HOMOGENEOUS CATALYSIS
IN GAS PHASE REACTIONS

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Ph.D.

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Finally I wish to acknowledge the support of the Mond Division of Imperial Chemical Industries Ltd., in providing the facilities and financial support for this project.

PREFACE

In this thesis the text of each chapter has been followed immediately by the tables and figures relevant to that chapter. The numbering system adopted throughout immediately indicates the position of a section, table or figure. Thus figure 4.05 will be found as the fifth figure (.05) at the end of chapter four (4.) whilst table 3.10 is the tenth table (.10) in chapter three (3.). Further subdivision where required has been designated by (a) (b) etc. The Appendices and Bibliography appear at the end of the thesis.

The abbreviations used for convenience throughout this report are as follows:

β TRI	for	1,1,2-trichloroethane.
α TRI	for	1,1,1-trichloroethane.
ECH	for	ethylene chlorohydrin.
VDC	for	1,1-dichloroethylene (vinylidene chloride).
c-DCE	for	cis 1,2-dichloroethylene.
t-DCE	for	trans 1,2-dichloroethylene.
VC	for	vinyl chloride.

Throughout the text occasional reference is made to bond strengths or free energy changes for certain reactions. Unless otherwise indicated the quoted values have been derived from "Thermochemical Kinetics" by S.W. Benson published by Wiley.

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ABSTRACT

The gas-phase, thermal decomposition of two chlorinated compounds -1,1,2-trichloroethane and ethylene chlorohydrin - have been investigated in an all-glass static reactor system at temperatures between 390°C and 484°C. The decompositions were followed both by pressure change and by detailed product analysis. Both compounds exhibit two modes of breakdown. 1,1,2-trichloroethane decomposes into 1,1-dichloroethylene or 1,2-dichloroethylene with elimination of HCl, whilst ethylene chlorohydrin undergoes dehydration to vinyl chloride or dehydrochlorination to acetaldehyde.

The effects of chain accelerators and chain inhibitors on these decompositions have been studied. The experimental evidence points to the existence of two separate modes of decomposition for each substrate - namely a radical chain mode and a molecular mode. The detailed nature of these mechanisms is discussed in the light of the experimental results.

The homogeneous gas phase catalysis of these decompositions is also described. The choice of the gas phase catalysts was made on the basis of the currently accepted theories of radical chain and molecular reactions. The effect of these additions on the overall rate and, in particular, on the selectivity of these decompositions was investigated. Changes in the selectivity of the chain processes were observed with HBr and H_2S addition. These are discussed with reference to the existing knowledge regarding selectivity. The effect of Lewis acid and base additives on the molecular modes of decomposition was shown to be small and is compared to the much greater effects observed in analogous liquid phase and heterogeneous systems.

A mathematical model of the decomposition of ethylene chlorohydrin has been formulated. The decomposition of ethylene chlorohydrin alone was simplified to 29 elementary reactions. The solution of this scheme

involved the use of an IBM 360-50 computer and gave a numerical rather than an analytical result for the formation of the various products which were observed in the decomposition.

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CHAPTER 1

INTRODUCTION

In contrast to both heterogeneous catalysis and homogeneous liquid phase catalysis studies on homogeneous gas phase catalysis have not been reported frequently in the literature. Furthermore, these studies have been limited to relatively few systems and no systematic study of a wide range of catalytic agents has been undertaken (1-13; 19; 22-27).

The work described in this thesis has been concerned with the decomposition of two chlorinated compounds namely, 1,1,2-trichloroethane (βTRI) and ethylene chlorohydrin (ECH). In both cases two important modes of breakdown are possible.

βTRI dehydrochlorination can occur in two ways to give 1,1-dichloroethylene (more commonly known as vinylidene chloride) or 1,2-dichloroethylene. The latter product can exist in both cis and trans form.

$$CHCl_2CH_2Cl \xrightarrow{-HCl} \begin{cases} CCl_2 = CH_2 & \text{(vinylidene chloride)} \\ CHCl = CHCl & \text{(cis/trans dichloroethylene)} \end{cases}$$

In the case of ECH, the decomposition reactions involve dehydrochlorination to acetaldehyde or dehydration to vinyl chloride.

$$CH_2ClCH_2OH \longrightarrow CHCl = CH_2 + H_2O$$

$$CH_2ClCH_2OH \longrightarrow CH_3CHO + HCl$$

For both compounds the ability to promote particular modes of breakdown can provide the basis of commercially useful processes. For instance, the commercially preferred product from βTRI is vinylidene chloride. The high selectivity to vinylidene chloride which is observed in the liquid phase E2 elimination reaction involving βTRI + a basic reagent makes the reaction of βTRI and lime the preferred method of manufacture of vinylidene chloride (41,42). However, this process suffers from a disadvantage in that the reaction is not catalytic and the eliminated HCl is not recoverable as it forms calcium chloride and water.

Because of the potential usefulness of being able to control the orientation and character of elimination in such compounds an investigation was initiated into the effect of various additives on these decompositions.

1.01 The Basic Mechanisms of Gas Phase Decompositions

The mechanisms of gas phase decompositions can be divided into two main categories:-

(a) Radical chain reactions, (it should be pointed out that a few examples of non-chain radical reactions have also been reported in the literature (77)).

(b) Molecular reactions.

1.01(a) Radical Chain Reactions

Radical chain processes are initiated by a species undergoing homolytic bond fission with formation of radical species.

$$RX \rightleftharpoons R^\bullet + X^\bullet$$

The decomposition is then propagated by the further reaction of one of the radical species. Termination of the chain occurs via radical-radical recombination. A typical example of such a decomposition was proposed by Howlett (14) for the thermal decomposition for 1,2-dichloroethane.

Initiation: $CH_2Cl - CH_2Cl \longrightarrow CH_2Cl - CH_2^\bullet + Cl^\bullet$ (1.01)

Propagation: $Cl^\bullet + CH_2Cl - CH_2Cl \longrightarrow CH_2Cl - \dot{C}HCl + HCl$ (1.02)

$CH_2Cl - \dot{C}HCl \longrightarrow CH_2 = CHCl + Cl^\bullet$ (1.03)

Termination: $CH_2Cl - CH_2^\bullet + Cl^\bullet \longrightarrow CH_2Cl - CH_2Cl$ (or $CH_2 = CHCl + HCl$)(1.04)

The propagation steps involve the formation of vinyl chloride with regeneration of a chlorine atom. Consequently, the production of one chlorine atom by the initiation reaction may give rise to a considerable number of vinyl chloride molecules before termination occurs. The average ratio of the number of propagation steps to termination steps defines the chain length in the system.

An essential feature of a chain process is that the radical species formed in the first propagation step should readily decompose. In the example quoted above, and in the thermal decompositions of halohydrocarbons generally, the presence of a chlorine atom in a position β to the radical centre provides a convenient decomposition mechanism as the loss of a β-Cl atom is a relatively facile process ($E_{ACT} \approx 22$ kcal/mole).

In the past relatively simple schemes have been proposed for chain reactions. However, in recent years it has been realised that the kinetics of chain processes are frequently extremely complex. Problems of kinetic analysis arise from product interaction and a further complication is the likely involvement of the reactor surface. Although propagation reactions are normally of a homogeneous nature and these form the bulk of a chain reaction, the important processes of initiation and termination may very likely occur at the walls of the reaction vessel.

A common feature of chain processes is the existence of an induction period. This can be due to the relatively slow build up of the propagating species until a steady state condition is reached when the rate of initiation is the same as the rate of termination. Alternatively the induction period may result from autocatalysis as a result of the decomposition of the primary products or from the presence of a trace of an inhibitory impurity.

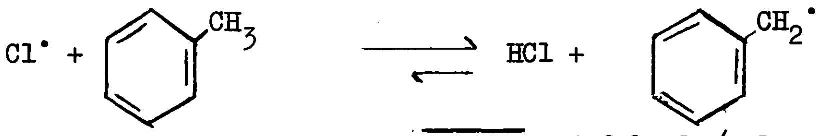
A chain decomposition reaction can normally be accelerated or retarded by the addition of suitable materials. Typical accelerators for chain decompositions involving halohydrocarbons are chlorine and carbon tetrachloride. These materials breakdown to radicals at a much higher rate than the principal reactant and this increases the rate of chain initiation. Barton has recorded (17) that the addition of 0.5% w/w of chlorine to 1,2-dichloroethane enhances the rate of dehydrochlorination 100-fold and suggests that the most likely reaction sequence is:-

$$Cl_2 + CH_2Cl - CH_2Cl \longrightarrow CH_2Cl - \dot{C}HCl + HCl + Cl^{\bullet} \qquad (1.05)$$

$$CH_2Cl - \dot{C}HCl \longrightarrow CH_2 = CHCl + Cl^{\bullet} \qquad (1.03)$$

with the chlorine atoms able to propagate the chains by hydrogen abstraction as shown previously, (equation 1.02 and 1.03). However, the above reaction indicates that the chlorine is itself destroyed in enhancing the chain and in this respect cannot be considered a true catalyst. Similar reasoning applies to other chain accelerators.

The inhibition of chain processes is achieved by the addition of materials such as toluene or propylene. The inhibiting action of these compounds depends on their ability to react with the normal propagating species to form a radical which is relatively unreactive toward chain propagation. The equilibrium of the reaction between chlorine atom and toluene is far to the right in the equation:-



$\Delta G = 21.8$ kcals/mole

Thus the removal of chlorine by toluene will compete favourably with the normal chain process and will produce the relatively unreactive benzyl radical. At one stage (52) it was assumed in discussing toluene inhibition that the only further reaction the benzyl radicals would undergo was dimerization to dibenzyl. In recent years it has been accepted that reactions in the presence of inhibitors are in fact very complex. The addition of inhibitor does not completely suppress chain reactions but only reduces them to a much lower level. Whether the residual reaction contributes significantly to the overall decomposition or not will depend on the extent of any underlying molecular process.

Inhibition need not necessarily involve toluene or propylene with the subsequent formation of a resonance stabilized radical. A saturated alkane can retard the radical chain decomposition of a chlorinated hydrocarbon because of the much lower activity of alkyl radicals as compared to chlorine atoms in hydrogen abstraction.

In certain chlorohydrocarbons free radical mechanisms do not occur because the substrate itself gives rise to radicals which do not possess a β-Cl atom. Thus the decompositions of ethyl chloride and 1,1-dichloroethane (18) are both unaffected by the addition of propylene and the reaction rates are much slower than those recorded for the chain decomposition of 1,2-dichloroethane. Taking ethyl chloride as our example, hydrogen abstraction by a chlorine atom can lead to two different radicals:-

$$\mathrm{Cl}^{\bullet} + \mathrm{CH_3 - CH_2Cl} \begin{array}{ll} \xrightarrow{-\mathrm{HCl}} \dot{\mathrm{C}}\mathrm{H_2 - CH_2Cl} & \qquad (A) \\ \xrightarrow[-\mathrm{HCl}]{} \mathrm{CH_3 - \dot{C}HCl} & \qquad (B) \end{array} \qquad .. (1.07)$$

Radical (A) can lose a β-Cl and thus continue the chain but (B) has no β-Cl. Furthermore, the loss of an $H^{\bullet}$ atom involves too much energy ($\Delta H = +39$ kcals) to proceed at a reasonable rate and thus the formation of (B) effectively stops the chain. If the rates of formation of (A) and (B) are assumed to be equal then each chlorine atom produced by initiation will on average lead to a chain length of approximately two. With 1,2-dichloroethane which did not form a "stopping" radical chain lengths of 10^5 or greater are obtained. Consequently, the rate of chain decomposition in ethyl chloride is negligible. In fact the rate of the dehydrochlorination reaction which is observed for ethyl chloride and 1,1-dichloroethane at 450°C is unaffected by chain inhibitors such as propylene (18) and a molecular mechanism is indicated as described in section 1.02.

True catalysis of chain processes can be brought about in certain conditions by the addition of a chain transfer agent. Catalysis by chain transfer involves the replacement of the slow rate determining step in a chain propagation sequence by two faster steps involving the catalytic agent. A typical example involves the HCl catalysed decomposition of dimethyl ether (19). In the absence of HCl the normal chain process occurs through methyl radicals:-

$$CH_3^{\bullet} + CH_3OCH_3 \longrightarrow CH_4 + \dot{C}H_2OCH_3 \qquad (1.08)$$

$$\dot{C}H_2OCH_3 \longrightarrow CH_2O + CH_3^{\bullet} \qquad (1.09)$$

The metathesis reaction (1.08) of methyl abstraction is slow ($E_{(1.08)} = 9.5$ kcal (20)). However, the corresponding methyl abstraction of hydrogen from HCl is much faster (E = 2.1 kcals (21)) and gives rise to the more reactive chlorine atom. Thus, in the presence of HCl, (1.08) is replaced by two faster reactions:-

$$\dot{C}H_3 + HCl \longrightarrow CH_4 + Cl^{\bullet} \qquad (1.10)$$

$$Cl^{\bullet} + CH_3OCH_3 \longrightarrow CH_2^{\bullet}OCH_3 + HCl \qquad (1.11)$$

The reformation of HCl in (1.11) indicates the true catalytic action of HCl in this process. Benson (19) observed that the addition of 20% HCl gave an eightfold increase in rate. Similar HCl catalysis has been observed in the pyrolysis of di-tertiary butyl peroxide (22) and in neopentane (23). In the decomposition of neopentane to isobutene and methane the catalysis is again considered as the replacement of chain propagation by methyl radicals to one involving chlorine atoms. The decomposition of di-tertiary butyl peroxide is more complex as primary decomposition can give isobutene oxide and t-butanol or isobutene, methane and acetone. However, the catalysis by HCl is rationalized as in the previous examples as a change in the chain propagating species from alkyl ($CH_3^\bullet$) or alkoxy ($t\text{-}BuO^\bullet$) to chlorine atom.

H_2S has also been found to act as an effective chain transfer agent where normal chain propagation occurs via alkyl radicals. The work of Imai and Toyama (24) on dimethyl ether decomposition demonstrated a tenfold increase in rate in the presence of H_2S. As with HCl the catalysis was believed to be due to the two reactions:-

$$CH_3^\bullet + H_2S \longrightarrow CH_4 + HS^\bullet \qquad (1.12)$$

$$HS^\bullet + CH_3OCH_3 \longrightarrow \dot{C}H_2OCH_3 + H_2S \qquad (1.13)$$

replacing the slower hydrogen abstraction by methyl shown previously (equation 1.08). The authors derived a value of 6.8 kcals for the activation energy in equation 1.13. They also noted that H_2S catalysed the secondary chain decomposition of formaldehyde. Similarly H_2S was found to catalyse the decomposition of acetaldehyde (25) by replacing

$$CH_3^\bullet + CH_3CHO \longrightarrow CH_4 + CH_3\dot{C}O \qquad (1.14)$$

by the two faster reactions:-

$$CH_3^\bullet + H_2S \longrightarrow CH_4 + HS^\bullet \qquad (1.15)$$

$$HS^\bullet + CH_3CHO \longrightarrow H_2S + CH_3\dot{C}O \qquad (1.16)$$

Imai and Toyama also observed a rate enhancement of acetaldehyde decomposition when methanethiol was present (26) and considered that the radical species $CH_3S^\bullet$ was propagating the chain. In this decomposition the thiol was also found to act as an alternative initiating source for the reaction ($CH_3SH \longrightarrow CH_3^\bullet + SH^\bullet$).

Hydrogen bromide catalysis of hydrocarbon oxidation reactions has been known for some time (27). The mechanism for the oxidation of

$i\text{-}C_4H_{10}$ is:-

$$tBu^{\bullet} + O_2 \longrightarrow t\text{-}BuO_2^{\bullet} \qquad (1.17)$$

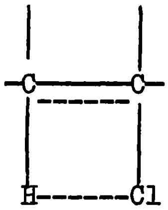
$$tBuO_2^{\bullet} + HBr \rightleftharpoons tBuO_2H + Br^{\bullet} \qquad (1.18)$$

$$i\text{-}C_4H_{10} + Br^{\bullet} \rightleftharpoons t\text{-}Bu^{\bullet} + HBr \qquad (1.19)$$

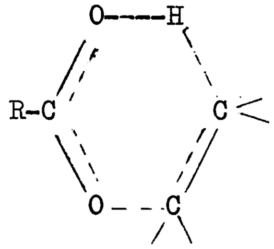
The rapid reaction (1.17) maintains the t-Bu˙ concentration at a low level and prevents the back reaction of (1.19) occurring. The forward reaction of (1.18) is exothermic by about 3 kcals and at the relatively low temperature used (150°C) the equilibrium of 1.18 lies well to the right. As with methanethiol in acetaldehyde HBr also acts as an initiating source in this reaction.

1.01(b) Molecular Reactions.

In the previous section it was pointed out that at temperatures around 450°C ethyl chloride or 1,1-dichloroethane decomposes at a rate which is unaffected by the addition of typical inhibitors such as propylene (18). Barton and Howlett concluded that the decomposition was occurring by a molecular process. Gas phase molecular decompositions have been observed for many classes of compounds such as esters, alcohols, xanthates, as well as alkyl halides. A review of kinetic data of such reactions has recently been published (81) and in addition an earlier review of Depuy and King (82) provides a good insight into the mechanism of the decompositions. The molecular mechanism for dehydrochlorination of alkyl halides is believed to involve a four centred transition state of the form:-



Alternatively for esters possessing a β-H in the alkyl group a six membered cyclic transition state has been postulated:-



with an overall decomposition into olefin and acid; thus for the ethyl ester:-

$$RCO_2CH_2CH_3 \longrightarrow RCO_2H + H_2C = CH_2$$

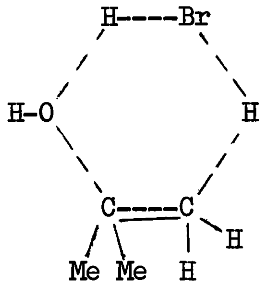
However, these cyclic transition states do not, per se, explain the widely variable effects of substituents on different classes of compound which have been observed in the literature (28,29). To explain the observed results, Maccoll and his co-workers postulated that the transition state in gas phase molecular eliminations contained a variable degree of charge separation. The complete dissociation of ions in the gas phase is most unlikely on energetic grounds as heterolytic bond dissociation energies of $\sim$300 kcals ($D(R^+X^-)$) are involved. However, the possible formation of a semi-ion pair which would involve partial heterolysis of a bond and therefore partial charge separation has received detailed consideration by Benson and Bose (30). They concluded that such a species was energetically feasible in the gas phase. Maccoll (29) has pointed out the great similarities which exist between eliminations in the gas phase and liquid phase E1 elimination reactions with regard to the effects of various substituents. The most striking effects of substitution are found in the alkyl halide series. The presence of an electron donating group on the α-carbon (i.e: the carbon attached to the halogen) enhances the rate considerably. Thus t-butyl chloride eliminates HCl 2.6×10^4 times faster than ethyl chloride owing to the electronic release from the methyl groups. An even greater catalysis is observed with -OMe substitution: α-methoxy ethyl chloride eliminating HCl 10^7 times faster than ethyl chloride at 330°C (31) due to a reduction of 23 kcal/mole in the activation energy. The importance of the immediate environment of the carbon-halogen bond is universally recognised in the literature for alkyl halide pyrolyses but the role of the carbon hydrogen bond does not appear to be fully resolved. The presence of electron releasing groups on this carbon atom (the β-carbon) slightly enhances the rate of HCl elimination indicating that the longer range forces on the carbon halogen bond are more important than the destabilizing effect expected on an intermediate possessing C-H polarization i.e: $C^{\delta-}$ ---- $H^{\delta+}$. Thus iso-butyl chloride eliminates HCl 3.2 times faster than ethyl chloride. Furthermore, the decomposition rates of s-butyl bromide and 4-brompentene-1 (32) are very similar although elimination of HBr from the latter compound involves the relatively facile removal of an allylic hydrogen. Both pieces of evidence point to the unimportance of the carbon hydrogen bond breaking process. In contrast, however, the isotope effects observed by Blades et al (33) in the molecular dehydrochlorination of 1,1,2,2-tetrachloroethane gave the relationship:-

$$\frac{k_H}{k_D} = 1.16 \exp (985/RT)$$

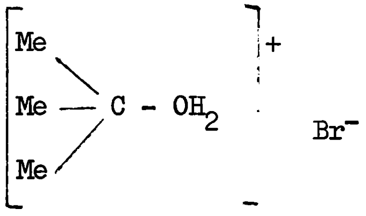
for the relative rates of HCl and DCl elimination. If the fission of the C-H bond were the rate determining step in HCl elimination then the activation energy difference for k_H/k_D would be 1,400 cals/mole i.e: the difference in zero point energy for C-H and C-D. The observed value of 985 cals/mole suggests that the C-H bond fission - whilst not completely rate determining - is important in HCl elimination. The similarity which was shown to exist between gas phase eliminations and E1 and SN1 reactions in solution led Maccoll and his co-workers to use the term "quasi-heterolytic" to describe the gas phase phenomenon.
As mentioned previously the alkyl halides were found to exhibit the greatest degree of "quasi heterolytic" character but other classes of compounds such as esters and alcohols show similar if smaller effects.

Homogeneous catalysis of molecular reactions in the gas phase has been reported in the literature by Stimson and his co-workers, (1-13). Their work has been concerned almost exclusively with hydrogen halide catalysis of the decomposition of various alcohols, ethers, acids and esters. No catalysis of alkyl halide decompositions has been reported.

In the catalysis of the decomposition of t-BuOH by HBr (1) various transition states were considered. The two extreme conditions of a concerted elimination (A) or the formation of an ion pair (B) are shown below:-

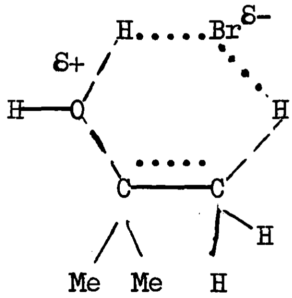


(A)



(B)

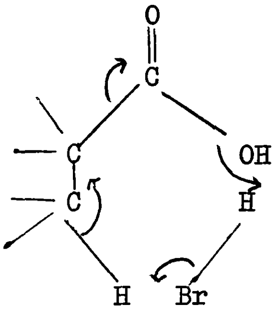
Maccoll (1) showed that the energy required to form (B) would be 100 kcals/mole whereas an activation energy of only 30 kcals/mole was observed experimentally. At the same time the existence of an uncharged transition state as designated by (A) would not explain the "quasi heterolytic" effects discussed above. The concept of an "intermediate" transition state was not developed further in this paper but one might envisage a partially polarized cyclic transition state possessing different degrees of bond breaking. If we represent almost complete bonds by a heavy dashed line and almost broken bonds by a dotted line then a typical partially polarized transition state is given by (C):-



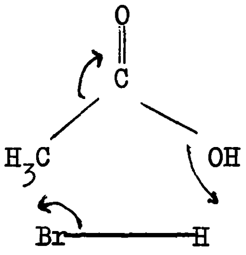
(C)

In this transition state protonation of the oxygen atom is almost complete whilst the bond between the hydrogen and the β-carbon has not been significantly broken.

The evidence obtained from the HBr catalysis of the decomposition of a series of methyl substituted acids again indicates the existence of a polarized transition state. The observed products from the catalysed decompositions of acetic (12), propionic (13), isobutyric (7), and trimethylacetic acids (6) changed from an alkyl bromide with acetic acid to an olefin with trimethylacetic acid. Initially this led to the postulation of two different cyclic transition states - a 7 centred one (D) for isobutyric and trimethylacetic acid and a 5 centred one (E) for acetic acid - in order to explain the formation of an olefin (from (D)) and an alkyl bromide (from (E)).

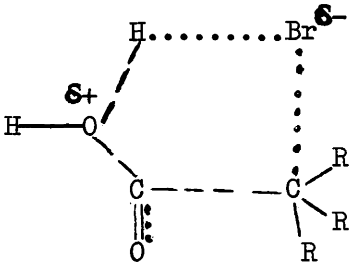


(D)



(E)

In the decomposition of propionic acid ethyl bromide was formed as the primary product. The subsequent rapid decomposition of ethyl bromide into ethylene suggested the possibility of the alkyl bromide also being formed as primary product in the decompositions of trimethylacetic and iso-butyric acid. The relative ease of HBr elimination from α-methyl substituted compounds would ensure rapid removal of the alkyl bromide to form the observed olefin. Furthermore, a comparison of the Arrhenius parameters for each decomposition (13) showed them to be very similar. These two factors made the concept of a common transition state appear more likely. The seven membered ring (D) cannot exist for acetic acid whilst the authors felt that the five membered ring (E) would be unlikely for trimethylacetic acid on steric grounds. Consequently, a "loose polar transition state" $(R_3C - CO - OH_2)^+Br^-$ was proposed in which the elimination of water and CO was followed by the decomposition of the alkyl bromide. However by analogy with t-BuOH the formation of this ion pair would require ∿100 kcals/mole and, in view of the observed activation energies of ∼33kcals/mole, ion pair formation appears unlikely. Consequently a 5 membered cyclic transition state is required similar to that proposed for t-BuOH (F).



R = H or CH_3

(F)

The above evidence indicates the strong possibility of ionic effects occurring in the gas phase and the possibility of alkyl halide decompositions being catalysed by additives finding more common application in liquid phase or heterogeneous systems.

1.02 Liquid Phase and Heterogeneous Dehydrochlorination

Dehydrochlorination reactions in both the liquid phase and in heterogeneous systems have received considerable attention in the literature. For the present purposes the review of the literature will be restricted to reactions involving dehydrochlorination of saturated chlorocarbons containing two carbon atoms with particular reference to 1,1,2-trichloroethane. The reagents available for dehydrochlorination fall into two broad classes of Lewis acids and bases. The typical effects of each class of compound is discussed below.

1.02(a) Dehydrochlorination by Lewis Acids

The presence of Lewis acids greatly enhances the rate of dehydrochlorination of a chlorinated hydrocarbon in both liquid and heterogeneous systems. Consideration of the published data about the effect of additional chlorine substitution on the relative rate of dehydrochlorination by typical Lewis acids (such as $FeCl_3$, $AlCl_3$) reveals that:-

(a) Increased α-substitution increases the rate.

(b) Increased β-substitution decreases the rate.

where the α-carbon is the atom from which the chlorine is removed. Thus the order of reactivity with $AlCl_3$ in the liquid phase has been reported by Susuki (34) to be:-

$CCl_3CH_3 > CCl_3CH_2Cl > CHCl_2CH_3 > CHCl_2CH_2Cl > CCl_3CHCl_2 > CHCl_2CHCl_2 >$

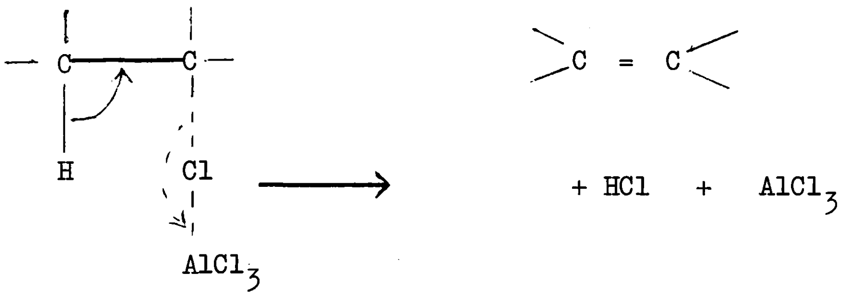
CH_2ClCH_2Cl

This order of reactivity with Lewis acids has been confirmed by Kulikova (35) and also by Mochida (36) who employed a heterogeneous system with silica-alumina and boron trioxide-alumina as typical acid catalysts.

The effects of Lewis acids are essentially catalytic and may be rationalized in terms of their known action in Friedel-Crafts type reactions. The Lewis acid attacks the most electronegative centre in the chlorocarbon molecule to give an intermediate complex which is most often represented as:-

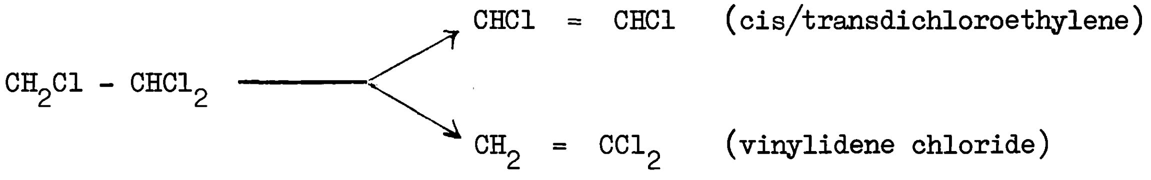
$$R^{\delta+} \text{-----} (Cl\text{-----}AlCl_3)^{\delta-}$$

i.e. a polarised transition state with the R-Cl bond partially broken. With a chlorocarbon substrate such a process reduces the activation energy for the formation of the transition state and HCl is more readily removed to form the olefin.



The effects of additional chlorine substitution can then be rationalised. The presence of an electronegative **Cl** on the αposition makes this centre more electronegative and this stabilises the complex by mesomeric interaction of the chlorine with the $\delta+$ charge. On the other hand the inductive withdrawal occasioned by the presence of a β-Cl will reduce the electronegativity of the α-carbon centre and hinder the Lewis acid effect.

The dehydrochlorination reaction with βTRI is unique in the C_2 series because different products are produced dependent on which C-Cl bond is broken.



The formation of different products makes βTRI a useful substrate in studying the stereospecificity of different additives.

In the case of Lewis acids where α-Cl substitution helps C-Cl bond break and β-Cl hinders we would expect a predominance of 1,2-dichloroethylene over vinylidene chloride. Formation of the former involves one α-Cl and one β-Cl whereas dehydrochlorination to vinylidene chloride occurs in the presence of two β-Cl substituents. The work of Mochida (36) on silica-alumina catalysts and Czarny on aluminium oxide (38) confirmed this view. In both cases the symmetrical dichloroethylene was formed in considerably greater amounts than the non-symmetrical product. In addition the cis isomer predominated over the trans. This has led both sets of workers to propose a high degree of concerted E2 character in the elimination process - the concerted mechanism giving rise to stereospecific formation of cis-1,2-dichloroethylene.

The use of metal sulphates as solid acid catalysts has given similar effects in the dehydrochlorination reaction of βTRI (37). No traces of vinylidene chloride were observed at 300°C with $NiSO_4$, $CoSO_4$, $MnSO_4$, $Cr_2(SO_4)_3$, $CuSO_4$, $CdSO_4$, $ZnSO_4$ and $Fe_2(SO_4)_3$. In addition the cis/trans ratio was very high ($>10/1$) suggesting, as previously, a considerable degree of E2 concerted mechanism.

An anomalous result has been obtained by Noller (39) and his co-workers. Using $MgSO_4$ they claim exclusive conversion of βTRI to vinylidene chloride. No satisfactory explanation of this effect is given in terms of acid-base characteristics. In addition their classification of reaction type by use of the derived activation energies for dehydrochlorination of C_2 chlorocarbons must be regarded with some caution as no account is taken of the wide spread of pre-exponential factors obtained. In terms of the observed conversions the order of reactivity over $MgSO_4$ would be:-

$CCl_3CH_3 > CHCl_2CH_3 > CH_2ClCH_3 > CHCl_2CH_2Cl > CH_2ClCH_2Cl$

which agrees well with the previously outlined concepts of substitution. Work done in these laboratories (40) with $MgSO_4$ and βTRI did not reproduce the results of Noller but showed that cis-1,2-dichloroethylene was the major product in accordance with the expected acidic effects of metal sulphates.

1.02(b) Dehydrochlorination by Lewis Bases

The action of a base in dehydrochlorination reactions is to assist in the removal of a proton from the substrate. Using $Ca(OH)_2$ in ethanol Suzuki (34) proposed that for additional chlorine atoms in the chlorocarbon

1. Increased α-substitution increases the rate of dehydrochlorination.

2. Increased β-substitution increases the rate of dehydrochlorination where the α-carbon again refers to that atom from which the chlorine is removed. The observed relative rates of dehydrochlorination were:-

$CCl_3CHCl_2 > CHCl_2CHCl_2 > CHCl_2.CHCl_2 > CCl_3CH_2Cl > CCl_3.CH_3 > CH_2Cl.CH_2Cl >$

$CHCl_2CH_3$

The greater rate observed with 1,1,2,2-tetrachloroethane in comparison to the 1,1,1,2-isomer (and βTRI compared to αTRI) indicates that the enhancement due to β-Cl is stronger than the enhancement from an α-Cl. The work of Mochida et al (36) using strontium oxide as a solid base agrees with the above order although 1,1,1,2-tetrachloroethane did not feature in their study.

The inductive withdrawal effect of additonal chlorine atoms attached to a carbon atom progressively weakens the C-H bond at this centre and makes it more susceptible to fission. The order of elimination has been correlated (36) with the "reactivity index of the delocalizability" of the C-H centre and the overall elimination has been considered as a stepwise <u>E2</u> process (known also as the Elcb mechanism) in which the C-H bond break is the rate determining step. This also explains the relatively minor effect of α -Cl substitution as the inductive effect on the C-H centre is reduced rapidly with distance through the molecule.

The above observation indicates that the effect of base on βTRI will be to form vinylidene chloride preferentially. Commercial exploitation has been made of this feature in preparing vinylidene chloride from βTRI without the formation of substantial amounts of 1,2-dichloroethylene. The use of $Ca(OH)_2$ with βTRI has been described in the patent literature (41, 42). The yield of vinylidene chloride was 95% in terms of the total dichloroethylene produced. Other inorganic bases such as alcoholic

KOH (43), ammonium hydroxide (44), and K_2CO_3 (39) have also been used to produce good yields of vinylidene chloride. Organic bases are also able to dehydrochlorinate βTRI selectively to vinylidene chloride. Using amines with a pk<7 such as trimethylamine and n-butylamine Ethyl Corporation (45) have claimed almost exclusive formation of vinylidene chloride. In all these examples the HCl formed is associated with the base. With the inorganic bases thermally stable chloride salts ($CaCl_2$ and KCl) are formed in a stoichiometric fashion and HCl is lost. The possibility of thermally decomposing the amine hydrochloride back into HCl and free amine has been considered and a degree of catalytic behaviour for the amine hydrochloride has been claimed (42) at temperatures above 200°C in the liquid phase. However, in any process the mechanical and chemical losses of the relatively expensive organic amine would have to be small to make this system more attractive (via useful by-product HCl) than that using an inexpensive base material. No examination of the use of bases in the gas phase has been reported.

1.02(c) Other Dehydrochlorinating Systems.

The dehydrochlorination of βTRI has been performed in the presence of other materials which do not fall into the Lewis acid or base category. None of these has produced exceptionally high reactivity or specificity. The use of coal impregnated with $BaCl_2$ (38) gave a dichloroethylene yield containing approximately 30% of vinylidene chloride at temperatures of 200° - 400°C. Pimenov (46) obtained a 45.0% selectivity to vinylidene chloride by using potassium fluoride on pumice at temperatures of 325-400°C. In the same paper the use of "high melting amines" were investigated as reactants which do not form stable compounds with HCl at the temperature used. 1,5-diaminonaphthalene on pumice gave a 27% selectivity to vinylidene chloride at 300°C suggesting that extensive base catalysis was not occurring under these conditions.

1.03 The Choice of the Substrate

In this investigation two chlorocarbon substrates were employed - 1,1,2-trichloroethane (βTRI) and ethylene chlorohydrin (ECH). The reasons for this choice may be summarised as follows.

(a) The gas phase reactions and decompositions of those compounds have not previously been studied in great detail and little consistency exists between the results from different sets of workers.

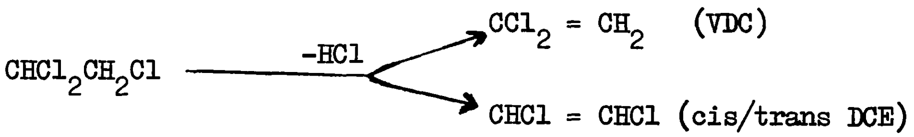
(b) The selectivity of an added catalyst can readily be observed with both substrates as different products are formed depending on the point of attack of the additive.

(c) There is a commercial interest in both substrates as starting materials for the manufacture of large tonnage materials (i.e. 1,1,1-trichloroethane via vinylidene chloride and vinyl chloride from ECH).

1.03(a) Previously published work into the thermal decomposition of βTRI

The published papers on the decomposition of βTRI (17, 47, 48, 49) have all concluded that at temperatures around 400-500°C βTRI decomposes predominantly via a radical mechanism. The addition of chlorine (17, 48) and oxygen (17) markedly enhanced the rate of reaction whereas typical inhibitors such as toluene (48) and propylene (47) considerably reduced the rate. The limiting rate attained on increasing addition of inhibitor led these authors to propose an underlying molecular mechanism of βTRI decomposition. A wide variation in the rate of decomposition has been recorded. The Arrhenius equations for the overall reaction are shown in table 1.01 (B). First order behaviour with respect to βTRI has been demonstrated (48, 49) but the same two sets of papers indicate considerable differences in the Arrhenius parameters and a difference of 2×10^3 in the value of the rate constant at 391.5°C - the temperature at which our investigation was carried out. The maximally inhibited rate in the presence of toluene as reported by the Japanese workers (48) is still 150 times greater than the uninhibited rate of Pimenov (49). One reason for this difference may be a heterogeneous catalysis of the decomposition in a steel reactor compared to a glass one. Marked catalysis of chlorocarbon decompositions in the presence of steel has been observed in previous work in this laboratory (50) and the existence of wall initiation reactions is a distinct possibility. Reference to table 1.01 also indicates marked differences in the rates observed in all-glass flow systems (17 and 49). Barton's value is almost 100 times greater than that of Pimenov. Other workers (47) have also found great irreproducibility in the reaction rate in glass reactors and it seems likely that the condition of the glass surface is a vital factor in determining the overall rate. In view of this surface effect discussions of the mechanism in terms of a purely homogeneous system (48, 49) must be treated with caution.

The selectivity of the reaction was considered by both Teramoto (48) and Pimenov (49). βTRI can undergo dehydrochlorination to give three dichloroethylenes - 1,1-dichloroethylene(VDC) and cis - or trans-1,2-dichloroethylene.



$$CHCl_2CH_2Cl \xrightarrow{-HCl} \begin{cases} CCl_2 = CH_2 & \text{(VDC)} \\ CHCl = CHCl & \text{(cis/trans DCE)} \end{cases}$$

Although, as mentioned above, the influence of the surface appears to be critical in determining the overall rate of chain decomposition, it is unlikely to affect the selectivity. This will depend solely on the competive chain propagation steps (k_2 and k_3) which involve chlorine atom abstraction of hydrogen from βTRI.

$$CHCl_2CH_2Cl + Cl^{\bullet} \xrightarrow{k_2} \overset{\bullet}{C}Cl_2CH_2Cl + HCl$$

$$CHCl_2CH_2Cl + Cl^{\bullet} \xrightarrow{k_3} CHCl_2\overset{\bullet}{C}HCl + HCl$$

The relative ease of β-Cl elimination ensures rapid conversion of these intermediate radicals into VDC and 1,2-dichloroethylenes respectively ($k_4$and k_5).

$$\overset{\bullet}{C}Cl_2CH_2Cl \xrightarrow{k_4} CCl_2 = CH_2 + Cl^{\bullet}$$

$$CHCl_2CHCl^{\bullet} \xrightarrow{k_5} CHCl = CHCl + Cl^{\bullet}$$

The chlorine atoms thus formed continue the chain process.

The relative rates of formation for the overall reaction as quoted in the literature are shown as a function of temperature in table 1.01 (F). At 391.5°C the proportion of VDC in steel is 39.1% (48) and in glass 40.1% (49). However at 453.5°C (the upper temperature in our investigation) these values have become 41% and 32.8% respectively. The rate data for chlorine abstraction of hydrogen from βTRI (51) suggests that abstraction of hydrogen from the dichloro centre (k_3) involves slightly less energy (0.6 kcals/mole) than that from the monochloro centre (k_4). Hence we might expect a slight decrease in the proportion of VDC obtained at increased temperatures. The activation energy difference of ∼5.2 kcals/mole claimed by the Russian workers appears far too great in this context. The value of Teramoto indicates a slight increase in VDC with temperature in contrast to the available rate data for the radical reaction. This may however be due to the influence of the underlying molecular mechanism which shows a strong temperature dependence of VDC formation (table 1.01(D)). Indeed the authors have estimated a value of 0.7 exp ($\pm$500/RT) for the radical reaction which would suggest an undetectable effect of temperature on the product ratio. Teramoto also demonstrated the absence of any isomerisation at 400–480°C between vinylidene chloride and 1,2-dichloroethylene. On the other hand cis-trans isomerisation would be expected to occur extensively (52) at these temperatures.

The rate of product formation in the maximally inhibited reaction (table 1.01 (D)) indicates a reduction in the proportion of VDC to 22.0% at 453.5°C and to 11.5% at 391.5°C. The selectivity of the inhibited reaction is thus substantially temperature dependent and also favours production of the symmetrical dichloroethylene at these temperatures. If the inhibited reaction truly represents a molecular reaction it would appear that the steel surface is again catalysing the decomposition as the rate at 391.5°C is faster than that obtained in glass by both Barton and Pimenov (see table 1.01 (C)).

1.03(b) Previously published work into the thermal decomposition of ECH

Previous work on the gas phase decomposition of ECH appears to be restricted to a minor entry by Lessig (53). During a general study into unimolecular decompositions of alkyl halides he observed 'complicated behaviour which did not obey first order kinetics'. The pressure change indicated a threefold increase in pressure with a 'half life' of 141 minutes at 368°C. A recent investigation into ECH decomposition in this laboratory showed that the major products from this reaction were acetaldehyde, carbon monoxide, methane, and vinyl chloride. It appeared reasonable to postulate a primary decomposition into acetaldehyde or vinyl chloride.

$$CH_2OHCH_2Cl \begin{array}{l} \nearrow CH_3CHO + HCl \\ \searrow CH_2 = CHCl + H_2O \end{array}$$

followed by a secondary decomposition of acetaldehyde into CH_4 and CO

In contrast to ECH the decomposition of acetaldehyde has received considerable attention in the literature. Recent publications of Laidler et al (54, 55) conveniently summarise previous work. They demonstrate that the decomposition into methane and CO proceeds via a chain process. It is obvious that the presence of ECH may provide alternative initiating propagating and terminating species for this decomposition and a detailed review of the kinetics of pure acetaldehyde decomposition would appear unwarranted.

TABLE 1.01 KINETICS OF β TRI DECOMPOSITION FROM PUBLISHED WORK.

WORKERS (REF)	BARTON (17)	TERAMOTO ET AL (48)	PIMENOV ET AL (49)
A TECHNIQUE EMPLOYED	GLASS FLOW REACTOR	STEEL FLOW REACTOR	QUARTZ GLASS FLOW REACTOR
OVERALL REACTION			
B $\log_{10} k_{ov.}$ (sec^{-1})	$9.74-\frac{38\times10^3}{4.575T}$	$9.9-\frac{34.3\times10^3}{4.575T}$	$16.57-\frac{64.5\times10^3}{4.575T}$
C $k_{ov.}$ (T=391.5°C)	1.74×10^{-3}	4.14×10^{-2}	2.25×10^{-5}
INHIBITED REACTION			
D $\log_{10} k_{inh.}$ (sec^{-1})	-	$6.5-\frac{27.3\times10^3}{4.575T}$	-
E $k_{inh.}$ (T=391.5°C)	-	3.31×10^{-3}	-
F $k_{VDC}/(k_{c-DCE} + k_{t-DCE})$	-		
(a) OVERALL REACTION (EX.B) AT 391.5°C	-	$1.6\exp\left(\frac{-1.2\times10^3}{RT}\right)$ 39.1 % VDC	$\frac{1}{(46.0\exp(-5200/RT) + 42.4\exp(-5700/RT))}$ 40.1 % VDC
(b) INHIBITED REACTION (EX.E)		$1.1\times10^3\left(\frac{-11.9\times10^3}{RT}\right)$	-
At 391.5°C		11.5 % VDC	-
At 453.5°C		22 % VDC	-

CHAPTER 2

EXPERIMENTAL

2.01 The General Technique

The thermal decompositions were studied by a conventional static reactor technique. The course of the reactions were followed both by analysis and by pressure measurement. A vacuum line system was used for handling gaseous reactants and products. The reactor was enclosed in a thermostatically controlled aluminium block furnace. The apparatus and mode of operation are described in detail below.

2.02 Apparatus.

Pyrex glass reactors were used throughout this work. The greater part of the investigation was carried out in an unpacked reactor. This was a cylindrical vessel 10 cm long and 7 cm in diameter with a volume of 326.2 cm^3 and a surface to volume ratio of 0.87 cm^{-1}. A packed vessel was also used during the study. This had similar external dimensions but possessed five, concentric, open-ended, glass cylinders which increased the surface to volume ratio to 5.06 cm^{-1} and decreased the volume to 259.9 cm^3. A third reactor was used to study the effect of a steel surface. This was again a pyrex cylinder of similar dimensions as before but containing a stainless steel cruciform insert 9 cm long which gave an area of steel surface of 244.6 cm^2. The volume of this reactor was 317 cm^3 and the surface of steel to volume ratio was 0.77 cm^{-1}.

Each reactor was fitted with separate inlet and outlet lines constructed of 2 mm capillary tubing. The provision of separate lines prevented high boiling product condensing out and contaminating the reactant storage and inlet sections. Both exit and inlet lines extended outside the containing furnace.

2.03 The Thermostat

The reactor was housed in a heated metal block thermostat (Fig.2.01). This consisted of a cylindrical aluminium block 20 cm high and 15 cm in diameter with a central well 16 cm deep and 7.2 cm in diameter into which the reactor fitted closely. The reactor rested on the bottom of the well and the block extended 6 cm above the top of the reactor. A groove on the outside of the block housed the platinum resistance thermometer of the temperature controller. In addition the metal block had two wells drilled into it suitable for thermocouples. As shown in figure 2.01 the wells were 1 cm in diameter and extended to the bottom of the reactor well to enable the temperature gradient up the reactor to be measured. The thermocouples used in this investigation were chrome-alumel and were pre-calibrated at three fixed temperatures (231.8°C, (M.Pt. of tin)); 327.4°C (lead); 419.5°C (zinc)).

The aluminium block stood in the central well of a firebrick lined electric furnace of external dimensions 50 cm^3. The temperature was controlled via the platinum resistance thermometer mentioned above through a Sirect Mark II Proportional Temperature Controller. Tests established that the temperature was maintained within ±0.2°C over prolonged periods. The variation in temperature across the block and in the centre of a reactor was also small ($<$0.2°C) but the vertical temperature gradient across the length of the reactor was less satisfactory, being of the order of 2°C. An improved temperature gradient ($<$1°C) has now been obtained in this laboratory with a redesigned furnace. For the purposes of this investigation however an accurate isothermal condition is of less importance than a reproducible mean temperature condition.

The accuracy of the absolute temperature was confirmed by studying the rate of decomposition of 1,1-dichloroethane at 453.5°C (the temperature at the mid-point of the reactor). This decomposition is known to be unimolecular (56, 57) and the first order rate constant, k_1, of 1.56×10^{-3} sec^{-1} agreed well with the value of 1.66×10^{-3} sec^{-1} obtained in a flow system in this laboratory. It also agrees reasonably well with the published value of Howlett which gives $k_1 = 1.32 \times 10^{-3} sec^{-1}$ at this temperature (56). The activation energy of 48.3 kcals/mole derived by Howlett indicates that the differences in the above results could arise from differences of ±1°C in the estimation of temperature. Hence the temperature in the block at a point corresponding to the mid-point of the reactor (5 cm from the bottom of the well) was used throughout as a measure of the temperature of the decomposition.

2.04 Vacuum System

The general layout of the vacuum system used in this investigation is shown in figure 2.02. The system was pumped by a mercury diffusion pump backed by a two-stage oil-pump and could be evacuated down to 10^{-5} torr. The design of the system ensured the separation of the reactants from the product recovery side as mentioned previously. The reactant section contained four 5000 cm^3 bulbs (A-D) for storing gases and two 150 cm^3 bulbs (F and G) for storing liquids at room temperature. The latter were wound with heating wire and lagged with the exception of the thimbles. An inlet point (e) was provided for the introduction of liquids and gases into the system. The inlet line a-d was also wound with heating wire (at 140°C) and lagged.

On the product exit section two points were provided for collection of reaction products for analysis (H and J). In addition the line b-k was wound with heating wire and lagged to give a temperature of 140°C. Gases not removed for analysis were condensed out in the two liquid nitrogen traps P and Q.

The remaining features of the system include a mercury manometer, M, for pressure calibration; a needle valve, K, for introducing nitrogen into the apparatus; and a by-pass line, N, which enabled evacuation of the reactant side without the passage of materials through the reactor.

2.05 Pressure Measurement

Pressure changes in the reactor were monitored by measuring the linear displacement of a glass bellows connected directly to the reactor as shown in figure 2.02. The system is shown more clearly in figure 2.03. The bellows (A) were glass blown from 2 mm capillary tubing which was subsequently connected to the reactor inlet line. The bellows were approximately 15 mm across and 8 mm in depth. On the upper side of the bellows the tubing was sealed with a length of glass rod (B). A glass shroud (D) was fitted around the bellows and terminated in a buttress joint level with the top of the rod B. With the aid of the asbestos sealing ring (H) a brass mount (E) was fitted to this joint. The brass cylinder (F) on this mount acted as a holder for a transducer (C). The head of the transducer rested lightly on the tip of the glass rod (B) and could be held rigidly in position by tightening the screw G. Linear displacement of the bellows thus caused a movement of the transducer head. In order to prevent condensation of reactor material in A the tube below the bellows and the glass outer casing (D) were wound with electrical heating wire and insulated. The entire head was then enclosed in a glass cylinder which excluded draughts from the system as these could give rise to sudden contractions of the measuring device.

A typical displacement of the bellows designed in this way was 0.05 mm for a pressure change of 200 torr. The signal obtained from the transducer head was passed to an amplifier. The amplifier used in this investigation is commercially available from Rank, Taylor, Hobson and is known as the 'Mitronic' Micro-Comparator. The output from the amplifier (0-250 μamp) was fed to a 'Servoscribe' strip chart recorder.

A 250 Ω resistance placed in parallel with the recorder enabled a full scale deflection of 100 mV to be obtained for an input of 250 μamp. This arrangement enables the output to be simultaneously recorded on a digital voltmeter or to be fed directly to an on-line computer system (Arugs 300) for direct calculation of first order log plots (see Appendix I). Under typical conditions the amplifier range 0.1 mm (from centre zero to full scale) would be used to provide full scale deflections for a 400 torr pressure change. In addition manual range changing could provide three more sensitive amplifier ranges (down to 3 μm full scale) and one less sensitive (0.3 mm full scale). Consequently different pressure regions could readily be studied.

2.06 Calibration and Operation of the Vacuum Line

The calibration of the pressure gauge was carried out by admitting nitrogen into the vacuum line and comparing the deflection in the chart recorder or the digital voltmeter with the change in manometer reading. A series of readings for each measuring range on the amplifier gave a linear plot (as shown in figure 2.04) up to full scale deflection of the recorder. The calibration factors obtained from these plots were correct to within ±1%.

The reactor volume was estimated by admitting a known pressure of HCl to the reactor at a known temperature. The HCl was subsequently analysed by the technique described below and the reactor volume could then be calculated. The consistency for three different pressures of HCl was found to be ±0.2%.

Liquid reactants were degassed and distilled into bulbs F or G of figure 2.02. To carry out a reaction the reactant was first heated and the capacity of bulb F or G was sufficient to ensure a rapid ingress of material into the reactor when taps f (or g) and a were opened with b and c closed. 200 torr of material could be introduced into the reactor within 3 secs. In addition the thermal capacity of the system was sufficiently large to ensure thermal equilibration of the material within that time. Consequently very little error arose from initial time and pressure estimation for a normal reaction. The pressure time curve was obtained for the entire reaction.

On completion of a reaction the products could be trapped out in a liquid nitrogen cooled sampling vessel (H or J) on opening b and h (or j) with k shut. Five minutes collection time was allowed and the sample trap was then isolated (using h or j) and the reaction vessel pumped out for a further five minutes by opening k before another reaction was performed. Between runs reactant material still present in the inlet line could be frozen back into the storage bulb and the inlet lines pumped out.

The heated glass stopcocks (a-k) on the vacuum line were lubricated with high vacuum silicone grease. Apiezon N was used on the remaining taps. The system was left in an evacuated condition when not in use and was tested daily for leaks.

2.07 Product Sampling and Analytical Technique.

2.07(a) HCl Analysis

In order to estimate the HCl present in a reaction mixture the products were frozen out into a previously evacuated trap cooled in liquid nitrogen. The liquid-sample trap used for this purpose is shown attached to H in figure 2.02. Five minutes collection time was allowed and the stopcock of the trap was then closed and the trap removed from the vacuum line. Water was carefully added to the contents of the trap which were then allowed to warm up to room temperature. The contents were transferred with washings to a titrating flask and titrated against standard ($\sim$N/50) borax solution using screened methyl red as indicator.

2.07(b) Preparation of Samples for Organic Analysis

The reaction products were frozen out either in a liquid-sample trap as for HCl analysis or in a gas-sample flask which is shown on tap G of figure 2.02. This consists of a 1000 cm^3 bulb fitted with a tap, thimble, and serum cap sampling point.

Liquid samples were prepared by adding a known volume of solvent (normally 5 cm^3) to the trap together with 0.2 cm^3 of water to absorb any HCl present. Removal of HCl is important as its presence can affect analysis by increasing certain peaks. In addition HCl will attack certain G.L.C. column packings (e.g. silicone oil). The contents of the trap were then warmed to room temperature and a fraction (normally 2 cm^3) of the organic phase was extracted by pipette and a known volume of the desired internal standard was added. The sample was then ready for analysis.

The procedure adopted for gas samples was to revaporize the sample into the bulb and carefully pressurize the contents with nitrogen to a pressure of around 820 torr. The internal standard (normally 1 cm^3 of propylene) was injected into the flask. 0.2 cm^3 of water was again added to absorb HCl. Mixing of the contents of the flask was facilitated by the presence of several glass beads. No evidence of poor mixing by this technique was ever indicated.

In every product system analysed it was necessary to ensure that the addition of 0.2 cm^3 of water did not affect the analysis by absorbing the organic species. In the case of ethylene chlorohydrin the addition of water decreased the concentration of this compound in the organic phase. However the addition of 0.2 g of sodium bicarbonate in this particular analysis satisfactorily removed HCl without affecting the chlorohydrin concentration. Water was also not added in the amine analysis work as it would again have leached out excess amine. However under these conditions the HCl is effectively bound up as amine hydrochloride and the need for water is eliminated. In the other systems the addition of water did not affect the analysis.

2.07(c) G.L.C. Conditions used for Analysis

Table 2.01 lists the various columns and the conditions used for the quantitative work performed in this investigation. Details of the type of sample (liquid or gas), the solvent, where applicable, and the internal standard are also included. In analyses (a) and (d) the compounds are arranged in the order of elution under the conditions used.

In addition to the above quantitative analyses semiquantitative analyses were also performed. 'Heavies' peaks which are mentioned at several points in the results were assessed on the PE226 as described in (c) of table 2.01. The facility of this machine to be accurately temperature programmed enabled realistic analysis of heavies peaks to be obtained by programming the machine between 60° and 130°C.

2.07(d) G.L.C. Calibration

In order to reduce the possibility of systematic error the technique adopted for G.L.C. calibration of liquid samples closely resembled the working up of the liquid sample described in the last section. For example in calibrating for (a) in table 2.01 amounts of each component were syringed into 5 cm^3 of CCl_4 contained in a sealed bottle. The weights of each were obtained by difference. 2 cm^3 of the resultant material were pipetted out and 8 mm^3 of trichlorethylene added as internal standard. 1 mm^3 of this solution was injected onto the column for analysis. For packed columns the ratio of peak area (peak height x width at $\frac{1}{2}$ peak height) of each component to that of the standard was measured. In the case of the capillary columns the elution time was too short to give an accurate measurement of the width of the peak and the analysis was performed on a peak height basis. Straight line calibration graphs were obtained for each component using five samples over the range of concentrations studied. Ethylene chlorohydrin (analysis (c) of table 2.01) was the only exception. A curved calibration graph was obtained in this case. This probably arose from the bad tailing effect shown by this compound.

Calibration of gas samples was carried out by injecting known volumes of each gaseous component into a gas sampling flask together with 1 cm^3 of the internal standard. Peak area ratios were again measured using 1 cm^3 injections onto the G.L.C. column. Straight line calibration graphs of peak area ratio against the number of moles of each component were obtained in all cases for five concentrations of each component. The temperature and atmospheric pressure existing during calibration were noted. Subsequent analyses then required small corrections to the volume of internal standard added to the flask owing to small day to day fluctuations in pressure and temperature. In this way the internal standard could always be designated in absolute terms as the number of moles injected into the 1000 cm^3 sampling flask and the peak area ratio could be normalized by reference to a constant number of moles of internal standard.

Random errors for specific G.L.C. calibration points amounted to ±5%. The most likely sources of error appear to be in the G.L.C. instrument itself and in the addition of the internal standard by volume. This accuracy is reflected in the mass balances shown in the results section and errors in G.L.C. analysis would appear to outweigh any other errors previously mentioned.

Small changes in calibration factors with time were also observed. In the case of (a) in table 2.01 over the period of twelve months the change in the average value for any calibration factor was <5% and was possibly caused by a slight deterioration in the column with time. The calibration factors were checked frequently to ensure their accuracy.

2.08 Purity of Materials

Previous work in this laboratory has shown that the presence of small traces of impurity in the starting material can lead to completely spurious results particularly when one is studying free radical reactions of long chain length. Consequently great care was taken over purification procedures.

2.08(a) Purification of βTRI

Readily available material was approximately 98% pure, the impurities consisting mainly of other halohydrocarbons. An initial study of the material also indicated the presence of peroxides. The technique developed to provide pure βTRI was as follows:

(i) βTRI (2000 cm^3) was washed with acidified 25% ferrous sulphate solution (200 cm^3) to remove peroxide, then with 10% potassium carbonate (200 cm^3) to remove acidic impurities and finally with water (2 x 150 cm^3). The βTRI was then dried for several days with 10 g $CaCl_2$.

(ii) βTRI was distilled at atmospheric pressure using a vacuum jacketed column 3' high and packed with glass helices. The top of the column was fitted with a reflux head and the reflux ratio was maintained at around 20 to 1. In this way 150 cm^3 fractions were taken and analysed. The most difficult impurity to remove from βTRI was 1-bromo-2-chloroethane (B.Pt 107°C) which possibly forms an azeotrope. 600 cm^3 of distillate collected late in the distillation were free from this impurity but contained considerable amounts of 1,1,1,2 tetrachloroethane.

(iii) The 600 cm^3 so obtained were redistilled and 300 cm^3 were collected containing no tetrachloroethane. However small quantities of low boiling materials were being formed in the distillation process (probably dichloroethylenes) and these were now the only visible contaminants on G.L.C. analysis.

(iv) A final distillation at reduced pressure (30-39 torr) and a temperature of 30-34°C removed the light boiling impurities and left 220 cm^3 of pure βTRI. G.L.C. analysis demonstrated the complete absence of impurities above the detection level of 10 ppm on both a polar (ODPN) and a non-polar (silicone oil) column. The use of the two columns of different characteristics reduces the possibility of an impurity peak being obscured by the peak from the pure material. The boiling point of this material at 760 torr was 114.2°C compared with the literature values of 113.5°C (58).

The material was stored in a dark cupboard in a brown bottle prepurged with nitrogen. This precaution was thought expedient in view of the peroxide formation which had been previously noted. The material has subsequently been kept for eighteen months without any peroxide or other impurities forming.

The technique of zone-refining has also been applied to βTRI. It was found that zone refining gave a pure specimen of βTRI provided the starting material contained less than 200 ppm of impurity.

However this process proved more time-consuming than distillation and the overall conclusion was that the distillation technique as outlined above provided the most satisfactory method of purification for βTRI.

2.08(b) Ethylene Chlorohydrin Purification

The ECH used in this study was obtained from B.D.H. Ltd. (Laboratory Reagent). The purity was >99%. The material was purified by distillation at atmospheric pressure as with βTRI. The purest 25% of the distillate as indicated by G.L.C. analyses was then subjected to a further distillation at reduced pressure. This satisfactorily removed an impurity boiling just below ECH which appeared to be being formed during the distillation at normal pressure. No impurity peaks were visible in the resultant material when analysed by G.L.C. indicating the absence of impurities above the 10 ppm level. The boiling point of this material was found by vapour pressure measurement to be 129.2°C. This compares with the literature value of 128.8°C (58).

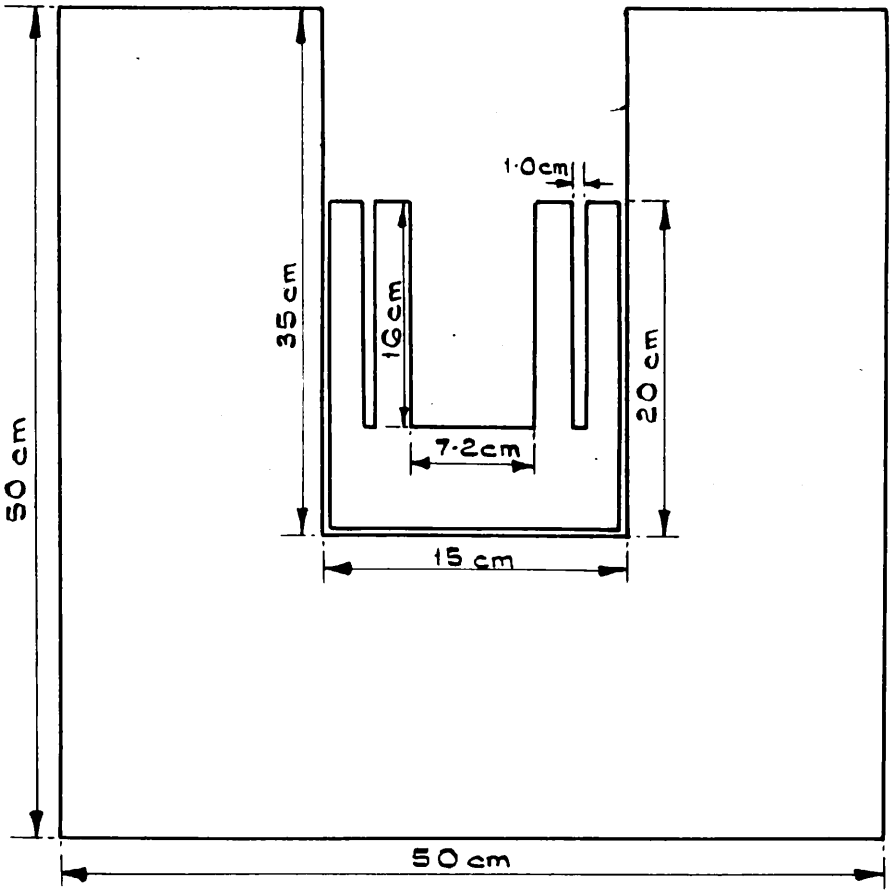
TABLE 2.01 DETAILS OF THE QUANTITATIVE ANALYSES PERFORMED BY G.L.C.

ANALYSIS	INTERNAL STANDARD	SAMPLE TYPE (SOLVENT)	G.L.C. CHARACTERISTICS.
βTRI DECOMPOSITION			
(a)VDC; t-DCE ;c-DCE toluene ; βTRI	TRI	LIQUID (CCl_4)	PERKIN ELMER F11-F.I.D.: N_2 CARRIER GAS 200' SILICONE OIL CAPILLARY COLUMN AT 57°C
(b) AMINES	TOLUENE*	LIQUID (CCl_4)	P.E. F11-F.I.D. N_2 CARRIER GAS 6' PACKED CARBOWAX 1500 on CELITE + AT 57°C
ECH DECOMPOSITION			
(c) ECH	CCl_4	LIQUID (βTRI)	PE 226-F.I.D. N_2 CARRIER GAS 200' SILICONE OIL CAPILLARY COLUMN AT 60°C
(d) CH_4; C_2H_4; C_3H_6 CH_3Cl; VC; CH_3CHO	C_3H_6	GAS -	PYE 104-F.I.D. N_2 CARRIER GAS 6' PACKED PORAPAK T AT 100°C
(e) CO	CH_4*	GAS	PYE 104 -KATHAROMETER He CARRIER GAS 6' MOLECULAR SIEVE AT 30 °C

* A PEAK COMMON TO TWO ANALYSES WAS USED AS A BASIS FOR THE QUANTITATIVE ANALYSIS OF ANOTHER COMPOUND.

