THE KINETICS AND MECHANISMS OF THE
THERMAL DECOMPOSITIONS OF CARBAMATES
IN THE GAS-PHASE

by

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I certify that all sources used and
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ABSTRACT

The chemistry of carbamates in the gas-phase has been investigated and two types of reactions are seen. The thermal decompositions of ethyl N-methyl-N-phenylcarbamate, ethyl N,N-dimethylcarbamate, isopropyl N,N-dimethylcarbamate, and *tert*-butyl N,N-dimethylcarbamate proceed exclusively according to the reaction

$$\text{Carbamate} \longrightarrow \text{amine} + \text{carbon dioxide} + \text{alkene}$$
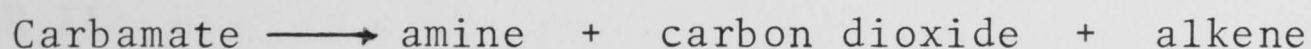
The decomposition of ethyl N-methylcarbamate proceeds by means of competing reactions: one reaction produces amine, carbon dioxide, and alkene, the other, the minor reaction, produces isocyanate and alcohol.

$$\text{MeNHCOOEt} \longrightarrow \begin{cases} \text{MeNH}_2 + \text{CO}_2 + \text{C}_2\text{H}_4 \\ \text{MeNCO} + \text{EtOH} \end{cases}$$
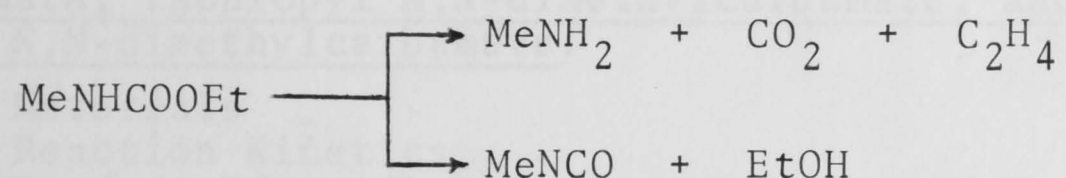
The olefin-forming reaction does not occur if the alkyl portion of the ester has no β-hydrogen atoms. Thus the decomposition of methyl N-methylcarbamate leads exclusively to methyl isocyanate and methanol.
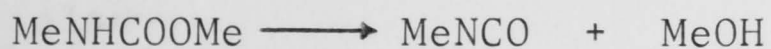
$$\text{MeNHCOOMe} \longrightarrow \text{MeNCO} + \text{MeOH}$$

All the decompositions follow the first-order rate law and rate constants are unaffected by the addition of free-radical inhibitors or by increase in the surface to volume ratio of the reaction vessel. First-order rate constants and Arrhenius parameters are reported. The reactions are believed to be unimolecular and homogeneous. The pattern of substituent effects is examined and indicates that the reactions involve heterolytic processes. Suitable transition states are discussed.

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CHAPTER I

INTRODUCTION

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INTRODUCTION

Thermal decompositions of organic compounds in the gas-phase may be classified into three general mechanistic types. These may be summarised as:

radical non-chain reactions

free-radical chain reactions

molecular reactions

(A) Radical Non-Chain Reactions.

The nature of this category of decomposition is such that bond fission is homolytic and the radical species formed do not set up self propagating chains. The observed activation energy is equivalent to the homolytic bond dissociation energy of the bond undergoing fission in the rate-determining step and the rate of the overall process is that of this slow step. The decomposition of allyl bromide is considered to occur by a radical non-chain mechanism[1].

(B) Free-Radical Chain Reactions.

This category of reactions occurs when free-radicals are initiated by homolytic bond fission and take part in propagating steps which generate products and regenerate the propagating radicals. The complex chain mechanisms may lead to simple overall kinetic laws[2]. The overall order of radical chain mechanisms depends upon the order of the initiation and termination steps and the dependence has been summarised[3] in Table 1.1. Propagation steps determine the major products of the reaction.

Criteria used to recognise radical chain mechanisms are the observed kinetics, the influence of radical inhibitors, and the nature of the products. Essentially each compound is judged

individually: the position of homolytic bond fission is taken to be at the weakest bond, and the role of those radicals which may be generated is examined to see if the possible assembly of element- ary processes can lead to the observed kinetics and products.

Table 1.1

Overall Orders of Reaction for Various Types of Initiation and Termination Reactions[a].

First-order initiation		Second-order initiation		Overall order
Simple termination	Third-body termination	Simple termination	Third-body termination	
		$\beta\beta$		2
$\beta\beta$		$\beta\mu$	$\beta\beta M$	$3/2$
$\beta\mu$	$\beta\beta M$	$\mu\mu$	$\beta\mu M$	1
$\mu\mu$	$\beta\mu M$		$\mu\mu M$	$\frac{1}{2}$
	$\mu\mu M$			0

[a] *A β radical is one which undergoes bimolecular propagation reactions, and μ radical one that undergoes unimolecular prop- agation reactions.*

(C) Molecular Reactions.

Molecular reactions may involve homolytic or heterolytic fission of the breaking bond. Heterolytic bond fission leads to reactions which are polar, and a body of evidence has been amassed in recent years to indicate that such reactions are important in the gas-phase. The evidence in support is based upon the parall- els the gas-phase reactions have with reactions in solution which have long been accepted as proceeding by a polar mechanism.

Maccoll reviewed the effect of substituents upon the rate constants for a number of reactions and concluded[7] that there exists a spectrum of reactions in which one extreme represents

molecular heterolytic processes, while the other represents
molecular homolytic processes. The decompositions of alkyl
halides and cyclobutanes represent the extreme cases of
heterolysis and homolysis respectively. Table 1.2 summarises
a number of elimination reactions together with the effect of
monomethyl and dimethyl substitution α to the reaction site.
Thus the large substituent effect on relative rate constants for
the alkyl halides contrast with the small substituent effect
observed for cyclobutane decomposition. This sensitivity to
substituents is considered diagnostic of heterolytic or polar
mechanisms.

The gas-phase chemistry of alkyl halides is reviewed here
because it provides a well documented case for polar molecular
reactions. Additionally, the decompositions of esters and related
compounds are reviewed since carbamates and esters are
structurally similar and in the event undergo similar reactions.

Table 1.2[a]

The Effect of Substitution on Relative Rate Constants.

System[b]	Temp(°C)	Parent	α-Methyl	α,α-Dimethyl
Chloride	360	1	150	25,000
Bromide	325	1	160	46,000
Iodide	285	1	102	35,000
Formate	400	1	20	720
Acetate	400	1	27	1,600
Isothiocyanate	307	1	35	690
Vinyl ether	350	1	13	126
Alcohol	525	1	10	38
Cyclobutane	450	1	1.5	3.4

[a] *Table adapted from ref.8.*   [b] *Parent compound is the ethyl compound except for cyclobutane.*

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(D) <u>The Thermal Decompositions of Alkyl Halides</u>

   The study of the elimination reactions of the alkyl halides

$$C_nH_{2n+1}X \rightarrow C_nH_{2n} + HX$$
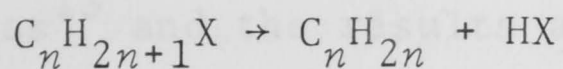
has shown that the reactions are generally first-order, unimolecular and homogeneous. The effect of α-methyl substitution has been widely studied[4-8] and resembles that in S_N1 or E1 reactions in solution which proceed by a polar mechanism. The gas-phase decompositions of the alkyl halides are considered to involve a considerable degree of heterolycity and the term "quasi-heterolytic" has been applied[15].

(a) <u>Surface Effects and Heterogeneous Processes</u>.

   Decompositions carried out in clean glass or pyrex vessels are complicated by the possibility of surface reactions thus for the decomposition of t-butyl chloride the rate is proportional to the surface area[9]. The rate constants for the heterogeneous mode of decomposition for a series of alkyl chlorides have been measured in a clean pyrex vessel and the proposed transition state is represented[10] by I:

$$
\begin{array}{cc}
||\\
-C\!\!-\!\!-\!\!-\!\!C-\\
||\\
HCl\\
\vdots\vdots\\
\overline{}\\
-+
\end{array}
$$
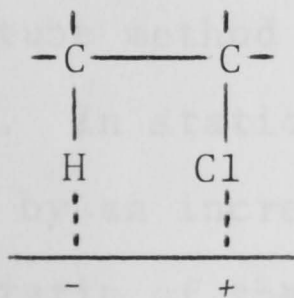
     + *and* - *represent polar sites on the glass surface.*

(I)

The polarization of the carbon-chlorine bond in (I) is considered to be more important than is polarization of the carbon-hydrogen bond. When a reaction process is allowed to deposit a carbonaceous coating on the glass surface[11], the rates are successively lowered to a reproducible value. Such coatings are thought to cover the polar sites on the glass surface thereby excluding the possibility

of heterogeneous reactions[12]. A study of the decomposition of
neo-pentane has been made in a "wall-less" flow reactor in which
the decomposing compound is separated from the wall by a barrier
of inert flowing gas[13] and the results are in excellent agreement
with shock-tube results[14].

The free electron content of pyrolytic carbon produced
from pyrolyses of *cis*-but-2-ene, ethyl chloride, and allyl bromide
was measured by Holbrook[15]. Only the e.s.r. spectrum of the
allyl bromide surface gave a strong signal (ca.10^{18}spins.g^{-1}.).
Holbrook and Rooney[16] demonstrated that the extent of isomerization
of but-2-ene in the presence of hydrogen chloride is dependent on
the origin of the pyrolytic carbon coating. Further investigations[17]
revealed that the concentration of free electrons at or near the
surface is important rather than the total number of free
electrons in the bulk of the carbon coating. The rates of
decomposition of isopropyl and n-butyl bromide (the latter as the
maximally inhibited reaction) are insensitive to the presence of
carbon coatings with different spin contents[18].

Most studies of alkyl halide decompositions have used the
static system, flow system, and the shock-tube method. Use of
the shock-tube method eliminates the possibility of heterogeneous
processes[8]. In static systems if the rate of a reaction is
unaffected by an increase (usually about tenfold) in the surface
to volume ratio of the reaction vessel, the reaction is considered
to be homogeneous. Arrhenius parameters obtained for alkyl halide
decompositions by the static and shock-tube method are in
excellent agreement (see Table 1.3) indicating that the reactions
are homogeneous.

(b) The Role of Radical Chain Reactions

For those compounds which decompose by competing radical

Table 1.3[a]

Rates of Reaction by Different Techniques

	Static		Dynamic	
Compound	log A	E(kcal.mole^{-1})	log A	E(kcal.mole^{-1})
EtCl	13.46	56.6	13.16	56.4
i-PrCl	13.40	50.5	13.64	51.1
t-BuCl	13.72	45.0	13.73	44.7

[a] *Table taken from reference 8.*

chain and molecular mechanisms, the addition of inhibitors (such as nitric oxide[19] and alkenes[20]) has been used to suppress the radical chain mechanism. Inhibitors have the ability to combine with chain-carrying radicals:

$$\overset{\bullet}{R} + NO \rightarrow RNO \rightarrow products$$
$$\overset{\bullet}{R} + CH_3 - CH = CH_2 \rightarrow RH + \overset{\bullet}{C}H_2 - CH = CH_2$$
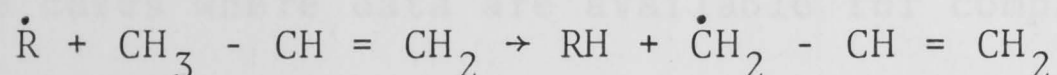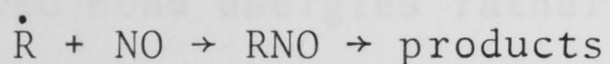
For alkyl halides the reaction which occurs when the process is maximally inhibited is considered to be a molecular process[20-22].

Studies of the decompositions of ethane and ethane-d$_6$ showed that the concentration of free radicals is not reduced to zero under conditions of maximal inhibition by nitric oxide[23,24] and it is suggested that this should also be the case for alkyl halides[71]. The inhibiting effect of nitric oxide (and other alkene-type inhibitors) is believed to be due to its ability to introduce new initiation and termination reactions rather than suppress all the existing chain processes[25-27], and mechanisms have been proposed which explain the observations that under certain conditions nitric oxide can either (a) increase, (b) decrease or (c) have no effect on the overall rate of a chain reaction.

Wojciechowski and Laidler[27] proposed that the alkyl

bromides pyrolyse by a radical chain mechanism which is
independent of the surface to volume ratio of the reaction vessel
and involves initiation and termination reactions on the surface.
Capon, Maccoll and Ross[28] applied the reasoning to the decomposition
of 3-bromopentane which followed first-order kinetics rather than
the 1.5 order predicted by the Wojciechowski-Laidler scheme, and
concluded that the bromide decomposes by a unimolecular mechanism.
Additional evidence supporting a unimolecular decomposition
mechanism for alkyl halides in the gas-phase is: (a) the absence
of induction periods, (b) pre-exponential terms ($ca.10^{13}sec^{-1}$)
in agreement with values predicted by the hard sphere collision
theory, (c) changeover to second-order kinetics at low pressures
of reagent[29], and (d) rate constants which correlate with
heterolytic bond energies rather than with homolytic bond energies
for those cases where data are available for comparison.

(c) The Effect of Substituents.

The polar nature of the unimolecular elimination reaction
is supported by the pattern of the effects of various substituents
upon the rate of the reaction. These results have been reviewed
in detail[8] and most of the data summarised here is taken from this
review.

(i) α-methyl[a] substitution

Systematic changes in the nature of the alkyl group have
been made in a series of alkyl bromides. Relative rates at 325°
are found to be:

$$C_2H_5Br : i-C_3H_7Br : t-C_4H_9Br = 1 : 160 : 46,000$$
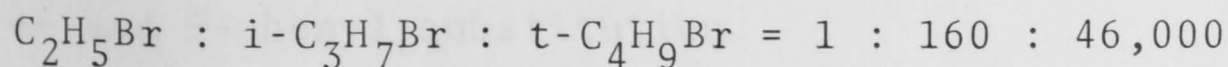
For alkyl chlorides and iodides the corresponding results are:

$$C_2H_5Cl : i-C_3H_7Cl : t-C_4H_9Cl = 1 : 150 : 25,000 \quad (T = 360°)$$

$$C_2H_5I : i-C_3H_7I : t-C_4H_9I = 1 : 102 : 35,400 \quad (T = 285°)$$

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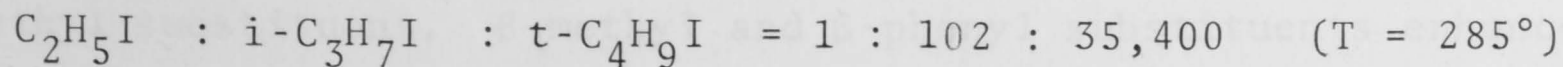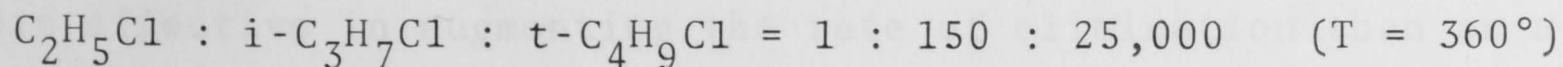
[a] The α-carbon is the one forming the C-X bond.

(ii) β-methyl substitution

Methyl substitution on the carbon atom β to the carbon-halogen bond has a much smaller effect on the rate constant than α-methyl substitution. Relative rates for alkyl bromides and chlorides are:

(Bromides) Ethyl : n-propyl : isobutyl = 1 : 3.4 : 7.3 (400°)

(Chlorides) Ethyl : n-propyl : isobutyl - 1 : 3.6 : 4.7 (440°)

Hughes and coworkers[30] have found that the S_N1 mechanism for solution reactions is also insensitive to β-methyl substitution.

(iii) α- and β-halo substitution

The inductive withdrawal effect of a β-halo substituent reduces the rate constant. The -I effect of an α-halo substituent is overshadowed by its mesomeric release of electrons to the C-X bond undergoing reaction thereby increasing the rate constant. Relative rates of elimination from the appropriate alkyl chlorides and bromides are:

$$CH_3CCl_3 : CH_3CHCl_2 : CH_3CH_2Cl : CH_2ClCH_2Cl = 32 : 8.2 : 1 : 0.55 \ (437°)$$

$$CH_3CHBr_2 : CH_3CH_2Br : CH_2BrCH_2Br = 9.6 : 1 : 0.25 \quad (416°)$$

These results parallel those observed for solution reactions[31].

(iv) If homolysis of the C-X bond is important in the transition state, the conjugation of the incipient double bond with a β-vinyl substituent would be expected to have a large augmenting effect on the rate. No such effect was found[32].

(v) α- and β-phenyl substitution.

The data in Table 1.4 show that an α-phenyl substituent is more effective in augmenting the rate of elimination than an α-methyl substituent. β-methyl and β-phenyl substituents enhance the rate of pyrolysis by approximately equal amounts.

Table 1.4

Relative Rate Constants for α- and β-phenyl Substitution

Compound	Rel. rates for α-substituents X=Cl (280°)	Rel. rates for α-substituents X=Br (280°)	Rel. rates for β-substituents X=Cl (425°)	Rel. rates for β-substituents X=Br (385°)
CH_3CHXCH_3	1	1	-	-
$PhCHXCH_3$	28	366	-	-
$(CH_3)_2CXCH_3$	113	675	-	-
$CH_3CH_2CH_2X$	-	-	1	1
$PhCH_2CH_2X$	-	-	1.8	0.7

The results show that electron availability at the breaking C-X bond rather than at the breaking C-H bond affects the rate of reaction.

(vi) α-methoxy substitution

Replacing an α-hydrogen atom by a methoxy group is known to greatly aid the formation of a carbonium ion in solution reactions[33] and has been found to have a similar effect in the pyrolytic elimination of HX from alkyl halides. At 200° relative rates are:

ethyl chloride : α-methoxyethyl chloride = 1 : 10^9

(vii) Deuteration of ethyl chloride[34a] and ethyl bromide[34b,35] decreases the rate of pyrolysis. This evidence suggests that the breaking of the β-carbon-hydrogen bond is involved in the rate-determining step. However, as Maccoll[6] has pointed out, this need not necessarily follow since deuteration might increase the heterolytic bond dissociation energy of the carbon-halogen bond.

(viii) At 325° the effects of variation of the halogen leaving group on the relative rates of pyrolysis are:

t-butyl chloride : bromide : iodide = 1 : 14 : 171

The same sequence is observed for the unimolecular solution reactions[36].

(ix) The direction of elimination to yield olefin is governed by the Saytzeff rule as would be appropriate for a polar reaction[36,57].

Thus the overall effect of electron-releasing groups at the α-carbon is to enhance the rate of elimination whereas β-methyl and β-phenyl groups affect the rate to a much smaller extent. This evidence suggests that the nature of the C-X bond rather than the β-C-H bond is important in determining the rate of elimination. This conclusion is supported by the similarities between the effects of substituents on the gas-phase elimination reactions and those on S_N1 or El solution reactions. Furthermore, Maccoll and Thomas showed that a correlation exists between the energies of activation for the gas-phase elimination reactions and the heterolytic bond dissociation energies $[E(HX) = 0.29D(R^+X^-)]$ whereas no correlation was found with the homolytic bond dissociation energies.

Maccoll and Thomas[7] proposed a transition state as represented by II:

$$\delta\delta^- \; C\!-\!\!-\!\!-\!\!-\!\!-\!\! C^{\delta+}$$
$$\delta\delta^+ \; H\!-\!-\!-\!-\!-\!Br^{\delta-}$$

(II)
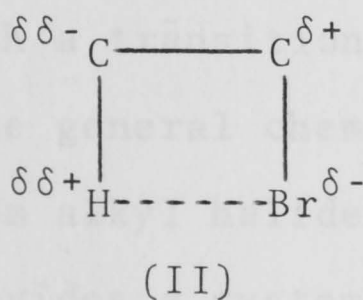
and suggested that simultaneous elongation and polarization of the C-Br bond may occur, followed by stabilization of the transition state due to polarization of the β-H atom. Ingold[33] favoured "a rate controlling step involving halogen heterolysis but no hydrogen loosening of any kind" i.e.,

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$$-\overset{\displaystyle |}{\underset{\displaystyle H}{C}}-\overset{\displaystyle |}{\underset{\displaystyle X}{C}}- \quad \xrightarrow{\text{slow}} \quad -\overset{\displaystyle |}{\underset{\displaystyle H}{C}}-\overset{\displaystyle |}{\underset{\displaystyle X^-}{\overset{+}{C}}}- \quad \xrightarrow{\text{fast}} \quad \overset{\diagdown}{\diagup}C=C\overset{\diagup}{\diagdown} + HX$$
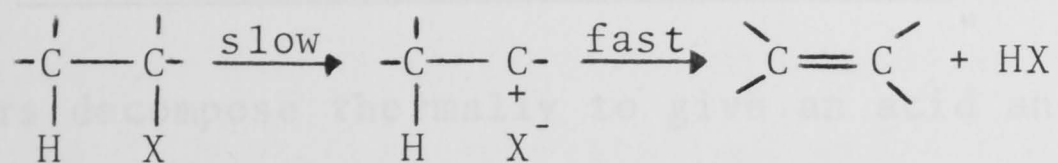
Calculations carried out for ethyl bromide showed that such a charged transition state cannot be ruled out on energetic grounds. The high value for the heterolytic bond dissociation is for separation of the formed ions to infinite separation. Where separation of the ion pair to 2.5 Å is performed the energy required[5] is about 55 kcal.mole^{-1}. Ethyl bromide is similar to all other alkyl halides for the purposes of this calculation.

Wagner-Meerwein rearrangements have been observed in the thermal decompositions of *neo*-pentyl chloride[37], *neo*-pentyl chloroformate[38], bornyl chloride[39] and isobornyl chloride[40]. These results are readily interpreted in terms of an ion-pair transition state. Kraus obtained straight lines from plots of Taft σ* constants against logarithms of rate constants for the decomposit-ions of alkyl chlorides and bromides and the large negative ρ-values were taken as evidence for the existence of polar transition states[41]. However, D-(+)-2-chlorooctane eliminated HCl at a rate faster than that required for racemization which seems to be evidence against such a transition state[42] in this case.

Surveying the general chemistry of the elimination of hydrogen halides from alkyl halides it does appear that a polar transition state provides a systematic description of the observed behaviour. There are a number of processes which present difficulties such as the reaction of D-(+)-2-chlorooctane and the role of radical processes in the fully inhibited reactions but the general description stands. The term "quasi-heterolysis" has been applied by Maccoll[5].

(E) <u>The Thermal Decompositions of Esters</u>

Esters decompose thermally to give an acid and olefin according to the reaction

$$RCOOC_nH_{2n+1} \rightarrow RCOOH + C_nH_{2n}$$
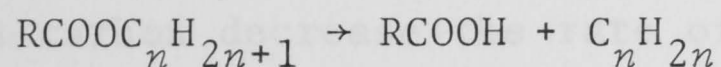
The structural requirement for reaction is that the carbon atom β to the alkyl-oxygen carries at least one hydrogen substituent to enable olefin formation[43]. A considerable quantity of work has been carried out, and in general reactions are considered to be first-order, homogeneous unimolecular eliminations. Some of the results however come from studies which have been carried out under preparative conditions.

(a) <u>Effects of Substituents on Reaction Rate</u>.

(i) Variation of Substituents in the Alkyl Portion of an Ester.

Significant differences on the rates of elimination are observed when the carbon atom α to the alkyl-oxygen is varied from primary, to secondary, to tertiary in a given ester. Relative rates are reported in Table 1.5.

<u>Table 1.5</u>[a]

Relative Rates for Elimination from Esters at 400°

Compound	Ethyl	Isopropyl	t-Butyl
Formates	1	20	720
Acetates	1	26	1660

[a] *Data taken from reference 6.*

The effects of substitution on the carbon β to the alkyl-oxygen are much smaller and are summarised in Table 1.6. In the

primary series β methylation lowers the rate slightly. In the
secondary series the only effect noticeable seems to be a small
increase in rate on continued substitution, and a similar result
appears to hold in the tertiary series. Electron withdrawing
groups on the β-carbon decrease the rate of elimination[44]. The
relative rates for ethyl acetate, 2-ethoxyacetate and 2-methoxy-
acetate are 1 : 0.37 : 0.32.

Table 1.6[a]

Effects of β-Methyl Substitution on Relative Rates
for Ester Pyrolyses

Temp(°C)	Primary series		
	Ethyl	n-Propyl	Isobutyl
489	1	0.91	0.46

	Secondary series		
	Isopropyl	s-Butyl	3-Methyl-2-pentyl
411	1	1.6	2.0
308	1	0.96	-

	Tertiary series		
	t-Butyl	t-Pentyl	2,3-Dimethyl-2-butyl
311	1	2.5	3.4
237	1	1.5	-

a *Table taken from ref.6.*

The relative importance of substituents on the α and β
carbon atoms are shown by the results of a study of the effects
of para substituents in the aryl rings of 1-aryl-2-phenylethyl
acetates (III) and 1-phenyl-2-arylethyl acetates (IV)[45].

X—⟨O⟩—CH—CH₂—⟨O⟩   ⟨O⟩—CH—CH₂—⟨O⟩—X

O—COCH₃   O—COCH₃
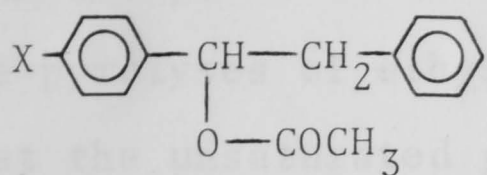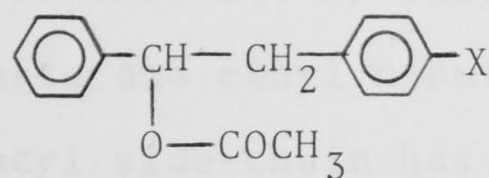
(III)   (IV)

Substituents in the 1-aryl compound have a greater influence over the rate of elimination than those in the 2-aryl compound which indicates that the breaking of the alkyl-oxygen bond is more important in the rate determining step than the breaking of the carbon-hydrogen bond. For the 1-aryl-2-phenylethyl acetates (III) variation of X leads to the observed rate sequence $CH_3O > CH_3 > H > Cl$, and a Hammett plot of $\log (k/k_o)$ versus σ has a negative ρ-value (-0.71) which is considered evidence that the reaction rate is affected by the electron availability at the breaking carbon-oxygen bond. The importance of the carbon-hydrogen bond has however been shown in the study[46] of the decompositions of γ-acetoisopropyl acetate and s-butyl acetate. At 309° the presence of the carbonyl group adjacent to the breaking carbon-hydrogen bond leads to the relative rates 108 : 1 favouring the pyrolysis of γ-acetoisopropyl acetate.

The rates of decomposition of ethyl and ethyl-d_5 acetates have been compared[47] and deuteration is found to reduce the rate of pyrolysis (k_H/k_D = 2.4 at 500°). Although this value is affected by secondary deuterium isotope effects (mainly rehybridization of the four unreacting deuterium atoms[46]), the results show that breaking of the carbon-hydrogen bond is important in the rate-determining step[48].

(ii) Variation of the Nature of the Acyl Portion of an Ester.

Varying the nature of the acyl group has little effect upon the rate of pyrolysis of esters. Thus varying R in RCOOEt

from methyl to *tert*-butyl[49] increases the rate by only *ca.* 10%.
The pyrolyses of ethyl *trans*-crotonate and ethyl n-butyrate show[50]
that the unsaturated group in the acyl side-chain has little
effect on the rate of pyrolysis.

Emovon[51] obtained Arrhenius parameters for the decompositions
of the *tert*-butyl esters of chloro- and dichloroacetic acid.
Relative rates for t-butyl acetate : t-butyl chloroacetate : t-
butyl dichloroacetate at 250° are 1 : 5.5 : 18.6. These rates in
the gas-phase follow the same sequence as the acid strengths of
the corresponding acids in aqueous solution. A similar comparison
with pK_a was made by Smith and Wetzel[52] for the decompositions of
the esters of cyclohexanol and although the use of K_a for such
comparisons is of doubtful validity[72,73] the results do show that
substituent and steric effects in the acyl portion of an ester
have little influence on the rate of elimination.

The stereochemistry of the pyrolyses of esters has been
studied and the cis nature of the elimination has been reported[53,54].
The acetates of both *threo*- and *erythro*-2-deutero-1,2-diphenyl-
ethanol give *trans*-stilbene on pyrolysis and while the olefin
from the *erythro* compound retained nearly all its deuterium, that
from the *threo* isomer lost most of its deuterium[55].

erythro

threo
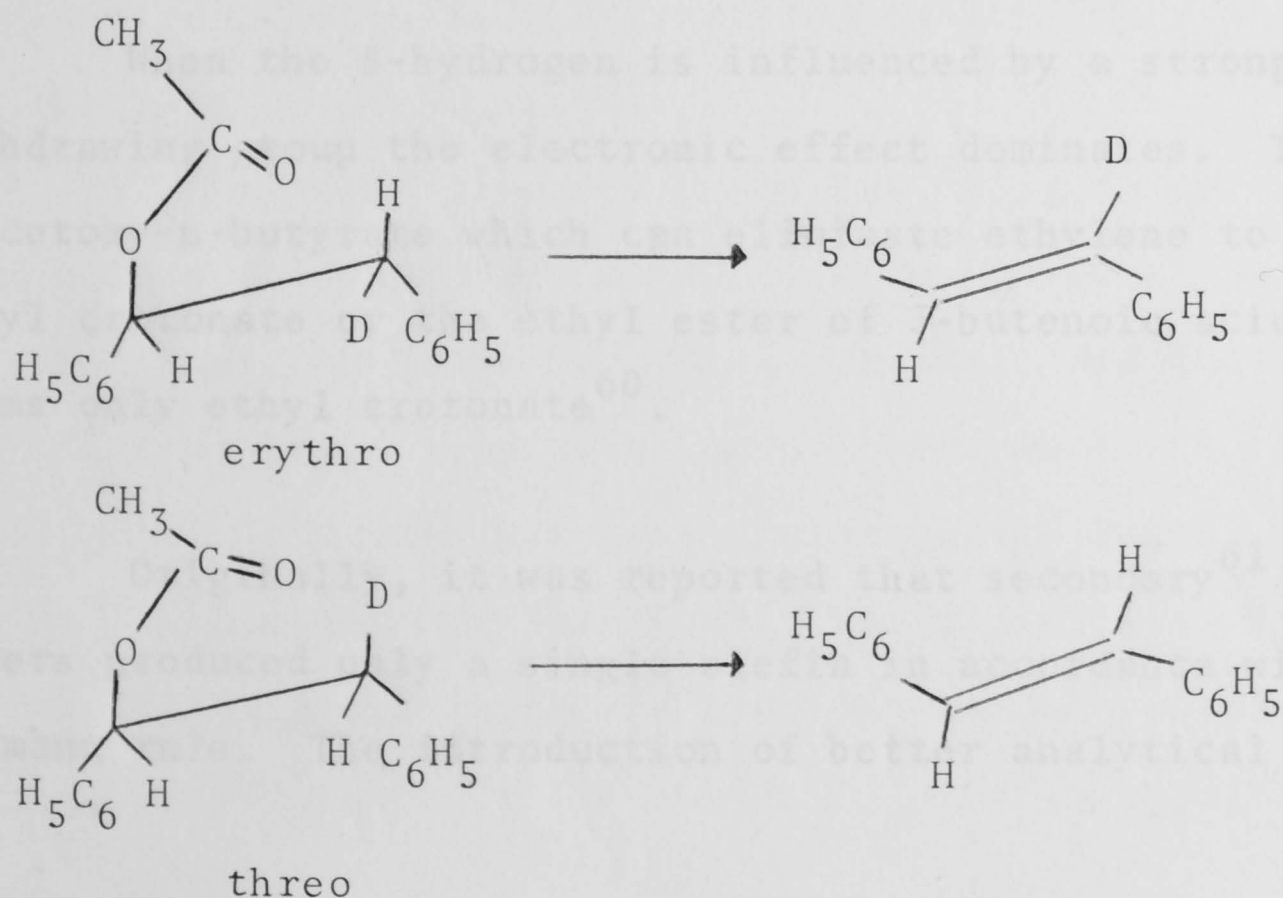
These results seem explained only by a mechanism in which a *cis*-β-hydrogen is eliminated, although a study of the direction of elimination from 1-methylcyclohexyl acetates showed that exact eclipsing of a β-H atom and the acetoxy group is not required in the transition state[56]. Significant amounts of other products have been produced during the pyrolyses of esters which cannot be explained in terms of a stereochemistry involving simple cis-elimination[53a,54,55]. Possible explanations offered are that these products are not primary products or that another mechanistic pathway is involved.

The direction of elimination has been determined mainly from experiments conducted under preparative conditions, and the results have been reviewed by De Puy and King[57] and by Smith and Kelly [58]. The important factors are listed as: (i) statistical effect (ii) steric effect and (iii) electronic effect.

Thus in the pyrolysis of *sec*-butyl acetate the ratio of olefins but-1-ene : but-2-ene = 57 : 43 is close to the 3 : 2 ratio expected on statistical grounds[59]. That twice as much *trans*-2-butene is formed as *cis*-2-butene is explained[56] in terms of a steric effect arising from the eclipsing of non-participating methyl groups in the transition state which generates cis-2-butene.

When the β-hydrogen is influenced by a strong electron withdrawing group the electronic effect dominates. Thus ethyl β-acetoxy-n-butyrate which can eliminate ethylene to form either ethyl crotonate or the ethyl ester of 3-butenoic acid in fact forms only ethyl crotonate[60].

Originally, it was reported that secondary[61] and tertiary[62] esters produced only a single olefin in accordance with the Hofmann rule. The introduction of better analytical techniques

confirmed the formation of minor proportions of Saytzeff-type olefins. The present interpretation of the published data is that the direction of elimination from esters is mainly controlled by the statistical effect. Superimposed on this effect are contributions from the electronic and steric effects.

Under the acidic conditions of reaction for the alkyl halides, isomerization of the initially formed olefin can occur. This is not the case for the esters.

(b) Mechanism of Pyrolysis of Esters.

Hurd and Blunck[43] originally proposed a cyclic, concerted six-membered transition state for ester pyrolysis. Since then, several modifications have been suggested which explain results not readily interpreted in terms of such a transition state.