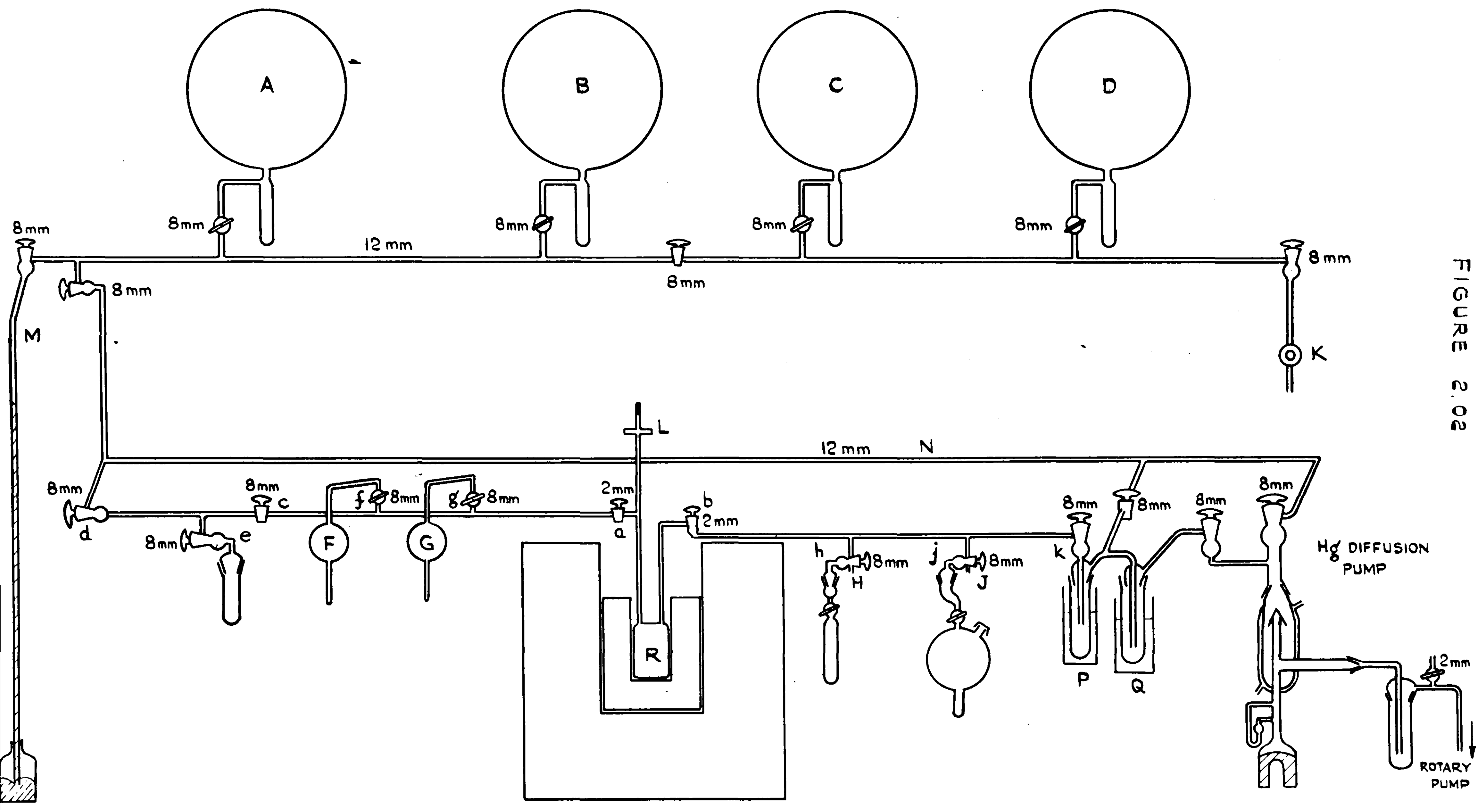
\+ CELITE WAS PREWASHED WITH 10% Na_2CO_3 solution (to prevent tailing of amine peak).

FIGURE 2.01



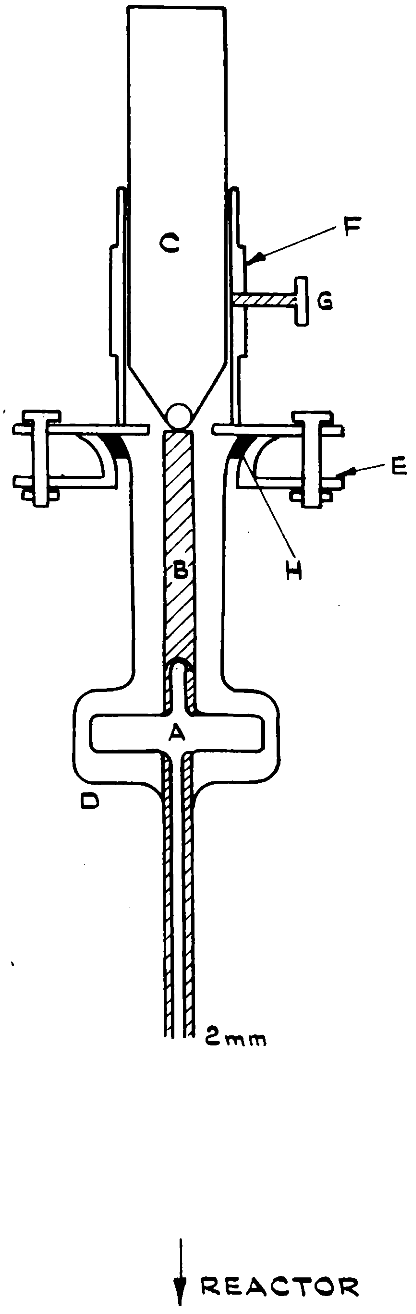
THE REACTOR FURNACE

FIGURE 2.02



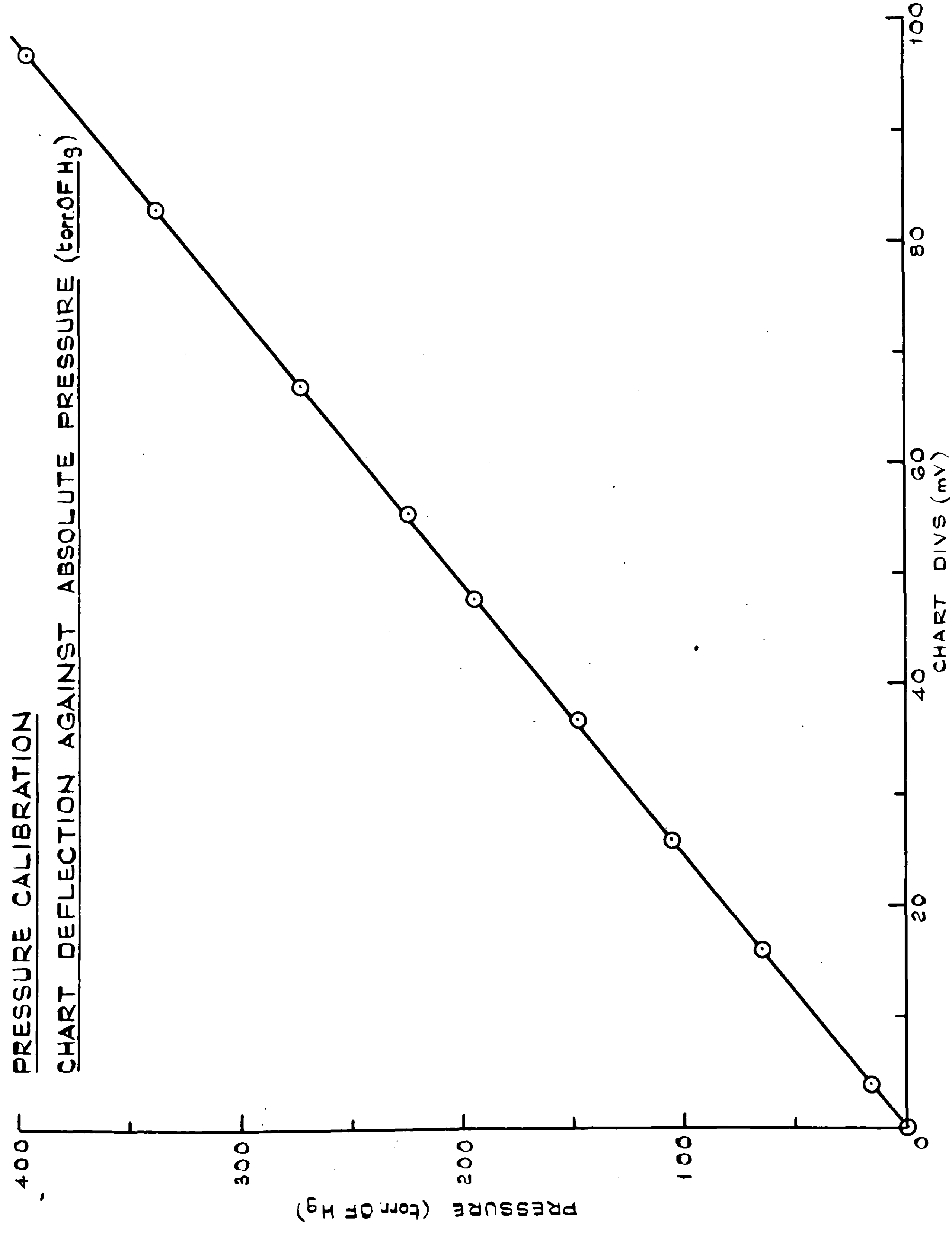
THE VACUUM LINE USED FOR THE KINETIC INVESTIGATION

FIGURE 2.03



THE PRESSURE MEASURING DEVICE

FIGURE 2.04



PRESSURE CALIBRATION

CHART DEFLECTION AGAINST ABSOLUTE PRESSURE (torr OF Hg)

CHAPTER 3

RESULTS FROM THE DECOMPOSITION OF 1,1,2-TRICHLOROETHANE

3.01 Stoichiometry of the Decomposition of βTRI

Previous workers (Chapter 1 section 1.03) have shown that βTRI decomposes at a conveniently measurable rate in the gas phase at temperatures around 400°C to give hydrogen chloride and a mixture of the three isomeric dichloroethylenes.

$$C_2H_3Cl_3 \longrightarrow C_2H_2Cl_2 + HCl \qquad (3.01)$$

In a constant volume reactor, as has been employed in this investigation, such a reaction should involve a twofold increase in pressure and the observed pressure change should be a direct measure of the extent of reaction. This is verified by comparing the pressure change with the HCl formed at various stages of the decomposition. The results are summarised in table 3.01 and figure 3.01. Close agreement is obtained between the % conversions calculated from either the pressure change or from HCl analysis and the theoretical 45° line (shown in figure 3.01) for βTRI decompositions up to 70%.

Alternatively, the % conversion may be calculated from G.L.C. analysis. The results shown in table 3.02 again demonstrate good agreement between the 45° ideal line and the % conversions calculated from pressure change and G.L.C. analysis. It should be pointed out that the % conversion from G.L.C. is based on the relative amounts of βTRI and dichloroethylene obtained by analysis. Comparison of the dichloroethylene amounts with p_o give conversions which do not correspond as closely to the "ideal" but this is associated with mass balance discrepancies which probably arise from small variations in internal standard addition.

A detailed G.L.C. analysis for trace products showed that only two other compounds were formed in decompositions of up to 75%. The first was identified as vinyl chloride from retention time data on two G.L.C.

columns. A linked GLC/Mass Spectroscopic study and NMR analysis identified the second peak as 1,2,3-trichlorobutadiene. At 75% conversion and 391.5°C these products were of the order of 140 ppm and 4,000 ppm respectively.

The absence of significant amounts of by-products coupled with the close agreement between the theoretical slope and the % conversions, as calculated from pressure change, G.L.C. analysis, and HCl analysis, confirms that up to 70% decomposition the reaction is adequately represented by equation 3.01 and that the measurement of pressure change is a valid method of following the reaction.

3.02 Order of Reaction

The concentration of the reacting species for a reaction stoichiometry of 1 mole→2 moles is represented by $(2p_o - p_t)$, where p_o represents the initial pressure and p_t the pressure at time t. First order log plots are obtained by plotting the logarithm of the function $\left(\frac{2p_o - p_t}{p_o}\right)$ against time. Figure 3.03 shows some typical plots obtained for βTRI at three different initial pressures. In individual runs the first order rate coefficient, which is proportional to the gradient of the log plot, increases with increasing decomposition suggesting either that the reaction order is less than one or, alternatively, that autocatalysis is involved. If the reaction order were less than one, the first order rate coefficients would be expected to decrease with increasing initial pressure. The data summarised in table 3.03 and figure 3.04 clearly indicate, however, that the first order rate coefficient estimated from the initial gradient of the log plot actually increases with initial pressure. Figure 3.05 shows a plot of the log of the initial rate against the log of the initial pressure of βTRI. A linear regression analysis on this data gave:-

$$\log \text{rate} = 2.006 \log p_o - 5.466$$

as the best fit. This line is shown in the figure and the gradient demonstrates clearly that the reaction order is second. The consistency of the second order rate coefficient (k_2) for varying initial pressures is shown in the last column of table 3.03. k_2 has the value of 0.142 $l.mol^{-1}sec^{-1}$.

The increase in the first order rate coefficient with decomposition must, therefore, be due to some form of autocatalysis. The effect of the principal products on the rate was briefly examined at 391.5°C. The addition of up to 100 torr of VDC or 1,2-dichloroethylene had a negligible effect on the rate of decomposition of 200 torr of βTRI as estimated from the initial gradient of the log plot. However an acceleration of initial rate was observed in the presence of HCl. Thus the addition of 100 torr of HCl to 200 torr of βTRI enhanced the initial rate of reaction by a factor of 2.

It seems likely therefore that the autocatalysis observed with % conversion of βTRI was associated with the production of HCl.

Table 3.04 shows that variation in initial pressure and in the degree of conversion has no significant effect on the product pattern. In all cases this agrees within the limits of experimental error. These data also feature in figure 3.08 which shows the product pattern against the percentage conversion for various conditions.

3.03 The Reproducibility of Reaction Rate.

The previous section has demonstrated the close correspondence to second order kinetics for the initial rates of a series of runs at varying initial pressures. Table 3.05 indicates that for a relatively constant initial pressure of approximately 214 torr the value of k_2 for a series of runs at 391.5°C was within ± 15% of the average value of 0.14 $l\ mol^{-1}\ sec^{-1}$ which suggests reasonable reproducibility.

However, table 3.06 demonstrates that subsequent experiments have given rate constants falling outside these limits and variations of up to ±50% have been observed. Previous workers (17, 47) have noted similar irreproducibility in βTRI decompositions. The only explanation of this effect appears to be an extreme sensitivity of the reaction to the condition of the carbonaceous coating which forms on the surface of the reactor. It should be pointed out that this fluctuation appears to be entirely random and that the values of k_2 shown in tables 3.04 and 3.05 represent a good average value. Furthermore, table 3.06 demonstrates that even though appreciable scatter can exist in the reaction rate there is still no significant variation in the distribution of the dichloroethylenes produced in the decomposition. These results are also plotted in figure 3.08.

3.04 The Effects of Temperature

The effect of temperature on both reaction rate and product distribution was examined. The results are summarised in table 3.07. There is a small but significant decrease in the proportion of VDC formed at higher temperatures indicating a decrease in the selectivity of formation of this compound. The difference between the mean values of product distribution at 391.5°C and 453.5°C would suggest that the activation energy for forming VDC is $\sim$ 2.5 kcals/mole less than that for forming the symmetrical dichloroethylene. However, the measured difference is so small that the experimental error from G.L.C. analysis puts large limits of error on this value (±1.5 kcals/mole). The precise significance of this temperature dependence is discussed later.

The average value for the observed rate constants is also shown in table 3.07. At the higher temperatures these were too fast to measure accurately. Owing to the irreproducibility of rate at 391.5°C as described in section 3.03 any estimate of Arrhenius parameters from activation energy plots would require a considerable number of experiments. This appeared unjustified in the present study and no attempt has been made to estimate the activation energy or the pre-exponential factor for βTRI.

3.05 Effects of Packing

The effect of surface was studied by comparing the results from the empty vessel (surface to volume ratio = 0.87 cm^{-1}) with results from a similar reactor containing five concentric glass cylinders (S/V = 5.06 cm^{-1}). The results are shown in tables 3.08(a) and (b). The product distribution is unaffected by the increased surface (table 3.08(b)) at 391.5°C or 453.5°C. The values obtained at 391.5°C are also included in figure 3.08.

The second order rate constant is shown in table 3.08(a). At the lower temperature second order kinetics are again observed, the value of k_2 remaining constant from 200-400 torr initial pressure. The rate in the packed vessel at both temperatures is about two thirds of the average value obtained in the empty vessel. This may indicate a positive decrease in rate with packing but the values obtained are within the observed scatter of results shown in table 3.06 and the significance of the observed decrease is, therefore, not proven.

3.06 The Addition of Carbon Tetrachloride as a Chain Accelerating Agent.

Carbon tetrachloride is known to exert a powerful accelerating influence on decompositions of chlorocarbons which proceed via a radical chain mechanism (75). The results from small additions ($<$4 torr) of CCl_4 are summarised in table 3.09.

Owing to the possibility of a change in the order of reaction with added CCl_4 a comparison of the initial rate of reaction for initial pressures $\sim$160 torr, has been shown in the table in preference to a comparison of rate constants. Figure 3.06 shows the increase in rate obtained from added CCl_4 and indicates that 3.44 torr (2.15%) of CCl_4 produce a 15-fold increase in initial rate.

However, the addition of CCl_4 causes no change in the product distribution (table 3.09 and figure 3.08) when compared to the normal decomposition.

A plot of the logarithm of the initial rate against the logarithm of the CCl_4 concentration is shown in figure 3.07. The line drawn through these points has a slope of 0.75 and represents the order of reaction with respect to CCl_4. It should be pointed out that this value depends on the accuracy of measurement of the fast rates involved and also on the assumption that negligible amounts of CCl_4 are consumed in the initial stages of reaction.

3.07 The Addition of Inhibitor

In a system which reacts predominantly by a free radical chain process the addition of a chain inhibiting agent reduces the rate by preferentially reacting with the chain propagating species thereby quenching the chain reaction. In general the process of inhibition may be represented by the equation:-

$$RH + X^{\bullet} \xrightarrow[\longleftarrow]{\hspace{2cm}} R^{\bullet} + HX$$

where $R^{\bullet}$ is a relatively unreactive radical in comparison with X° . Toluene and propylene are recognized as being powerful chain inhibitors as they will undergo hydrogen atom transfer to form the benzyl and allyl radicals respectively. Both these radicals are relatively stable and, therefore, less reactive toward chain propagation.

3.07(a) The Addition of Toluene

The results obtained from the addition of toluene to βTRI at 453.5°C are shown in table 3.10. The addition of small amounts of toluene caused a dramatic reduction of reaction rate and the higher temperature was required to obtain measurable rates of reaction. For a constant initial pressure of βTRI the rate of reaction can be represented by the first order rate constant (k_1). The decrease in k_1 with toluene addition is shown in figure 3.09. 1% toluene decreases the rate by a factor of 40 but after 3.5% addition the rate appears to reach a limiting value which does not change for additions of toluene up to 11%. Furthermore the log plots obtained from the minimum rate conditions were linear up to 10%

conversion which was the highest level studied.

The table below indicates that the first order rate coefficients estimated from the gradients of the log plots were constant for a range of initial pressures (p_o) of βTRI in the presence of > 8% toluene.

p_o βTRI (torr)	101.0	156.9	204.1	252.5	291.9	353.6
% TOLUENE	20.5	13.2	11.2	8.2	12.2	12.6
$k_1 \times 10^4 sec^{-1}$	1.62	1.57	1.58	1.61	1.65	1.62

k_1 FOR VARIOUS INITIAL PRESSURES OF βTRI IN THE PRESENCE OF TOLUENE

First order kinetics are indicated for the inhibited decomposition of βTRI. The change from second order behaviour for the uninhibited decomposition to first order in the inhibited decomposition is strong evidence for an accompanying change in the principal mode of decomposition of βTRI.

The effect of toluene on the absolute amounts of dichloroethylenes formed in five minute reactions is shown in figure 3.10. This graph provides a more sensitive indication than figure 3.09 of the amounts of toluene necessary to attain maximum inhibition and indicates that 6% toluene is required to produce limiting values in the amounts of dichloroethylene formed for a p_o of 200 torr. These values are then maintained for toluene concentrations up to 12% indicating the absence of any substantial side reaction involving toluene and dichloroethylene. The amount of VDC formed in the presence of toluene has fallen to a particularly low level and a graph of the % product distribution (figure 3.11) indicates a reduction to around 6% for toluene concentrations > 6% compared to 41.4% in the uninhibited reaction at this temperature. Another interesting feature of figure 3.11 is the greater relative increase in cis-dichloroethylene compared to the trans isomer. Toluene would be expected to inhibit the cis/trans isomerisation process (52) and the direction of change indicates that the cis dichloroethylene is the preferred product from the inhibited gas phase decomposition.

3.07(b) The Addition of Propylene

Table 3.11 shows that the addition of propylene to βTRI also caused a severe retardation in rate and a change in the product pattern. Figure 3.09 demonstrates that the decrease in rate with propylene coincides with the curve obtained previously for toluene and that a similar minimum value is obtained for propylene concentrations of $> 2\%$.

The absolute amounts of dichloroethylenes produced from five minute reactions are shown in figure 3.10. Although the general correspondence with the toluene results is good, the VDC values do fall slightly lower for propylene than for toluene. This is reflected in the product distribution graph of figure 3.12 which indicates a minimum value of 4.3% compared to 5.8% with toluene whilst the cis/trans values are in good agreement (59.5%/36.2% for propylene; 57.7%/36.5% for toluene).

The lower level of % VDC obtained with propylene might have arisen from a preferential reaction of VDC with propylene (or more probably with the allyl radical). However experiments carried out with mixtures of VDC and propylene at 453.5°C did not indicate the formation of any side product. It seems highly probable therefore that the observed differences in the VDC level obtained in the presence of toluene and propylene have arisen from a small amount of residual chain reaction.

Between 6-11% concentrations of inhibitor (figure 3.10) the amount of VDC produced is constant for each inhibitor used. This implies that in this range of inhibitor concentration chlorine atoms are making a negligible contribution to chain propagation. It follows that the residual chain activity must have arisen from chain propagation via benzyl or allyl radicals. On this basis the observed difference in the minimum levels of VDC obtained suggests that benzyl radical is slightly more reactive than allyl in hydrogen abstraction from βTRI.

3.07(c) Formation of Minor Products in the Presence of an Inhibitor.

Detailed GLC analysis of the products from five minute reactions indicated the presence of vinyl chloride in amounts below 1% of the total material present. No other compounds were observed.

For extended reactions in the presence of inhibitor, a graph of the amounts of product formed against pressure change (figure 3.13) showed negligible fall off up to 25% conversion (30 minute reaction time) in the presence of 10% propylene. This implies that only minor amounts of byproduct could be being formed. In contrast to the uninhibited decomposition, no 1,2,3-trichlorobutadiene was detected by GLC analysis when either inhibitor was present. However, two new peaks were observed. These gave different retention times for toluene and propylene and in the case of toluene further examination of these products by GLC/MS link showed them to be isomeric compounds of formula C_9H_9Cl. The same two compounds have been observed in the products of reaction between toluene and 1,2-dichloroethylene at 453.5°C and have been assigned as the cis and trans isomers of 1-chloro-3-phenyl prop-1-ene. By contrast the reaction of vinylidene chloride with toluene is slower and produces a different C_9H_9Cl none of which was detected in the trace analysis.

3.08 The Addition of Chain Transfer Agents

3.08(a) Hydrogen Sulphide

The effect of H_2S addition on the rate of decomposition of βTRI is shown in figure 3.09 and table 3.13. As in the case of more typical inhibitors the first order rate coefficient decreases rapidly with increasing additions although not as sharply as with toluene or propylene.

Figure 3.14 shows the absolute amounts of dichloroethylene formed in five minute reactions with varying amounts of H_2S (see table 3.13).

The fall off in VDC formed is not as great as that obtained from toluene addition and a slight enhancement is indicated at 10% H_2S addition. In contrast the amounts of 1,2-dichloroethylene formed fall off at 10% H_2S after appearing to be levelling out at 5% addition. A secondary reaction of these compounds with H_2S is indicated and several new peaks were observed in GLC analysis. The identification of thiophene and chlorothiophenes by GLC/Mass Spectroscopic link substantiates this theory. The thiophene was confirmed by retention time data on our GLC. These compounds probably arise from $SH^\bullet$ addition to two molecules of dichloroethylene with $Cl^\bullet$ elimination followed by ring closure with HCl or Cl_2 elimination.

The effect of H_2S on the product distribution is shown more clearly in figure 3.15. The VDC is only suppressed to a level of around 30% (compare toluene in figure 3.11) at 4% H_2S addition before beginning to rise. As explained above this rise is due to a small enhancement in VDC formation and a fall off in the other products due to secondary reactions.

The decrease in rate with H_2S obviously implies some form of suppression of the normal chain activity. The proportion of reaction occurring via a molecular process thus becomes important. Assuming that the molecular reaction is represented by the <u>minimum</u> values shown in figure 3.10 then subtraction of these amounts from the data of figure 3.14 will provide a measure of the amounts and distribution of the products being formed by the residual chain activity present in H_2S addition. Using the values at 5% H_2S addition, as this represents the minimum value for VDC, the proportion of VDC in the product distribution from radical chain is 62% compared to the value of 41.4% obtained from the normal chain decomposition at 453.5°C. This suggests that the addition of H_2S has increased the selectivity of the radical chain process towards VDC formation. This is further discussed in Chapter 6.

3.08(b) Hydrogen Bromide

The results of experiments with added HBr on the decomposition of βTRI at 391.5°C are summarised in table 3.14. Figure 3.16 shows a marked increase in rate for additions of up to 5% HBr. Above this level the rate becomes independent of HBr concentration.

Figure 3.17 shows the amounts of product formed with increasing HBr additions. The VDC continues to rise for HBr additions up to 10% whereas the 1,2-dichloroethylenes remain constant after 1% addition. The good mass balances shown in table 3.14 demonstrate the absence of major secondary reactions removing dichloroethylenes. In addition run T809 was of 10 minutes duration and 90% conversion but the product distribution is in excellent agreement with T800, an equivalent run of five minutes duration. Again the inference is that negligible side reaction involving the dichloroethylenes is occurring. The fate of HBr in the system was not investigated.

Figure 3.18 shows the increasing proportion of VDC in the products as the HBr level increases. At 10% HBr the VDC has increased to 60% compared to the value of 43.8% obtained in the absence of HBr (T703). Thus HBr is both catalyzing the overall decomposition and selectively enhancing the VDC formation. This result is discussed in more detail in Chapter 6.

TABLE. 3.01 COMPARISON OF % CONVERSION FROM Δp AND FROM HCl ANALYSIS AT 391.5°C

RUN	po (torr)	Δp (torr)	HCl (torr)	% CONVERSION	
				Ex Δp	Ex HCl
T267	196.2	1.9	1.9	1.0	1.0
T279	205.4	11.9	12.4	5.8	6.0
T280	208.8	24.7	24.9	11.8	11.9
T268	178.9	33.6	33.7	18.8	18.8
T278	199.7	46.1	45.5	23.1	22.8
T277	214.3	50.9	52.6	23.8	24.6
T271	193.1	66.4	65.8	34.4	34.1
T284	206.0	78.0	78.2	37.9	38.0
T273	193.0	80.2	82.4	41.6	42.7
T275	182.8	90.9	93.2	49.7	51.0
T262	222.0	115.6	112.7	52.0	50.8
T263	213.1	141.7	139.6	66.5	65.5

TABLE.3.02. COMPARISON OF % CONVERSION FROM Δp AND FROM G.L.C. ANALYSIS AT 391.5°C

RUN	po (torr)	Δp (torr)	G.L.C. ANALYSIS (torr)		% MASS BALANCE	% CONVERSION	
			pTRI	$\Sigma C_2H_2Cl_2$		Ex Δp	Ex G.L.C.
T281	200.0	14.9	181.2	16.1	98.6	7.5	8.2
T288	198.7	19.7	173.2	22.4	98.5	9.9	11.5
T282	209.8	24.4	183.4	26.7	100.2	11.6	12.7
T301	48.9	8.3	38.2	7.8	94.0	17.0	16.9
T283	202.4	42.4	152.9	47.3	98.9	20.9	23.4
T299	268.5	64.6	200.9	65.6	99.3	24.1	24.6
T541	206.0	65.3	141.4	68.6	102.0	31.7	32.7
T544	210.5	68.1	148.5	73.6	105.5	32.4	33.1
T285	190.5	65.8	116.1	64.8	95.0	34.5	35.8
T300	105.0	42.4	64.3	41.3	100.6	40.4	39.1
T274	193.0	89.5	107.1	99.2	106.9	46.4	48.0
T287	193.6	135.3	60.3	133.9	100.3	69.9	69.0
T293	187.8	126.1	58.9	125.4	98.1	67.1	68.0

TABLE 3.03 EFFECT OF INITIAL PRESSURE ON FIRST AND SECOND ORDER RATE COEFFICIENT AT 391.5°C

RUN	po		$k_1 x 10^4$ (sec^{-1})	INITIAL RATE = $k_1 p_o$ ($torr.sec^{-1}$)	log p_o	log(rate)	k_2 ($l,mol^{-1} sec^{-1}$)
	(torr)	$mole.l^{-1}$ x 10^3					
T210	81.1	1.95	2.94	.0238	1.909	-1.623	.151
T212	142.0	3.41	4.70	.0667	2.152	-1.176	.138
T207	181.0	4.34	6.80	.123	2.258	-0.910	.156
T208	210.0	5.04	7.62	.160	2.322	-0.796	.151
T214	210.2	5.04	7.02	.148	2.323	-0.831	.139
T216	215.1	5.16	7.95	.171	2.333	-0.767	.154
T209	216.0	5.18	7.82	.169	2.334	-0.772	.151
T215	218.9	5.25	6.75	.148	2.340	-0.830	.129
T211	284.3	6.82	10.70	.304	2.454	-0.517	.157
T213	371.8	8.92	12.00	.446	2.570	-0.351	.135

TABLE. 3.04 EFFECT OF THE VARIATION IN p_o ON THE PRODUCT DISTRIBUTION AT 391.5°C

RUN	p_o(torr)	% CONVERSION	% PRODUCT DISTRIBUTION		
			VDC	t-DCE	c-DCE
T226	237.0	32.9	46.0	22.9	31.1
T299	268.5	24.1	44.1	24.4	31.5
T300	105.0	40.4	43.8	24.6	31.6
T301	48.9	17.0	46.1	23.0	30.9

TABLE 3.05 THE VARIABILITY IN k_2 AT 391.5°C FOR A CONSTANT p_o (213.6± 5.3 torr)

RUN	p_o		k_2
	(torr)	(mole.l.$^{-1}$)	(l. mole^{-1} sec^{-1})
T208	210.0	5.04 x 10^{-3}	.151
T209	216.0	5.18 x "	.151
T214	210.2	5.04 x "	.139
T215	218.9	5.25 x "	.128
T216	215.1	5.16 x "	.154
T218	215.1	5.16 x "	.161
T239	208.3	5.00 x "	.143
T240	216.0	5.18 x "	.144
T244	210.0	5.04 x "	.123
T245	216.3	5.19 x "	.119
AVERAGE	213.6 ±5.3	(5.13±0.13)x 10^3	.140 ±.021

TABLE 3.06 EFFECT OF VARIABILITY IN k_2 ON THE PRODUCT DISTRIBUTION OBTAINED AT 391.5°C

RUN	p_o		k_2	%	% PRODUCT DISTRIBUTION		
	(torr)	(mole.l^{-1} x 10^{-3})	(l.mole^{-1}sec^{-1})	CONVSN.	VDC	t-DCE	c-DCE
T245	216.3	5.19	.119	59.8	45.4	24.7	29.9
T274	193.0	4.63	.189	46.4	45.3	24.9	29.8
T282	209.8	5.04	.081	11.6	45.2	23.4	31.4
T283	202.4	4.86	.074	21.0	44.7	24.8	30.5
T287	193.6	4.65	.220	69.9	44.7	25.0	30.3
T541	206.0	4.94	.115	31.6	44.5	22.4	33.1
T544	210.5	5.05	.158	32.4	45.0	22.3	32.7
AVERAGE	205±12	4.94±.29	.137±.083		45.0±0.5	23.8±1.5	31.2±1.9

TABLE 3.07 EFFECT OF TEMPERATURE ON k_2 AND PRODUCT DISTRIBUTION

TEMP °C	k_2 ($l.mol^{-1}.sec^{-1}$)		% PRODUCT DISTRIBUTION				$^1/_T \times 10^3$	$\log \frac{k_{VDC}}{k_{1,2-DCE}}$
	VALUE	NO OF RUNS AVGD.	VDC	t-DCE	c-DCE	NO OF RUNS AVGD.		
391.5	0.142 ± .04	11	45.0 ± 0.5	23.8 ± 1.5	31.2 ± 1.9	8	1.505	-.087
413.5	0.421 ± .02	2	42.8	23.9	33.3	1	1.457	-.125
453.5	2.430 ± .50	5	41.4 ± 0	26.0 ± 0.2	32.6 ± 0.2	2	1.378	-.151

TABLE 3.08(a) EFFECT OF PACKING ON k_2

RUN	TEMP °C	p_o (torr)	p_o (mole.l^{-1})	k_2 (l.mol.$^{-1}$ sec^{-1})
T250	391.5	203.6	4.89×10^{-3}	.114
T249	"	205.4	4.93 x "	.108
T254	"	224.3	5.38 x "	.089
T253	"	233.1	5.59 x "	.087
T252	"	260.9	6.26 x "	.084
T251	"	396.0	9.50 x "	.100
AVERAGE				.097 ± .017
UNPACKED VESSEL				.142 ± .040
T694	453.5	196.4	4.32×10^{-3}	1.42
T697	"	199.8	4.39 x "	1.56
T698	"	204.2	4.49 x "	1.46
T695	"	204.6	4.50 x "	1.56
AVERAGE				1.50 ± 0.08
UNPACKED VESSEL				2.43 ± 0.5

TABLE 3.08(b) EFFECT OF PACKING ON THE PRODUCT DISTRIBUTION.

RUN	% CONVSN	TEMP °C	% PRODUCT DISTRIBUTION		
			VDC	t-DCE	c-DCE
T253	42.0	391.5	46.1	23.1	30.8
UNPACKED		"	45.0 ± 0.5	23.8 ± 1.5	31.2 ± 1.9
T694	87.6	453.5	42.0	24.6	33.4
UNPACKED		"	41.4	25.9	32.7

TABLE 3.09 EFFECT OF CCl_4 ON RATE AND PRODUCT RATIO AT 391.5°C

RUN	p_o (torr)	p_{CCl4} (torr)	Initial Rate (torr.sec^{-1})	$\log_{10}p_{CCl4}$	log (rate)	% CONVN	% PRODUCT DISTRIBUTION		
							VDC	t-DCE	c-DCE
STANDARD	166.0	-	.100	-	-		45.0	23.8	31.2
T307	166.4	0.53	.383	-0.274	-0.417	20.9	45.6	24.3	30.1
T304	167.0	1.34	.752	+0.126	-0.125	51.4	44.2	25.1	30.7
T303	166.0	1.84	1.038	+0.265	+0.016	43.1	45.2	25.0	29.8
T305	159.3	3.44	1.431	+0.537	+0.157	67.3	45.1	25.2	29.7

TABLE 3.10 EFFECT OF TOLUENE ON RATE (as k_1) AND PRODUCT FORMATION FOR 5 MIN REACTIONS AT 453.5°C

RUN	p_o (torr)	% TOLUENE	$k_1 x10^4$ (sec^{-1})	PRODUCT ANALYSIS(MOLESx10^4) (% PRODUCT DISTRIBUTION)				p_o (molesx10^4)	% MASS BALANCE
				βTRI	VDC	t-DCE	c-DCE		
UN-INHBD	200	0	107.0		(41.4)	(25.9)	(32.7)		
T753	202.8	0.22	3.72	13.720	.453 (27.2)	.471 (28.3)	.739 (44.5)	14.6	105.2
T757	211.8	0.42	2.86	13.068	.236 (20.1)	.353 (30.0)	.587 (49.9)	15.2	94.0
T347	209.0	0.66	2.73	14.132	.200 (17.4)	.377 (32.8)	.572 (49.8)	15.0	101.8
T348	210.0	1.6	2.05	13.365	.094 (11.0)	.303 (35.4)	.458 (53.6)	15.1	94.5
T349	208.5	1.6	2.16	13.991	.093 (10.7)	.310 (35.6)	.468 (53.7)	15.0	99.0
T346	198.2	1.8	2.21	14.180	.092 (11.2)	.288 (35.2)	.439 (53.6)	14.4	104.0
T345	201.1	3.5	1.82	14.429	.052 (7.3)	.263 (36.6)	.403 (56.1)	14.5	104.2
T392	182.5	6.5	1.96	12.342	.048 (6.8)	.269 (37.1)	.397 (56.1)	13.0	100.3
T344	204.4	7.3	1.96	14.457	.042 (5.9)	.262 (36.8)	.408 (57.3)	14.7	103.3
T422	200.9	8.2	1.80	13.049	.037 (5.5)	.254 (37.6)	.385 (56.9)	14.4	95.4
T621	206.0	9.3	1.85	13.449	.035 (5.2)	.233 (34.9)	.399 (59.9)	14.8	95.2
T737	204.0	9.7	1.73	14.076	.035 (5.0)	.239 (34.9)	.411 (60.1)	14.7	100.2
T386	205.4	10.2	1.68	14.221	.040 (6.0)	.240 (35.7)	.391 (58.3)	14.8	100.8
T565	201.6	10.5	1.75	13.226	.035 (4.9)	.262 (36.8)	.416 (58.3)	14.5	96.0
T353	205.0	11.2	2.05	14.330	.037 (5.7)	.228 (35.1)	.385 (59.2)	14.8	101.0

TABLE 3.11 EFFECT OF PROPYLENE ON RATE (as k_1) AND PRODUCT FORMATION FOR 5 MIN REACTIONS AT 453.5°C

RUN	p_o (torr)	% C_3H_6	$k_1 x10^4$ (sec^{-1})	PRODUCT ANALYSIS (molesx10^4) (% PRODUCT DISTRIBUTION)					
				βTRI	VDC	t-DCE	c-DCE	(molesx10^4)	BALANCE
UN-INHBD.	200	0	107.0		(41.4)	(25.9)	(32.7)		
T742	200.3	0.22	11.9	9.119	2.122 (38.7)	1.394 (25.4)	1.973 (35.9)	14.4	101.4
T744	207.3	0.95	2.59	15.018	.162 (15.8)	.323 (31.4)	.541 (52.8)	14.9	107.2
T740	206.9	1.8	1.71	14.681	.060 (7.5)	.275 (34.8)	.456 (57.7)	14.9	104.0
T739	206.4	4.2	1.75	14.772	.036 (4.9)	.256 (35.5)	.431 (59.6)	14.9	104.0
T745	203.2	6.0	1.57	14.280	.019 (3.1)	.222 (35.3)	.388 (61.6)	14.6	102.0
T755	204.4	6.5	1.83	14.298	.030 (4.4)	.240 (36.2)	.394 (59.4)	14.7	101.8
T754	206.4	8.1	1.75	15.776	.030 (4.4)	.246 (36.1)	.409 (59.5)	14.9	105.3
T741	196.2	10.4	1.77	13.849	.027 (3.8)	.253 (36.4)	.414 (59.8)	14.1	102.8

TABLE 3.12 PRODUCT FORMATION AND PRESSURE INCREASE WITH TIME AT 453.5°C IN THE PRESENCE OF ~10% PROPYLENE

RUN	p_o (torr)	% C_3H_6	TIME (mins)	Δp (torr)	% CONVSN.	PRODUCT ANALYSIS (moles x 10^4)			
						βTRI	VDC	t-DCE	c-DCE
T741	196.2	10.4	5	10.6	5.3	13.849	.027	.253	.414
T760	203.6	9.7	10	20.0	9.8	14.013	.036	.481	.801
T761	199.5	10.3	15	27.7	13.9	12.796	.063	.747	1.205
T763	204.8	10.0	20	36.3	17.7	11.506	.091	1.000	1.608
T765	203.6	10.3	25	46.5	22.8	10.513	.114	1.266	2.005
T762	185.2	11.3	30	49.8	26.9	9.862	.130	1.341	2.137

TABLE 3.13 EFFECT OF H_2S ON RATE (as k_1) AND PRODUCT FORMATION FOR 5 MIN. REACTIONS AT 453.5°C

RUN	p_o (torr)	% H_2S	$k_1 x10^4$ (sec^{-1})	PRODUCT ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)				p_c molesx10^4)	% MASS BALANCE
				βTRI	VDC	t-DCE	c-DCE		
STANDARD	200.0	0	107.0		(41.4)	(25.9)	(32.7)		
T342	201.7	0.49	31.4	-	-	-	-		
T341	201.7	0.52	10.4	-	-	-	-		
T334	187.8	1.20	5.9	-	-	-	-		
T333	205.4	1.29	5.9	11.550	1.03 (34.8)	0.86 (29.0)	1.07 (36.2)	14.8	98.0
T340	201.0	2.7	3.34	12.65	0.47 (30.8)	0.44 (29.1)	0.61 (40.1)	14.5	97.8
T335	215.0	4.8	2.81	13.62	0.44 (30.0)	0.46 (30.9)	0.58 (39.1)	15.4	98.0
T336	203.5	10.6	3.59	13.27	0.47 (38.9)	0.33 (27.0)	0.41 (34.1)	14.6	99.1

TABLE 3.14 EFFECT OF HBr ON THE INITIAL RATE AND ON THE PRODUCT FORMATION FOR 5 MIN. REACTIONS AT 453.5°C

RUN	p_o (torr)	% HBr	INITIAL RATE (torr.sec^{-1})	PRODUCT ANALYSIS (molesx10^4) (% PRODUCT DISTRIBUTION)				p_o (molesx10^4)	% MASS BAL:
				βTRI	VDC	t-DCE	c-DCE		
T793	203.6	0	.113	13.014	1.377 (43.8)	.702 (22.3)	1.066 (33.9)	16.0	100.5
T794	205.6	0.68	.736	7.392	3.852 (44.4)	2.037 (23.5)	2.787 (32.1)	16.2	99.4
T795	197.9	5.32	1.168	3.808	6.169 (53.9)	2.227 (19.5)	3.035 (26.6)	15.6	97.5
T803	199.1	6.81	1.105	4.078	6.454 (56.2)	2.122 (18.5)	2.912 (25.3)	15.7	99.0
T813	215.8	8.96	1.245	-	-	-	-		
T810	202.8	9.78	1.213	-	-	-	-		
T800	199.1	9.90	1.085	3.858	7.065 (59.7)	2.017 (17.0)	2.761 (23.3)	15.7	100.0
	10 MINUTE REACTION								
T809	206.4	9.69	1.205	1.678	8.327 (59.8)	2.359 (17.0)	3.240 (23.2)	16.2	96.3

FIGURE 3.01

β TRI DECOMPOSITION AT 391·5°C

PRODUCTION OF HCl COMPARED TO THE PRESSURE CHANGE

[SOLID LINE INDICATES THE IDEAL]

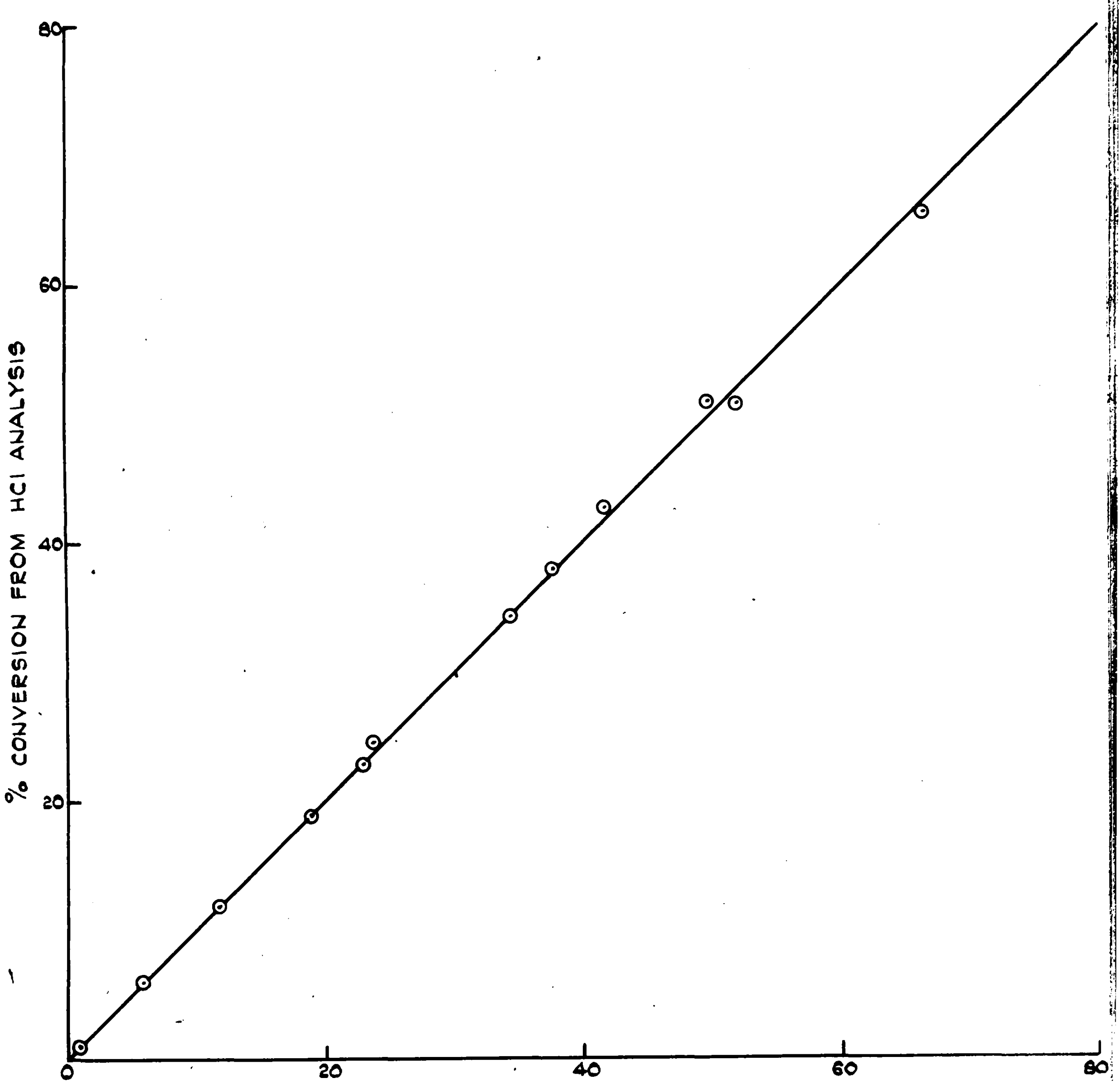


FIGURE 3.02

β TRI DECOMPOSITION AT 391·5°C

PRODUCTION OF DICHLOROETHYLENES COMPARED TO THE PRESSURE CHANGE

[SOLID LINE INDICATES THE IDEAL]

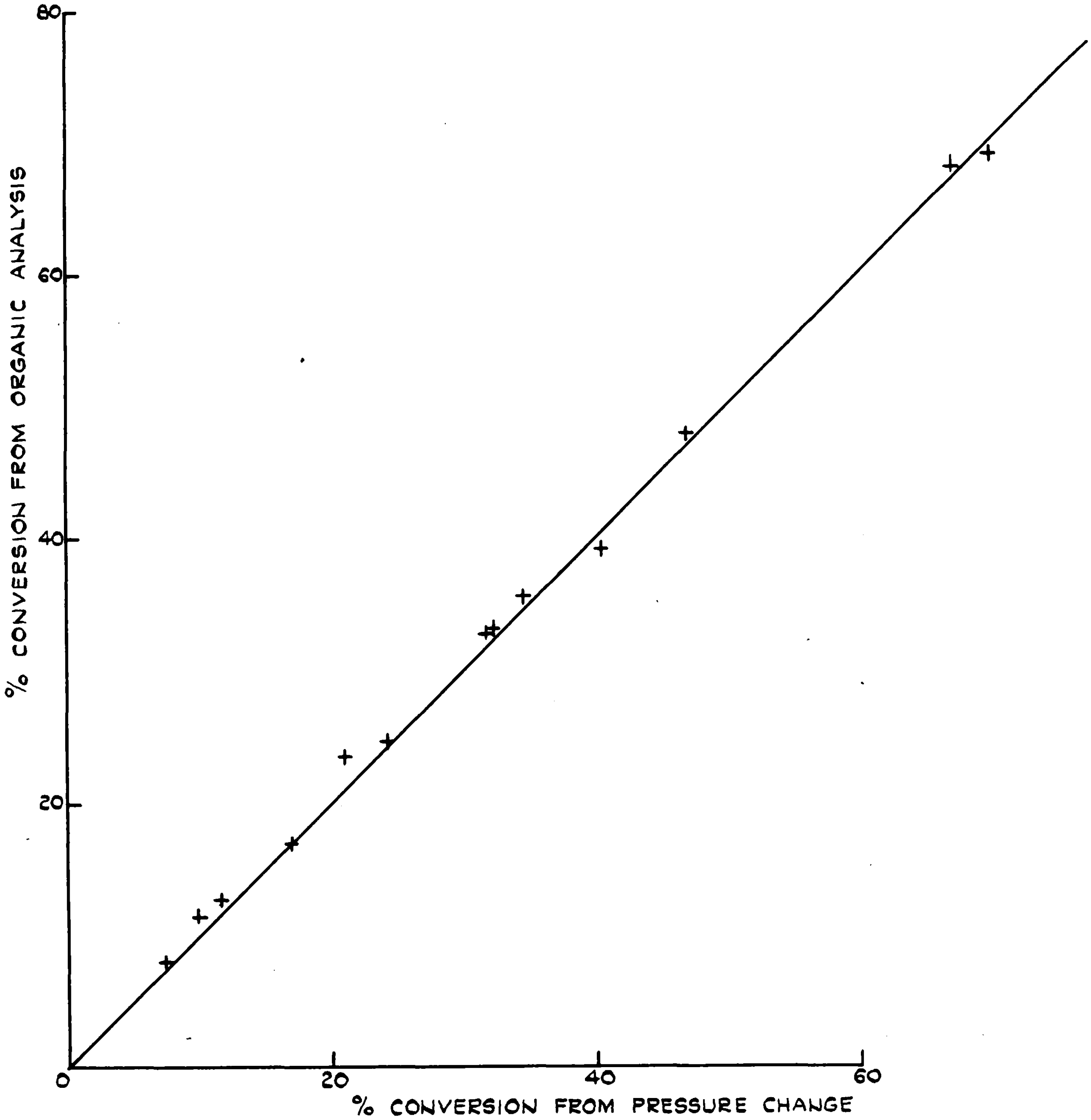
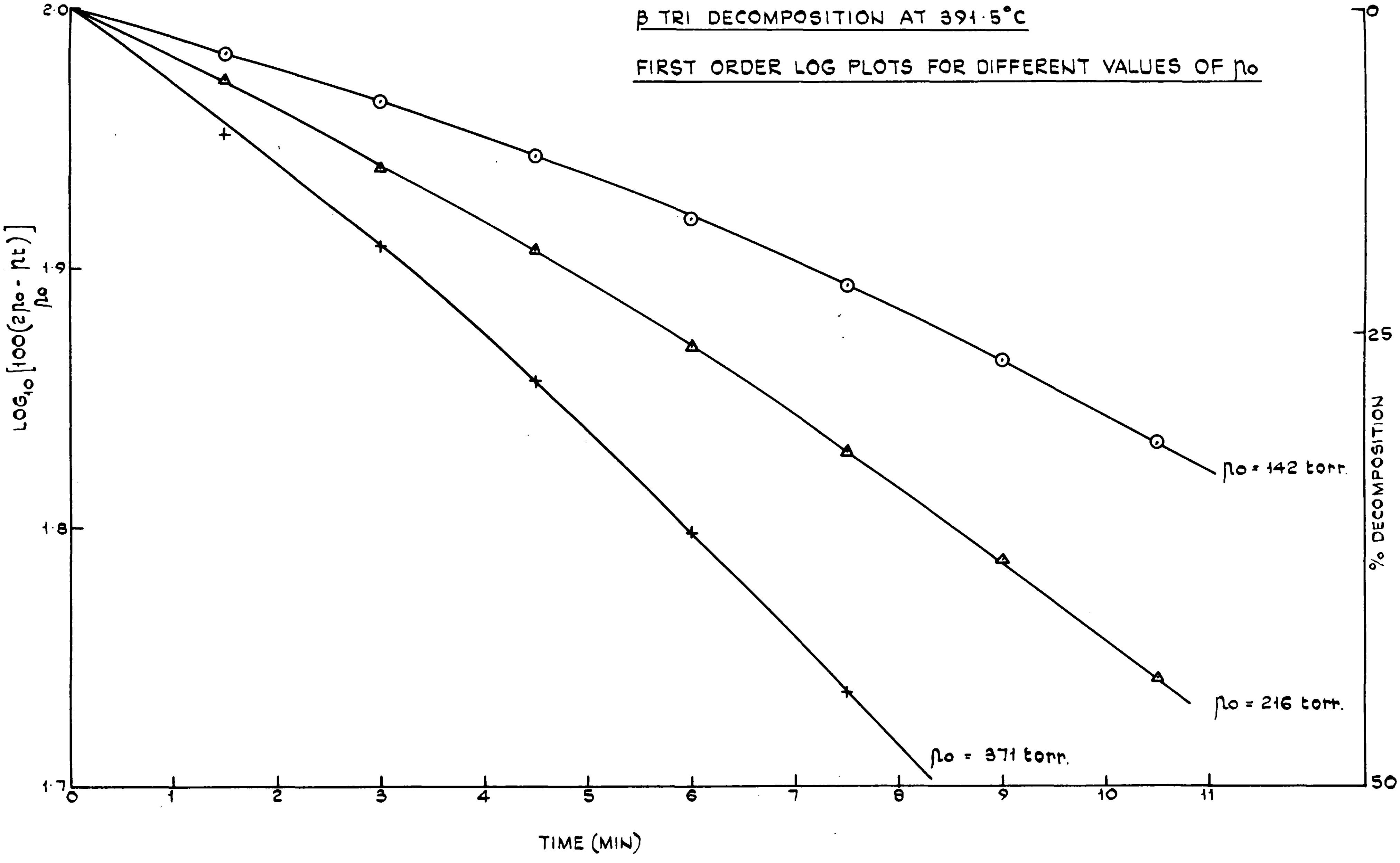


FIGURE 3.03



β TRI DECOMPOSITION AT 391·5°C

FIRST ORDER LOG PLOTS FOR DIFFERENT VALUES OF p_o

FIGURE 3.04

β TRI DECOMPOSITION AT 391·5°C

VARIATION OF INITIAL RATE WITH INITIAL PRESSURE

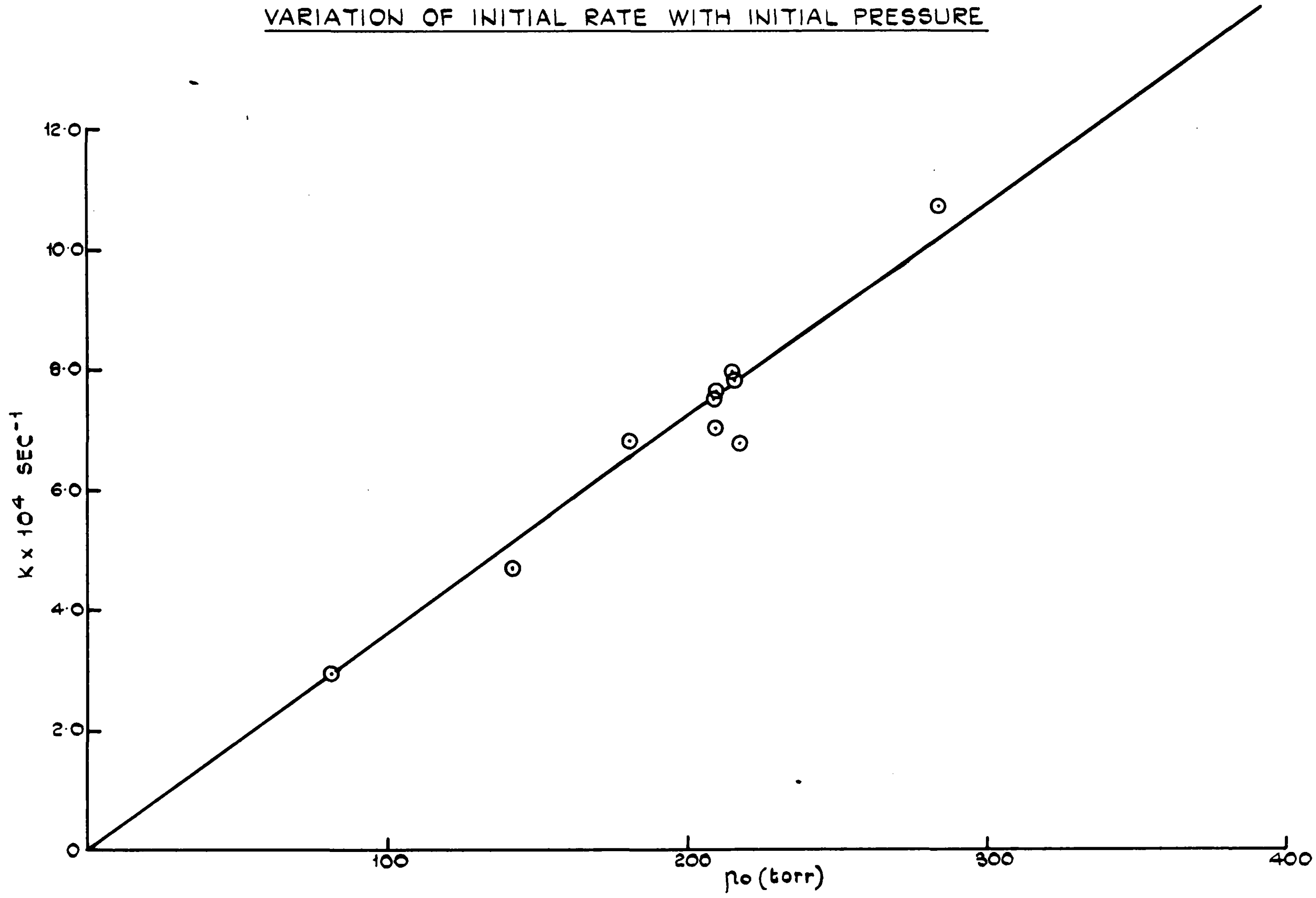


FIGURE 3.05

β TRI DECOMPOSITION AT 391·5°C

LÓG/LOG PLOT OF INITIAL RATE OF DECOMPOSITION AGAINST INITIAL PRESSURE.

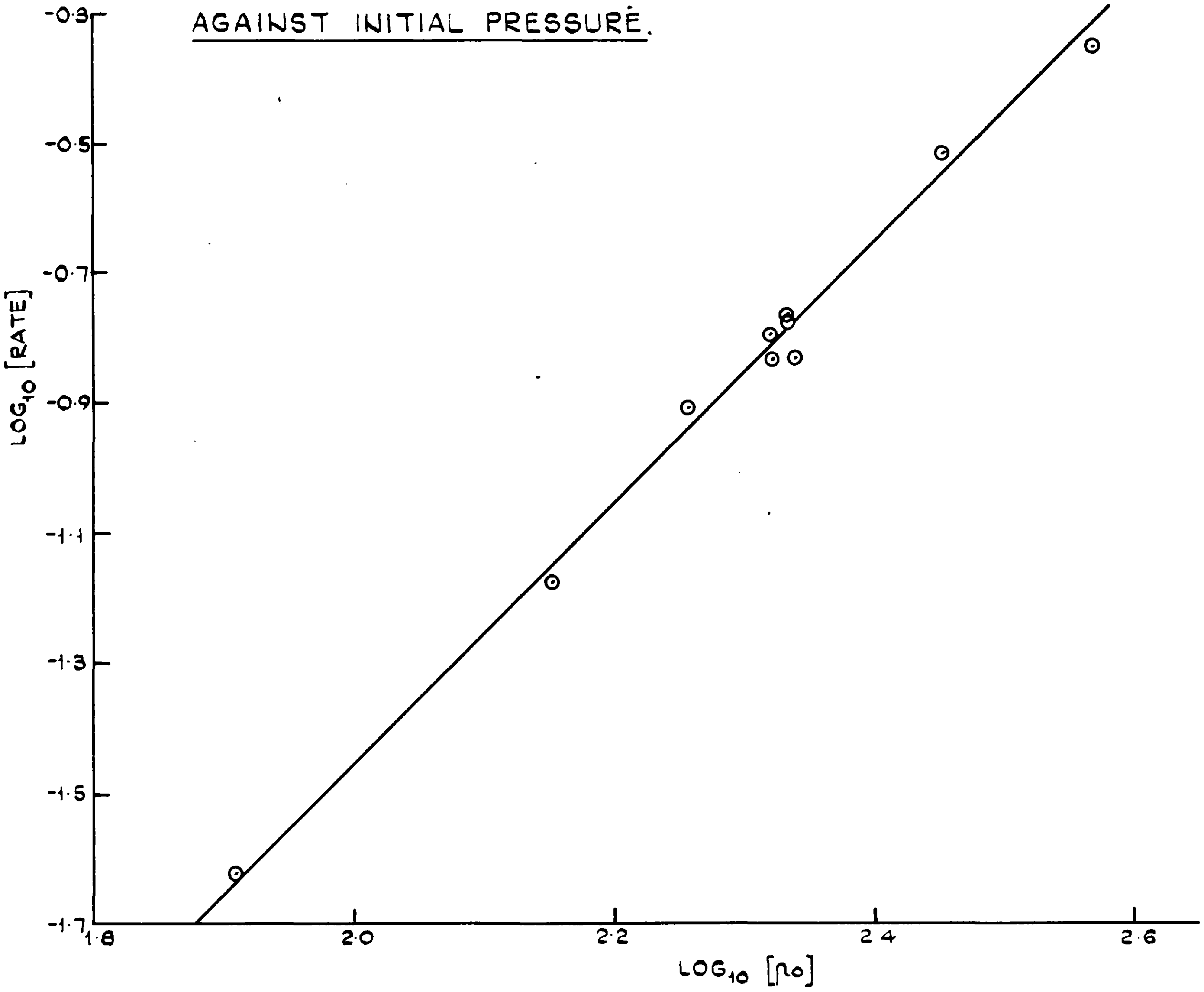


FIGURE 3.06

β TRI DECOMPOSITION AT 391·5 °C. [Po ≈ 160 torr]

EFFECT OF CCl_4 ON THE INITIAL RATE OF DECOMPOSITION

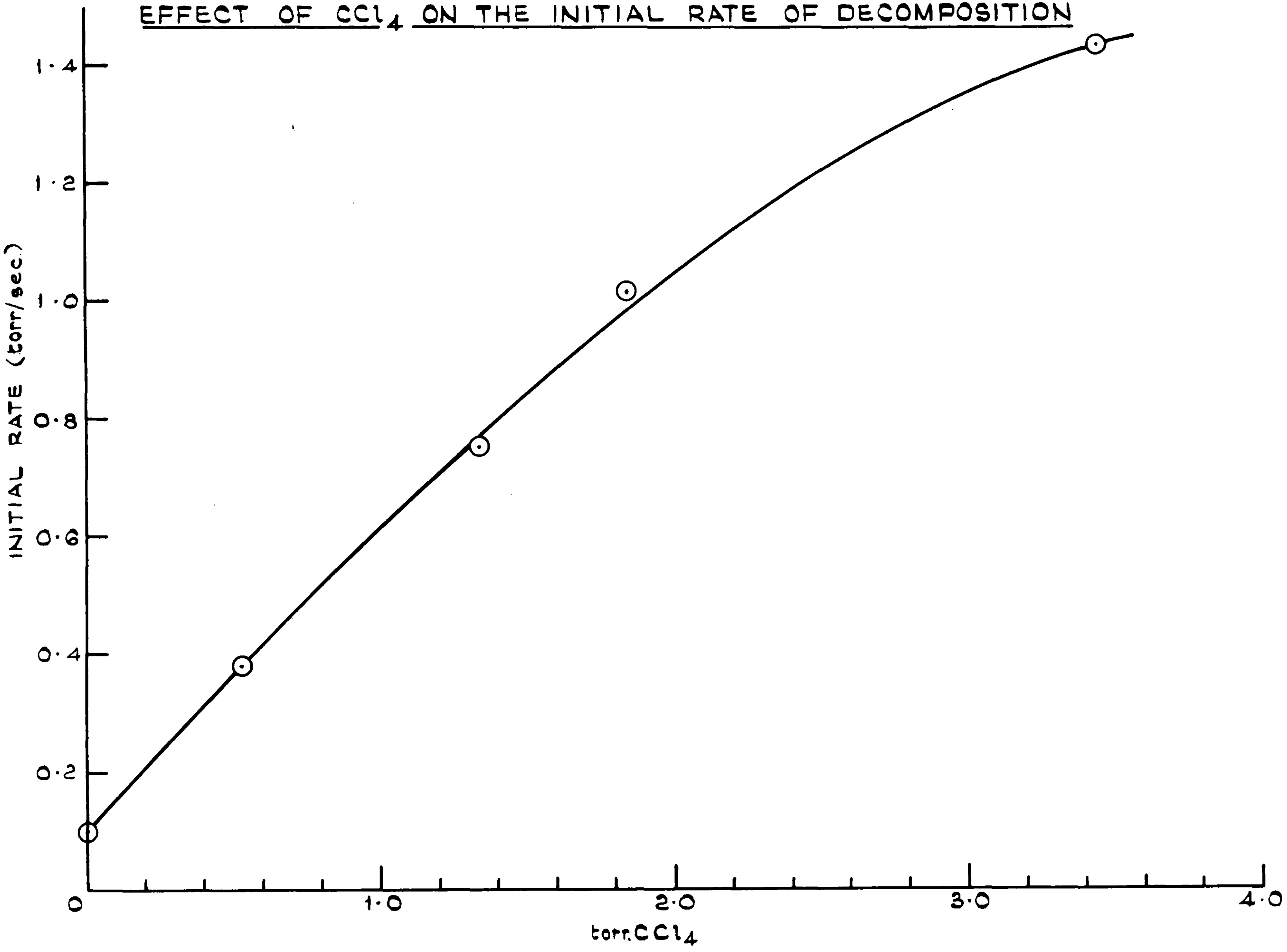
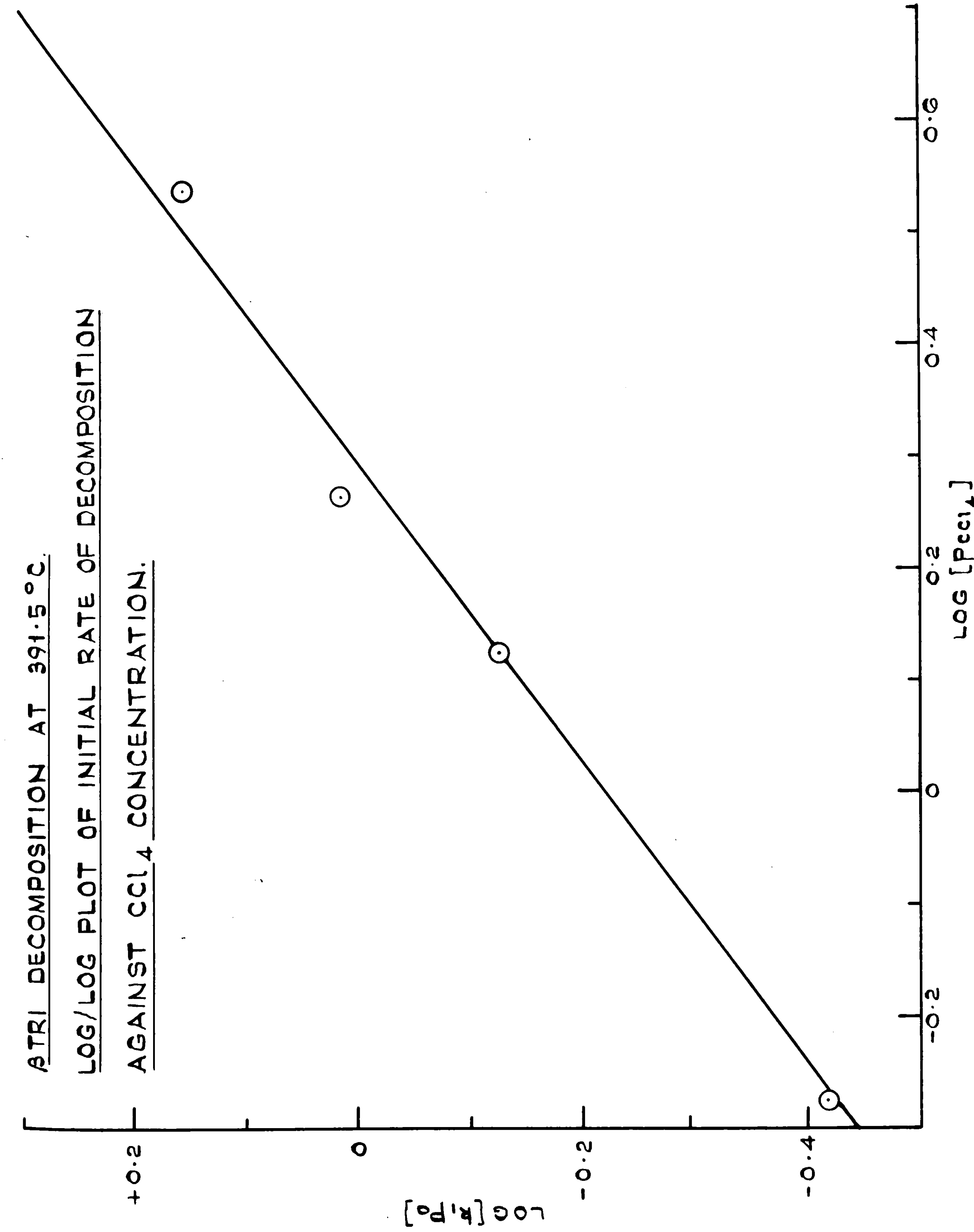


FIGURE 3.07



βTRI DECOMPOSITION AT 391·5 °C.