Maccoll[63] proposed that the pyrolysis of esters is governed by the nucleophilic attack of the carbonyl-oxygen atom on the β-hydrogen atom and suggested an analogy with the E2 reaction in a polar solvent. If this is the case, the vinyl alkyl ethers would be expected to decompose at a slower rate than the esters. Since esters and vinyl alkyl ethers decompose at about the same rate, this mode of reaction is not important in determining the rate of pyrolysis[57].

It has been proposed by De Puy, King and Froemsdorf[64] that some double-bond character develops between the carbon atoms in the transition state for ester pyrolysis and that no appreciable charge separation occurs between the breaking C-H and C-O bonds. This view has been challenged by Smith, Bagley and Taylor[45] who maintain that "olefin stability is of little importance in determining the stability of the esters in contrast to the character of the C-O bond". In the pyrolysis of 1,2-di-

arylethyl acetates, substituents in the 1-aryl ring (which influence the breaking of the C-O bond) have a greater effect on the rate of pyrolysis than substituents in the 2-aryl ring (which influence the breaking of the C-H bond). Thus although the alkyl-oxygen and carbon-hydrogen bonds break simultaneously, the rate of pyrolysis is mainly influenced by the character of the breaking C-O bond.

This conclusion is supported by the results of Taylor, Smith and Wetzel[65] who found that the effects of substituents in the aryl ring of 1-arylethyl acetates is described by a plot of $\log (k/k_o)$ versus σ^+ and had a $\rho = -0.66$. This value compares with $\rho = -1.4$ observed in the corresponding 1-arylethyl chlorides[66] and is considered to establish that ester pyrolysis is not as dependant on polar substituent effects and is not as heterolytic. Lum and Smith[67] showed that substitution of a cyclopropyl group in the α-position of a secondary or tertiary ester had only a minor effect on the gas-phase rate of pyrolysis which further supports these conclusions. An α-cyclopropyl group brings about a marked activation in the rate of solvolysis reactions and is 246 times more effective than an α-isopropyl group.

On the other hand, Scheer, Kooyman and Sixma[44] favour an ion-pair intermediate mechanism for aliphatic esters according to the scheme:

$$R^1COOR^2 \underset{\longleftarrow}{\xrightarrow{rapid}} [R^1COO^- \;^+R^2] \xrightarrow{slow} R^1COOH + Olefin$$
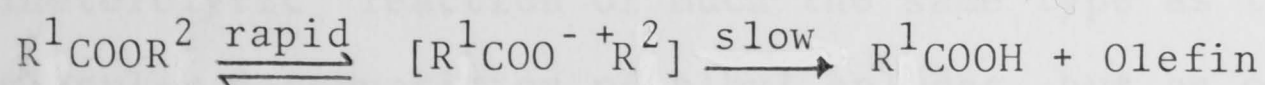
The deuterium isotope effect observed in ethyl-d_5 acetate[47] is well explained by such a mechanism. Additionally the rearrangements observed by Emovon[69] for bicyclic esters are satisfactorily interpreted by such a scheme. Evidence against such an ion-pair intermediate is that the observed ρ-values ($\rho = -0.66$ for

1-arylethyl acetates[65]) are not sufficiently negative and the presence of an α-cyclopropyl group[67] has little effect on the reaction rate. Ion-pair gas-phase reactions are expected[58] to show ρ-values between -3 and -5. Smith, Voorhees and Kelly[68] studied the partial pyrolysis of MeCO—[18]OEt and using mass spectrometric analysis showed that no scrambling of the oxygens occurred in the unpyrolysed ester. This result rules out the existence of a rapid equilibrium between an ion-pair intermediate and the ground state ester at least for this compound.

It is now generally agreed that the pyrolysis of esters is best represented by the polarized transition state V.

$$\left\{ R-C \begin{matrix} O \\ O \end{matrix} \right\}^{\delta-} \left\{ \begin{matrix} H \\ C \end{matrix} \right\}^{\delta+}$$

(V)
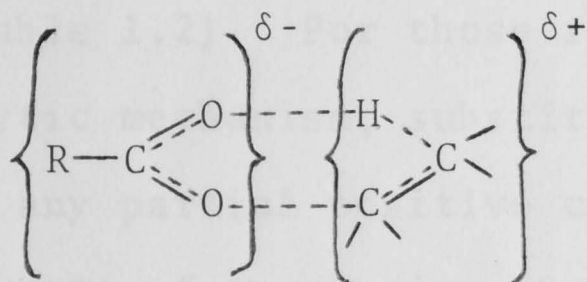
where δ indicates a smaller degree of charge transfer than in the transition state for alkyl halide pyrolysis. Maccoll[46] describes such a polarized transition state as one in which "both the ease of breaking of the alkyl-oxygen bond and the ease of breaking of the β-carbon-hydrogen bond in the heterolytic sense are of importance in increasing the rate of pyrolysis of esters. The unimolecular decompositions of esters is best thought of as a quasiheterolytic reaction of much the same type as the unimolecular decomposition of alkyl halides, but as one in which substituent effects on the heterolysis of the alkyl-oxygen bond are greatly reduced".
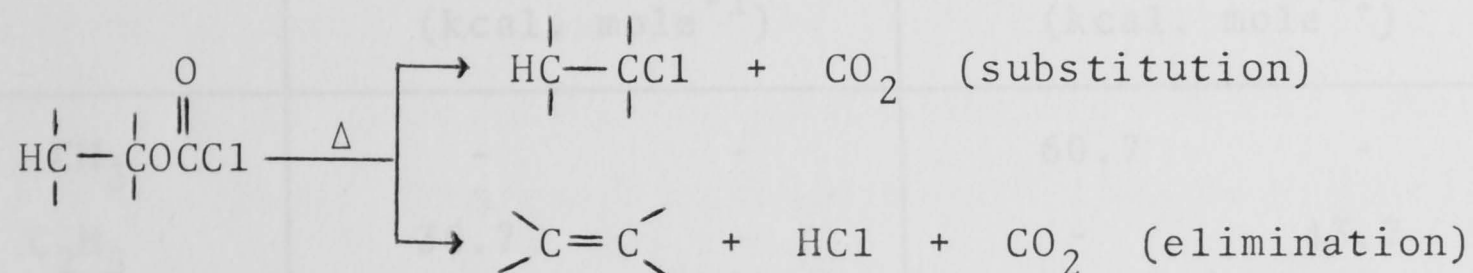
Such a transition state is in agreement with the observations that α-substituents have a greater effect on the rate constant than β-substituents, and it explains the observed stereochemistry

and β-deuterium isotope effect. However, the formation of rearranged products is difficult to explain as it seems that Wagner-Meerwein rearrangements require that a carbonium ion be formed on a primary or secondary carbon adjacent to a quaternary carbon. Emovon[69] carried out carefully controlled gas-phase decompositions of bornyl and isobornyl acetates and found that some rearrangement apparently does occur. Bornylene is the expected product of cis-elimination. Besides bornylene substantial amount of tricyclene and camphene were produced and explained in terms of a rearrangement mechanism in the gas-phase.

Unimolecular, homogeneous gas-phase reactions can be considered as either proceeding by a heterolytic or homolytic mechanism (see Table 1.2). For those reactions which proceed by a mainly heterolytic mechanism, substituents which stabilize the tendency to form any partial positive charge on the α-carbon atom enhance the rate of pyrolysis. On the other hand conjugation in the transition state is a major factor which increases the rate of pyrolysis of reactions proceeding by a homolytic mechanism. The rates of pyrolyses of cyclobutanes which are considered to decompose by a homolytic mechanism[7] are markedly affected by conjugation of a β-vinyl substituent with the forming double bond. Thus isopropenylcyclobutane[70] decomposes 900 times faster at 390° than does cyclobutane. However, the rate constant for the pyrolysis of 1-methylbut-3-enyl acetate is ca. twice that for s-butyl acetate[46] showing that homolytic bond fission is not important in the transition state for ester pyrolysis. Thus although the intimate nature of the transition state may be debated, and may in fact vary from ester to ester, agreement that the eliminations are essentially polar seems general.

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(F) Other Related Reactions

(a) Chloroformates

The aliphatic chloroformates have been reported to decompose by two paths in the gas-phase:

$$HC-COCCl \xrightarrow{\Delta} \begin{cases} HC-CCl + CO_2 \quad \text{(substitution)} \\ \\ \ce{>C=C<} + HCl + CO_2 \quad \text{(elimination)} \end{cases}$$

Lewis and coworkers[74-76] studied the effect of α-methylation on the rate of the substitution reaction. Relative rates for the decomposition of ROCOCl at 240° are: Me : Et : i-Pr = 1 : 2.2 : 220. These results indicate the rather polar nature of the proposed[57] four-centred transition state

$$R \cdots \underset{Cl}{\overset{O}{\diamond}} \cdots C = O$$
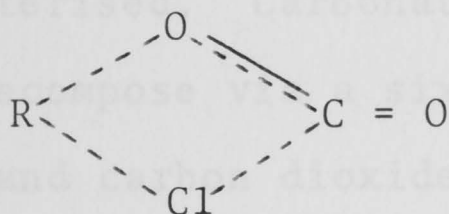
The olefin-forming reaction was placed in the category of unimolecular, cyclic cis-elimination reactions. From the observation that *neo*-pentyl chloroformate gave rearranged products[76], it was concluded that the six-membered transition state for the elimination reaction has a substantial amount of charge separation. Later, Lewis and Newman[58] pointed out that heterogeneous contributions may have been considerable for these pyrolyses.

The decompositions of the chloroformates have been reinvestigated by Johnson and Stimson[77] whose results (Table 1.7) were obtained under carefully controlled conditions in seasoned vessels. They believe that the substitution reactions are heterogeneous.

Table 1.7

Activation Energies for the Pyrolyses of Chloroformates (ROCOCl).

R	[a]E_s	E_e	[b]E_s	E_e
	(kcal. mole^{-1})		(kcal. mole^{-1})	
CH_3	-	-	60.7	-
C_2H_5	36.7	-	-	43.7
i-C_3H_7	26.2	37.2	-	41.7

[a] *Results of Lewis and coworkers.* [b] *Results of Johnson and Stimson.*

(b) Carbonates

The thermally induced reactions of carbonates have not been thoroughly characterised. Carbonates possessing a β-hydrogen atom are believed to decompose via a six-membered transition state to an olefin, alcohol and carbon dioxide. Gordon and Norris[78] showed that the decompositions of methyl ethyl and diethyl carbonates are homogeneous, unimolecular reactions.

Smith and Yates[79] obtained ρ-values from plots of logarithms of relative rates against σ$^+$-values for the pyrolysis of meta- and para-substituted 1-arylethyl methyl carbonates and 1-arylethyl acetates. The ρ-values were 0.97 and 0.66 respectively indicating that the transition states for the pyrolyses of carbonates and acetates are similar and that a partial positive charge is formed on the α-carbon atom.

(c) Xanthates

Xanthate esters of an alcohol containing a β-hydrogen atom decompose to an olefin, carbon oxysulphide and a mercaptan.

$$R'OCSR \longrightarrow Olefin + COS + RSH$$
(with S double-bonded to C)
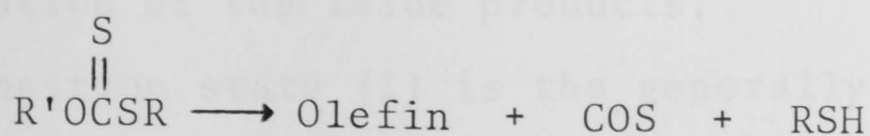
Most of the pyrolyses studied have been carried out in the liquid phase and are reviewed by Nace[80].

The elimination of a cis-β-hydrogen atom was demonstrated in the decompositions of the methyl xanthates of cis- and trans-2-phenylcyclohexanol[53a]. Examples of trans-elimination have also been reported[81,82] indicating that the reactions are not mechanist-ically homogeneous. Rearranged products have also been found[83].

The olefin-forming reactions of the chloroformates, carbonates and xanthates belong to the category of unimolecular, cyclic cis-elimination reactions. They differ from the carboxylic esters in that two possible six-centred transition states (I) and (II) are available which lead to the observed products. The two alternative transition states are illustrated for carbonate decomposition:

(I)

(II)
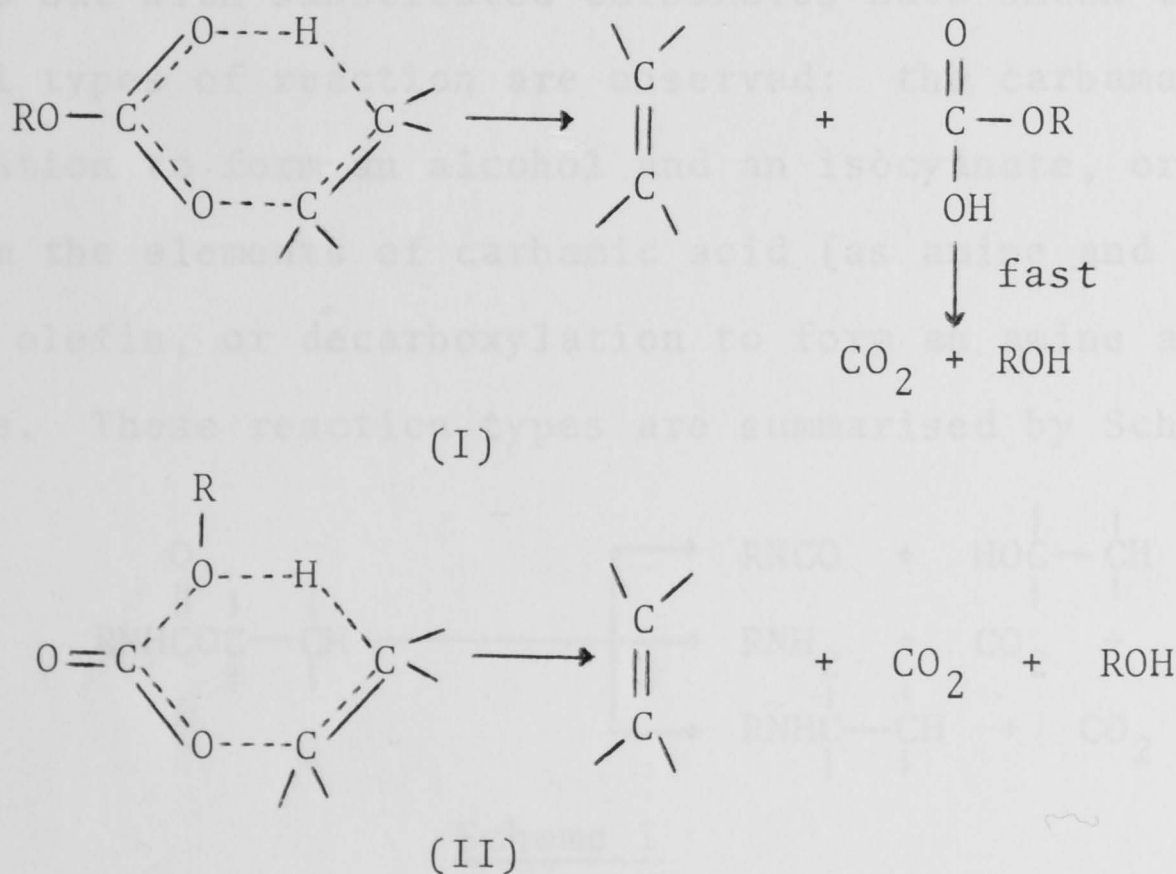
Transition state (I) leads to the formation of an olefin and an unstable carbonic acid which decomposes in a fast step to carbon dioxide and an alcohol. Transition state (II) leads to the direct formation of the three products.

Transition state (I) is the generally accepted path for

the pyrolysis of carbonates and xanthates[78]. Bader and Bourns[84] studied the decomposition of S-methyl-*trans*-2-methyl-1-indanyl xanthate. They measured the kinetic isotope effects for the thio-ether sulphur, thion sulphur and carbonyl-carbon atoms and showed that the experimental results support mechanism I.

(G)   Reactions of Carbamates.

Carbamic acids structurally resemble carbonic acids and are regarded as less stable and have no independent existence in solution.   The structural similarity leads to an expectation that thermal fragmentations of carbamates ought resemble those of carbonate esters, and to esters generally.

Most studies of the reactions of carbamates have been confined to solution chemistry and to thermal fragmentations which occur under distillation conditions.   Thus thermal degradations carried out with substituted carbamates have shown that three general types of reaction are observed: the carbamate may undergo elimination to form an alcohol and an isocyanate, or elimination to form the elements of carbamic acid (as amine and carbon dioxide) and an olefin, or decarboxylation to form an amine and carbon dioxide.   These reaction types are summarised by Scheme I.

$$RNHCOC-CH \longrightarrow \begin{cases} RNCO + HOC-CH \\ RNH_2 + CO_2 + \,\diagup C = C \diagdown \\ RNHC-CH + CO_2 \end{cases}$$
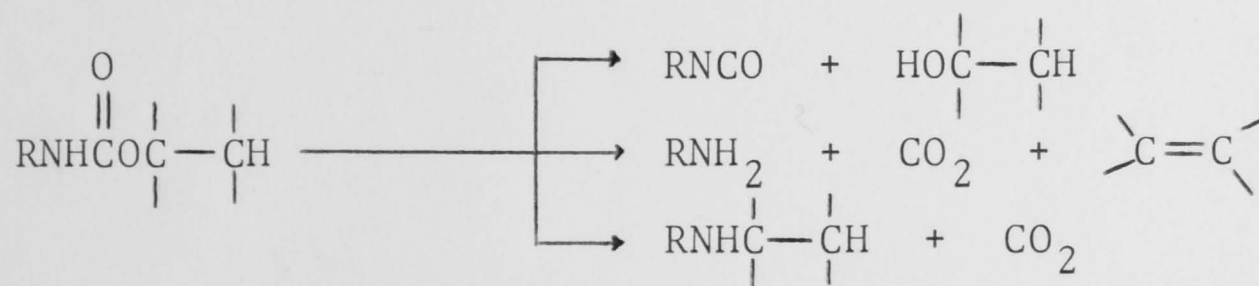
Scheme I

Additionally, the thermal stability of carbamates varies greatly depending upon structure, so that those formed from tertiary alcohols decompose more readily than those from primary or secondary alcohols.[85]

It seemed that an investigation into the kinetics and

mechanisms of reactions of carbamates ought provide information into their chemistry. Accordingly an investigation was undertaken and is now reported.

CHAPTER II

APPARATUS AND TECHNIQUES.

(A) <u>Apparatus</u>.

A conventional static system was used and the essentials are illustrated diagrammatically in Figure 2.1.

Reactions took place in a cylindrical pyrex vessel connected to the vacuum line, via the "pot-tap" (C_1), by 1.5 mm bore capillary tubing and separated from the precision-bore manometer (G_1) by a glass diaphragm gauge. The pot-tap and capillary tubing were wound with resistance wire (Brightray C, 1.7 ohm. ft^{-1}) and electrically heated to prevent reactant or product condensation. The windings were lagged with asbestos tape. The gauge was heated with a small electrical radiator.

The remainder of the vacuum line was constructed of 20 mm pyrex tubing. Crank-type vacuum taps (B_1-B_7) and ground glass joints were lubricated with Apiezon N grease. The tap C_1 which was maintained at a temperature between 200 and 250° was lubricated with Dow-Corning High Vacuum Silicone Grease. Gaseous reagents were stored in 5-litre bulbs (D_1-D_4) fitted with Springham greaseless taps and the remainder of the taps (E_1-E_4) were of the same type. The storage bulbs were covered with filament tape as a precaution against implosion. The pressure in the line was readily reduced to ca. 5×10^{-4} torr by a three-stage mercury diffusion pump (A_1) backed by a Metrovac G.D.R.I. two-stage oil pump. Waste materials were collected in traps cooled by liquid nitrogen.

The reaction vessel fitted into a central well (5 cm diameter x 25 cm deep) in the cylindrical aluminium block furnace. The furnace was wound with insulated layers of resistance wire and held in a container filled with asbestos wool. A resistance thermometer and thermocouple were placed in holes next to the reaction vessel. The temperature of the furnace was held
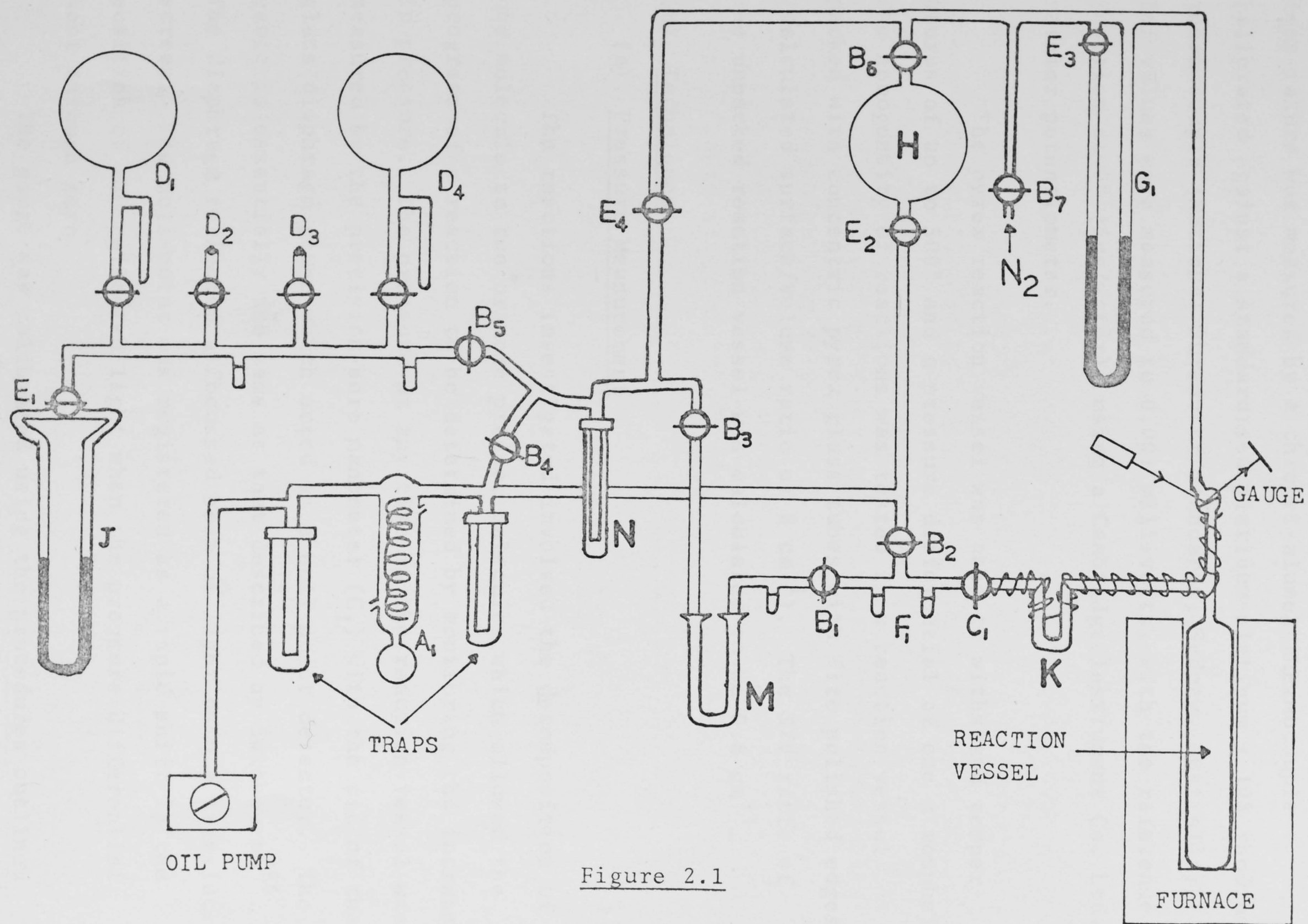
Figure 2.1

constant to $\pm 0.2°$ by an A.E.I.Ltd. RT3/R2 Temperature Controller

in conjunction with a platinum resistance thermometer. The

temperature was measured by a chromel-alumel thermocouple

calibrated against a standardised platinum-platinum + 10% rhodium

thermocouple (National Bureau of Standards, Sydney, Australia).

Emf values were measured to 0.001 millivolts, with the reference

junction at 0° (ice/water), using a Cambridge Instrument Co. Ltd.

vernier potentiometer.

The pyrex reaction vessel was able to withstand temper-
atures of up to 500° and a pressure differential of one atmosphere.
The homogeneity of reactions was tested in a reaction vessel
packed with concentric pyrex glass tubes with fire polished edges
(calculated surface/volume ratio of 8 cm^{-1}). The S/V ratio of
the unpacked reaction vessel was calculated to be 0.8 cm^{-1}.

(B) Techniques

(a) Pressure Measurement

The reactions investigated involved the decomposition of

one molecule to two or more product molecules which allowed the

progress of a reaction to be determined by monitoring the increase

in pressure. The pressure at any time in the reaction vessel was

measured by the precision-bore manometer (G_1) with the aid of the

glass diaphragm gauge which acted as a null-point detector. The

gauge is essentially the same as that described by Swinbourne[86].

The diaphragm reflected a focussed beam of light onto a translucent

screen. The null-point was registered as a rapid shift in the

position of the reflected light when the pressure differential

went through zero.

The gauge was calibrated using the procedures outlined

below:-

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Taps B_4, B_3, B_1, C_1, E_4 and E_3 were opened to the pumps and taps B_7, B_6, B_5 and B_2 left closed. After allowing 30 min for both sides of the manometer (G_1) to pump down, taps E_3 and B_4 were closed. Through a capillary leak at tap B_7, a pressure of dry oxygen-free nitrogen was admitted into the manometer and the reaction vessel. After allowing 10 min for temperature equilibration, taps C_1 and E_4 were closed and the actual pressure inside the reaction vessel read off a vernier scale attached to the manometer. The pressure in the manometer was then reduced by opening and closing tap B_6 to the empty ballast flask (H). The experimental pressure reading was obtained by allowing nitrogen to enter through tap B_7 which was rapidly closed when the null-point was registered. The results in Table 2.1 show that the value for the gauge correction did not vary over a pressure range of $ca.$ 50 to 410 mm.

Table 2.1

Calibration of the Diaphragm Gauge

Actual Pressure (mm)	Pressure Measured (mm)	Gauge Correction (mm)
51.0	54.2	-3.2
96.5	99.5	-3.0
167.3	170.4	-3.1
245.7	248.6	-2.9
362.1	365.1	-3.0
410.2	413.0	-2.8
		Mean: -3.0

(b)   Outgassing of Reagents

All reagents used were outgassed before being admitted into the reaction vessel. Liquids were contained in tap-vessels and attached to section F_1 (bounded by taps B_1, B_2 and C_1) of the vacuum line. The removal of dissolved oxygen and other permanent gases was accomplished by freezing the reagent in liquid nitrogen, opening to the pumps, then closing the tap-vessel and allowing the reagent to thaw. This procedure was repeated several times.

Gaseous reagents were transferred from storage cylinders to the 5-litre bulbs (D_1-D_4). Pressures of ca. one atmosphere, measured out by manometer (J), were admitted into the bulbs. Dissolved oxygen was removed by the freeze-pump-thaw technique. Readily condensable impurities were removed by passing the gas several times through a trap cooled by an acetone/dry ice mixture.

(c)   Introduction of Reagents into the Reaction Vessel.

Two methods were used:-

(i)   The "Distill-in" technique. The reaction vessel was evacuated for 10 min by opening taps B_2 and C_1 to the pumps. Tap B_2 was then closed and the capillary U-bend (K) cooled in liquid nitrogen. A sample of compound was then distilled from a tap-vessel into the U-bend where it froze to a solid plug. Tap C_1 was closed and the compound was volatilised into the reaction vessel by heating the U-bend with a small bunsen flame. To prevent reactant or product condensation, the U-bend was heated during the course of a kinetic run.

Some of the compounds studied had a low vapour pressure at room temperature. To facilitate sample entry into the capillary U-bend, section F_1 was wound with resistance wire and

electrically heated. During the distillation process, the compound in the tap-vessel was gently heated by a stream of hot air.

(ii) The "Blow-in" technique. This method was used to introduce gases into the reaction vessel. An amount of gas was condensed in section F_1 and allowed to warm to ambient temperature. The gas was admitted to the reaction vessel by rotating tap C_1 through the open position. Care was taken not to build up a pressure greater than an atmosphere in section F_1.

(d) Volume of the Reaction Vessel

Hydrogen bromide was blown-into the reaction vessel and its pressure and temperature measured. It was collected at liquid nitrogen temperatures in a tap-vessel fitted with a side-arm which was sealed by a serum cap. Distilled water was injected through the serum cap by a hypodermic syringe and the contents vigorously shaken. The serum cap was then removed and the acid titrated with 0.1M sodium hydroxide solution (phenolphthalein indicator). Using the ideal gas law

$$V = nRT/P$$

the volume of the reaction vessel (295 cm^3 ± 1%) was determined.

(e) Coating the Reaction Vessel Surface.

The reaction vessel was coated with the decomposition products of cyclopropane or isobutene at $ca.$ 490°. Finally, the surface was "seasoned" with the decomposition products of the compound under investigation. The packed reaction vessel was treated in the same way. Rate constants obtained in this system were reproducible and independent of a tenfold variation in the S/V ratio of the reaction vessel.

(f) Regreasing the Pot-tap.

The heated pot-tap (C_1) required regreasing once a week.
During the regreasing process the possibility of air entering
the reaction vessel had to be eliminated. This was achieved by
blocking the capillary U-bend (K) with a frozen plug of *tert*-
butyl isopropyl ether before removing the tap. This procedure
was found to be satisfactory and values obtained for rate constants
before and after the regreasing process were the same (within
experimental precision).

(g) Procedures used in carrying out Kinetic Runs.

A sample of the compound under investigation was added
to the reaction vessel by the "distill-in" method. The zero of
time was taken when half the sample was volatilised into the
reaction vessel and progress of the reaction was followed by
measuring the increase in pressure with time. The accuracy of
pressure measurements was $\pm$ 0.2 mm. The initial pressure of the
compound was obtained by extrapolation of the total pressure to
zero time.

Compounds were also decomposed in the presence of
additives. For runs with an added gas, the gas was blown into
the reaction vessel and its pressure measured. It was then
frozen at -196° into the R.H.S. of the capillary U-bend and a
sample of the compound under investigation added to the L.H.S.
of the U-bend by the distill-in method. The reagents were
volatilized into the reaction vessel and the total pressure
extrapolated to zero time. The initial pressure of the component
under investigation was obtained by subtracting the pressure of
gas added from the total initial pressure of the two component
system.

When calculating rate constants no allowance was made for

the "dead space" i.e., that part of the reaction vessel where no significant reaction takes place. The small volume in the capillary tubing and gauge was no greater than 2% of the total volume.

(C) Gas-liquid Chromatography.

Reaction products were separated and quantitatively analysed using a F & M 500 gas-chromatograph. The instrument incorporates a thermal conductivity detector in conjunction with a Wheatstone bridge connected to a potentiometric single-pen recorder. Both the injection port and block were maintained at 200°. The following procedures were used in the quantitative analysis of reaction mixtures.

(a) The Quantitative Analysis of Gaseous Products.

The gaseous fraction of the reaction mixture was separated from the liquid fraction by opening tap C_1 and pumping the reaction mixture through U-bend (M) cooled in an acetone/dry ice mixture and collecting the gaseous fraction in trap (N) at liquid nitrogen temperatures. The gases were transferred to a tap-vessel fitted with a side-arm which was sealed by a serum cap. Where g.l.c. analyses were carried out with an added reference standard, an amount of this standard was measured out in the reaction vessel and transferred to the tap-vessel. The tap-vessel was pressurized with helium to *ca.* one atmosphere and the gases mixed to ensure the formation of a homogeneous mixture. Mixing was normally carried over 24 hr and the process was aided by using a small magnetic stirrer bar inside the tap-vessel. Samples were withdrawn through the serum cap using a gas-tight syringe and injected onto a column.

Estimation of Ethylene. Ethylene was estimated using nitrous oxide as a reference standard. A Porapak Q column

(72 x ¼ in; helium flow rate: 43 ml.min^{-1}) at 35° was used which separated authentic samples of nitrous oxide and ethylene with retention times 465 and 675 sec, respectively. The calibration curve is shown in Figure 2.2 and describes results obtained from eight standard mixtures with an accuracy of 1%.

Estimation of Propene. Propene was estimated using isobutene as a reference standard. Propene and isobutene were separated by a Porapak Q column (42 x ¼ in; helium flow rate: 45 ml.min^{-1}) at 135° with retention times 135 and 298 sec, respectively. The calibration curve is shown in Figure 2.3.

Estimation of Isobutene. Propene was used as a reference standard in the estimation of isobutene. The calibration curve presented in Figure 2.3 was used.

The molar ratio of carbon dioxide to ethylene formed on the decomposition of ethyl N-methyl-N-phenylcarbamate was determined using a Porapak Q column (42 x ¼ in; helium flow rate: 65 ml.min^{-1}) at 50°. Carbon dioxide and ethylene were separated with retention times 90 and 145 sec, respectively. Since the expected molar ratio was 1.0, a calibration curve was prepared (Figure 2.4) covering the molar ratio carbon dioxide : ethylene = 0.89 : 1.13.

(b)   The Quantitative Analysis of Liquid Products.

The reaction mixture was collected in a trap at liquid nitrogen temperatures and the required pressure of reference compound was measured in the reaction vessel and added to the trap. The resultant mixture was allowed to warm to ambient temperature and then flushed out with a small amount of anhydrous diethyl ether into a 10 ml round-bottom flask. A homogeneous solution was formed by stirring with a magnetic micro-bar stirrer.