LOG/LOG PLOT OF INITIAL RATE OF DECOMPOSITION AGAINST CCl_4 CONCENTRATION.

FIGURE 3.08

βTRI DECOMPOSITION AT 391·5°C.

EFFECT OF CERTAIN VARIABLES ON THE PRODUCT RATIO OBTAINED AT DIFFERENT CONVERSIONS.

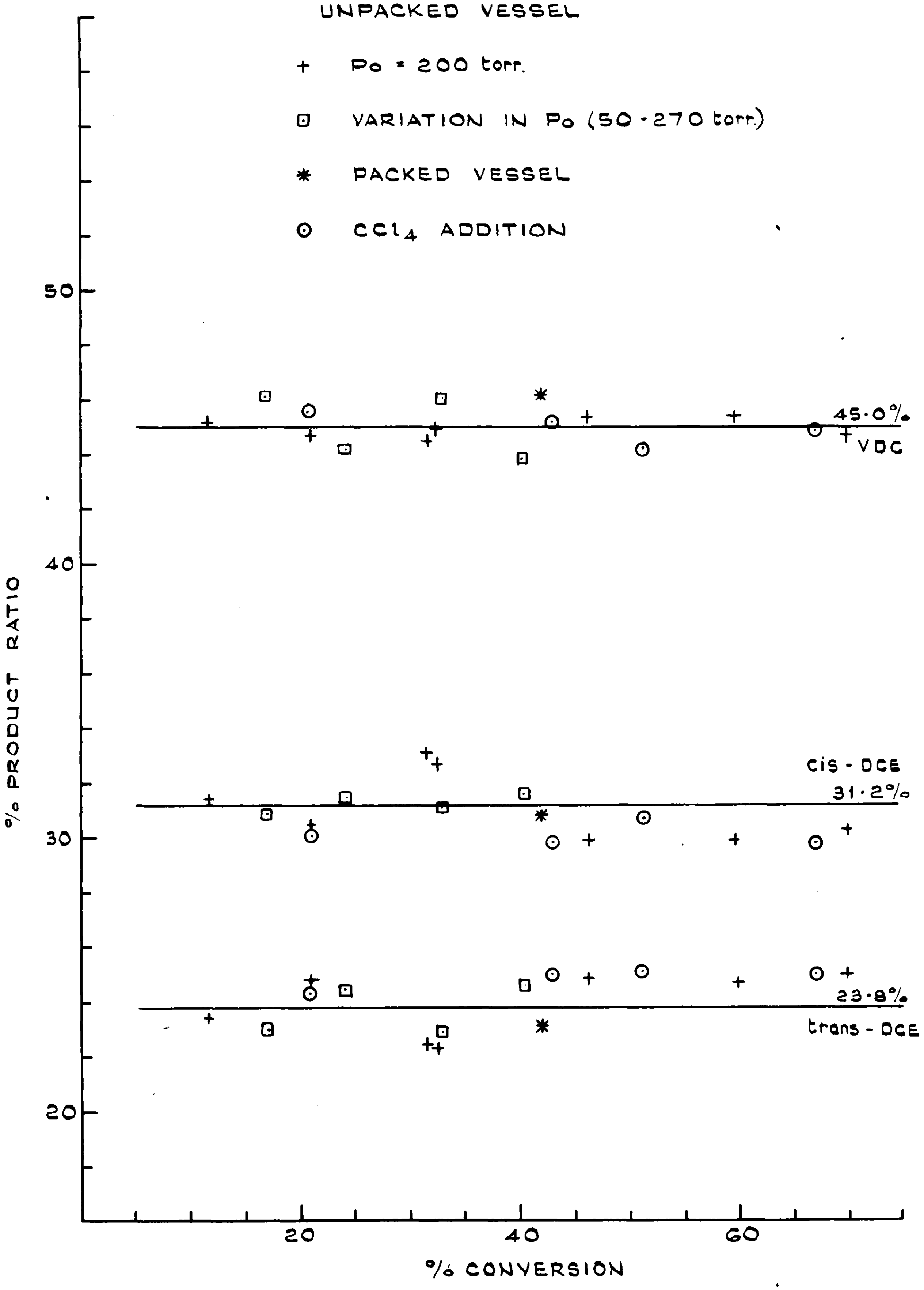


FIGURE 3.09

βTRI DECOMPOSITION AT 453·5 °C
EFFECT OF VARIOUS ADDITIVES ON THE FIRST ORDER RATE CONSTANT OF DECOMPOSITION [Po = 200 torr]

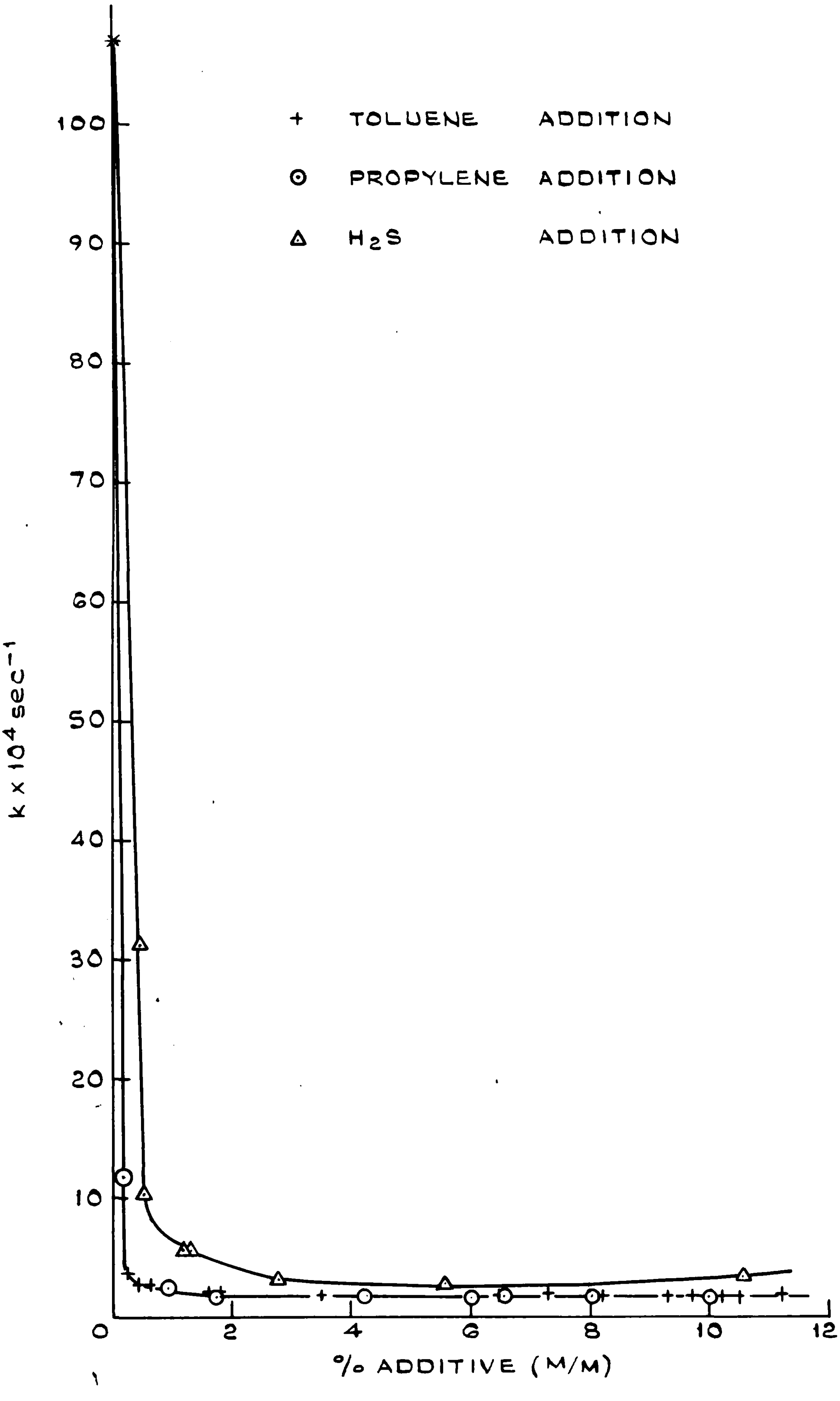
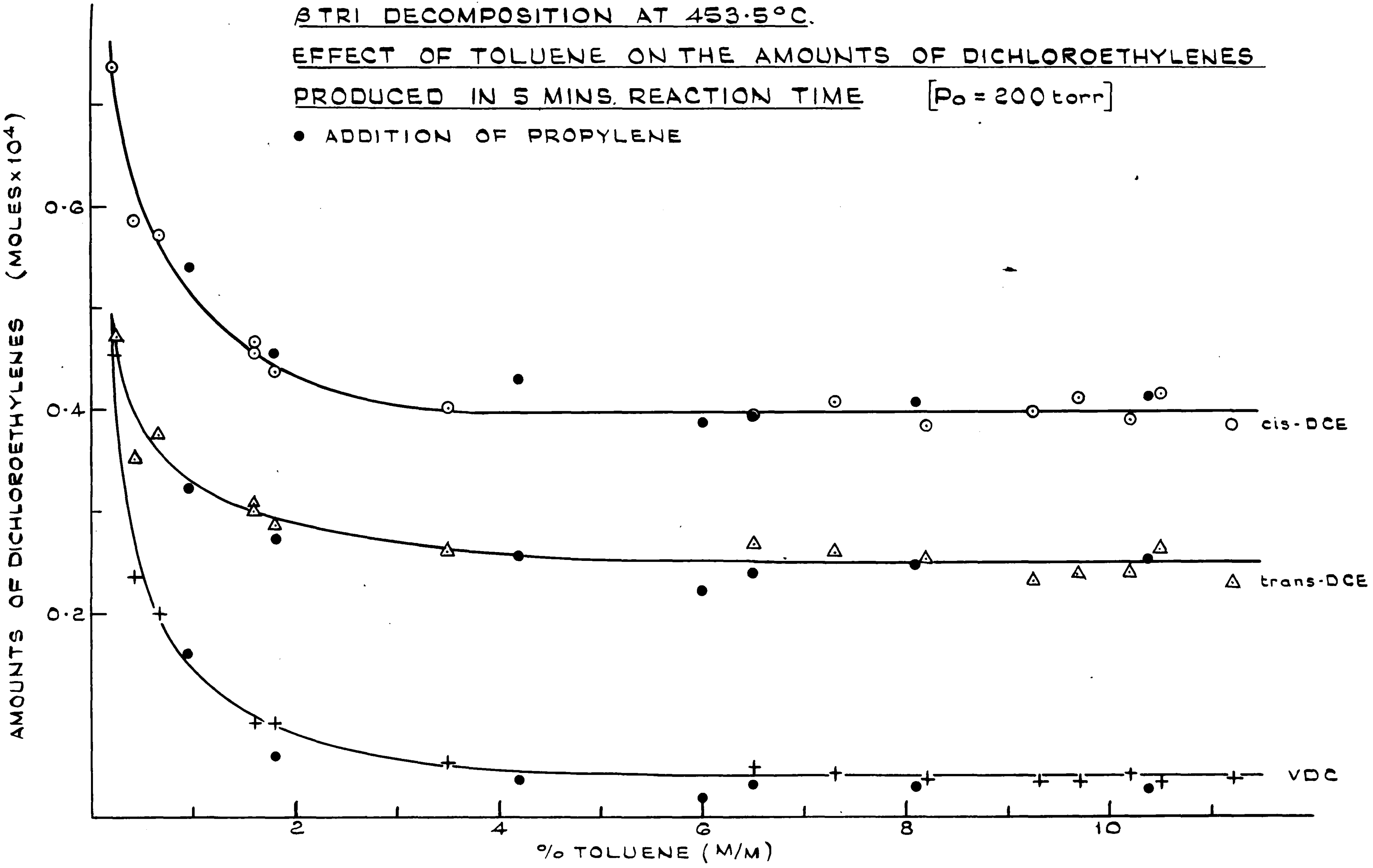


FIGURE 3·10



βTRI DECOMPOSITION AT 453·5°C.

EFFECT OF TOLUENE ON THE AMOUNTS OF DICHLOROETHYLENES PRODUCED IN 5 MINS. REACTION TIME [P_o = 200 torr]

● ADDITION OF PROPYLENE

FIGURE 3.11

β TRI DECOMPOSITION AT 453·5°C

EFFECT OF TOLUENE ON THE PRODUCT DISTRIBUTION OBTAINED

FROM 5 MIN REACTIONS [p_0 = 200 torr]

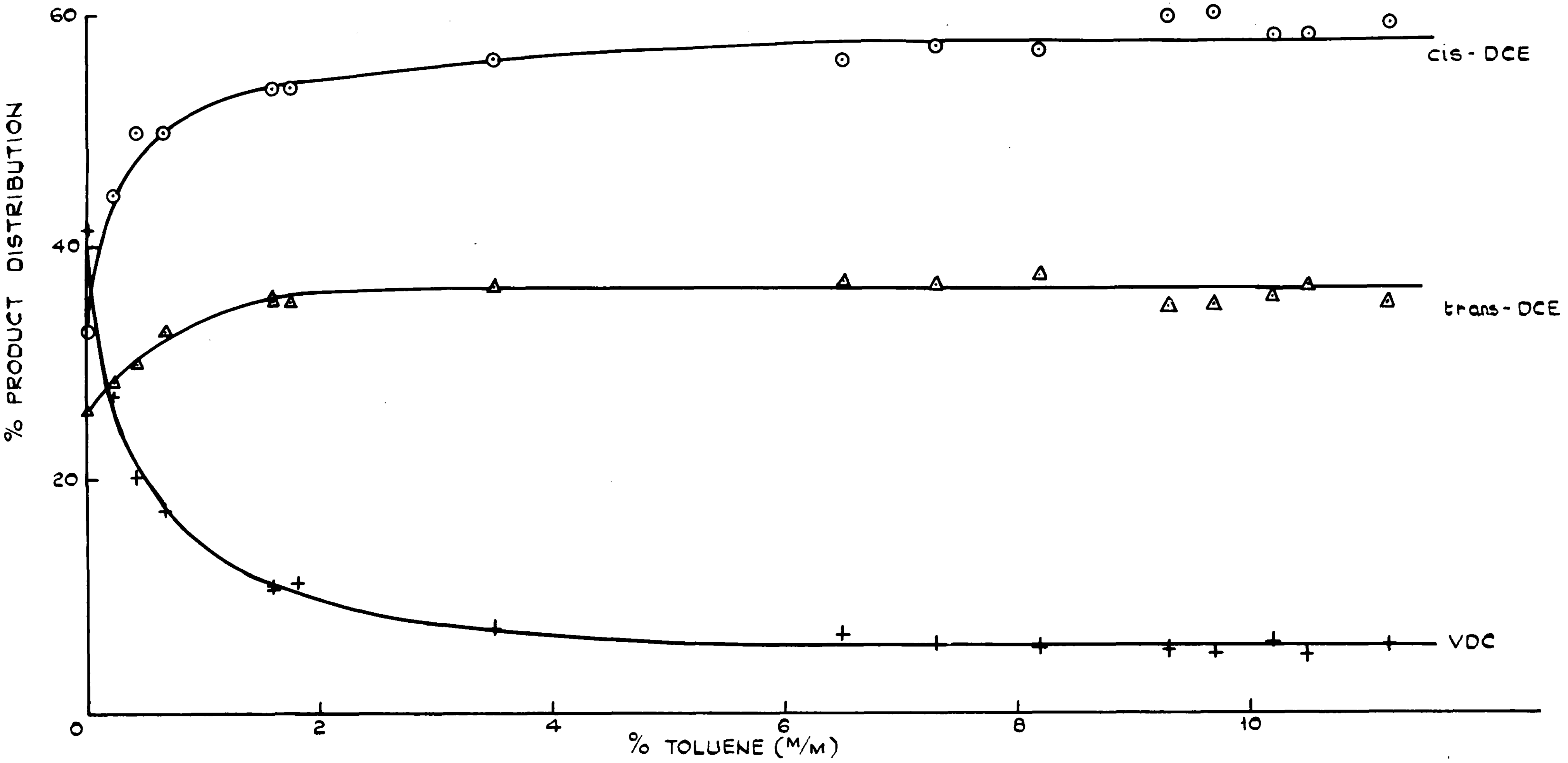


FIGURE 3.12

β TRI DECOMPOSITION AT 453·5°C

EFFECT OF PROPYLENE ON THE PRODUCT DISTRIBUTION OBTAINED

FROM 5 MIN REACTION TIMES [P_o = 200 torr]

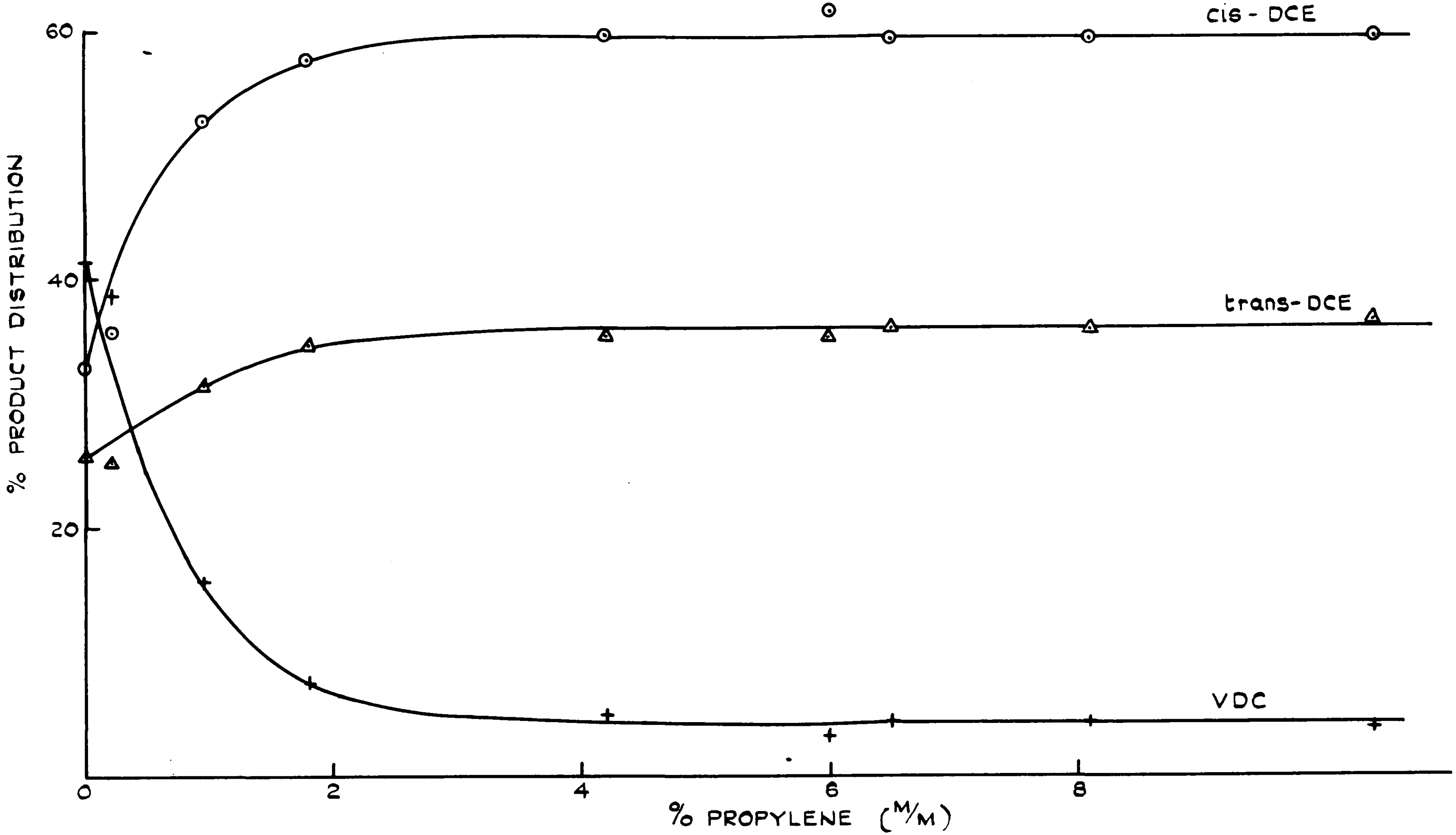


FIGURE 3.13

β TRI DECOMPOSITION AT 453·5°C
IN THE PRESENCE OF 10% PROPYLENE
PRODUCT FORMATION AGAINST ΔP
FOR Po = ~ 200 torr

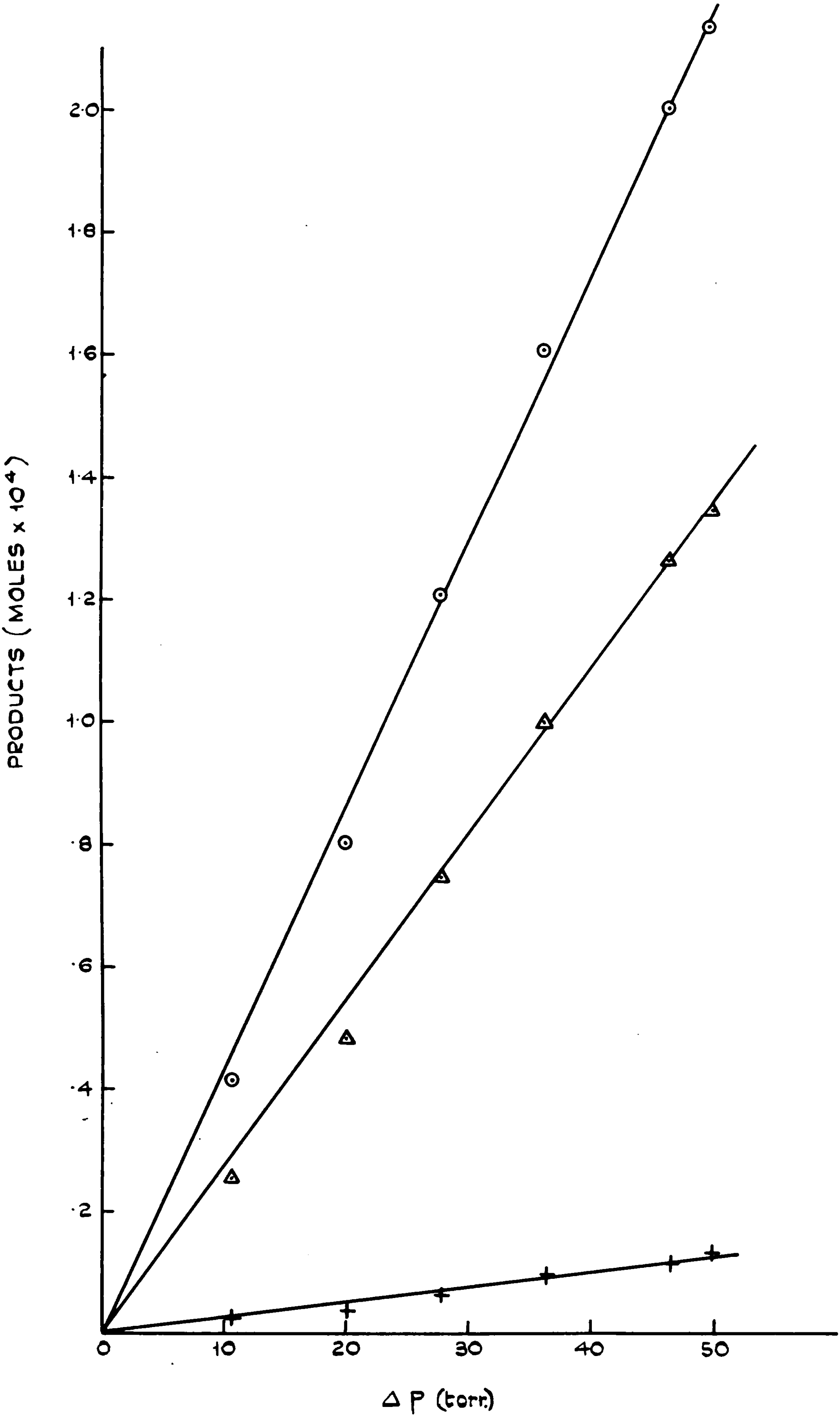


FIGURE 3·14

β TRI DECOMPOSITION AT 453·5°C

EFFECT OF H_2S ON AMOUNTS OF DICHLOROETHYLENES PRODUCED IN 5 MINS REACTION TIME. [Po = 200 torr]

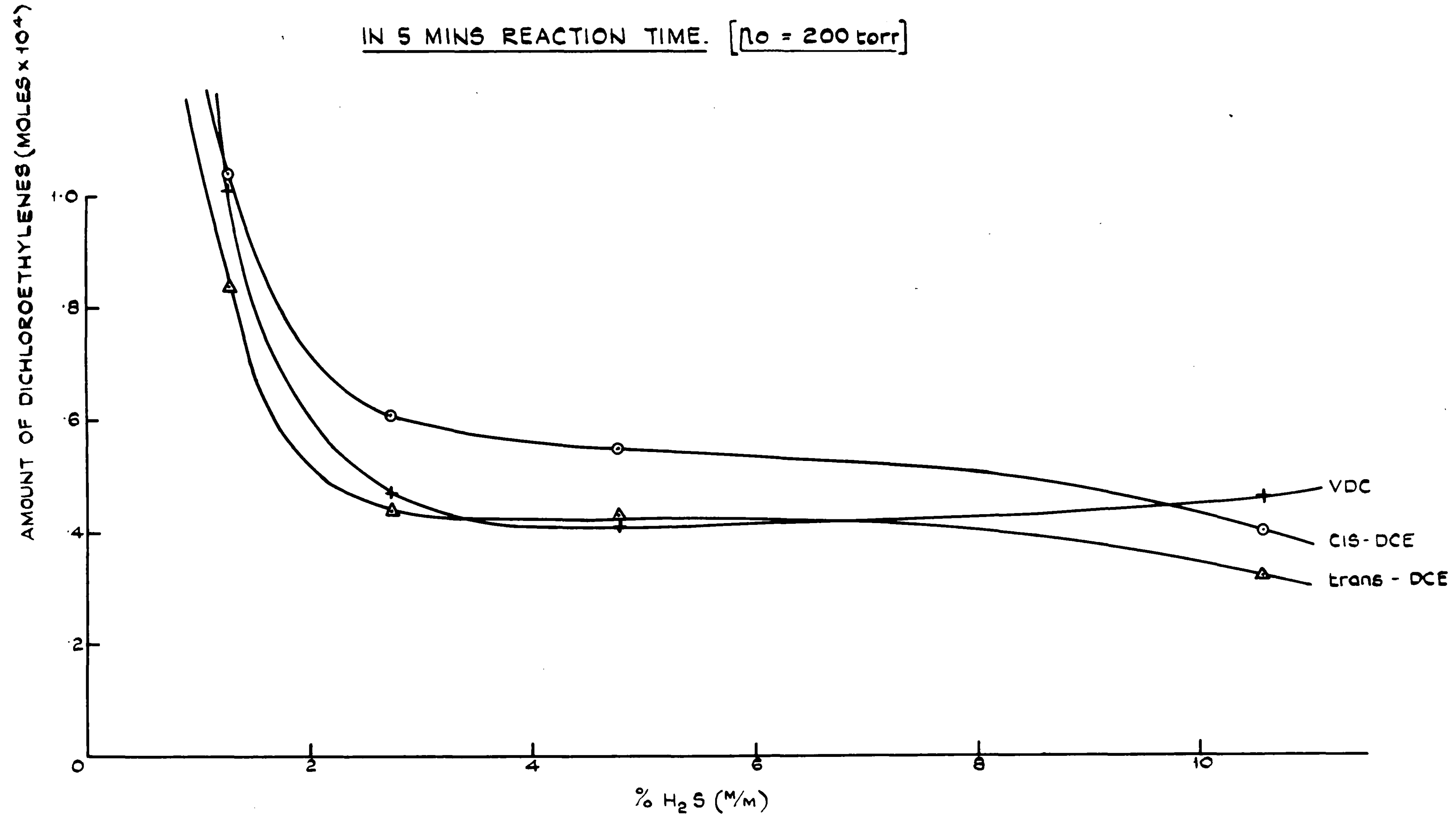


FIGURE 3.15

β TRI DECOMPOSITION AT 453·5°C

EFFECT OF H_2S ON PRODUCT DISTRIBUTION OBTAINED

FROM 5 min REACTION TIMES [p_o = 200 torr]

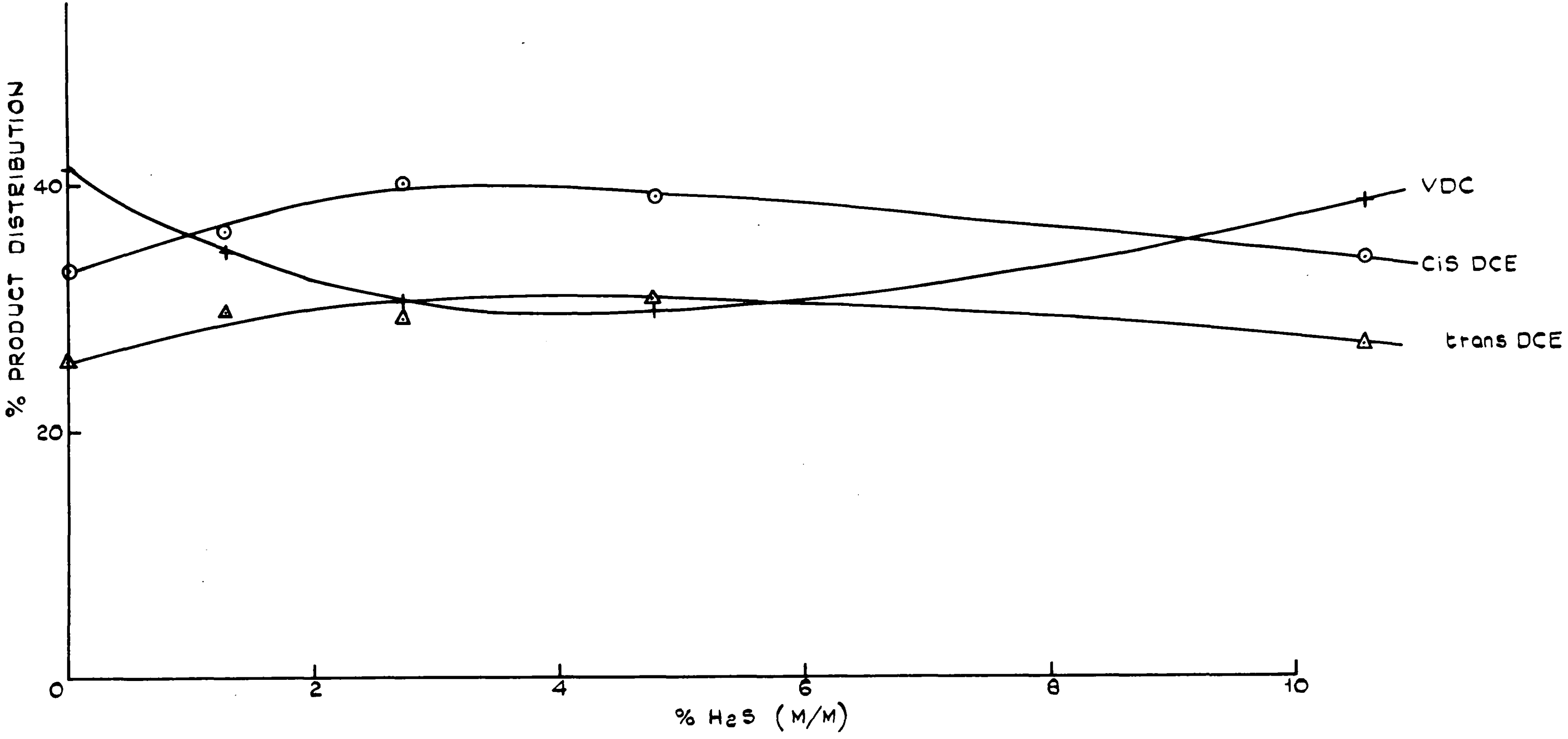


FIGURE 3.16

β TRI DECOMPOSITION AT 391·5°C

EFFECT OF HBr ON THE INITIAL RATE FOR $p_o \approx 200$ torr

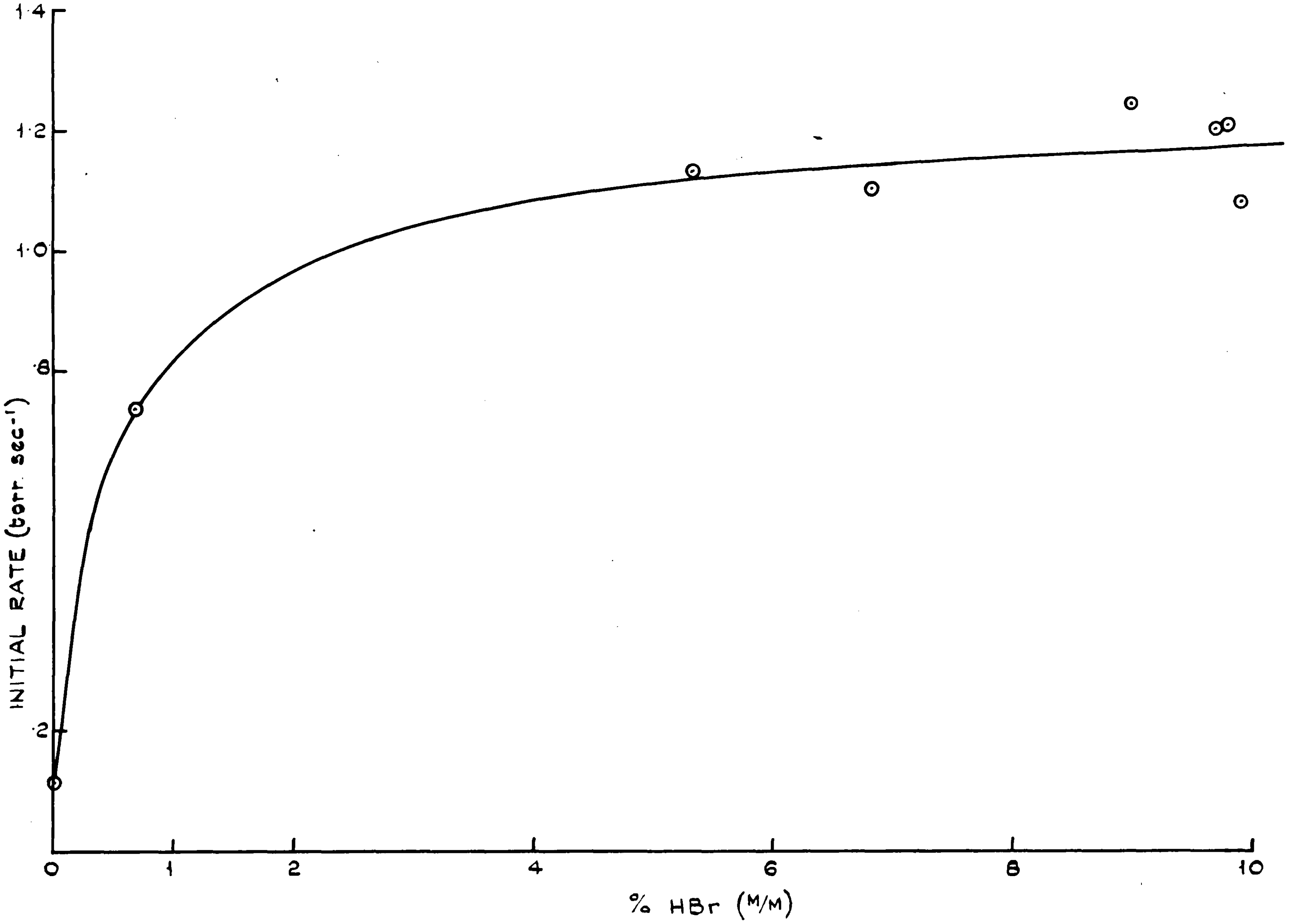


FIGURE 3·17

β TRI DECOMPOSITION AT 391·5°C
EFFECT OF HBr ON THE AMOUNTS OF PRODUCT
FORMED FROM 5 MIN REACTIONS (p_o = 200 torr)

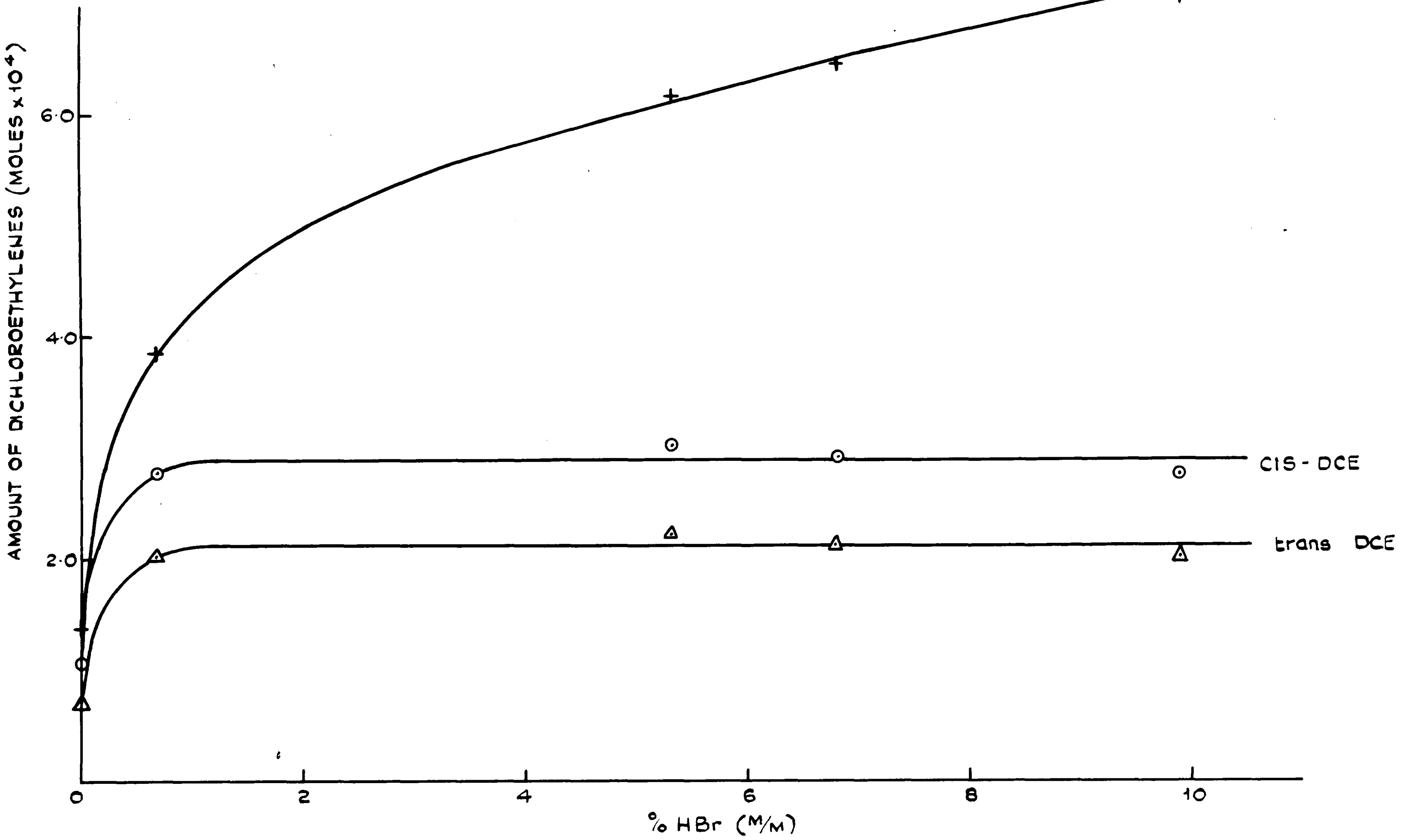
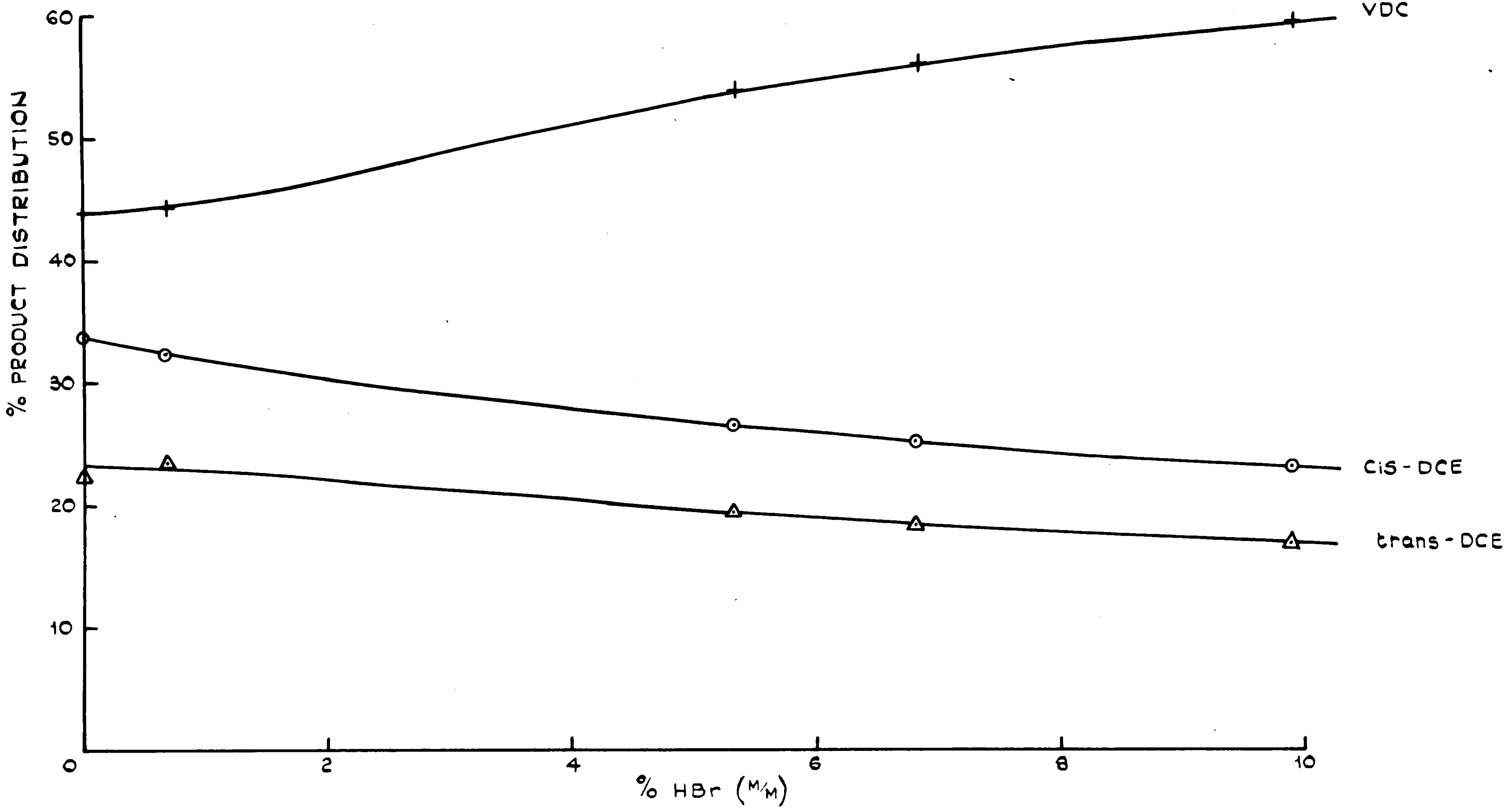


FIGURE 3.18

β TRI DECOMPOSITION AT 391·5°C

EFFECT OF HBr ON THE PRODUCT DISTRIBUTION OBTAINED FROM 5 min REACTION [p_o = 200 torr]



CHAPTER 4

RESULTS FROM THE DECOMPOSITION OF ETHYLENE CHLOROHYDRIN

4.01 Stoichiometry of the Decomposition of ECH

4.01(a) The Formation of the Major Products

The major products arising from the decomposition of ECH are acetaldehyde, vinyl chloride, carbon monoxide and methane. The latter two compounds are formed from the secondary decomposition of the acetaldehyde produced in the primary reaction

$$CH_2OHCH_2Cl \rightarrow CH_3CHO + HCl \quad \ldots\ldots\ldots\ldots\ldots \quad 4.01$$

$$CH_2OHCH_2Cl \rightarrow CH_2{:}CHCl + H_2O \quad \ldots\ldots\ldots\ldots \quad 4.02$$

$$CH_3CHO \rightarrow CH_4 + CO \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 4.03$$

In an empty glass reactor at a temperature of 454.9°C and an initial pressure of ECH of $\sim$200 torr the amounts of the major organic products formed as a function of time are as summarized in table 4.01 and figure 4.01. The methane curve shows the typical behaviour of a secondary product, its rate of formation increasing with the build-up of acetaldehyde in the system. The overall rate of dehydrochlorination can be estimated from the sum of the acetaldehyde and methane curves and this demonstrates that the dehydrochlorination reaction of ECH (equation 4.01) is considerably more favoured than the dehydration route (equation 4.02) which leads to vinyl chloride. The ratio of dehydration to dehydrochlorination is shown in figure 4.09 as a function of % conversion of ECH (line A). The relative rate of dehydration increases with % conversion from 0.05 at 5% conversion to 0.09 at 40%. The reasons for this are further discussed in section 4.05. In figure 4.09 values are only quoted for $>5\%$ conversion because at lower conversions small errors in VC analysis have a large effect on the dehydration/dehydrochlorination ratio.

The value shown in table 4.01 for % conversion was obtained by summing the VC, CH_3CHO and CH_4 values which have been expressed in the table as percentages of p_o.Equations 4.01, 4.02 and 4.03 show that this will provide a correct estimate of % conversion in the absence of any important side reactions.

4.01(b) CO/CH_4 Balance

The major reactions in the decomposition should lead to equal amounts of methane and CO (equation 4.03). The products from several runs at 454.9°C were analysed for methane and CO using a katharometer detector. Table 4.02 shows that the amounts formed with time follow each other closely. A slight excess of CO over methane was indicated and a ratio of 1.16 ± 0.03 was recorded for all the reactions analyzed. It will be demonstrated later that this excess can be partly accounted for by the existence of certain side reactions but in calculating the pressure change of a reaction the values of CO and CH_4 may be considered equal. In figure 4.02 the formation of CO and CH_4 with time have been plotted using the CH_4 curve of figure 4.01 as the absolute standard.

4.01(c) The Comparison between GLC Analysis of Products and Pressure-Time Data

The evidence presented in the preceding section shows that the principal reactions occurring in the decomposition of ECH are:

$$CH_2OHCH_2Cl \rightarrow CH_3CHO + HCl$$

$$CH_2OHCH_2Cl \rightarrow CH_2CHCl + H_2O$$

$$CH_2OHCH_2Cl \rightarrow CH_4 + CO + HCl$$

Each mole of ECH which decomposes gives rise to 1 mole of HCl or 1 mole of H_2O. Thus the EXCESS pressure, which is the pressure increase observed in the pressure-time curve, is equivalent to the term $\Sigma(CH_3CHO+VC+CH_4+CO)$. Table 4.03 and figure 4.03 show excellent agreement between this term and Δp for a temperature of 454.9°C and reaction times of < 30 mins. The discrepancy between the product sum and the observed pressure increase at longer reaction times is indicative of side reactions involving removal of the products. This is discussed further in section 4.04.

4.01(d) Analysis of ECH

The correlation between Δp and $\Sigma(CH_3CHO+VC+CH_4+CO)$ indicates that the occurrence of any appreciable side-reaction was unlikely at ECH conversions below $\sim$33%. It was important however to confirm this point by direct measurement of the amount of unreacted ECH. A difficulty was encountered in analysing for ECH. Owing to its high boiling point ECH could not be estimated reliably by the gas sampling technique and it was necessary to trap out the products in solution. Initial analyses of the solution showed that the amounts of ECH detected at moderate conversions were 20% less than would have been expected on the basis of the corresponding measurement for $\Sigma(CH_3CHO+VC+CH_4)$. However detailed analysis revealed the presence of substantial quantities of a high boiling product. A GLC/Mass Spectroscopic investigation of this compound suggested that it was the dichloro acetal: $CH_3CH(OCH_2CH_2Cl)_2$. Further tests established that this compound was not present in the gaseous product leaving the reactor but was formed when the frozen products were allowed to warm up in the solvent to ambient temperatures. Formation of acetals under these conditions from hydroxy compounds and acetaldehyde is a well-documented reaction (59). It was impossible to prevent the formation of the acetal in the solvent. Consequently the alternative course was adopted of preparing a pure sample of the acetal and calibrating it on the GLC. The amount of ECH present in the gases leaving the reactor was then assessed by determining the amounts of ECH and the acetal in solution. It was assumed that 1 mole of the acetal was formed from 1 mole of acetaldehyde and 2 moles of ECH.

For any particular reaction the % conversion may thus be estimated from the ECH analysis obtained by the above method. This result can be compared with a gas sample analysis performed on the products of a similar reaction. The results obtained are summarised in table 4.04 and the relationship between the observed pressure increase and the two methods of estimating the % conversion is shown in figure 4.04. In view of the difficulties in obtaining the ECH analysis the figures agree well and confirm the absence of important side reactions below 40% conversion. The results shown in figure 4.03 would suggest that the % conversion of run E202 will be low owing to the occurrence of side reactions.

The overall conclusion is that the combined gas-sample analysis of acetaldehyde, vinyl chloride, and methane provides a satisfactory measure of the course of the decomposition of ECH.

4.02 Order of Reaction and Rate of Reaction

Because of the additional pressure increase arising from the secondary decomposition of acetaldehyde the use of the term $(2p_o-p_t)$ as an expression for the concentration of reactant at time t will only be valid during the initial stages of the reaction when the amounts of secondary products (CH_4 and CO) are negligible.

It has been shown in the previous section that for conversions below 30% at 454.9°C the % pressure increase can be satisfactorily represented by $\Sigma\%(CH_3CHO+VC+2CH_4)$ and the % ECH conversion by $\Sigma\%(CH_3CHO+VC+CH_4)$. Figure 4.05(a) shows a plot of these two terms derived from the data of table 4.01. Deviation from linearity is observed above 4% conversion. This figure enables true % conversions to be estimated from the observed pressure change in a reaction and a corrected first order log plot may thus be obtained. Figure 4.05(b) shows a corrected plot for a reaction proceeding up to 15% conversion (A). The linearity of this indicates good first order behaviour for the first 15% of reaction. The uncorrected log plot (B) derived directly from pressure measurement $(2p_o-pt/_{po})$ has also been shown in figure 4.05(b). The initial gradient to this curve agrees well with the slope of the corrected plot indicating that the initial gradient obtained from the pressure time curve would provide a reasonably accurate measure of the reaction rate constant.

Variation in the initial pressure of ECH gave very little variation in the first order rate constant as estimated from the initial gradient of the log plots.

The table below shows a constant value for k over an initial pressure range of 100-350 mm.

Run	E42	E43	E43A	E45
P_o torr	195.8	341.1	103.8	151.8
k_1 sec^{-1}	1.88×10^{-4}	1.89×10^{-4}	1.92×10^{-4}	1.83×10^{-4}

Effect of variation of p_o on the value of k at 454.9°C.

Thus to a first approximation the decomposition of ECH is obeying first order kinetics at low conversions over the range of pressures studied.

4.03 The Effect of Temperature.

The decomposition of ECH was studied at two other temperatures, 484.0°C and 439.5°C. Table 4.05 and figures 4.06 and 4.07 indicate the formation of the major products with time at these two temperatures. The ratio of dehydration to dehydrochlorination remains similar to that obtained at 454.9°C (figure 4.09). The correlation between $\% \Delta p$ and $\Sigma(CH_3CHO+VC+CH_4+CO)$ is shown in table 4.06 and figure 4.03. The CO concentration has again been assumed equal to the CH_4. For reaction times of less than 15 minutes at any temperature any discrepancy between the two values is within experimental error.

Table 4.07 shows the average first order rate constant obtained at each temperature from the initial gradient of the first order log plots.

The Arrhenius plot of log k against $^1/T$ is shown in figure 4.08. The rate expression obtained from the straight line shown in the figure is:

$$\log_{10} k_1 = 13.32 - 56{,}800/4.575T$$

It should be recognised that this equation is only approximate as it falls outside the limits of experimental error for the extreme temperatures. Although curvature of Arrhenius plots can be obtained for reactions involving a change in mechanism (and therefore in activation energy) considerably more experimental evidence would be required to determine the effect of the experimental error involved. This was not undertaken in the present study as the above approximation is adequate for our needs.

4.04 The Formation of Side Products

The decomposition of ECH produces several minor products. The most important of these have been identified as ethylene, methyl chloride, and propylene. GLC analysis also revealed trace amounts of propane and acetylene and Mass spectroscopic evidence suggested traces of methanol although this has not been confirmed by our own analytical techniques.

Table 4.08 and figures 4.10, 4.11, 4.12 show the production of the three major side products as a function of time for the three temperatures employed in this investigation. The ethylene and methyl chloride curves follow each other closely at all stages of the decomposition. The product curves are all sigmoid and the ethylene and methyl chloride curves are of similar form to the methane curve indicating the secondary nature of their formation. The propylene curves possess an even greater degree of sigmoid character. These features are shown more clearly for the highest temperature (484.0°C) in figure 4.13 where the side products are plotted against % conversion as measured by $\Sigma\%(CH_3CHO+VC+CH_4)$. Above 70% conversion the ethylene and methyl chloride curves flatten out, whereas the rate of formation of propylene is still slightly increasing above 80% conversion.

4.05 The Addition of Inhibitor

The effects of toluene and propylene on the decomposition of ECH were investigated. The results are summarised below.

4.05(a) Effect on the Reaction Rate

In contrast to βTRI decomposition, the addition of inhibitor caused only a marginal decrease in the initial first order rate constant, k_1, obtained for the decomposition of ECH. The results are shown in table 4.09 which indicate a $\sim$20% reduction in k_1 for 50% addition of toluene or propylene. In comparison the pressure change for 45 minute reactions in the presence of inhibitor show a 40% reduction for 50% addition of inhibitor. This indicates a greater degree of radical chain character in the later stages of the normal decomposition than at the beginning. The effect of varying amounts of inhibitor on the pressure change associated with 45 minute reactions is shown in figure 4.14. The decrease in Δp is relatively gradual particularly with toluene and even with 50% addition a minimum value has not been attained. This behaviour is in marked contrast to the inhibition observed with βTRI where 1% toluene suppressed the rate by X50 (figure 3.09).

4.05(b) Effect on Reaction Products

The formation of major products as a function of time in the presence of 50% toluene is shown in table 4.10 and figure 4.15. In comparison to figure 4.01 the most obvious change is the large reduction in the rate of formation of methane. This is to be expected as the decomposition of acetaldehyde is known to proceed via a free radical mechanism (54), and there is no evidence for a significant molecular mode of decomposition under these reaction conditions. The large decrease in methane production also confirms the previous observation in section (a) that a greater proportion of inhibition occurs at the later stages of reaction than at the beginning.

However the addition of 50% toluene has not fully suppressed this secondary decomposition and toluene is thus not as powerful an inhibitor in this reaction as might be expected from its reported inhibiting efficiency in other systems.

Consideration of the amounts of product formed in the early stages of the decomposition show that toluene has reduced the rate of primary decomposition to about 80% of its value in the uninhibited reaction. Of particular interest is the reduction in the dehydration to dehydrochlorination ratio from 0.090 to 0.036 for 45 min reactions. This is shown as curve B in figure 4.09.

The result obtained from propylene addition shows a similar overall reduction in product formation (figure 4.15). However a higher value of dehydration to dehydrochlorination ratio (0.056) is obtained compared to that for toluene (0.036).

The effect of toluene on the formation of minor products (table 4.11 and figure 4.16) is to considerably reduce their rate of production, indicating a high proportion of radical chain character in their mechanism of formation. The methyl chloride and ethylene curves do not follow each other as closely as in the uninhibited reaction.

The above results demonstrate the existence of chain mechanisms particularly in the secondary decomposition of acetaldehyde and in the formation of side products. In the primary decomposition the relatively small reduction in rate coupled with the change in selectivity of dehydration and dehydrochlorination suggest the presence of two decomposition modes, a radical chain and a molecular process which is uninhibited by the addition of toluene. The reduction in dehydration ratio with toluene further suggests that the molecular decomposition produces proportionately less VC than the chain process. The absence of complete suppression of methane formation with 50% toluene and the difference between the dehydration/dehydrochlorination ratio with toluene and propylene means that complete suppression of the chain processes cannot be assumed and is indeed unlikely under these conditions.

4.06 The Effect of Surface

4.06(a) Increase in Surface Area

The results shown in table 4.12 summarise the effects observed using a packed vessel of surface to volume ratio 5.06 cm^{-1} (compared to 0.87 cm^{-1} for the empty vessel). The initial first order rate constant is somewhat enhanced in comparison to the value of 1.88×10^{-4} sec^{-1} obtained at the same temperature in the empty vessel. However this rate constant is subject to fluctuation (table 4.12).

The formation of the major organic products is shown as a function of time in figure 4.17. The pattern is basically similar to the unpacked vessel results (figure 4.01) but the dehydration to dehydrochlorination ratio has decreased from 0.091 to 0.057 for 45 minute reactions. The ratio is shown as line C in figure 4.09. Comparison of the VC formation rates for the two systems (table 4.01 and 4.12) indicate a slower rate of production of this compound in the packed vessel.

The formation of minor products (figure 4.18) also shows similar features to the unpacked vessel (figure 4.10) but the overall rates are again somewhat reduced particularly for propylene and methyl chloride.

The effect of 50% toluene addition in the packed reactor is fairly small. Table 4.12 indicates that the initial rate constant does not alter outside the normal limits of variation and the formation of all products are not reduced to the same extent as in the unpacked vessel. The dehydration/dechlorination ratio is reduced with 50% toluene from 0.049 to 0.035 for a 20 minute reaction.

The conclusion from this study is that the effect of increasing surface is to somewhat enhance the primary decomposition rate. This effect is relatively small and the values obtained for dehydration/dehydrochlorination ratios and the DECREASE in the rate of production of VC in the packed vessel suggest that this enhancement is associated with the unimolecular decomposition and that the radical chain component of the overall mechanism is REDUCED by increasing surface. Assuming that methane and the side products are being predominantly formed by a chain mechanism, as in the unpacked vessel, then the effect of toluene is not as great as in the unpacked vessel because these particular products are not decreased to the same extent as previously.

4.06(b) The Effect of a Steel Surface

A glass reactor containing a stainless steel insert as described in chapter 2 was employed to study the effects of the steel surface on the decomposition of ECH. A considerable enhancement in the rate of decomposition was observed and it was necessary to reduce the temperature of the reactor to 400°C to obtain measurable rates. The reactor had been 'coked up' prior to use by allowing 1,2-dichloroethylene to remain in the reactor for several weeks at 400°C. Notwithstanding this precaution, the rate of reaction was found to vary considerably from day to day indicating an extreme sensitivity of the reaction to the surface condition. Table 4.13 shows a set of results obtained at a relatively constant ($4.0\text{x}10^{-3}$ ± 10%) value of initial first order rate constant. Prior to Run E31S involving the addition of toluene, the rate constant had increased 50% to $6.2\text{x}10^{-3}\text{sec}^{-1}$. Thus sensible comparisons of rate and product formation can only be made with adjacent runs.

Figure 4.19(a) illustrates the build up of major products with time and figure 4.19(b) shows the more important by-products. The enhanced rate in steel is obviously due to a catalysis of the dehydrochlorination reaction leading to increased amounts of acetaldehyde. Thus, at 80% decomposition of ECH, acetaldehyde and its decomposition product, methane, account for all but 2% of the products and the dehydration/dehydrochlorination ratio has dropped from 0.09 in glass to 0.007 in steel. The formation of acetaldehyde has been catalysed to a much greater extent than the decomposition of acetaldehyde and this is reflected in a much higher concentration maximum (i.e. 67%) than was observed in glass at 454.9°C (25%).

Another reaction which has been catalysed is the formation of ethylene which is now far in excess of the methyl chloride curve in figure 4.19(b). The absence of sigmoid character in the ethylene curve indicates that this compound is now being formed as a primary product. This is most likely to be occurring by a heterogenous mechanism on the steel surface. Similar effects have been noted for 1,2-dichloroethane in steel (50).

Comparison of Runs E30S and E32S with E31S show that the addition of 55% toluene has a very small effect on the overall rate. The reduction in rate constant is within experimental error and this is reflected in the product analysis, which shows a negligible drop in the major product, acetaldehyde. Toluene reduces the amounts of VC and methane indicating again some degree of chain character in their formation. The absence of any measurable reduction in the ethylene figure supports the concept of a non-radical process producing ethylene in the steel vessel.