Figure 2.2

G.L.C. CALIBRATION CURVE FOR ESTIMATION OF ETHYLENE.
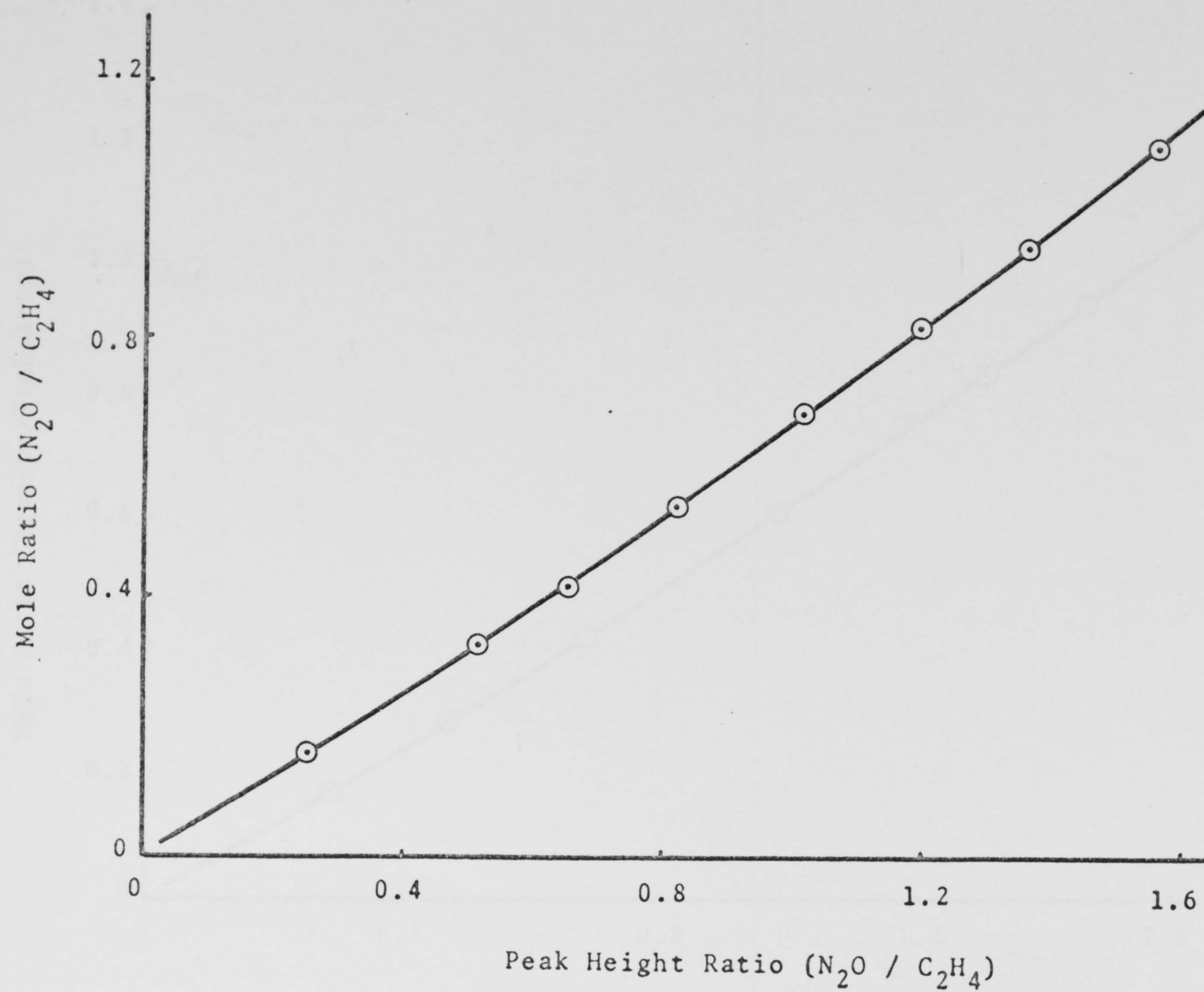
G.L.C. CALIBRATION CURVE FOR ESTIMATION OF PROPENE and ISOBUTENE.

Figure 2.3
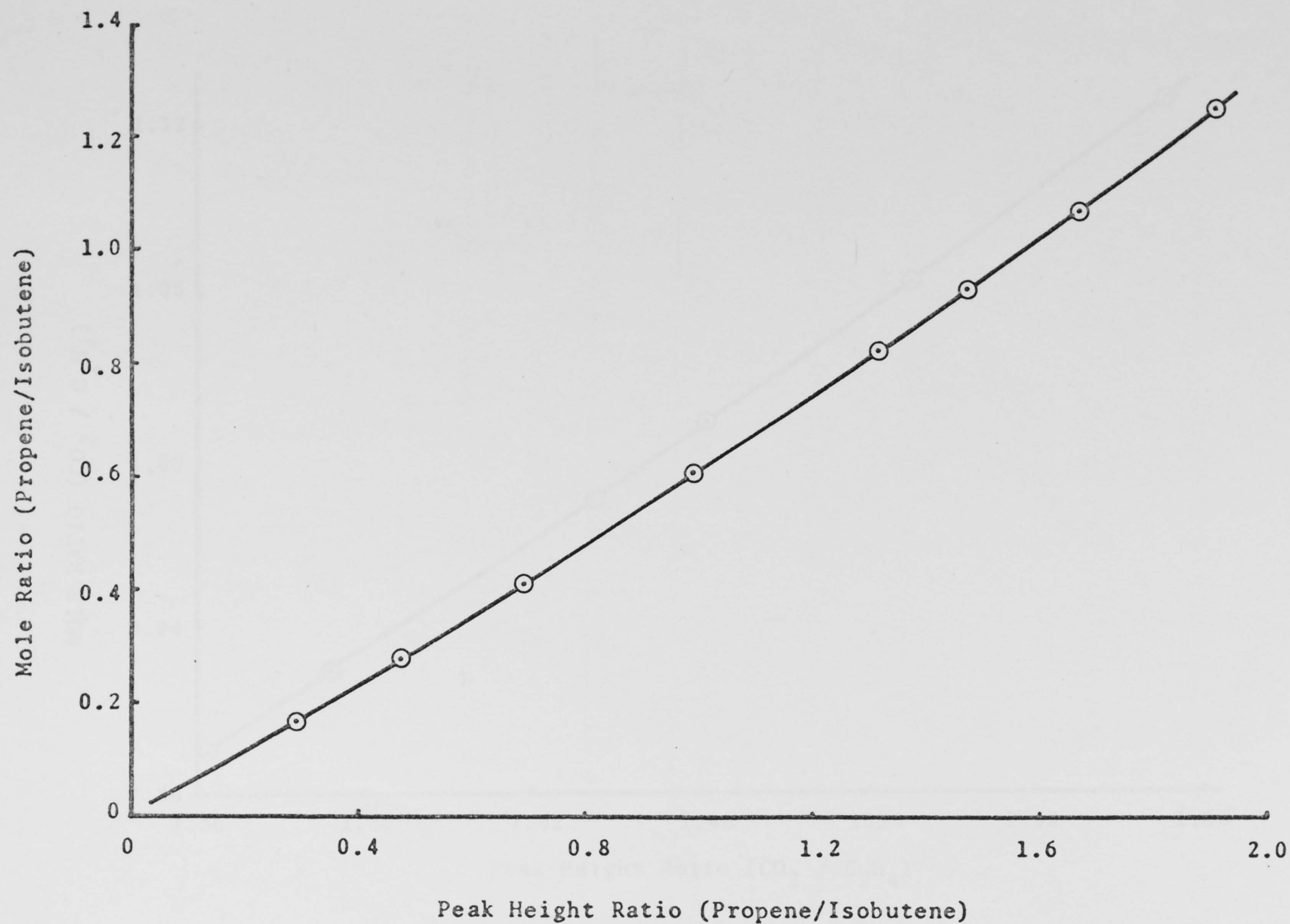
Figure 2.4

G.L.C. CALIBRATION CURVE.
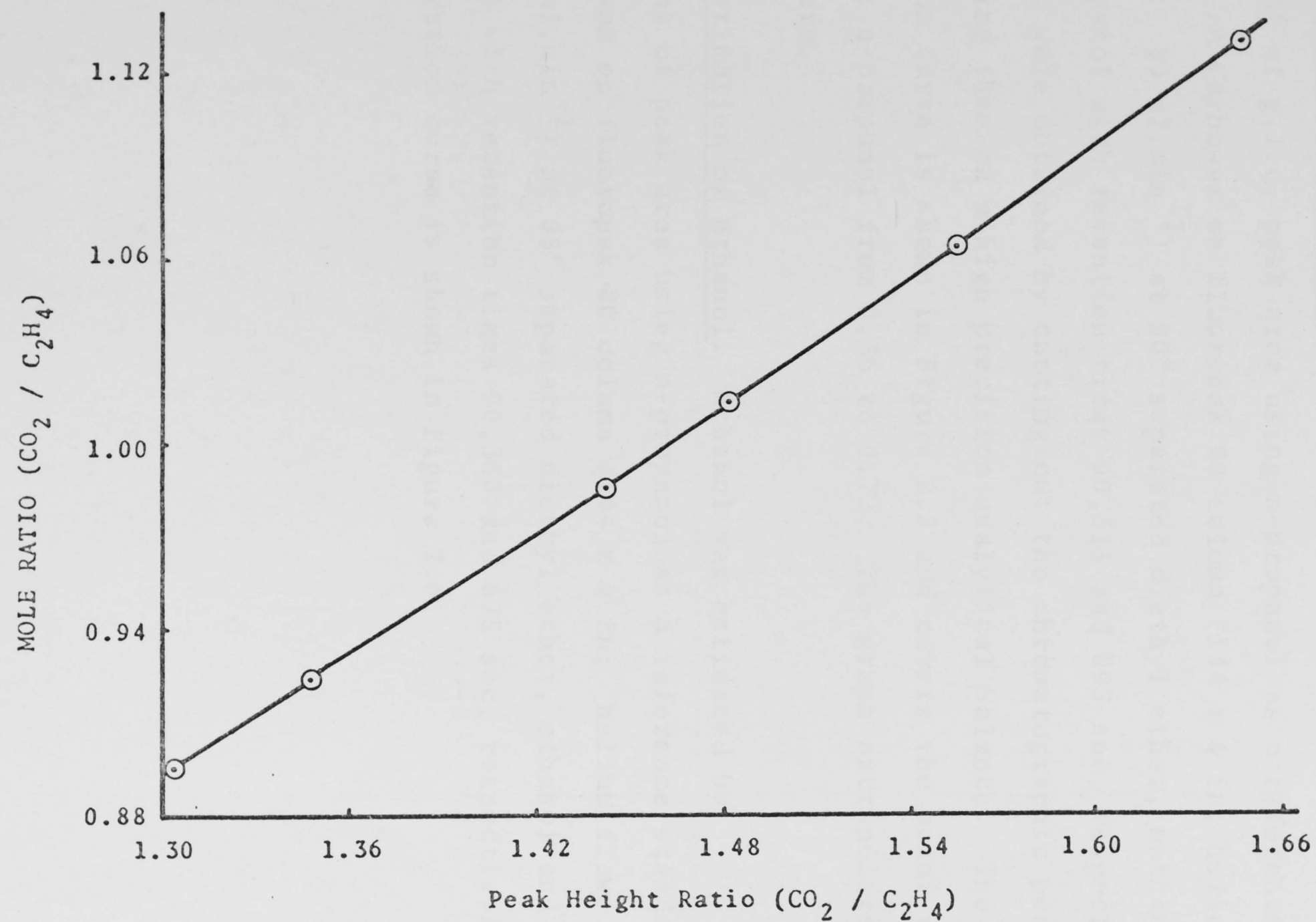
Samples were withdrawn with a microlitre syringe and injected onto a column.

Estimation of Methanol. Methanol was estimated by measurement of g.l.c. peak area using n-propanol as a reference standard. A Carbowax on fluoropak 80 column (144 x ¼ in; helium flow rate: 80 ml.min^{-1}) at 90° separated diethyl ether, methanol and n-propanol with retention times 90,315 and 695 sec, respectively. Peak areas were obtained by cutting out the chromatographic peaks and weighing them on a high precision analytical balance. The calibration curve is shown in Figure 2.5 and covers the molar ratio methanol : n-propanol from 0.36 to 0.72. The graph extrapolates through zero.

Estimation of Ethanol. Ethanol was estimated by measurement of peak area using n-propanol as a reference standard. The Carbowax on fluoropak 80 column (144 x ¼ in; helium flow rate: 95 ml.min^{-1}) at 85° separated diethyl ether, ethanol and n-propanol with retention times 90,360 and 675 sec, respectively. The calibration curve is shown in Figure 2.6.

Figure 2.5

G.L.C. CALIBRATION CURVE FOR
ESTIMATION OF METHANOL.

Figure 2.6

G.L.C. CALIBRATION CURVE FOR
ESTIMATION OF ETHANOL.

CHAPTER III

THE THERMAL DECOMPOSITIONS OF
ETHYL N-METHYL-N-PHENYLCARBAMATE,
ISOPROPYL N,N-DIMETHYLCARBAMATE, and
tert-BUTYL N,N-DIMETHYLCARBAMATE.

TERMINOLOGY

The following abbreviations are used

EMPC = Ethyl N-methyl-N-phenylcarbamate

PMMC = Isopropyl N,N-dimethylcarbamate

BMMC = *tert*-Butyl N,N-dimethylcarbamate

The thermal decompositions of ethyl N-methyl-N-phenyl-carbamate, isopropyl N,N-dimethylcarbamate, and *tert*-butyl N,N-dimethylcarbamate are considered together in this chapter for convenience. They each display a similar behaviour, have a corresponding reaction stoicheiometry, and follow similar reaction kinetics.
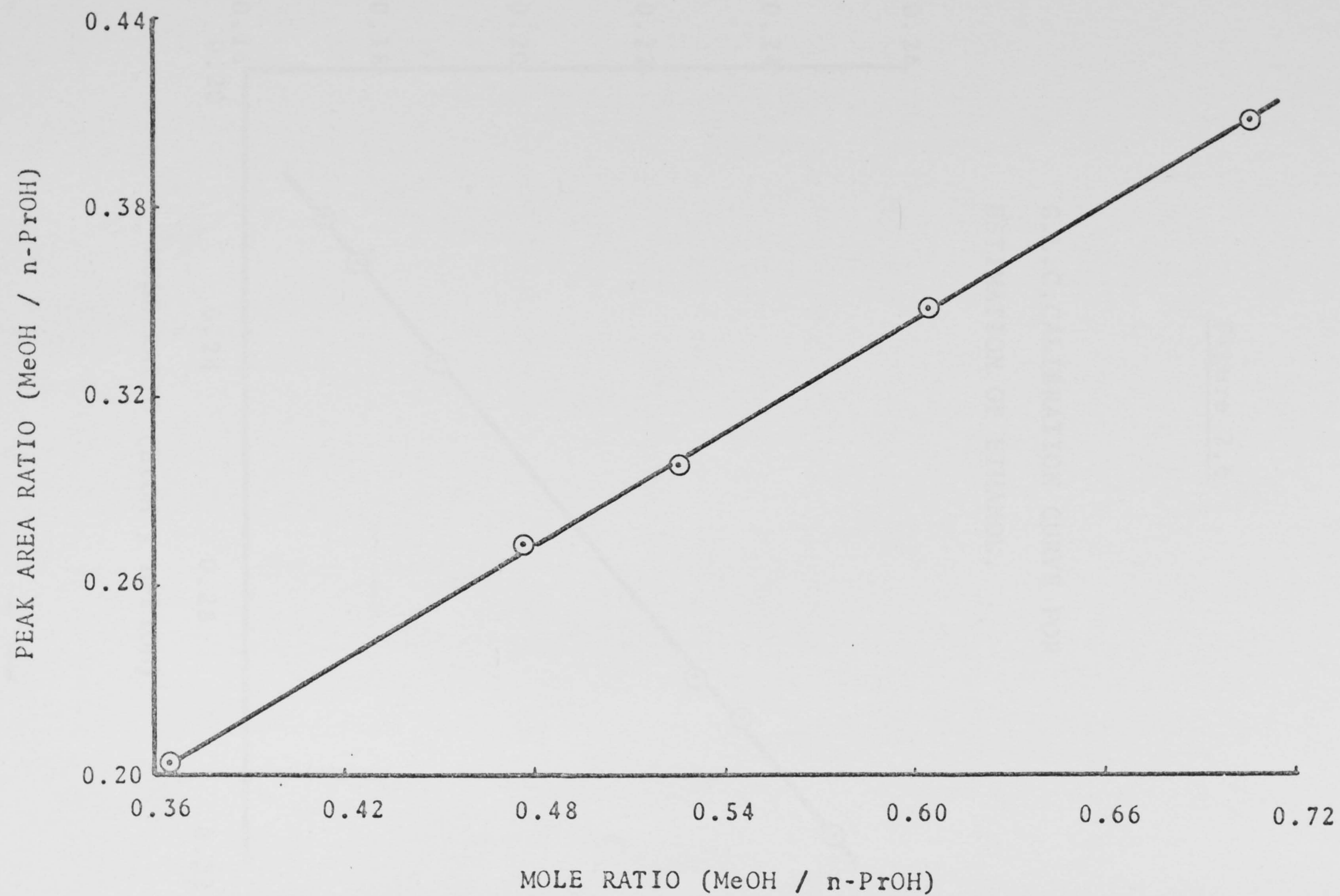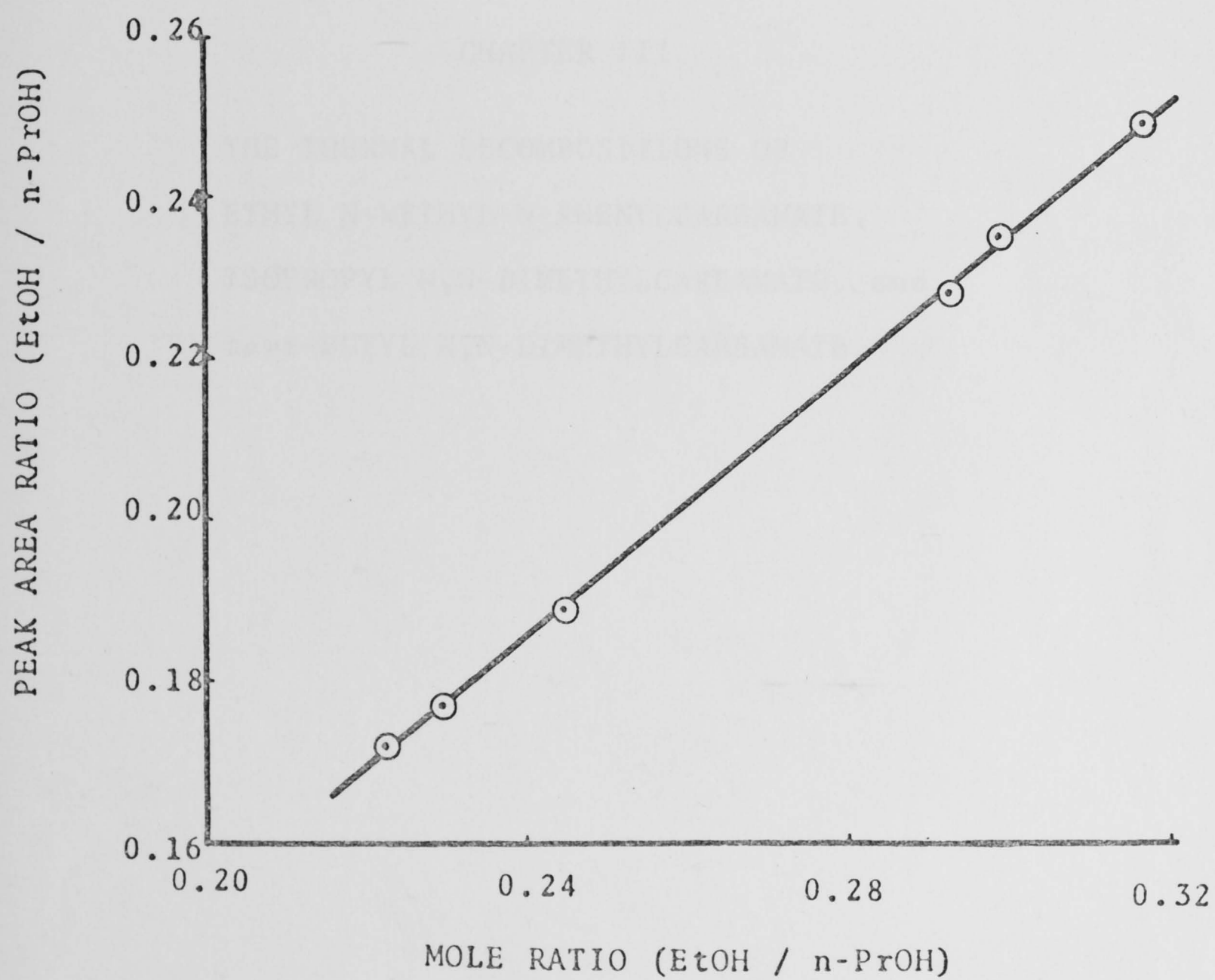
(A) Materials

The materials used in the studies were prepared and purified in the following manner:

Ethyl N-methyl-N-phenylcarbamate was prepared from ethyl chloroformate and N-methylaniline by a method analogous to that of Hartman and Brethen[87] for the preparation of ethyl N-methyl-carbamate. After fractionation through a 6-in. column of Fenske helices, the compound had b.p. $120°/13$ mm and n_D^{20} 1.5157 (lit.[88] $136-139°/20$ mm) (Found: C, 67.1; H, 7.2; N, 7.5. Calc. for $C_{10}H_{13}NO_2$: C, 67.0; H, 7.3; N, 7.8%).

Isopropyl N,N-dimethylcarbamate was prepared from isopropyl chloroformate (Pfaltz and Bauer, Inc.) and dimethylamine. After fractionation the compound had b.p. $52\pm0.2°/12$ mm and n_D^{20} 1.4125 (no literature values are available) (Found: C, 55.1; H, 10.2; N, 10.8. Calc. for $C_6H_{13}NO_2$: C, 54.9; H, 10.0; N, 10.7%).

tert-Butyl N,N-dimethylcarbamate was prepared by a method analogous to that of McLamore, P'An and Bavley[89] for the preparation of carbamates of tertiary acetylenic carbinols.

tert-Butyl alcohol (30 gm) was added to 60 gm of phenyl chloroformate (prepared from phosgene and phenol[90]) in 150 ml of anhydrous pyridine at 0°. To an ether solution of the resultant mixed carbonate was added 200 ml of liquid dimethylamine and the

mixture was stirred at the reflux temperature (Dry-Ice condenser) for 12 hr. After fractionation through an 18-in. spinning band column, the compound had b.p. 44-45°/13-14 mm and n_D^{20} 1.4163 (Found: C, 58.0; H, 10.3; N, 9.6. Calc for $C_7H_{15}NO_2$: C, 57.9; H, 10.4; N, 9.6%). N.m.r. spectrum* ($CDCl_3$): δ 1.53 (9H, singlet, C-methyl protons), 2.93 (6H, singlet, N-methyl protons). The n.m.r. spectrum is shown in Figure 3.1. t-Butyl N,N-dimethyl-carbamate has not been prepare before. In addition to the micro-analyses which lead to the correct empirical formula, and the n.m.r. spectrum which confirms the structure, the mass spectrum has been recorded using a Varian CH7 instrument and is now reported. The spectrum was obtained with an ionization potential of 70eV, an ion current of 3.5 pA and shows peaks at m/e 145 (relative abundance 15%), 130(4%), 90(30%), 89(8%), 86(8%), 72(60%), 58(9%), 57(100%), 56(9%), 45(32%), 44(26%), 43(13%), 42(15%), 41(40%), 32(8%), 31(11%), 29(26%) and 28(13%).

The instability of t-BuOCOCl at room temperature makes the preparation of this carbamate by the method of Hartman and Brethen impossible.

Ethylene (C.I.G.) was introduced into the vacuum line, outgassed, and purified by several distillations through a trap cooled in an acetone/dry ice mixture and stored in a 5-litre bulb. No impurities were detected by g.l.c. analysis.

Carbon dioxide (C.I.G.) and Nitrous oxide (C.I.G; Medical grade) were treated in the same way as ethylene and stored in 5-litre bulbs.

Cyclohexene (B.D.H. Laboratory Reagent) was freed from peroxides by shaking with dilute acidified ferrous sulphate, washed with

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* δ in p.p.m. (at 33.4° and 60 M.H.z). Internal standard Me_4Si.

Figure 3.1

N.m.r. spectrum of

tert-Butyl N,N-dimethylcarbamate.
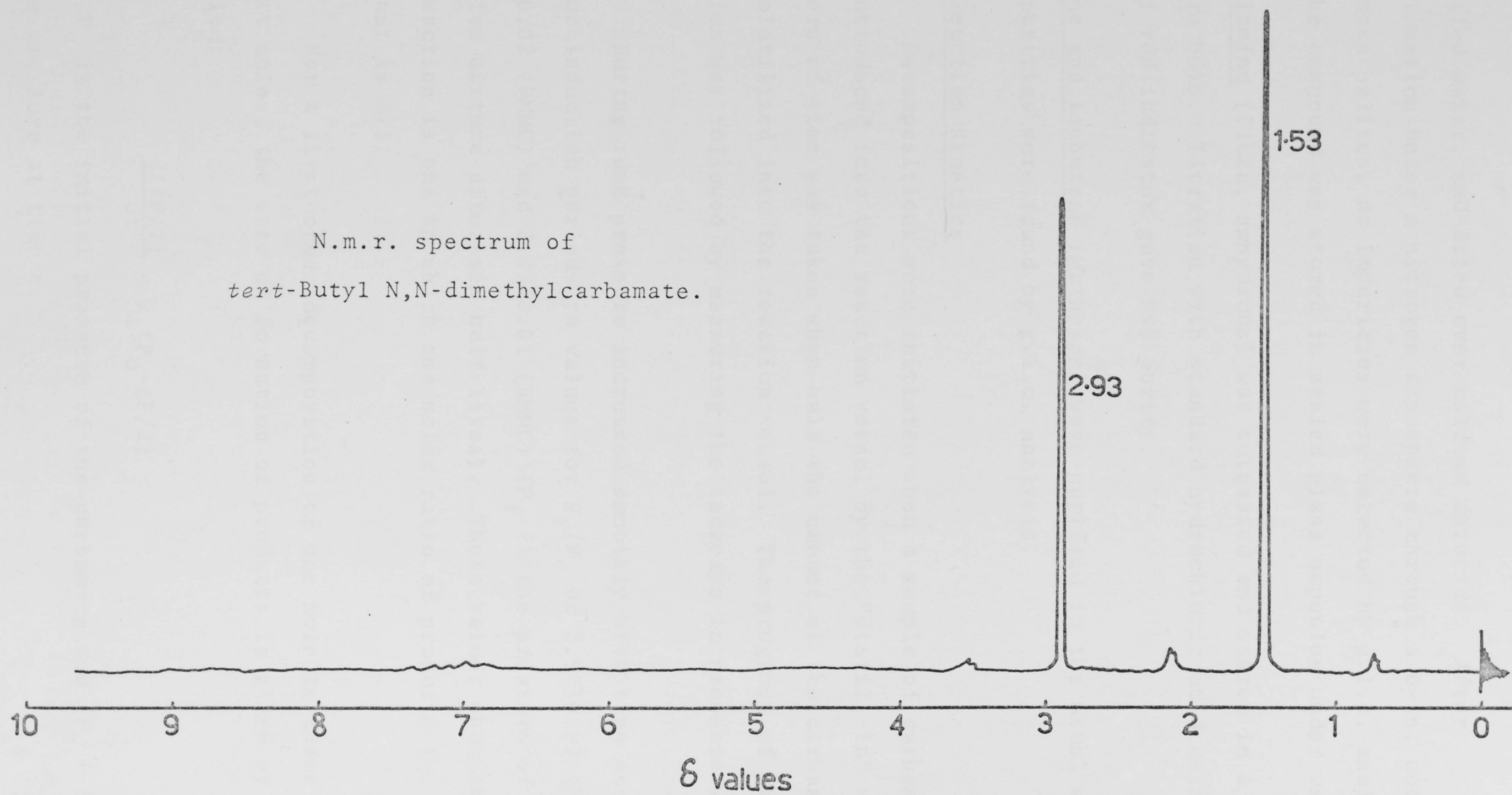
distilled water, and dried over calcium chloride. After
fractionation under a nitrogen atmosphere through a 6-in. column
of Fenske helices, no impurities were detected by g.l.c. analysis
and the compound was stored in sealed glass ampoules under vacuum.

Methylamine (Fluka, anhydrous) was outgassed and stored in a
5-litre bulb. Titration with standard hydrochloric acid using
methyl red indicator gave 99% purity.

Propene and Isobutene (Matheson) were purified in the usual manner.
No impurities were found by g.l.c. analysis.

(B) Reaction Kinetics

Decompositions were initiated when a sample of carbamate
was introduced into the reaction vessel by the "distill-in" method.
The zero of time was taken when half the amount of the carbamate
was volatilized into the reaction vessel. The progress of each
reaction was followed by measuring the increase in pressure with
time.

During runs pressure increased smoothly with time and
without induction periods to values for P_f/P_o of $2.97^{\pm}0.02$ (EMPC),
$2.96^{\pm}0.02$ (PMMC) and $2.97^{\pm}0.01$ (BMMC) (P_f is the pressure of the
reaction mixture after six half-lives). These values show that
the reaction is one in which the molar ratio of products to
reactant is 3:1.

For a first-order decomposition of one mole to three
product moles, the rate of formation of products is given by the
equation:

$$\frac{d(\Delta P/2)}{dt} = k_1(P_o - \Delta P/2)$$

where P_o is the initial pressure of the carbamate and $(P_o + \Delta P)$
is the pressure at time t.

Integrating this equation leads to:

$$\ln\left(\frac{P_O}{P_O - \Delta P/2}\right) = k_1 t$$

or $\qquad \log (P_O - \Delta P/2) = \dfrac{-k_1 t}{2.303} + \log P_O$

For each of the three carbamates discussed in this chapter the first-order rate constants (k_1) were obtained from the slopes of the plots of $\log (P_O - \Delta P/2)$ against time. A typical pressure-time curve (broken line) and first-order log-plot to 59% reaction for the decomposition of 132.0 mm of ethyl N-methyl-N-phenyl-carbamate (Table 3.1) at 360.2° are shown in Figure 3.2. The data in Table 3.1 point up the method of calculation employed. The pressure at zero time is obtained by extrapolation, usually from about t∿0.5 min. Rather than calculate the appropriate log term for each set of pressure-time values, the results were described by a smooth curve, and pressures for selected times were read off and log terms calculated. Figures 3.3 and 3.4 are typical and show that the decompositions of isopropyl and *tert*-butyl N,N-dimethylcarbamates follow the first-order rate law to *ca.* 60% reaction, i.e., as far as reactions were followed kinetically.

The rates of decomposition of each of the carbamates were measured over a 50-60° temperature range and at each temperature for a five- or sixfold variation in the initial pressure. Rate constants calculated from these data are reported in Table 3.9 (EMPC), Table 3.10 (PMMC), and Table 3.11 (BMMC), and are independent of the initial pressure which confirms the kinetic order of the reactions.

(C) Product Identification.

The products of the reactions were identified using gas-liquid chromatography and mass spectrometry. Results obtained

Figure 3.2
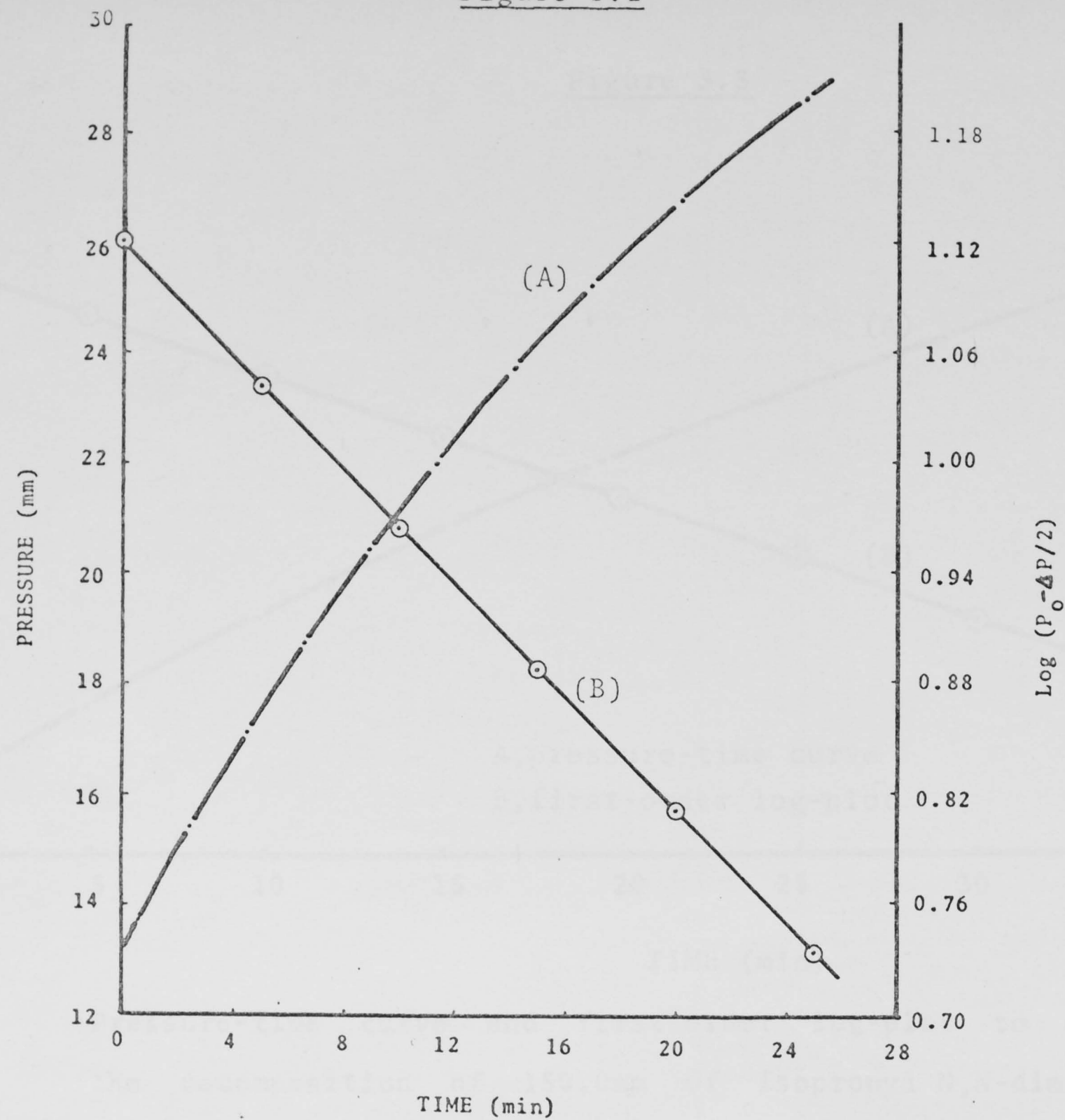
Pressure-time curve and first-order log-plot to 59% reaction for the decomposition of 132.0mm Of Ethyl N-methyl-N-phenyl-carbamate at 360.2°

A,pressure-time curve
B,first-order log-plot

Figure 3.3
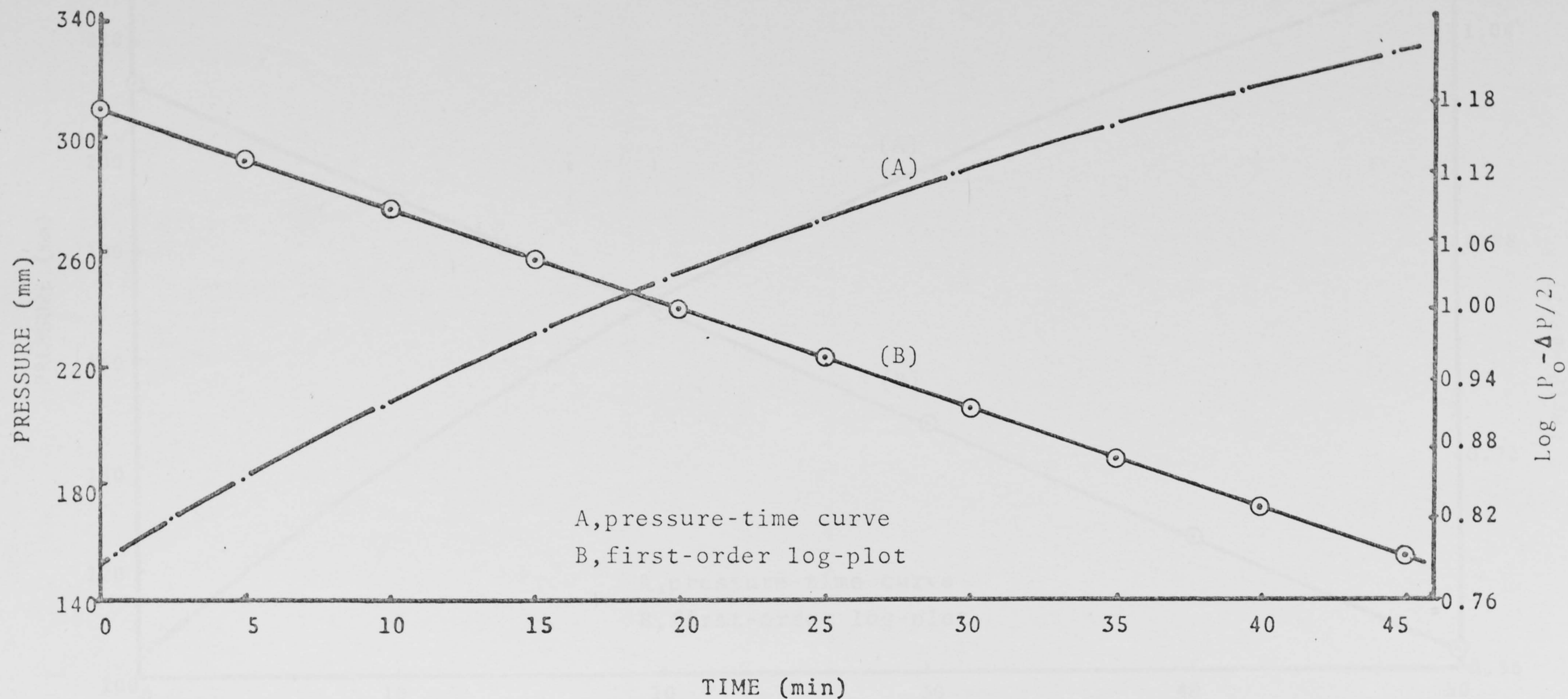
Pressure-time curve and first-order log-plot to 59% reaction for
the decomposition of 150.0mm of Isopropyl N,N-dimethylcarbamate at 299.6°

Figure 3.4

A,pressure-time curve
B,first-order log-plot
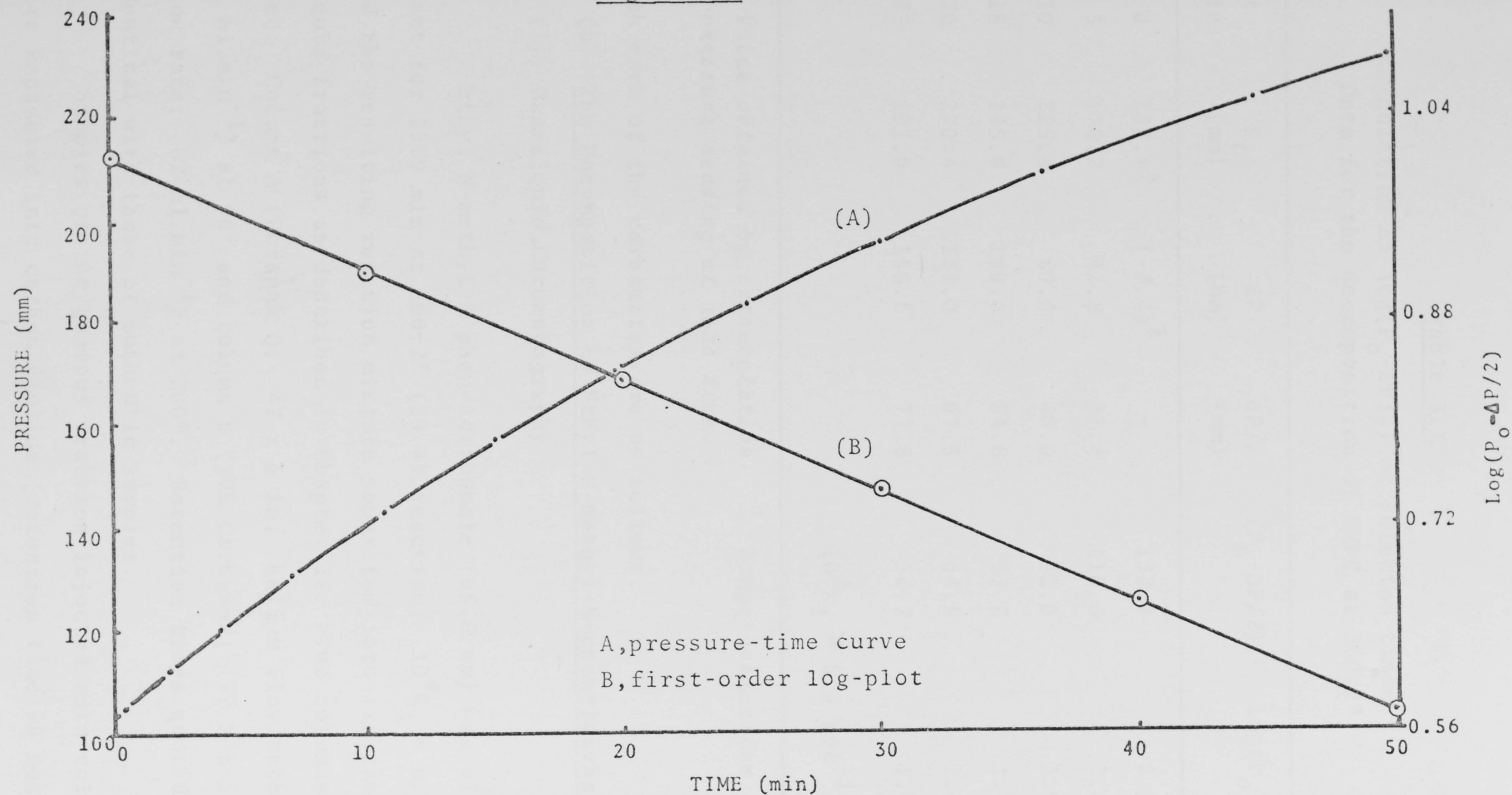
Pressure-time curve and first-order log-plot to 63% reaction for
the decomposition of 102.2mm of t-Butyl N,N-dimethylcarbamate at 231.9°

Table 3.1

Calculation of $\log(P_o - \Delta P/2)$ at selected times.
Data for the decomposition of EMPC at 360.2°

t (min)	P_t (mm)	ΔP (mm)	$\Delta P/2$ (mm)	$(P_o - \Delta P/2)$	$\log(P_o - \Delta P/2)$
0	135.4[a]	(-3.4)[b]	-	132.0	2.1206
5	178.2	42.8	21.4	110.6	2.0437
10	215.4	80.0	40.0	92.0	1.9638
15	245.0	109.6	54.8	77.2	1.8876
20	270.4	135.0	67.5	64.5	1.8096
25	291.0	155.6	77.8	54.2	1.7340

$$10^4 k_1 = 5.9 \ sec^{-1}$$

[a] *Value obtained by extrapolation.* [b] *Gauge correction applied to pressure reading at zero time.*

with each of the carbamates are as follows:

(a) The Decomposition of Ethyl N-methyl-N-phenylcarbamate.

(i) Gas-liquid Chromatography

Ethyl N-methyl-N-phenylcarbamate (95.6 mm) was allowed to react for 25.0 min at 360.2° (59.4% reaction; $10^4 k_1 = 6.0 \ sec^{-1}$), and the resulting reaction mixture separated into its gaseous and liquid fractions as described in Chapter II. Two columns were used: Column A (Porapak Q; 42 x ¼ in; helium flow rate: 65 ml.min^{-1}) at 50° and column B (20% Carbowax; 72 x ¼ in; helium flow rate: 62 ml.min^{-1}) at 200°. Retention times quoted were identical with those of authentic samples.

Samples of the gaseous fraction injected onto column A were separated into carbon dioxide (retention time 90 sec) and

ethylene (145 sec). Samples of the liquid fraction injected onto column B were separated into N-methylaniline (180 sec) and unreacted ethyl N-methyl-N-phenylcarbamate (315 sec). Further analyses led to similar results.

(ii) Mass Spectrometry.

In a series of determinations the carbamate was allowed to react at 360.2° for a suitable time, and the reaction mixture was separated into gaseous and liquid fractions as before. The gaseous fraction of the reaction mixture was connected to the inlet system of an A.E.I. MSIO mass spectrometer (ion current: 50µA; ionization potential: 70eV) and the mass spectrum obtained (Figure 3.5). The peak at m/e 44 is the parent peak for carbon dioxide. The remainder of the spectrum can be attributed to the fragmentation of ethylene (parent peak: m/e 28).

When the liquid fraction of the reaction mixture was separated by g.l.c., the compound with retention time 180 sec was collected (in a capillary U-bend held at -80°) as it was eluted from the column. Its mass spectrum (Figure 3.6) showed prominent peaks at m/e 107 (relative abundance 82%), 106(100%), 79(17%), 77(29%), 65(9%), 51(21%), and 39(13%) and corresponds to that for an authentic sample of N-methylaniline[91].

Thus both mass spectrometric analysis and gas-liquid chromatographic methods show that the detectable products are N-methylaniline, carbon dioxide and ethylene, and the reaction for the decomposition is:

$$PhN(Me)COOC_2H_5 \longrightarrow PhNHMe + CO_2 + C_2H_4$$
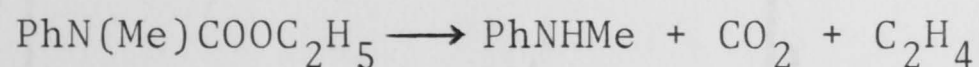
(b) The Decomposition of Isopropyl N,N-dimethylcarbamate.

(i) Gas-liquid Chromatography.

Isopropyl N,N-dimethylcarbamate (116.8 mm) was allowed to

Figure 3.5

MASS SPECTRUM OF THE GASEOUS FRACTION
FROM THE DECOMPOSITION OF EMPC.
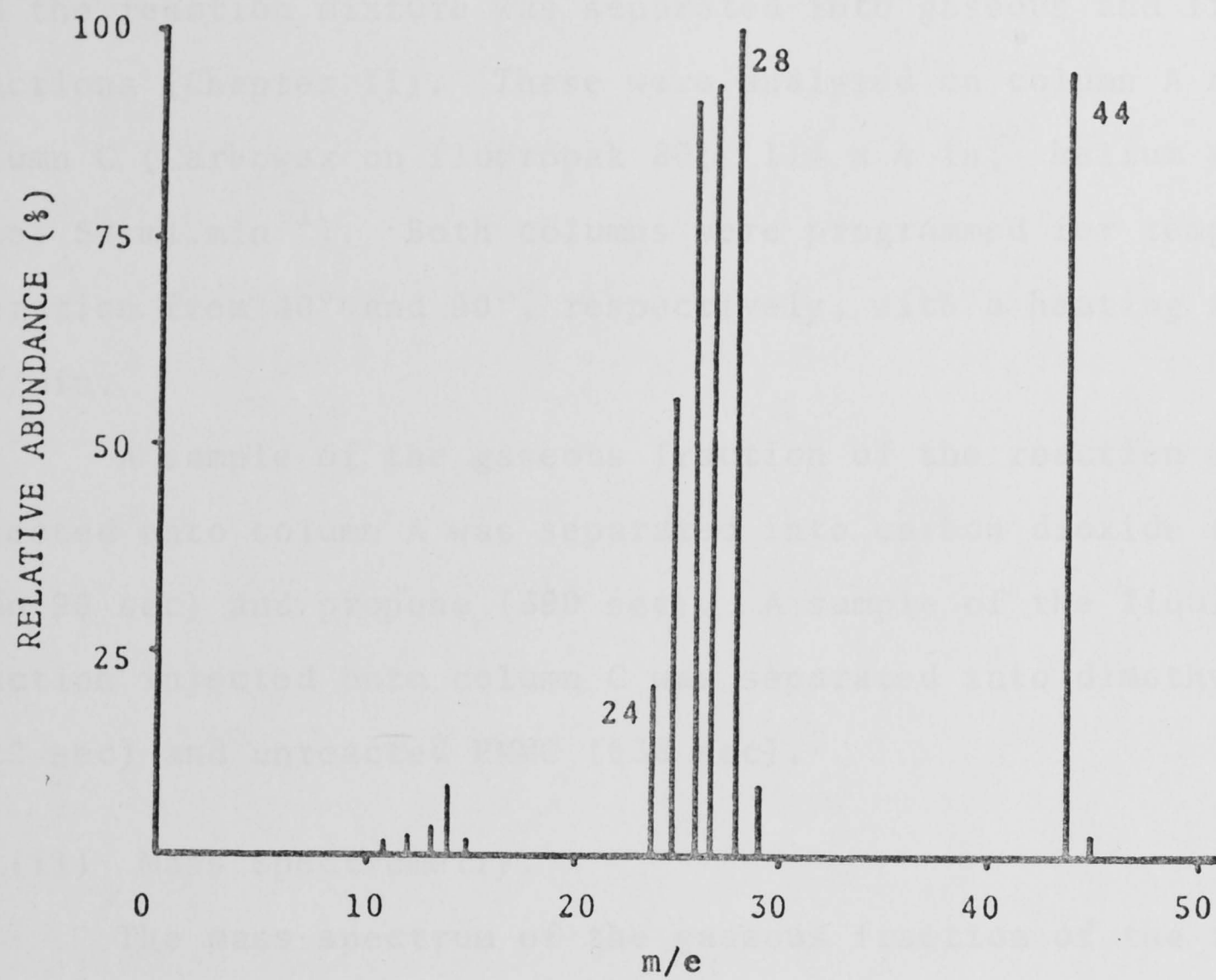
Figure 3.6
MASS SPECTRUM OF THE COMPOUND SEPARATED BY G.L.C.
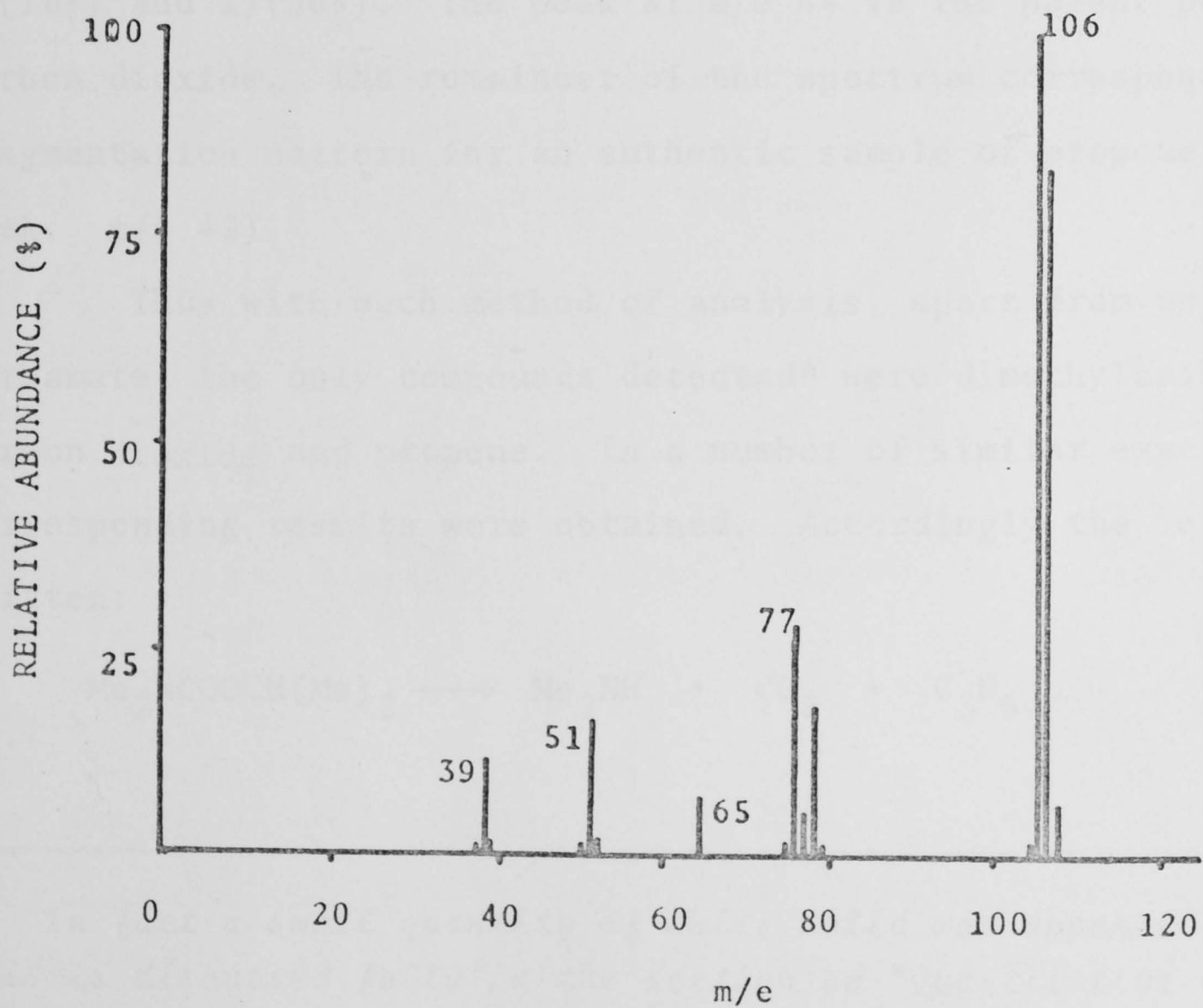
react for 45 min at 299.6° (59.3% reaction; $10^4k_1 = 3.3 \text{ sec}^{-1}$) and the reaction mixture was separated into gaseous and liquid fractions (Chapter II). These were analysed on column A and column C (Carbowax on fluoropak 80; 114 x ¼ in; helium flow rate: 58 ml.min^{-1}). Both columns were programmed for temperature operation from 40° and 90°, respectively, with a heating rate of 12°/min.

A sample of the gaseous fraction of the reaction mixture injected onto column A was separated into carbon dioxide (retention time 90 sec) and propene (390 sec). A sample of the liquid fraction injected onto column C was separated into dimethylamine (112 sec) and unreacted PMMC (638 sec).

(ii) Mass Spectrometry.

The mass spectrum of the gaseous fraction of the reaction mixture is shown in Figure 3.7 and had peaks at m/e 44 (relative abundance 68%), 42(70%), 41(100%), 40(32%), 39(83%), 38(25%), 37(18%) and 27(36%). The peak at m/e 44 is the parent peak for carbon dioxide. The remainder of the spectrum corresponds to the fragmentation pattern for an authentic sample of propene (parent peak: m/e 42).

Thus with each method of analysis, apart from unreacted carbamate, the only compounds detected* were dimethylamine, carbon dioxide and propene. In a number of similar experiments corresponding results were obtained. Accordingly the reaction is written:

$$Me_2NCOOCH(Me)_2 \longrightarrow Me_2NH + CO_2 + C_3H_6$$

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* *In fact a small quantity of white solid was apparent but this is discussed fully in the section on "Quantitative analysis" in this chapter.*

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(c)   The Decomposition of *tert*-Butyl N,N-dimethylcarbamate

(i)   Gas-liquid Chromatography

tert-Butyl N,N-dimethylcarbamate (70.6 mm) was allowed to react for 50 min at 231.9° (62.9% reaction; $10^4 k_1 = 3.3$ sec^{-1}) and the reaction mixture was separated into gaseous and liquid fractions (Chapter II) which were analysed on column A (Porapak Q; 42 x ¼ in; helium flow rate: 53 $ml.min^{-1}$) and column C (Carbowax on fluoropak 80; 144 x ¼ in; helium flow rate: 95 $ml.min^{-1}$). Both columns were programmed for temperature operation from 45° and 90° with a heating rate of 18°/min and 12°/min, respectively.

A sample of the gaseous fraction of the reaction mixture injected onto column A was separated into carbon dioxide (90 sec) and isobutene (485 sec). A sample of the liquid fraction injected onto column C was separated into dimethylamine (95 sec) and unreacted BMMC (600 sec). No other compounds were detected.*

(ii) Mass Spectrometry.

The mass spectrum (Figure 3.8) of the compound separated by column C with retention time 95 sec showed prominent peaks at m/e 45 (relative abundance 45%), 44(100%), 43(17%), 42(14%), 28(22%) and 18(11%) which corresponds to the spectrum for an authentic sample of dimethylamine.[92]

The results of a number of qualitative analyses which used both g.l.c. and mass-spectrometric techniques give similar results to those outlined and lead to the conclusion that the reaction is:

$$Me_2NCOOC(Me)_3 \longrightarrow Me_2NH + CO_2 + i\text{-}C_4H_8$$
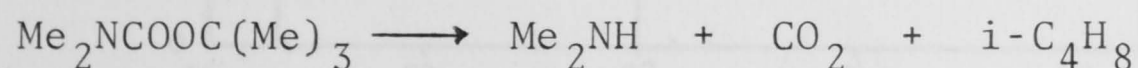
(D)   Quantitative Analyses.

Rates of reaction have been obtained by monitoring the rates of increase of pressure and interpreting these in terms of

* *See footnote on preceding page.*

Figure 3.7

MASS SPECTRUM OF GASEOUS FRACTION
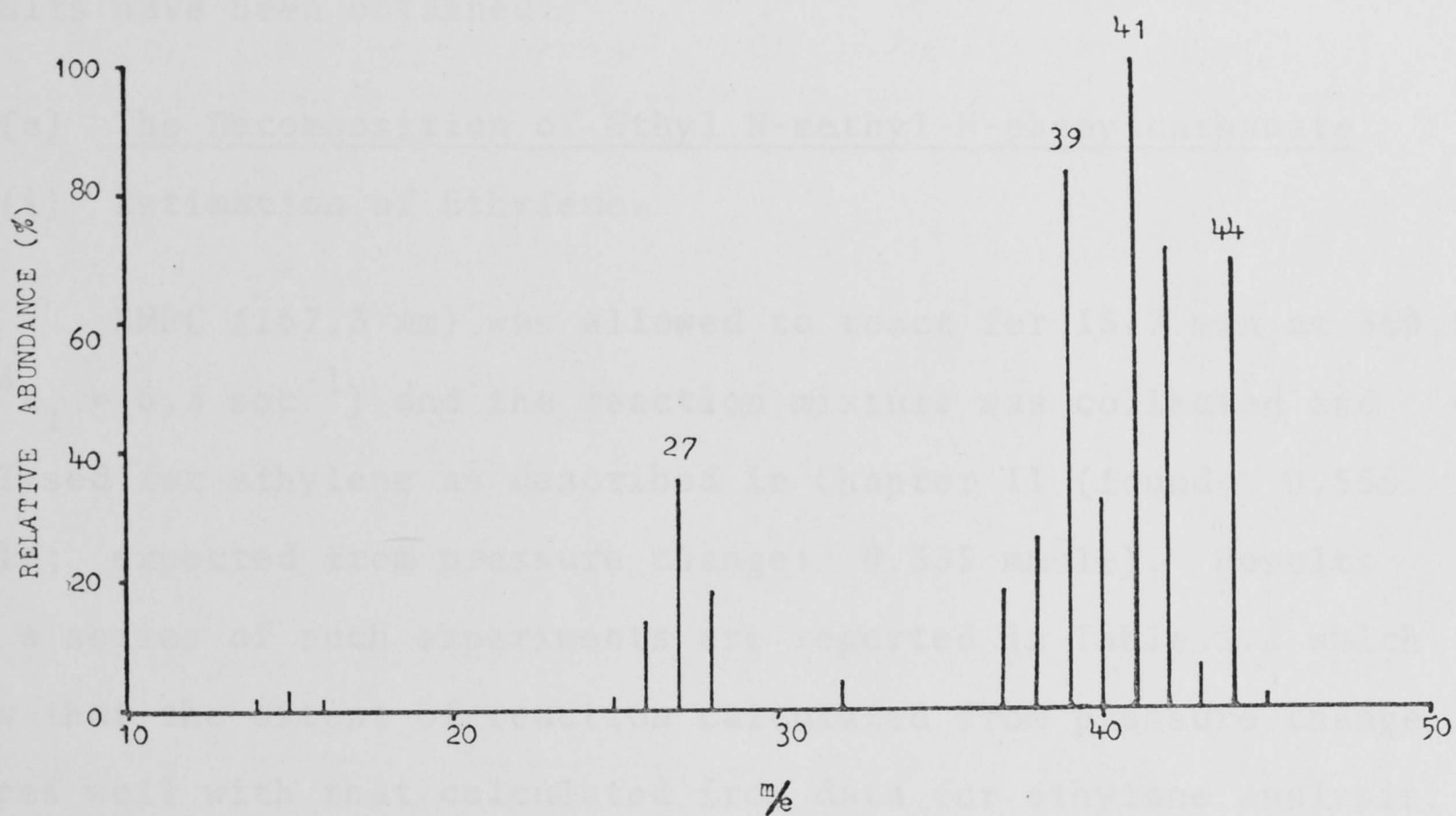
Figure 3.8

MASS SPECTRUM OF DIMETHYLAMINE SEPARATED BY G.L.C.
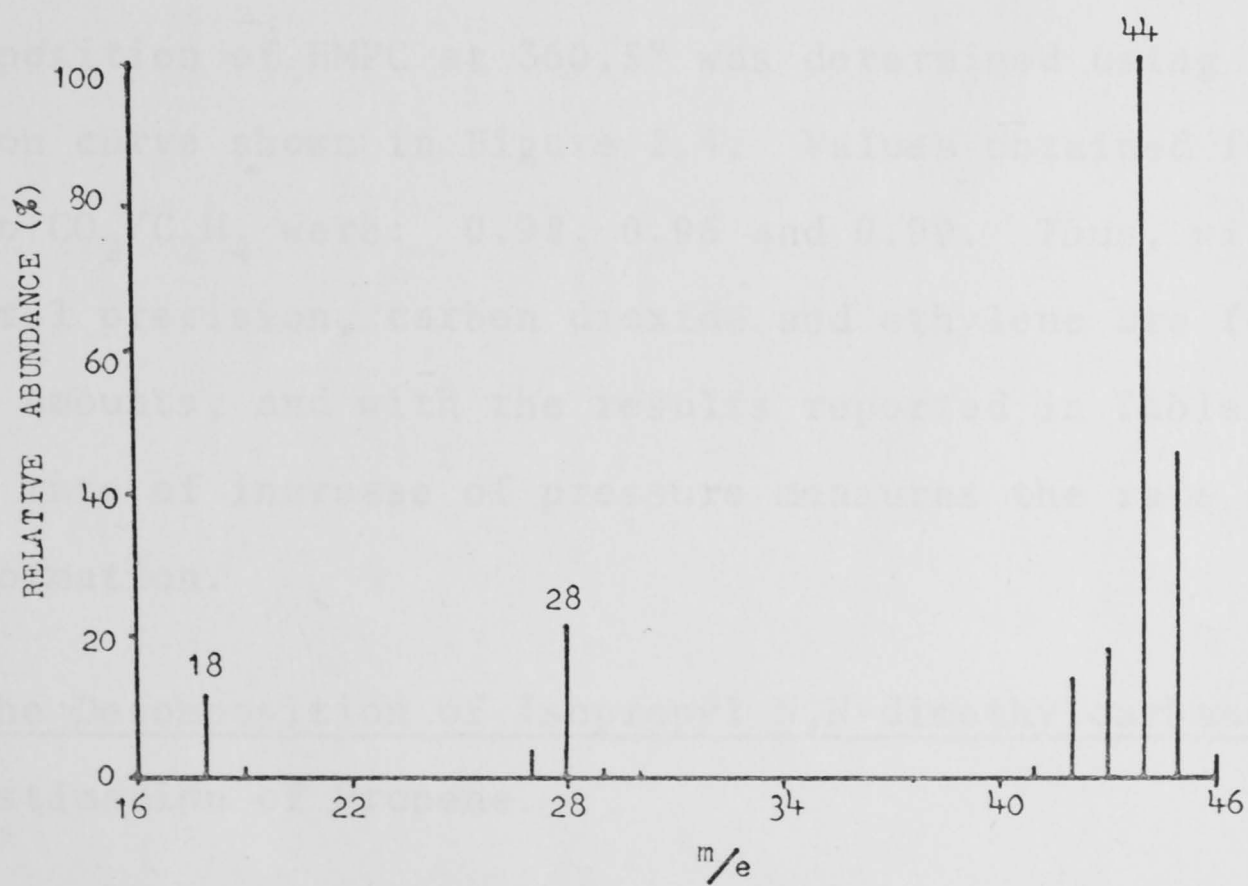
the stoicheiometry in which one mole of reactant generates three moles of products. Analytical determinations carried out for a number of such runs show that the rates of pressure change correspond to rates of formation of the products. The following results have been obtained:

(a) The Decomposition of Ethyl N-methyl-N-phenylcarbamate

(i) Estimation of Ethylene.

EMPC (167.3 mm) was allowed to react for 15.7 min at 360.5° $(10^4 k_1 = 6.3 \ sec^{-1})$ and the reaction mixture was collected and analysed for ethylene as described in Chapter II (found: 0.556 mmole; expected from pressure change: 0.555 mmole). Results for a series of such experiments are reported in Table 3.2 which show that the extent of reaction calculated from pressure change agrees well with that calculated from data for ethylene analysis.

(ii) Determination of the mole ratio CO_2/C_2H_4.

The mole ratio of carbon dioxide to ethylene produced by the decomposition of EMPC at 360.5° was determined using the calibration curve shown in Figure 2.4. Values obtained for the mole ratio CO_2/C_2H_4 were: 0.98, 0.96 and 0.99. Thus, within experimental precision, carbon dioxide and ethylene are formed in equimolar amounts, and with the results reported in Table 3.2 show that rate of increase of pressure measures the rate of carbon dioxide formation.

(b) The Decomposition of Isopropyl N,N-dimethylcarbamate

(i) Estimation of Propene.

PMMC (181.8 mm) was allowed to react for 24.0 min at 299.6° $(10^4 k_1 = 3.3 \ sec^{-1})$ and the reaction mixture collected and analysed for propene as described in Chapter II (found: 0.563

Table 3.2

DECOMPOSITION OF ETHYL N-METHYL-N-PHENYLCARBAMATE AT 360.5°.
Comparison of extents of reaction determined by pressure
change and by ethylene analysis.

P_o [a] (mm)	P_o (mmol)	$10^4 k_1$ (sec^{-1})	Reaction(%) by Pressure	Ethylene (mmol) Calc.	Found	Reaction(%) by Ethylene Anal.
176	1.31	6.2	20.8	0.272	0.273	20.8
195	1.45	6.3	27.4	0.398	0.413	28.5
167	1.24	6.3	29.0	0.361	0.369	29.8
182	1.36	6.2	33.0	0.447	0.450	33.1
167	1.24	6.3	44.7	0.555	0.556	44.8
166	1.24	6.2	50.9	0.629	0.640	51.6
165	1.23	6.1	59.7	0.733	0.750	61.0
146	1.09	6.2	61.5	0.669	0.674	61.8

[a] P_o is the initial pressure of EMPC.

Table 3.3

DECOMPOSITION OF ISOPROPYL N,N-DIMETHYLCARBAMATE AT 299.6°.
Comparison of extents of reaction determined by pressure
change and by analyses for propene.

P_o [a] (mm)	P_o (mmol)	$10^4 k_1$ (sec^{-1})	Reaction(%) by Pressure	Propene (mmol) Calc.	Found	Reaction(%) by Propene Anal.
205	1.69	3.3	18.1	0.306	0.310	18.3
177	1.46	3.4	19.9	0.291	0.288	19.7
188	1.55	3.4	25.0	0.388	0.383	24.7
159	1.31	3.3	28.0	0.367	0.357	27.3
182	1.50	3.3	35.8	0.536	0.533	35.5
182	1.50	3.3	37.8	0.567	0.563	37.5
164	1.35	3.2	39.2	0.529	0.511	37.9
168	1.38	3.3	44.6	0.619	0.612	44.3
162	1.33	3.3	50.9	0.679	0.694	52.2
150	1.24	3.3	54.4	0.672	0.659	53.1
152	1.25	3.3	58.8	0.736	0.719	57.5

[a] P_o is the initial pressure of PMMC.

mmole; expected by pressure change: 0.567 mmole). Analytical results are summarised in Table 3.3. The correlation between propene calculated from pressure data with that found by analysis establishes that the rate of pressure change measures the rate of propene formation.