4.07 Addition of CCl_4 as a Chain Accelerating Agent

The addition of small amounts of CCl_4 caused a considerable increase in the rate of reaction. Table 4.14 and figure 4.20 show the increase in the initial first order rate constant for increasing additions of CCl_4 to 200 torr of ECH. The addition of 4% CCl_4 increased the rate by a factor of 3. The pressure increase over 15 minutes reaction is also shown in table 4.14 and indicates an increase of 5 in Δp when compared to the normal reaction. As previously observed with inhibitors (section 4.05) the increased effect of CCl_4 as the reaction proceeds reflects the increasing degree of chain character in the system caused by the secondary chain-decomposition of acetaldehyde.

Table 4.15 and figures 4.21(a) and (b) show the formation of products with time in the presence of a constant (1.5%) amount of CCl_4. Comparison with figure 4.01 demonstrates that a considerably faster rate of decomposition of ECH is obtained in the presence of CCl_4 due to the greater rate of chain initiation.

Table 4.15 and curve D of figure 4.09 also demonstrate an increase in the ratio of dehydration to dehydrochlorination. It has previously been mentioned (section 4.05) that the radical chain process in ECH decomposition produced relatively more VC than the molecular process. Thus the addition of a chain accelerating agent would be expected to produce proportionately more VC by enhancing the chain contribution to the overall decomposition.

Figure 4.21b also indicates an increase in the rate of production of side products. This is again to be expected as the predominance of a radical chain mechanism for the formation of these compounds has already been postulated. There is some divergence of the methyl chloride and ethylene curves after 10 minutes. The reason for this was not investigated further but the most likely cause would be further reaction of ethylene with other radicals in the system.

4.08 The Addition of Chain Transfer Agents

4.08(a) Hydrogen Chloride

Previous results have shown that the production of vinyl chloride from ECH is slightly enhanced with time (figure 4.01) and that in addition there is a gradual increase in the dehydration/dehydrochlorination ratio (figure 4.09 line A) with increasing conversion of ECH. These observations could be accounted for by an enhancement in chain component of the ECH decomposition reaction as % conversion increases. HCl has been reported in the literature (19, 22, 23) as exerting a catalytic effect on various chain decomposition processes and the production of HCl in the ECH decomposition makes this compound an obvious candidate for further study as a possible chain transfer agent.

The effect of 50% HCl addition on the initial rate of ECH decomposition is to enhance that rate by a factor of two. Figure 4.22(a) and table 4.16 shows the formation of the major products with time under conditions of 50% HCl addition. The VC value has increased relative to the other products and this is reflected by an increasing dehydration/dehydrochlorination ratio as shown in figure 4.09, line E. The increase in VC formation is most obvious in the early stages of decomposition, the difference between lines A and E decreasing with % conversion due presumably to the build up of HCl in the standard decomposition reaction.

Figure 4.22(b) shows the formation of minor products as a function of time in the presence of 50% HCl. The propylene amounts have doubled in comparison to the normal reaction (figure 4.10). The methyl chloride has also increased slightly. There was no obvious explanation for the considerable scatter observed in the ethylene values.

It is concluded that HCl does act as a catalyst of the chain component of ECH decomposition.

4.08(b) Hydrogen Bromide

The addition of small amounts of HBr to ECH caused considerable changes in the decomposition characteristics. The pressure-time curves showed accelerating rates of pressure changes over 15 minute reaction periods involving pressure increases of up to 126% of p_o. The initial rates expressed as first order rate constants show considerable scatter (table 4.17) but there is undoubtedly a marked catalytic effect. The pressure change obtained from 15 mins reactions is also shown in table 4.17. The scatter is again high but the catalysis is again evident.

The possible loss of HBr in this system was not investigated specifically. However, comparison of E97, containing only 0.93% HBr, with E101 - a normal reaction - did suggest that catalysis was still occurring after 15 minutes reaction the rate of pressure change after 15 minutes being 0.098 torr/sec for E97 and 0.052 torr/sec for E101.

The formation of products as a function of time in the presence of $\sim$2.2% HBr is shown in table 4.18 and figure 4.23. Catalysis of the primary decomposition process is observed but a more striking consequence of adding HBr is the enhancement of the secondary decomposition involving the formation of methane. HBr is obviously acting as a selective catalyst in this decomposition with a much stronger preference for the acetaldehyde chain decomposition than the ECH decomposition. This catalysis gives rise to the considerable increase in Δp which was observed in table 4.18 and also produces a much lower maximum concentration of acetaldehyde (8% compared to $\sim$25% in figure 4.01). Comparison between table 4.01 and 4.18 indicates that HBr does exert some catalysis on the primary decomposition. Furthermore there is a small increase in the dehydration/dehydrochlorination ratio (F in figure 4.09) which suggests that this catalysis is acting via the chain mechanism. This is confirmed by the enhancement in the minor product formation as illustrated in table 4.18 and figure 4.23(b).

TABLE 4.01 PRODUCT FORMATION WITH TIME AT 454.9°C ($p_o \approx$ 200torr)

RUN	p_o (torr)	TIME (mins)	PRODUCT ANALYSIS (As % of p_o) VC	CH$_3$CHO	CH$_4$	$\frac{\text{de-H}_2\text{O}}{\text{de-HCl}}$*	% CONVSN.+
E35	214.8	1	.09	.63	.02	-	0.7
E26	203.1	2	.12	2.08	.06	-	2.3
E10	195.0	2.25	.06	2.76	.04	-	2.9
E19	199.1	3	.18	3.71	.30	-	4.2
E27	191.0	5	.29	5.32	.20	.053	5.8
E25	200.7	10	.66	8.65	.81	.069	10.1
E17	197.9	15	1.06	13.23	1.87	.070	16.2
E18	189.4	25	2.17	19.22	5.76	.087	27.2
E38	196.3	30	2.74	21.43	8.77	.091	32.9
E28	198.3	35	3.01	20.75	12.42	.091	36.2
E88	206.3	35	3.44	22.59	14.08	.093	40.1
E20	196.7	45	3.98	23.90	19.64	.091	47.5

* VALUES ONLY REALISTIC FOR % CONVERSIONS >5% OWING TO SMALL DEGREE OF DE-H_2O.

+ % CONVERSION $= \sum \%$ (CH_3CHO + VC + CH_4).

TABLE 4.02 CORRELATION BETWEEN CO AND CH_4 FORMED AT 454.9°C (p_o= 200 torr)

RUN	p_o (torr)	TIME (mins)	$^{CO}/_{CH_4}$
E 137	202.4	5	1.16
E 133	193.9	10	1.14
E 132	194.4	15	1.17
E135	193.9	20	1.19
E139	189.9	25	1.14
E136	197.6	30	1.18
E138	209.7	38	1.16
E134	198.8	45	1.13
		AVERAGE 1.16 ± .03	

TABLE 4.03 CORRELATION BETWEEN % PRESSURE CHANGE AND % PRODUCT FORMATION AT 454.9°C

RUN	p_o(torr)	Δp(torr)	TIME (mins)	%($CH_3CHO+VC+CH_4+CO$)*	$\Delta p/p_o \times 100$
E27	191.0	10.1	5	6.0	5.3
E25	200.7	21.4	10	10.9	10.6
E17	197.9	34.7	15	17.9	17.6
E18	189.4	64.9	25	32.9	34.3
E38	196.3	82.6	30	41.7	42.1
E28	198.3	108.0	35	48.6	54.5
E20	196.7	141.6	45	67.2	71.3

* CO assumed equal to CH_4.

TABLE 4.04 COMPARISON OF % CONVERSION CALCULATED FROM ECH ANALYSIS AND FROM PRODUCT ANALYSIS AT 454.9°C

RUN	P_o (torr)	Δp (torr)	% CONVERSION	
			Ex ECH ANALYSIS	% ($CH_3CHO+VC+CH_4$)
E170	209.9	11.8	3.9	
E171	207.3	14.4		5.5
E201	206.8	19.2	9.0	
E200	202.5	22.6		10.9
E216	209.9	62.3	29.4	
E217	203.3	63.6		29.5
E232	203.3	74.9		34.0
E235	207.7	75.3	37.9	
E233	201.2	99.3		39.1
E234	211.2	109.3	42.6	
E209	208.6	232.2	71.8	
E202	214.7	296.5		78.1

TABLE 4.05 THE FORMATION OF PRODUCTS WITH TIME AT 484.0° AND 439.5°C

RUN	TEMP (°C)	p_o (torr)	TIME (mins)	% PRODUCT ANALYSIS (% of p_o)			* de-H_2O / de-HCl	+ % CONVSN.
				VC	CH_3CHO	CH_4		
E124	484.0	195.1	1.25	.36	5.80	.27	.059	6.4
E118	"	204.7	2	.65	9.31	1.30	.061	11.3
E121	"	192.7	4	1.66	15.60	3.05	.089	20.3
E117	"	190.3	5	1.77	14.86	4.92	.089	21.6
E122	"	200.1	6	2.74	22.54	8.10	.089	33.4
E116	"	194.7	10	4.33	23.99	18.72	.102	47.0
E120	"	194.7	15	7.65	19.76	49.48	.110	76.9
E123	"	198.8	25	8.07	12.80	66.04	.102	86.9
E130	439.5	202.0	5	0.09	2.05	0.04	-	2.2
E126	"	189.9	10	0.21	4.53	0.14	-	4.9
E129	"	193.9	20	0.51	7.27	0.58	.065	8.4
E131	"	193.9	30	0.92	11.65	1.51	.070	14.1
E128	"	186.6	45	1.71	17.39	4.17	.079	23.3
E127	"	190.3	60	2.64	18.59	9.51	.094	30.7

* + see table 4.01.

TABLE 4.06 CORRELATION BETWEEN % PRESSURE CHANGE AND % PRODUCT FORMATION

RUN	TEMP (^oC)	p_o (torr)	Δp (torr)	TIME (mins)	%($CH_3CHO+VC+CH_4+CO$)*	$\Delta p/_{po}$ x 100
E124	484.0	195.1	12.9	1.25	6.7	6.6
E121	"	192.7	48.1	4	23.4	24.9
E117	"	193.9	52.8	5	26.5	27.3
E122	"	190.3	80.8	6	41.5	42.5
E116	"	200.1	131.0	10	65.8	65.5
E120	"	194.7	253.7	15	126.4	130.3
E130	439.5	202.0	3.6	5	2.2	1.8
E126	"	189.9	8.9	10	5.0	4.7
E129	"	193.9	19.8	20	8.9	10.2
E131	"	193.9	33.1	30	15.6	17.1
E128	"	186.6	54.5	45	27.3	29.2
E127	"	190.3	84.4	60	40.3	44.4

* CO ASSUMED EQUAL TO CH_4.

TABLE 4.07 VARIATION OF RATE WITH TEMPERATURE.

TEMP (^{o}C)	$k_1 \times 10^4$ (sec^{-1})		$\log_{10}(k_1 \times 10^5)$	$^1/_T \times 10^3$
	VALUE	NO.OF RUNS AVERAGED		
439.5	0.93 ± .05	5	.969 ± .024	1.403
454.9	1.88 ± .05	5	1.274 ± .012	1.374
484.0	10.80 ± .80	5	2.033 ± .034	1.321

TABLE 4.08 FORMATION OF MINOR PRODUCTS WITH TIME AT 454.9; 484.0, AND 439.5°C

RUN	TEMP	p_o (torr)	TIME (mins)	MINOR PRODUCT ANALYSIS (AS % of Po)			% CONVSN.
				CH_2H_4	CH_3Cl	C_3H_6	
E26	454.9	203.1	2	.013	-	N.D	2.3
E27	"	191.0	5	.030	.029	N.D	5.8
E25	"	200.7	10	.071	.062	N.D	10.1
E17	"	197.9	15	.123	.123	N.D	16.2
E18	"	189.4	25	.288	.200	N.D	27.2
E38	"	196.3	30	.326	.282	.071	32.9
E28	"	198.3	35	.390	.377	.117	36.2
E20	"	196.7	45	.545	.443	.200	47.5
E124	484.0	195.1	1.25	.034	.037	.002	6.4
E118	"	204.7	2	.076	.063	.006	11.3
E121	"	192.7	4	.188	.182	.018	20.3
E117	"	193.9	5	.200	.183	.029	21.6
E122	"	190.3	6	.317	.289	.050	33.4
E116	"	200.1	10	.531	.494	.162	47.0
E120	"	194.7	15	1.059	1.082	.655	76.9
E123	"	198.8	25	1.070	1.103	.935	86.9
E130	439.5	202.0	5	.011	.008	N.D	2.2
E126	"	189.9	10	.026	.020	N.D	4.9
E129	"	193.9	20	.055	.050	.003	8.4
E131	"	193.9	30	.117	.089	.008	14.1
E128	"	186.6	45	.227	.171	.030	23.3
E127	"	190.3	60	.370	.269	.081	30.7

TABLE.4.09 EFFECT OF INHIBITOR ON INITIAL RATE AND PRESSURE CHANGE FOR 45 MINS. REACTIONS AT 454.9°C

RUN	p_o (torr)	% INHIBITOR	k_1 (sec^{-1})	Δp at 45MINS	$\Delta p/p_o$ x 100
		TOLUENE			
E20	198.6	0	1.88×10^4	141.6	71.1
E36	199.0	6.3	1.77×10^4	124.5	62.6
E50	206.3	21.9	1.62×10^4	103.8	49.8
E51	200.3	31.2	1.60×10^4	91.9	45.9
E49	201.9	50.1	1.57×10^4	86.6	42.9
		PROPYLENE			
E74	197.5	0	1.91×10^4	149.5	75.7
E73	196.7	6.2	1.71×10^4	100.8	51.2
E72	199.9	12.3	1.67×10^4	93.9	47.0
E71	201.5	22.0	1.73×10^4	97.5	48.4
E70	199.5	48.5	1.64×10^4	87.9	44.0

TABLE 4.10 PRODUCT FORMATION WITH TIME AT 454.9°C IN THE PRESENCE OF 50% INHIBITOR.

RUN	p_o (torr)	% TOLUENE	TIME (mins)	PRODUCT ANALYSIS (AS % of p_o) VC			*$\frac{\text{de-H}_2\text{O}}{\text{de-HCl}}$	+ % CONVSN.
				VC	CH_3CHO	CH_4		
E58	202.3	48.6	2	.03	1.65	.01	-	1.7
E52	198.3	51.2	5	.07	4.39	.07	-	4.5
E54	201.5	50.8	10	.18	8.31	.30	.020	8.8
E53	193.8	51.5	15	.34	11.25	.56	.029	12.1
E57	201.9	46.3	20	.47	15.89	.98	.028	17.3
E55	199.5	49.9	25	.58	19.14	1.51	.028	21.2
E56	197.9	47.2	35	.90	23.89	3.12	.033	27.9
E49	201.9	50.1	45	1.22	27.92	5.58	.036	34.7
		% PROPYLENE						
E70	199.5	48.5	45	2.00	29.70	4.31	.059	36.0

* + see table 4.01

TABLE 4.11 FORMATION OF MINOR PRODUCTS WITH TIME AT 454.9°C IN THE PRESENCE OF 50% INHIBITOR

RUN	p_o (torr)	% TOLUENE	TIME	% CONVSN.	MINOR PRODUCT ANALYSIS (AS % of P_o)		
					C_2H_4	CH_3Cl	C_3H_6
E58	202.3	48.6	2	1.7	.003	.003	N.D
E52	198.3	51.2	5	4.5	.011	-	N.D.
E54	201.5	50.8	10	8.8	.028	.017	N.D
E53	193.8	51.5	15	12.1	.037	.025	N.D
E57	201.9	46.3	20	17.3	.054	.036	.002
E55	199.5	49.9	25	21.2	.057	.045	.003
E56	197.9	47.2	35	27.9	.114	.069	.008
E49	201.9	50.1	45	34.7	.169	.105	.019

TABLE 4.12 EFFECT OF PACKING ON RATE AND PRODUCT FORMATION AT 454.9°C

RUN	p_o (torr)	k x 10^4 (sec^{-1})	TIME (mins)	PRODUCT ANALYSIS (AS % OF P_o)			% CONVSN. OF ECH	$\frac{de\text{-}H_2O}{de\text{-}HCl}$
				VC	CH_3CHO	CH_4		
E193	201.2	2.92	10	.53	11.20	1.01	12.7	.043
E195	205.9	2.43	20	1.12	19.44	3.54	24.1	.049
E198	209.0	3.09	30	1.96	26.60	9.73	38.3	.054
E197	193.3	2.59	45	2.71	28.83	18.33	49.9	.057
ADDITION OF 50% TOLUENE.								
E211	226.4	2.44	20	.77	19.43	2.65	22.9	.035

		TIME	MINOR PRODUCT ANALYSIS (As % of P_o)		
			C_2H_2	CH_3Cl	C_3H_6
E193	AS ABOVE	10	.082	.059	.004
E195	" "	20	.183	.123	.016
E198	" "	30	.333	.210	.051
E197	" "	45	.462	.305	.115
ADDITION OF 50% TOLUENE					
E211	AS ABOVE	20	.159	.076	.006

TABLE 4.13 EFFECT OF STEEL ON INITIAL RATE (AS k_1) AND PRODUCT FORMATION AT 400°C

RUN	p_o (torr)	Δp (torr)	$k_1 x10^4$ (sec^{-1})	TIME (mins)	PRODUCT ANALYSIS (AS % of p_o)					
					VC	CH_3CHO	CH_4	C_2H_4	CH_3Cl	C_3H_6
E13S	210.2	42.0	41.1	2	.075	20.23	.134	.353	.003	N.D
E10S	209.8	67.9	38.2	4	.118	28.20	.415	.457	.006	.001
E4S	199.3	92.1	41.9	5	.110	41.43	.865	.386	.007	.001
E16S	205.7	88.5	42.9	6	.236	38.90	1.03	.614	.013	.002
E12S	210.2	127.2	43.5	8	.283	51.83	2.32	.625	.018	.002
E5S	204.3	126.3	37.3	10	.279	54.13	2.82	.675	.024	.004
E11S	209.8	143.2	36.1	12	.373	55.73	4.43	.774	.060	.005
E17S	213.4	204.7	41.0	20	.680	65.06	13.82	1.036	.055	.013
E14S	186.5	208.9	39.4	30	.602	59.35	22.34	1.126	.065	.022
E30S	214.2	162.0	61.8	10	.348	62.11	4.47	.664	.019	.004
E31S*	204.7	138.2	51.7	10	.259	61.65	2.34	.686	.013	.003
E32S	213.8	143.4	54.0	10	-	-	-	-	-	-

* RUN CONTAINING 55.2% TOLUENE

TABLE 4.14. EFFECT OF CCl_4 ON THE INITIAL RATE (AS k_1) AND THE PRESSURE CHANGE FOR 15 MINS. REACTIONS AT 454.9°C

RUN	p_o (torr)	% CCl_4	k_1 (sec^{-1})	Δp AT 15MIN (torr)	$^{\Delta p}/_{p_o}$ x 100
E75	204.7	0	1.91×10^4	38.3	18.7
E76	205.1	.06	2.30 x "	45.1	22.0
E86	189.0	.58	3.74 x "	84.6	44.8
E79	212.8	.98	4.10 x "	122.1	57.4
E81	199.9	1.49	4.29 x "	122.5	61.3
E77	193.4	1.65	4.58 x "	121.3	62.7
E83	205.5	2.18	4.82 x "	154.8	75.3
E84	201.1	3.01	5.30 x "	177.3	88.2
E85	198.3	3.23	5.58 x "	179.3	90.4
E87	197.1	3.72	5.78 x "	180.1	91.4
E78	201.1	4.01	5.70 x "	187.8	93.4

TABLE 4.15 EFFECT OF ~1.5% CCl_4 ON THE PRODUCT ANALYSIS AT 454.9°C

RUN	p_o (torr)	$\%CCl_4$	TIME (mins)	PRODUCT ANALYSIS (AS % OF p_o)			* de-H_2O / de-HCl	+ % CONVSN.
				VC	CH_3CHO	CH_4		
E82	203.5	1.48	5	2.01	8.35	2.31	.188	13.2
E80	201.5	1.50	10	4.61	14.64	10.03	.186	32.1
E81	199.9	1.49	15	5.84	15.53	18.06	.174	43.4
				C_2H_4	CH_3Cl	C_3H_6		
E82	AS ABOVE			.332	.323	.034		
E80	" "			.799	.855	.159		
E81	" "			.957	1.062	.346		

* + SEE TABLE 4.01

TABLE 4.16 EFFECT OF 50% HCl ADDITION ON THE PRODUCT FORMATION AT 454.9°C

RUN	p_o (torr)	Δp (torr)	TIME (mins)	PRODUCT ANALYSIS (AS % OF P_o)			$\frac{\text{de-}H_2O}{\text{de-HCl}}$	+% CONVSN.
				VC	CH_3CHO	CH_4		
E41	196.3	8.5	2	.52	3.52	.20	-	4.4
E64	199.1	21.4	5	.90	7.34	.62	.113	8.9
E65	193.0	58.0	12	2.44	15.27	4.53	.123	22.2
E40	202.3	86.2	20.5	3.49	20.99	8.99	.116	33.5
E39	200.3	124.2	30	4.43	24.51	16.29	.109	45.2
				C_2H_4	CH_3Cl	C_3H_6		
E41	AS ABOVE			.028	.033	N.D		
E64	"	"		.088	.063	.005		
E65	"	"		.227	.168	.033		
E40	"	"		.205	.260	.084		
E39	"	"		.282	.350	.162		

* + see table 4.01

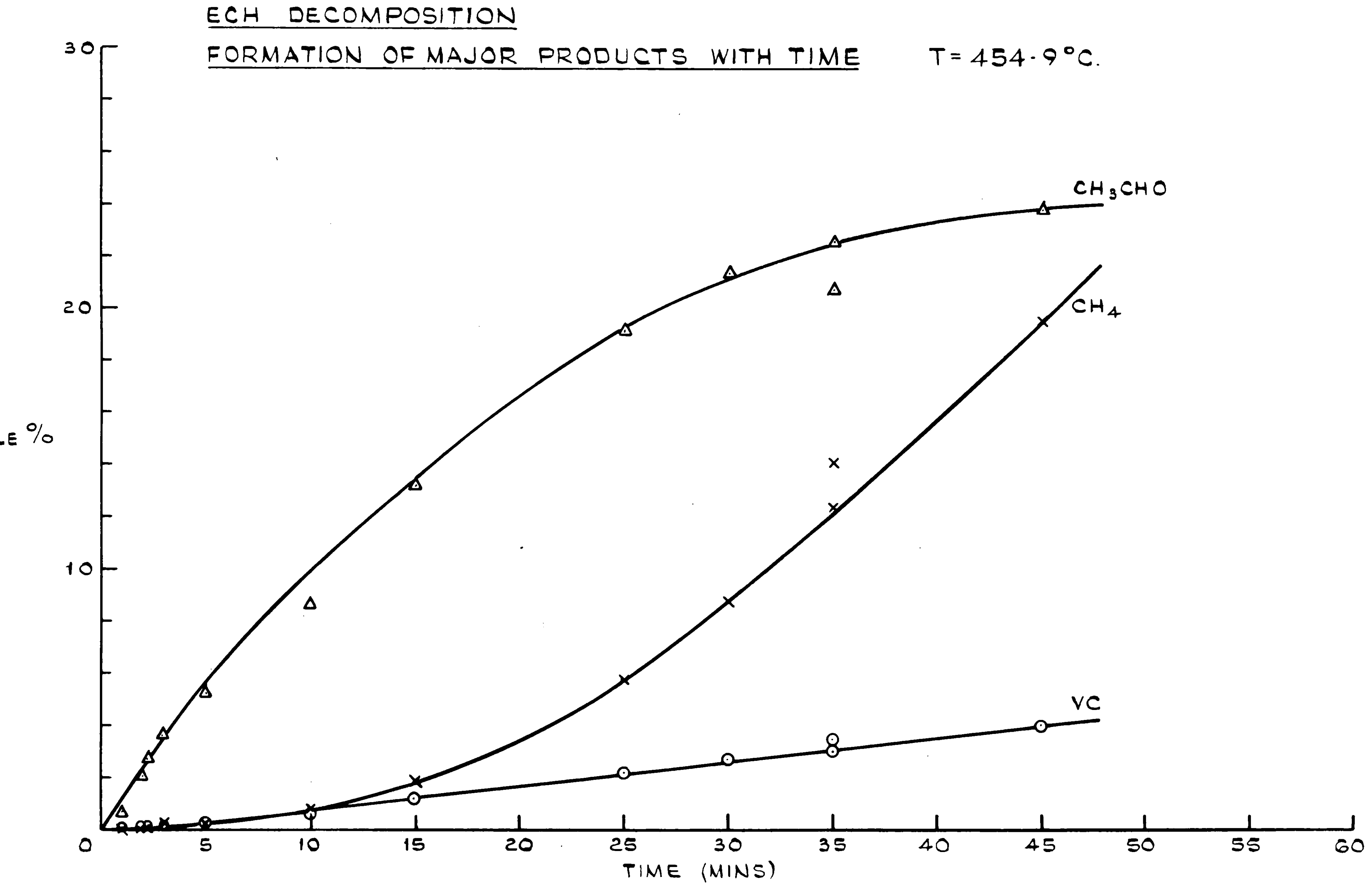
TABLE 4.17 EFFECT OF HBr ON THE INITIAL RATE (AS k_1) AND THE PRESSURE CHANGE AFTER 15 MINS. REACTION AT 454.9°C.

RUN	p_o (torr)	% HBr	k_1 (sec^{-1})	Δp (torr)	$\Delta p/p_o$ x 100
E101	202.3	0	1.96×10^4	39.1	19.3
E97	203.5	.91	2.93 x "	70.1	34.5
E89	206.3	1.05	3.80 x "	93.1	45.1
E102	201.1	1.40	3.58 x "	87.5	43.5
E105	201.5	1.80	6.58 x "	141.0	70.0
E98	190.2	2.18	6.26 x "	145.9	76.7
E90	205.9	2.29	4.25 x "	140.2	68.1
E94	216.0	2.44	3.95 x "	150.3	69.6
E104	205.9	2.58	11.48 x "	218.8	106.3
E96	203.5	2.67	11.08 x "	239.8	117.9
E91	200.7	3.27	5.44 x "	189.0	94.2
E92	204.3	3.85	12.02 x "	257.5	126.0

TABLE 4.18 EFFECT OF ~2.2% HBr ON PRODUCT FORMATION AT 454.9°C

RUN	p_o (torr)	%HBr	TIME (mins)	PRODUCT ANALYSIS (AS % OF p_o)			$\frac{\text{de-}H_2O}{\text{de-HCl}}$*	% CONVSN.+
				VC	CH_3CHO	CH_4		
E100	206.3	2.11	5	1.25	5.91	9.08	.084	16.1
E99	202.7	2.11	10	2.90	7.75	20.18	.104	34.0
E98	190.2	2.18	15	4.38	7.62	32.77	.108	44.5
				C_2H_4	CH_3Cl	C_3H_6		
E100	AS ABOVE			.209	.129	.010		
E99	" "			.361	.310	.059		
E98	" "			.468	.451	.151		

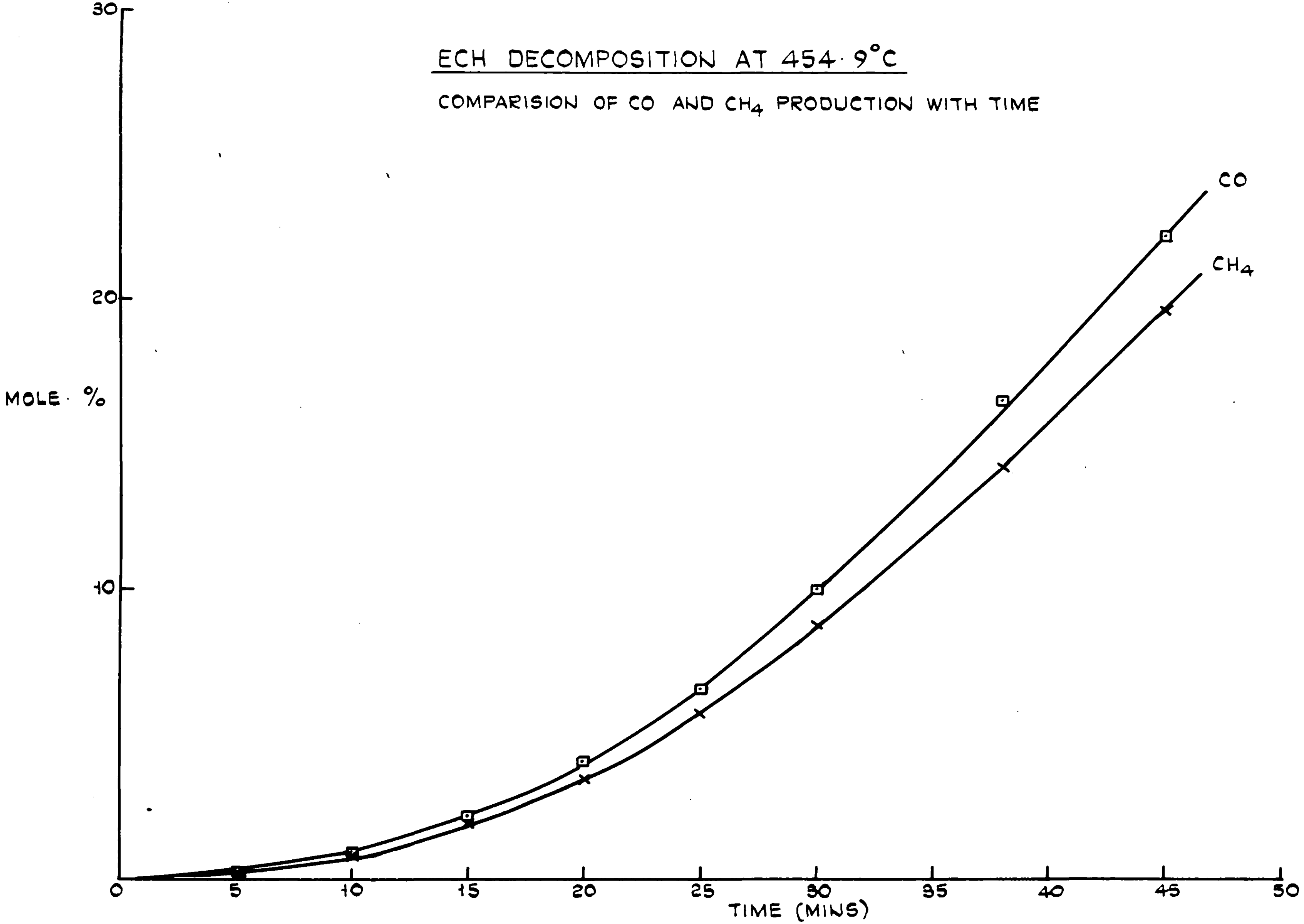
FIGURE 4.01



ECH DECOMPOSITION

FORMATION OF MAJOR PRODUCTS WITH TIME T= 454·9°C.

FIGURE 4.02



ECH DECOMPOSITION AT 454·9°C

COMPARISION OF CO AND CH_4 PRODUCTION WITH TIME

ECH DECOMPOSITION COMPARISON OF PRESSURE CHANGE AND PRODUCT FORMATION AT THREE TEMPERATURES

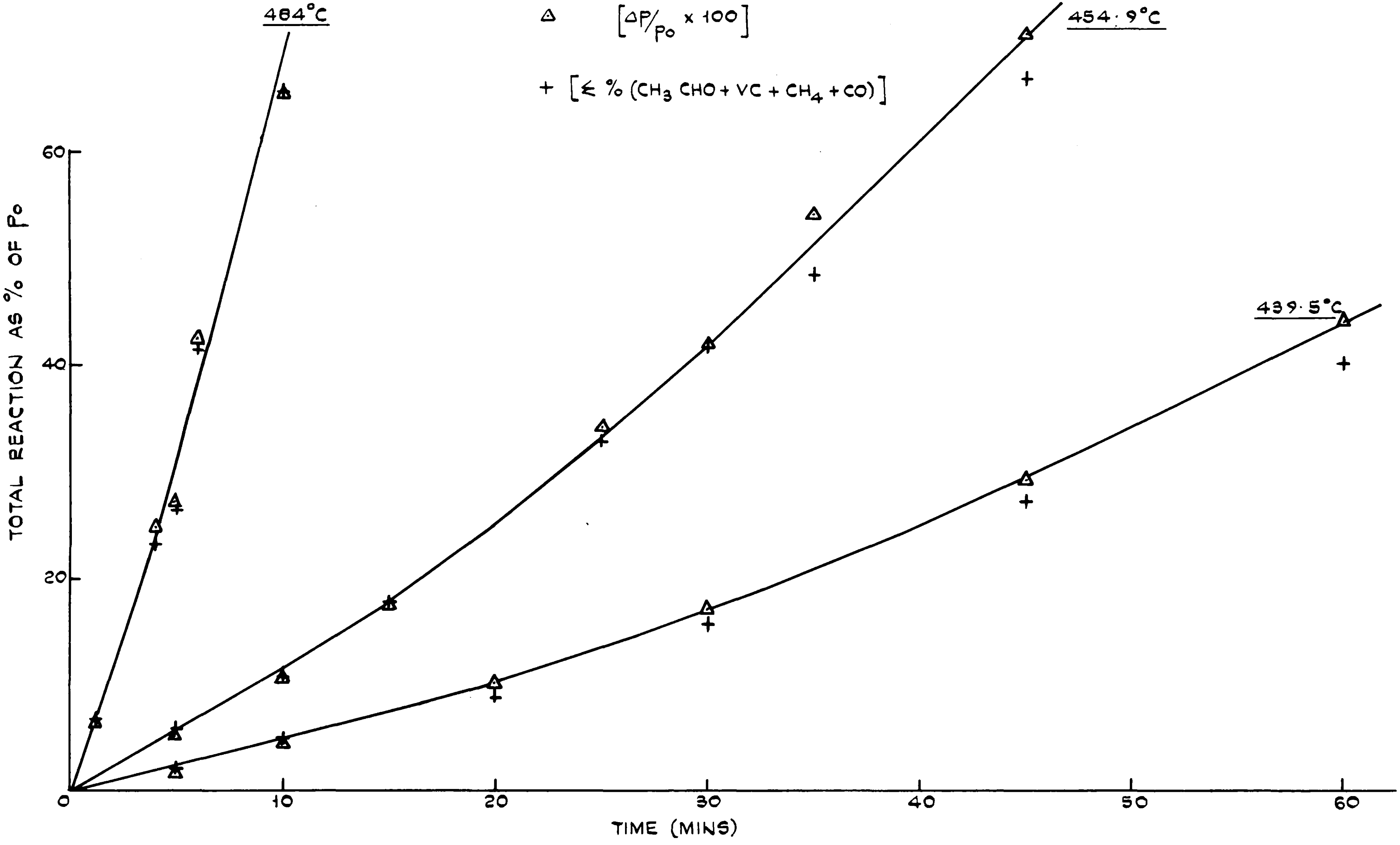


FIGURE 4.03

FIGURE 4.04

ECH DECOMPOSITION AT 454·9°C

RELATIONSHIP BETWEEN % CONVERSION AND ΔP

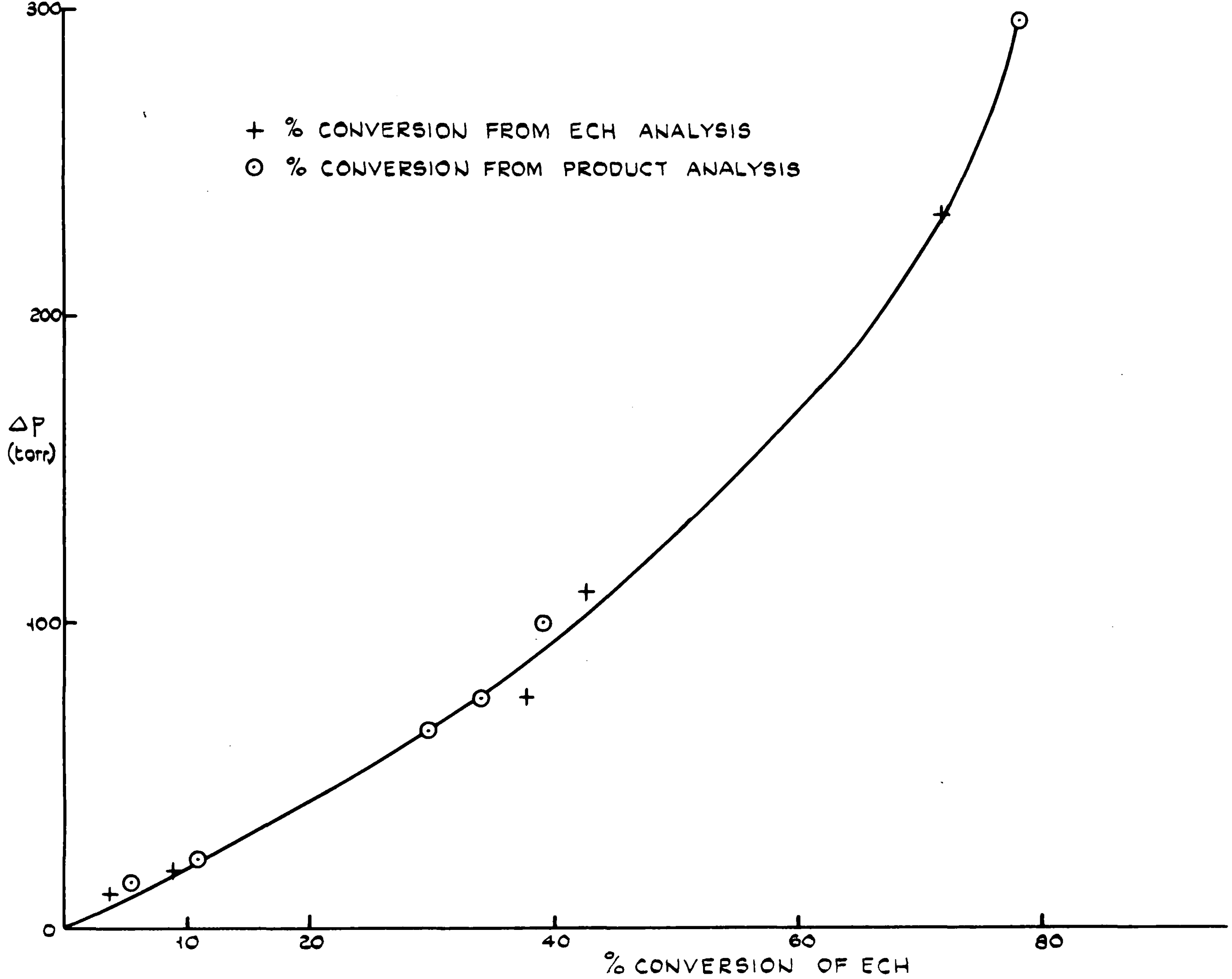


FIGURE 4.05 (a)

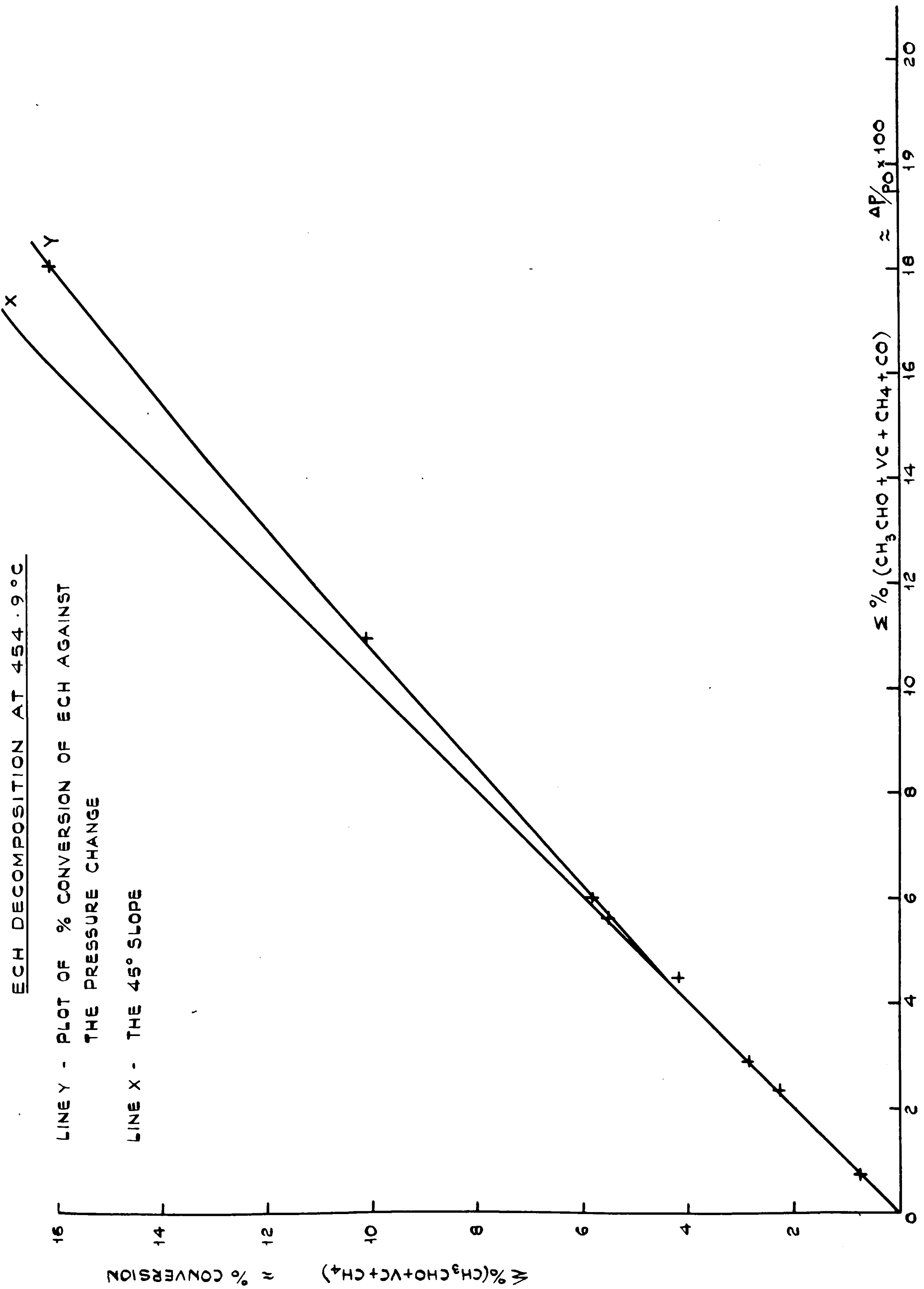

ECH DECOMPOSITION AT 454.9°C
LINE Y - PLOT OF % CONVERSION OF ECH AGAINST THE PRESSURE CHANGE
LINE X - THE 45° SLOPE
X
Y
0
2
4
6
8
10
12
14
16
18
19
20
$\Sigma\%(CH_3CHO+VC+CH_4+CO) \approx \Delta P/P_0 \times 100$
$\Sigma\%(CH_3CHO+VC+CH_4) \approx$ % CONVERSION

FIGURE 4.05 (b)

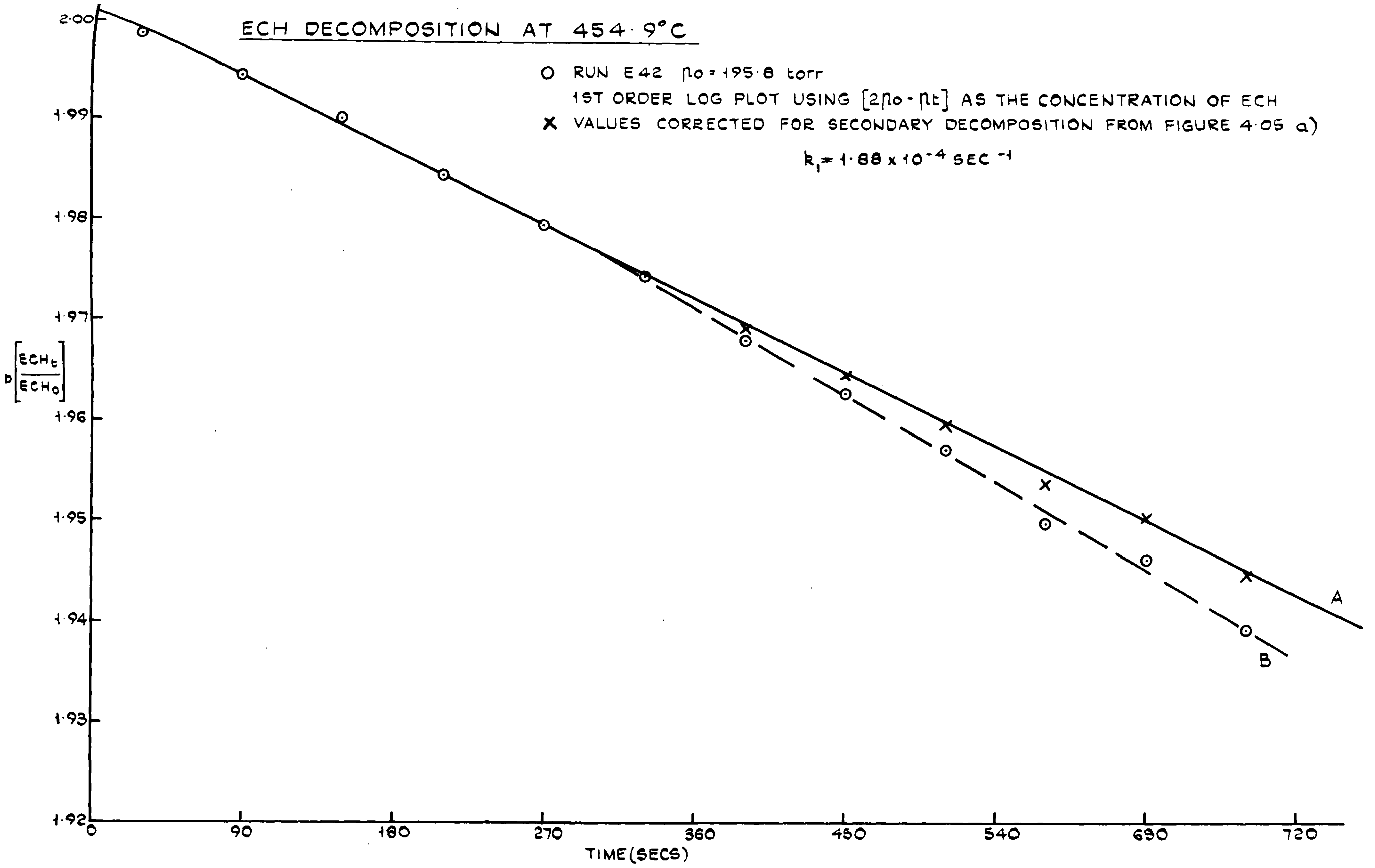

ECH DECOMPOSITION AT 454·9°C
O RUN E42 p_o = 195·8 torr
1ST ORDER LOG PLOT USING $[2p_o - p_t]$ AS THE CONCENTRATION OF ECH
X VALUES CORRECTED FOR SECONDARY DECOMPOSITION FROM FIGURE 4·05 a)
$k_1 = 1{\cdot}88 \times 10^{-4}$ SEC^{-1}
A
B
$D\left[\frac{ECH_t}{ECH_o}\right]$
2·00
1·99
1·98
1·97
1·96
1·95
1·94
1·93
1·92
0
90
180
270
360
450
540
630
720
TIME (SECS)

FIGURE 4.06

ECH DECOMPOSITION AT 484°C

FORMATION OF MAJOR ORGANIC PRODUCTS WITH TIME [p_0 = 200 torr]

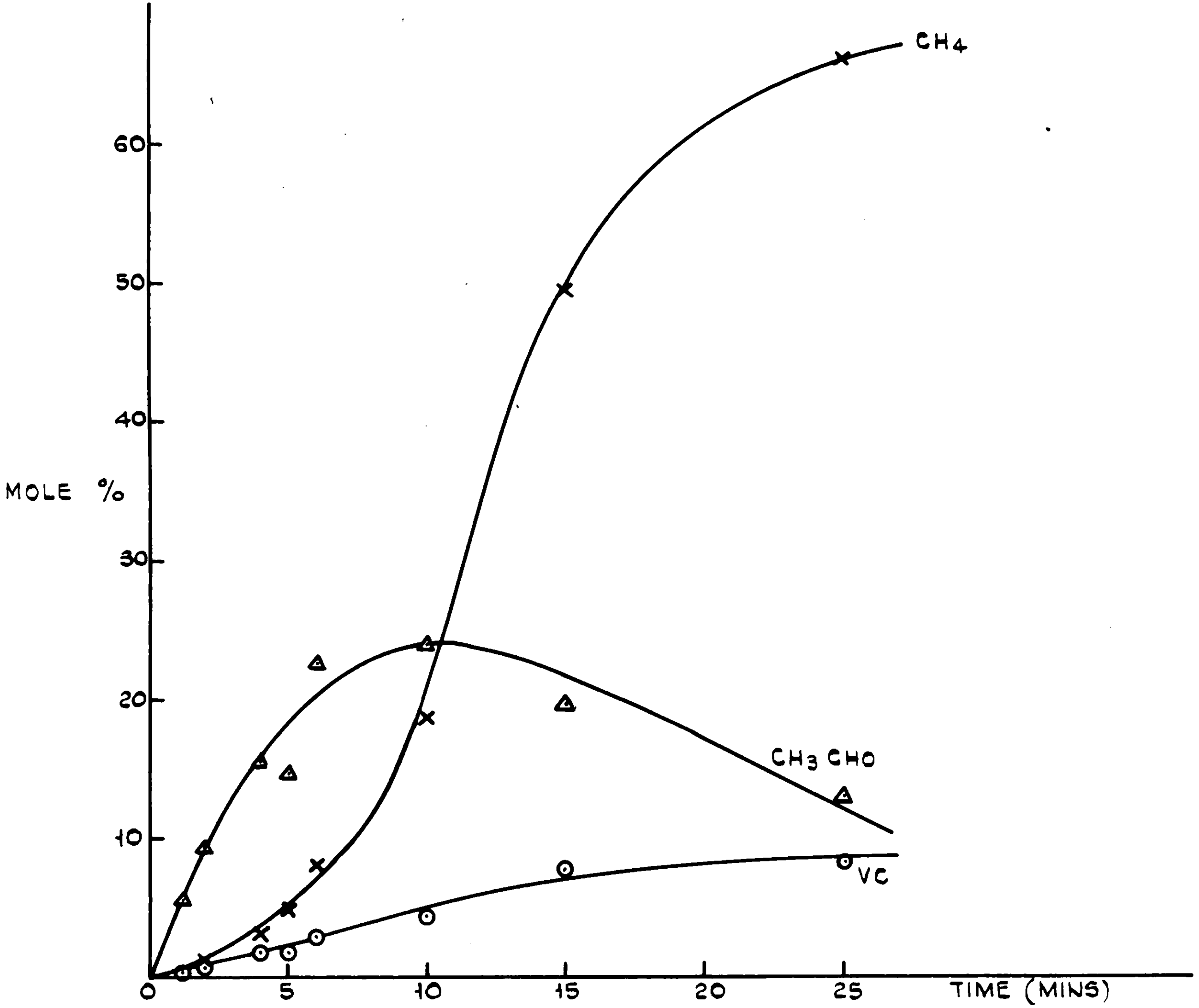


FIGURE 4.07

ECH DECOMPOSITION AT 439·5°C

FORMATION OF MAJOR ORGANIC PRODUCTS AS A FUNCTION OF TIME

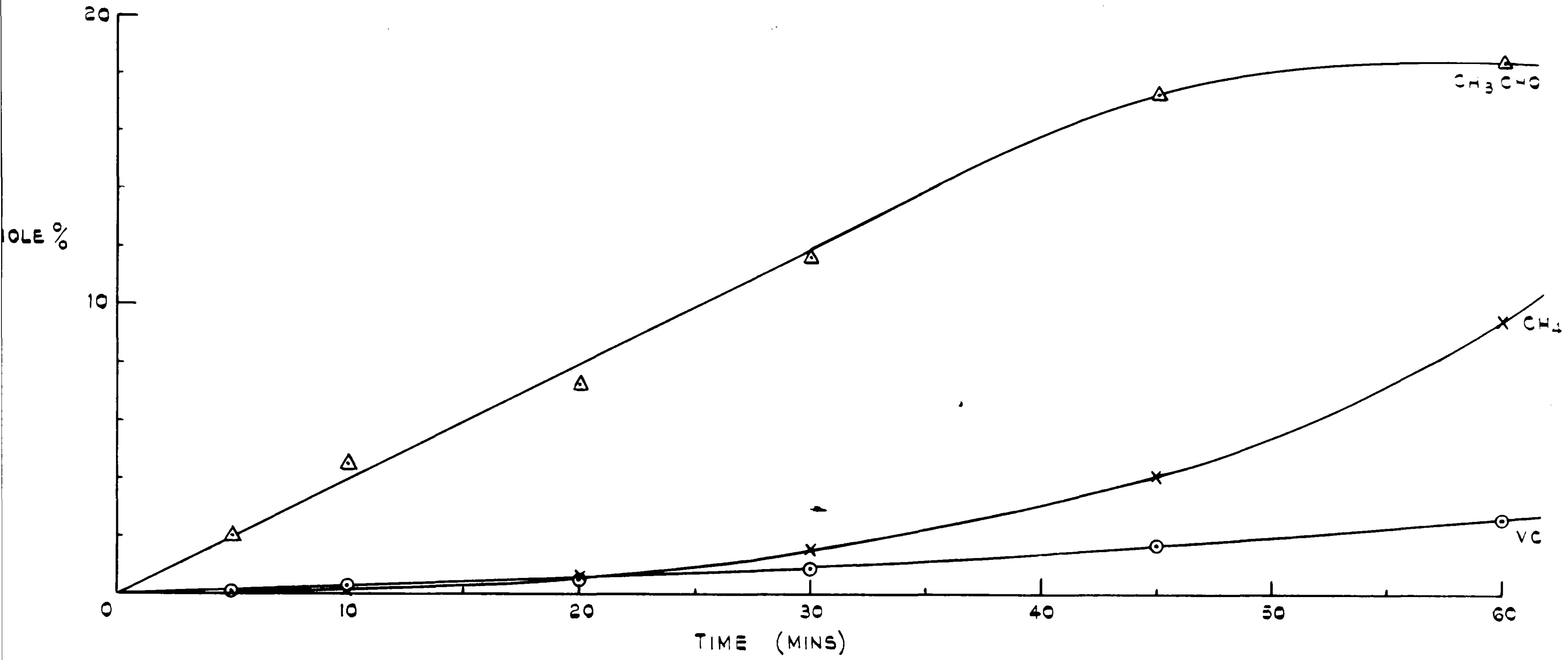
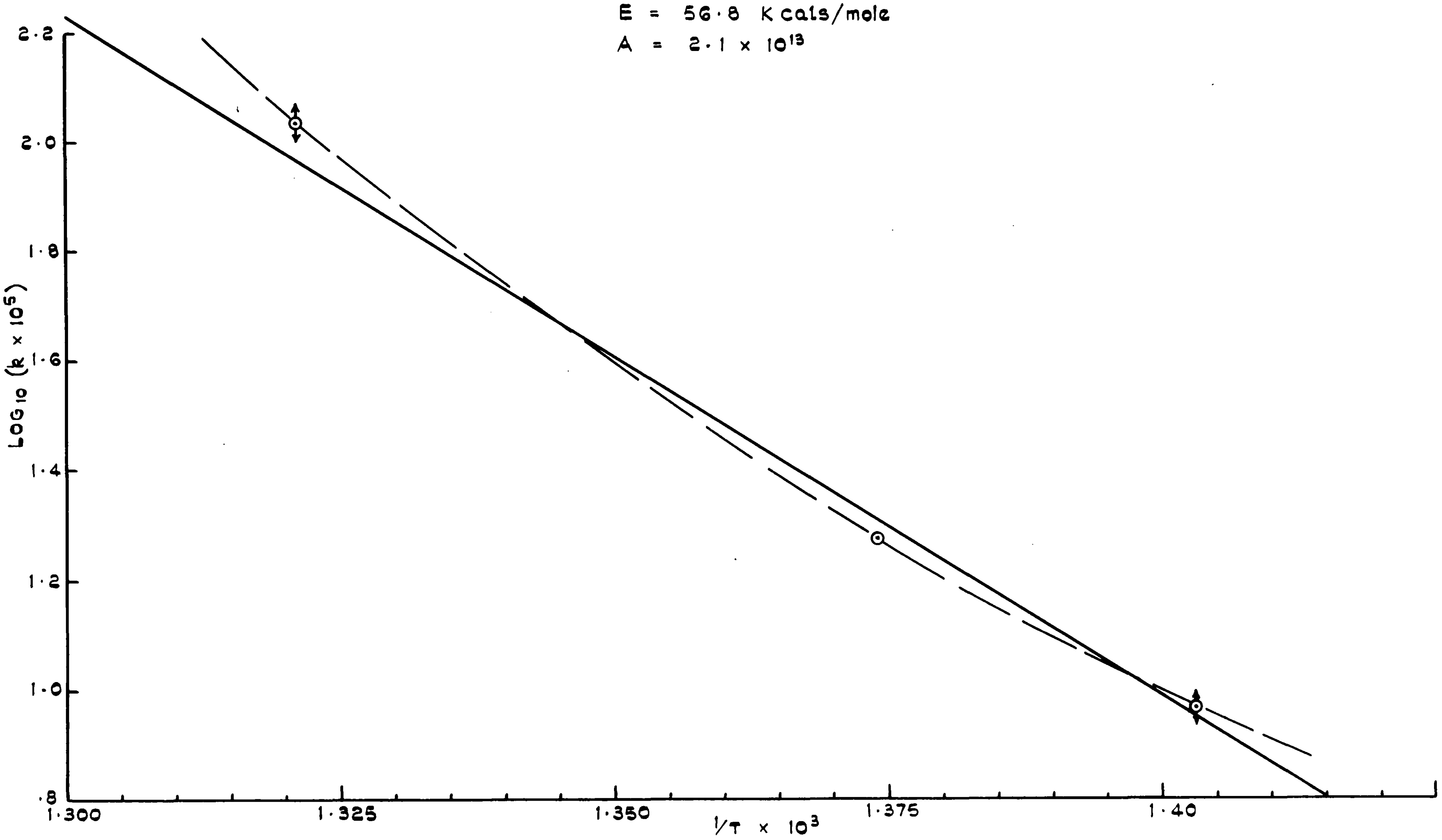


FIGURE 4.08

ECH DECOMPOSITION - ARRHENIUS PLOT



E = 56·8 K cals/mole

A = $2\cdot1 \times 10^{13}$

FIGURE 4.09

ECH DECOMPOSITION

RATIO OF DEHYDRATION TO DEHYDROCHLORINATION

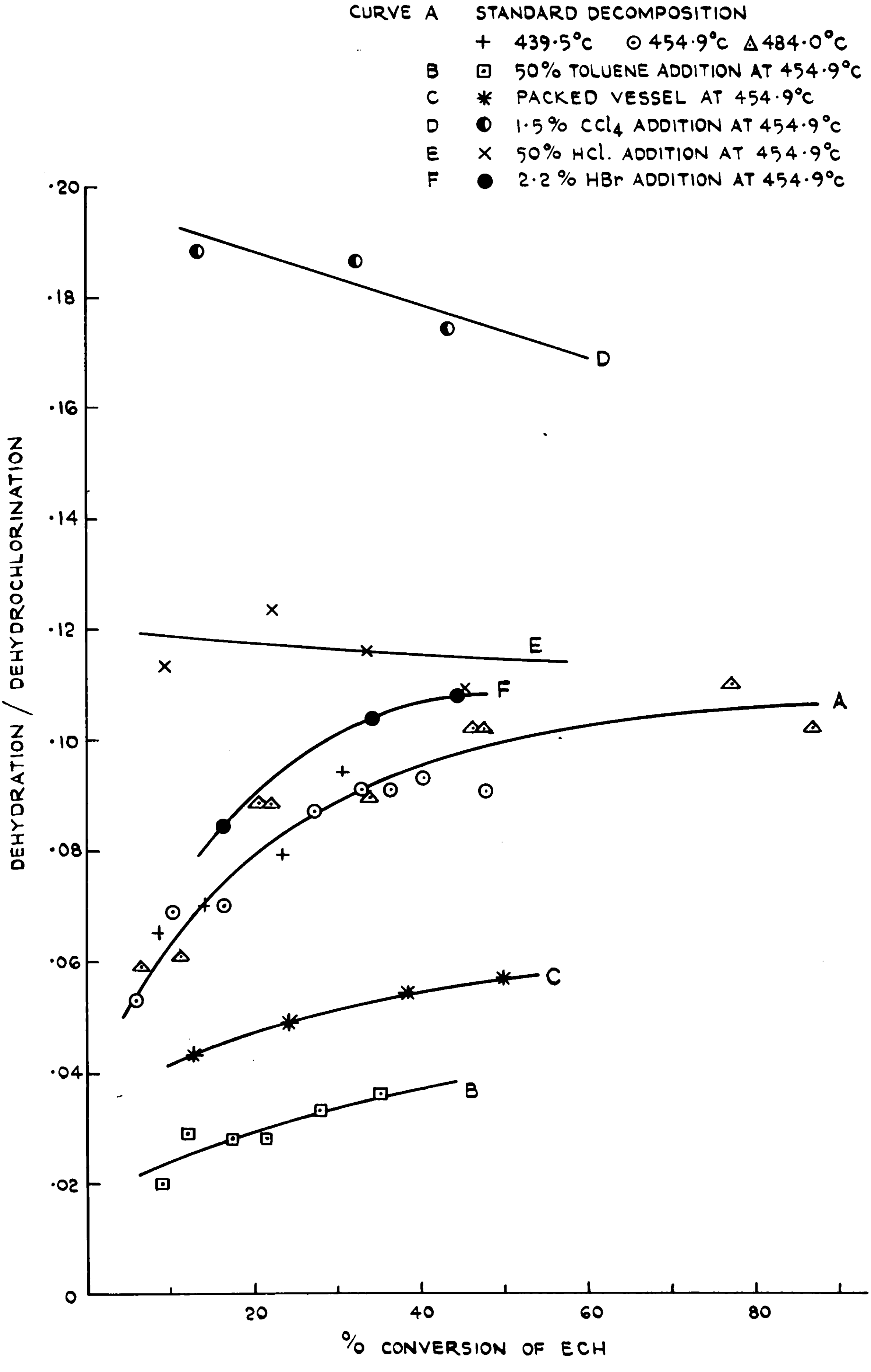
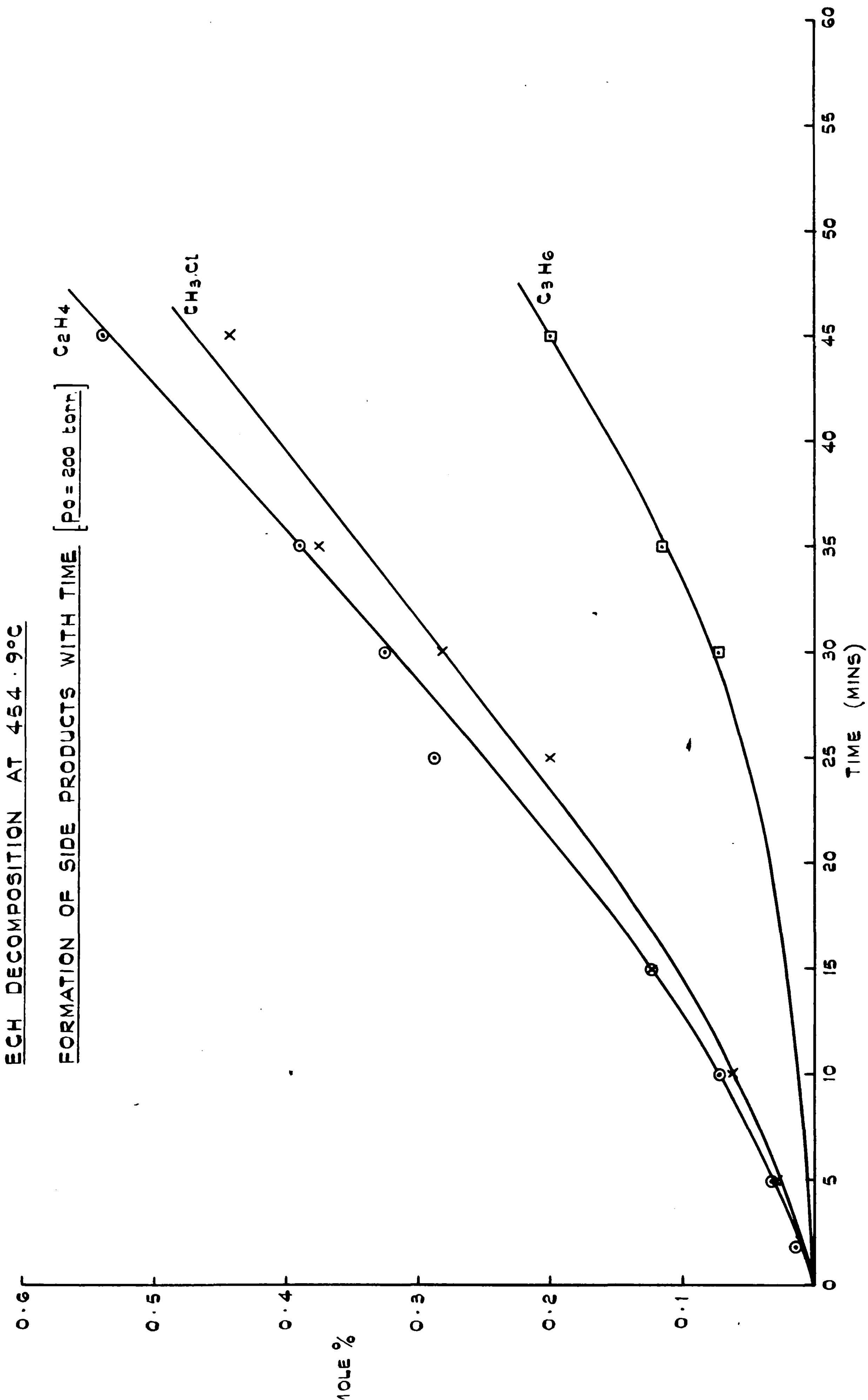


FIGURE 4.10



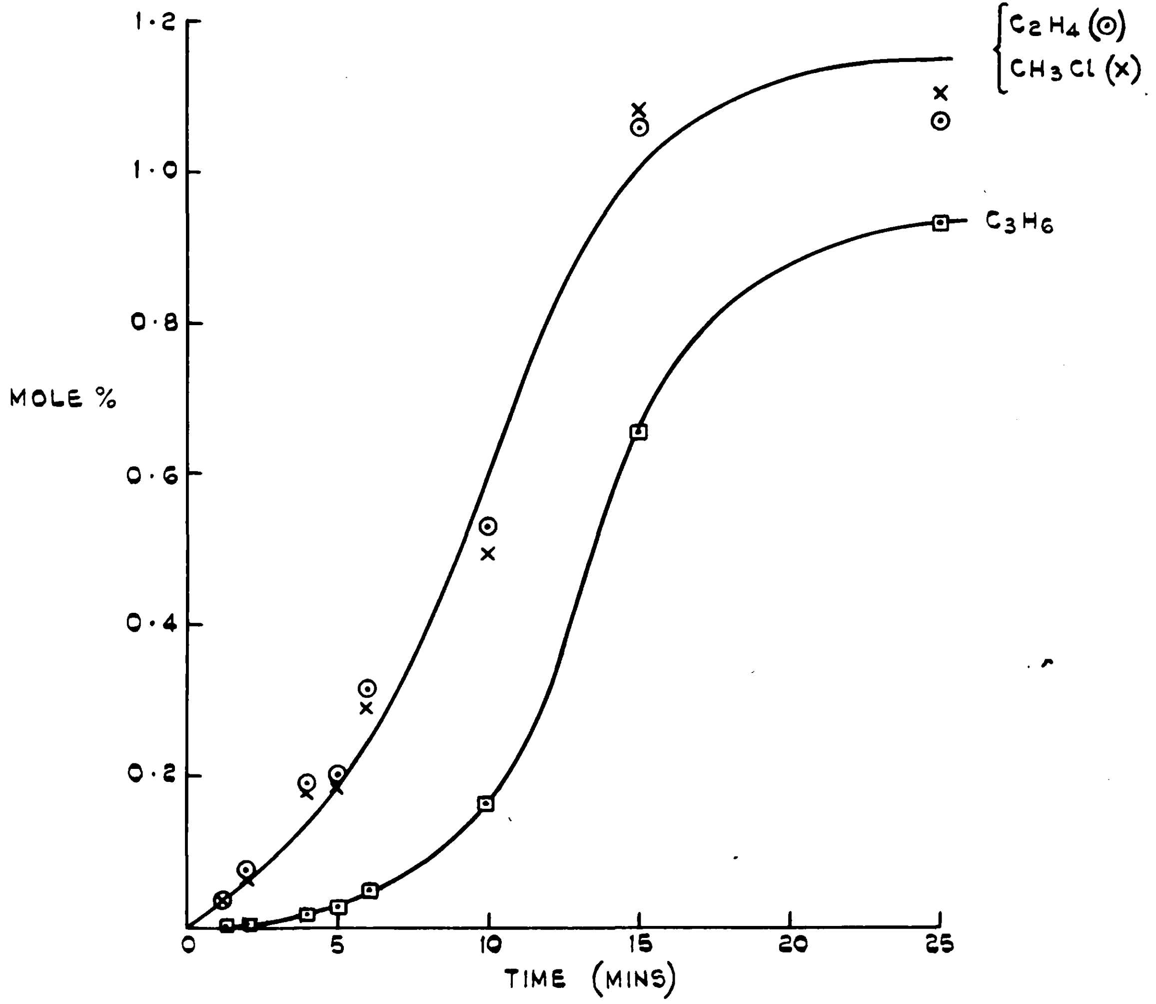
ECH DECOMPOSITION AT 454·9°C

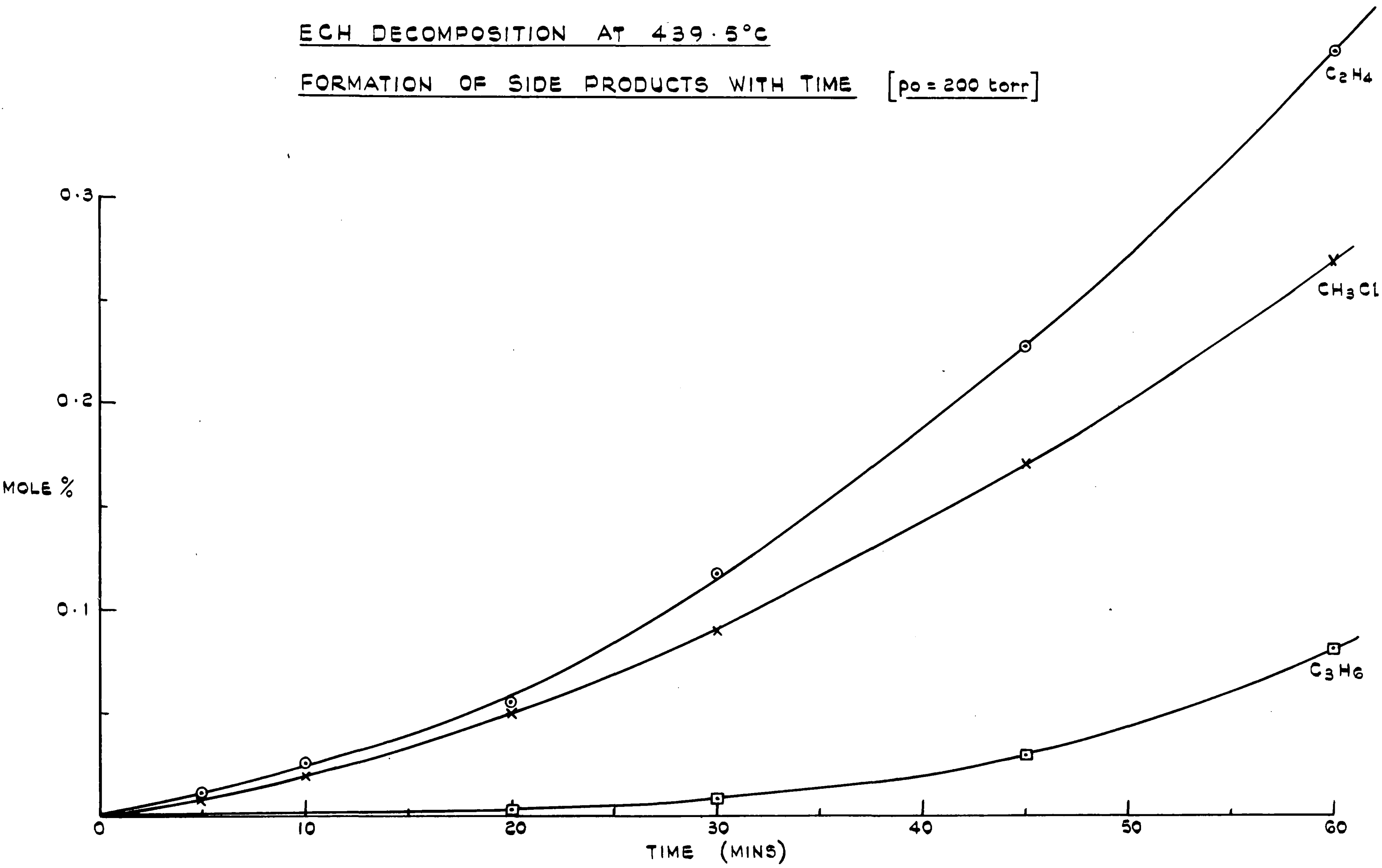
FORMATION OF SIDE PRODUCTS WITH TIME [Po = 200 torr]

FIGURE 4.11

ECH DECOMPOSITION AT 484·0°C

FORMATION OF SIDE PRODUCTS WITH TIME [po = 200 torr]





ECH DECOMPOSITION AT 439·5°C

FORMATION OF SIDE PRODUCTS WITH TIME [po = 200 torr]

FIGURE 4.12

FIGURE 4.13

ECH DECOMPOSITION AT 484°C

FORMATION OF SIDE PRODUCTS AS A FUNCTION OF CONVERSION OF ECH

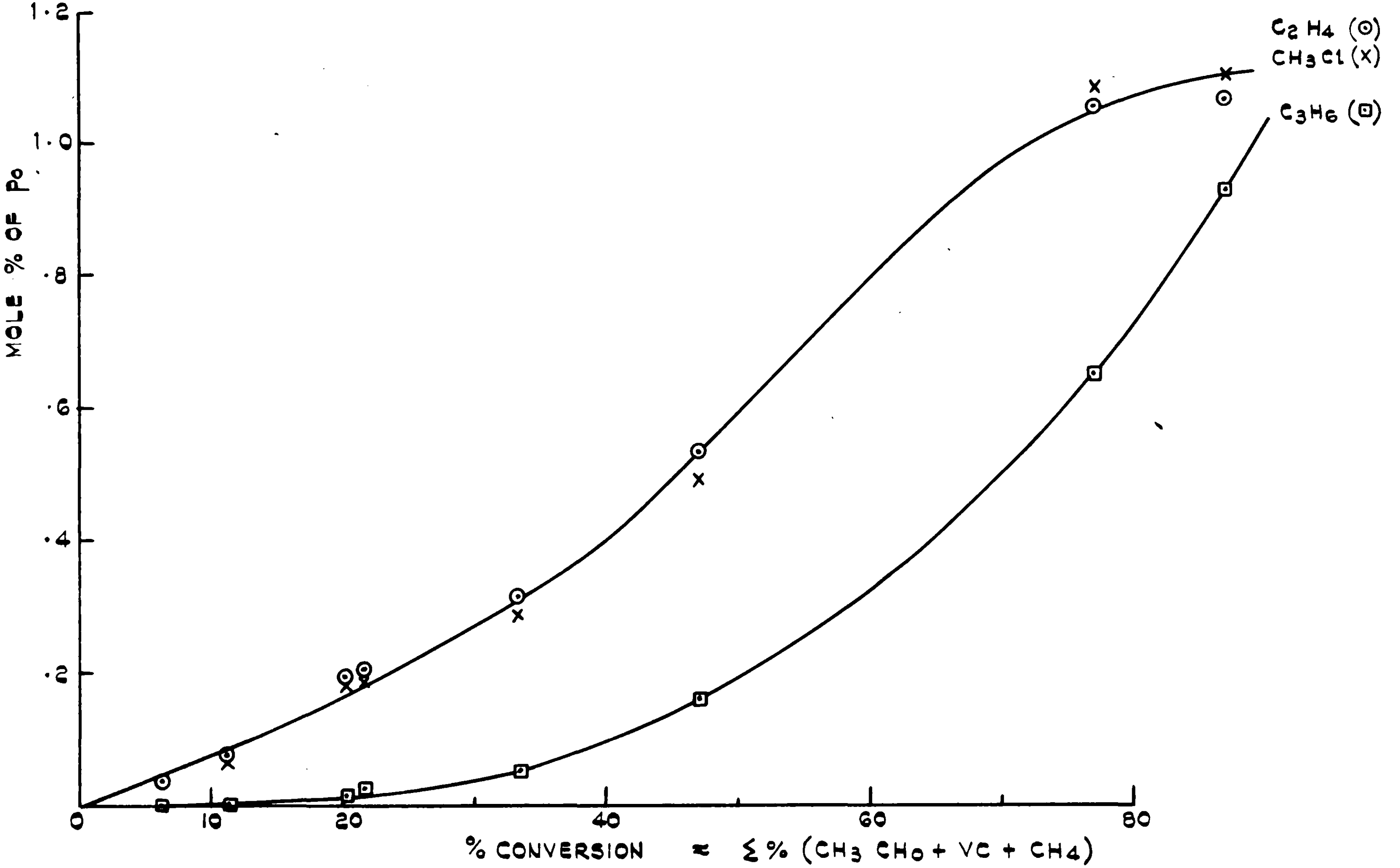
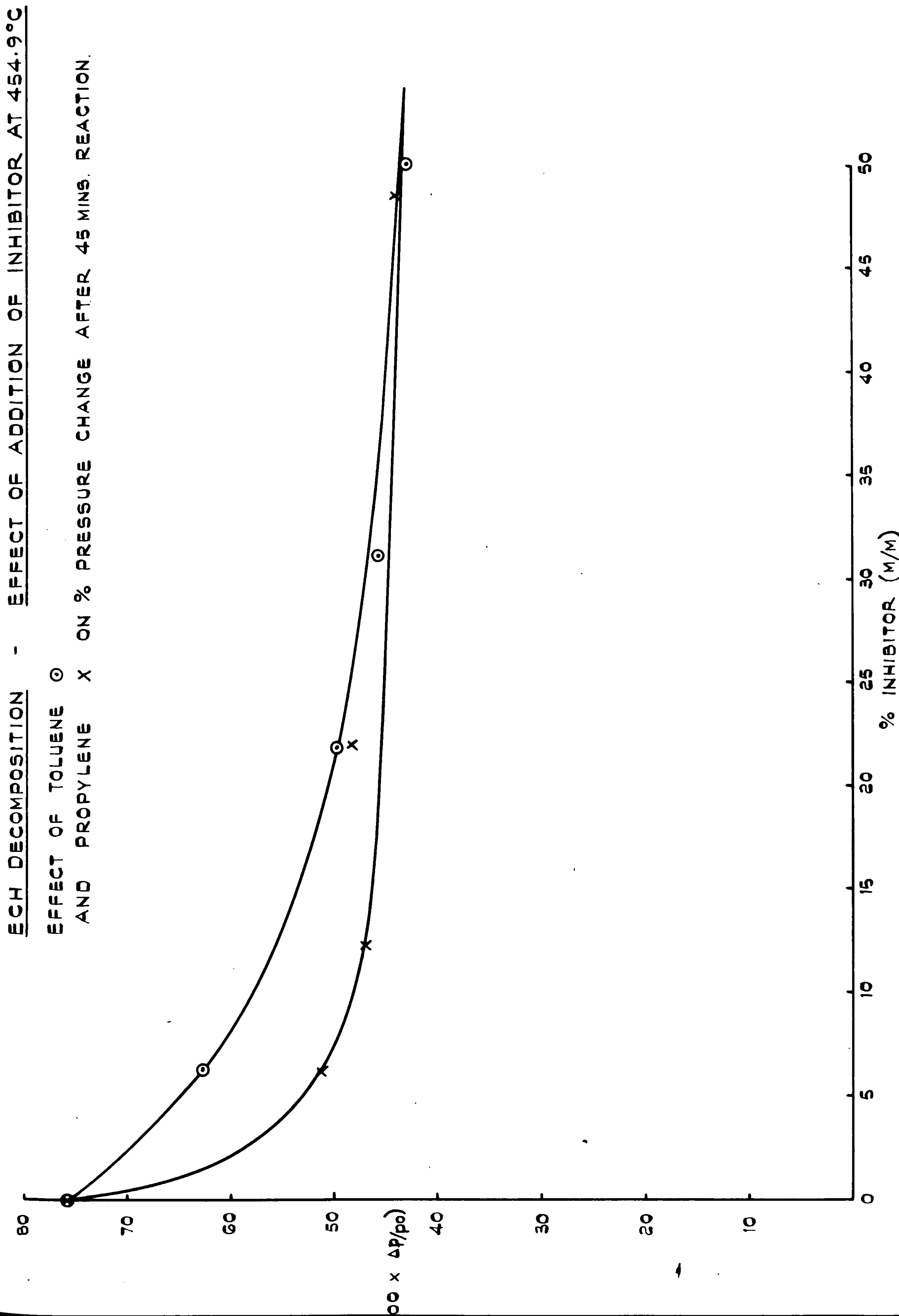


FIGURE 4.14



ECH DECOMPOSITION - EFFECT OF ADDITION OF INHIBITOR AT 454.9°C

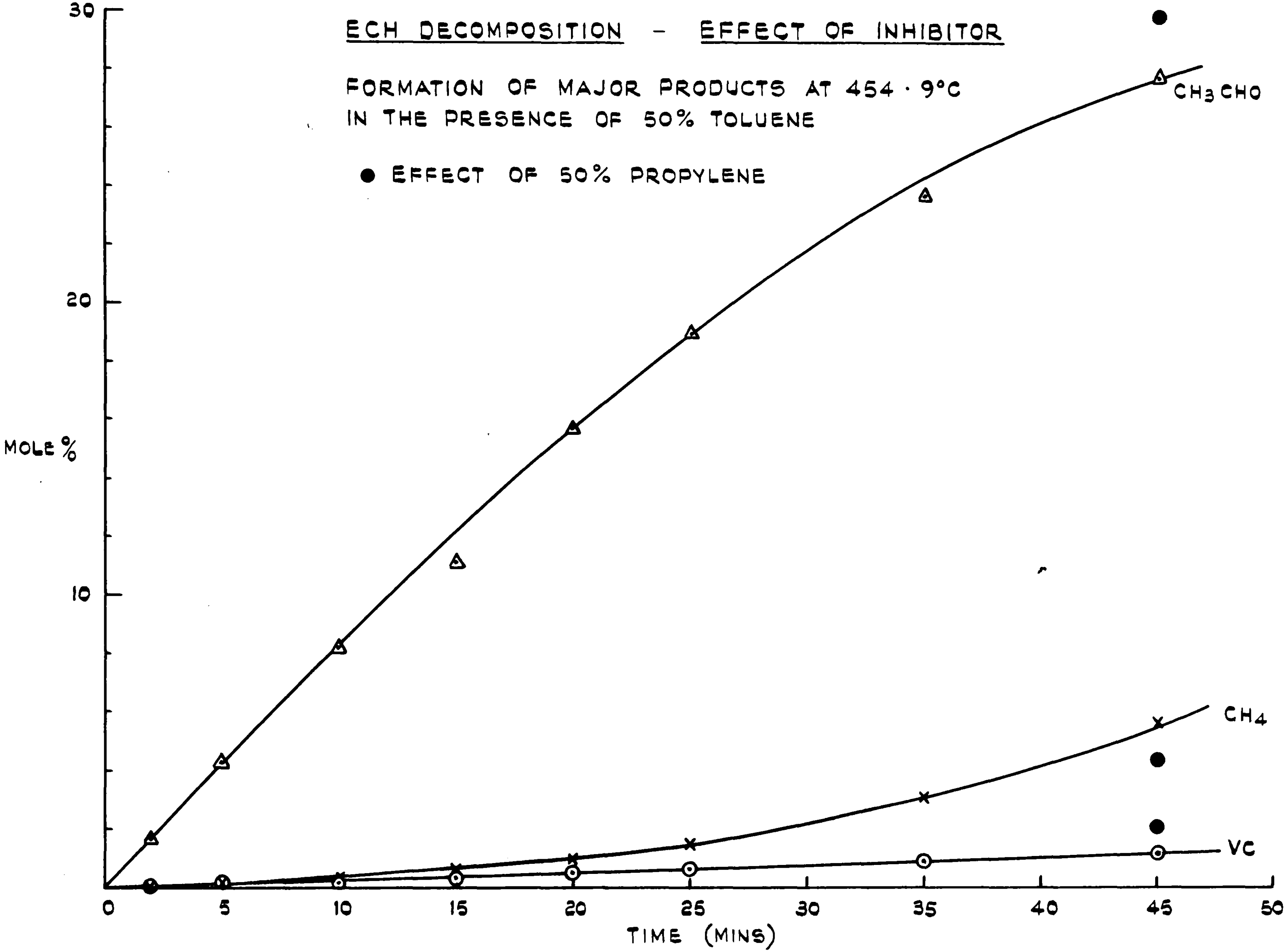

ECH DECOMPOSITION - EFFECT OF INHIBITOR
FORMATION OF MAJOR PRODUCTS AT 454·9°C
IN THE PRESENCE OF 50% TOLUENE
● EFFECT OF 50% PROPYLENE
CH3CHO
CH4
VC
MOLE %
30
20
10
0
5
10
15
20
25
30
35
40
45
50
TIME (MINS)

FIGURE 4.15

FIGURE 4.16

ECH DECOMPOSITION AT 454·9 °C

FORMATION OF MINOR PRODUCTS WITH TIME IN THE PRESENCE OF 50% TOLUENE

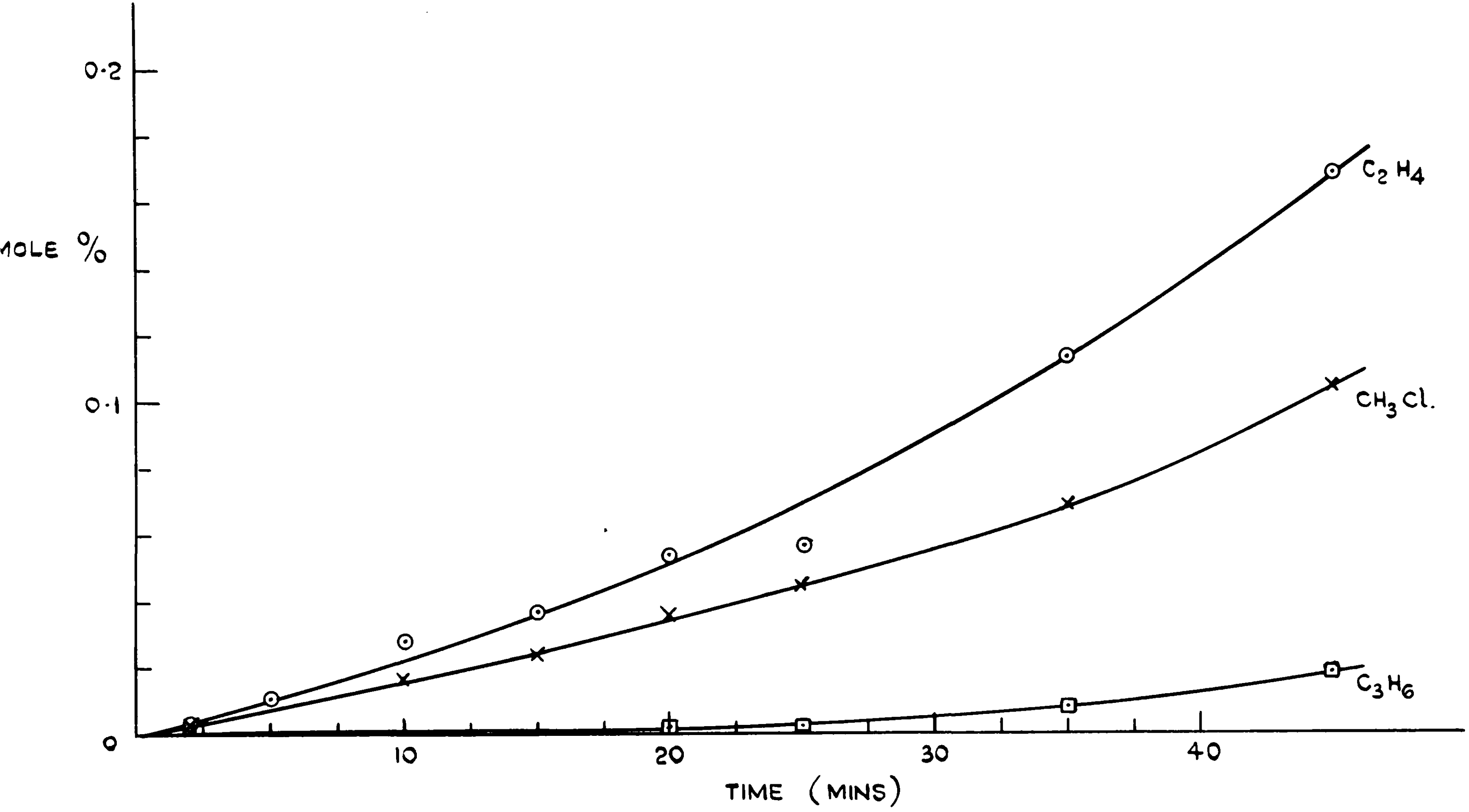


FIGURE 4.17

ECH DECOMPOSITION AT 454·9°C IN A PACKED VESSEL

FORMATION OF MAJOR PRODUCTS WITH TIME

SOLID POINTS - EFFECT OF 50% TOLUENE (■ REFERS TO CH_4)

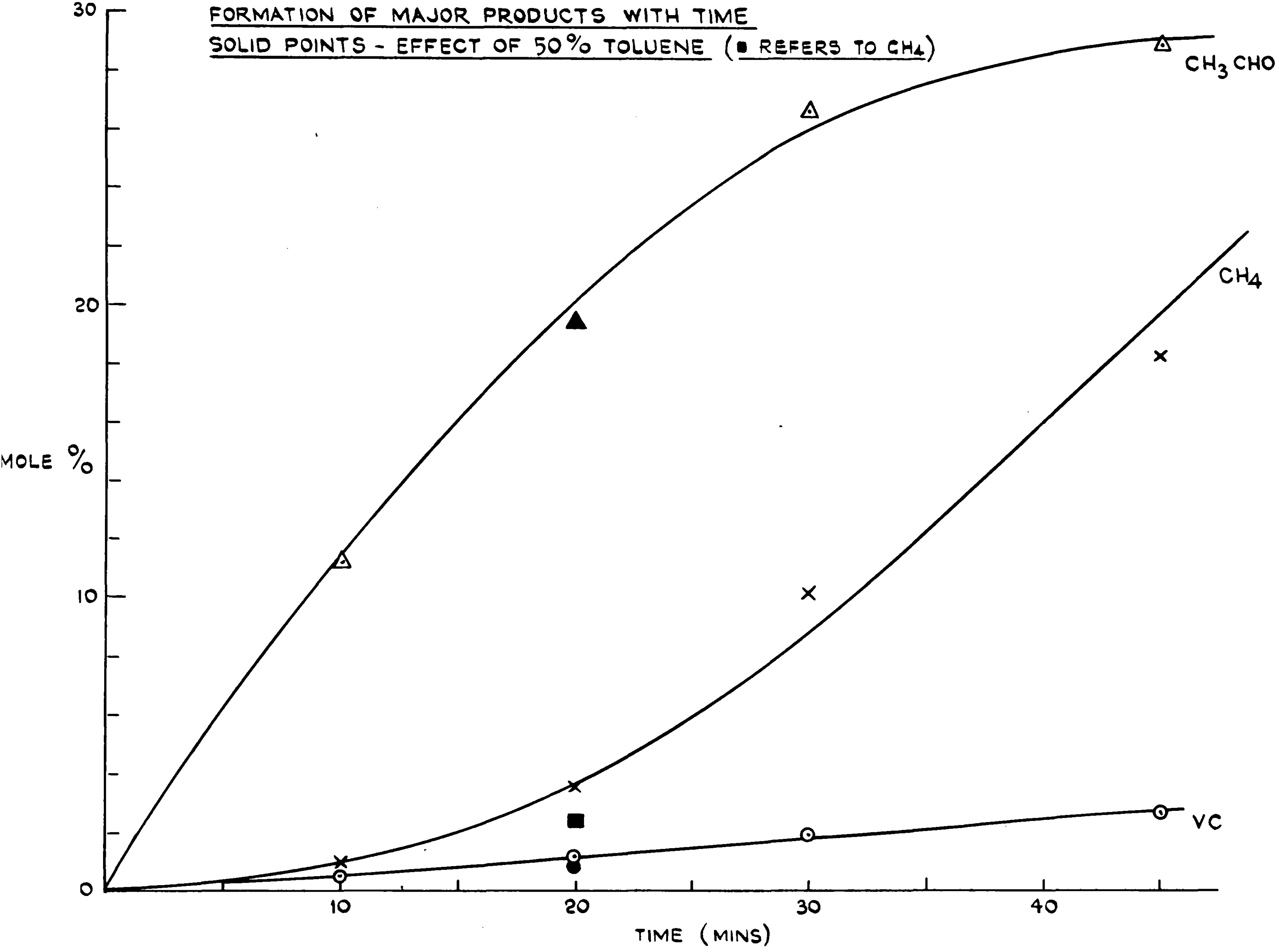
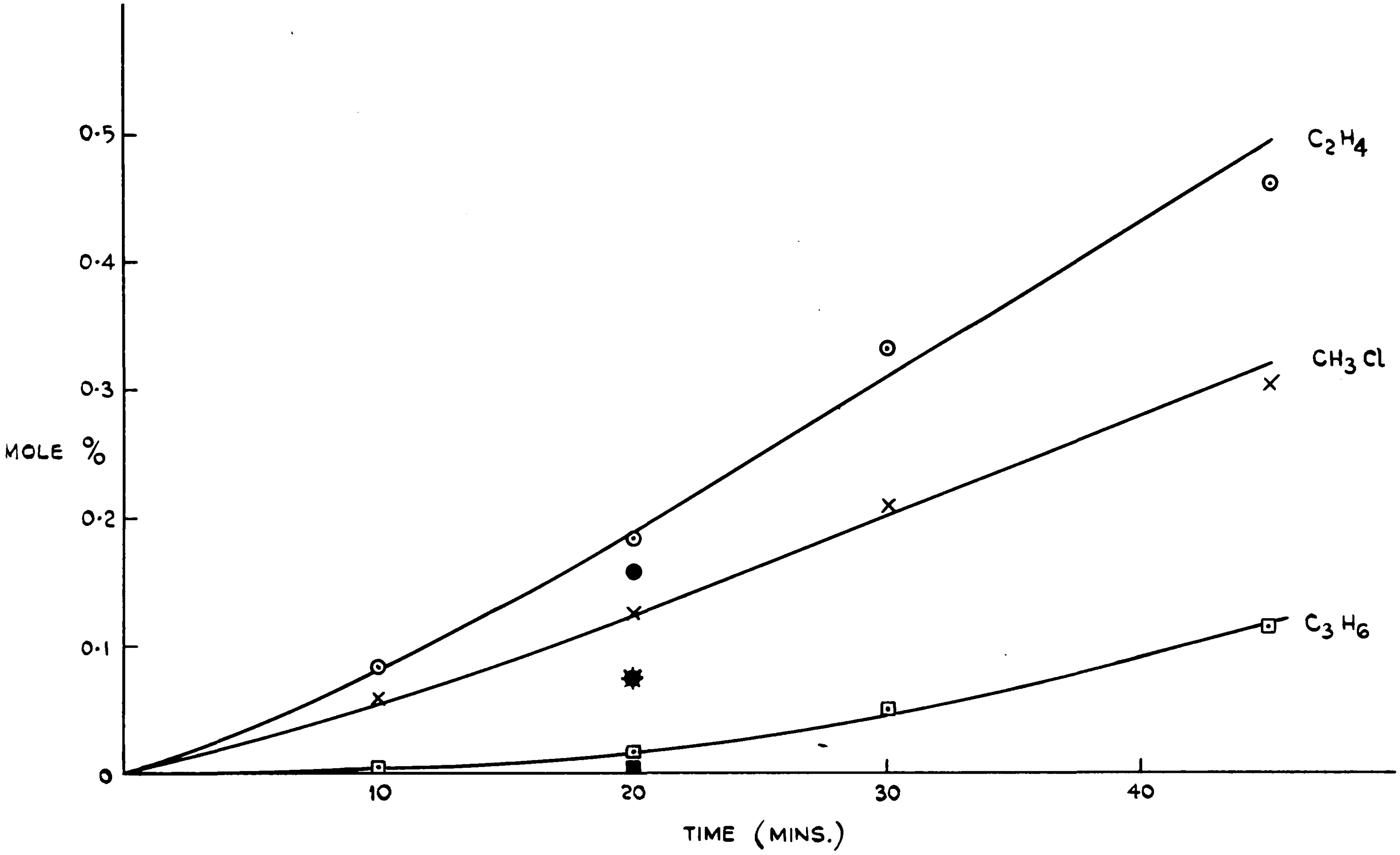


FIGURE 4. 18

ECH DECOMPOSITION AT 454·9°C IN A PACKED VESSEL

FORMATION OF MINOR PRODUCTS WITH TIME

SOLID POINTS - EFFECT OF 50% TOLUENE ADDITION



ECH DECOMPOSITION IN STEEL AT 400°C

FORMATION OF PRODUCTS WITH TIME

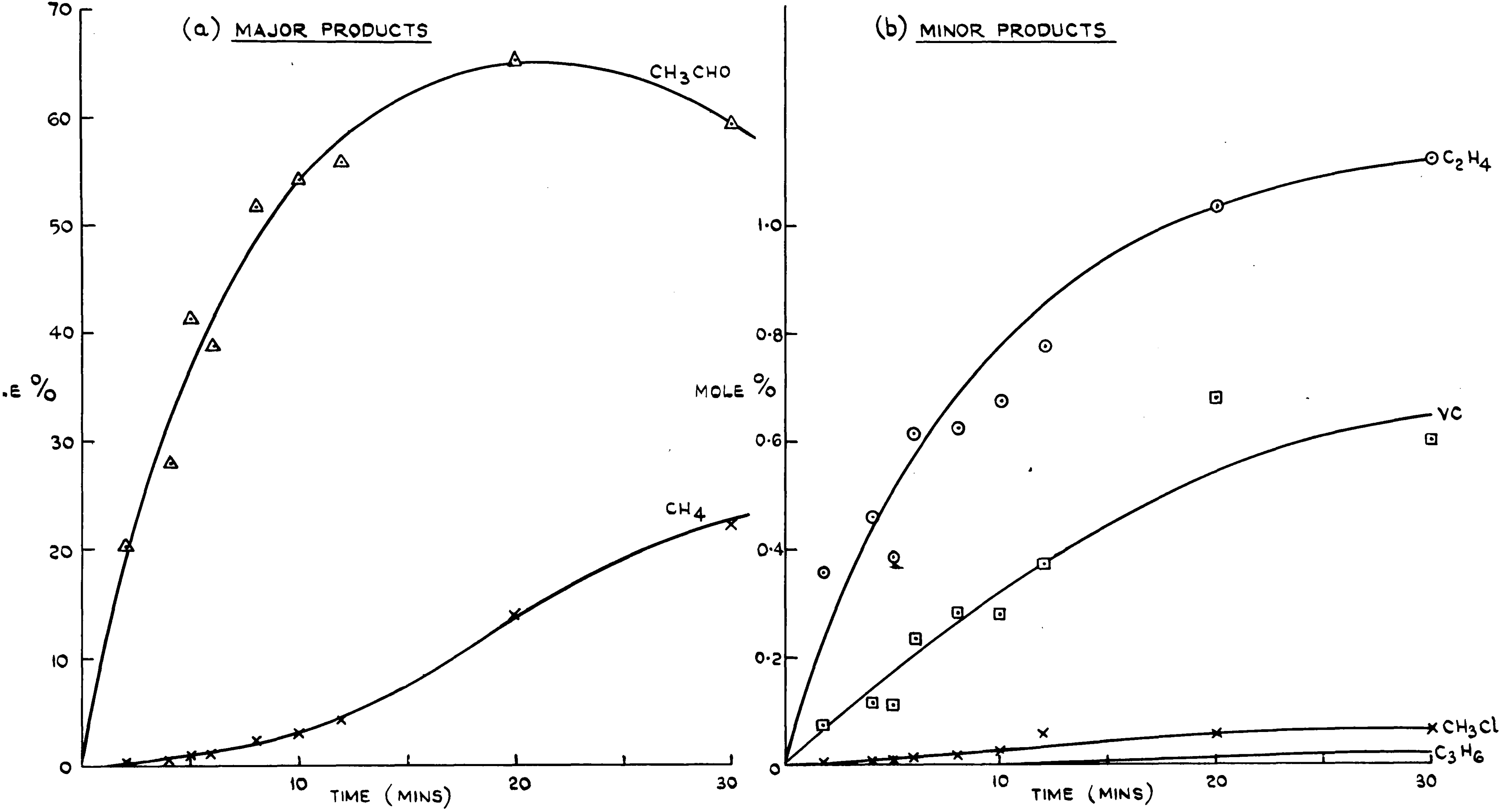
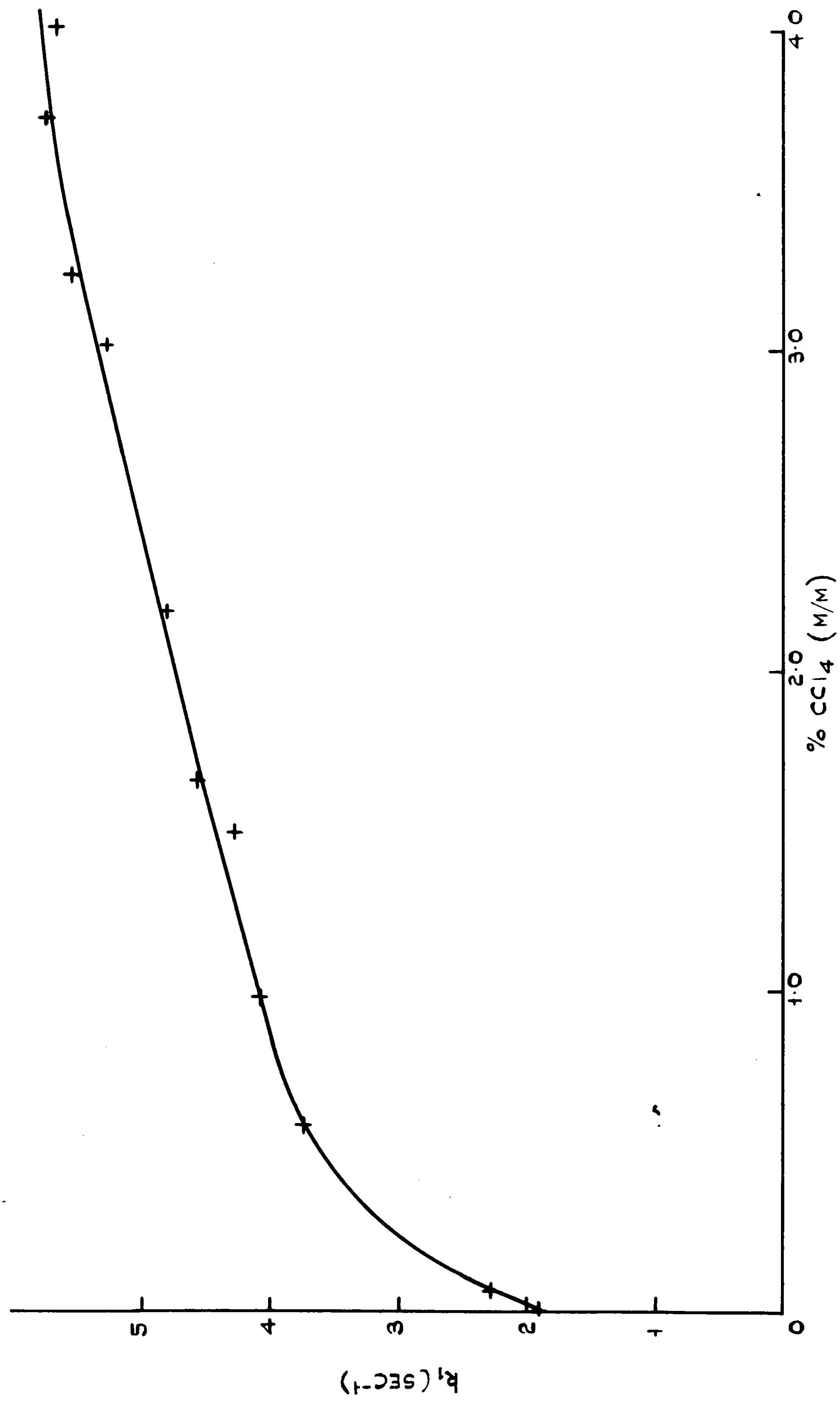


FIGURE 4.19 (a) AND (b)

FIGURE 4.20

ECH DECOMPOSITION AT 454·9°C

EFFECT OF CCl_4 ADDITION ON THE INITIAL FIRST ORDER RATE CONSTANT (k_1)



ECH DECOMPOSITION - EFFECT OF CHAIN ACCELERATORS (CCl_4) ON PRODUCT FORMATION AT 454·9°C

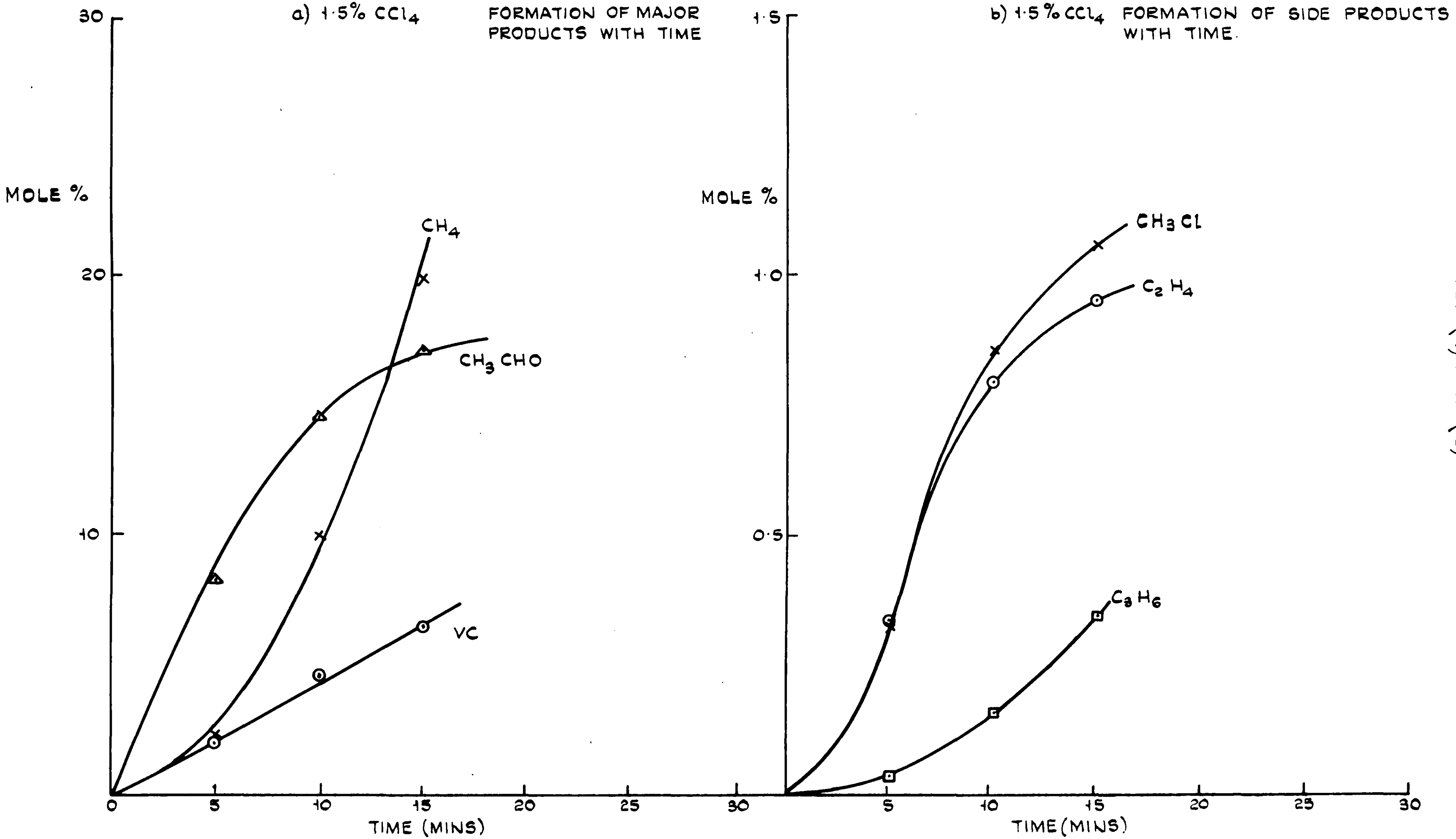


FIGURE 4.21 (a) AND (b)

ECH DECOMPOSITION AT 454·9°C

EFFECT OF 50% HCl ADDITION ON PRODUCT FORMATION

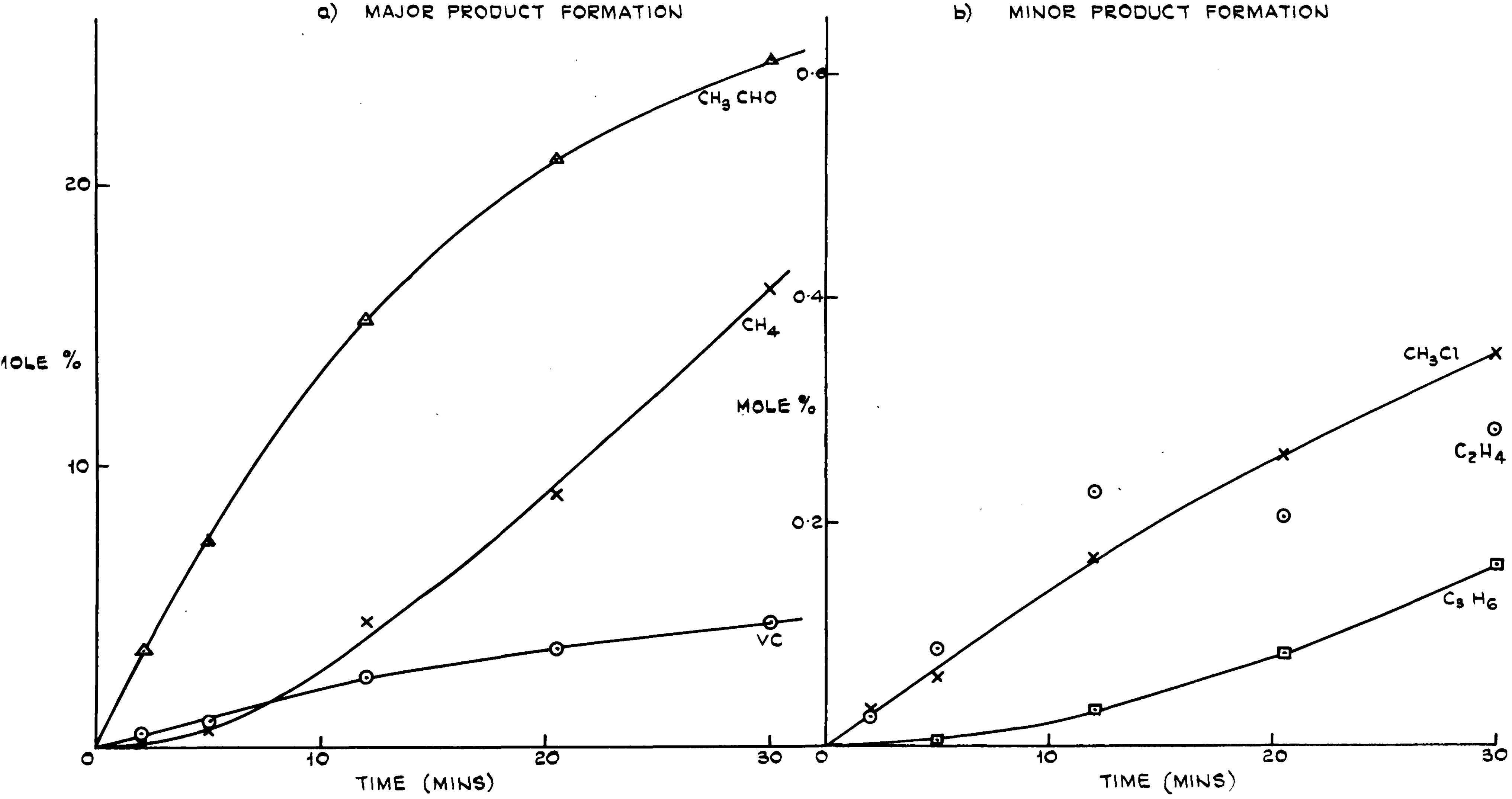


FIGURE 4.22 (a) AND (b)

ECH DECOMPOSITION - EFFECT OF HBr ON PRODUCT FORMATION AT 454·9°C

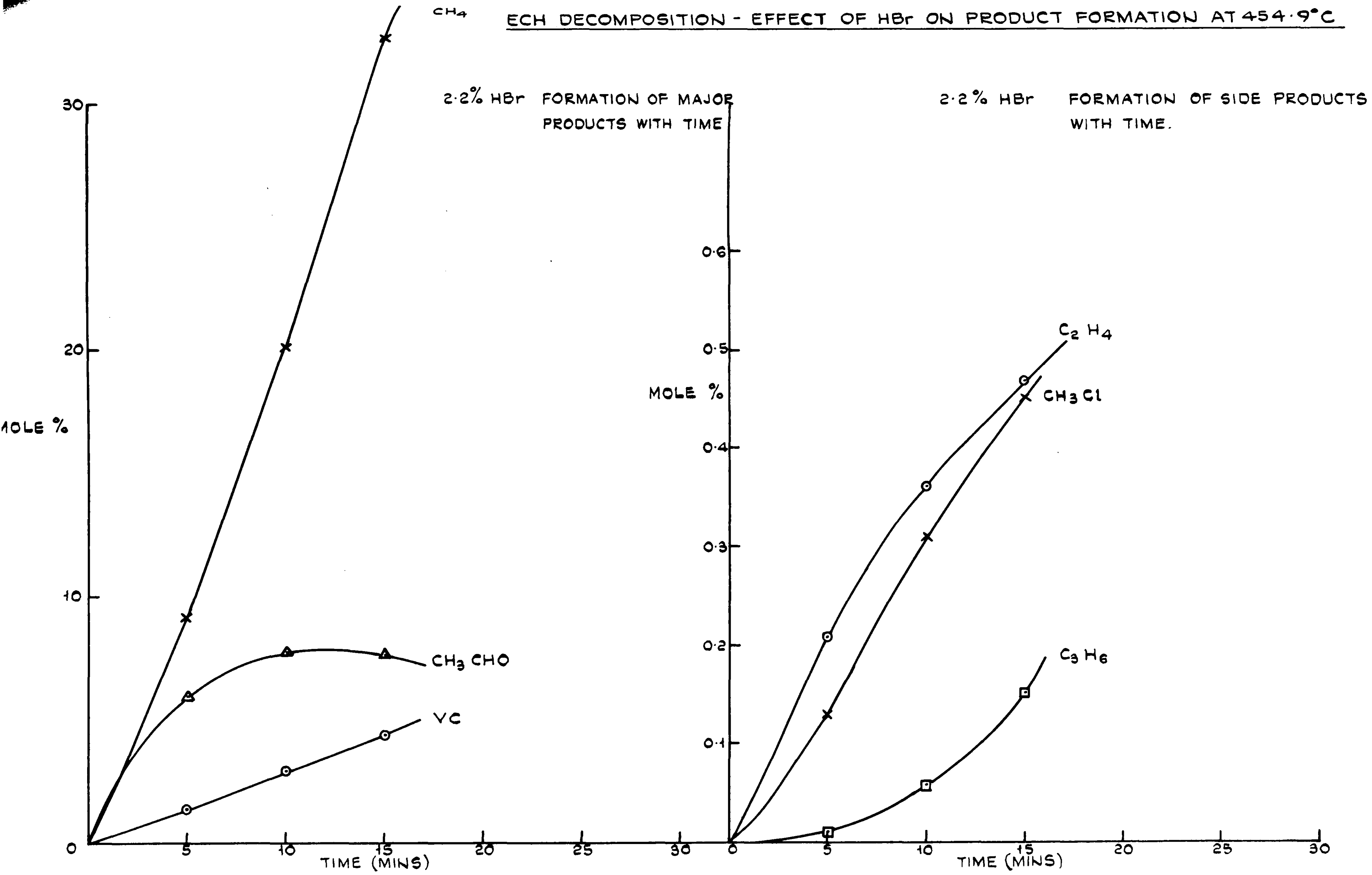


FIGURE 4.23 (a) AND (b)

CHAPTER 5

RESULTS FROM THE CATALYSIS OF THE MOLECULAR DECOMPOSITION

The previous two chapters have demonstrated that both βTRI and ECH possess molecular modes of decomposition in addition to those involving radical chain processes. In the case of βTRI this molecular process was virtually isolated by the addition of amounts of toluene in excess of 6%. For ECH however the isolation of the molecular reaction was not obtained as readily. In the present chapter we are concerned with catalysis of the molecular decomposition with particular reference to the selectivity of βTRI dehydrochlorination.

The underlying concepts behind this investigation have previously been described in chapter 1. The results described in this chapter have been arranged in terms of the classes of compound being investigated for possible catalytic effects.

A THE EFFECTS OF LEWIS ACIDS

The information available in the literature (see section 1.02) indicates that, in heterogeneous or condensed systems, Lewis acids such as $FeCl_3$, $AlCl_3$ catalyse the dehydrochlorination reaction of chlorocarbons. It was also observed in chapter 4 that the presence of a steel surface considerably enhanced the molecular dehydrochlorination of ECH under conditions where iron chloride would have been formed by the reaction of HCl on the steel. Consequently, a study of possible homogeneous gas phase catalysis between the substrate and suitably volatile Lewis acids was undertaken. The use of $FeCl_3$ would have required considerable modification to the apparatus owing to condensation problems. Consequently BCl_3 and $SnCl_4$ were used as typical Lewis acids. These compounds being respectively a gas and a liquid at room temperature were more readily manipulated on the vacuum line.

5.01 Boron Trichloride

5.01(a) The Addition of BCl_3 to ECH

The effect of 20% BCl_3 addition on the decomposition of ECH alone at 454.9°C is shown in table 5.01 and figures 5.01(a) and (b). Comparison of the % conversion figures with those of table 4.01 demonstrate a rate enhancement of between 2 and 2.5 in the presence of BCl_3. However the major product curves in figure 5.01(a) are more similar to those obtained in the presence of CCl_4 (figure 4.20(a)) than to those from steel (figure 4.18(a)). Furthermore, E155 and E157 demonstrate that the addition of toluene retards the rate of decomposition. Thus the major effect of BCl_3 in this reaction involves a catalysis of the radical chain component of reaction.

Figure 5.01(b) shows the production of minor products in the presence of 20% BCl_3 and the effect of toluene on their formation. The rates of formation were greater than those of the uncatalysed decomposition (figure 4.10) and they were retarded by toluene as would be expected for free radical processes. An interesting consequence of BCl_3 addition was the divergence of the ethylene and methyl chloride curves. Previously these two products had followed each other closely in both the normal and the uninhibited decompositions. In the presence of BCl_3 however ethylene production was enhanced over methyl chloride and the disappearance of the sigmoid character in the initial stages of the ethylene curve indicated an increasing degree of formation from a primary process. The effect of toluene was to reduce the amounts of methyl chloride and ethylene by the same absolute amount and this suggested that the ethylene was being formed in part from a primary molecular process. In this respect BCl_3 is showing a similar (albeit much weaker) effect to that obtained with a steel surface (see paragraph 4.06(b)).

5.01(b) Addition of BCl_3 to βTRI

The addition of BCl_3 had no effect on the decomposition of βTRI proceeding under conditions of maximum inhibition (> 6% toluene) at 453.5°C. Table 5.02 shows no significant changes in either the rate of conversion or in the amounts and distribution of the major products for 10% BCl_3 addition. Consequently BCl_3 is unable to exert any Lewis acid behaviour on the inhibited βTRI decomposition.

In the absence of toluene, BCl_3 produced no positive effect on the pressure change associated with 2 minutes decomposition at 453.5°C. Table 5.02 also shows clearly the absence of any change in the product distribution with BCl_3.

This last result demonstrated an interesting contrast between the effect of BCl_3 on the chain components of the ECH and βTRI decomposition. The radical chain acceleration obtained for ECH in the presence of BCl_3 was obviously not solely due to BCl_3 initiation or a similar enhancement would have been observed with βTRI. The production of radicals from BCl_3 must therefore be in some part due to the presence of ECH or its products.

5.02 The Addition of Stannic Chloride to βTRI

Experiment T643 in table 5.03 shows that 10% $SnCl_4$ increased the production of the three dichloroethylenes from an inhibited βTRI decomposition at 453.5°C. Although the enhanced rate could have been due to a catalysis of the molecular reaction it could also have arisen from a re-establishment of the radical chain reaction. Experiments with increasing amounts of toluene (table 5.03 and figure 5.02) indicated that in the presence of 10% $SnCl_4$ maximum inhibition is not achieved until 15% toluene addition. At this point the proportion of VDC in the products was 13% (figure 5.03) but comparison of T644 with T662 shows that the absolute amounts of all the dichloroethylenes had still increased in the presence of $SnCl_4$ and that the selectivity of this increase toward VDC production was 45%.

One reason for the larger amounts of toluene required to attain maximum inhibition is associated with the disappearance of toluene during the reaction.

Thus in T643 the initial pressure of 21.1 torr of toluene had been reduced to 15.1 torr after 5 minutes reaction. Consequently the initial pressures of toluene do not represent its true concentration in the system. This loss of toluene was associated with the formation of a 'heavies' peak in the GLC analysis which was identified as benzyl chloride. The absence of benzyl chloride when $SnCl_4$ was not used suggests that the chlorine atom is arising from $SnCl_4$. The implications of this together with a discussion into the likely mode of catalysis of $SnCl_4$ are contained in Chapter 6.

B THE EFFECT OF LEWIS BASES ON THE MOLECULAR DECOMPOSITION OF βTRI

5.03 The Addition of Oxygen Containing Species to βTRI

The effects of various compounds containing an oxygen atom which must have at least one pair of unshared electrons are summarised in table 5.04. For comparison "blank" experiments containing no additive other than toluene are shown at the beginning and end of the table.

5.03(a) Water

Water has no significant effect on the decomposition of βTRI. A very small increase in VDC production is recorded which remains constant for additions of water between 1.5% and 10%. The reasons for this "zero-order" behaviour are not obvious but the effect is clearly not very significant.

5.03(b) Methanol

The single experiment performed with 10% methanol indicated no catalysis. As with the runs involving water addition the mass balances were low. This could be due to side reactions involving methanol and the dichloroethylenes but this point was not substantiated.

5.03(c) Dimethyl Ether

10% dimethyl ether addition increases the proportion of VDC in the product analysis to above 9%. The two experiments T414 and T416 indicate a reproducible effect and the mass balances are good. Comparison with T386 and T422 indicate an increase in the three dichloroethylene products such that the increase in VDC only represents 50% of the overall catalysis. This again indicates either a non-selective catalysis or small degree of chain character which is not quenched in the presence of 9% toluene.

In the experiments with dimethyl ether the conversion as estimated from pressure change was higher than that from GLC analysis (8.2% compared to 5.4% in T416). The good mass balances for these experiments suggest that this excess pressure cannot arise from side reactions which involve more than a fractional amount of βTRI or its products. It would therefore appear that the excess pressure is stemming from the decomposition of dimethyl ether. HCl is known to catalyse the chain decomposition of dimethyl ether (19) to methane and formaldehyde which subsequently decomposes to hydrogen and CO. However, methane was not detected in the products of reaction of βTRI, toluene and dimethyl ether. Furthermore a mixture of dimethyl ether, HCl and toluene failed to produce any measurable pressure change over a five minute period at 453.5°C.

It thus appears that the presence of βTRI is required to produce the additional increase in pressure observed with dimethyl ether and that the ether decomposition may not lead to the normal products. An analogous situation of βTRI "catalysis" is discussed in Section 5.05.

5.03(d) Tetrahydrofuran

THF produced no catalysis of the inhibited decomposition of βTRI. The small drop in the proportion of VDC is not significant within the error limits. In addition the % conversion from pressure change agrees well with that from GLC analysis indicating that THF is more stable than dimethyl ether under these conditions. THF should possess similar basic properties to dimethyl ether but these could be offset by restrictive steric requirements for the cyclic molecule.

5.03(e) Carbon Monoxide

Carbon monoxide does not show any catalytic behaviour towards βTRI. The volatility of CO at liquid nitrogen temperatures does not allow complete trapping out of the products owing to the residual pressure. About 85%

of the products were collected and the product analysis in T417 and T418 have been corrected to an assumed 100% mass balance.

The overall conclusion arising from these results is that negligible catalytic activity is observed with the majority of oxygen containing compounds investigated. Dimethyl ether did give a small catalysis of a non-selective nature but the results were complicated by a side reaction assumed to involve the decomposition of the ether.

5.04 The Addition of Sulphur Containing Species to βTRI

The effect of H_2S, $(CH_3)_2S$ and thiophene on the inhibited decomposition of βTRI are shown in Table 5.05. Again two experiments containing no base additive are included for reference purposes (T386 and T422).

5.04(a) Hydrogen Sulphide

The addition of 10% H_2S (T387) produces a more marked catalysis of VDC production than any of the oxygen containing additives. The product formation with % H_2S is shown graphically in figure 5.04. T388 and T423 demonstrate the reproducibility of the effects obtained. The amounts of cis and trans dichloroethylene drop slightly above 5% H_2S addition. This could be due to a side reaction involving loss of the 1,2-dichloroethylene. Such a small decrease ($<$ 1% of the total number of moles present) would not be a significant factor in the % mass balance which is seen to remain within experimental error of 100%. The effect of increasing H_2S addition on the product distribution is shown in figure 5.05. At 10.1% addition of H_2S the VDC has risen to 21.4%.

The % conversion estimated from the percent pressure change (T388) was 6.8% compared to 5.2% as derived from GLC Analysis. This discrepancy also suggests some degree of side reaction. Consequently the assessment of the catalytic affect is complex. The enhancement in the amount of VDC produced does, however, suggest a degree of catalytic behaviour and the constancy of the 1,2-dichloroethylene values up to 5% H_2S addition further indicate an element of selectivity in this catalyst.

5.04(b) Thiophene

The single reaction performed in the presence of 10% thiophene is shown in the table 5.05. The absence of any catalytic effect from this compound is demonstrated clearly by comparison with T422.

5.04(c) Dimethyl Sulphide

The effect of dimethyl sulphide on the inhibited βTRI decomposition was investigated. The results of table 5.05 and figure 5.06 indicated an initial rise in the amounts of the three dichloroethylenes produced. The VDC continued to rise with increasing additions of dimethyl sulphide up to 10%. However, the amounts of 1,2 dichloroethylenes fell off above 2% additions and at higher additions, the mass balances became poor. Furthermore "excess" pressure was also recorded. In T487 for example the % conversion derived from product formation was 6.6% whereas from pressure change a figure of 14.5% was obtained. The inference is that a high proportion of side reaction is involved which confuses the interpretation of the results and in the absence of a startling catalysis from dimethyl sulphide no further work was undertaken on this compound.

5.05 The Addition of Nitrogen Containing Species to βTRI

Table 5.06 indicates the catalytic effects obtained from a series of amine bases from ammonia through primary, secondary, and tertiary amines. As before two runs containing no base are included for comparison purposes. The last column of table 5.06 indicates the difference between the % conversions measured by pressure increase and by GLC conversion. In the absence of base the excess pressure is negligible but with 10% addition of base the excess pressure becomes considerable indicating amine decomposition. This is discussed in greater detail in section 5.06.

5.05(a) Ammonia

The addition of 10% NH_3 to the maximally inhibited βTRI decomposition led to a small acceleration in the rate of formation of the dichloroethylenes. The effect was relatively non-selective with catalysis to VDC corresponding to 42% of the overall increase in dehydrochlorination. This increased the overall proportion of VDC from 5.5% to 11%. In addition a small excess pressure of 4.1 torr (2.1%) was observed but the possibility of side reactions was not investigated any further.

5.05(b) n-Butylamine

T478 shows that the catalytic effect obtained from a primary amine was greater than that observed with ammonia - as would be expected from normal considerations of basic strength. The amount of VDC produced showed an increase of 5 over the uncatalyzed decomposition and this was reflected in the proportion of VDC in the final product distribution. This had increased to 20%. The production of 1,2-dichloroethylenes was catalysed to a smaller degree and comparison of T478 with T422 indicates that the selectivity of the n-$BuNH_2$ catalysis (i.e.: the excess amounts produced in T478) was 59% toward VDC production. An "excess" pressure was also recorded which was four times greater than that observed with ammonia.

5.05(c) Dimethylamine

The addition of the secondary amine caused the strongest selective effect observed in the amine series. T431 in table 5.06 shows that 10% addition of dimethylamine catalysed the overall production of dichloroethylene to a similar extent as 10% n-butylamine (i.e. to approximately 40%). The selective catalysis of the secondary amine toward VDC production was 74% of this excess decomposition and this increased the overall VDC figure to 23.5% of the total product.