(ii) Estimation of Dimethylamine

PMMC (173.9 mm) reacted for 35.0 min at 299.6° ($10^4 k_1$ = 3.3 sec^{-1}) and the reaction mixture was collected at -196° and transferred to a tap-vessel. Distilled water was added through a serum cap with a hypodermic syringe and the solution shaken. The serum cap was removed and the dimethylamine was titrated with 0.05M hydrochloric acid using methyl red as the indicator. Results are shown in Table 3.4. Control runs were carried out in which PMMC was collected in the tap-vessel without having been heated in the reaction vessel, and no titre with hydrochloric acid was obtained.

The decomposition of PMMC is believed to follow a stoicheiometry which produces a molar ratio of CO_2/Me_2NH = 1. In control runs, equal pressures of carbon dioxide and dimethylamine were collected in a tap-vessel, distilled water added, and the amine titrated. The control experiments (Table 3.5) showed amounts of amine determined were 1.5% less than the theoretical amounts. This effect may be explained by the presence of residual carbon dioxide during the determinations[93]. This correction was applied to the results reported in Table 3.4.

(iii) Estimation of Carbon dioxide.

PMMC (145.1 mm) was allowed to react for 23.5 min at 299.6° ($10^4 k_1$ = 3.3 sec^{-1}) and the reaction mixture collected at -196° and transferred to a tap-vessel. The carbon dioxide was

Table 3.4

DECOMPOSITION OF ISOPROPYL N,N-DIMETHYLCARBAMATE AT 299.6°.
Comparison of extents of reaction determined by pressure
change and by dimethylamine analysis.

P_o[a] (mm)	P_o (mmol)	$10^4 k_1$ (sec^{-1})	Reaction(%) by Pressure	[b]DMA (mmol) Calc.	Found[c]	Reaction(%) by Anal.
168	1.38	3.3	28.8	0.397	0.388	28.1
182	1.50	3.3	45.0	0.675	0.655	43.7
194	1.59	3.3	45.0	0.716	0.696	43.8
174	1.43	3.3	49.6	0.710	0.689	48.2
144	1.19	3.3	52.8	0.628	0.615	51.7
134	1.10	3.3	55.0	0.605	0.589	53.5
148	1.22	3.3	59.1	0.721	0.706	57.9

[a] *Initial pressure of PMMC.* [b] *DMA denotes dimethylamine.*
Correction factor of 1.5% included in these results (see text).

Table 3.5

Press. dimethylamine added (mm)	Press. carbon dioxide added (mm)	Press. dimethylamine by titration (mm)
72.0	71.3	71.1
71.5	70.3	70.3
84.0	83.1	82.6

Table 3.6

DECOMPOSITION OF ISOPROPYL N,N-DIMETHYLCARBAMATE AT 299.6°.
G.L.C. ANALYSIS FOR CARBON DIOXIDE

P_o[a] (mm)	$10^4 k_1$ (sec^{-1})	ΔP (mm)	CO_2 (mm) Calc.	Found	CO_2 by Analysis (% of calc. amount)
202.0	3.3	104.6	52.3	37.6	71.9
117.8	3.2	112.2	56.1	41.7	74.3
145.1	3.3	107.8	53.9	42.1	78.1
167.2	3.3	127.2	63.6	48.1	75.6

[a] P_o *is the initial pressure of PMMC.*

quantitatively analysed by g.l.c. peak-heights using ethylene as a marker. The calibration curve presented in Figure 2.4 was used. The results reported in Table 3.6 show that only ca.70-80% of the amount of carbon dioxide anticipated from pressure change data is recovered. A similar effect was observed in the study of *tert*-butyl N,N-dimethylcarbamate.

In control runs, approximately equal pressures of carbon dioxide and dimethylamine were measured out in the reaction vessel and mixed in a tap-vessel. A white compound was observed to form on the walls inside the tap-vessel. Analysis for carbon dioxide gave values similar to those in Table 3.6, i.e., only ca. 70-80% of the added carbon dioxide was recovered. These results are explained in terms of a reaction between carbon dioxide and the amine to form a carbamate salt and is discussed further on page 50.

(c)   The Decomposition of *tert*-Butyl N,N-dimethylcarbamate.

(i)   Estimation of Isobutene

BMMC (162.4 mm) was allowed to react for 9.3 min at 240.1° $(10^4 k_1 = 6.3 \text{ sec}^{-1})$. Isobutene was quantitatively determined by g.l.c. (Chapter II) using propene as a reference standard. The calibration curve is presented in Figure 2.3. Analytical results are reported in Table 3.7 and show excellent agreement between the extent of reaction calculated from pressure change and from isobutene analysis which establishes that the rate of isobutene formation is measured by the rate of pressure change.

(ii)   Estimation of Dimethylamine.

BMMC (148 mm) was allowed to react for 15.4 min at 240.1° $(10^4 k_1 = 6.4 \text{ sec}^{-1})$ and the reaction mixture collected and analysed for dimethylamine as described on page 46 (found: 0.593 mmol; expected by pressure change: 0.606 mmol). Analytical results are reported in Table 3.8 and established that amine

Table 3.7

DECOMPOSITION OF *tert*-BUTYL N,N-DIMETHYLCARBAMATE AT 240.1°.

Comparison of extents of reaction determined by pressure
change and by isobutene analysis.

$P_o{}^a$ (mm)	P_o (mmol)	$10^4 k_1$ (sec^{-1})	Reaction(%) by Pressure	Isobutene (mmol) Calc.	Found.	Reaction(%) by Anal.
145	1.33	6.5	21.3	0.283	0.290	21.8
187	1.72	6.4	26.9	0.463	0.473	27.5
162	1.49	6.3	29.7	0.442	0.431	28.9
127	1.67	6.3	38.5	0.643	0.650	38.9
165	1.52	6.5	43.7	0.664	0.681	44.8
144	1.32	6.4	55.3	0.730	0.740	56.1
178	1.64	6.4	61.0	1.00	1.02	62.2

a *P_o is the initial pressure of BMMC.*

Table 3.8

DECOMPOSITION OF *tert*-BUTYL N,N-DIMETHYLCARBAMATE AT 240.1°.

Comparison of extents of reaction determined by pressure
change and by dimethylamine analysis.

$P_o{}^a$ (mm)	P_o (mmol)	$10^4 k_1$ (sec^{-1})	Reaction(%) by Pressure	^{b}DMA (mmol) Calc.	Found^c	Reaction (%) by DMA Anal.
159	1.46	6.5	27.3	0.398	0.388	26.6
172	1.58	6.4	38.7	0.611	0.600	38.0
148	1.36	6.4	44.6	0.606	0.593	43.6
142	1.31	6.5	50.2	0.658	0.640	48.8
151	1.39	6.3	56.5	0.785	0.771	55.5
167	1.54	6.4	58.9	0.907	0.890	57.8

a *P_o is initial pressure of BMMC.*   b *DMA denotes dimethylamine.*

c *Correction factor of 1.5% included in these results.*

formation follows the first-order rate law and is measured by the rate constants reported.

(iii) Estimation of Carbon dioxide

BMMC (136.0 mm) was allowed to react for 25.0 min at 240.1° ($10^4 k_1$ = 6.5 sec^{-1}) and the reaction mixture collected and analysed for carbon dioxide (the procedure used is described on page 46). Essentially similar results were obtained to those reported for isopropyl N,N-dimethylcarbamate in Table 3.6 namely, only about 75% of the anticipated amount of carbon dioxide was found. The discrepancies noted between rate constants calculated from pressure data and the quantity of carbon dioxide detected analytically are considered below.

(E) Reactions involving Carbon dioxide.

With both isopropyl N,N-dimethylcarbamate and t-butyl N,N-dimethylcarbamate although analyses showed that both olefin and amine formation were measured by the rate constants calculated from pressure data, carbon dioxide by analysis was recovered in amounts *ca.* 70-80% of those anticipated from the rate constants.

When products from each of these reactions were collected it was observed that an amount of solid material was deposited in the collecting vessel. The following evidence now establishes that carbon dioxide reacts with various amines to produce a solid product.

Carbon dioxide (89.2 mm) was measured out in the reaction vessel and condensed in the capillary U-bend. A previously measured quantity of methylamine (190.1 mm) was added, and both reagents were volatilised into the reaction vessel at 320°. Total pressure was measured and found to be 279.5 mm. This value did not vary over a period of 2 hours. Eight such experiments were conducted at temperatures ranging from 215-405° and gave

corresponding results. No reaction leading to a pressure change occurs between carbon dioxide and the amine at these temperatures. Similar results were obtained when ethylamine or dimethylamine were used.

Ethylamine (246 mm) was condensed into a tap-vessel at -196° which contained carbon dioxide (119 mm). On warming to room temperature a white solid was deposited. The residual gases were pumped away and a sample of the solid was analysed:
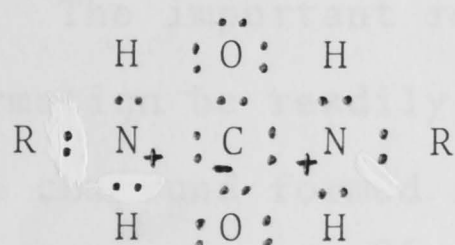
Found: C, 44.67; H, 10.59; N, 20.98%

Calc. for $C_5H_{14}N_2O_2$: C, 44.75; H, 10.52; N, 20.88%.

The evidence is interpreted in terms of the reaction

$$2C_2H_5NH_2 + CO_2 \longrightarrow C_5H_{14}N_2O_2$$
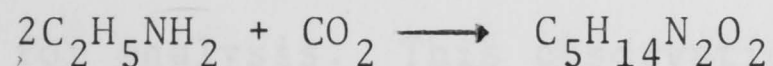
which takes place when amine and carbon dioxide are mixed at room temperature, but not at the temperatures 215-405° at which the pyrolyses of carbamates are conducted. Thus the reaction interferes only with analyses of products.

Hayashi[94] studied the physicochemical properties of the compounds formed from the reaction of a variety of amines with carbon dioxide and proposed that the compounds have the following electronic formula:

$$\begin{array}{ccccc} H & :\overset{..}{O}: & H \\ R:\overset{..}{\underset{..}{N}}_+ & :\overset{..}{\underset{..}{C}}: & \overset{..}{\underset{..}{N}}_+:R \\ H & :\overset{..}{O}: & H \end{array}$$

This formula treats both amine groups as being identical and indistinguishable by chemical reactions. However, Werner[95] considers that these compounds are substituted ammonium carbamates since he was able to prepare several substituted ammonium carbamates by replacing the amine in the electropositive group by a more basic one. Wright and Moore[96] studied the reactions of

aralkylamines with carbon dioxide and also concluded that the resulting compounds can be considered as substituted ammonium carbamates. They proposed the electronic formula:

$$\left[\begin{array}{c} H \\ \cdot\cdot \\ R : N : H \\ \cdot\cdot \\ H \end{array}\right]^{+} \left[\begin{array}{cc} :O: & H \\ \cdot\cdot\cdot\cdot & \cdot\cdot \\ C & :N: \ R \\ \cdot\cdot & \cdot\cdot \\ :O: & \end{array}\right]^{-}$$
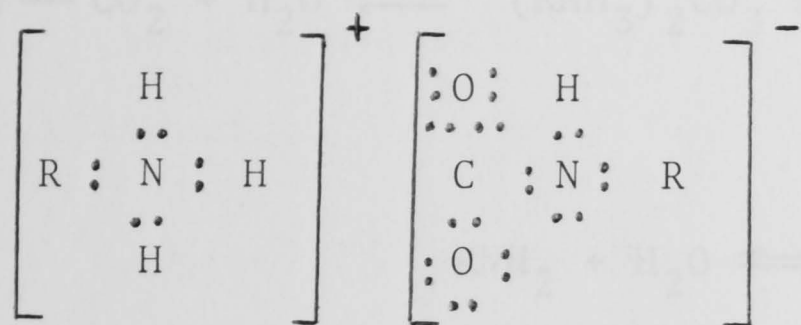
The carbon dioxide produced by the decomposition of ethyl N-methyl-N-phenylcarbamate was found to be in a 1:1 molar ratio with the amount of ethylene formed which shows that no carbon dioxide reacted with N-methylaniline when the reaction products are collected for analysis. This observation is in accord with the results of Wright and Moore[96] who show that only aromatic amines such as β-arylethylamine ($ArCH_2CH_2NH_2$) react readily with carbon dioxide.

It is noteworthy that although analyses of carbon dioxide are complicated, those of amine are not. Carbon dioxide was detected directly by g.l.c. analyses. Analyses for amine were by titration with standard acid solutions. A number of structures for the solid are possible, but the most probable is a substituted ammonium carbamate. The important requirement is that any amine removed by salt formation be readily hydrolysed under the analytical conditions. If the compound formed is a carbamate salt as favoured by Werner [95] and Wright and Moore[96], hydrolysis can occur according to the scheme:

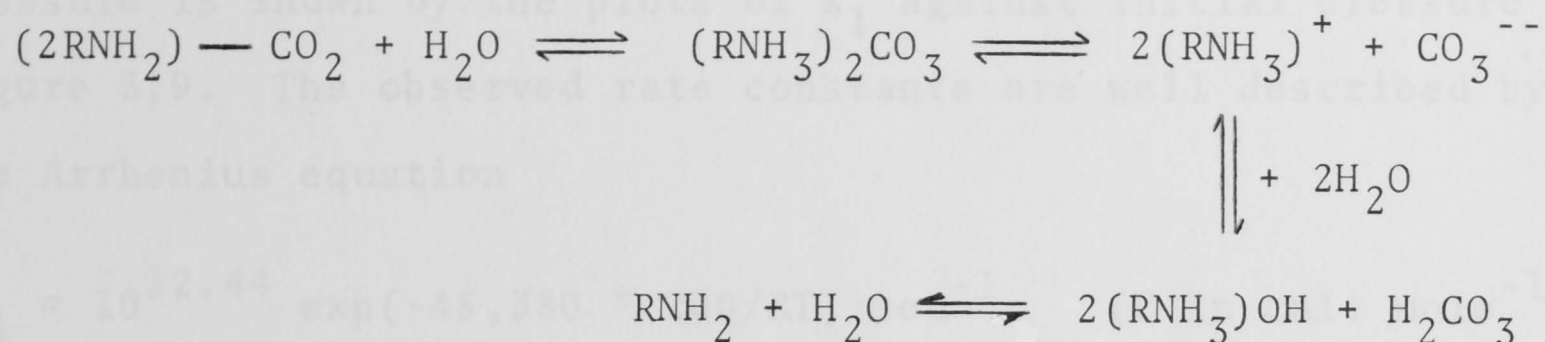$$RNHCOOH_3NR \ + \ nH_2O \longrightarrow RNHCOO^-_{(aq)} \ + \ H_3NR^+_{(aq)}$$
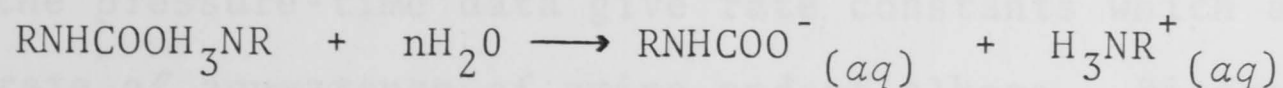
Carbamic acids are not known in the free state and decompose into carbon dioxide and amine, so that the result of the analysis will be to regenerate and estimate the amine involved in salt formation.

If on the other hand the compound is not a simple salt

but has the structure favoured by Hayashi[94], then the scheme proposed by Hayashi undoubtedly occurs.

$$(2RNH_2) - CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3 \rightleftharpoons 2(RNH_3)^+ + CO_3^{--}$$

$$\Updownarrow + 2H_2O$$

$$RNH_2 + H_2O \rightleftharpoons 2(RNH_3)OH + H_2CO_3$$

Hayashi considers that the degree of hydrolysis is large, so that the result would again be that the total amine would be estimated in the titration procedure.

Thus in the decompositions of both the *tert*-butyl- and the isopropyl N,N-dimethylcarbamate the rate of pressure change measures the rate of alkene formation and the rate of amine formation. That the analyses for carbon dioxide are lower than predicted by the rate constants is satisfactorily explained by the reaction of carbon dioxide with amine. One may speculate that the origin of the 1.5% correction factor applied to data reported in Table 3.4 may have some connection with the carbon dioxide reaction system.

(F) Summary

The results reported show that each of the carbamates decompose by a first-order process according to the general reaction:

$$Carbamate \longrightarrow Amine + Alkene + CO_2$$
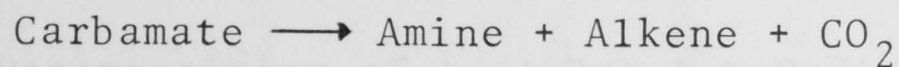
and the pressure-time data give rate constants which also measure the rate of appearance of amine and of alkene. Discrepancies apparent in determining carbon dioxide quantitatively are satisfactorily explained by the formation of the adduct with amines.

(a) The Decomposition of Ethyl N-methyl-N-phenylcarbamate.

The rate constants obtained at each temperature are

reported in Table 3.9 which also gives the variation in initial pressures. Lack of dependance of the rate constants on initial pressure is shown by the plots of k_1 against initial pressure in Figure 3.9. The observed rate constants are well described by the Arrhenius equation

$$k_1 = 10^{12.44} \exp(-45,380 \pm 200/RT) \ sec^{-1} \qquad (E \ in \ cal. \ mole^{-1})$$

the values for which were obtained by the method of least squares (Appendix 1). The plot of $(5 + \log k_1)$ against $10^3/T$ is linear (Figure 3.10). Rate constants obtained in a packed reaction vessel (S/V 8 cm^{-1}) conform to the above Arrhenius equation (Table 3.9; Figure 3.10) which is taken as evidence of the homogeneity of the reaction.

(b) The Decomposition of Isopropyl N,N-dimethylcarbamate.

Rate constants obtained in the range 272-329° are reported in Table 3.10 and are given by the equation

$$k_1 = 10^{13.04} \exp(-43,310 \pm 200/RT) \ sec^{-1} \qquad (E \ in \ cal. \ mole^{-1})$$

The plot of $(5 + \log k_1)$ against $10^3/T$ is linear (Figure 3.11) and rate constants obtained in a packed reaction vessel lie on this line indicating that the reaction is homogeneous. As required by the first-order rate law, rate constants are independent of a sixfold variation in P_o (Figure 3.12).

(c) The Decomposition of *tert*-Butyl N,N-dimethylcarbamate.

BMMC decomposes in the range 212-260° and the rate constants (Table 3.11) are given by the equation:

$$k_1 = 10^{12.87} \exp(-37,740 \pm 400/RT) \ sec^{-1} \qquad (E \ in \ cal. \ mole^{-1})$$

A plot of $(5 + \log k_1)$ against $10^3/T$ is linear (Figure 3.13) and rate constants obtained in a reaction vessel with S/V 8 cm^{-1}

Figure 3.9

VARIATION OF FIRST-ORDER RATE CONSTANT WITH INITIAL PRESSURE OF ETHYL N-METHYL-N-PHENYLCARBAMATE.

Figure 3.10

Variation of first-order rate constant with temperature for the decomposition of Ethyl N-methyl-N-phenylcarbamate.

⊙ ORDINARY RUNS
△ WITH CYCLOHEXENE
⊡ PACKED VESSEL

Figure 3.11

Variation of first-order rate constant with temperature for the decomposition of isopropyl N,N-dimethylcarbamate.

⊙ runs in unpacked vessel
⊡ runs in packed vessel

$10^3/T$

$5 + \log k_1$ (k_1 in sec^{-1})

Figure 3.12

VARIATION OF FIRST-ORDER RATE CONSTANT WITH INITIAL PRESSURE OF ISOPROPYL N,N-DIMETHYLCARBAMATE.

PRESSURE OF ISOPROPYL N,N-DIMETHYLCARBAMATE (mm).

Figure 3.13

Variation of first-order rate constant with temperature for the decomposition of t-butyl N,N-dimethylcarbamate.

⊙ runs in unpacked vessel

▣ runs in packed vessel
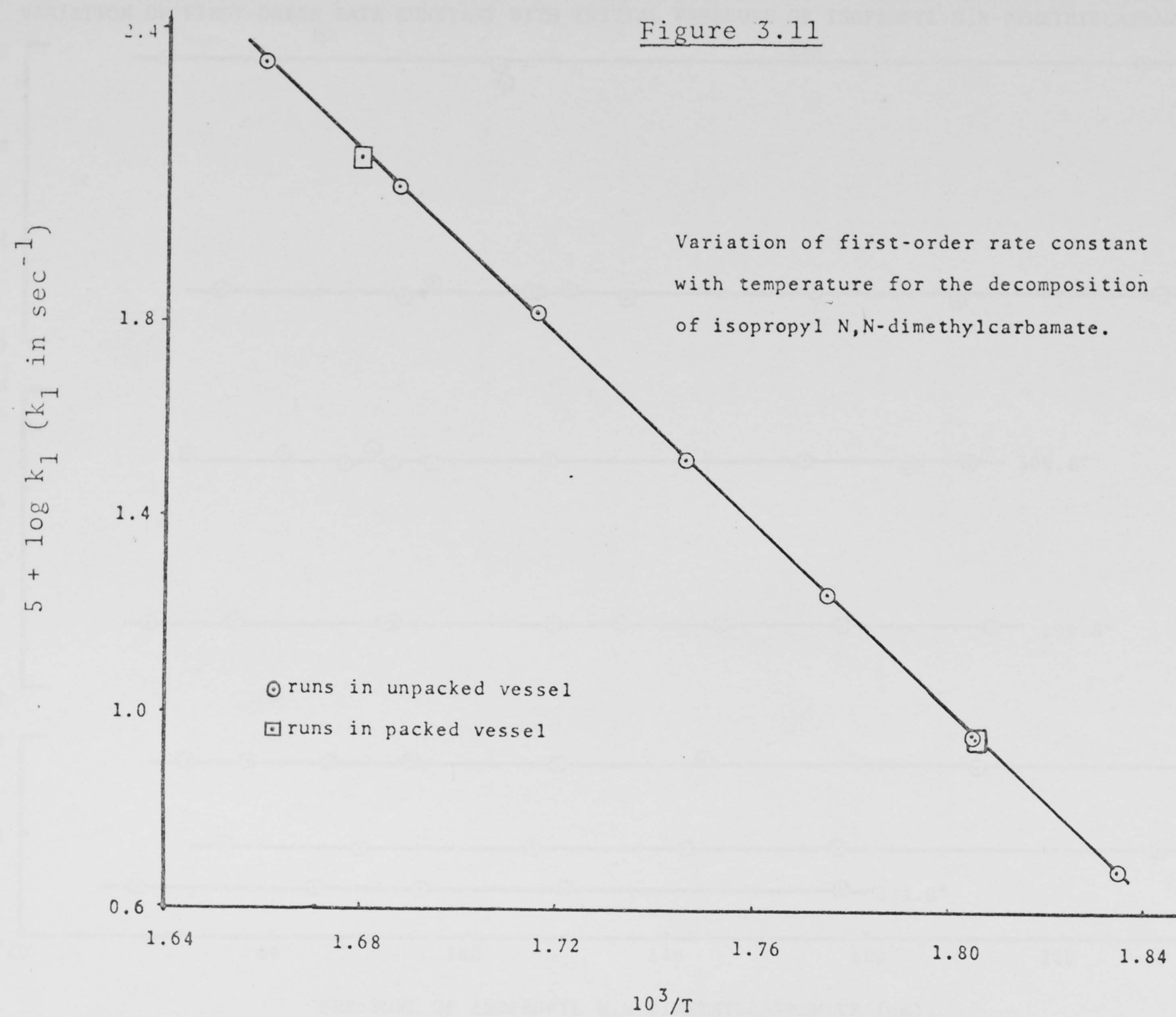
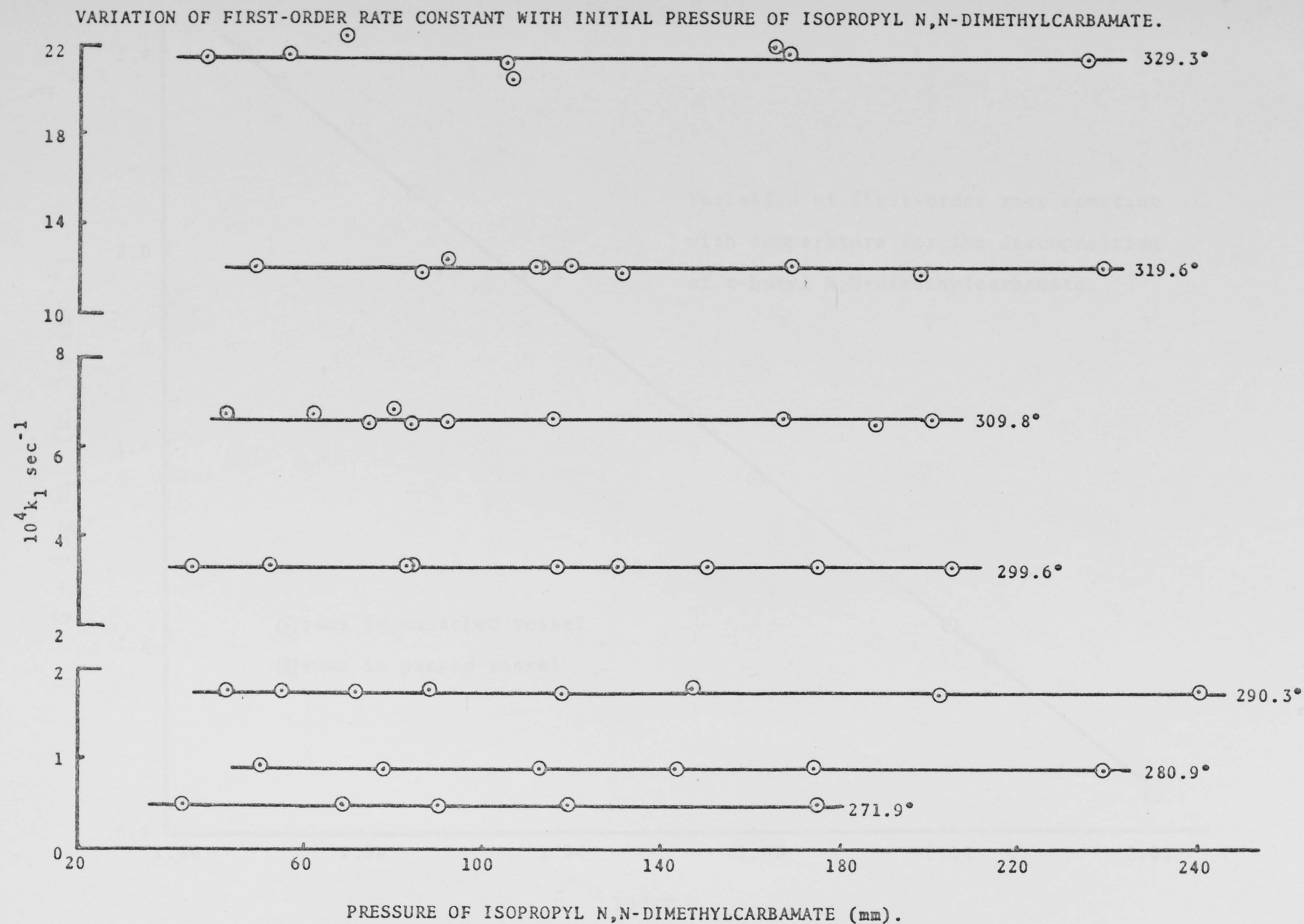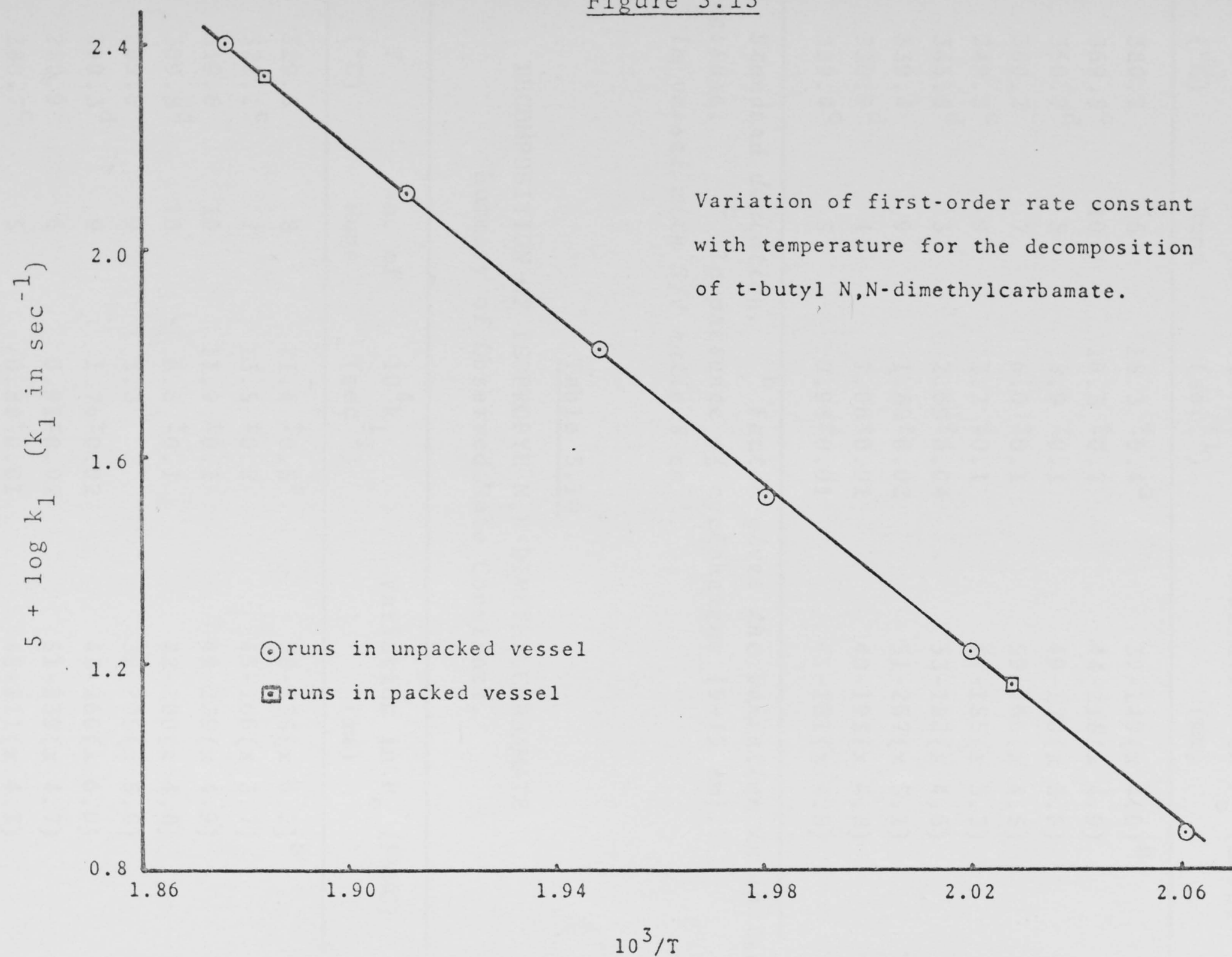This is page 55 (top right), a body page with two data tables.

Table 3.9

DECOMPOSITION OF ETHYL N-METHYL-N-PHENYLCARBAMATE.

Summary of Observed Rate Constants.

T (°C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (EMPC) (mm)
380.2	6	18.3 $\pm$0.4[a]	37-149(x 4.0)[b]
369.8[c]	10	10.3 $\pm$0.2	44-218(x 4.9)
366.7[d]	5	8.9 $\pm$0.1	49-170(x 3.5)
360.2	7	6.0 $\pm$0.1	59-266(x 4.5)
349.5[c]	9	3.2 $\pm$0.1	47-155(x 3.3)
345.8[d]	3	2.69$\pm$0.04	33-152(x 4.6)
339.4	9	1.80$\pm$0.02	51-257(x 5.1)
330.9[d]	4	1.06$\pm$0.01	40-193(x 4.8)
329.4[c]	5	0.95$\pm$0.01	41-181(x 4.5)

[a] *Standard deviation.* [b] *Factor gives the variation in initial pressure.* [c] *In presence of cyclohexene (5-15 cm).* [d] *In vessel with S/V ratio 8 cm^{-1}.*

Table 3.10

DECOMPOSITION OF ISOPROPYL N,N-DIMETHYLCARBAMATE

Summary of Observed Rate Constants.

T (°C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (PMMC) (mm)
329.3	8	21.4 $\pm$0.5[a]	38-235(x 6.2)[b]
322.2[c]	7	13.5 $\pm$0.2	45-166(x 3.7)
319.6	10	11.9 $\pm$0.2	49-239(x 4.9)
309.8[d]	10	6.6 $\pm$0.1	42-200(x 4.8)
299.6	9	3.3	35-205(x 5.8)
290.3[d]	9	1.76$\pm$0.02	43-260(x 6.0)
280.9	6	0.91$\pm$0.02	51-239(x 4.7)
280.7[c]	5	0.88$\pm$0.01	45-211(x 4.7)
271.9	5	0.48$\pm$0.01	33-175(x 5.3)

[a] *Standard deviation.* [b] *Factor gives variation in initial pressure.* [c] *In vessel with S/V 8 cm^{-1}.* [d] *In presence of cyclohexene.*

(Table 3.11) conform to the above Arrhenius equation (Figure 3.13).
The first-order rate constants are shown to be independent of the
initial pressure of BMMC in Figure 3.14.

Table 3.11

DECOMPOSITION OF *tert*-BUTYL N,N-DIMETHYLCARBAMATE.

Summary of Observed Rate Constants

T (°C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (BMMC) (mm)
259.9	9	25.2 ±0.7[a]	36-248(x 6.9)[b]
257.7[c]	3	21.9 ±0.2	41-207(x 5.0)
250.2	6	12.9 ±0.2	38-198(x 5.2)
240.1	7	6.4 ±0.1	40-187(x 4.7)
231.9	9	3.3 ±0.1	33-178(x 5.4)
221.9	6	1.66±0.02	40-190(x 4.8)
220.0[c]	4	1.45±0.01	37-191(x 5.2)
212.1	3	0.75±0.01	28-154(x 5.5)

[a] *Standard deviation.* [b] *Factor gives variation in initial pressure.* [c] *In vessel with S/V ratio 8 cm^{-1}.*

(G) The Effect of Additives.