The % excess pressure recorded in T431 is greater than the % of amine added. This implies that the pressure change involved in the amine decomposition must be greater than that represented by a stoichiometry of 1 mole → 2 moles.

5.05(d) Trimethylamine

The addition of varying amounts of trimethylamine to the chain inhibited βTRI decomposition is shown in experiments T567-T623 of table 5.06. Graphs of the amounts of dichloroethylene formed and of the product distribution are shown in figures 5.07 and 5.08 respectively. The similarity of results between T622 and T623 demonstrates good reproducibility for adjacent runs but over a greater period of time some variation in the results was observed (T568). Average values for 10% addition obtained from these figures indicate a similar overall catalytic effect to that obtained for dimethylamine (i.e.: 40% rate enhancement) but a decrease in the selectivity of that catalysis towards VDC production. VDC now represents ∿53% of the total catalysed product (compared to 74% with dimethylamine) and the overall ratio of VDC is 18.3%. This figure is slightly lower than that obtained for n-butylamine and suggests a considerable decrease in the basic effect of the tertiary amine due presumably to steric effects. The pressure change arising from amine decomposition is noticeably smaller than that obtained with a corresponding quantity of dimethylamine.

5.05(e) Triethylamine

Triethylamine would be expected to give a similar catalytic effect to trimethylamine. T586 shows that this was the case. The overall catalysis for ∿10% addition compare closely and the selectivity toward VDC was 54% compared to 53% for trimethylamine. The excess pressure is also similar.

5.06 Amine Decomposition at 453.5°C

The last column of table 5.06 showed clearly the development of excess pressure in the decomposition of βTRI with amines. This excess pressure is believed to be due to a decomposition of the amine involving an increase in the number of moles in the system. An investigation of the literature revealed very little information about the gas-phase decomposition of aliphatic amines at temperatures around 450°C. A study of t-butylamine (60) suggested that this material would decompose very slowly at 453°C by a molecular mechanism ($k \simeq 4 \times 10^{-6}$ sec^{-1} at 453.5°C). Similar rate parameters have been obtained for N-methylbenzylamine (61) and benzylamine (62). At first sight, therefore, the proposed rapid decomposition of amine in the inhibited βTRI system appears atypical. Consequently an investigation into the reasons underlying this effect was undertaken.

5.06(a) The Stoichiometry of the Decomposition.

The % conversion of βTRI derived from the pressure increase is given by ($\Delta p/_{po}$ x 100). In the presence of amine the figure obtained in this way is too high owing to the pressure increase arising from the decomposition of the amine. Table 5.07(a) and curve A of figure 5.09 shows the % conversion calculated in this way for different reaction times in the presence of 10% triethylamine. The % conversion obtained from GLC analysis of the same reactions is shown in table 5.07(b) and curve B of figure 5.09. The difference between the two lines represents the excess pressure arising from amine decomposition. After 30 minutes the two curves become approximately parallel suggesting that the amine decomposition reaction has almost reached completion and subsequent pressure changes are solely due to the normal decomposition of βTRI to dichloroethylenes. The "excess conversion" is approximately 23% in terms of the initial concentration of βTRI. Consequently the decomposition of triethylamine (which was 10% of the initial βTRI must have an approximate stoichiometry of 1 mole→3.3 moles of products (i.e: 10%→10% + 23%). The implication is that the decomposition is complex because an integral number of moles are not formed.

A final observation concerns curve C of figure 5.09. This is the % conversion calculated from GLC analysis of the products divided by the <u>initial pressure</u> of βTRI (rather than by the sum of (βTRI + dichloroethylenes) obtained from GLC analysis (see table 3.07(b)). Comparison with curve B shows no divergence for reaction times less than 14 minutes. The small divergence at longer reaction times suggests the possibility of some side reactions involving dichloroethylene removal. The absence of a large discrepancy between B and C is, however, conclusive evidence that the difference between curve A and curve B is not due to a removal of dichloroethylene by secondary reaction and must, therefore, definitely arise from amine decomposition.

5.06(b) Catalysis by the Amine as a Function of Time

The previous paragraph indicated the likely complexity of the amine decomposition reaction. The removal of amine by decomposition would be expected to cause a diminution in the catalytic effect with time. Table 5.07(b) and figure 5.10 show the % product distribution as a function of time. The observed decrease in the ratio of VDC would be the expected effect of amine disappearance. By comparison, the figures of table 5.08 show no variation in the product ratio with time in the absence of amine. Figure 5.11 shows the absolute amounts of products formed with and without amine addition. A slight catalysis of the formation of cis/trans dichloroethylene is observed but this appears to remain relatively constant up to 10 minutes. The VDC, however, is formed six times faster in the amine catalysed reaction over the first minute. At the end of ten minutes this has been considerably reduced and the two curves showing VDC formation in the presence and absence of amine have become almost parallel. This suggests that only small amounts of amine are present after 10 minutes decomposition. In figure 5.09, however, the continuing divergence of the "excess" pressure curve (A) from the % GLC conversion curve (B) after 10 minutes reaction suggested that further secondary decomposition of the amine products was occurring.

5.06(c) Analysis of the Amine.

Triethylamine was analysed by GLC using a Carbowax column as previously indicated in table 2.01. At the temperatures of the reaction (453.5°C) it was considered that triethylamine and HCl would coexist without forming an amine hydrochloride. However, preparation of a liquid sample for analysis would inevitably lead to combination of equimolar amounts of amine and HCl. The amine analysis would thus represent the excess amount of amine compared to the HCl produced by the dehydrochlorination reaction.

This may be conveniently termed the "free" amine, and is shown in table 5.07(b) and as curve A in figure 5.12. Assuming that all the HCl in the reaction product arose from βTRI dehydrochlorination then the total HCl can be represented by the sum of the individual dichloroethylene concentrations in moles, (table 5.07(b)). Thus curve B represents the formation of HCl in these reactions. Consequently the total amine present in the gas phase may be obtained by summing the two curves A and B up to 3.2 minutes and this gives the solid line of curve C. After the disappearance of "free" amine at 3.2 minutes this curve has to be estimated. This has been done by drawing a smooth curve which follows first order kinetics. At ten minutes reaction time the amine is > 90% decomposed and this agrees well with the almost complete disappearance of catalytic effect toward VDC production at this time. The VDC curves shown in figure 5.11 have been magnified in figure 5.13. The difference between the two curves A and B represents the triethylamine catalysed VDC production. If one as$_2H_5)_3N$ a second order reaction for the catalysis between βTRI and $(C_2H_5)_3N$ then

$$\frac{d\ VDC'}{dt} = k_c\ (\beta TRI)\ ((C_2H_5)_3N)$$

where VDC' is the excess VDC produced by the second order catalysed reaction having the rate constant k_c.

Now at all times during the catalysis the $(\beta TRI) > 10 \times ((C_2H_5)_3N)$. Consequently the reaction may be considered pseudounimolecular and only dependent on the amine concentration:-

i.e. $$\frac{d\ (VDC')}{dt} = k_c'\ ((C_2H_5)_3N)$$

where $k_c' = k_c(\beta TRI)$

Integration yields:-

$$(VDC') = k_c' \int_0^t ((C_2H_5)_3N).\ dt + c.$$

(and c should = 0 from the boundary condition at time t = 0.)

The graph of (VDC') against $\int_0^t ((C_2H_5)_3N).dt$ is shown in figure 5.14 from the results compiled in table 5.09. Two different conditions are considered. The solid line shows the best straight line fit for the results derived from curve C of figure 5.12. This assumes complete dissociation of any amine hydrochloride into free amine and HCl under the conditions of the decomposition. The broken line of figure 5.14 is that derived from the "free" amine curve (A) of figure 5.12 which, therefore, assumes no amine hydrochloride dissociation. The former provides the better fit over the complete range of data. The vertical line which arises in the curve derived from the "free" amine intergration is indicative of the continuing catalysed production of VDC after the "free" amine has disappeared (3.2 minutes). The conclusion is that the effect observed with amines at 453.5°C is a true catalysis rather than a stoichiometric reaction involving the formation of undissociated amine hydrochloride.

5.06(d) Identification of the Products of Triethylamine Decomposition

The routine GLC analysis on the liquid sample indicated the presence of some "light" components arising from the decomposition of triethylamine. These were further investigated qualitatively by inspecting a gas sample from a 20 minute reaction on a Porapak T column. The major peak appeared to be ethane and this was five times greater than a second peak which proved to be methane. Ethylene was also observed as a shoulder on the ethane peak and appeared to be of similar size to methane. Tentative assignments were also given to several small peaks. These were propylene, propane, methyl chloride and butane. Further discussion of the possible mechanism of decomposition is contained in Chapter 6.

5.06(e) The Decomposition of Trimethylamine

Unlike triethylamine, trimethylamine could not be satisfactorily analysed on Carbowax as it had the same retention time as VC which was formed in this reaction as a minor product. In addition GLC analysis was made difficult by the presence of a non-condensable gas which was formed by trimethylamine decomposition. Investigation of a gas sample showed this to be methane. The presence of residual gas during freezing out of the reaction products prevents complete collection of the components and erroneous mass balances result. The formation of products with time is shown in table 5.10 and figure 5.15 for reaction time <10 minutes where the discrepancy due to residual gas pressure will be relatively small. For the 10 minute reaction a mass deficit of $\sim 6\%$ indicated the maximum error from this source. A very similar pattern to that for triethylamine is observed (figure 5.11).

5.07 Catalytic Effect of Triethylamine in a Packed Vessel

The preceding sections have indicated a small but positive catalysis by certain Lewis bases toward dehydrochlorination of βTRI. Although the position is complicated by catalyst decomposition the catalysis has been shown to favour VDC formation particularly in the early stages of a reaction. It would thus appear that the base is able to exert a small ionic effect on the substrate. It has been observed in chapter 1 that the gas phase is an unfavourable medium for ionic reactions owing to its low dielectric constant. Hence it is important to decide if the catalysis observed is a true gas-phase reaction or is proceeding on the walls of the reactor. The walls could provide a local environment of relative high dielectric character (63) and this could be the favoured reaction centre.

The two experiments T720 and T726 at the end of tables 5.07(a) and (b) indicate the results obtained from a packed glass vessel containing five times the surface area of the normal reactor. If a surface reaction were responsible for the amine catalysis then the VDC ratio should markedly increase in the packed vessel. Comparison of T720 with T586 and T726 with T587 shows that this is not the case. Very similar results are obtained with the proportion of VDC slightly lower in the 5 minute run in the packed vessel. The % conversion is also similar and the excess pressure caused by amine decomposition agree well ($\Delta p/p_0 \times 100$ in table 5.07(a)).

To enable direct comparison of the amounts of product formed, the values obtained from the packed vessel have to be corrected for the difference in volume between the two reactors. This involves multiplying the original analyses by 1.256 and these corrected values are shown in the table 5.07(a) and (b).

Again considering this correction and the differences in the two reactor systems the results are remarkably similar and indicate conclusively that the amine catalysis is a true gas phase catalysis.

5.08 Amine Catalysis at Lower Temperatures

5.08(a) 370-392°C

The analysis of the catalytic effect of amines on the molecular decomposition of βTRI at temperatures of 453.5°C is complicated by two factors. In the first place the normal molecular decomposition is proceeding at a faster rate than the observed catalysis and secondly the catalytic agent itself decomposes. To reduce both these effects a lower reaction temperature was employed. At 391.5°C the molecular decomposition of βTRI proceeds very slowly. Trimethylamine, n-butylamine, and dimethylamine were added in 10% quantities to the inhibited βTRI decomposition (10% toluene present). The GLC conversions obtained for 5 minute reaction times were negligible ($<0.5\%$). In addition no excess pressure was recorded indicating the absence of amine decomposition at these temperatures. A further experiment with n-butylamine at 373.7°C again showed negligible conversion and pressure change over 5 minutes and analysis for the amine confirmed that no decomposition of the catalyst had occurred.

5.08(b) Liquid Phase Dehydrochlorination of βTRI by Amines

The preceding paragraph has demonstrated negligible effects from amines in the gas phase between 370-392°C. The absence of amine decomposition at these temperatures (unlike 453.5°C) implies that they are unable to react with βTRI not only in a catalytic but also in a stoichiometric manner. A stoichiometric reaction with 10% amine would give rise eventually to 10%

conversion of βTRI and the formation of the amine hydrochloride. This type of reaction has been observed in the liquid phase. Ethyl Corporation (45) have claimed specific dehydrochlorination of βTRI to VDC by certain amines at temperatures around 80°C. In the present investigation into the effect of amines one of the examples quoted in the Ethyl patent has been repeated. This involved heating equimolar quantities of βTRI and n-butylamine from 50-80°C over a period of 45 minutes. The resultant product indicated a 56% conversion of βTRI to dichloroethylenes in which the yield of VDC was 99%. These figures were in good agreement with the patent claims of 63% and 96.3% respectively and indicate the facility with which amines will remove HCl from βTRI in the liquid phase. The solid material formed in this reaction (n-butylamine hydrochloride) was reprecipitated from hot chloroform with petroleum ether, filtered and stored in a vacuum desiccator over NaOH. The melting point of this compound was 220°C which is 25° higher than that quoted in the literature (76) for n-butylamine hydrochloride. However elemental analysis, Mass Spectrometry, and IR data confirmed that the compound was indeed n-butylamine hydrochloride. The elemental analysis accounted for 98.9% of the sample as C,N,H, and Cl and gave the experical formula $C_4 H_{11.9} N_{1.04} Cl_{1.06}$. This material was used to study the decomposition characteristics of a typical amine hydrochloride as described in the next section.

5.08(c) Amine Hydrochloride Dissociation and Investigation of a Stoichiometric Reaction

Figure 5.16 shows the results of a differential thermal analysis study on the n-butylamine hydrochloride prepared above. The melting point of the hydrochloride is shown clearly as an endothermic peak at ~ 220°C. The straight line before the melting point implies the absence of any decomposition below 220°C. After the material has melted, a small downward trend in the trace is observed between 225° and 310°C. This could possibly be caused by a slow evolution of HCl and amine from the molten hydrochloride.

The large endothermic change observed at 330°C must involve boiling or a rapid decomposition of the hydrochloride into HCl and amine in the gas phase. Thus above 330°C one might expect considerable dissociation into free amine and HCl. However below this temperature n-butylamine hydrochloride appears to be reasonably stable. Thus below 330°C n-butylamine might be expected to exert a stoichiometric effect in dehydrochlorinating βTRI. However gas phase reactions of 15 minutes duration at 300.6°C and 223.5°C involving 50% addition of n-butylamine to βTRI gave very small conversions ($<1\%$). The small traces of dichloroethylene which were observed were however exclusively VDC. Another GLC peak found corresponded to VC formed presumably by direct dechlorination. The ratio of VDC peak to VC was about 2::1.

The conclusion is that the amine does not react readily in the gas phase under temperature conditions which would favour the production of the amine hydrochloride (i.e. <300°C). In this respect it differs markedly from the liquid phase system which readily gives dehydrochlorination of βTRI at temperatures below 100°C. Possible reasons for this difference are discussed in Chapter 6.

TABLE 5.01 EFFECT OF BCl_3 ON PRODUCT FORMATION WITH TIME AT 454.9°C

RUN	p_o (torr)	%BCl_3	TIME (mins)	PRODUCT ANALYSIS (AS % OF p_o)						% CONVSN.
				VC	CH_3CHO	CH_4	C_2H_4	CH_3Cl	C_3H_6	
E153	197.2	19.5	2	0.47	3.98	0.24	.053	.016	.001	4.7
E151	196.3	19.8	5	1.40	9.37	1.86	.165	.047	.016	12.7
E150	216.5	19.2	10	2.86	15.63	8.03	.339	.127	.080	26.5
E149	214.9	18.8	15	4.50	18.13	17.97	.472	.249	.217	40.6
E152	210.9	19.5	20	5.78	17.07	25.93	.522	.357	.365	48.8
+E157	219.0	21.6	10	.91	10.31	1.51	.195	.031	.010	12.7
+E155	221.4	19.7	15	1.77	16.06	4.06	.310	.082	.029	21.9

* % CONVERSION = % (CH_3CHO + VC + CH_4)

+ RUNS INVOLVING ADDITION OF TOLUENE - E157 has 16.6% E155 has 21.0%

TABLE 5.02 EFFECT OF BCl_3 ON βTRI DECOMPOSITION AT 453.5°C

RUN	p_o	% TOLUENE	% BCl_3	TIME (mins)	PRODUCT ANALYSIS (moles x 10^4) (PRODUCT RATIO)				% CONVSN.
					βTRI	VDC	t-DCE	c-DCE	
INHIBITED DECOMPOSITION									
T560	199.9	11.2	0	10	12.820	.065 (4.9)	.498 (37.5)	.765 (57.6)	9.4
T561	212.2	10.1	9.6	10	13.263	.080 (5.6)	.534 (37.3)	.816 (57.1)	9.7
UNINHIBITED DECOMPOSITION									
T563	210.6	0	0	2	4.540	4.008 (40.6)	2.584 (26.2)	3.270 (33.2)	68.5
T564	204.8	0	9.6	2	7.048	3.009 (40.4)	1.941 (26.0)	2.506 (33.6)	51.4

TABLE 5.03 βTRI DECOMPOSITION - EFFECT OF 10% $SnCl_4$ ON THE PRODUCT FORMATION OBTAINED UNDER VARYING ADDITIONS OF TOLUENE AT 453.5°C

RUN	p_o (torr)	% TOLUENE (INITIALLY)	% $SnCl_4$	TIME (mins)	PRODUCT ANALYSIS (% DISTRIB) (moles x 10^4)				% CONVSN.
					βTRI	VDC	t-DCE	c-DCE	
T660	204.0	0	10.6	3	.786	5.447 (42.5)	3.125 (24.4)	4.249 (33.1)	94.1
T662	206.0	10.6	0	5	13.367	.028 (4.2)	.232 (35.1)	.401 (60.7)	4.7
T643	209.7	10.1	10.7	5	13.320	.134 (14.7)	.281 (30.9)	.494 (54.4)	6.4
T644	206.4	20.3	11.2	5	13.029	.108 (13.0)	.261 (31.3)	.464 (55.7)	6.0
T661	208.0	23.8	10.6	5	12.697	.100 (12.3)	.255 (31.3)	.459 (56.4)	6.0
T648	206.0	30.0	9.9	5	13.147	.125 (14.2)	.268 (30.3)	.481 (55.5)	6.3
T646	214.7	49.3	9.7	5	13.498	.108 (12.8)	.258 (30.8)	.472 (56.4)	5.8

TABLE 5.04 EFFECT OF OXYGEN CONTAINING LEWIS BASES ON THE PRODUCT PATTERN OBTAINED FROM 5 MINUTE DECOMPOSITION REACTIONS OF INHIBITED βTRI AT 453.5°C

RUN	p_o (torr)	BASE	% BASE	% TOLUENE	ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)				% MASS BALANCE.
					βTRI	VDC	t-DCE	c-DCE	
T386	205.4	-	-	10.2	14.221	.041 (6.0)	.246 (35.7)	.401 (58.3)	100.8
T407	215.2	H_2O	1.5	8.6	13.978	.050 (6.8)	.268 (36.4)	.418 (56.8)	95.0
T405	209.9	"	5.2	10.3	13.470	.049 (6.9)	.266 (37.3)	.398 (55.8)	94.4
T406	219.5	"	10.1	9.3	14.010	.052 (6.9)	.277 (36.7)	.426 (56.4)	93.2
T410	187.6	CH_3OH	10.6	9.0	11.895	.032 (5.8)	.200 (35.8)	.324 (58.4)	93.1
T414	192.0	$(CH_3)_2O$	10.1	9.1	13.070	.068 (9.8)	.264 (35.4)	.415 (54.8)	100.0
T416	202.4	"	10.2	9.0	13.680	.074 (9.8)	.266 (35.4)	.412 (54.8)	99.0
T420	205.8	T.HF	9.6	8.5	13.537	.030 (4.5)	.252 (38.1)	.380 (57.4)	95.9
T419	194.1	"	10.5	8.2	12.374	.028 (4.4)	.246 (38.1)	.371 (57.5)	93.0
T418	191.0	CO	10.2	7.8	13.080	.035 (5.3)	.252 (37.4)	.386 (57.3)	* see text
T417	195.1	"	11.6	6.8	13.320	.038 (5.4)	.261 (37.4)	.400 (57.2)	* " "
T422	200.9	-	-	8.2	13.049	.037 (5.5)	.254 (37.6)	.385 (56.9)	95.4

* NON-CONDENSABLE CO LEADS TO LOW MASS BALANCES WHEN TRAPPING OUT PRODUCTS.

TABLE 5.05 EFFECT OF SULPHUR CONTAINING LEWIS BASES ON THE PRODUCT PATTERN OBTAINED FROM 5 MINUTE DECOMPOSITION REACTIONS OF INHIBITED βTRI AT 453.5°C

RUN	p_o (torr)	BASE	% BASE	% TOLUENE	ANALYSIS(moles x 10^4) (% PRODUCT DISTRIBUTION)				% MASS BALANCE
					βTRI	VDC	t-DCE	c-DCE	
T386	205.4	-	-	10.2	14.221	.041 (6.0)	.246 (35.7)	.401 (58.3)	100.8
T389	189.0	H_2S	1.7	6.6	12.899	.075 (10.5)	.250 (35.1)	.388 (54.4)	100.0
T423	208.0	"	4.4	8.5	13.194	.116 (15.1)	.261 (33.9)	.392 (51.0)	97.3
T388	200.1	"	4.5	6.6	13.701	.103 (13.8)	.252 (33.8)	.391 (52.4)	100.1
T387	192.0	"	10.1	6.6	13.280	.148 (21.4)	.214 (31.0)	.327 (47.6)	101.6
T421	194.4	THIO-PHENE	10.4	8.8	13.031	.036 (5.5)	.242 (37.1)	.375 (57.4)	100.1
T489	200.0	$(CH_3)_2S$	2.4	7.5	13.503	.149 (16.9)	.287 (32.5)	.447 (50.6)	100.0
T488	198.5	"	2.6	7.5	13.681	.154 (17.4)	.289 (32.6)	.444 (50.0)	102.0
T490	202.6	"	5.7	7.0	12.828	.251 (28.9)	.259 (29.8)	.359 (41.3)	94.0
T487	196.0	"	9.5	6.5	12.400	.290 (33.2)	.236 (27.0)	.347 (39.8)	94.3
T422	199.6	-	-	8.2	13.049	.037 (5.5)	.254 (37.6)	.385 (56.9)	96.7

TABLE 5.06 EFFECT OF NITROGEN CONTAINING LEWIS BASES ON THE PRODUCT PATTERN OBTAINED FROM 5 MINUTE DECOMPOSITION REACTIONS OF INHIBITED βTRI AT 453.5°C

RUN	p_o (torr)	BASE	% BASE	% TOLUENE	ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)				EXCESS$_{\Delta p}$ (as % p_o)
					βTRI	VDC	t-DCE	c-DCE	
T422	197.6	-	-	8.2	13.049	.037 (5.5)	.254 (37.6)	.385 (56.9)	0.2
T428	197.4	NH_3	10.6	8.2	13.896	.088 (11.0)	.273 (34.3)	.436 (54.7)	2.1
T478	212.6	$n\text{-}BuNH_2$	9.6	8.7	13.010	.185 (20.0)	.301 (32.5)	.441 (47.5)	8.5
T433	202.8	$(CH_3)_2NH$	1.7	9.6	12.921	.127 (15.1)	.307 (36.5)	.407 (48.4)	0.4
T432	211.3	"	5.2	10.7	13.070	.168 (19.0)	.299 (33.8)	.418 (47.2)	5.5
T431	194.5	"	10.8	7.7	11.541	.216 (23.5)	.292 (31.8)	.410 (44.7)	14.5
T567	206.5	$(CH_3)_3N$	2.9	10.1	13.564	.065 (8.0)	.297 (36.6)	.450 (55.4)	0.5
T566	210.5	"	4.9	9.8	13.531	.107 (12.2)	.308 (34.9)	.466 (52.9)	1.8
T568	206.0	"	9.6	9.7	12.650	.181 (18.0)	.332 (33.1)	.491 (48.9)	6.5
T622	208.1	"	10.1	9.0	12.740	.164 (18.5)	.276 (31.2)	.446 (50.3)	6.4
T623	208.9	"	10.1	10.1	13.021	.165 (18.4)	.280 (31.3)	.449 (50.3)	6.2
T586	204.0	$(C_2H_5)_3N$	10.1	9.6	12.946	.169 (18.3)	.293 (31.7)	.461 (50.0)	7.1
T621	206.0	-	-	9.3	13.449	.035 (5.2)	.233 (34.9)	.399 (59.9)	0

TABLE 5.07(a) EFFECT OF 10% $(C_2H_5)_3N$ ON THE PRESSURE INCREASE OBSERVED WITH TIME IN THE INHIBITED βTRI DECOMPOSITION AT 453.5°C

RUN	p_o (torr)	% $(C_2H_5)_3N$	% TOLUENE	TIME (mins)	Δp (torr)	$\frac{\Delta p}{p_o} \times 100$
T585	203.0	10.0	10.0	0.5	-	-
T588	203.6	10.0	9.5	1	4.5	1.6
T582	208.1	9.8	9.4	2	11.4	5.5
T591	197.1	10.3	9.9	2.5	13.5	6.8
T586	204.0	10.1	9.6	5	28.1	13.8
T587	203.2	10.1	9.8	10	53.4	26.3
T614	203.2	10.0	9.5	20	86.9	42.8
T611	204.0	8.8	10.0	30	102.8	50.5
T613	202.4	10.4	10.1	45	127.8	63.0
PACKED VESSEL						
T720	208.1	9.1	10.0	5	33.1	15.9
T726	208.6	10.4	9.8	10	60.5	29.0

TABLE 5.07(b) CONTINUATION OF TABLE 5.07(a) PRODUCT FORMATION AND % CONVERSION EX G.L.C. ANALYSIS

RUN (CONT)	ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)						% MASS BALANCE	TIME	% CONVERSION	
	$(C_2H_5)_3N$	βTRI	VDC	t-DCE	c-DCE	ΣDCE			EX GLC.	$\frac{\Sigma DCE}{p_o}$
T585	1.160	14.300	.033 (26.6)	.036 (28.7)	.056 (44.7)	.125	99.2	0.5	0.9	0.9
T588	.850	13.762	.057 (25.6)	.064 (29.2)	.099 (45.2)	.220	95.9	1	1.4	1.5
T582	.435	13.495	.100 (23.8)	.124 (29.4)	.198 (46.8)	.422	93.0	2	3.0	2.8
T591	.286	13.354	.108 (21.6)	.151 (30.5)	.233 (47.9)	.492	97.2	2.5	3.4	3.5
T586	0	12.950	.169 (18.3)	.293 (31.7)	.461 (50.0)	.923	94.5	5	6.7	6.3
T587	0	12.332	.261 (15.4)	.584 (34.5)	.849 (50.1)	1.694	95.9	10	12.0	11.6
T614	0	11.410	.461 (14.6)	1.055 (33.5)	1.631 (51.9)	3.147	97.2	20	21.6	21.3
T611	0	9.585	.559 (13.3)	1.472 (35.1)	2.167 (51.6)	4.198	94.0	30	30.5	28.6
T613	0	8.413	.676 (12.2)	1.932 (35.0)	2.912 (52.8)	5.520	95.2	45	39.5	37.8
PACKED VESSEL										
T720	0	13.660	.145 (15.9)	.282 (31.1)	.481 (53.0)	.908	96.7	5	6.2	6.1
T726	0	12.221	.255 (15.4)	.532 (31.2)	.911 (53.4)	1.698	92.6	10	12.3	11.3

TABLE 5.08 PRODUCT FORMATION WITH TIME IN THE INHIBITED βTRI DECOMPOSITION AT 453.5°C

RUN	p_o (torr)	% TOLUENE	TIME (mins)	ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)				% MASS BALANCE
				βTRI	VDC	t-DCE	c-DCE	
T593	208.9	9.5	1	14.580	.011 (6.7)	.062 (37.7)	.092 (55.6)	98.0
T592	201.6	9.9	2.5	13.755	.023 (6.2)	.139 (36.8)	.216 (57.0)	97.2
T594	198.7	10.2	5	13.508	.049 (6.7)	.268 (36.8)	.411 (56.5)	99.2
T596	202.4	9.5	7.5	13.020	.071 (6.5)	.403 (37.0)	.617 (56.5)	96.7
T597	206.4	9.5	10	12.878	.095 (6.5)	.541 (37.0)	.826 (56.5)	96.0

TABLE 5.09 AMINE CATALYSED PRODUCTION OF VDC AND THE TIME INTEGRATED $(C_2H_5)_3N$ CONCENTRATION

TIME	$((C_2H_5)_3N)$ EX CURVE C IN FIG.5.12	$\int_0^t ((C_2H_5)_3N).dt$ EX CURVE C	VDC' A-B IN FIG 5.13	"FREE" AMINE EX CURVE A FIG.5.10	$\int_0^t$("FREE"AMINE)dt
(mins)	(moles x 10^4)	(moles x 10^4 x mins)	(moles x 10^4)	(moles x 10^4)	(moles x 10^4 x mins)
0	1.480	0	0	1.480	0
.2	1.374	.285	.0104	1.325	.280
.4	1.285	.551	.0214	1.192	.531
.6	1.211	.800	.0306	1.075	.758
.8	1.148	1.036	.0400	.965	.962
1.0	1.090	1.260	.0474	.867	1.145
1.5	.971	1.774	.0654	.650	1.522
2.0	.870	2.234	.0786	.456	1.797
2.5	.771	2.644	.0900	.262	1.977
3.0	.681	3.006	.0990	.077	2.061
4.0	.521	3.605	.1136	0	2.067
5.0	.402	4.065	.1250	0	2.067
6.0	.306	4.416	.1344	0	2.067
7.0	.232	4.684	.1432	0	2.067
9.0	.129	5.042	.1580	0	2.067

TABLE 5.10 PRODUCT FORMATION WITH TIME IN THE PRESENCE OF 10% $(CH_3)_3N$ FOR THE INHIBITED β TRI DECOMPOSITION AT 453.5°C

RUN	p_o (torr)	%$(CH_3)_3N$	% TOLUENE	TIME (mins)	$\frac{\Delta p}{p_o}$ x 100	* ANALYSIS (moles x 10^4) (% PRODUCT DISTRIBUTION)			
						βTRI	VDC	t-DCE	c-DCE
T624	207.7	10.9	9.6	1	1.6	14.283	.039 (19.4)	.065 (32.0)	.098 (48.6)
T623	207.7	10.2	10.1	2.5	6.1	13.741	.092 (19.8)	.145 (31.0)	.230 (49.2)
T622	208.1	10.1	9.0	5	12.9	12.740	.164 (18.5)	.276 (31.2)	.446 (50.3)
T626	206.9	9.9	10.4	10	24.9	11.548	.264 (16.4)	.509 (31.7)	.834 (51.9)

* MASS BALANCE LOW DUE TO FORMATION OF NON-CONDENSABLE GAS. MAXIMUM ERROR OBTAINED IN T626 WAS 6% LOW.

ECH DECOMPOSITION IN GLASS AT 454·9°C

EFFECT OF 20% BCl_3 ON PRODUCT FORMATION

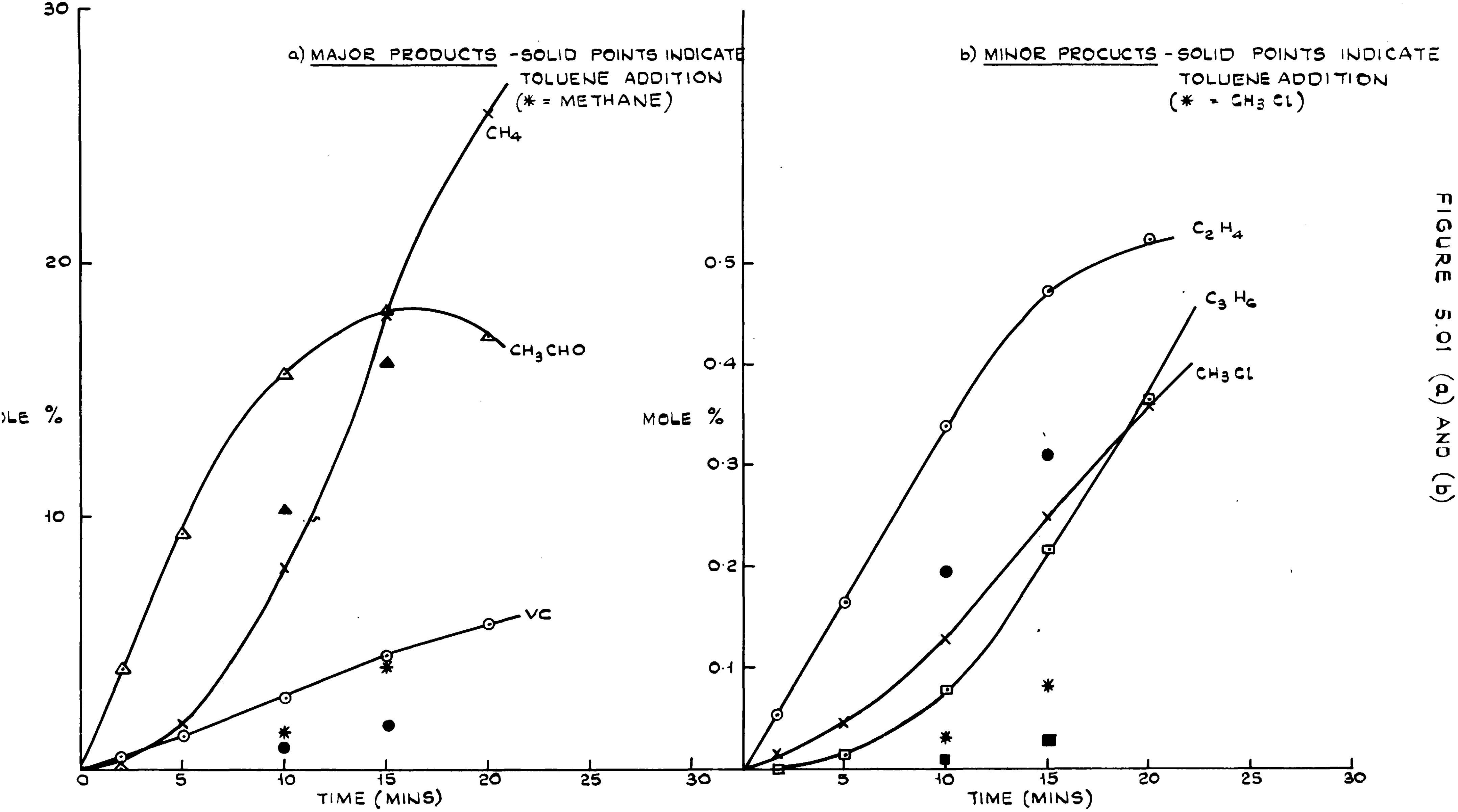
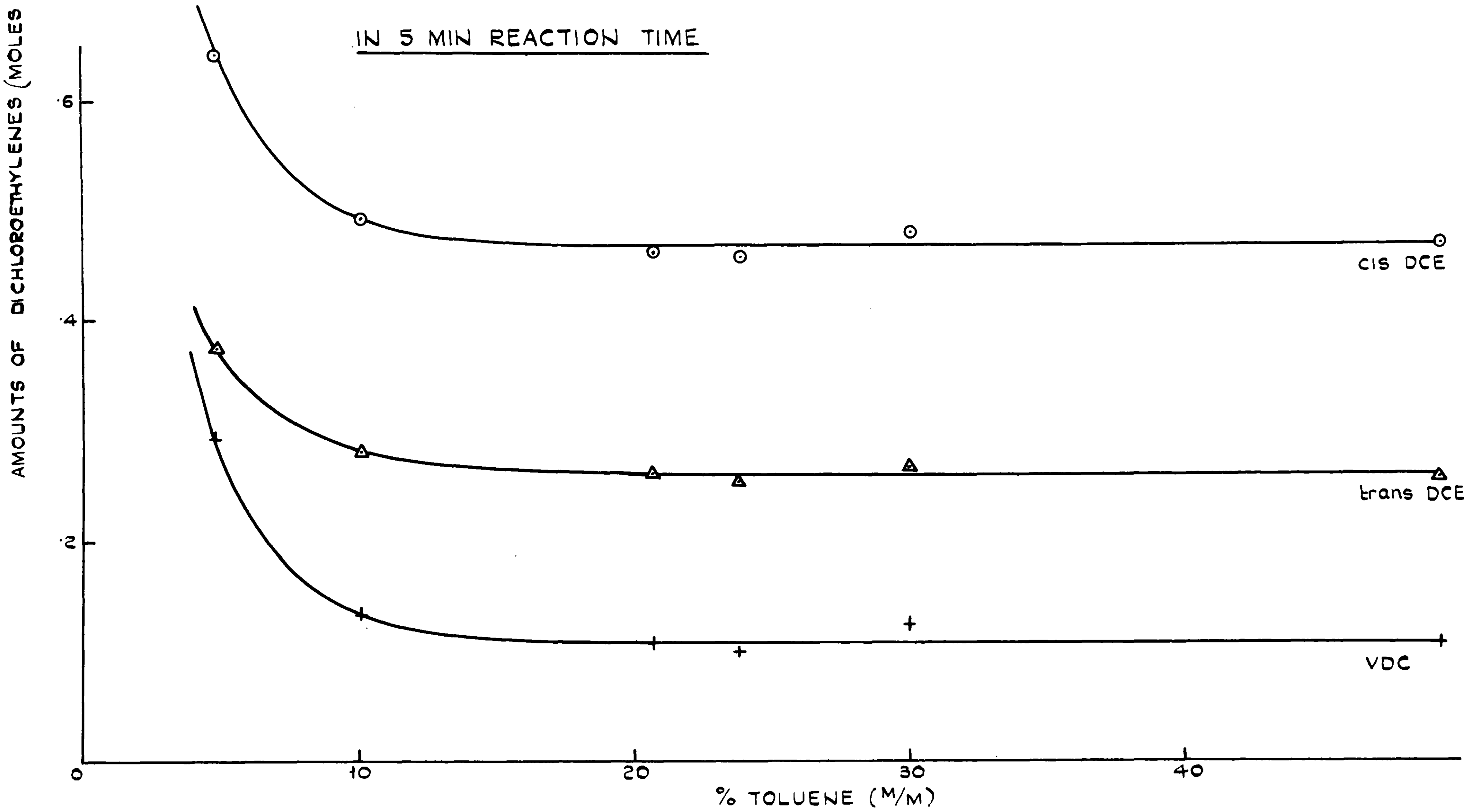


FIGURE 5.01 (a) AND (b)

FIGURE 5·02



β TRI DECOMPOSITION AT 453·5°C IN THE PRESENCE OF 10% $SnCl_4$

EFFECT OF TOLUENE ON THE AMOUNTS OF DICHOROETHYLENES FORMED

IN 5 MIN REACTION TIME

FIGURE 5.03

β TRI DECOMPOSITION AT 453·5°C IN THE PRESENCE OF 10% $SnCl_4$

EFFECT OF TOLUENE ON PRODUCT DISTRIBUTION OBTAINED FROM 5 MINS. REACTION TIMES

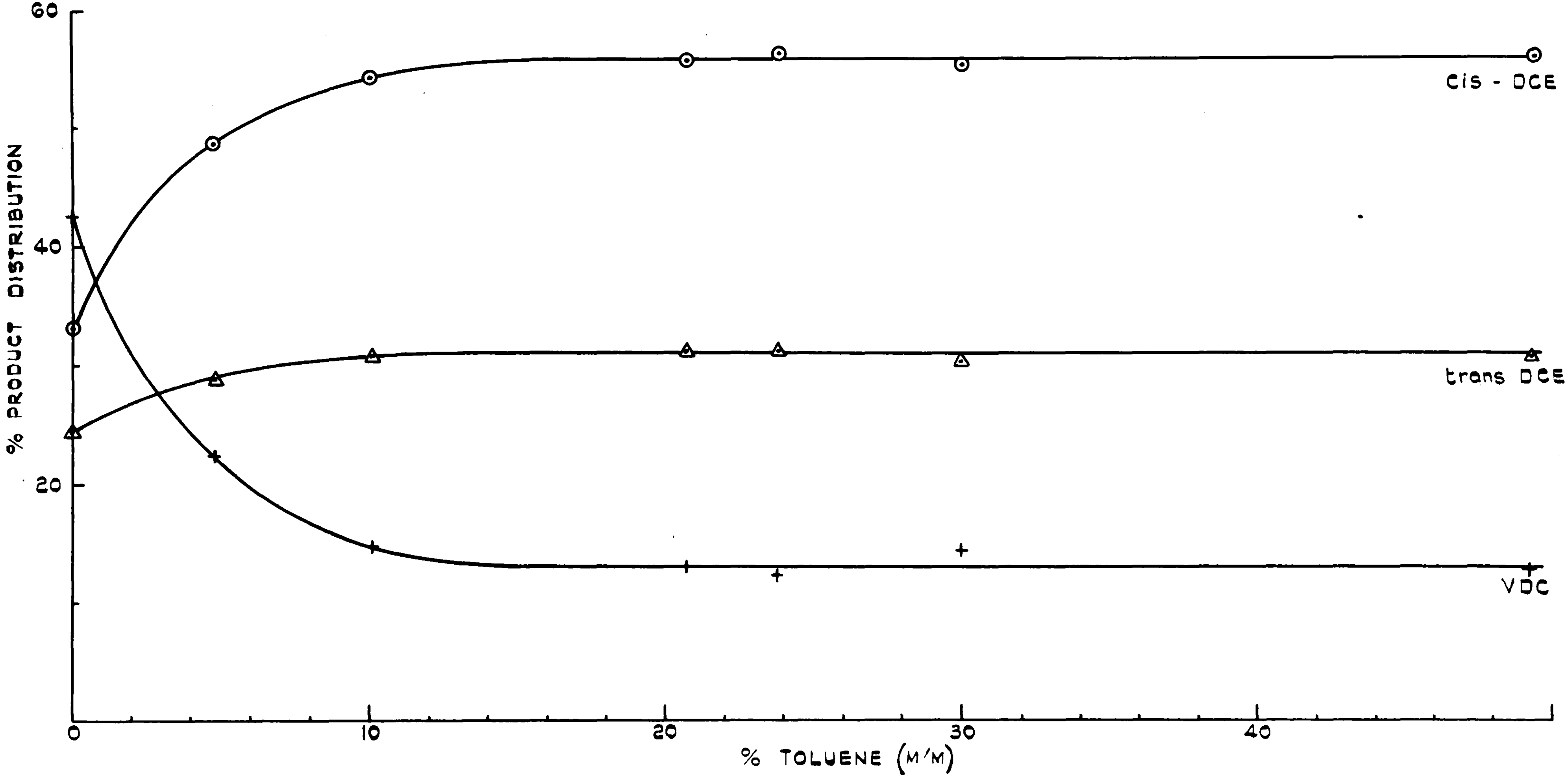


FIGURE 5.04

β TRI DECOMPOSITION AT 453°C- CHAIN INHIBITED REACTION (> 6·6 % TOLUENE)
EFFECT OF H_2S ON AMOUNTS OF PRODUCT FORMED IN 5 MINS REACTION TIMES

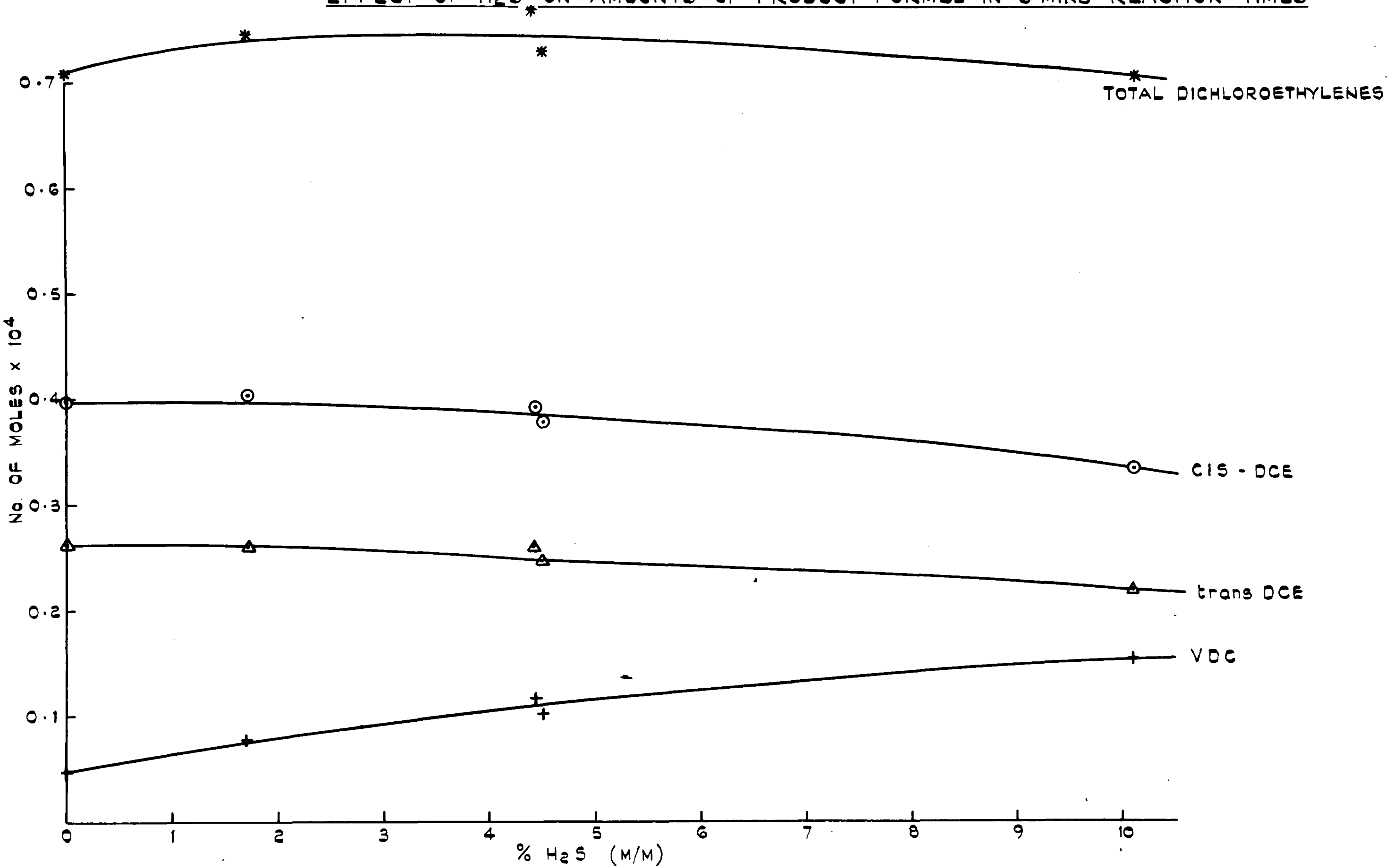


FIGURE 5.05

β TRI DECOMPOSITION AT 453·5°C - CHAIN INHIBITED REACTION (>6·6% TOLUENE)
EFFECT OF H_2S ON PRODUCT DISTRIBUTION FROM 5 MINS REACTION TIMES

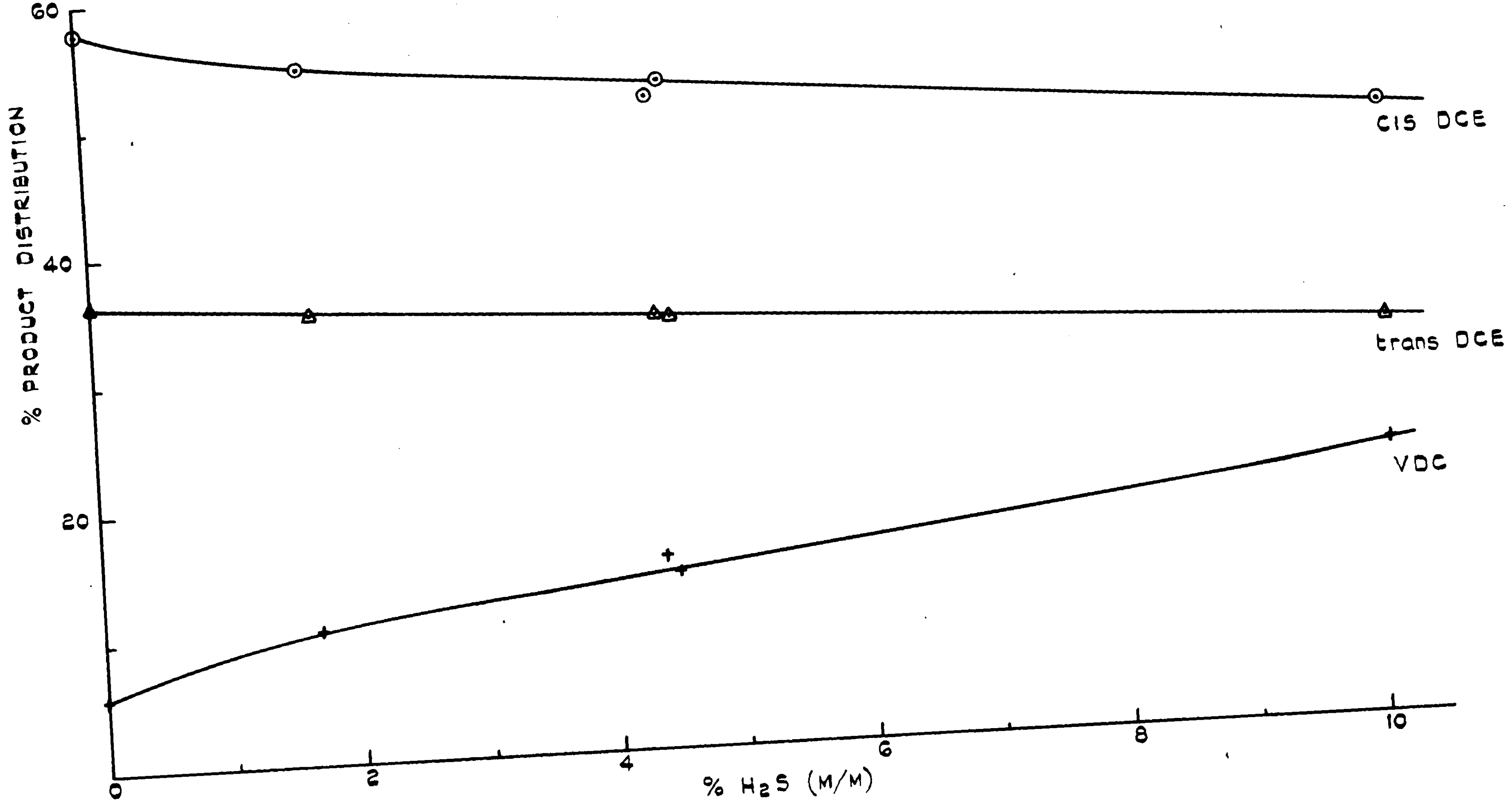


FIGURE 5.06

β TRI DECOMPOSITION AT 453·5°C - CHAIN INHIBITED REACTION (7% TOLUENE)
EFFECT OF $(CH_3)_2S$ ON AMOUNTS OF PRODUCT FORMED IN 5 MINS
REACTION TIME FOR Po = 200 torr

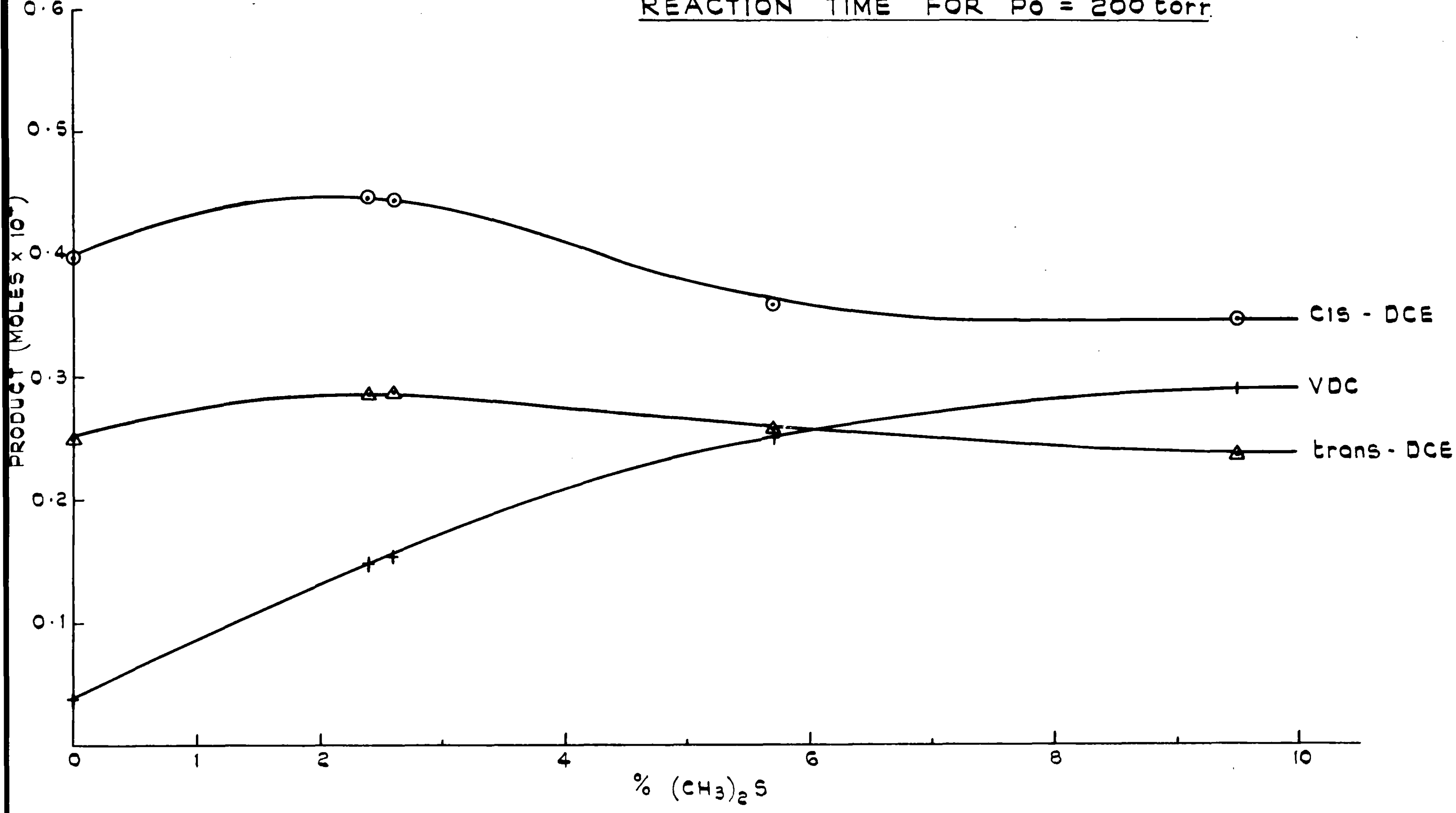


FIGURE 5.07

β TRI DECOMPOSITION AT 453·5°C - CHAIN INHIBITED REACTION

EFFECT OF TRIMETHYLAMINE ON THE AMOUNTS OF PRODUCT FORMED FROM 5 MIN. REACTIONS

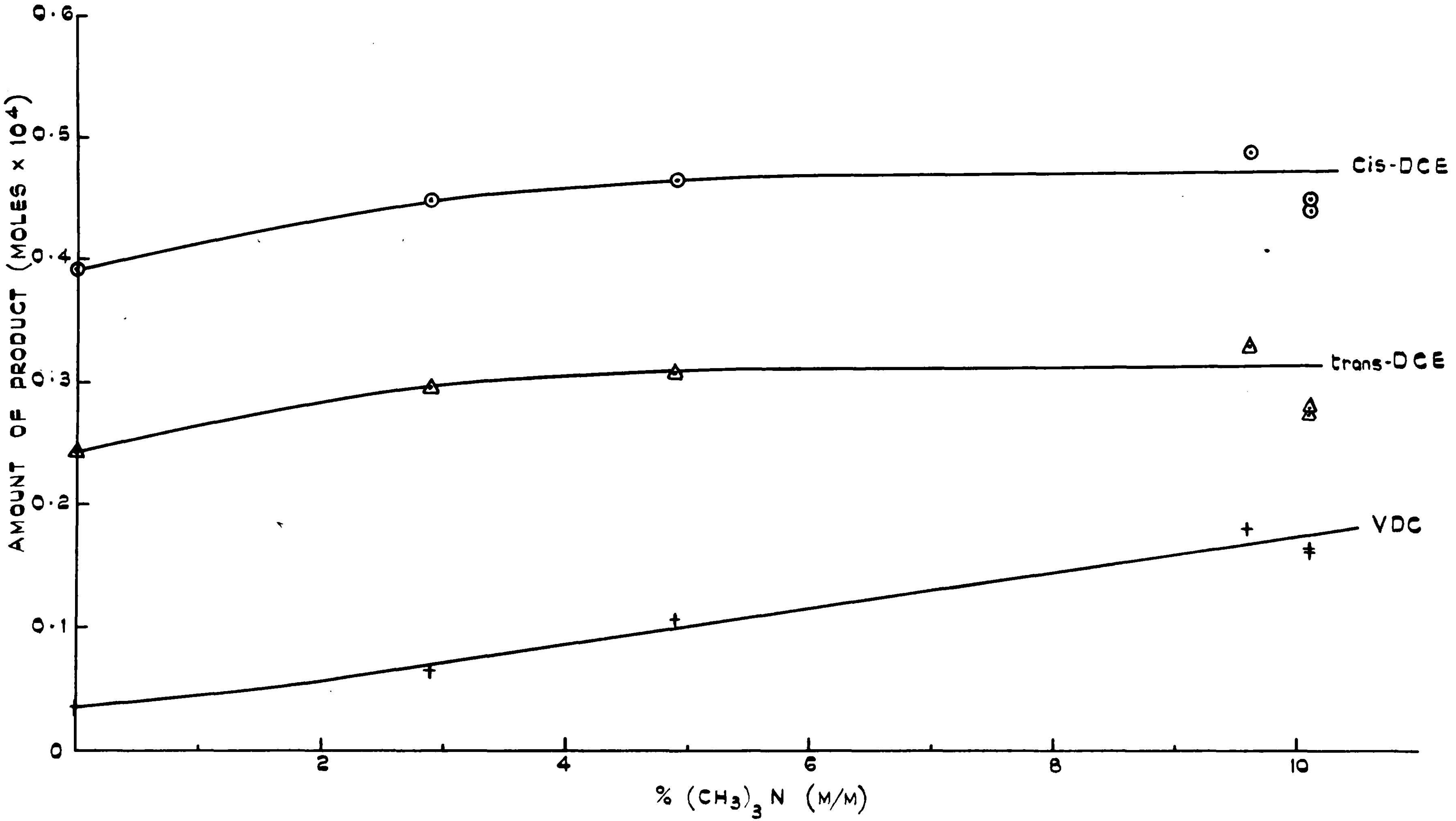


FIGURE 5·08

β TRI DECOMPOSITION AT 453·5°C - CHAIN INHIBITED REACTION
EFFECT OF TRIMETHYLAMINE OF THE PRODUCT DISTRIBUTION OBTAINED
FROM 5 MIN REACTIONS.

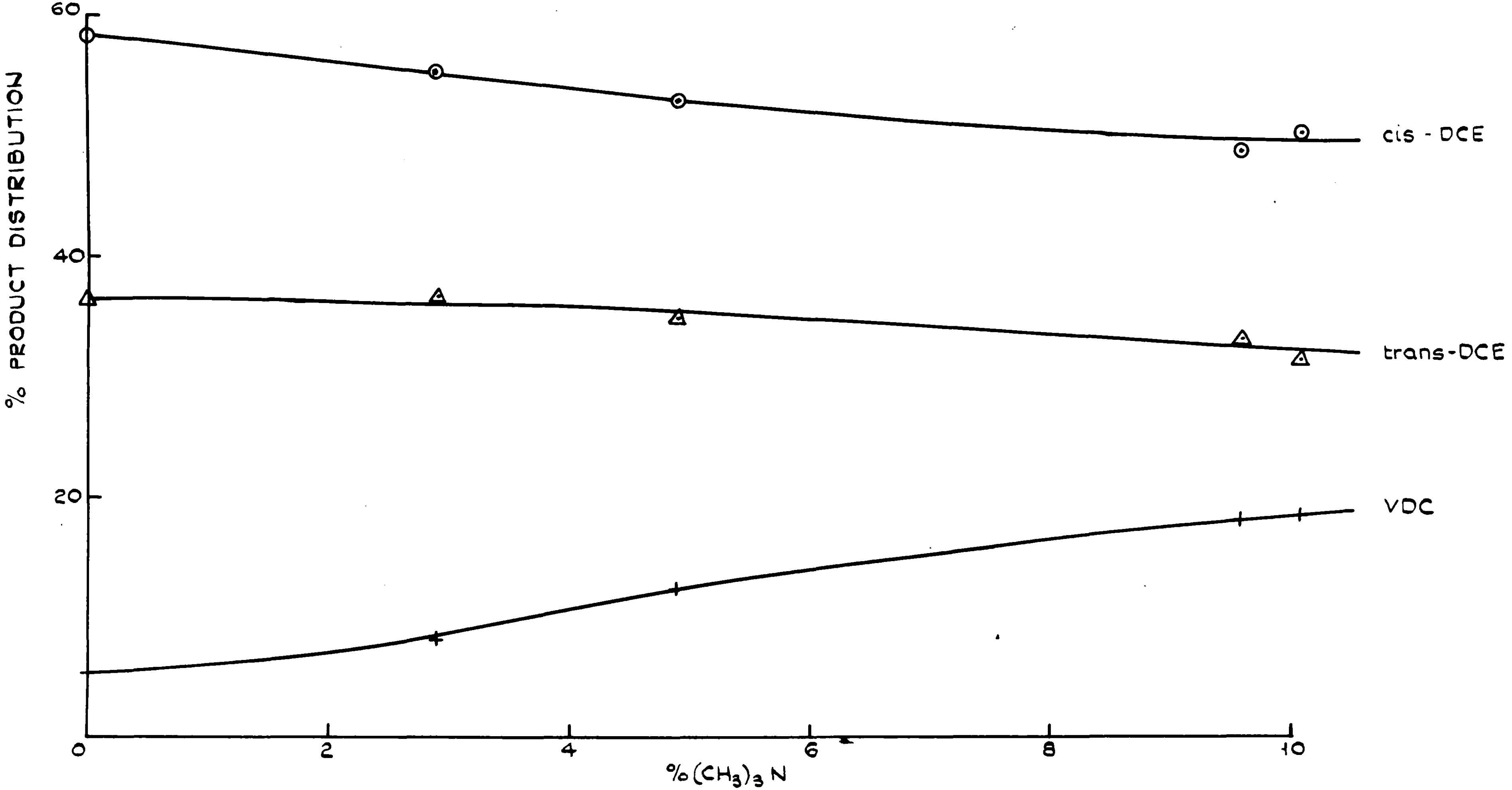
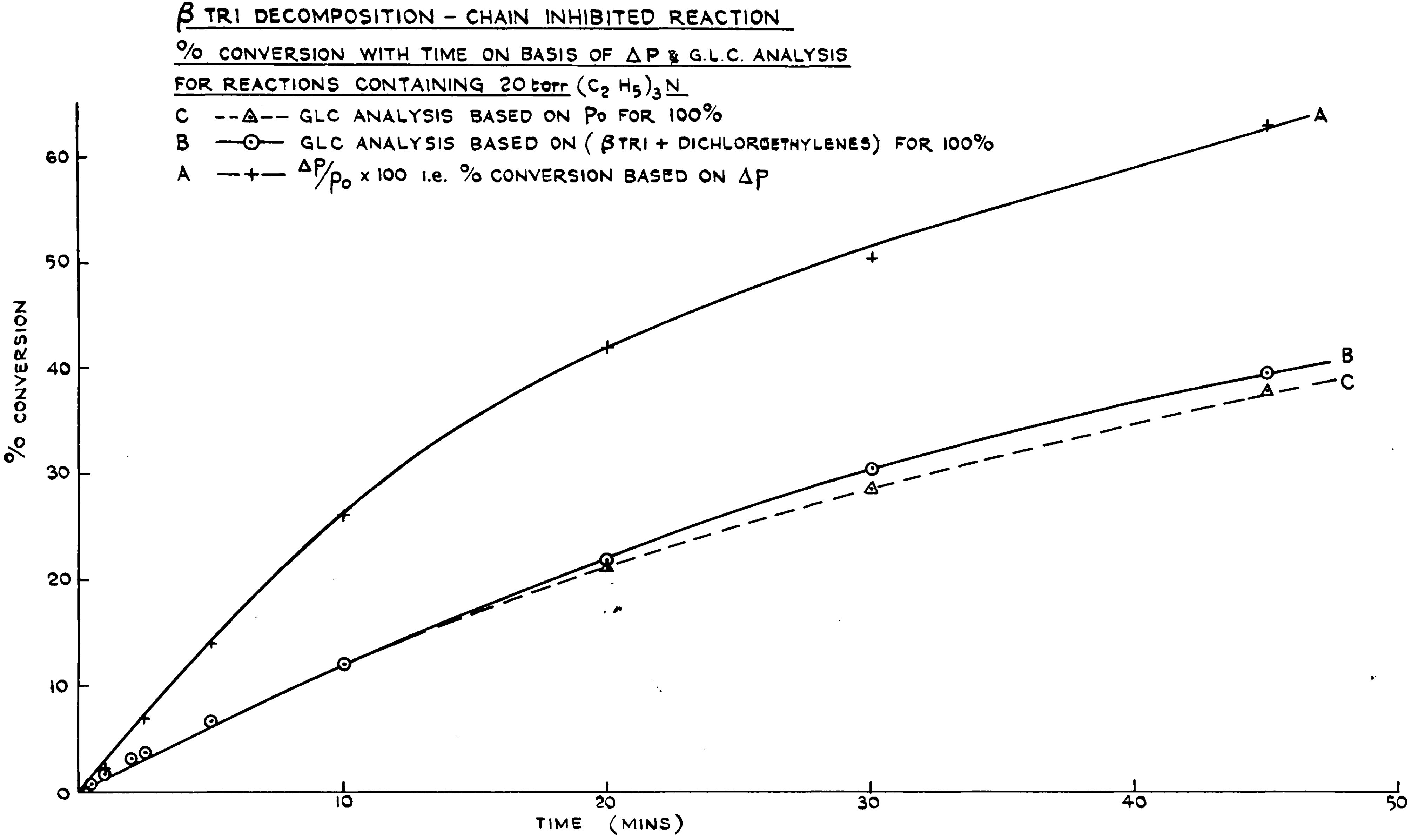


FIGURE 5.09



β TRI DECOMPOSITION - CHAIN INHIBITED REACTION

% CONVERSION WITH TIME ON BASIS OF ΔP & G.L.C. ANALYSIS

FOR REACTIONS CONTAINING 20 torr $(C_2H_5)_3N$

FIGURE 5.10

β TRI DECOMPOSITION - CHAIN INHIBITED REACTION AT 453·5°C

TRIETHYLAMINE ADDITION (~9%)

EFFECT OF TIME OF REACTION ON PRODUCT DISTRIBUTION.

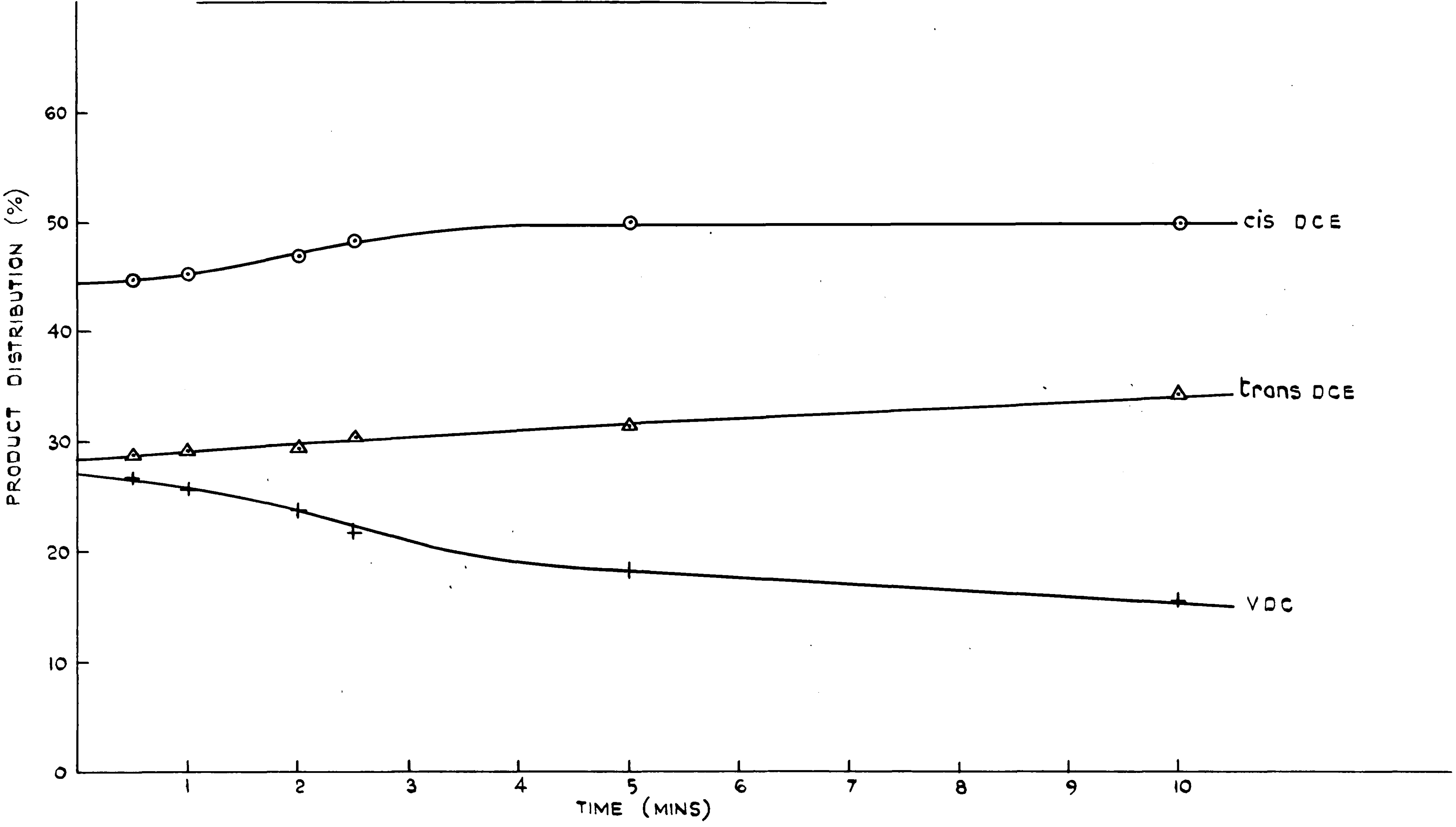


FIGURE 5.11

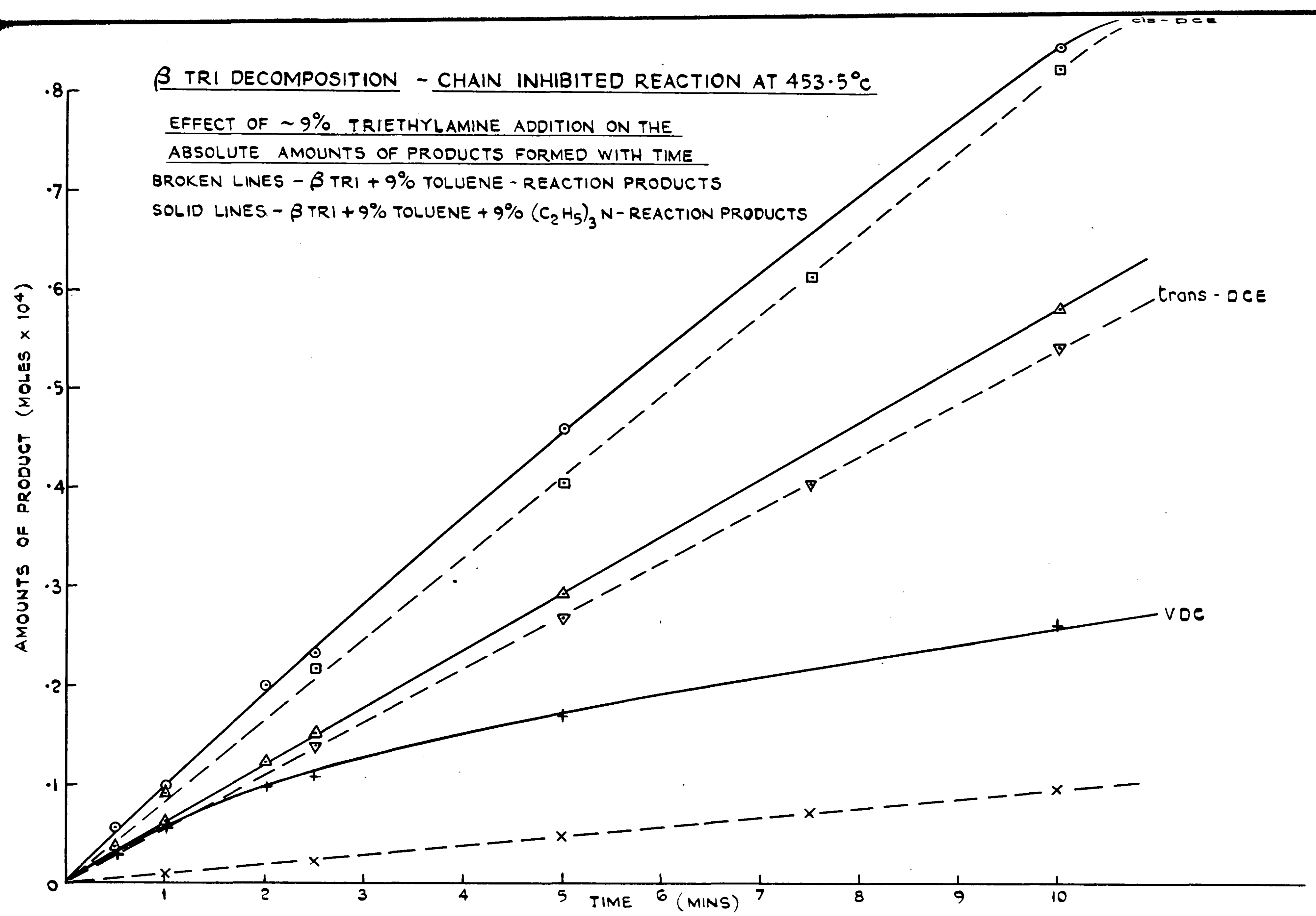
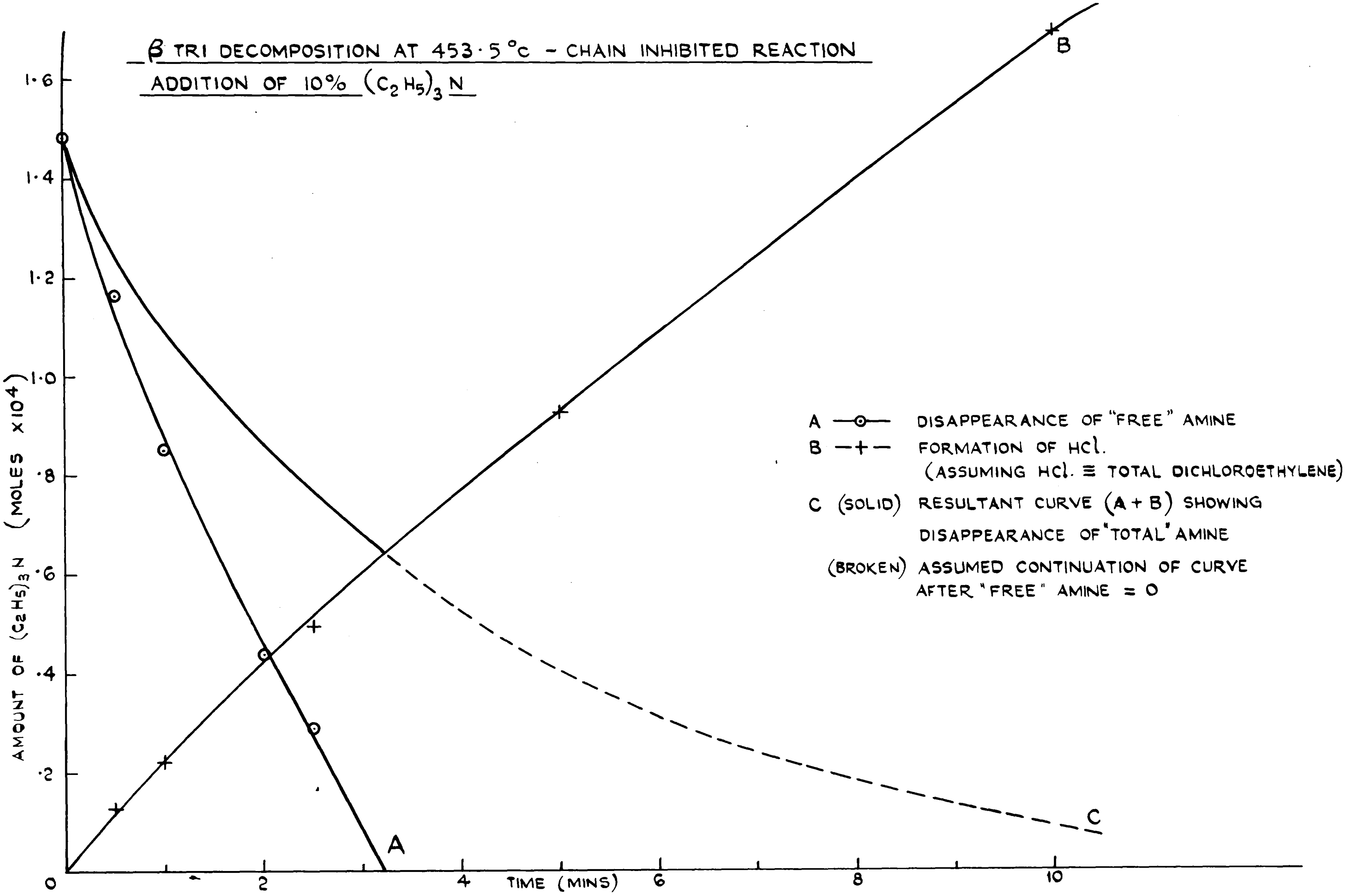

β TRI DECOMPOSITION - CHAIN INHIBITED REACTION AT 453·5°C
EFFECT OF ~9% TRIETHYLAMINE ADDITION ON THE ABSOLUTE AMOUNTS OF PRODUCTS FORMED WITH TIME
BROKEN LINES - β TRI + 9% TOLUENE - REACTION PRODUCTS
SOLID LINES - β TRI + 9% TOLUENE + 9% $(C_2H_5)_3N$ - REACTION PRODUCTS
cis - DCE
trans - DCE
VDC
AMOUNTS OF PRODUCT (MOLES × 10^4)
·8
·7
·6
·5
·4
·3
·2
·1
0
1
2
3
4
5
6
7
8
9
10
TIME (MINS)

FIGURE 5.12



β TRI DECOMPOSITION AT 453·5 °C – CHAIN INHIBITED REACTION

ADDITION OF 10% $(C_2H_5)_3N$

FIGURE 5.13

β TRI DECOMPOSITION AT 453·5°C - CHAIN INHIBITED REACTION (~10% TOLUENE)

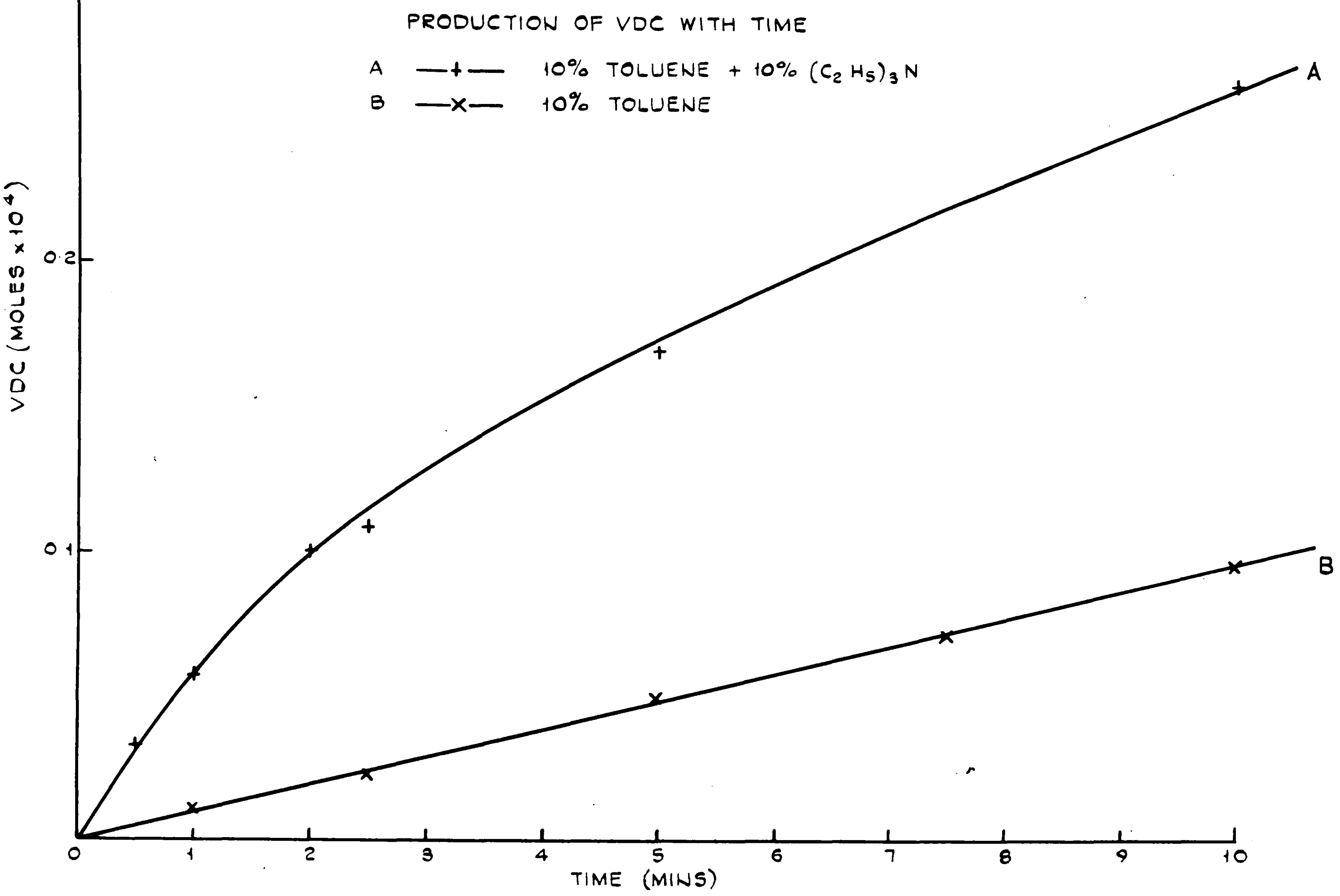
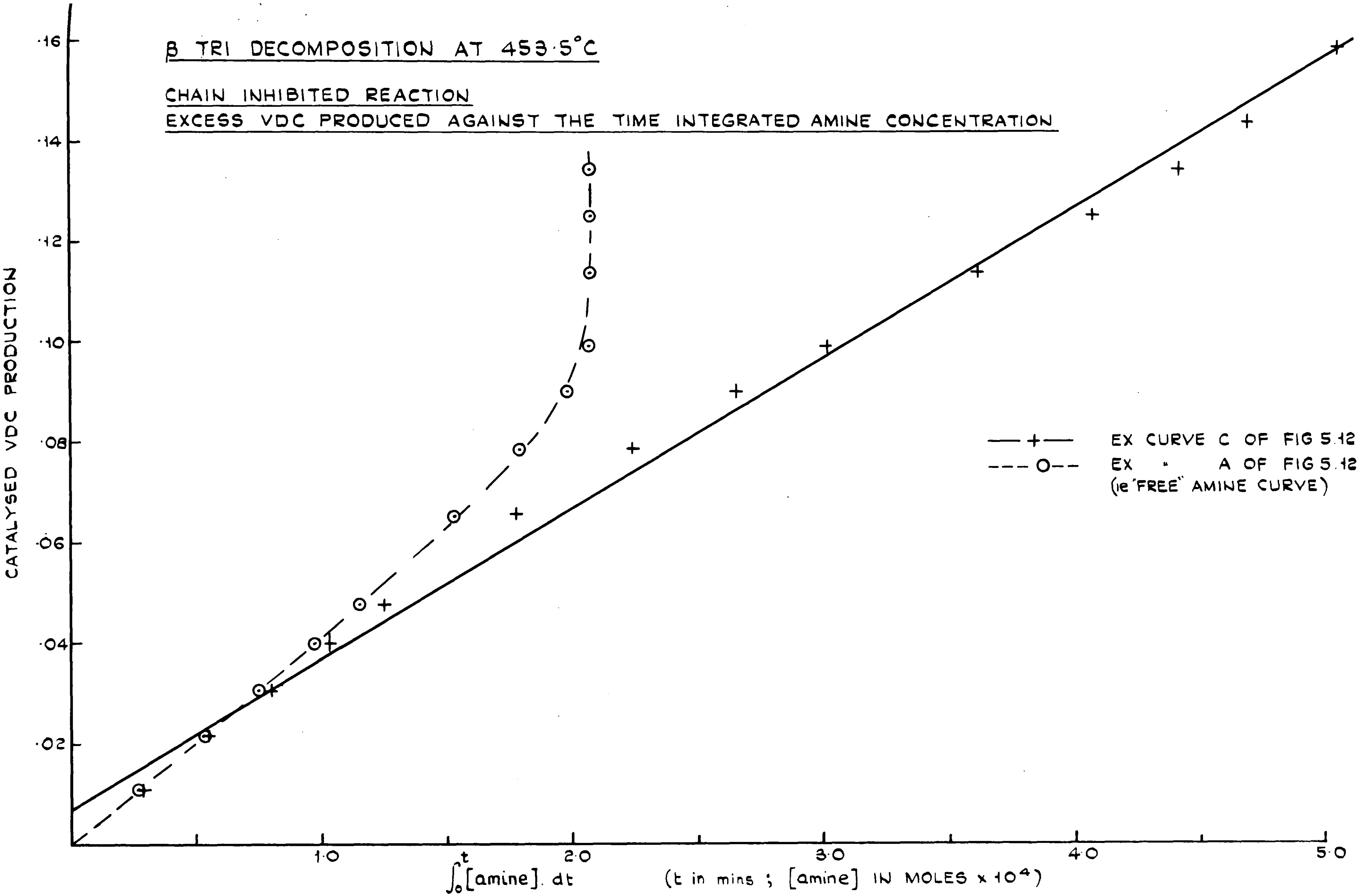
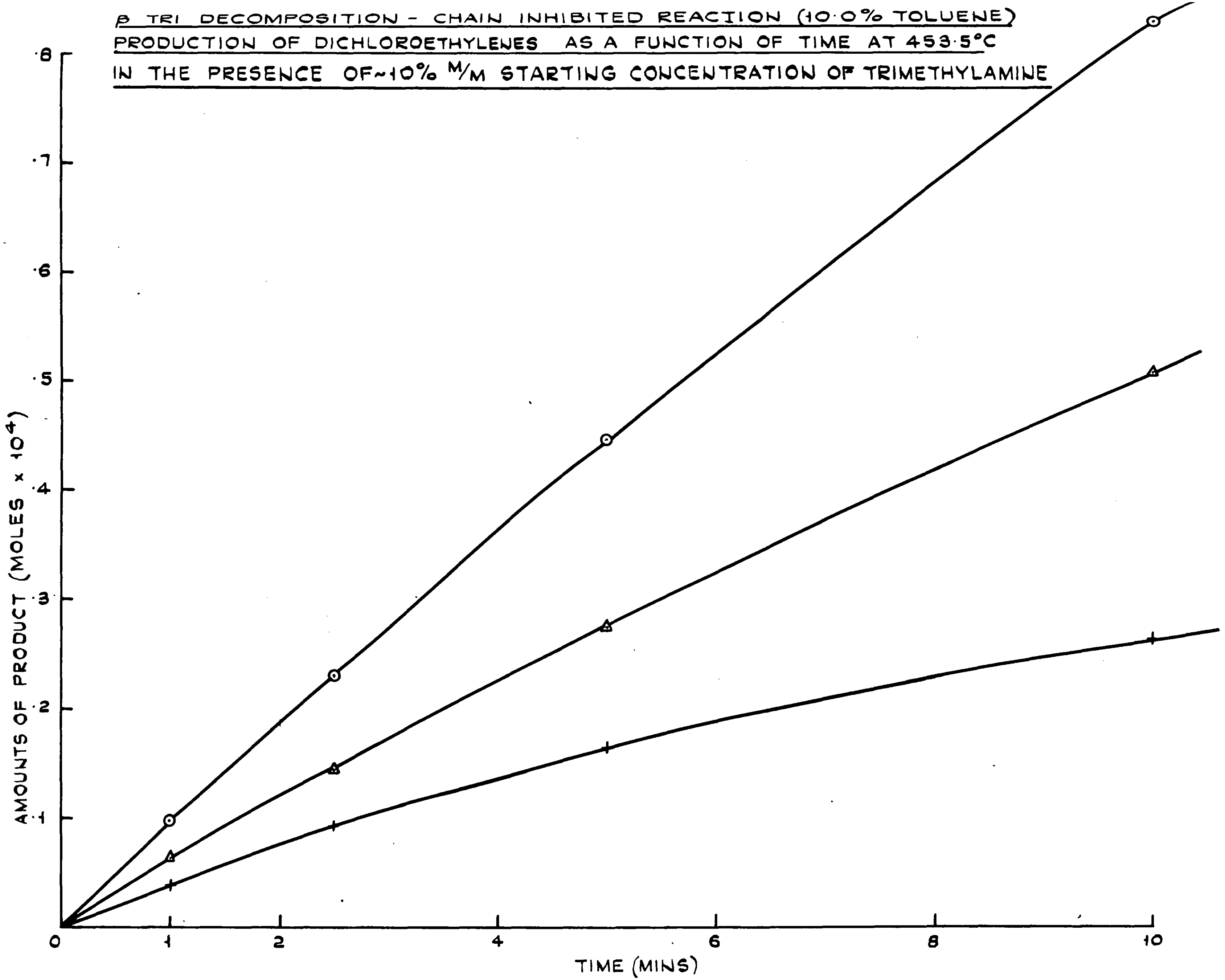


FIGURE 5.14


β TRI DECOMPOSITION AT 453·5°C
CHAIN INHIBITED REACTION
EXCESS VDC PRODUCED AGAINST THE TIME INTEGRATED AMINE CONCENTRATION
CATALYSED VDC PRODUCTION
·16
·14
·12
·10
·08
·06
·04
·02
1·0
2·0
3·0
4·0
5·0
$\int_0^t [\text{amine}].\,dt$ (t in mins ; [amine] IN MOLES × 10^4)
—+— EX CURVE C OF FIG 5.12
---O-- EX " A OF FIG 5.12
(ie "FREE" AMINE CURVE)



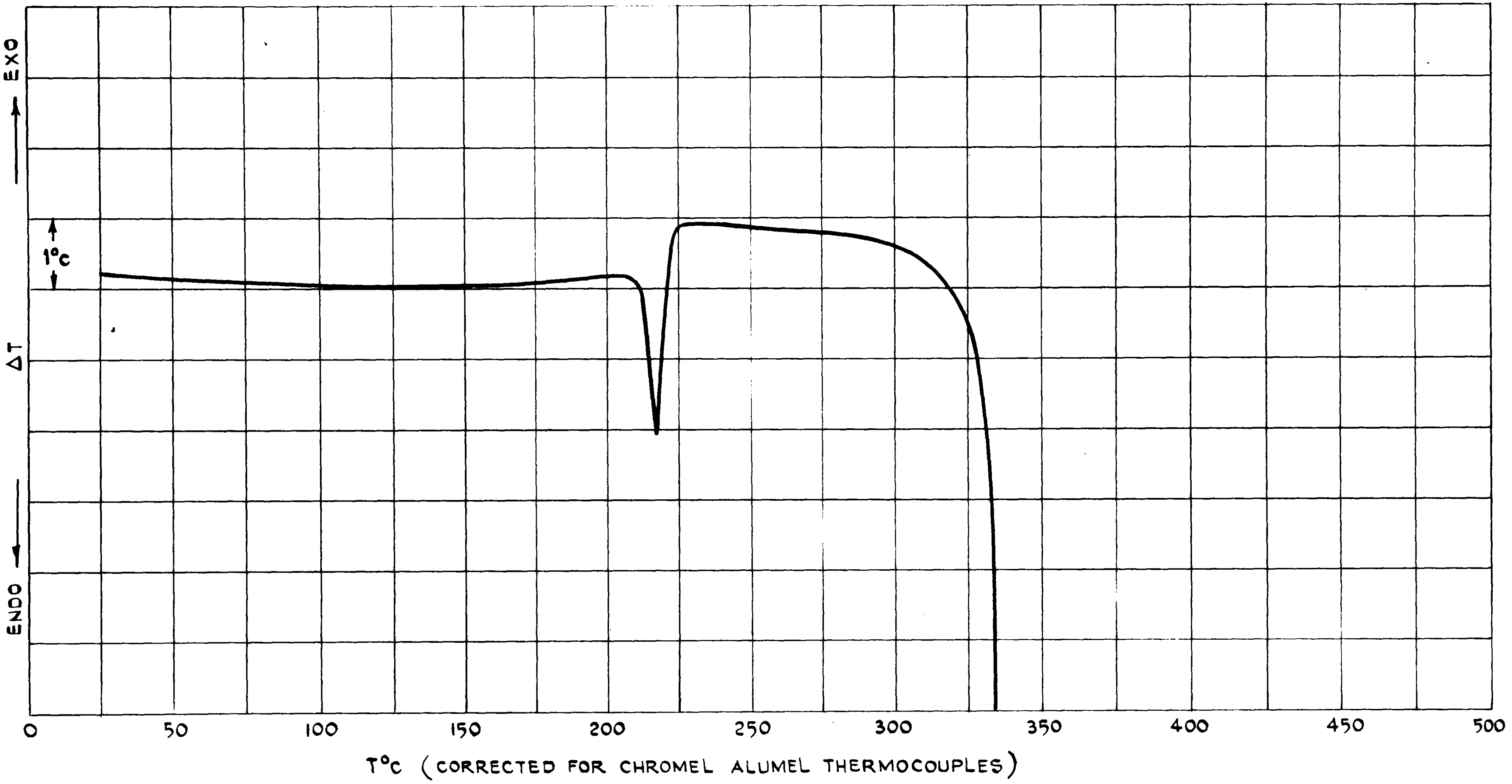
β TRI DECOMPOSITION - CHAIN INHIBITED REACTION (10·0% TOLUENE)
PRODUCTION OF DICHLOROETHYLENES AS A FUNCTION OF TIME AT 453·5°C
IN THE PRESENCE OF ~10% M/M STARTING CONCENTRATION OF TRIMETHYLAMINE

FIGURE 5·15

FIGURE 5.16

DIFFERENTIAL THERMAL ANALYSIS OF n-BUTYLAMINE HYDROCHLORIDE (PROTECTED THERMOCOUPLE)

HEATING RATE OF 20 °C/MIN.



CHAPTER 6

DISCUSSION

6.01 The Decomposition Reactions in the Absence of Additives

It has been shown in the preceeding chapters that the thermal decompositions of both βTRI and ECH, although differing in detail, proceed partly by free radical chain and partly by molecular mechanisms. The ability of both systems to sustain a chain reaction was demonstrated by the rate accelerations observed in the presence of CCl_4. On the other hand whilst the addition of a chain inhibitor such as toluene or propylene retarded the rates of decomposition it did not completely eliminate them.

6.01(a) The Decomposition of βTRI

In the case of βTRI decomposition at 391.5°C we have observed irreproducibility in rate. This had been noted in previous work on this system (17, 47) and we believe that the chain decomposition is sensitive to the condition of the surface. The catalysis observed with HCl (section 3.02) also appears to arise from a surface effect. Two sets of previous workers (48, 49) have proposed homogeneous reaction schemes for the decomposition and both have derived first order expressions using identical chain propagation reactions but somewhat different initiation and termination reactions. In contrast to the first order kinetics observed by these workers we have observed second-order kinetics with respect to βTRI under our conditions of reaction. The order of a chain reaction is normally determined by the nature of the initiation and termination steps. If we adopt a simple unimolecular C-Cl bond fission as our initiating process **for** βTRI the subsequent β-Cl loss would be rapid and the overall initiation reaction can be written

$$CH_2ClCHCl_2 \xrightarrow{k_i} CH_2{=}CHCl + 2Cl^{\bullet}$$

The order of this chain process is then decided by the number and the type of the radicals involved in the termination process. The "type" of radical is conveniently described by the nomenclature originally proposed by Martens (73). β radical is one involved in a second order chain propagation step e.g. the chlorine atom in the reaction:-

$$Cl^{\bullet} + CH_2Cl.CHCl_2 \longrightarrow CH_2Cl.\dot{C}Cl_2 + HCl$$

Alternatively a μ radical is one involved in a first order chain propagation step:-

$$CH_2Cl.\dot{C}Cl_2 \longrightarrow CH_2{=}\,CCl_2 + Cl^{\bullet}$$

Two conditions exist which will establish the order of a chain reaction as second.

(1) If a β radical can terminate by a unimolecular process (i.e: on the wall)

$$Cl^{\bullet} \xrightarrow{k_t} \text{termination.}$$

(2) If the termination reaction occurs between a β and a μ radical and if in addition the decomposition of the μ radical is in its pressure dependent region. This latter condition may be represented by:-

i.e. $$CH_2Cl.\dot{C}Cl_2 + M \longrightarrow CH_2{=}CCl_2 + \dot{C}l + M$$

and the termination reaction by:

$$Cl^{\bullet} + CH_2Cl\dot{C}Cl_2 \longrightarrow CH_2Cl.CCl_3$$

It is to be expected from theory that at pressures around 200 torr the above radical decomposition would be in its pressure dependent region. In previous work in this laboratory on the decomposition of the $CH_2ClCH_2^{\bullet}$ radical the addition of an inert gas (CO_2) had no effect on the overall rate of 1,2-dichloroethane decomposition implying that the μ radical was not involved in termination and that termination (1) was correct. If we assume that a similar result would be obtained for βTRI then the proposed mechanism for βTRI decomposition becomes

$$CH_2ClCHCl_2 \xrightarrow{k_i} CH_2{=}CHCl + 2Cl^{\circ} \qquad \text{......} (6.02)$$

$$Cl^{\bullet} + CH_2ClCHCl_2 \xrightarrow{k_3} CH_2ClCCl_2^{\bullet} + HCl \qquad \text{.......}(6.03)$$

$$\dot{Cl} + CH_2ClCHCl_2 \xrightarrow{k_4} \dot{C}HCl\ CHCl_2 + HCl \qquad .....(6.04)$$

$$CH_2Cl\dot{C}Cl_2 \xrightarrow{k_5} CH_2 = CCl_2 + Cl^{\bullet} \qquad .....(6.05)$$

$$\dot{C}HCl\ CHCl_2 \xrightarrow{k_6} CHCl = CHCl + Cl^{\bullet} \qquad .....(6.06)$$

$$Cl^{\bullet} \xrightarrow{k_t} \text{termination} \qquad .....(6.07)$$

Then using the steady state approximation:-

Rate of chain initiation = Rate of chain termination.

$$\therefore \quad 2\,k_i\,(\beta TRI) = k_t\,(Cl^{\bullet})$$

$$Cl^{\bullet} = \frac{2k_i}{k_t}\,(\beta TRI)$$

Rate of decomposition of βTRI = $k_i(\beta TRI) + (k_3 + k_4)(\beta TRI)(Cl^{\bullet})$

for a chain length $>$100 the loss of βTRI by chain initiation may be ignored

$$\therefore \quad \text{Rate of decomposition of } \beta TRI = (k_3 + k_4)(\beta TRI)(Cl^{\bullet})$$

$$= \frac{2k_i}{k_t}(k_3 + k_4)(\beta TRI)^2$$

The proposed termination reaction must certainly occur on the wall but at the same time the absence of a large effect on the rate when a packed vessel was employed indicates that the initiation reaction is also dependent on the surface. Such an effect would also explain the wide variation in the reaction rates observed by different groups of workers. These have already been discussed in chapter 1. The rate of reaction observed in this investigation was similar to that obtained by Barton (17). At 391.5°C and 200 torr initial pressure the data of table 3.05 enables us to calculate an initial first order rate "constant" of 7.1×10^{-4} sec^{-1}. This can be compared directly with the value of 17.4×10^{-4} sec^{-1} obtained by Barton, who expressed his rate constant as a first order value but did not verify this point experimentally.

Although the initiation and termination reactions affect the overall rate of decomposition, the selectivity of the reaction is determined solely by the relative rates of hydrogen abstraction from the two carbon centres (k_3 and k_4). If the rates of abstraction of any hydrogen atom in βTRI were equivalent then the statistical distribution of hydrogen atoms would be expected to give 33% VDC and 67% 1,2-dichloroethylene. In the present study the VDC proportion was 45.3% and this infers a favoured abstraction from the $CHCl_2$- end of the molecule. Goldfinger et al (51) showed that:-

$$\log_{10}k_3 = 9.95 \pm 0.20 - \frac{(3.10 \pm 0.30) \times 10^3}{4.575T}$$

$$\log_{10}k_4 = 10.15 \pm 0.20 - \frac{(3.70 \pm 0.30) \times 10^3}{4.575T}$$

These data were obtained photochemically at 50-150°C and extrapolation to 391.5°C will be subject to error, however the value obtained at this temperature gives a VDC distribution of 49± 12%. The errors are unavoidably large - as the calculation involves the difference of two large numbers - but the experimental value of 45.3% lies well within the error limits.

An additional feature of these equations is the lower activation energy for k_3. Although the errors involved in comparing k_3 and k_4 reduce the significance of this result it does indicate that a decrease in the proportion of VDC formed would be expected at higher temperatures. This is in agreement with the result observed experimentally in section 3.04.

As we have adopted the same propagation steps as previous workers on βTRI decomposition one should expect the same product ratios at a given temperature. Our value of 45.3% VDC at 391.5°C was obtained from the overall reaction and must therefore be affected by the proportion of molecular reaction occurring. However inhibition studies have indicated that this reaction is at least 50 times slower than the chain process and one can assume a negligible contribution from the molecular mechanism. On the other hand the decomposition in steel as studied by Teramoto possessed a larger molecular component (i.e: $\frac{1}{10}$ th of the reaction), which would affect the overall proportion of VDC observed. Use of the equation

$$\frac{\text{Proportion of VDC}}{\text{Proportion of 1,2.DCE}} = 0.7 \exp\left(\pm\frac{500}{RT}\right)$$

which Teramoto derived for the radical reaction leads to a value of 41.7 ± 9.3 % VDC which is acceptably close to our value. The value of 40.1 % VDC obtained in Pimenov's work was again derived from the overall reaction. The amount of molecular reaction occurring was not assessed by Pimenov and may have been considerable as the observed reaction was much slower than that measured by ourselves or Barton, indicating a suppression of the radical component of decomposition.

Our results also demonstrated no change in the proportion of VDC formed at 391.5°C under varying conditions of initial pressure, rate, % conversion, surface volume ratio and CCl_4 addition. This would be the expected result if as postulated, k_3 and k_4 were solely responsible for determining product selectivity. One may conclude that the propagation steps shown in equations 6.03, 6.04, 6.05 and 6.06 represent the most likely mechanism of chain propagation. An additional conclusion is that the contribution of the molecular component of decomposition is negligible under the variable conditions mentioned above.

The previous paragraphs have shown that the normal βTRI decomposition propagated by chlorine atoms gives a small selectivity toward VDC production. Chlorine atoms are known to be highly reactive and non-selective in chlorocarbon decompositions and the introduction of a more selective hydrogen abstracting agent might be expected to enhance the proportion of VDC formed. The addition of 10% HBr (section 3.08(b)) increased the proportion of VDC to 60% indicating a change in the chain propagating reactions. The reaction:-

$$HBr + Cl^{\bullet} \longrightarrow Br^{\bullet} + HCl \quad \ldots\ldots\ldots \qquad (6.08)$$

has a ΔG value of -15.1 kcals/mole (74). The high reactivity of chlorine atoms will ensure the production of bromine atoms in the system. These would be expected to extract hydrogen more slowly and more selectively than chlorine. Typical activation energies for hydrogen abstraction from chloroalkanes are 12 kcals and 3 kcals/mole respectively. This would lead to a build up of bromine atom concentration in the system thereby increasing the rate of abstraction by bromine and ensuring that a considerable proportion of the abstraction reaction occurred through bromine atoms. The observed enhancement in selectivity to VDC confirms this agrument. The addition of HBr also caused an overall acceleration of the chain process. This is most likely due to a new initiation reaction involving the fission of the relatively weak HBr bond (85.5 kcals). Such an effect has been frequently observed in chain decompositions.

A similar change in the selectivity of the chain process was observed on the addition of H_2S to βTRI (section 3.08 (a)). In this case a retardation in rate was observed and the proportion of molecular reaction occurring had to be subtracted from the overall rate. The selectivity of 5% H_2S was thus shown to give 62% VDC in the radical reaction. In a similar manner to HBr in equation 6.08 the reaction:-

$$H_2S + Cl^{\bullet} \longrightarrow SH^{\bullet} + HCl \qquad \ldots\ldots\ldots\ldots \quad (6.09)$$

has a ΔG of -13.8 kcals/mole (74) and the build up of a reasonable concentration of $SH^{\bullet}$ radicals will ensure the occurrence of the more selective and slower hydrogen abstraction process via $SH^{\bullet}$. In the absence of any additional initiation reaction arising from H_2S then a reduction in overall rate, which was the observed effect in the presence of H_2S, is to be expected owing to the replacement of a reactive atom ($Cl^{\bullet}$) by a less reactive one ($SH^{\bullet}$).

6.01(b) The Decomposition of ECH.

The normal βTRI decomposition at 391.5°C occurs predominantly by a radical mechanism. With ECH at 454.9°C this was not the case - the molecular decomposition providing ~75% of the reaction. The selectivity of the radical decomposition is complicated by this factor and is more readily understood after a discussion of the effects of inhibitors.

The mechanism of the chain process may be thought of in a similar manner to that proposed for βTRI. Thus:-

$$CH_2OHCH_2Cl \xrightarrow{k_{10}\ (wall)} CH_2OHCH_2^{\bullet} + Cl^{\bullet} \qquad ....(6.10)$$

$$Cl^{\bullet} + CH_2OHCH_2Cl \xrightarrow{k_{11}} \dot{C}HOHCH_2Cl + HCl \qquad ....(6.11)$$

$$Cl^{\bullet} + CH_2OHCH_2Cl \xrightarrow{k_{12}} CH_2OH\dot{C}HCl + HCl \qquad ....(6.12)$$

$$\dot{C}HOHCH_2Cl \xrightarrow{k_{13}} \underset{\substack{\downarrow \\ CH_3\ CHO}}{(CHOH{=}CH_2)} + Cl^{\bullet} \qquad ....(6.13)$$

$$CH_2OH\dot{C}HCl \xrightarrow{k_{14}} CH_2{=}\ CHCl + OH^{\bullet} \qquad ...(6.14)$$

$$2CH_2OHCHCl^{\bullet} \xrightarrow{k_{15}} (CH_2OHCHCl)_2 \qquad ...(6.15)$$

It will be seen later that the termination process shown (equation 6.15) is the one most likely to occur according to concentration effects.

The enol formed in equation 6.13 would rapidly adopt the more stable aldehyde structure. The loss of an hydroxyl group (6.14) to form vinyl chloride is more difficult ($E_{ACT} \cong 35$ kcals/mole) than the loss of a $\beta Cl^{\bullet}$ ($E_{ACT} \approx 22$ kcals/mole) and if the initial rates of hydrogen abstraction are similar ($k_{11} \approx k_{12}$) then one would expect the vinyl chloride precursor $CH_2OH\text{-}\dot{C}HCl$ to build up and provide a major source of chain termination as shown in equation 6.15. Reaction 6.14 also supplies an hydroxyl radical which will be sufficiently reactive to play a part in subsequent chain propagation. An alternative site for hydrogen abstraction is from the O-H group. This process would be expected to be relatively slow as the O-H bond strength is ≈ 103 kcals/mole compared to ≈ 97 kcals/mole for the typical C-H bond. Furthermore the decomposition of the resultant radical $CH_2ClCH_2O^{\bullet}$ would occur rapidly and yield formaldehyde. The absence of formaldehyde, or its decomposition product hydrogen, from the routine analysis indicated that the hydrogen abstraction from O-H was insignificantly small and could be ignored.

A further complication of the ECH pyrolysis is the secondary decomposition of acetaldehyde into carbon monoxide and methane. Previous work (54, 55) has shown that at these temperatures acetaldehyde decomposes readily by a radical chain mechanism but a molecular mechanism is not known. The mechanism involves hydrogen abstraction from the relatively weak aldehydic C-H position (E=86.5 kcal/mole) with subsequent decomposition of the acetyl radical.

$$CH_3CHO + X^\bullet \longrightarrow CH_3\dot{C}O + HX \qquad ...(6.16)$$

$$CH_3\dot{C}O \longrightarrow CH_3^\bullet + CO \qquad ...(6.17)$$

In our system X could be $Cl^\bullet$ or $OH^\bullet$ arising from the primary decomposition or $CH_3^\bullet$ derived from the above reactions. $CH_3^\bullet$ is also able to abstract hydrogen from ECH and aid propagation of the primary decomposition.

The complicated nature of the decomposition indicated that a satisfactory analytical result from steady state theory would be unobtainable. Hence computational methods involving a numerical solution were adopted and these are described later.

The chain transfer agents used in ECH decomposition were HCl and HBr. Published data (20, 21, 64) suggests that methyl abstracts hydrogen far more readily from HCl and HBr than from halocarbons. In general the reactivity of $CH_3^\bullet$ is less than $Cl^\bullet$ and the consequent build up of $CH_3^\bullet$ in the system will make the reaction:-

$$CH_3^\bullet + HX \longrightarrow CH_4 + X^\bullet$$

$(X^\bullet = \dot{B}r \text{ or } \dot{C}l)$

an important one. HCl is formed as a decomposition product and consequently the addition of excess HCl to the system would not be expected to produce a dramatic effect. The small amount of chain catalysis which was observed (section 4.08(a)) was most probably due to the above reaction replacing some methyl radicals by chlorine atoms.

In the presence of H-Br a preferential catalysis of the secondary decomposition was observed (section 4.08(b)). The selectivity of bromine atoms has previously been discussed in this chapter in connection with βTRI decomposition. In ECH decomposition the relative weakness of the aldehydic

C-H bond will ensure a strong preferential attack from bromine atoms at this point. The likely chain transfer scheme may be thus written:-

$$CH_3^{\bullet} + HBr \longrightarrow CH_4 + Br^{\bullet} \qquad ...(6.18)$$

$$Br^{\bullet} + CH_3CHO \longrightarrow CH_3\dot{C}O + HBr \qquad ...(6.19)$$

$$CH_3\dot{C}O \longrightarrow CH_3^{\bullet} + CO \qquad ...(6.17)$$

The replacement of the reaction

$$CH_3^{\bullet} + CH_3CHO \longrightarrow CH_4 + CH_3CO$$

by reactions 6.18 and 6.19 leads to the observed catalysis. In the presence of HBr the formation of side products ($CH_3Cl, CH_2{=}CH_2, CH_3{-}CH{=}CH_2$) was maintained. The proposed mechanism for their formation involved $CH_3^{\bullet}$ as an attacking radical, and because there was no serious depletion of side products this mechanism requires that the concentration of $CH_3^{\bullet}$ is likewise maintained. This point was also considered further in section 6.03.

6.02 Chain Inhibition and the Extent of Unimolecular Decomposition

The decompositions of both βTRI and ECH were retarded by the addition of inhibitors thus suggesting the likelihood of a radical chain mode of decomposition. In the absence of complete suppression of the reaction the question arises as to whether the residual reaction is still occurring wholly by chain or whether an underlying molecular mechanism also exists which would be unaffected by chain inhibitors.

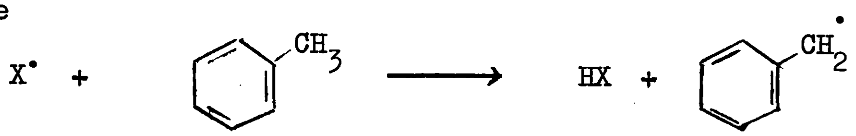
In the past several authors have argued against the existence of unimolecular reactions (65) on the grounds that the inhibitor provided an alternative (and slower) chain propagating species. The absence of any inhibitory effect in certain reactions was rationalized as an equivalent change occurring in the rates of the initiation and termination steps which gave the same overall rate whether inhibitor was present or not.

More recently however the likely existence of unimolecular mechanisms has been recognized. For example in chapter II of a recent review by Benson and O'Neal (81) the authors outline the reasons for accepting an underlying molecular reaction in the decomposition of ethyl bromide. At the same time they point out (chapter V section 2.0) that the relatively unreactive radicals produced by inhibitors may still be able to sustain a chain reaction by hydrogen abstraction. Thus in any discussion involving radical chain and molecular mechanisms not only is it necessary to establish that an underlying molecular mechanism exists but also what extent of the residual reaction is involved.

In our studies on βTRI and ECH inhibition the retarding effect of increasing amounts of inhibitor on the rates of reaction were quite different. With βTRI (figure 3.09) the rate dropped dramatically for very small additions of toluene and appeared to reach a limiting value at ~3% toluene. For ECH however the rate reduced slowly (figure 4.14) and had not reached a limit at 50% toluene addition. However one effect is common to both - namely a change in the product distribution as toluene is added. For βTRI figure 3.11 shows the considerable decrease in the proportion of VDC formed whilst figure 6.01 demonstrates that with ECH the dehydration to dehydrochlorination ratio decreases steadily from 0.09 to 0.036 for 45 minute reactions as the addition of toluene is increased from 0 to 50%. This evidence suggests the existence of two mechanisms for each decomposition, one affected by inhibitors whilst the other remains unaffected. This is confirmed in the case of βTRI where the second order kinetics observed for the uninhibited reaction give way to first order kinetics for the maximally inhibited decomposition. In the case of ECH decomposition table 6.01 summarizes the results obtained from 10 minute reactions of ECH in the presence of various additives. The ratio of the formation of acetaldehyde to vinyl chloride is shown in the last column of the table. This ratio varies widely from 5.7 for the CCl_4 accelerated reaction to 36 for the reaction inhibited by toluene (B). However if one assumes complete chain inhibition by toluene then subtraction of this latter result from the others should give the amount of reaction occurring via a radical chain process and should produce an approximately constant ratio in the last column. For the normal decomposition and those with CCl_4 and HCl (F, G, and H) the ratio is reasonably constant. The higher value obtained with HBr arises from a change in the nature of the propagating species and is further discussed in section 6.03. The relatively constant ratio obtained from the "chain" component of reaction lends support to the view that the change in selectivity observed with added toluene arises from a dual mechanism.

For both reactions the inhibitory effect involves the replacement of reactive radicals by unreactive ones:-

for toluene



for propylene

$$X^{\bullet} + CH_3 - CH = CH_2 \longrightarrow HX + \dot{C}H_2\text{-}CH{=}CH_2$$

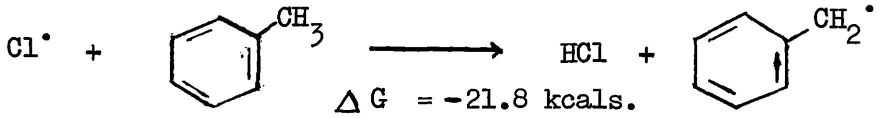
where $X^{\bullet}$ is $Cl^{\bullet}$ in βTRI decomposition.

and $X^{\bullet}$ is $Cl^{\bullet}$,$OH^{\bullet}$,$CH_3^{\bullet}$ in ECH decomposition.

The process involved is analogous to the chain transfer process discussed previously with the important difference that the inhibitory radicals are too sluggish to continue chain propagation. Furthermore we have shown that any selectivity in chain transfer will favour VDC production (e.g: the results with HBr). Hence it is unlikely that the major change in selectivity (a decrease in the proportion of VDC) observed with toluene has arisen through a chain transfer process in which benzyl is abstracting hydrogen.

Thus we believe that βTRI and ECH both possess radical chain and molecular modes of decomposition.

The second consideration was the extent of inhibited reaction occurring by the molecular mode. This was particularly important for βTRI because we wished to study the effects of additives on the molecular mechanism. The reduction of the rate of βTRI decomposition to the same minimum value in the presence of both toluene and propylene suggested that the amount of chain reaction occurring at this point must be negligible. The more sensitive indication of maximum inhibition which was derived from the amount of product formed in 5 minute reaction (figure 3.10) showed that 6% toluene was required to reach a true minimum value. The equality of the product amounts for 6 and 10% toluene suggested that chlorine atom propagation of the chain had been reduced to negligible amounts by the replacement of chlorine atoms with benzyl radicals.



..(6.20)

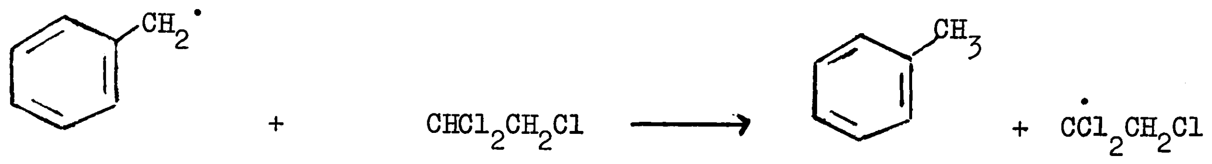
With propylene a similar plateau was observed (figure 3.12) in the amounts of product formed and again one may assume complete suppression of chain propagation by chlorine atom for propylene concentrations above 5%.

$$Cl^{\bullet} + CH_3 - CH = CH_2 \longrightarrow HCl + \dot{C}H_2 - CH = CH_2 \quad ..(6.21)$$

$$\Delta G = -18.3 \text{ kcals.}$$

However the minimum amount of VDC formed was slightly less in the presence of propylene than with toluene (i.e.: 4.2% of the total product formed with propylene but 5.8% with toluene). Although this change could arise from a side reaction which removed VDC (e.g: allyl radical adding to VDC) no addition products were observed and in addition the linearity of the amounts of product formed with time (figure 3.13) implies that any such reaction is small up to 15% decomposition. It seems highly probable therefore that the excess VDC observed in the presence of toluene is arising from a very slow chain propagation involving hydrogen abstraction by benzyl radical. If this is the case the previous discussion on selectivity (section 6.01(a)) would suggest a favoured selectivity toward VDC formation.

The abstraction reaction we are considering:-



$\Delta G = + 7.5$ kcals

will obviously be very unfavourable in comparison to the analogous abstraction by chlorine atom ($\Delta G = - 14.3$ kcals) but the possibility of benzyl radical leading to the small amount of VDC produced cannot be excluded. Similarly the allyl radical may also give rise to a small degree of chain propagation (for the above reaction with allyl $\Delta G = + 4.0$ kcals). Thus we cannot be certain that the molecular reaction has been completely isolated under conditions of maximum inhibition. One can only conclude that a molecular reaction exists and that under these conditions of maximum inhibition with toluene or propylene the chain propagation by chlorine atoms is negligible. Thus any chain process which occurs must occur through the benzyl or allyl radical and is unlikely to provide more than 5% of the total reaction observed at maximum inhibition. In considering the effect of additives on the inhibited βTRI decomposition we must be constantly aware of the possibility of enhancing a small amount of chain reaction.

In the case of ECH decomposition it is even more difficult to reach a definite conclusion about the extent of reaction occurring by a molecular process. The change in product distribution with inhibitor addition does imply two modes of decomposition but the following points are strong evidence that the chain reaction is not fully suppressed in the presence of 50% toluene.

(a) In the inhibition curves (figure 4.14) the failure to attain a limiting value, the difference between the rate obtained with propylene and toluene, and the difference in product distribution (figure 4.15) under conditions of 50% addition of inhibitor all suggest that the radical chain process has not been completely eliminated.

(b) With 50% inhibitor acetaldehyde was still undergoing decomposition to methane (figure 4.15). This reaction is known to proceed via a free radical mechanism (54, 55, 67, 68) and the existence of an underlying molecular mechanism has not been demonstrated.

(c) In figure 4.09 curve B indicated a change in the dehydration to dehydrochlorination ratio with % conversion in the presence of 50% toluene.

This is difficult to rationalize in terms of a molecular mechanism and suggests some radical chain character which could be affected by the production of HCl as in curve A.

(d) The decomposition of ethyl chloride is known to proceed via a molecular mechanism. The rate can be represented by the Arrhenius expression (81) :-

$$\log k = 13.43 - \frac{56.6\text{x}10^3}{4.575T}$$

which is equivalent to $k_{EtCl} = 2.75 \times 10^{-4}$ sec^{-1} at 454.9°C.

The data on ethanol is more limited but the work of Freeman (71) suggests an upper limit for molecular decomposition of $k_{EtOH} = 1.1 \times 10^{-5}$ sec^{-1} at 525°C. On the assumption of a similar A factor to EtCl this would infer an activation energy of 67.1 kcals/mole and a rate constant at 454.9°C of $k_{EtOH} = 1.86 \times 10^{-7}$ sec^{-1}.

Although the effects of the additional substituents in ECH are unknown it appears unlikely that they would disturb these values by a large factor. Furthermore, in agreement with previously published work (28) on the effect of electron withdrawing β substituents any effect would be expected to slow the rate down (28).

In the presence of 50% toluene a rate constant of 1.44×10^{-4} sec^{-1} is obtained from the rate of acetaldehyde formation. This is reasonably close to the value expected from ethyl chloride. On the other hand the rate constant derived for dehydration under the same conditions would be 4×10^{-6} sec^{-1} which is 20 times faster than the value estimated for ethyl alcohol. It is unlikely that a β-Cl would lead to a 20fold increase in rate and the conclusion is that the production of VC in the presence of 50% toluene may still be occurring largely by chain.

A comparison of figure 4.15 with 4.01 shows that the proportional decrease in the methane with added inhibitor (in the presence of a reasonably constant amount of acetaldehyde) agrees closely with that observed for vinyl chloride. If one assumes that methane is arising solely from a chain process then a similar assumption could be inferred for VC formation. The 1000fold difference calculated above for the molecular decompositions of EtOH and EtCl is in agreement with this.

A proportional reduction in the acetaldehyde figure obtained at 50% toluene addition yields the estimated values shown under J in table 6.01 for the extent of molecular reaction. The use of J rather than B in calculating the chain component of reaction makes very little difference to the ratios observed in the last column of rows F - I.

Two factors appear important in discussing the marked difference in the effects of toluene on the decompositions of βTRI and ECH. The first of these concerns the chain lengths of the two decompositions. As mentioned previously typical chain lengths of $>10^5$ have been observed for chlorocarbons which can eliminate a β-Cl after hydrogen abstraction from any carbon atom. βTRI falls into this class of compound and consequently the removal of a small amount of chlorine atoms has a dramatic effect on the overall rate. In the case of ECH the radical $CH_2OH\dot{C}HCl$ cannot eliminate a β-Cl. The hydroxyl group can be eliminated but this is energetically less favourable (by about 12 kcals/mole) than β-Cl elimination. At the same time this process is more favourable than the elimination of a hydrogen atom. The $CH_2OH\dot{C}HCl$ species will provide a partial "stop" to the chain process through side reactions particularly those involving termination. Thus ECH falls between the extreme cases of long chain length associated with βTRI and the negligible chain activity of species such as ethyl chloride. The resultant intermediate chain length means that the effect of inhibitor will not be as dramatic as in βTRI.

The second feature of importance concerns the species involved in the hydrogen abstraction process. For βTRI, inhibition involves the rapid replacement of chlorine atoms by benzyl radicals which have a high energy barrier to hydrogen abstraction from βTRI. In ECH decomposition $\dot{\mathrm{C}}\mathrm{l}$, $\dot{\mathrm{O}}\mathrm{H}$ and $\dot{\mathrm{C}}\mathrm{H}_3$ may all propagate the chain process and the literature (69) reveals that hydrogen abstraction by methyl from a saturated alkyl group will proceed at a similar rate as that from toluene. Consequently it will be impossible to completely suppress the methyl propagated chain by 50% toluene. In addition the power of the inhibitor depends on the relative ease with which it can lose a hydrogen atom compared to other species in the system. The aldehydic C-H bond in acetaldehyde is also weak and will provide effective competition to toluene or propylene as a site for hydrogen atom abstraction. Abstraction from acetaldehyde will, of course, sustain the chain by subsequent decomposition of the acetyl radical into $CH_3^{\bullet}$ and CO.

6.03 The Mathematical Model of the ECH Decomposition.

The mechanism of ECH decomposition and the effects of additives on the rate and the product distribution have been discussed in the previous sections. The complex kinetic interactions involved in the decomposition indicated the need for a mathematical model to test the validity of the postulated mechanism.

The model at our disposal was developed by the Mathematics Department of I.C.I. Mond Division following work done at the Central Instrument Research Laboratory of I.C.I. Ltd. The model has previously been employed in connection with a study carried out in this laboratory into the thermal dehydrochlorination of 1,2-dichloroethane.

The use of the model involved the tabulation of the series of elementary reactions which were thought to occur in the decomposition process.

The rate constant for each reaction was then defined in terms of its activation energy and pre-exponential factor. The model treats the reactions as homogeneous steps and, when supplied with the temperature of reaction and the initial pressures of the components, is able to predict the formation of any species as a function of time.

The rate parameters were obtained from published rate data whenever possible. In the absence of direct information they were estimated with due regard to the thermodynamics of that reaction and the known rate parameters for similar systems. A knowledge of the rate parameters for the reverse reaction and the thermodynamics of the system gave an alternative method for calculating the rate parameters for the forward reaction.

In the initial stages of model fitting the aim was to achieve a close fit to the experimental product-time curves whilst maintaining realistic rate parameters for each reaction. The existence of two competing mechanisms producing interacting products meant that the rates and product distribution had to be fitted simultaneously. Following the evidence of section 6.02 the molecular dehydrochlorination reaction was made considerably faster (10^3) then molecular dehydration (i.e: the VC was considered to be almost completely formed by a chain process).

The model prediction of the concentrations of intermediates allowed an assessment to be made of the likely importance of individual reactions in the scheme. Thus the observation that the species $CH_2OHCH\dot{C}l$ was building up in the system showed that not only termination reactions but also hydrogen transfer reactions involving this species were important. In contrast it was observed that all termination and hydrogen transfer reactions involving radicals of low concentration, such as $\dot{C}HOHCH_2Cl$ and $Cl^{\bullet}$, could be omitted without altering the product pattern.

Various reactions which were initially included in the reaction scheme were subsequently omitted without affecting the product pattern or rate. Thus the reaction involving hydrogen abstraction from the wrong end of the acetaldehyde molecule was eventually omitted.

$$CH_3CHO + X^{\bullet} \longrightarrow \dot{C}H_2CHO + HX$$

Hydrogen abstraction from the CH_3 -group involves the fission of a bond some 12 kcals/mole more endothermic than the alternative - CHO site and would thus be expected to occur far less readily. For similar reasons hydrogen abstraction from the hydroxyl group in ECH was also dropped from the initial scheme:-

$$X^{\bullet} + CH_2ClCH_2OH \longrightarrow CH_2ClCH_2O^{\bullet} + HX.$$

Eventually the mechanism shown in Appendix II A was accepted as the most probable. The molecular decompositions into acetaldehyde is shown in reaction (27) whilst reaction (28) contains the much slower rate of molecular formation of vinyl chloride. The remaining reactions are all radical reactions describing the primary and secondary decompositions and the formation of side-products. The pre-exponential factor for the initiation process (reaction (1)) was selected on the grounds that it gave a sensible rate of initiation when combined with an activation energy close to the energy of the bond undergoing fission. The process of initiation is almost certainly heterogeneous and consequently the high A factor has no chemical significance in the context of a homogeneous molecular decomposition. Termination of the chain was provided for by radical-radical combination (reactions (24), (25), (26)). As mentioned previously only those radicals in the greatest concentration need be considered because the recombination rate parameters are very similar for all species. The only exception to this rule is atom-atom recombination where a third body is required to dissipate the excess energy and prevent re-fragmentation. At low pressures this will considerably reduce the likelihood of atom-atom recombination, however in the present system chlorine atom recombination has already been excluded on concentration grounds but this point is relevant in the case of HBr addition which is discussed later.

Reactions (2)-(13) are all involved with the main chain processes occurring in the decomposition. These have already been discussed in section 6.01.

The formation of side products is shown in reactions (17)-(21). The observed adherence between the methyl chloride and ethylene curves (e.g: figure 4.10) suggested that they might arise from the same process. Investigation of the literature data involving chlorine abstraction from C_2 chlorocarbons by methyl radical (69) showed that reaction (17) could be expected to occur in ECH decomposition. Subsequent elimination of -OH from $CH_2CH_2\dot{O}H$ (reaction (18)) leads to ethylene. Methyl abstraction of hydroxyl would be expected to be slower (reaction (19)) and the resultant amount of methanol would not have been detected under our analysis conditions. However its inclusion does provide an alternative source of ethylene formation which could explain the slight excess of ethylene over methyl chloride which is normally observed. Reaction (21) suggests the most likely mechanism for propylene formation namely methyl attack on vinyl chloride (to form $CH_3 - CHCl - CH_2^{\bullet}$) with rapid elimination of -Cl.

The other reactions in the system are the hydrogen transfer reactions which are considered important. Reaction (14) shows the rapid exchange existing between methyl radical and HCl. This has the important consequence of maintaining the chlorine atom activity in the system in the later stages of decomposition. The reverse of this reaction has also been included (reaction (15)) because it is also known to be very fast and the possibility exists of attaining an equilibrium between $CH_3^{\bullet}$ and $Cl^{\bullet}$ in the system. On the other hand the reverse of reaction (16) is unnecessary as it will occur relatively slowly owing to the endothermicity involved in such a reaction. Finally reactions (22) and (29) involve the two most prominent hydrogen transfer reactions with $CH_2OHCH\dot{C}l$ - the radical species found to build up to the greatest concentration. These are of major importance in the system because along with the termination reactions (25) and (26) they provide the explanation in our scheme of the observed chain selectivity to acetaldehyde.