Studies of the rates of decompositions of the carbamates
were carried out in systems which contained added cyclohexene
and added amines. Results are reported in Table 3.12 which shows
that no additive had any effect on the observed rate constants.

Carbamates are known to undergo transesterification
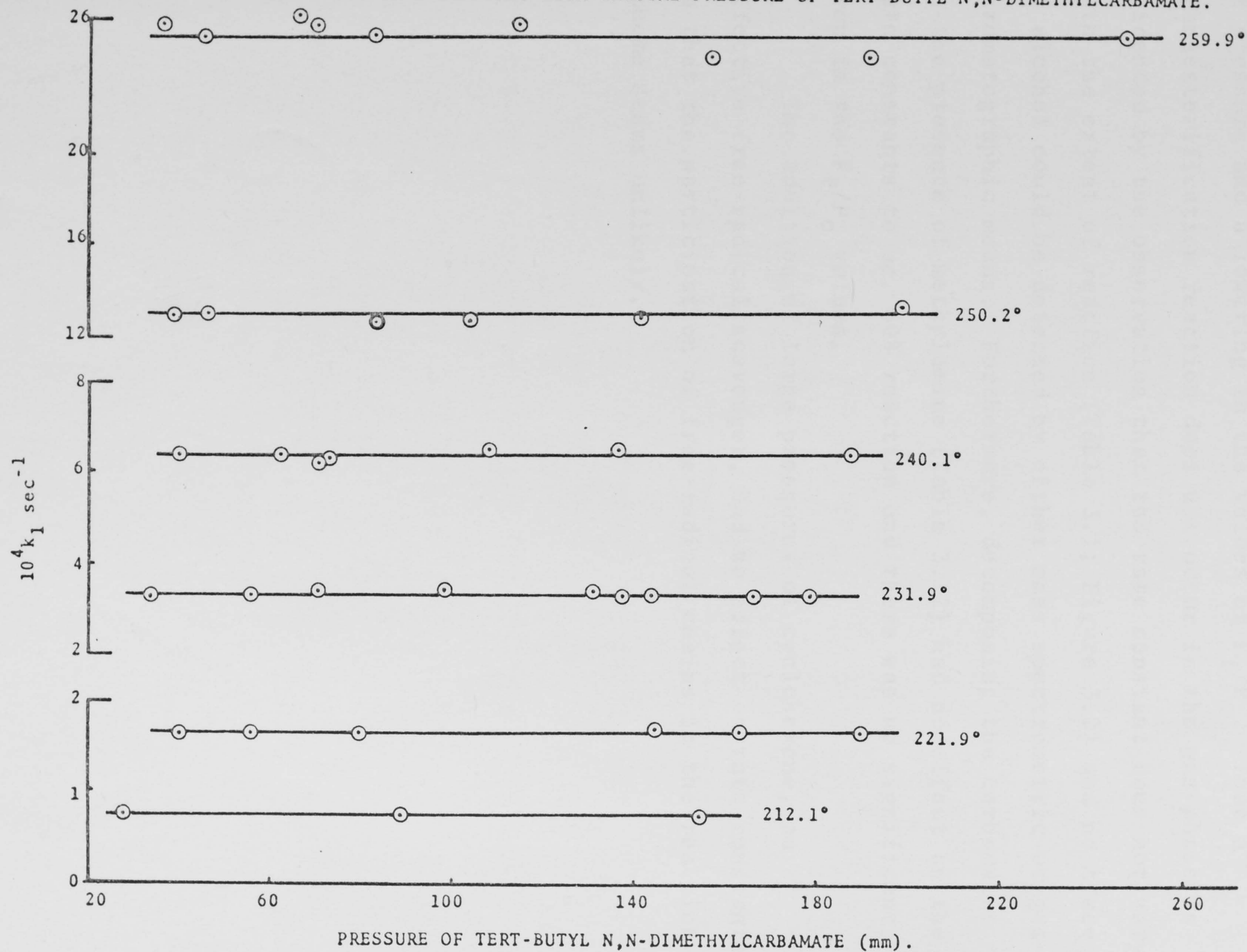reactions of the type

$$RNHCOOR' + R''NH_2 \rightleftharpoons RNHCONHR'' + R'OH$$
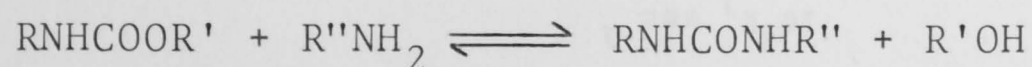
No trace of such a reaction was found in the gas-phase. The
stoicheiometry of the transesterification reaction compared

Figure 3.14

VARIATION OF FIRST-ORDER RATE CONSTANT WITH INITIAL PRESSURE OF TERT-BUTYL N,N-DIMETHYLCARBAMATE.

with that of the decomposition of EMPC, PMMC and BMMC is such that reaction of the product amine with unpyrolysed carbamate would bring about a drop away from the first-order rate of change of pressure and a lowering in the values of P_f/P_o. That a transesterification reaction does not occur in the gas-phase is evidenced by the observation that the rate constant does not vary with the extent of reaction (Table 3.1; Figure 3.2) and no trace of alcohol could be detected by either mass spectrometric or gas-chromatographic means. Furthermore, decomposing the carbamates in the presence of methylamine (Table 3.12) had no effect on the rate constants to ca. 60% reaction and there was no significant drop in the P_f/P_o values.

The addition of large pressures of cyclohexene, an effective free-radical scavenger, had no effect on rate constants, so that the participation of free-radical chains in the reaction scheme seems unlikely.

Table 3.12

THE EFFECT OF ADDITIVES

P_o(carbamate) (mm)	Additive	P(additive) (mm)	$10^4 k_1$ (sec^{-1})	P_{f/P_o}
EMPC (Temp: 349.5°)				
Mean value for k_1 without additives			3.3	2.98
67.6	cyclohexene	149.7	3.3	2.98
72.4	cyclohexene	113.8	3.3	-
98.8	cyclohexene	51.7	3.2	-
EMPC (Temp: 360.2°)				
Mean value for k_1 without additives			6.0	2.98
143.1	methylamine	70.3	6.1	-
83.2	methylamine	179.7	6.0	2.97
115.2	methylamine	131.1	6.1	2.97
73.8	methylamine	117.1	5.9	-
PMMC (Temp: 309.8°)				
Mean value for k_1 without additives			6.6	2.97
80.6	cyclohexene	191.7	6.8	-
84.0	cyclohexene	110.3	6.5	2.96
115.5	cyclohexene	91.1	6.6	-
187.5	cyclohexene	50.1	6.5	2.97
PMMC (Temp: 290.3°)				
Mean value for k_1 without additives			1.76	2.97
120.6	methylamine	73.3	1.77	-
113.4	methylamine	94.1	1.76	2.97
71.1	methylamine	118.8	1.76	-
BMMC (Temp: 250.2°)				
Mean value for k_1 without additives			12.9	2.98
103.4	cyclohexene	90.6	12.7	-
8.32	cyclohexene	100.5	12.6	2.98
198.0	cyclohexene	66.6	13.3	-

(A).Ethyl N-methyl-N-phenylcarbamate.

(i).Runs in reaction vessel, S/V = 0.8cm^{-1}

Temp.380.2°

P_O(mm)   37.1;68.0;75.0;82.0;101.0;149.2

$10^4k_1(s^{-1})$ 18.3;18.3;18.9;17.9;18.4 ;17.9

                                   Mean:10^4k_1=18.3 sec^{-1}

Temp.369.8°

P_O(mm)   44.3;65.4;64.0;65.2;84.0;87.8;100.2;130.0;164.4;218.2

$10^4k_1(s^{-1})$ 10.5;10.6;10.4;10.2;10.2;10.1;10.3 ;10.4 ;10.5 ;10.2

$P(C_6H_{10})$(mm)^a 110.5;97.1   90.1

                                   Mean:10^4k_1=10.3 sec^{-1}

Temp.360.2°

P_O(mm)   58.8;68.0;85.8;104.8;113.8;132.0;266.3

$10^4k_1(s^{-1})$ 6.1 ;5.9 ;6.0 ;5.9 ; 6.1 ; 5.9 ; 6.0

                                   Mean:10^4k_1=6.0 sec^{-1}

Temp.349.5°

P_O(mm)   46.8;69.0;67.6;72.4;74.8;98.8;103.0;122.6;154.6

$10^4k_1(s^{-1})$ 3.2 ;3.2 ;3.3 ;3.3 ;3.3 ;3.2 ; 3.2 ; 3.3 ; 3.3

$P(C_6H_{10})$(mm)   149.7;113.8   51.7

                                   Mean:10^4k_1=3.3 sec^{-1}

Temp.339.4°

P_O(mm)   50.8;61.0;76.0;74.2;95.1;113.6;138.8;166.4;257.3

$10^4k_1(s^{-1})$ 1.79;1.80;1.77;1.81;1.78; 1.78; 1.79; 1.82; 1.83

                                   Mean:10^4k_1=1.80 sec^{-1}

Temp.329.4°

P_O(mm)   40.6;57.0;80.6;109.8;181.4

$10^4k_1(s^{-1})$ 0.95;o.97;0.95;0.95;0.95

$P(C_6H_{10})$(mm)   81.0;73.1

                                   Mean:10^4k_1=0.95 sec^{-1}

---

^{a}Pressure of cyclohexene

(ii).Runs in packed reaction vessel, $S/V = 8cm^{-1}$

Temp.366.7°

$P_o(mm)$ 49.2;78.8;95.0;142.0;170.0

$10^4k_1(s^{-1})$ 8.9; 9.0; 9.1; 8.7; 8.9

Mean:10^4k_1=8.9 sec^{-1}

Temp.345.8°   Temp.330.9°

$P_o(mm)$ 33.1;95.6;151.6 $P_o(mm)$ 40.4;82.2;135.7;193.1

$10^4k_1(s^{-1})$ 2.73;2.64;2.69 $10^4k_1(s^{-1})$ 1.07;1.06;1.06;1.05

Mean:10^4k_1=2.69 sec^{-1} Mean:10^4k_1=1.06 sec^{-1}

(B).Isopropyl N,N-dimethylcarbamate.

(i).Runs in reaction vessel, $S/V = 0.8cm^{-1}$

Temp.329.3°

$P_o(mm)$ 37.9;56.9;69.5;105.0;106.5;155.1;158.6;234.9

$10^4k_1(s^{-1})$ 21.4;21.5;22.3; 21.1; 20.4; 21.8; 21.5; 21.3

Mean:10^4k_1=21.4 sec^{-1}

Temp.319.6°

$P_o(mm)$ 49.0;92.0;86.6;112.0;114.0;120.0;130.8;168.8;197.6;238.7

$10^4k_1(s^{-1})$ 12.0;12.3;11.7; 12.0; 11.9; 11.9; 11.5; 12.0; 11.5;11.9

Mean:10^4k_1=11.9 sec^{-1}

Temp.309.8°

$P_o(mm)$ 42.5;61.9;74.6;80.6;84.0;92.0;115.5;167.0;187.5;200.1

$10^4k_1(s^{-1})$ 6.7; 6.7; 6.5; 6.8; 6.5; 6.5; 6.6; 6.6; 6.5; 6.6

$P(C_6H_{10})(mm)$ 91.1;50.1;191.7   Mean:10^4k_1=6.6 sec^{-1}

Temp.299.6°

$P_o(mm)$ 35.1;52.3;84.7;83.3;116.8;130.1;150.0;174.7;204.5

$10^4k_1(s^{-1})$ 3.3; 3.3; 3.3; 3.3; 3.3; 3.3; 3.3; 3.3; 3.3; 3.3

Mean:10^4k_1=3.3 sec^{-1}

Temp.290.3°

$P_o(mm)$ 43.0;55.0;71.7;73.0;88.1;118.0;147.0;202.0;260.5

$10^4k_1(s^{-1})$ 1.76;1.75;1.74;1.77;1.77; 1.74; 1.79; 1.73; 1.77

Mean:10^4k_1=1.76 sec^{-1}

Temp.280.9°

P_o(mm)   50.6;77.8;113.0;143.4;174.2;238.6

$10^4k_1(s^{-1})$ 0.92;o.87;0.91; 0.91; 0.92; 0.90

Mean:10^4k_1=0.91 sec^{-1}

Temp.271.9°

P_o(mm)   32.9;69.0;90.4;119.2;174.8

$10^4k_1(s^{-1})$ 0.48;0.49;0.48; 0.49; 0.48

Mean:10^4k_1=0.48 sec^{-1}

(ii).Runs in packed reaction vessel, S/V = 8cm^{-1}

Temp.322.2°

P_o(mm)   44.6;67.2;70.0;106.4;120.8;149.8;166.2

$10^4k_1(s^{-1})$ 13.6;13.5;13.4; 13.7; 13.2; 13.6; 13.5

Mean:10^4k_1=13.5 sec^{-1}

Temp.280.7°

P_o(mm)   44.7;102.0;140.2;151.6;211.1

$10^4k_1(s^{-1})$ 0.88;0.88; 0.87; 0.89; 0.88

Mean:10^4k_1=0.88 sec^{-1}

(C).Tert-butyl N,N-dimethylcarbamate.

(i).Runs in reaction vessel, S/V = 0.8cm^{-1}

Temp.259.9°

P_o(mm)   36.3;44.9;65.8;69.4;82.4;114.0;156.6;191.0;247.6

$10^4k_1(s^{-1})$ 25.8;25.2;26.2;25.7;25.2; 25.7; 24.1; 24.1; 25.2

Mean:10^4k_1=25.2 sec^{-1}

Temp.250.2°

P_o(mm)   103.4;141.2;83.2;46.0;38.4;198.0

$10^4k_1(s^{-1})$ 12.7; 12.8;12.6;13.0;12.9; 13.3

$P(C_6H_{10})$(mm)   90.6;   100.5;66.6

Mean:10^4k_1=12.9 sec^{-1}

Temp. 240.1°

P_o(mm)   39.8; 62.2; 70.6; 73.2; 108.2; 136.0; 187.2

$10^4 k_1 (s^{-1})$ 6.4; 6.4; 6.2; 6.3; 6.5 ; 6.5 ; 6.4

Mean: $10^4 k_1 = 6.4$ sec^{-1}

Temp. 231.9°

P_o(mm)   33.4; 55.4; 70.6; 97.8; 131.0; 137.2; 144.0; 166.0; 178.2

$10^4 k_1 (s^{-1})$ 3.3; 3.3; 3.4; 3.4; 3.4 ; 3.3 ; 3.3 ; 3.3 ; 3.3

Mean: $10^4 k_1 = 3.3$ sec^{-1}

Temp. 221.9°

P_o(mm)   40.0; 55.6; 79.4; 144.2; 162.8; 189.6;

$10^4 k_1 (s^{-1})$ 1.66; 1.64; 1.64; 1.70; 1.67; 1.66;

$P(C_6 H_{10})$(mm)   67.8   111.1

Mean: $10^4 k_1 = 1.66$ sec^{-1}

Temp. 212.1°

P_o(mm)   27.6; 88.8; 154.0

$10^4 K_1 (s^{-1})$ 0.77; 0.74; 0.74

Mean: $10^4 k_1 = 0.75$ sec^{-1}

(ii). Runs in a packed vessel, $S/V = 8$cm^{-1}

Temp. 257.7°

P_o(mm)   41.3; 147.9; 206.6

$10^4 k_1 (s^{-1})$ 22.1; 21.7; 21.9

Mean: $10^4 k_1 = 21.9$ sec^{-1}

Temp. 220.0°

P_o(mm)   37.1; 73.3; 158.2; 191.1

$10^4 k_1 (s^{-1})$ 1.43; 1.46; 1.46; 1.44

Mean: $10^4 k_1 = 1.45$ sec^{-1}

CHAPTER IV

THE THERMAL DECOMPOSITION OF
ETHYL N-METHYLCARBAMATE.

(A) Materials

Ethyl N-methylcarbamate (B.D.H. Laboratory Reagent) was fractionated through a 12-in column of Fenske helices and had b.p. $64.1 \pm 0.2°/9\text{-}10$ mm and n_D^{22} 1.4176 (Found: C, 46.4; H, 8.8; N, 13.4%. Calc. for $C_4H_9NO_2$: C, 46.6; H, 8.8; N, 13.6%).

(B) The Thermal Decomposition

Ethyl N-methylcarbamate was pyrolysed over the temperature range 331° to 381° and rates of pressure change were measured in the usual manner. When these pressure-time data were interpreted in terms of a first-order reaction having a stoicheiometry in which one mole of reagent produces three moles of products (as outlined in Chapter III) the first-order plots were non-linear, and showed observable derivations after *ca*. 10-15% reaction (Figure 4.1). Furthermore, the slope of the log-plot steadily decreased with time:

Time interval(min):   0-5;   5-10;   10-15;   15-20;   20-25;   25-30.
$10^5 k_1 (sec^{-1})$:   26.8;   26.4;   25.8;   25.5;   24.9;   24.5.

Analyses for ethylene were carried out at various extents of reaction, and amounts of ethylene found do not correlate with the percentage reaction calculated from pressure data interpreted in terms of the stoicheiometry in which one mole gives three moles. Results are reported in Table 4.1. The decomposition is not a simple process as observed for EMPC, PMMC, and BMMC and is explained in terms of competing reactions.

(C) Identification of Products

Products were identified in the main using gas-liquid chromatography. Three columns were used: Column A (Porapak Q; 42 x ¼ in; helium flow rate: $65ml.min^{-1}$; column temperature: 50°),

Figure 4.1

Pressure-time curve and log-plot (assuming 1 mole gives 3 moles) for the decomposition of 158.0mm of Ethyl N-methylcarbamate at 351.3° (ΔP = 116.8mm).
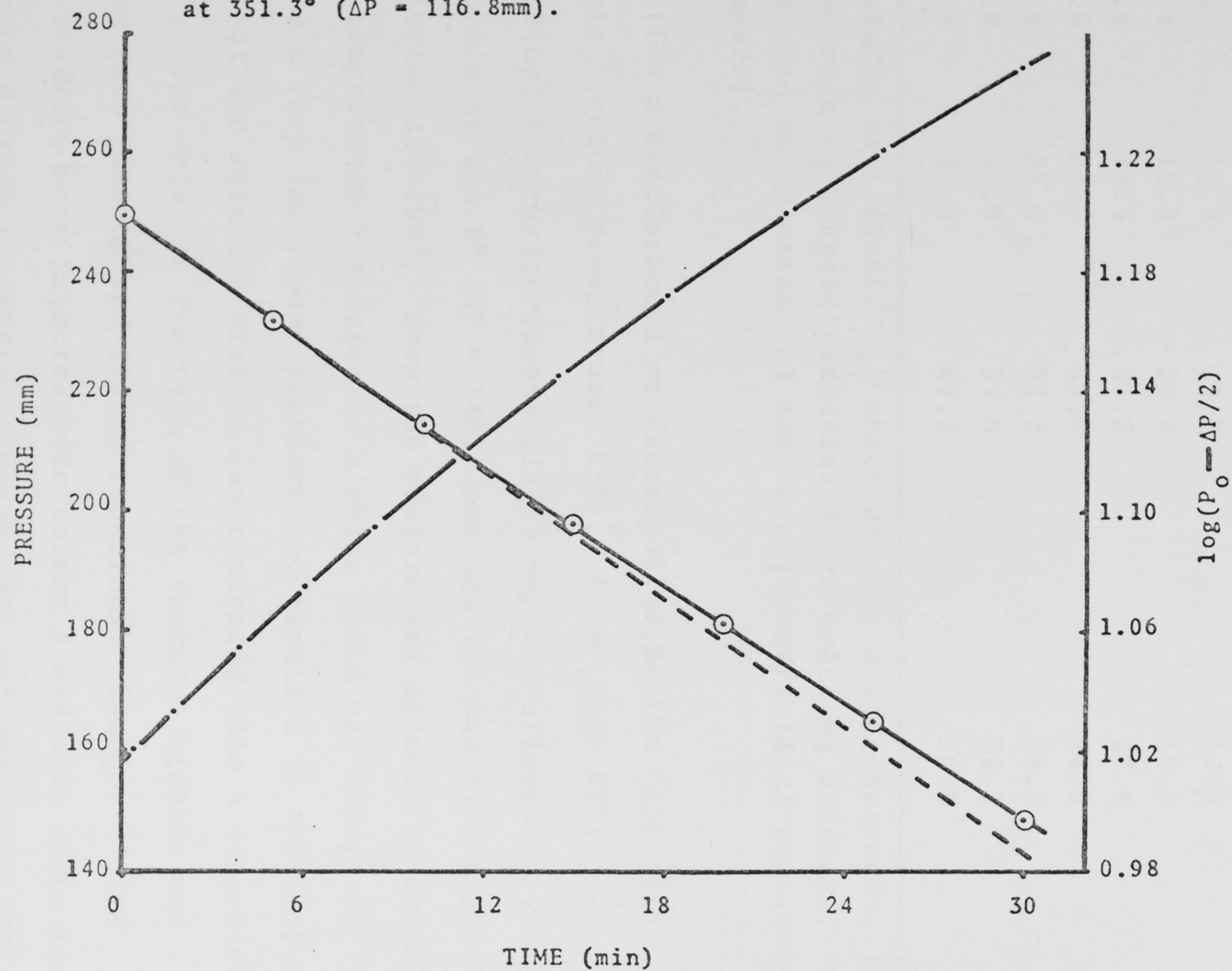
Table 4.1

Extents of Reaction at 351.3° by Ethylene Analysis
and by Pressure Data

P_o(carbamate) (mm)	Time (min)	% Reaction (by pressure)[a]	% Reaction (by ethylene analysis)[b]
167.0	10.9	15.9	14.0
150.8	15.0	20.9	18.6
148.0	18.5	24.9	22.6
174.0	22.0	29.0	24.9
179.6	25.0	32.3	28.3
158.0	30.0	37.0	32.1
168.2	35.0	41.3	36.5

[a] *Calculated as $(100 \times \Delta P / 2P_o)$ which assumes a stoicheiometry in which one mole of reagent generates three moles of products.*
[b] *Calculated as (pressure of ethylene formed/initial pressure of carbamate).*

column B(144 x ¼in;Carbowax on fluoropak 80,helium flow rate: 120 ml.min^{-1};column temperature: 85°)*, [see page 122]

Ethyl N-methylcarbamate (173.5 mm) was allowed to react for 9.26 min at 373.8° (ΔP = 140.7 mm) and the reaction mixture was collected at -196°. When the mixture was allowed to warm to ambient temperature formation of a white solid was observed. This solid had a very low vapour pressure and remained in the trap when the rest of the reaction mixture was condensed into a tap-vessel at -196°. The volatile fraction of the reaction mixture was separated into gaseous and liquid fractions. Samples of the gaseous fraction were injected onto column A and were separated into carbon dioxide (retention time 90 sec) and ethylene (145 sec). Samples of the liquid fraction were injected onto column B and methylamine (125 sec) was clearly separated. Samples of the liquid fraction injected onto column C were separated into peaks corresponding with ethanol (200 sec) and ethyl N-methylcarbamate

(470 sec). All retention times quoted are identical with those obtained for authentic samples.

A series of such experiments were carried out and product analysis gave similar results.

Products were also examined using an A.E.I. Ltd. MSIO mass spectrometer. Ethyl N-methylcarbamate (189.4 mm) was allowed to react for 18.8 min at 360.7° (ΔP = 147.0 mm) and the reaction mixture collected at -196° and transferred to a tap-vessel. The tap-vessel was connected to the inlet system of the mass spectrometer, and, as the mixture warmed from -196° to ambient temperature, samples were drawn off and their spectra recorded. In this way the reaction mixture was divided roughly into three fractions. Fraction 1 (Figure 4.2) corresponds to the mass spectrum of ethylene (parent peak: m/e 28) and carbon dioxide (parent peak: m/e 44). Fraction 2 corresponds to the mass spectrum of ethanol (Figure 4.3) together with minor peaks corresponding to the fragmentation of ethyl N-methylcarbamate which is not rigidly excluded from this fraction. Fraction 3(Figure 4.4) corresponds to the mass spectrum for an authentic sample of the carbamate[97]. It was difficult to identify methylamine by this method of analysis since its fragmentation peaks are obscured by those of the other components of the reaction mixture.

The white solid formed was characterised using the following techniques. The solid was pumped steadily for some time to remove any volatile material, and the n.m.r. spectrum was obtained on a Perkin-Elmer spectrometer in the solvent deuterochloroform. The spectrum, recorded at 33.4° and 60 M.H.z. using tetramethyl-silane as an internal standard, is reproduced in Figure 4.5. Results are: δ(p.p.m.) 2.74 (6H, singlet, N-methyl protons),
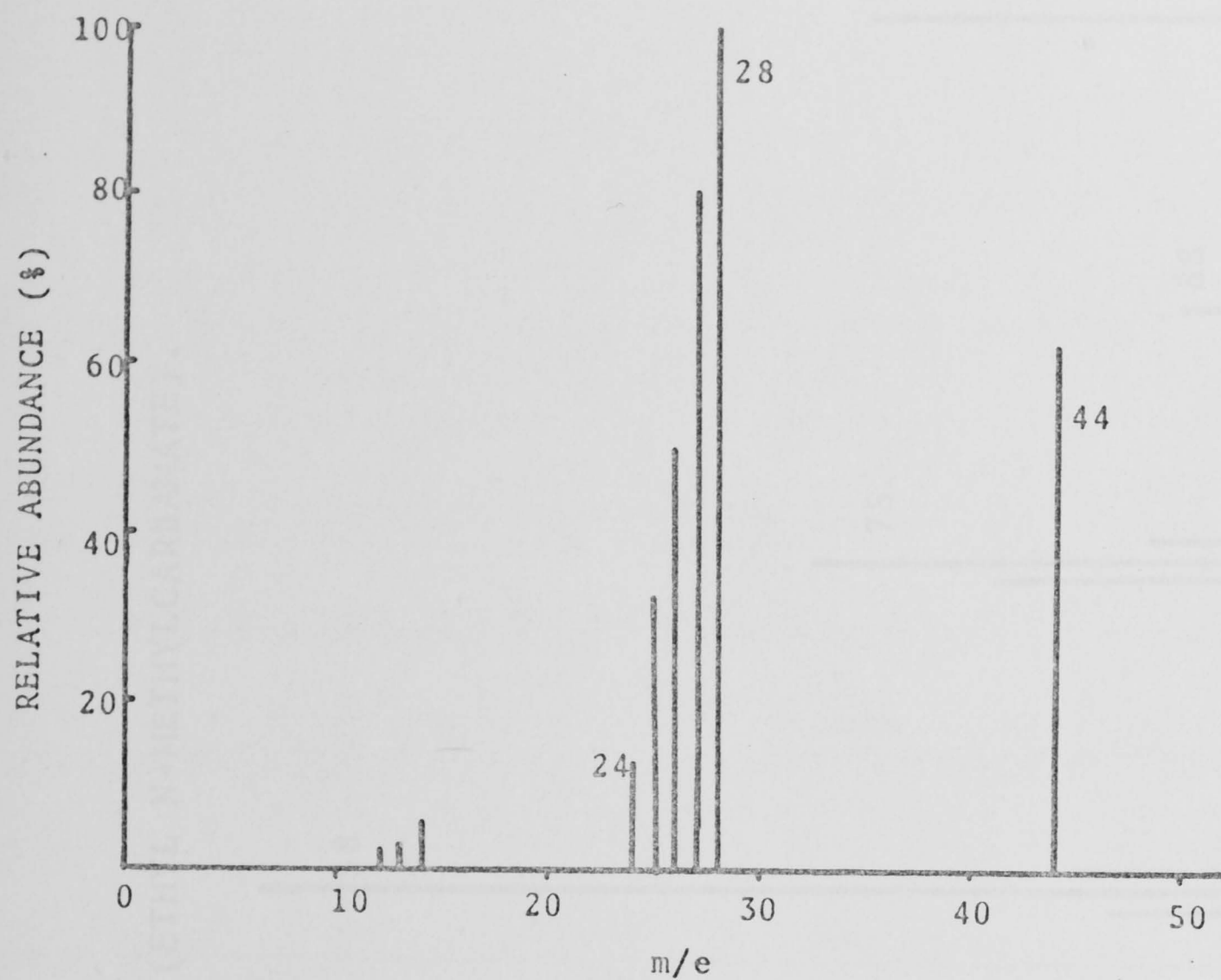
Figure 4.2
MASS SPECTRUM OF FRACTION 1

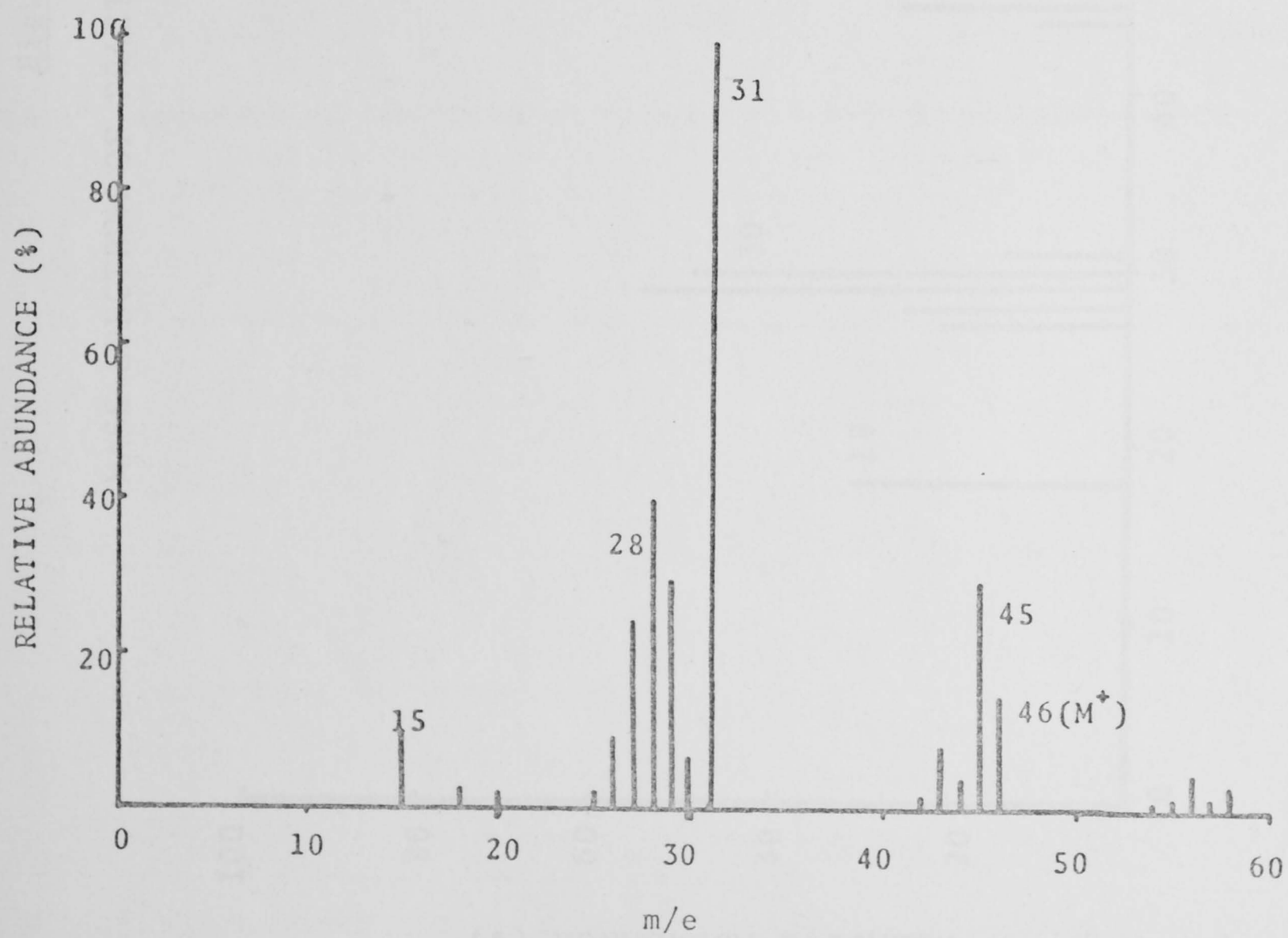
Figure 4.3
MASS SPECTRUM OF FRACTION 2

Figure 4.4

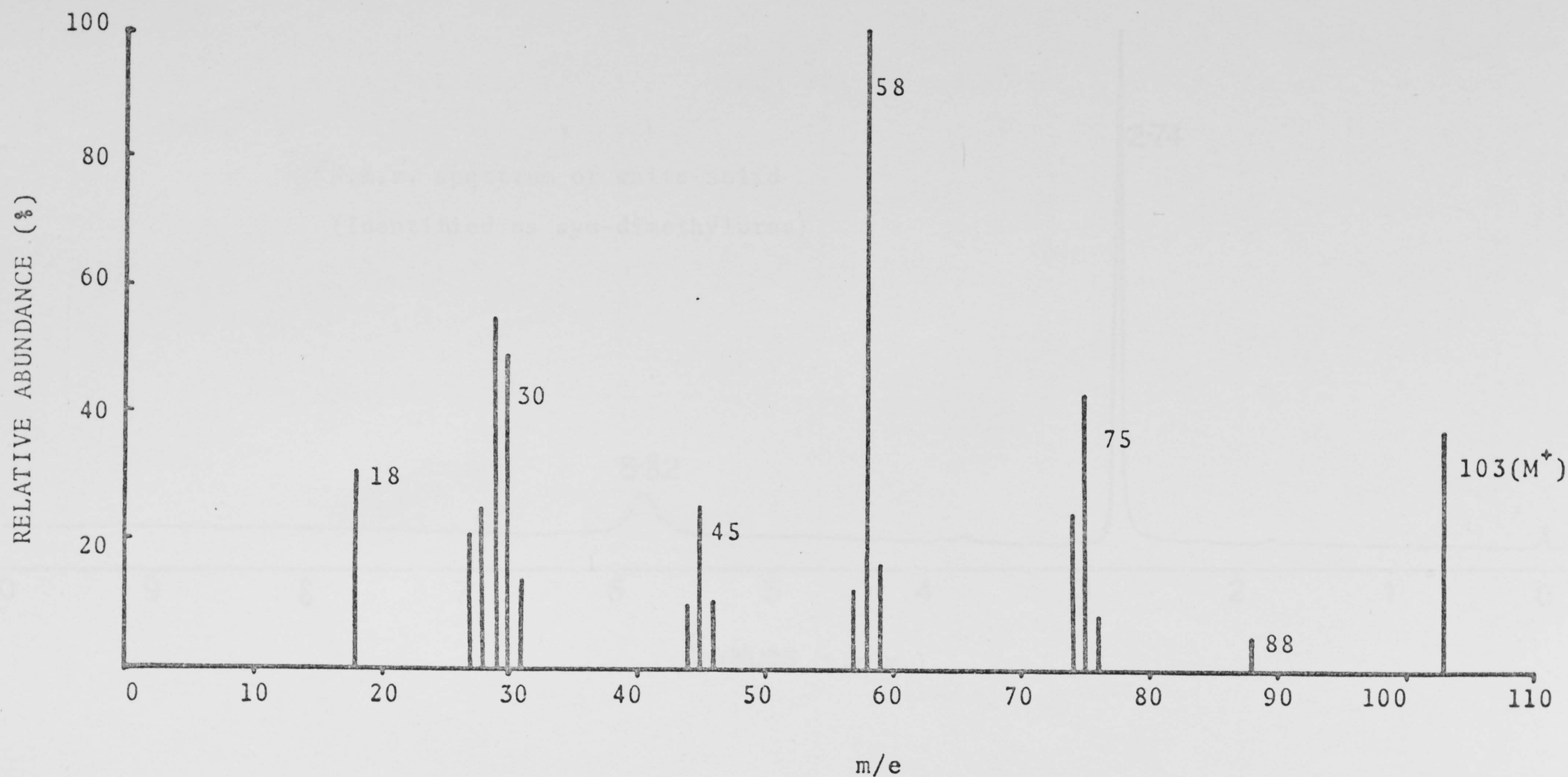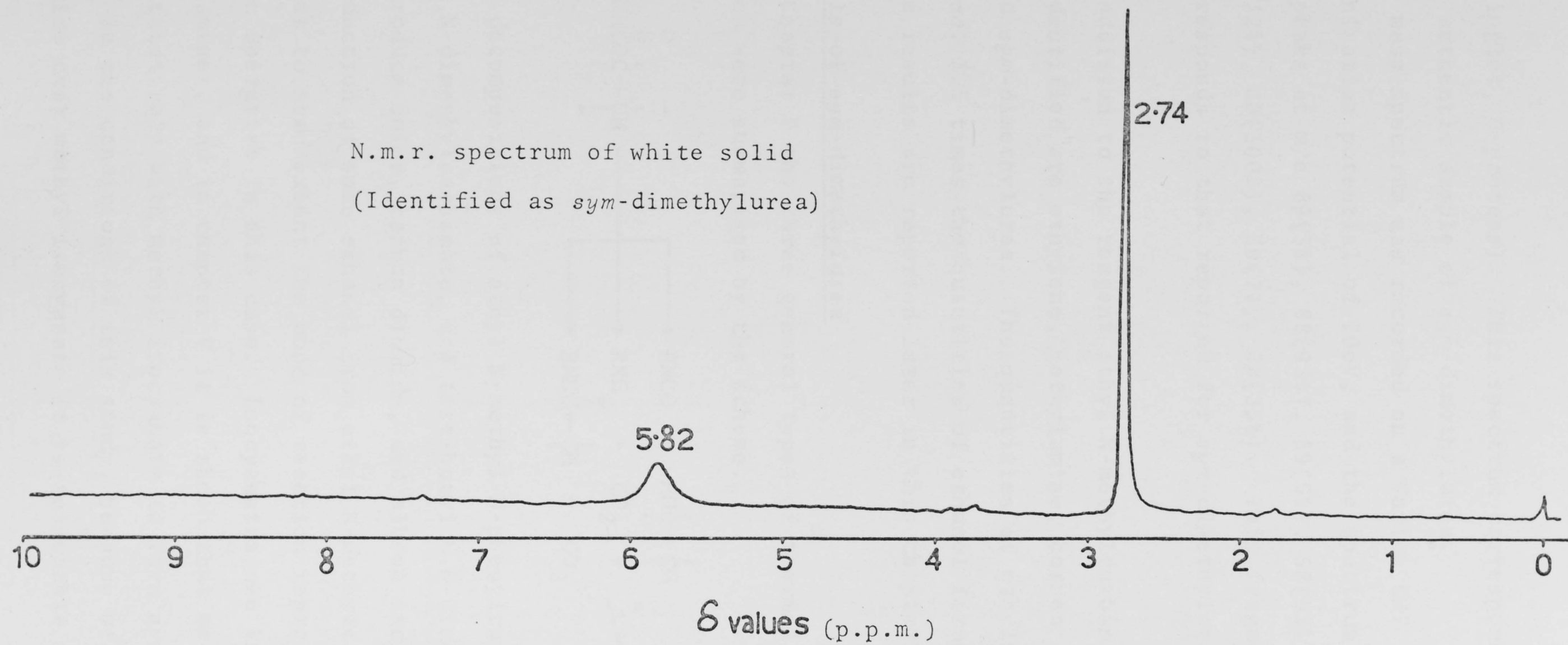MASS SPECTRUM OF FRACTION 3
(ETHYL N-METHYLCARBAMATE).