The fit of the model to the experimental results at 454.9°C and 200 torr initial pressure of ECH is shown in figure 6.02 for the overall decomposition. The fit to the product-time curves is seen in figure 6.03 for the major products and figure 6.04 for the minor products. The agreement between experimental and predicted values is excellent up to 33% decomposition (30 minutes reaction time). Above this point any deviation could well be the result of additional side reactions which have not been included in the scheme. For example propylene is formed in the reaction but no attempt has been made to include the known inhibitory effect of this compound into the reaction scheme.

The model was also run at different temperatures and figures 6.05 and 6.06 show very similar trends for both the experimental and predicted values. Further slight adjustments to some of the Arrhenius parameters would undoubtedly provide a better fit to the observed effects of temperature variation but such refinement was considered unnecessary at this stage.

If one accepts the validity of this model several interesting points emerge from the computed result.

1. As the reaction proceeds and the proportion of acetaldehyde to ECH increases there is no comparable swing from $Cl^{\bullet}$ to $CH_3^{\bullet}$ radicals (reaction (1) compared to reaction (9)). Thus at two minutes the CH_3/Cl ratio is 200/1 whilst after 50 minutes the ratio had actually decreased to 114/1. This decrease which appeared unexpected at first sight was presumably due to the increasing absolute concentration of $CH_3^{\bullet}$ radicals leading to a greater degree of chain termination. The absence of any swing to $CH_3^{\bullet}$ radicals indicates the importance of reaction (14) involving H atom abstraction by $CH_3^{\bullet}$ from HCl.

2. is $7.9 \times 10^4(ECH)(CH_3^{\bullet})$. The ratio of CH_3/Cl as$_{Cl\cdot}$) whereas reaction (11) is $7.9 \times 10^4(ECH)(CH_3^{\bullet})$. The ratio of CH_3/Cl as outlined above in 1

demonstrates that the rate of (2) is at least 250 times faster than the rate of (11) and hence the contribution of $CH_3^\bullet$ toward hydrogen abstraction from ECH is insignificantly small in comparison to that of $Cl^\bullet$. The proportion of chain reaction occurring via $OH^\bullet$propagation (reaction (4)) is substantial initially but falls off as the relative concentration of chlorine atom to hydroxyl increases. This increase is also due to reaction (14) which provides a convenient source of chlorine atoms during the decomposition.

3. The selectivity of the chain decomposition as described previously (5/1 in favour of acetaldehyde formation) can be explained by the relative rates of decomposition of the two types of radical precursor. Thus the rate of formation of these radicals, $\dot{C}HOHCH_2Cl$ and $CH_2OH\dot{C}HCl$ have been considered equal (e.g: reactions (2) and (5)). The subsequent loss of a β-Cl occurs readily and converts $\dot{C}HOHCH_2Cl$ into acetaldehyde (via a keto-enol type transformation). Thus this radical species is maintained in low concentration and side reactions will be negligible. The formation of vinyl chloride by the loss of an hydroxyl group from $CH_2OH\dot{C}HCl$ is more difficult. The concentration of this radical builds up in the system and other reactions such as termination reactions ((25) and (26)) and hydrogen transfer reactions ((22) and (29)) become likely. These side reactions are responsible for the lower selectivity to VC in the chain decomposition.

4. The rate parameters for the formation of side products (reactions (17) to (21)) have all been estimated but are in close accord with similar systems appearing in the literature. For example chlorine atom abstraction from hexachlorethane by methyl radical has been measured (69) and the rate parameters used in reaction (17) are similar. The reasonable agreement between the experimental and predicted product curves shown in figure 6.04 indicate that the postulated mechanism is feasible explanation of the formation of these side products.

One of the most interesting effects on ECH decomposition occurred with the addition of HBr (section 4.08(b)). The great enhancement of CH_4

production suggested the presence of a selective catalysis arising from a bromine propagated chain. The overall catalysis which was observed in the initial stages of the decomposition indicated an additional initiation reaction whilst the production of $CH_3Cl, CH_2{=}CH_2$, and $CH_3{-}CH{=}CH_2$ suggested that the concentration of $CH_3^{\bullet}$ had not been seriously depleted by HBr.

In order to incorporate the effects of HBr into the standard decomposition scheme ten additional reactions were included in the scheme. These are shown in Appendix II B, together with the relevant Arrhenius parameters. It should again be pointed out that the initiation reaction (30) is not chemically significant. Wall initiation seems likely for HBr and furthermore in our reaction the $H^{\bullet}$atom is regarded as being associated with the wall where it might form hydrogen. It does not become involved in the chain ; hence reaction (30) should simply be considered as a means of enhancing initiation.

The fit between experimental and predicted product curves is shown in figure 6.07. It is a feature in reactions involving hydrogen abstraction by bromine for the activation energy to be only slightly (1-2 kcal) greater than the endothermicity of the reaction. At the same time bromine exhibits considerable selectivity in hydrogen abstraction because the H-Br bond is relatively weak (85.5 kcals/mole) and its formation does not therefore provide a high driving force from the thermodynamic standpoint. Thus $\dot{Br}$ will far more readily abstract H from the aldehydic group (-CHO) of bond strength 86.5 kcals/mole than from an alkyl type group of bond energy between 94-97 kcals/mole. Thus reaction (32) occurs far more readily than (33) or (34). Furthermore reaction (31) takes place rapidly to reform $Br^{\bullet}$ and in this manner acetaldehyde is selectively decomposed.

An essential feature of the proposed mechanism is that the addition of HBr should not seriously deplete the concentration of $CH_3^{\bullet}$ (via reaction (31)) because the normal side products were still observed and the proposed mechanism for their formation involves methyl radical attack on ECH or VC. The fit between the experimental and predicted values for major product formation is shown in figure 6.07. Under these conditions the methyl radical concentration is not depleted and the normal side products were still observed. In fact the model predicts higher concentrations of side products than was observed in practice and further modification is required to reduce the $CH_3^\bullet$ concentration.

6.04 Catalysis of the Molecular Decomposition

The addition of Lewis acids to ECH and βTRI increased the rate of decomposition in certain cases. However the evidence indicated that a molecular catalysis was not involved. Thus the rate enhancement observed with boron trichloride on ECH was considerably depressed by the addition of 20% toluene (figure 5.01) and this indicated that the BCl_3 was predominantly enhancing the chain reaction. Furthermore the product pattern was very similar to that obtained with added CCl_4. We may infer from this that BCl_3 supplies additional chlorine atoms to the system thereby aiding chain decomposition. On the other hand the absence of any effect from BCl_3 on either the uninhibited or the inhibited decomposition of βTRI does indicate that BCl_3, unlike CCl_4, requires the presence of ECH or its products in order to promote this activity.

The addition of $SnCl_4$ to βTRI in the presence of toluene led to an enhanced production of the three dichloroethylenes (section 5.02). However various factors point to this enhancement arising from an increase in the chain activity in the presence of $SnCl_4$.

(1) With 10% $SnCl_4$ maximum inhibition is not obtained with 15% toluene addition (figure 5.02) compared to 6% in the absence of $SnCl_4$.

(2) Benzyl chloride was formed in the presence of $SnCl_4$ and toluene. This compound was not found in the normal decomposition but has been observed in the products of a CCl_4 accelerated βTRI decomposition. Again an enhancement in chain activity is indicated. The benzyl radical will

exist in relatively high concentration in the inhibited system and benzyl chloride would most probably be formed by benzyl abstraction of chlorine from $SnCl_4$. This would suggest a readily broken Sn-Cl bond in stannic chloride and the likelihood of this molecule enhancing chain activity.

(3) The additional amounts of dichloroethylenes formed in the presence of 10% $SnCl_4$ indicated a selectivity of 45% toward VDC production. This is equivalent to that usually observed in the chain decomposition (figure 3.08).

(4) As mentioned previously (section 1.02) a typical Lewis acid effect on βTRI would be expected to give preferential formation of 1,2-dichloroethylene as the intermediate complex ($R^{\delta+}$----$(Cl$--$SnCl_4)^{\delta-}$) would form more readily at the more electronegative dichloro centre. Consequently the formation of 45% VDC is unexpectedly high if $SnCl_4$ were acting in the character of a Lewis acid.

The above factors suggest strongly that the effect of $SnCl_4$ on the inhibited βTRI decomposition also involves an acceleration of the radical chain processes.

One may conclude therefore that the Lewis acid effects which existed in heterogeneous and liquid phase systems are unimportant in a homogeneous gas phase system.

Similarly the effects of Lewis base additions were very small in comparison to the results obtained in the liquid phase. The reaction rate observed with a variety of base systems was only marginally greater than the rate of the inhibited reaction itself. Furthermore the molar amount of excess product formed in the typical five minute decomposition reaction never exceeded the molar amount of base added to the system. Therefore it was impossible to determine on these grounds whether the excess reaction arose from a catalytic effect or a stoichiometric reaction. A further complication was the apparent decomposition of a number of the bases studied.

The reactions of inhibited βTRI with amines have been studied in greater detail to ensure that in the first instance the absence of any large effect is not due to other factors such as amine removal from the system; and secondly to determine if the observed product enhancement arose from a truly homogeneous molecular reaction. The important features arising from this study were:-

1. The amine hydrochloride (n-butylamine hydrochloride) was shown to be reasonably stable up to temperatures of 330°C. Thus the equilibrium:-

$$R.NH_2 + HCl \rightleftharpoons RNH_2.HCl$$

   below 330°C lies far to the right. However reactions with βTRI at temperatures at 223.5° and 300.6°C gave negligible conversions indicating the absence of a strong stoichiometric extraction of HCl by n-butylamine under these conditions. This underlines the considerable difference between the gas phase and the liquid phase reaction involving βTRI and amines.

2. At temperatures of 453.5°C the absence of any effect of packing indicated that the production of excess dichloroethylene in the presence of triethylamine was not occurring at the surface of the reactor.

3. The rate of production of excess VDC at 453.5°C decreased with time as would be expected from the observed decrease in triethylamine concentration which arose from decomposition of the base. However excess VDC was still being formed under conditions where all the amine would have disappeared from the system if a stable amine hydrochloride had been formed with the product HCl. On the other hand the assumption of complete dissociation of the amine hydrochloride into free amine and HCl gave good agreement between the excess VDC production and the decreasing amine concentration. The inference is that the reaction is truly catalytic and does not involve stoichiometric production of an amine hydrochloride.

The above factors indicate that, although there is a severe reduction in the ease of HCl abstraction by amines in passing from the liquid phase into the gas phase, the small effect observed does arise from a homogeneous catalysis. What is as yet unresolved is whether the catalysis is occurring via a molecular reaction or alternatively whether the decomposition of the amine has given rise to a chain catalysis. Although the decomposition of t-butylamine (60) was originally described as being of a molecular nature, Benson has recently criticized the conclusion (81) and indicated the likelihood of a radical chain decomposition. In the present investigation it is also felt that the decomposition of amines occurs via a chain mechanism which is catalysed by βTRI. Additional studies have established that:-

(a) The amine does not decompose significantly in the absence of βTRI

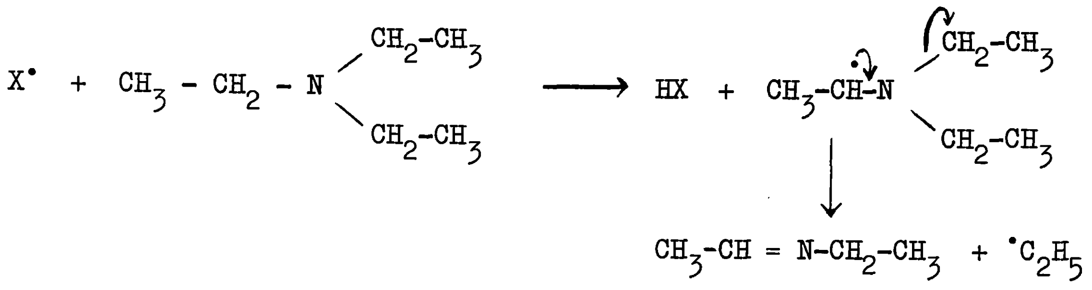
(b) The decomposition of the amine is enhanced considerably in the presence of CCl_4

(c) The presence of toluene reduces but does not eliminate the decomposition of the amine in the presence of CCl_4 or βTRI

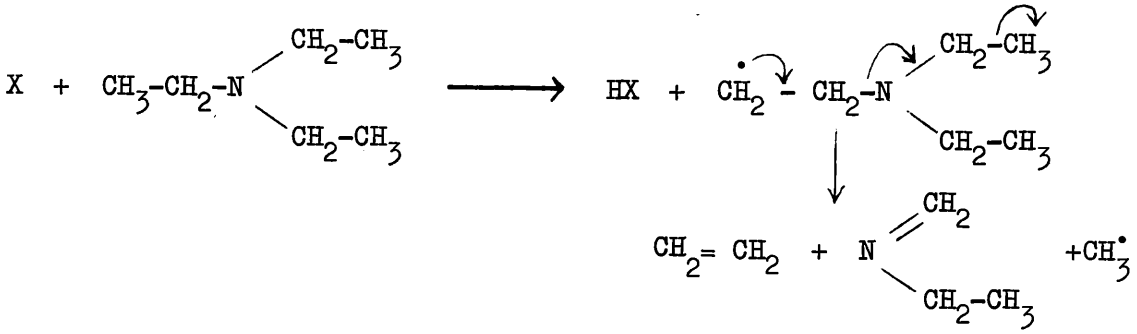
(d) Ethane is a major product arising from the decomposition and methane and ethylene are also formed in reduced amounts.

Literature data (69) reveals that the C-H bond in an α position to the nitrogen atom in an amine is relatively weak. Thus $CH_3^{\bullet}$ abstracts hydrogen from triethylamine with a reported activation energy of 5.3 kcals/mole which is low compared to other alkyl group substrates. It seems likely that the slow decomposition of the pure amine is due to a slow initiation reaction but that in the presence of a suitable initiator (e.g: CCl_4 or βTRI) a chain decomposition occurs which is difficult to suppress with normal inhibitors. In this respect the amine decomposition is similar to the decomposition of ECH which was also found difficult to inhibit. A suitable scheme for the decomposition which also gives rise to the observed products is as follows:-

(1)



(2)



$X^\bullet$ could be $Cl^\bullet$ arising from the initiator (CCl_4 or βTRI) or $CH_3^\bullet$ from scheme (2) or $C_2H_5^\bullet$ from scheme (1). The latter two continue the chain giving rise to CH_4 and C_2H_6. Reaction (1) will be the preferred abstraction process leading to ethane whereas methane and ethylene are formed from reaction (2). Further abstraction of hydrogen from the primary products is to be expected and the final likely products involve the formation of 3 or 4 moles of product from each mole of amine - in good agreement with the observed stoichiometry ofl mole going to 3.3 moles (section 5.06(a)). Furthermore the secondary decomposition of the imine product explains the observed continuation of the pressure change after the cessation of the VDC catalysis (section 5.06(b)).

Thus a radical chain process provides a satisfactory explanation for all the observed features of the amine decomposition reaction and one must consider whether the existence of the radical components of this chain mechanism have caused the observed catalysis of HCl elimination from βTRI. Figure 5.11 indicated a very high selectivity of VDC formation ($\sim$75%) in the catalyzed reaction arising from triethylamine addition. The amine decomposition reaction produces alkyl radicals which are relatively unselective in their modes of hydrogen abstraction whereas the observed selectivity of ~75% is greater than that obtained in the presence of highly selective species such as bromine atoms. On the other hand molecular catalysis by the amine would be expected to produce high selectivity toward VDC production and on these grounds it may be reasonably assumed that the catalysis observed in the presence of amine is stemming from a molecular reaction.

The main point arising from the work on Lewis acids and bases is the clear distinction between the gas phase and liquid phase in terms of reactivity. It must be concluded that this difference is dependent on the ability of the condensed phase to reduce the energy of the partially polarized transition state by solvation. Thus the transition state in the amine catalysed removal of HCl from βTRI may be represented as

$$(R_3N\ \text{--}\ H)^{\delta+}\ \text{--}\ \overset{\delta-}{CCl_2}\ \text{——}\ CH_2Cl$$

that is, an intermediate state in which the H-C bond at the dichloro centre has been partially broken and the N-H bond partially formed with a subsequent separation of charge. In the liquid phase the solvating action of the medium reduces the energy required to attain this partially polarized transition state and consequently the abstraction of HCl occurs far more readily than in the gas phase where such solvation is impossible.

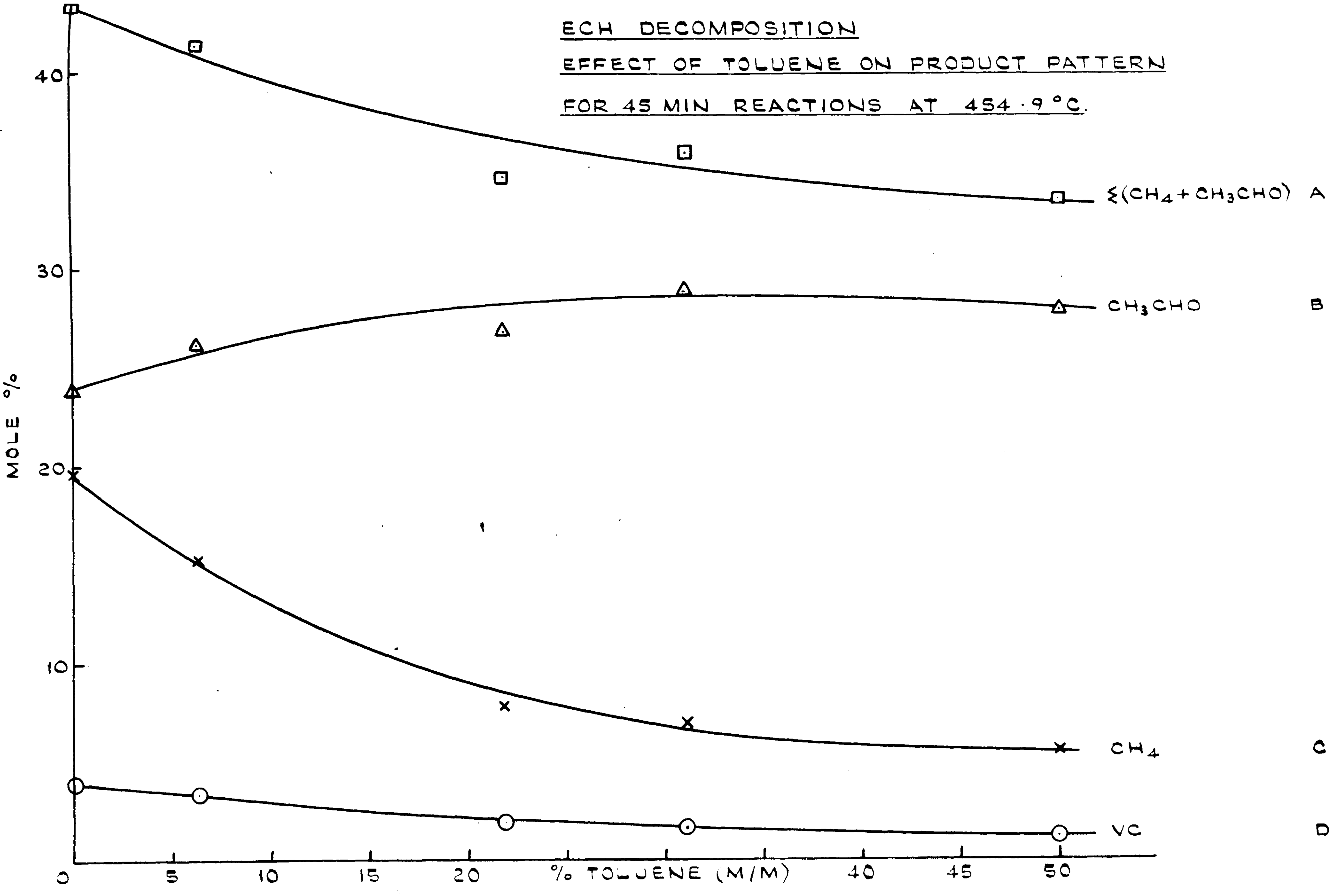
A similar argument applies to the intermediate transition state expected in the catalysis by Lewis acids. Thus the partially polarized intermediate, which may be denoted by $R^{\delta+}\text{--}(Cl\ \text{--}\ MCl_n)^{\delta-}$ for a Lewis acid MCl_n and a chlorocarbon substrate, RCl, will be stabilized by solvation in the liquid phase but not in the gas phase. Thus although previously published work has emphasized the importance of the C-Cl bond fission in the gas phase molecular elimination of HCl from alkyl chlorides (28,29) we have found no evidence to indicate that this bond break can be enhanced by the addition of Lewis acids.

TABLE 6.01 ECH DECOMPOSITION AT 454.9°C - 10 MIN.REACTIONS WITH p_o = 200 torr. THE SELECTIVITY OF THE OVERALL REACTION AND THE RADICAL REACTION IN THE PRESENCE OF VARIOUS ADDITIVES

EXPT.	REACTION	FIGURE NO.	MAJOR PRODUCTS (MOLE % OF P_o)			* DE-HCl	+ DE-HCl / DE-H_2O
			VC	CH_3CHO	CH_4		
A	ECH alone	4.01	0.66	10.0	0.80	10.8	16
B	ECH + 50% TOLUENE	4.15	0.24	8.3	0.30	8.6	36
C	ECH + 1.5% CCl_4	4.21(a)	4.20	14.6	9.50	24.1	5.7
D	ECH + 50% HCl	4.22(a)	2.05	13.3	2.75	16.05	7.8
E	ECH + 2.2% HBr	4.23(a)	2.80	7.7	20.10	27.8	10.0
F	EXPT.A - EXPT. B.	-	0.42	1.7	0.5	2.2	5.2
G	" C - " B	-	3.96	6.3	9.2	15.5	3.9
H	" D - " B	-	1.81	5.0	2.45	7.45	4.1
I	" E - " B	-	2.56	-0.6	19.8	19.2	7.5
J	CALCULATED MOLECULAR COMPONENT	-	0	7.3	0	7.3	-

* DE-HCl The figures in this column indicate the total amount of dehydrochlorination occurring i.e: ($CH_3CHO+CH_4$)

+ $\frac{\text{DE-HCl}}{\text{DE-}H_2O}$ The ratio of dehydrochlorination to dehydration is given by $\frac{(CH_3CHO + CH_4)}{VC}$



ECH DECOMPOSITION

EFFECT OF TOLUENE ON PRODUCT PATTERN

FOR 45 MIN REACTIONS AT 454·9 °C.

FIGURE 6·01

FIGURE 6.02

MATHEMATICAL MODEL

THE % DECOMPOSITION OF ECH AT 454·9 °C [po=200 torr]

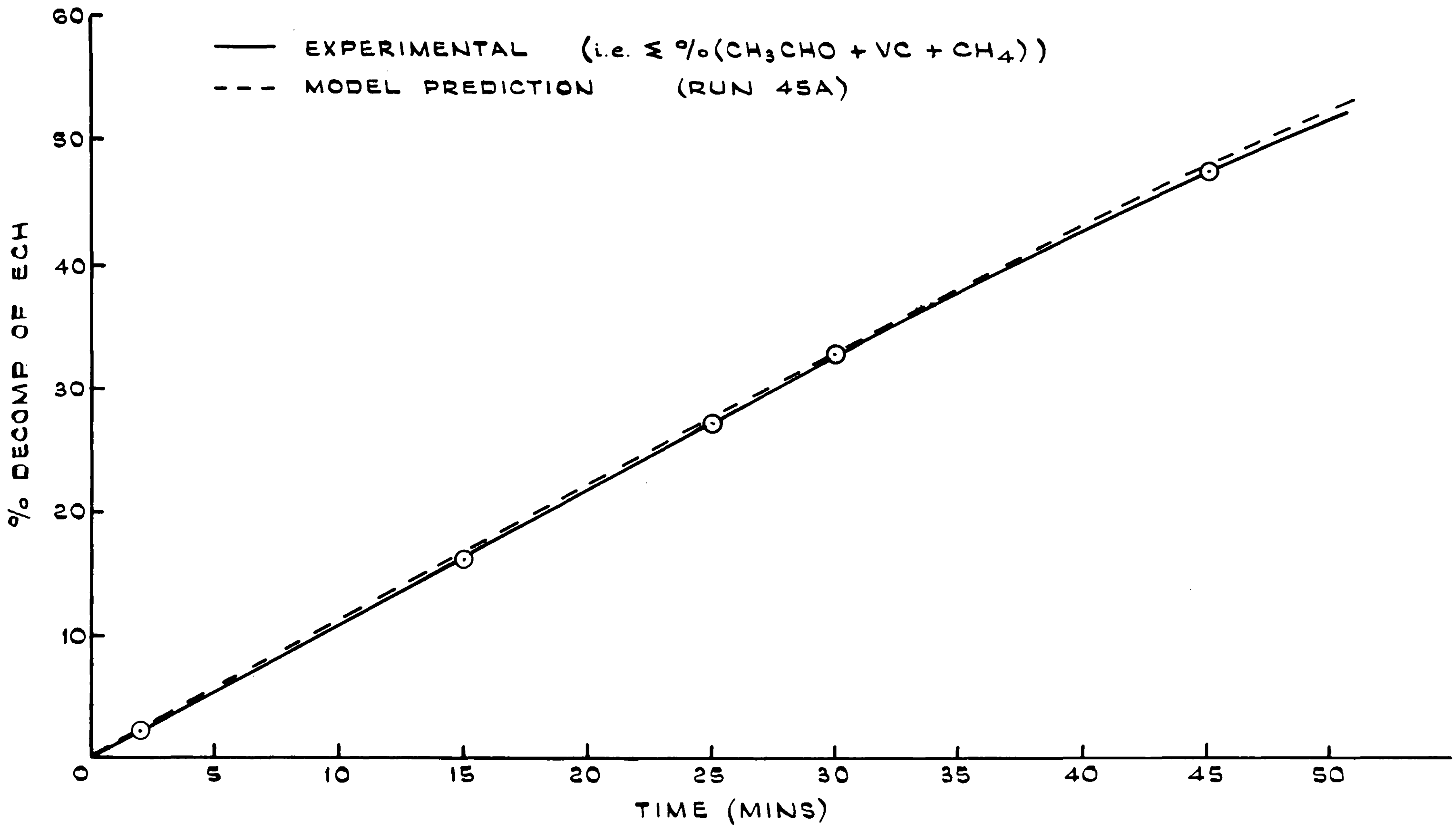


FIGURE 6·03

MATHEMATICAL MODEL - ECH DECOMPOSITION AT 454·9 °C. [Po = 200 torr]

FORMATION OF MAJOR PRODUCTS WITH TIME.

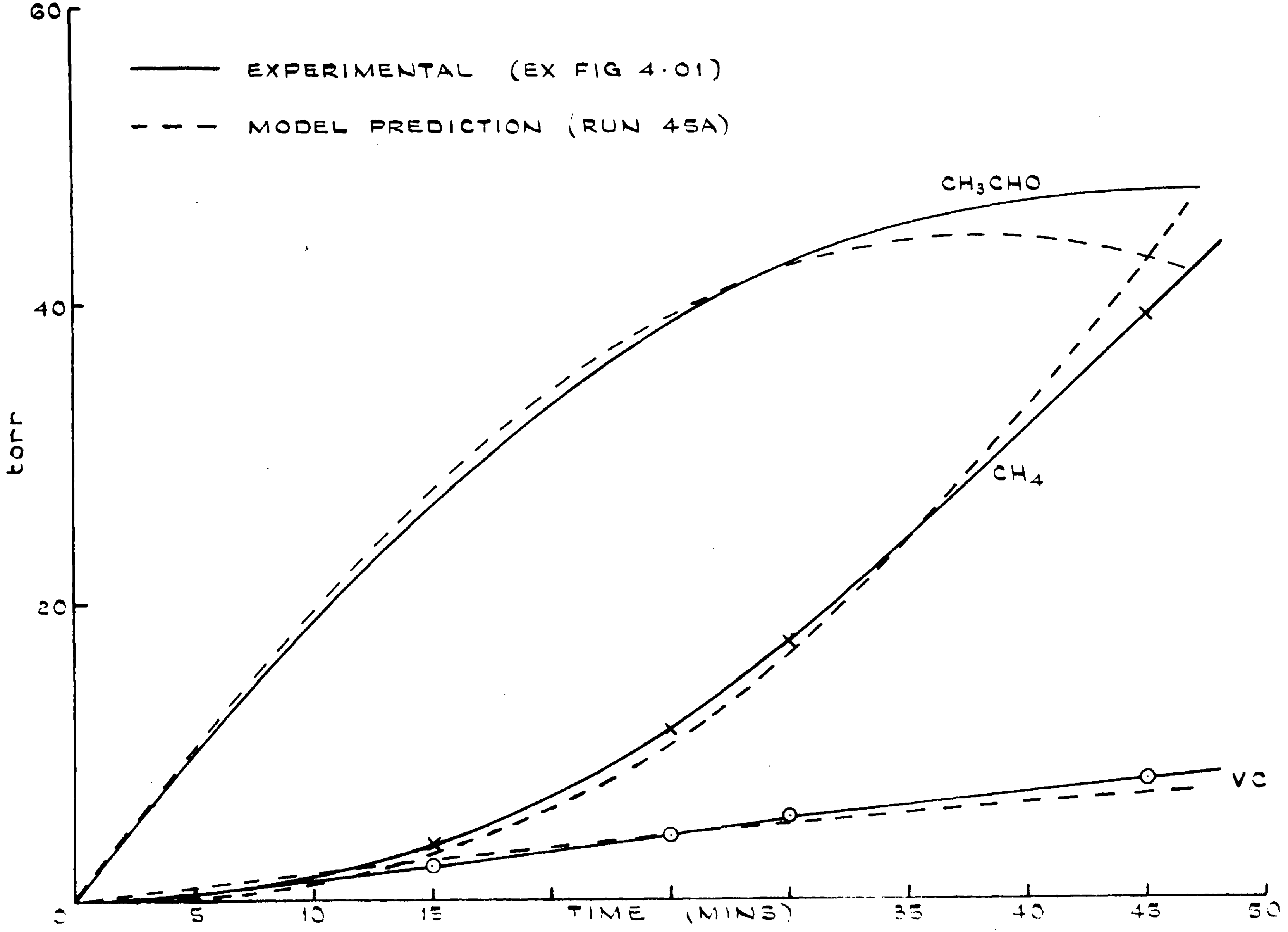


FIGURE 6·04

MATHEMATICAL MODEL - ECH DECOMPOSITION AT 454·9°C. [po = 200 torr]

FORMATION OF MINOR PRODUCTS WITH TIME

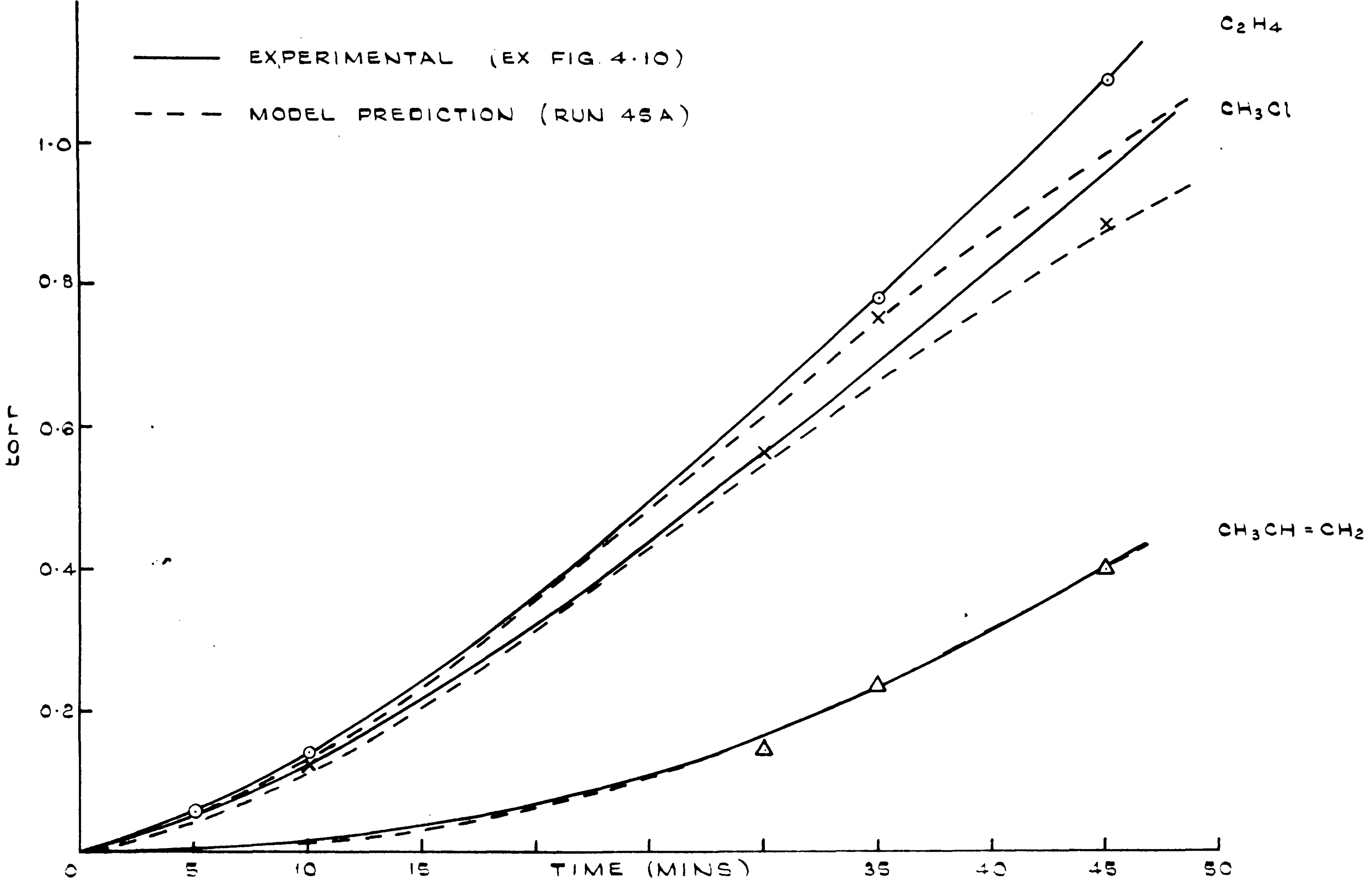
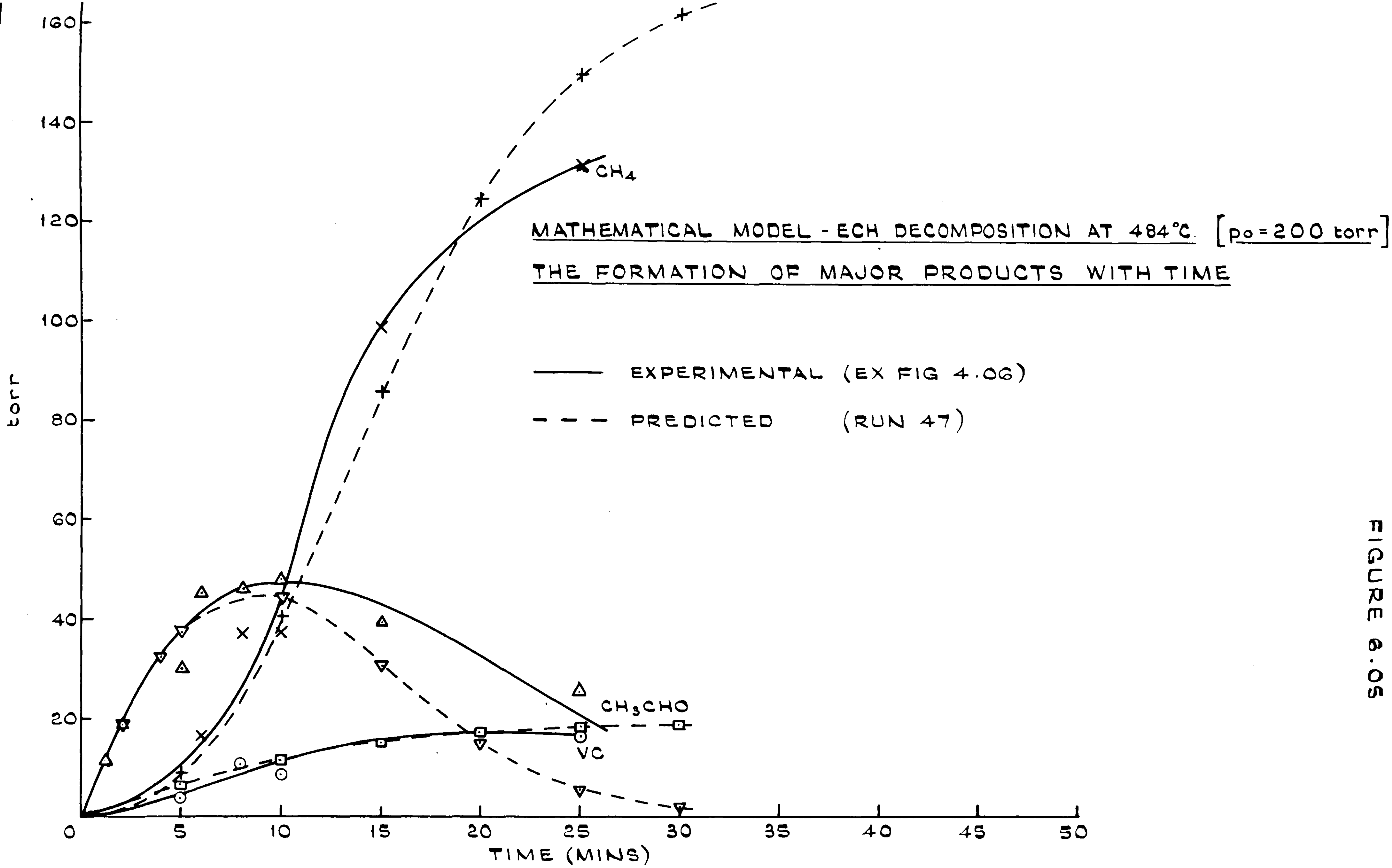


FIGURE 6.05



MATHEMATICAL MODEL - ECH DECOMPOSITION AT 484°C [po = 200 torr]

THE FORMATION OF MAJOR PRODUCTS WITH TIME

MATHEMATICAL MODEL - ECH DECOMPOSITION AT 439·5°C [Po = 200 torr]

FORMATION OF MAJOR ORGANIC PRODUCTS WITH TIME

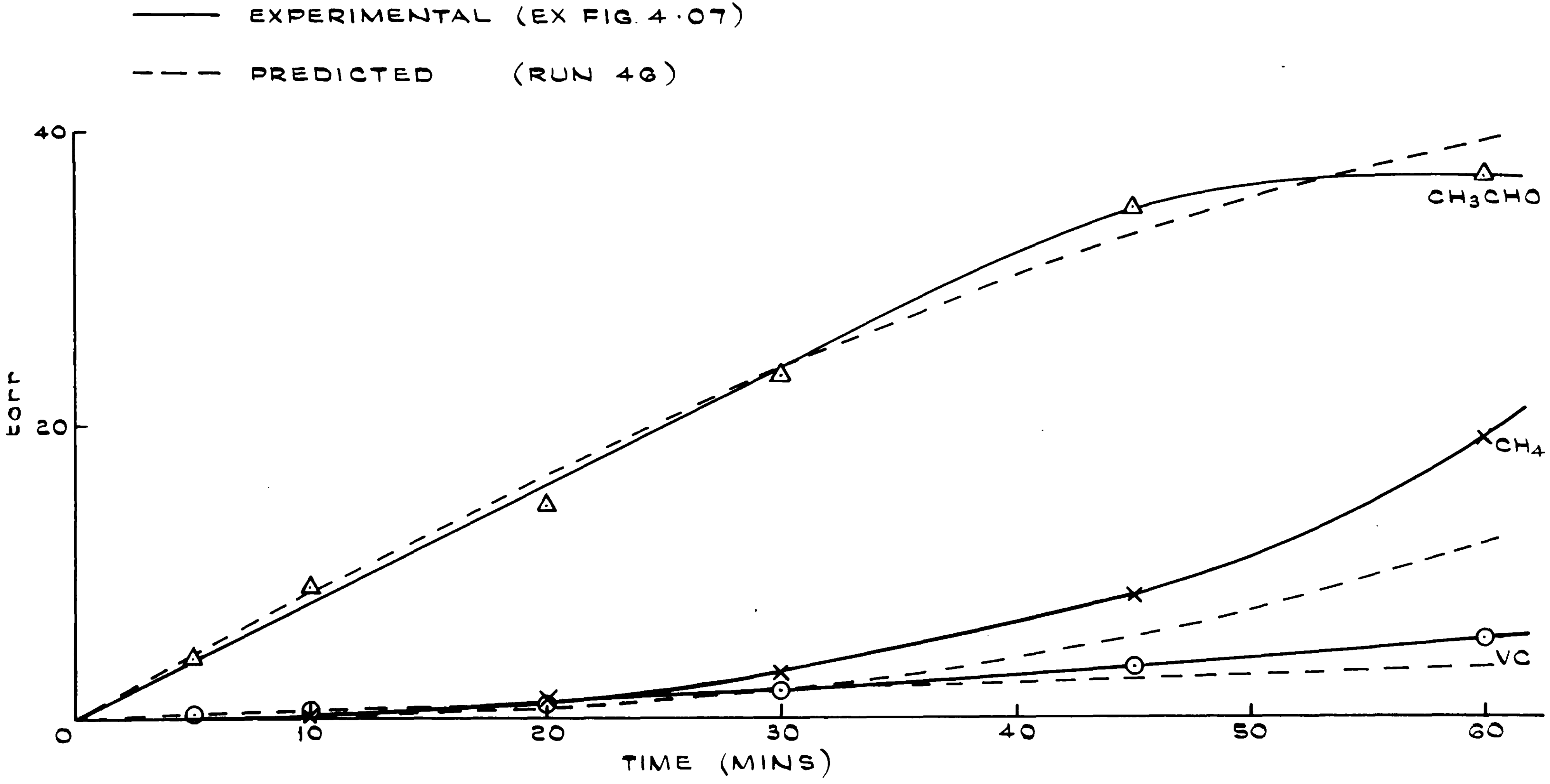


FIGURE 6.06

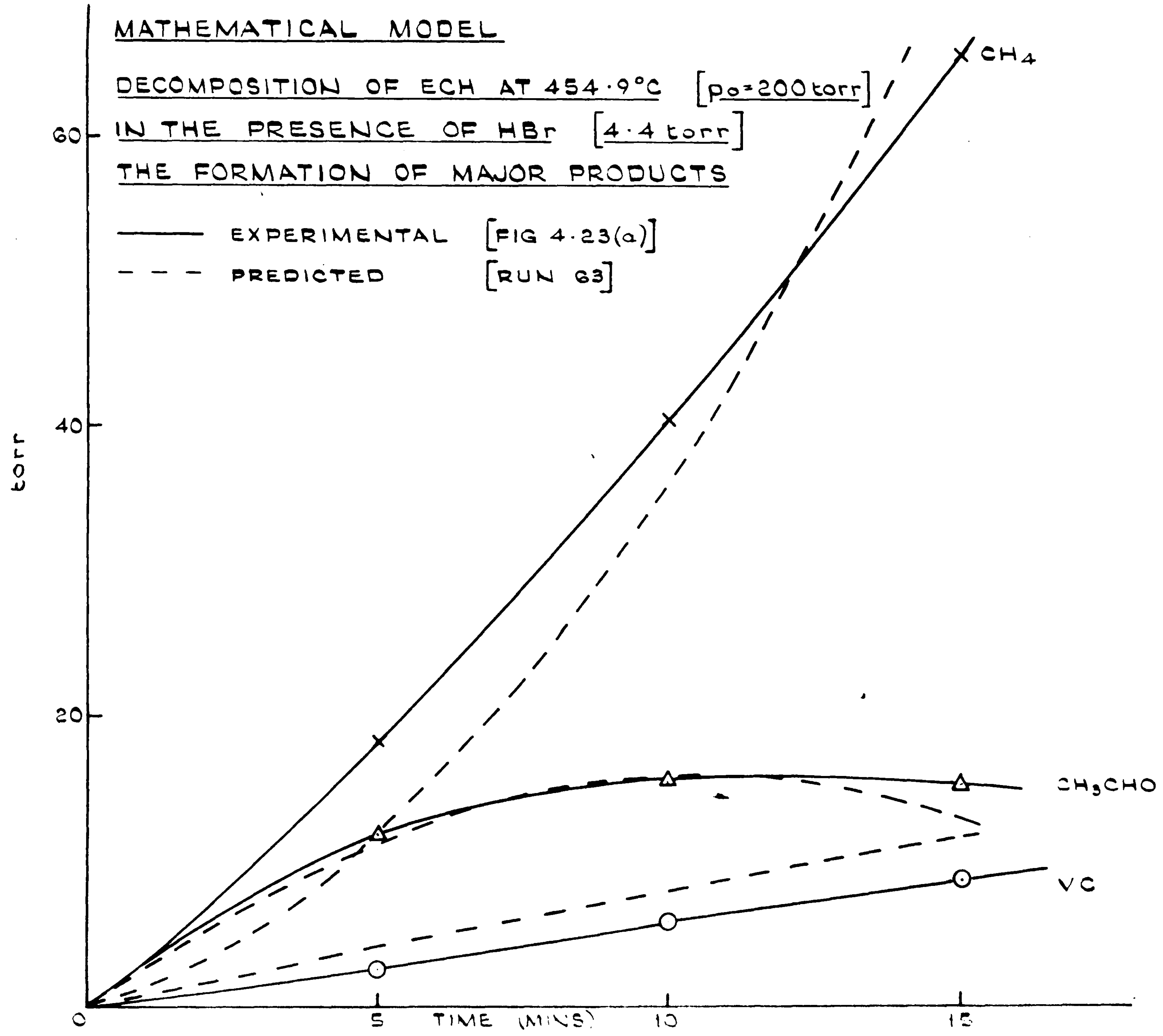

MATHEMATICAL MODEL
DECOMPOSITION OF ECH AT 454·9°C [Po=200 torr]
IN THE PRESENCE OF HBr [4·4 torr]
THE FORMATION OF MAJOR PRODUCTS
EXPERIMENTAL [FIG 4·23(a)]
PREDICTED [RUN 63]
CH4
CH3CHO
VC
torr
60
40
20
0
5
10
15
TIME (MINS)

FIGURE 6·07

CHAPTER 7

CONCLUSIONS

The thermal dehydrochlorination of βTRI at 391.5°C in an all-glass, static reactor system occurs predominantly by a radical chain process and is accelerated by HCl, one of the products of the decomposition. The irreproducible rate obtained in this and in other studies is attributed to an extreme sensitivity of the initiation and termination steps to the condition of the reactor surface. Owing to this irreproducibility in rate a detailed kinetic investigation of the decomposition was not undertaken but in the region of 80-370 torr second order kinetics were observed for the initial rate. Comparison with similar systems suggests that this probably arises from a wall termination reaction involving a chlorine atom.

The homogeneous nature of the propagation steps is demonstrated by the invariability of the product distribution (45.3% VDC) under reaction conditions which included additions of chain accelerators and variations in surface to volume ratio and in initial pressure. The effects of temperature and selective chain transfer agents on the product distribution have demonstrated that the formation of VDC by a radical chain process is energetically more favourable than the formation of the 1,2-dichloroethylene isomers but the calculated energy difference is small and no set of reaction conditions have been found which gave a selectivity to VDC of >60%.

In the presence of chain inhibitors the evidence indicates the existence of a molecular reaction which favours the production of 1,2-dichloroethylene. However even in the region of maximum inhibition the radical process is not completely suppressed and a small amount of chain reaction is still occurring through the inhibitor radical (e.g: benzyl or allyl).

The thermal decomposition of ECH at 454.9°C also occurs both by a radical chain and a molecular process. Both processes favour dehydrochlorination rather than dehydration. The molecular process, which was responsible for 75% of the total decomposition of ECH on its own at 454.9°C, exhibited a selectivity of 25/1 in favour of acetaldehyde over vinyl chloride. The slow suppression of the radical chain decomposition by inhibitor in this system as compared to the βTRI decomposition arises from the shorter chain length involved in the ECH decomposition and the presence of a relatively weak C-H bond (from the -CHO group in acetaldehyde). This acts as an effective competitor to the inhibition process and is able to sustain the chain reaction through decomposition of the acetyl radical.

The selectivity of the chain process was 4/1 in favour of acetaldehyde. The mathematical model has demonstrated that this selectivity is explicable in terms of the relative rates of decomposition of the radical precursors of acetaldehyde and vinyl chloride (i.e: $\dot{\mathrm{C}}\mathrm{HOHCH_2Cl}$ and $\mathrm{CH_2OH\dot{C}HCl}$). In addition the formation of methyl chloride and ethylene is satisfactorily explained by a methyl radical abstracting a chlorine atom from ECH which loses a β-OH radical to form ethylene.

$$\mathrm{CH_3^{\bullet} + CH_2OHCH_2Cl \longrightarrow CH_3Cl + CH_2OHCH_2^{\bullet}}$$
$$\mathrm{CH_2OHCH_2^{\bullet} \longrightarrow CH_2{=}CH_2 + OH^{\bullet}}$$

Also propylene arises from the methyl radical addition to vinyl chloride with β-Cl elimination

$$\mathrm{CH_3^{\bullet} + CHCl = CH_2 \longrightarrow CH_3 - CHCl - CH_2^{\bullet}}$$
$$\mathrm{CH_3\text{-}CHCl\text{-}CH_2^{\bullet} \longrightarrow CH_3\text{-}CH{=}CH_2 + Cl^{\bullet}}$$

In the decomposition of ECH in the presence of HBr the selectivity of the bromine atom in hydrogen abstraction is responsible for the enhanced production of methane from the secondary decomposition of acetaldehyde.

The investigation into the area of molecular catalysis of thermal decompositions has demonstrated the absence of any large effects. Rate enhancements observed with typical Lewis acids such as $\mathrm{BCl_3}$ on ECH and $\mathrm{SnCl_4}$ on βTRI involved accelerations of the chain reaction rather than the molecular decomposition. The small effect obtained with amines on βTRI arises from a homogeneous catalytic cycle rather than a stoichiometric reaction. Furthermore the high selectivity to VDC is consistent with a molecular rather than a chain process. The investigation highlights the large reactivity difference between the gas phase and liquid phase reaction of amines and βTRI. The higher reactivity observed in the liquid systems demonstrates the importance of solvation in stabilizing the partially polarized transition state expected in these systems.

APPENDIX I

Computerization of First Order Log Plots

In section 2.05 it was pointed out that the amplified output from the pressure gauge attached to the reactor could be fed directly to a recorder to provide a visual trace of the pressure-time curve. Simultaneously the output could be registered on an Argus 300 computer which was programmed to convert the value so obtained into logarithmic values of the resultant concentration thereby eliminating the need for tedious calculation of first order log plots. An interrupt line at the apparatus site enabled direct stop/start control of the computation.

After the paper tape programme had been fed into the computer the desired time interval between pressure readings was manually inserted via the keyboard. Then the ON switch of the interrupt line was depressed and the baseline was tracked for about a minute. After depressing the OFF switch the operator introduced the reactant into the reactor by the method described in section 2.06. The operator then depressed the ON switch again and the output readings from the pressure gauge were recorded at the specified time intervals. This process continued until the STOP switch was depressed after which another reaction could be immediately performed if the same time interval were required or alternatively the time interval could be manually changed. A typical print out is shown in table A.01 for 1,1-dichloroethane which is believed to be a first order reaction. The run number is followed by a value for the base pressure (p_b) as determined from the initial tracking. It should be observed that all the pressure values are recorded in mV and are an amplification (x 100) of the voltage across the recorder. Conversion to true pressure readings (in torr) could be achieved with a suitable calibration factor but this is unnecessary for the first order log plot calculation and the evaluation of the true initial pressure was derived from the recorder trace.

The first reading after the introduction of the reactant gave the initial "pressure" (p_o) for use in the log plot calculation. The absolute value registered by the computer was equivalent to (p_o) + (p_b) but the programme automatically subtracts (p_b) from the value and prints out the value of (p_o) against a time (t) = 0. The subsequent values of (p_t) were all obtained in a similar manner to give the values listed in the second column. The time of reaction is listed in the first column.

In a constant volume system where 1 mole of reactant forms 2 moles of product then the increase in pressure at time t (i.e: $p_t - p_o$) is a direct measure of the amount of reactant which has disappeared. Thus if (A_t) represents the concentration of reactant at time t then $(A_t) = p_o - (p_t - p_o) = 2p_o - p_t$ and

$$\frac{(A_t)}{(A_o)} = \frac{2p_o - p_t}{p_o}$$

The computer programme evaluated the logarithm of this function (multiplied by 100 to maintain a positive value) for each value of p_t. This is shown in the third column of table A.01. A paper tape output of the log values and the time of reaction enabled automatic log plotting of the results. The log plot derived from these results is shown in figure A.01.

The linearity of this plot shows the first order nature of the reaction and the rate constant is derived from the gradient of the plot multiplied by 2.303. The final column of the computer print out indicates the % decomposition of the reactant.

TABLE A.01 ON-LINE COMPUTER PRINT OUT FROM THE DECOMPOSITION OF 1,1-DICHLOROETHANE AT 453.5°C

RUN NUMBER 16

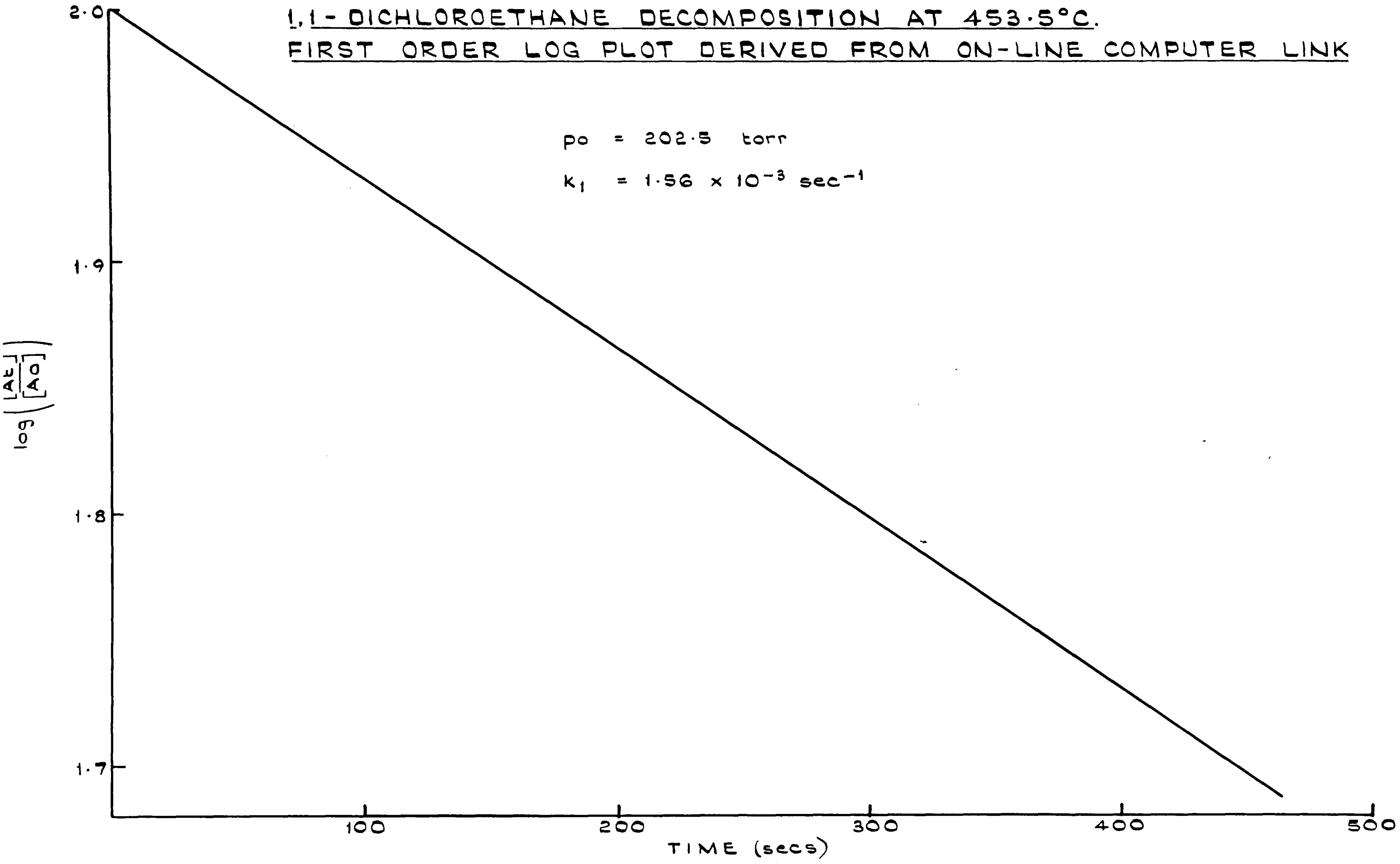
BASE PRESSURE IS 364.0

t (secs)	p_t	$\log_{10}\left(100\left(\frac{(A_t)}{(A_o)}\right)\right)$	% DECOMPOSITION $\left(= 100\left(\frac{A_o - A_t}{A_o}\right)\right)$
0	4049.5	2.0	0
20	4168.1	1.9871	2.93
40	4285.3	1.9739	5.82
60	4403.7	1.9602	8.75
80	4519.4	1.9464	11.60
100	4632.9	1.9324	14.41
120	4736.7	1.9192	16.97
140	4840.0	1.9057	19.52
160	4938.2	1.8924	21.95
180	5033.4	1.8791	24.30
200	5129.1	1.8653	26.66
220	5219.4	1.8519	28.89
240	5307.4	1.8384	31.06
260	5395.7	1.8245	33.24
280	5480.0	1.8107	35.32
300	5557.4	1.7977	37.24
320	5639.0	1.7835	39.25
340	5711.9	1.7704	41.05
360	5785.4	1.7569	42.87
380	5856.2	1.7434	44.62
400	5922.3	1.7304	46.25
420	5993.1	1.7160	48.00
440	6052.7	1.7036	49.47
460	6116.2	1.6899	51.03

FINISHED

FIGURE A·01

1,1-DICHLOROETHANE DECOMPOSITION AT 453·5°C.
FIRST ORDER LOG PLOT DERIVED FROM ON-LINE COMPUTER LINK


$p_o = 202{\cdot}5$ torr

$k_1 = 1{\cdot}56 \times 10^{-3}$ sec^{-1}

APPENDIX II

KINETIC MODEL OF THE DECOMPOSITION OF ETHYLENE CHLOROHYDRIN

A The Decomposition of ECH in the Absence of Catalysts.

NO.	REACTION	log A*	E+	REF
(1)	$CH_2OHCH_2Cl \longrightarrow \dot{C}H_2CH_2OH + Cl^{\bullet}$	16.0	79.9	
(2)	$Cl^{\bullet} + CH_2OHCH_2Cl \longrightarrow \dot{C}HOHCH_2Cl + HCl$	10.5	3.0	
(3)	$\dot{C}HOHCH_2Cl \longrightarrow CH_3CHO + Cl^{\bullet}$	13.5	24.0	
(4)	$OH^{\bullet} + CH_2OHCH_2Cl \longrightarrow \dot{C}HOHCH_2Cl + H_2O$	11.0	7.0	
(5)	$Cl^{\bullet} + CH_2OHCH_2Cl \longrightarrow CH_2OH\dot{C}HCl + HCl$	10.5	3.0	
(6)	$CH_2OH\dot{C}HCl \longrightarrow CH_2{=}CHCl + OH^{\bullet}$	13.5	35.0	
(7)	$OH^{\bullet} + CH_2OHCH_2Cl \longrightarrow CH_2OH\dot{C}HCl + H_2O$	11.0	7.0	
(8)	$Cl^{\bullet} + CH_3CHO \longrightarrow CH_3CO^{\bullet} + HCl$	11.0	2.0	
(9)	$CH_3CO^{\bullet} \longrightarrow CH_3^{\bullet} + CO$	10.3	15.0	
(10)	$OH^{\bullet} + CH_3CHO \longrightarrow CH_3CO^{\bullet} + H_2O$	10.5	4.0	69.
(11)	$CH_3^{\bullet} + CH_2OHCH_2Cl \longrightarrow \dot{C}HOHCH_2Cl + CH_4$	8.5	12.0	
(12)	$CH_3^{\bullet} + CH_2OHCH_2Cl \longrightarrow CH_2OH\dot{C}HCl + CH_4$	8.5	12.0	
(13)	$CH_3^{\bullet} + CH_3CHO \longrightarrow CH_3CO^{\bullet} + CH_4$	8.9	7.6	78.

* Units of A are 1 $mole^{-1}sec^{-1}$ for bimolecular and sec^{-1} for unimolecular

\+ Units of E are kcals/mole

NO	REACTION	$\log_{10}A$	E	REF
(14)	$CH_3^\bullet + HCl \longrightarrow CH_4 + Cl^\bullet$	8.71	2.33	(a) 79
(15)	$Cl^\bullet + CH_4 \longrightarrow HCl + CH_3^\bullet$	10.42	3.85	79
(16)	$OH^\bullet + CH_4 \longrightarrow H_2O + CH_3^\bullet$	11.4	8.0	69
(17)	$CH_3^\bullet + CH_2OHCH_2Cl \longrightarrow CH_2OHCH_2^\bullet + CH_3Cl$	8.9	10.0	
(18)	$CH_2OHCH_2^\bullet \longrightarrow CH_2{=}CH_2 + OH^\bullet$	13.5	34.0	
(19)	$CH_3^\bullet + CH_2OHCH_2Cl \longrightarrow \dot{C}H_2CH_2Cl + CH_3OH$	7.7	9.0	
(20)	$\dot{C}H_2CH_2Cl \longrightarrow CH_2{=}CH_2 + Cl^\bullet$	13.9	23.6	80
(21)	$CH_3^\bullet + CH_2{=}CHCl \longrightarrow CH_3CH{=}CH_2 + Cl^\bullet$	9.0	6.5	
(22)	$HCl + CH_2OH\dot{C}HCl \longrightarrow CH_2OHCH_2Cl + Cl^\bullet$	9.5	10.3	
(24)	$CH_3^\bullet + CH_3^\bullet \longrightarrow C_2H_6$	10.3	0.0	72
(25)	$CH_2OH\dot{C}HCl + CH_3^\bullet \longrightarrow CH_2OHCHClCH_3$	10.3	0.0	
(26)	$CH_2OH\dot{C}HCl + CH_2OH\dot{C}HCl \longrightarrow (CH_2OHCHCl)_2$	9.9	0.0	
(27)	$CH_2OHCH_2Cl \longrightarrow CH_3CHO + HCl + U.DEHX^*$	13.21	56.8	
(28)	$CH_2OHCH_2Cl \longrightarrow CH_2{=}CHCl + H_2O + U.DEH_2O^*$	13.14	67.1	
(29)	$CH_2OH\dot{C}HCl + CH_2OHCH_2Cl \longrightarrow CH_2OHCH_2Cl + \dot{C}HOHCH_2Cl$	8.5	12.0	

* U.DEHX is included in (27) to give a measure of the amount of dehydrochlorination occurring by a unimolecular process.

U.DEH_2O is similarly included in reaction (28) as a measure of unimolecular dehydration.

B The Effect of HBr on the Decomposition of ECH

Additional Reactions to be Included with Part A

NO	REACTION	$\log_{10} A$	E	REF
(30)	$HBr \xrightarrow{\text{wall}} H(\text{wall}) + Br^{\bullet}$	17.5	74.0	
(31)	$CH_3^{\bullet} + HBr \longrightarrow CH_4 + Br^{\bullet}$	8.5	1.43	(a)64
(32)	$Br^{\bullet} + CH_3CHO \longrightarrow CH_3\dot{C}O + HBr$	11.0	4.0	
(33)	$Br^{\bullet} + CH_2OHCH_2Cl \longrightarrow \dot{C}HOHCH_2Cl + HBr$	10.8	12.0	
(34)	$Br^{\bullet} + CH_2OHCH_2Cl \longrightarrow CH_2OH\dot{C}HCl + HBr$	10.8	12.0	
(35)	$Cl^{\bullet} + HBr \longrightarrow HCl + Br^{\bullet}$	10.5	1.0	
(36)	$OH^{\bullet} + HBr \longrightarrow H_2O + Br^{\bullet}$	10.5	1.0	
(37)	$CH_3^{\bullet} + Br^{\bullet} \longrightarrow CH_3Br$	10.3	0.0	
(38)	$Br^{\bullet} + CH_2OH\dot{C}HCl \longrightarrow CH_2OHCHClBr$	10.3	0.0	
(39)	$CH_2OH\dot{C}HCl + HBr \longrightarrow CH_2ClCH_2OH + Br^{\bullet}$	9.0	6.0	

(a) Calculated from the reverse reaction, which was obtained from the indicated reference, together with the thermodynamic quantities derived from reference (74).

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