Figure 4.5

N.m.r. spectrum of white solid
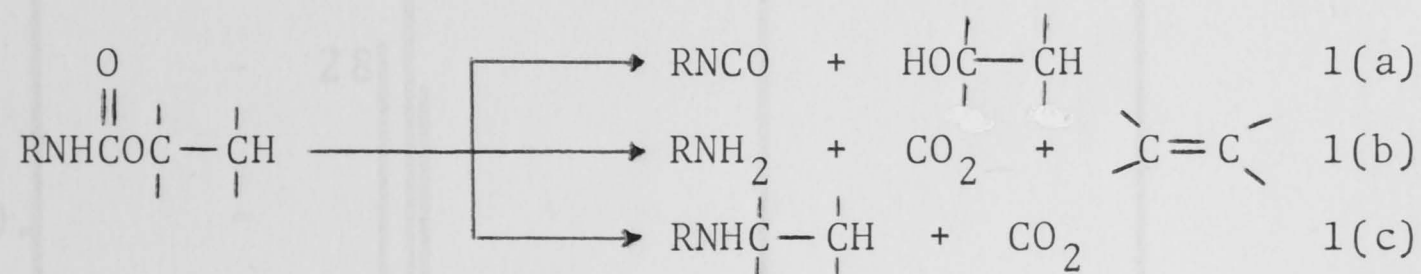
(Identified as *sym*-dimethylurea)

5.82 (2H, singlet, N-protons). This spectrum corresponds with that for an authentic sample of *sym*-dimethylurea.

The mass spectrum was recorded on a Varian CH7 instrument using an ionisation potential of 70eV, and the spectrum (Figure 4.6) shows peaks at m/e 89(3%), 88(93%), 59(5%), 58(62%), 57(5%), 44(5%), 31(32%), 30(100%), 29(7%), 28(35%). This fragmentation pattern corresponds to that reported for *sym*-dimethylurea[98].

In addition to the reagent ethyl N-methylcarbamate, the compounds identified are ethylene, methylamine, carbon dioxide, ethanol, and *sym*-dimethylurea. The quantities of ethylene formed seem to be *ca.* 3.5 times the quantities of ethanol formed. Quantitative results are reported later in this chapter.

(D) The Role of *sym*-dimethylurea

In Chapter I the three general types of thermal degradations of carbamates were summarised by the scheme.

$$
RNHCO\overset{\mid}{C}-\overset{\mid}{C}H \longrightarrow
\begin{cases}
RNCO + HO\overset{\mid}{C}-\overset{\mid}{C}H & 1(a) \\
RNH_2 + CO_2 + \enspace C=C & 1(b) \\
RNH\overset{\mid}{C}-\overset{\mid}{C}H + CO_2 & 1(c)
\end{cases}
$$

The decompositions of ethyl N-methyl-N-phenylcarbamate, isopropyl N,N-dimethylcarbamate, and tert-butyl N,N-dimethyl-carbamate produce amine, carbon dioxide, and alkene exclusively, but the production of some ethanol from ethyl N-methylcarbamate suggests that to some extent the mode of reaction represented by (1a) is also operative in this case. Isocyanates are known to react with amines, and in chapter V it is shown that methylamine reacts quantitatively with methyl isocyanate to form *sym*-dimethyl-urea. Thus in the conditions of this study, because of the excess of methylamine over methyl isocyanate it is reasonable that no free

Figure 4.6

MASS SPECTRUM OF THE WHITE SOLID.

(IDENTIFIED AS SYM-DIMETHYLUREA)
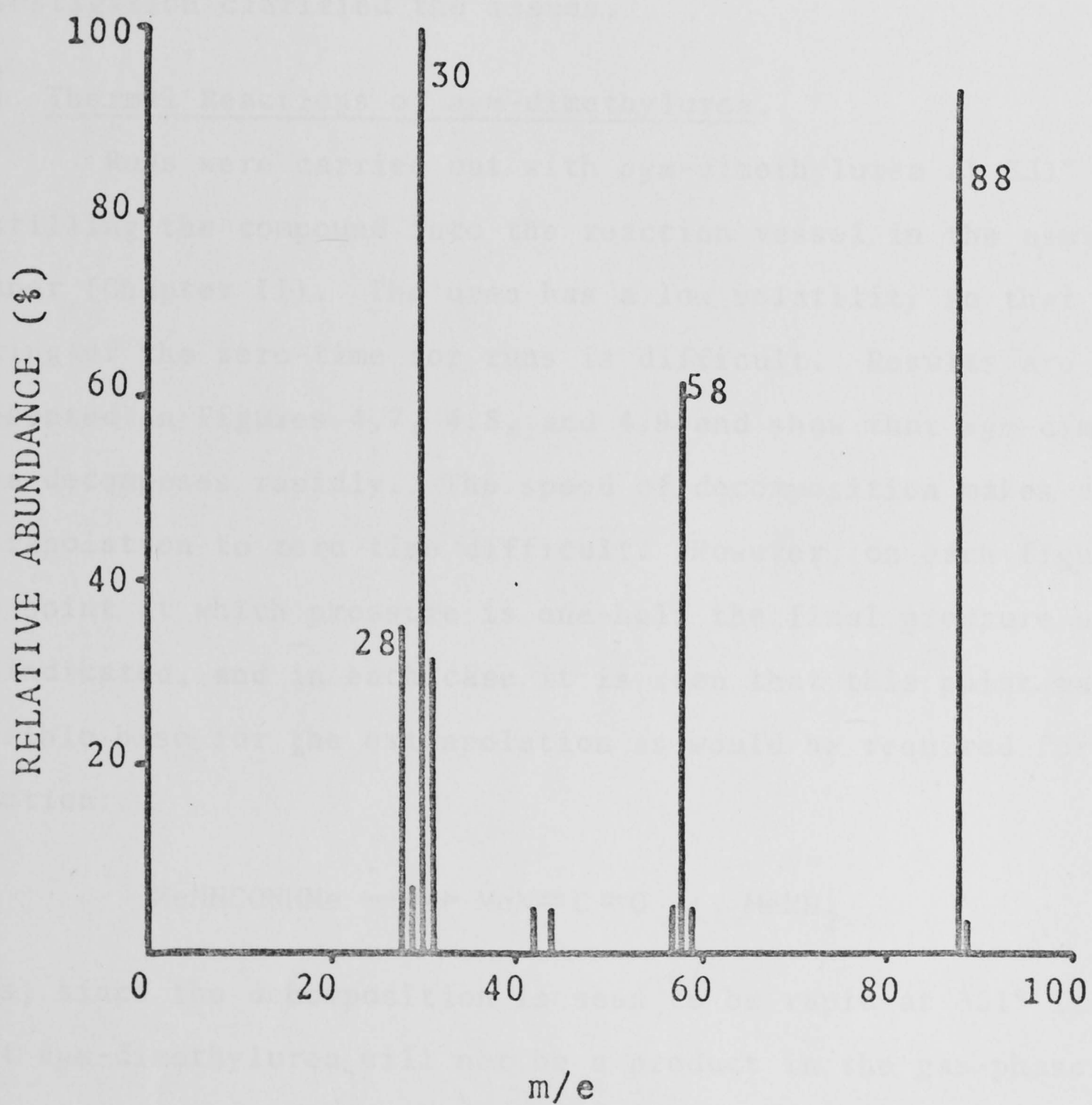
isocyanate is detected, but that conversion to the urea according to the reaction:

$$MeNH_2 + MeN=C=O \longrightarrow MeNHCONHMe$$

takes place quantitatively. The problem is whether this takes place in the reaction vessel during runs, or later, on the vacuum line during the analytical procedures. The following investigation clarified the issues.

(E) Thermal Reactions of *sym*-dimethylurea.
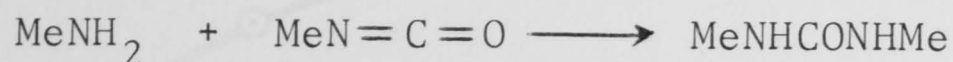
Runs were carried out with *sym*-dimethylurea at 331° by distilling the compound into the reaction vessel in the usual manner (Chapter II). The urea has a low volatility so that precise fixing of the zero-time for runs is difficult. Results are presented in Figures 4.7, 4.8, and 4.9 and show that *sym*-dimethylurea decomposes rapidly. The speed of decomposition makes accurate extrapolation to zero time difficult. However, on each figure, the point at which pressure is one-half the final pressure achieved is indicated, and in each case it is seen that this point makes a sensible base for the extrapolation as would be required for the reaction:

$$MeNHCONHMe \longrightarrow MeN=C=O + MeNH_2$$
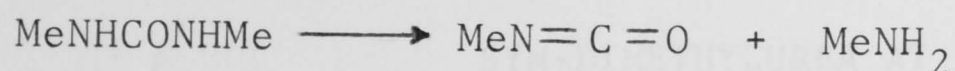
Thus, since the decomposition is seen to be rapid at 331° it seems that *sym*-dimethylurea will not be a product in the gas-phase decomposition of ethyl N-methylcarbamate. Condensing the reaction mixtures led to the formation of *sym*-dimethylurea. In a further experiment, *sym*-dimethylurea (*ca.* 55 mm) was allowed to react at 331° for 20 min (Figure 4.9) and the reaction mixture was condensed at -196° in the U-bend adjacent to the reaction vessel. On redistilling the condensate back into the reaction vessel the

Figure 4.7

THE THERMAL DECOMPOSITION OF
SYM-DIMETHYLUREA AT 331°

$P_o \approx 55$mm

← point where $p = \frac{1}{2}p_f$

PRESSURE (mm)

TIME (min)

THE THERMAL DECOMPOSITION OF
SYM-DIMETHYLUREA AT 331°

$P_o \approx 78$mm
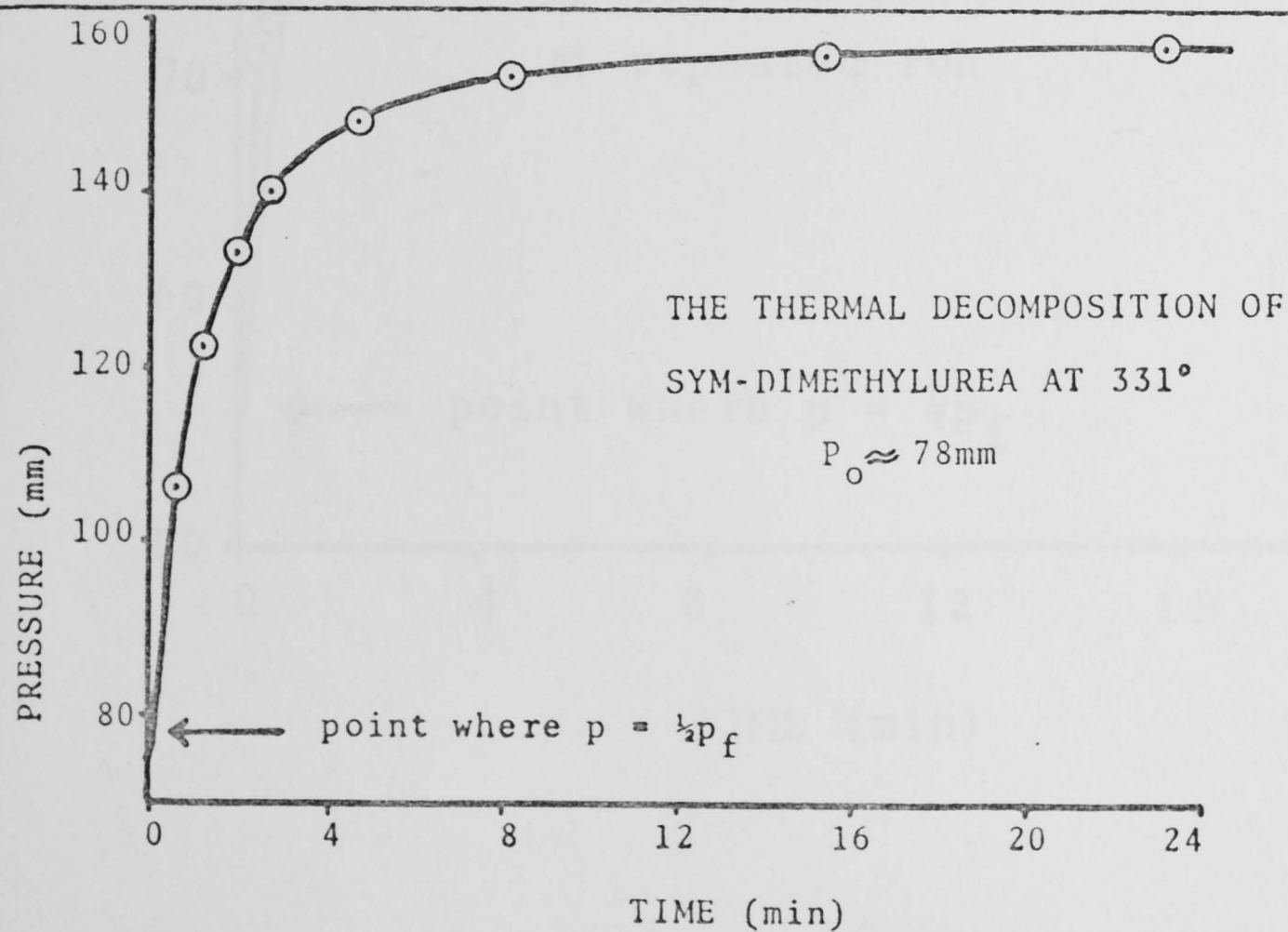
← point where $p = \frac{1}{2}p_f$

PRESSURE (mm)

TIME (min)
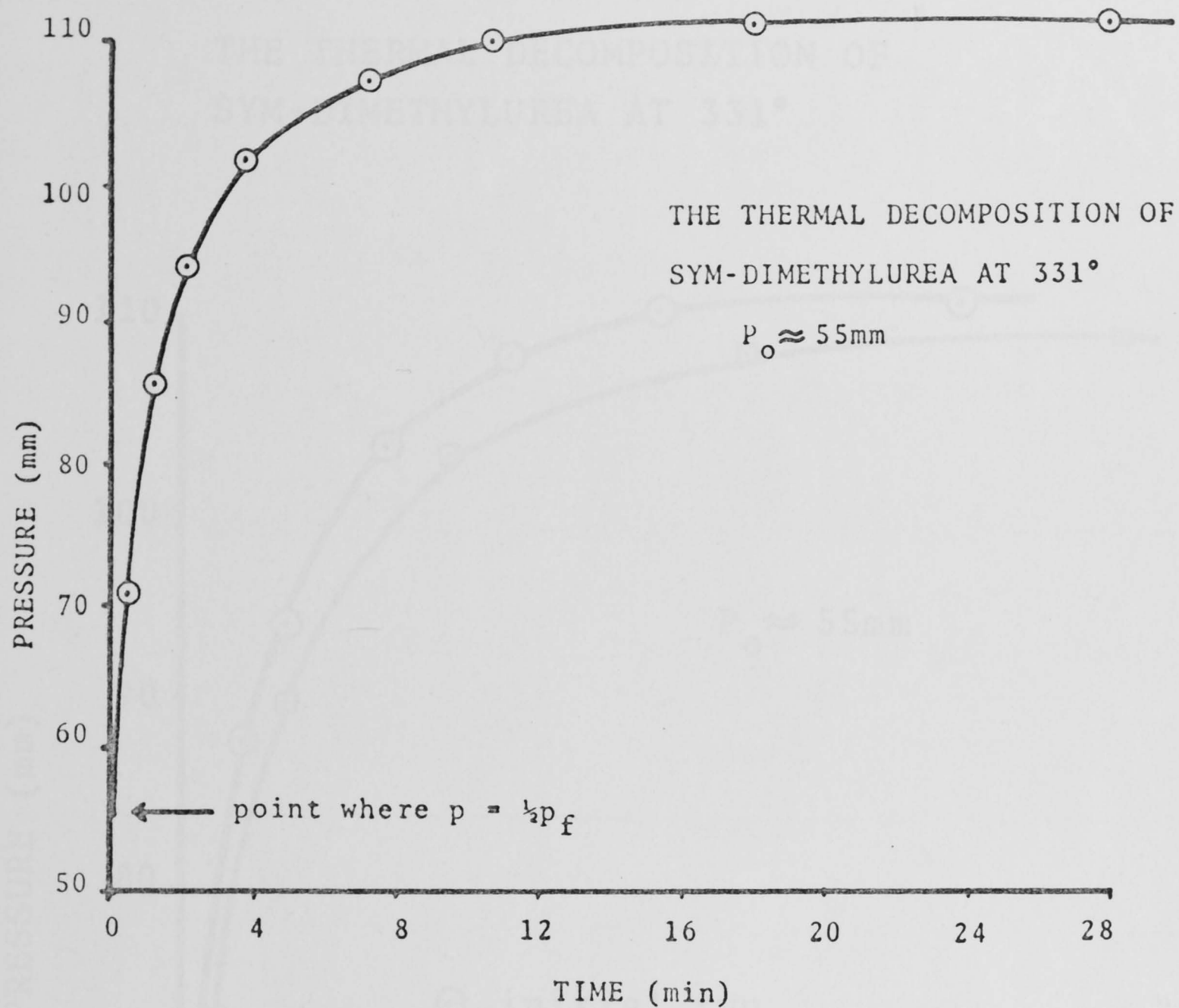
Figure 4.8

Figure 4.9

THE THERMAL DECOMPOSITION OF
SYM-DIMETHYLUREA AT 331°

$P_o \approx 55mm$

⊙ initial run
⊡ repeated run

⟵ point where $p = \frac{1}{2}p_f$

PRESSURE (mm)

TIME (min)
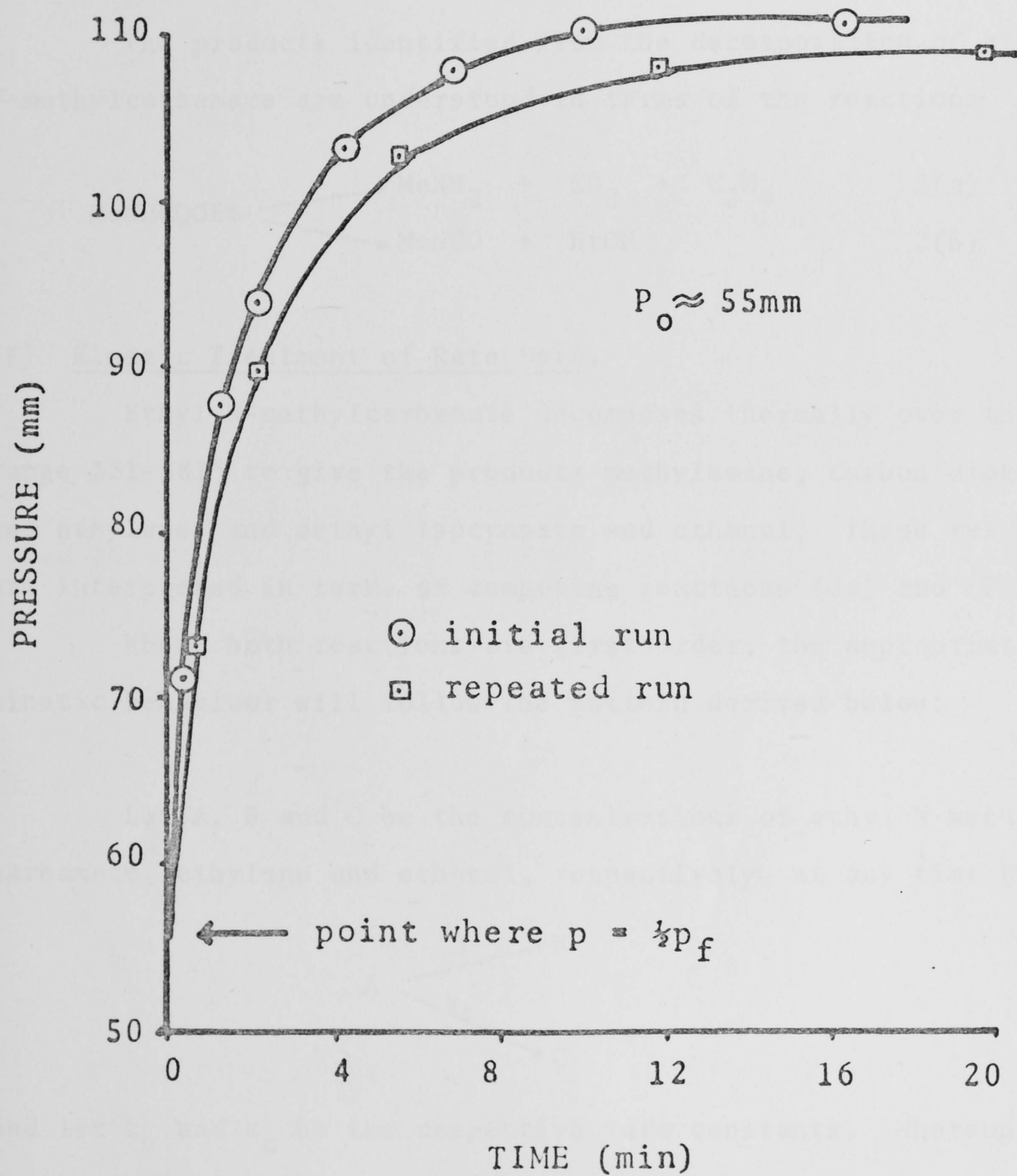
pressure-time curve (shown in Figure 4.9) was the same (within the limits of experiment) as the initial pressure-time curve. Thus the evidence is that methyl isocyanate reacts with methyl-amine during the analytical stages, but not within the reaction vessel, and is characterised by the formation of *sym*-dimethylurea.

The products identified from the decomposition of ethyl N-methylcarbamate are understood in terms of the reactions

$$MeNHCOOEt \quad \begin{array}{l} \nearrow MeNH_2 + CO_2 + C_2H_4 \qquad\qquad 2(a) \\ \searrow MeNCO + EtOH \qquad\qquad\qquad\quad 2(b) \end{array}$$
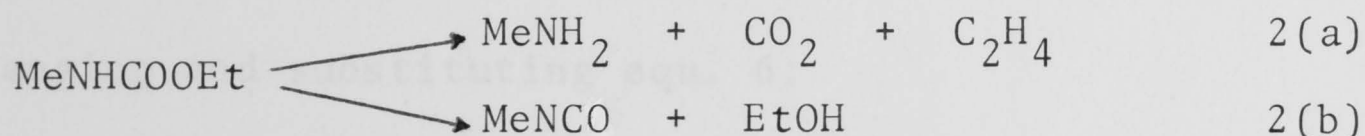
(F) Kinetic Treatment of Rate Data.

Ethyl N-methylcarbamate decomposes thermally over the range 331-381° to give the products methylamine, carbon dioxide, and ethylene, and methyl isocyanate and ethanol. These results are interpreted in terms of competing reactions (2a) and (2b).

Where both reactions are first-order, the appropriate kinetic behaviour will follow the pattern derived below:

Let A, B and C be the concentrations of ethyl N-methyl-carbamate, ethylene and ethanol, respectively, at any time (t)

$$A \quad \begin{array}{l} \xrightarrow{k_b} B \\ \searrow_{k_c} \\ \qquad C \end{array}$$
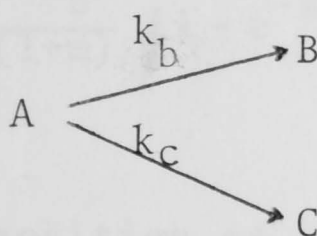
and let k_b and k_c be the respective rate constants. Whereupon:

$$A_o = A + B + C \qquad\qquad (A_o \text{ is the conc. of A at } t=0) \qquad (3)$$

$$\frac{C}{B} = \frac{k_c}{k_b} = m \qquad\qquad (Let \ \frac{k_c}{k_b} = m) \qquad\qquad\qquad (4)$$

$$A_o = B_\infty + C_\infty \quad (B_\infty \text{ is the conc. of B at } t = \infty) \quad (5)$$

$$\therefore \quad A_o = B_\infty (1 + m) \quad (6)$$

The rate of formation of ethylene is given by the equation:

$$\frac{dB}{dt} = k_b A = k_b [A_o - B(1+m)] \quad (7)$$

or

$$\frac{dB}{dt} = k_b A_o - k_b B(1+m) \quad (8)$$

Rearranging and substituting equ. 6:

$$\frac{1}{k_b(1+m)} \cdot \frac{dB}{dt} = \frac{A_o}{(1+m)} - B = B_\infty - B \quad (9)$$

or

$$\frac{dB}{(B_\infty - B)} = (k_b + k_c)dt = k_b(1+m)dt \quad (10)$$

Integrating:

$$\ln\left(\frac{B_\infty - B}{B_\infty}\right) = -k_b(1+m)t \quad (11)$$

or

$$B = B_\infty [1 - e^{-k_b(1+m)t}] \quad (12)$$

$$\therefore \quad B = \frac{A_o}{(1+m)} [1 - e^{-k_b(1+m)t}] \quad (13)$$

For the decomposition of ethyl N-methylcarbamate, the progress of the reaction was measured by monitoring the increase in pressure with time. Since the carbamate decomposes by two simultaneous reactions producing three mole of products for the ethylene forming reaction and two mole of products for the ethanol forming reaction, the total pressure (P_t) at any time (t) is:

$$P_t = A + 3B + 2C \quad (14)$$

where A donates the pressure of A, B the pressure of B, and C the pressure of C. Additionally, if P_o is the initial pressure of carbamate, the relationship is:

$$\frac{\Delta P}{P_o} = \frac{A + 3B + 2C - A_o}{A_o} \qquad (15)$$

Substituting equ. 3 leads to the simplified form:

$$\frac{\Delta P}{P_o} = \frac{2B + C}{A_o} \qquad (16)$$

or
$$\frac{\Delta P}{P_o} = \frac{B}{A_o}(2+m) \qquad (17)$$

Substituting the value for B (equ.17) into equ. 13 leads to:

$$\frac{\Delta P}{P_o} = \frac{(m+2)}{(m+1)}[1 - e^{-k_b(1+m)t}] \qquad (18)$$

or
$$\ln\left[1 - \frac{\Delta P(m+1)}{P_o(m+2)}\right] = -k_b(1+m)t \qquad (19)$$

This last form (equation 19) is the equation in terms of pressure which will describe the pressure-time data for the decomposition of ethyl N-methylcarbamate if the model assumed viz: simultaneous reaction by equations (2a) and (2b) is the correct one.

During runs pressure increased smoothly with time and without induction periods. Pressure-time data for a typical run at 351.3° are presented in Table 4.2. The method of obtaining the value for "m" is presented in the section on quantitative analysis.

Figure 4.10 shows that the plot of $\log[1-\Delta P(m+1)/P_o(m+2)]$ against time is linear. The value for k_b is calculated from the the slope of the line. Using equ.4 and m = 0.30, k_c is obtained.

Figure 4.10

Pressure-time curve and the plot of $\log\left[1 - \Delta P(m+1)/P_0(m+2)\right]$ for the decomposition of 158.0mm of Ethyl N-methylcarbamate at 351.3° ($\Delta P = 116.8$mm).

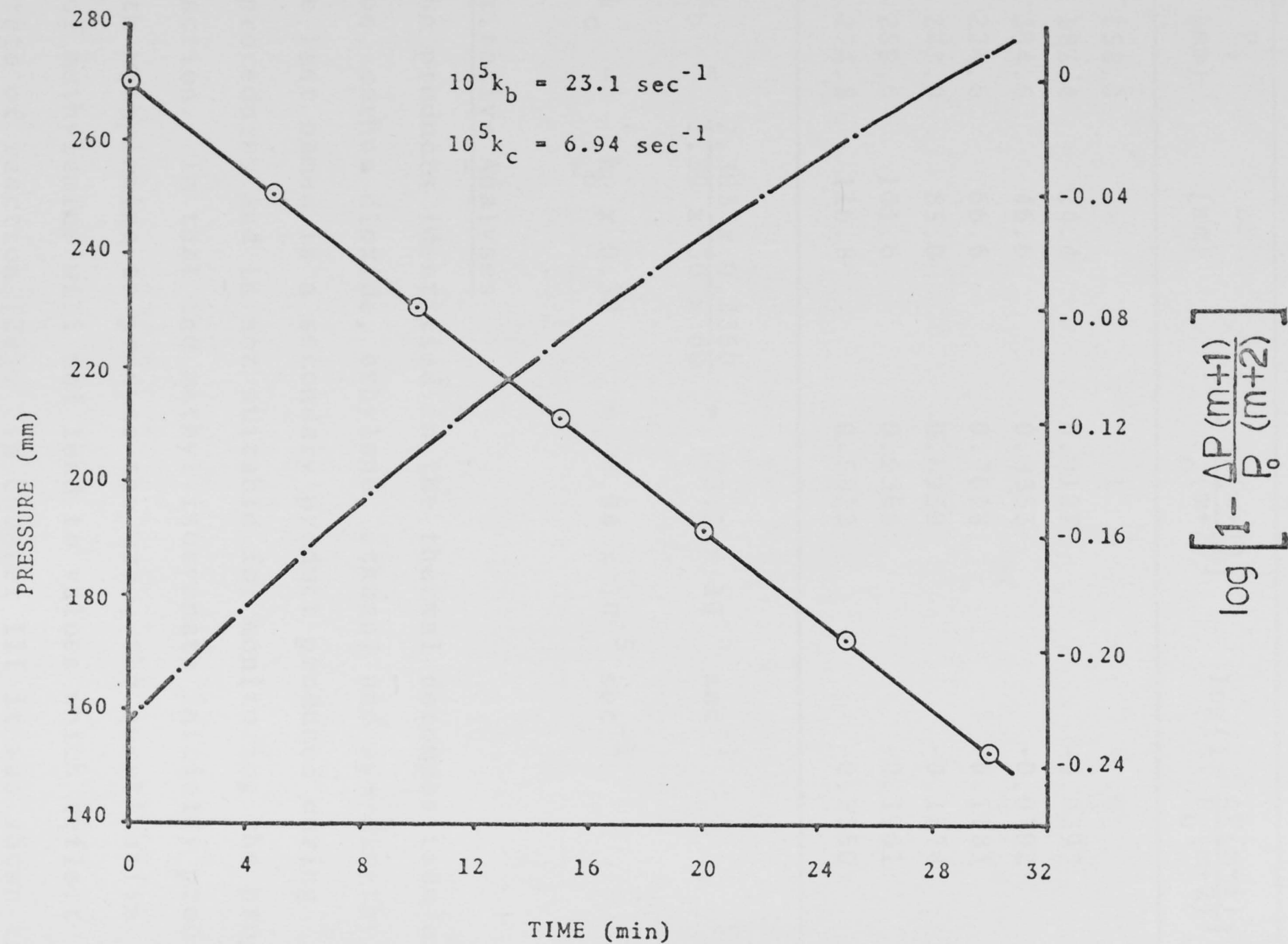$10^5 k_b = 23.1 \text{ sec}^{-1}$

$10^5 k_c = 6.94 \text{ sec}^{-1}$

Table 4.2

THE THERMAL DECOMPOSITION OF ETHYL N-METHYLCARBAMATE.

Rate Data for a Typical Run at 351.3°

t (min)	P_t (mm)	ΔP (mm)	$[1 - \frac{\Delta P(m+1)}{P_o(m+2)}]$	$\log[1 - \frac{\Delta P(m+1)}{P_o(m+2)}]$
0	158.0	-	1	0
5	182.4	24.4	0.9127	-0.0397
10	204.6	46.6	0.8333	-0.0792
15	224.6	66.6	0.7618	-0.1181
20	243.0	85.0	0.6959	-0.1574
25	259.6	101.6	0.6366	-0.1961
30	274.8	116.8	0.5822	-0.2350

$$k_b = \frac{2.303 \times 0.2350}{1.30 \times 30 \times 60} = 23.1 \times 10^{-5} \text{ sec}^{-1}$$

$$k_c = k_b \times 0.30 = 6.94 \times 10^{-5} \text{ sec}^{-1}$$

(G) Quantitative Analyses

The products identified in the thermal decomposition are methylamine, carbon dioxide, ethylene, ethanol and *sym*-dimethyl-urea. The last named is a secondary product produced during analysis procedures and is not suitable for monitoring the progress of the reaction. In that the methyl isocyanate initially produced reacts with methylamine to produce the urea, the quantitative analysis of methylamine will not lead to values which reflect only the rate of reaction (2a). In Chapter III it was shown that amines such as methylamine react with carbon dioxide to produce an adduct so that carbon dioxide analyses detect *ca*. 60-70% of the gas formed in the decompositions. The result is that ethylene and ethanol appear to be the only products which can be estimated quantitatively to provide a measure of the rates of reactions (2a) and (2b).

During product identification in this chapter the white solid formed was shown to be *sym*-dimethylurea. The results presented in Chapter III show that an adduct between carbon dioxide and methylamine should almost certainly form to an extent. That this was not detected is due to the method of handling which deliberately avoided this complication in that: Of the volatile materials only the liquid and gaseous fractions were analysed, and the solid formed was pumped thoroughly to remove volatile materials. The carbon dioxide-methylamine adduct is comparatively volatile and is removed by such treatment.

Calculations of rate constants from the pressure-time data require values for "m" which was defined in section F. The analyses of ethanol and ethylene are now described, and the values of "m" are tabulated.

(a) Estimation of Ethylene

Ethylene produced by the decomposition of ethyl N-methyl-carbamate at 351.3° was separated and estimated by g.l.c. analysis using nitrous oxide as a standard reference and measuring peak-heights relative to those of nitrous oxide. Procedures are outlined in Chapter II. Determinations were carried out at differing extents of reaction, and results are reported in Table 4.3. Table 4.3 also lists percent ethylene where ethylene is related to the initial pressure of carbamate. Results are plotted against time in Figure 4.11. Similar graphs were obtained at each temperature studied and were used in determining the value for "m" at each temperature.

(b) Estimation of Ethanol.

Analysis for ethanol is complicated by several factors.
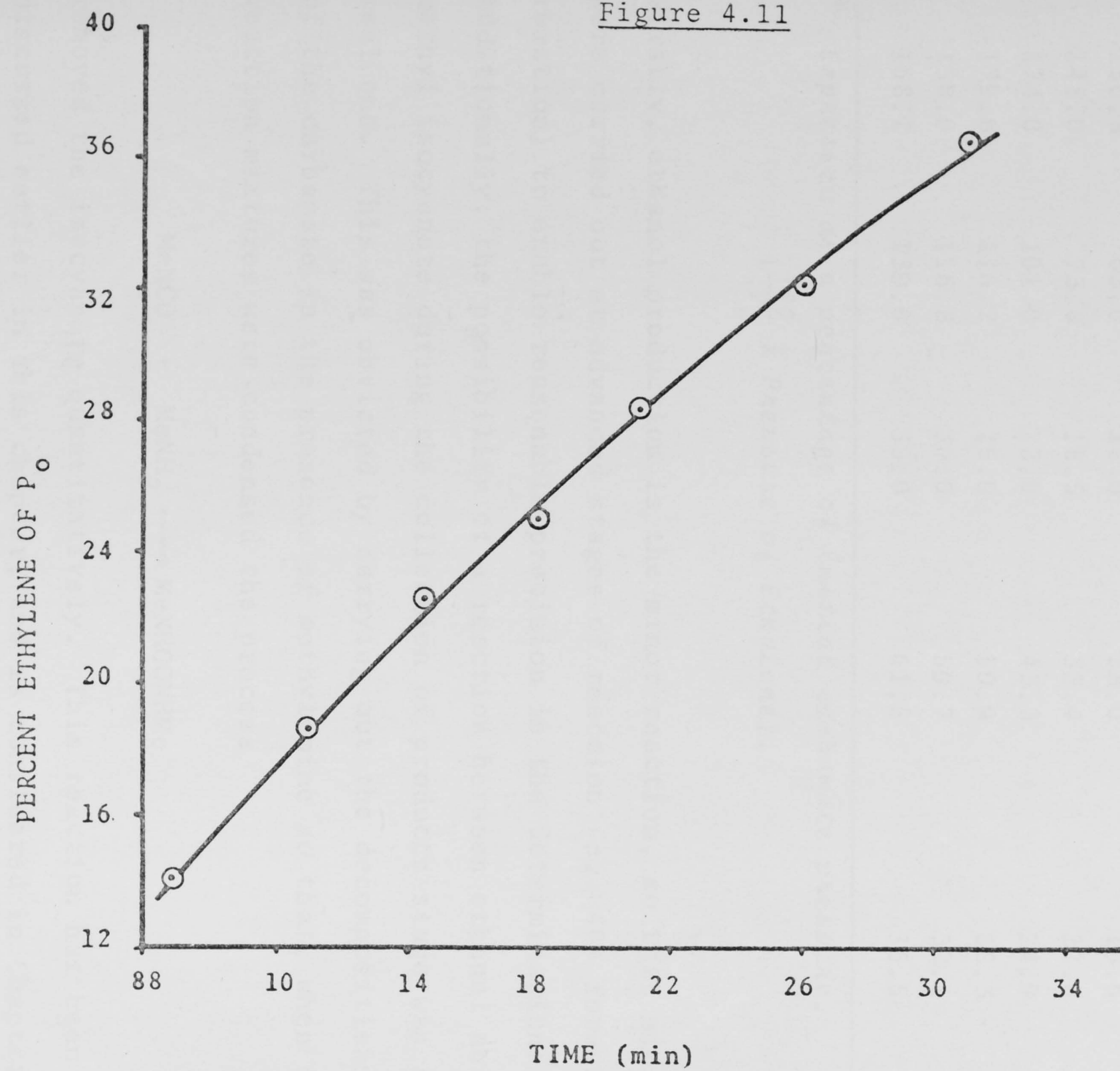
Figure 4.11

Table 4.3

Estimation of Ethylene Formed at 351.3°

P_O(carbamate) (mm)	ΔP (mm)	Reaction time (min)	Pressure of Ethylene (mm)	Reaction (%) by Ethylene Anal.[a]
167.0	53.1	10.9	23.4	14.0
150.8	63.0	15.0	28.0	18.6
148.0	73.8	18.5	33.4	22.6
174.0	101.0	22.0	43.3	24.9
179.6	116.2	25.0	50.9	28.3
158.0	116.8	30.0	50.7	32.1
168.2	139.0	35.0	61.5	36.5

[a] *Expressed as a percentage of initial carbamate pressure,*

$$(\frac{100}{P_O} \text{ x Pressure of Ethylene}).$$

Firstly, ethanol production is the minor reaction, so that analyses were carried out at advanced stages of reaction (*ca.* 40% forward reaction) to enable reasonable precision in the determinations. Additionally, the possibility of a reaction between ethanol and methyl isocyanate during the collection of products stage was a real one. This was obviated by carrying out the decompositions of the carbamate in the presence of methylamine so that, when the reaction mixtures were condensed the process

$$\text{MeNCO} + \text{MeNH}_2 \longrightarrow \text{MeNHCONHMe}$$
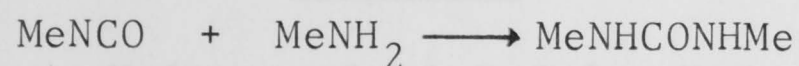
removed the isocyanate quantitatively. This reaction has been discussed earlier in this chapter, and is considered in Chapter V and shown to be quantitative. The effect of amines on the carbamate decomposition has also been studied and shown not to affect the reaction.

In general ethyl N-methylcarbamate was decomposed in the presence of methylamine (in about twice the quantity of the ethylene

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produced) and the reaction mixture was collected, and the ethanol
estimated as described in Chapter II. Results are expressed as
a percentage of the initial pressure of carbamate used in the
particular run. Thus at 351.3° ethyl N-methylcarbamate (166.0 mm)
was allowed to react for 35.0 min in the presence of 138.4 mm of
methylamine (ΔP = 138.6 mm) and the reaction mixture was collected,
and analysis for ethanol gave a value of 11.0%. Amounts of
ethanol produced in two further determinations carried out after
35 min were 10.7 and 11.3%. Sets of analyses were carried out at
each temperature in the range.

(H) Calculation of "m" and First-order Rate Constants.

The reaction scheme proposed involves two simultaneous
first-order processes and if this model is the correct one then
the ratio of ethanol to ethylene will remain constant throughout
the reaction. Thus, at 351.3° after 35 min, the mean percentage
of ethanol (related to initial pressure of carbamate) is 11.0%
whereas the data in Figure 4.11 show that the percentage of
ethylene is 36.2%. Comparison of these values leads to the value
of m = 0.30 at 351.3°. Similar procedures were used to calculate
m at each temperature. Values obtained are listed in Table 4.4.

Table 4.4

Values calculated for "m"

Temp.(°C)	331.1°;	340.9°;	351.3°;	360.7°;	373.8°;	381.2°
"m"	0.33;	0.31;	0.30;	0.29;	0.27;	0.27

These values for "m" were used in conjunction with
equation 19 and satisfactory plots were obtained (see Figure 4.10),
and values of k_b were calculated. The relationship, $k_c = mk_b$

was used to obtain corresponding values for k_c, and both sets of constants are listed in Table 4.5.

Table 4.5

Values of First-order Rate Constants, k_b and k_c.

Temp(°C)	No. of Runs	Variation in P_o (mm)	$10^5 k_b$ (sec^{-1})	$10^5 k_c$ (sec^{-1})
381.2	10	45-239(x 5.3)[a]	$125^{\pm}3$	33.8 ± 0.9[b]
373.8	7	39-229(x 5.9)	$85^{\pm}1$	23.0 ± 0.3
360.7	12	49-250(x 5.1)	$40^{\pm}1$	11.6 ± 0.2
351.3	10	48-259(x 5.4)	$23.2^{\pm}0.3$	6.9 ± 0.1
340.9	10	58-238(x 4.1)	$12.3^{\pm}0.3$	3.8 ± 0.1
331.1	9	42-247(x 5.9)	$6.7^{\pm}0.2$	$2.21^{\pm}0.05$

[a] *Factor gives variation in initial pressure.*
[b] *Standard deviation.*

The kinetic model chosen successfully describes the pressure-time data for each reaction. Additionally, the validity was tested at each temperature by examining the effect of a sixfold variation of initial pressure of carbamate on each of the rate constants k_b and k_c. The results are presented graphically in Figures 4.12 and 4.13 and clearly establish that the constants k_b and k_c accurately describe the rate processes, and justify the kinetic treatment and the assumptions implicit in that treatment.

The variation of these rate constants with temperature is described by the Arrhenius equations:

$$k_b = 10^{12.47} \exp(-46,020 \pm 200/RT) \ sec^{-1} \qquad (E \ in \ cal.mole^{-1})$$

$$and \ k_c = 10^{10.91} \exp(-43,070 \pm 750/RT) \ sec^{-1} \qquad (E \ in \ cal.mole^{-1})$$

Figure 4.12

VARIATION OF k_b WITH INITIAL PRESSURE OF ETHYL N-METHYLCARBAMATE.
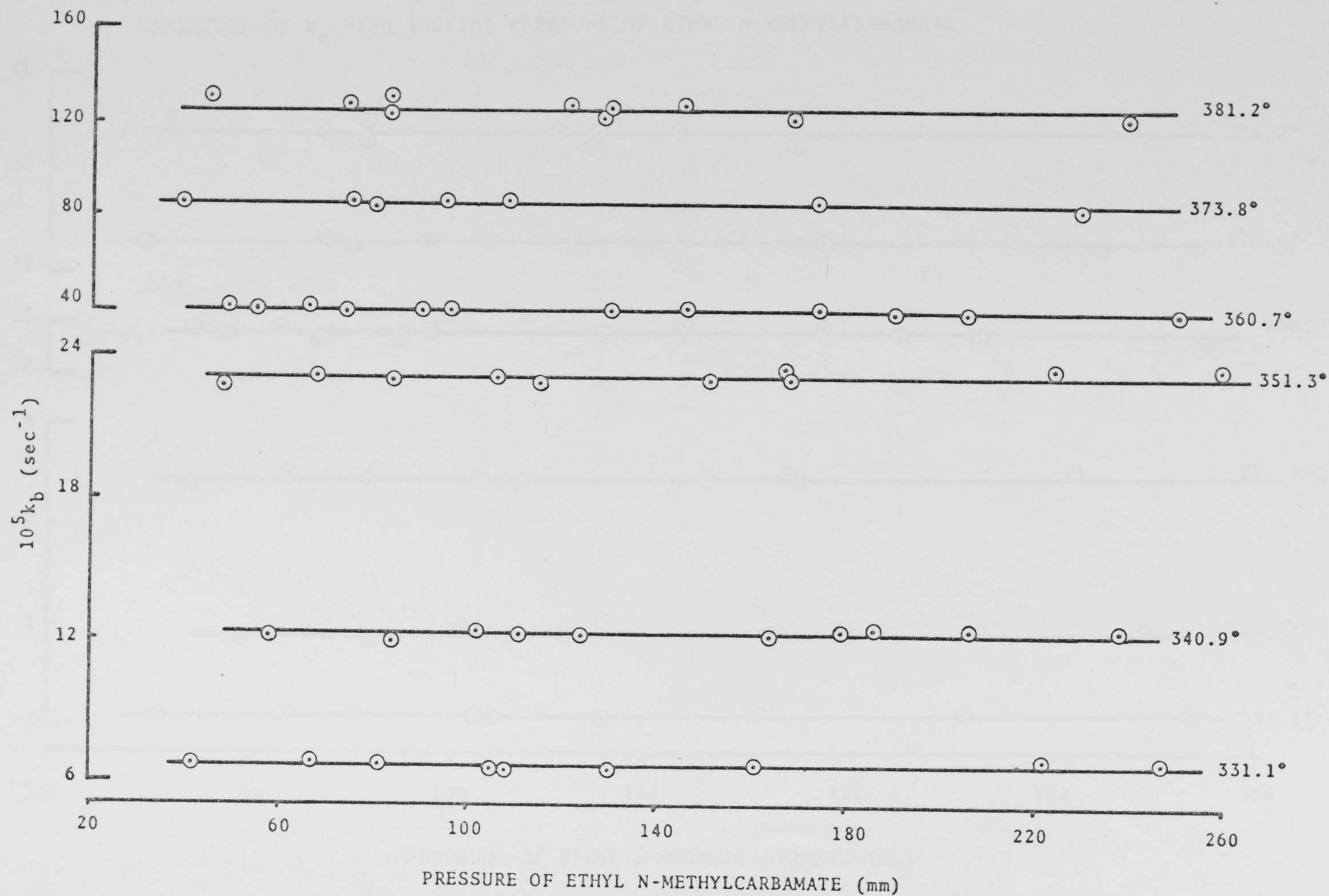
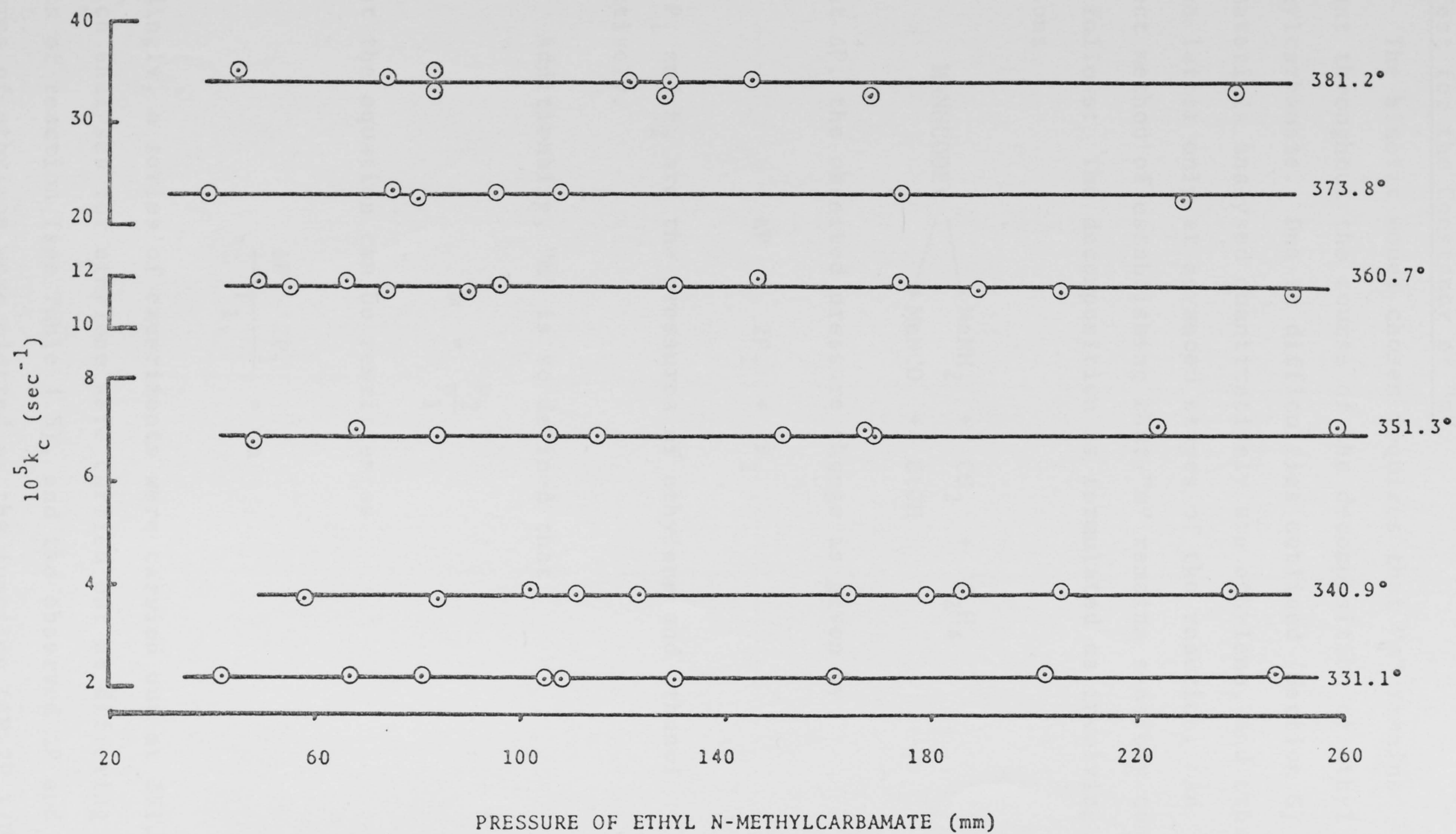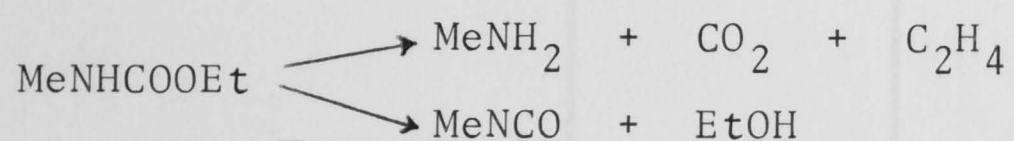PRESSURE OF ETHYL N-METHYLCARBAMATE (mm)

Figure 4.13

VARIATION OF k_c WITH INITIAL PRESSURE OF ETHYL N-METHYLCARBAMATE

(J)   Test for the Constancy of "m".

The kinetic model chosen requires that "m" remains
constant throughout the course of the decomposition of ethyl
N-methylcarbamate. Due to difficulties outlined (Section G) the
only materials analysed quantitatively are ethylene, and ethanol,
and the latter only at advanced stages of the reaction. An
indirect method of establishing that "m" remains sensibly constant
is as follows: The decomposition is formulated as involving the
reactions

$$\text{MeNHCOOEt} \begin{array}{l} \longrightarrow \text{MeNH}_2 \;+\; CO_2 \;+\; C_2H_4 \\ \longrightarrow \text{MeNCO} \;+\; \text{EtOH} \end{array}$$

so that ΔP, the observed pressure change is given by

$$\Delta P \;=\; 2P_1 \;+\; P_2$$

where P_1 and P_2 are the pressures of ethylene and ethanol
respectively.

Additionally, "m" is so defined that

$$m \;=\; \frac{P_2}{P_1}$$

so that the equation can be rewritten as

$$\frac{\Delta P \,-\, 2P_1}{P_1} \;=\; m$$

Accordingly, a series of experiments were carried out at 351.3°
in which analyses for ethylene were carried out at differing
extents of reaction (see Table 4.3), and the observed ΔP and
pressures of ethylene were plotted as the function $(\Delta P - 2P_1)/P_1$
against P_1. The results are shown in Figure 4.14. The line

Figure 4.14
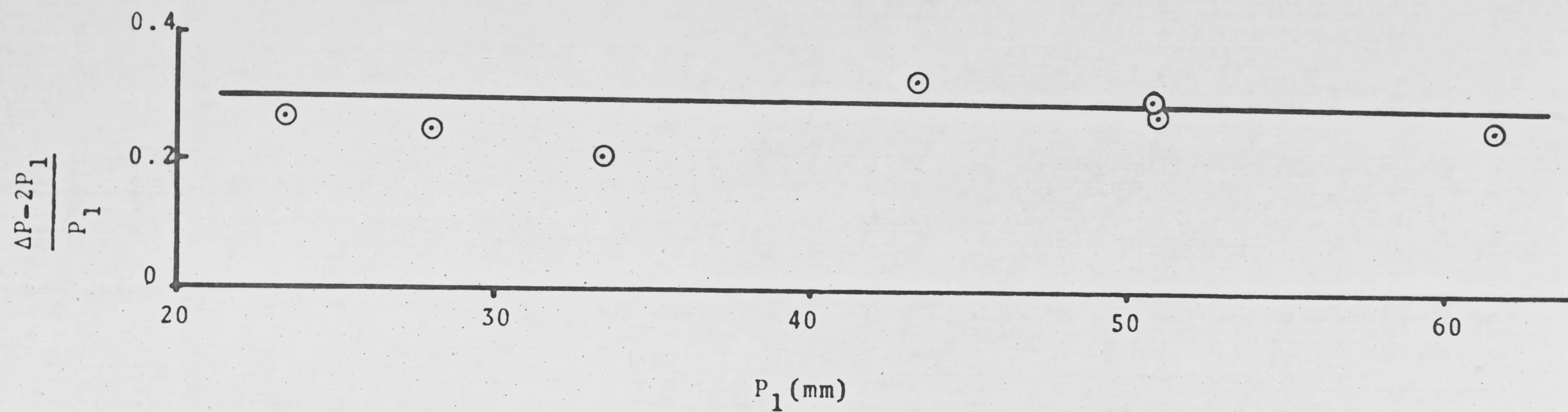
drawn shows the value for "m" obtained from the analyses of
ethanol at advanced stages of reaction and for ethylene (Section
H). The agreement is satisfactory and shows that $(\Delta P - 2P_1)/P_1$
shows no trend away from "m" and provides useful corroborative
evidence that the kinetic model is valid.

(K) Effect of Additives.

Analyses for ethanol were carried out using a technique
involving the carrying out of a decomposition of ethyl N-methyl-
carbamate in the presence of methylamine. Since the possibility
of transesterification reactions existed

$$R'NHCOOR^2 + R^3NH_2 \longrightarrow R'NHCONHR^3 + R^2OH$$
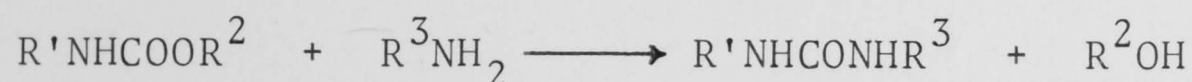
and because sym-dimethylurea had been detected among the products,
(Sections C, D.) runs were carried out in the presence of methyl-
amine and ethylamine. The addition of up to 208 mm of amine had
no effect on rate. Results are listed in Table 4.6. Additionally,
the addition of pressures of up to 126 mm of isobutene had no
effect on rate, so that the existence of a free-radical chain-
mechanism seems unlikely.

Runs were carried out in a reaction vessel having a S/V
ratio = 8.0 cm^{-1} (compared with S/V = 0.8 cm^{-1} normally used).
The values obtained are listed in Table 4.7 and show that the
reaction is essentially homogeneous.

Table 4.6

EFFECT OF ADDITIVES AT 351.3°

P_o(carbamate) (mm)	Additive	P(additive) (mm)	$10^5 k_b$ (sec^{-1})	$10^5 k_c$ (sec^{-1})
111.3	no additive	-	23.1	6.9
168.1	no additive	-	23.2	7.0
68.7	isobutene	126.4	22.9	6.9
111.5	isobutene	106.7	23.5	7.1
132.5	isobutene	73.4	23.0	6.9
85.3	ethylene	99.9	23.1	6.9
78.3	ethylene	110.8	23.4	7.0
78.0	methylamine	128.3	23.6	7.1
69.2	methylamine	208.0	23.5	7.0
82.0	methylamine	79.9	23.1	6.9
92.4	ethylamine	67.2	23.1	6.9
58.6	ethylamine	154.1	23.2	7.0

Table 4.7

RATE CONSTANTS OBTAINED IN REACTION VESSEL WITH S/V = 8.0 cm^{-1}.

Temp. (°C)	$10^5 k_b$[a] (sec^{-1})	$10^5 k_c$[a] (sec^{-1})	$10^5 k_b$ (calc)	$10^5 k_c$ (calc)[b]
373.8	86	23.4	84	23.0
340.9	12.5	3.9	12.4	3.8

[a] *Mean of 5 runs.* [b] *Calc. from Arrhenius equation for vessel with S/V = 0.8 cm^{-1}.*

DETAILS OF ALL RUNS

1) Runs in reaction vessel with S/V = 0.8 cm^{-1}.

P_o*(mm)	$10^5 k_{\underline{b}_1}$ (sec^{-1})	$10^5 k_{\underline{c}_1}$ (sec^{-1})	P_o(mm)	$10^5 k_{\underline{b}_1}$ (sec^{-1})	$10^5 k_{\underline{c}_1}$ (sec^{-1})
Temp: 381.2°	m = 0.27		Temp: 373.8°	m = 0.27	
45.0	130	35.1	39.0	85	23.0
73.8	127	34.4	74.8	86	23.3
83.1	123	33.2	79.7	84	22.6
83.5	130	35.2	95.0	86	23.2
121.0	127	34.2	107.8	86	23.2
128.0	121	32.7	173.5	86	23.1
129.4	125	33.8	222.9	83	22.4
144.6	127	34.2		Mean: 85	Mean: 23.0
168.0	121	32.6			
239.0	122	32.8			
	Mean: 125	Mean: 33.8			

Temp: 360.7°	m = 0.29		Temp: 351.3°	m = 0.30	
49.0	41	11.8	48.2	22.7	6.8
54.8	40	11.6	68.5	23.2	7.0
66.1	41	11.8	83.7	23.0	6.9
73.9	39	11.4	105.8	23.1	6.9
90.2	39	11.4	114.6	22.9	6.9
96.3	40	11.6	150.8	23.0	6.9
129.6	40	11.6	167.0	23.5	7.0
145.7	41	11.9	168.2	23.1	6.9
174.2	41	11.8	223.8	23.6	7.1
189.4	39	11.5	259.4	23.6	7.1
205.2	39	11.4		Mean: 23.2	Mean: 6.9
250.0	39	11.3			
	Mean: 40	Mean: 11.6			

P_O (mm)	$10^5 k_{b_1}$ (sec^{-1})	$10^5 k_{c_1}$ (sec^{-1})	P_O (mm)	$10^5 k_{b_1}$ (sec^{-1})	$10^5 k_{c_1}$ (sec^{-1})
Temp: 340.9°	m = 0.31		Temp: 331.1°	m = 0.33	
57.8	12.1	3.7	42.2	6.7	2.20
84.1	11.9	3.7	67.0	6.8	2.23
102.4	12.4	3.9	81.4	6.7	2.23
111.0	12.2	3.8	104.9	6.5	2.15
123.8	12.2	3.8	107.8	6.5	2.15
163.7	12.2	3.8	129.7	6.5	2.14
179.2	12.4	3.8	161.1	6.7	2.22
185.7	12.5	3.9	222.0	7.0	2.30
205.6	12.5	3.9	246.6	6.9	2.28
237.6	12.5	3.9			
	Mean: 12.3	Mean: 3.8		Mean: 6.7	Mean: 2.21

CHAPTER V

THE THERMAL DECOMPOSITION OF
METHYL N-METHYLCARBAMATE

(A) Introduction

The thermal decompositions of ethyl N-methyl-N-phenyl-carbamate, isopropyl N,N-dimethylcarbamate and t-butyl N,N-dimethylcarbamate gave quantitative yields (see Chapter III) of amine, carbon dioxide, and alkene. No trace of an isocyanate forming reaction was observed. The decomposition of ethyl N-methylcarbamate proceeds (Chapter IV) by means of competing reactions; one reaction produces amine, carbon dioxide, and alkene, while the other is the minor reaction with a rate constant about 30% of that for alkene production and produces isocyanate and alcohol. Methyl carbamates are known to produce isocyanates and methanol under certain conditions; thus in a stream of nitrogen using precautions to separate the products to stop reversal of the reaction, methyl N-methylcarbamate pyrolyses to methyl isocyanate and methanol[101] at 430-440°. In order to characterise the isocyanate forming reaction further, a study of the kinetics of the decomposition of methyl N-methylcarbamate was undertaken.

(B) Materials

Methyl N-methylcarbamate was prepared from methyl chloroformate and methylamine and after fractionation through a 12-in column of Fenske helices had b.p. 54°/8 mm and n_D^{20} 1.4161 (lit.[99] 64-65°/14 mm, and n_D^{20} 1.4155) (Found: C, 40.1; H, 7.8; N, 15.7. Calc. for $C_3H_7NO_2$: C, 40.4; H, 7.9; N, 15.7%).

Methanol and n-Propanol (B.D.H. Laboratory grade reagent) were fractionated and dried using magnesium activated with iodine as outlined by Vogel[100].

Volumetric solutions were prepared by the appropriate dilution of May & Baker "Volucon" volumetric solutions.

82

(C)   Reaction Kinetics

The decomposition of methyl N-methylcarbamate occurred when a sample of the compound was introduced into the reaction vessel by the "distill-in" technique. The reaction was studied in the temperature range 370-422°. The progress of the reaction was followed by monitoring the rate of change of pressure.

The rate of reaction was very sensitive to the nature of the surface coating. Both the packed and unpacked reaction vessels were coated with the decomposition products of the carbamate until reproducible first-order rate constants were obtained. Between runs, the products were allowed to remain in the reaction vessel overnight.

During runs pressure increased smoothly with time and without induction periods to values for P_f/P_o of 1.97 ± 0.01 (where P_f and P_o have usual meanings) indicating a reaction in which the molar ratio of products to reactant is 2:1. Reactions were followed to *ca.* 40-50% reaction over the temperature range and rate constants were obtained from plots of the function $\log(P_o - \Delta P)$ against time (Figure 5.1).

(D)   Product Identification.

As a general procedure methyl N-methylcarbamate was allowed to react to 20-60% reaction, and the reaction mixture was collected at -196° and allowed to warm to ambient temperature. Samples of the resultant liquid were injected onto a Carbowax column (72 x ¼ in; helium flow rate: 76 ml.min^{-1}) at 125°. Methanol and unchanged carbamate were separated with retention times 55 sec and 380 sec respectively which corresponded with those of authentic samples. The only other peak was assigned to methyl isocyanate which, when the column temperature was reduced to 40°, had a retention time of 108 sec. Methyl N-methylcarbamate (132.8

Figure 5.1

Pressure-time curve and first-order log-plot for the decomposition of 240.0mm of methyl N-methylcarbamate at 401.1° (ΔP = 134.2mm ; $10^4 k_1$ = 6.8 sec^{-1}).
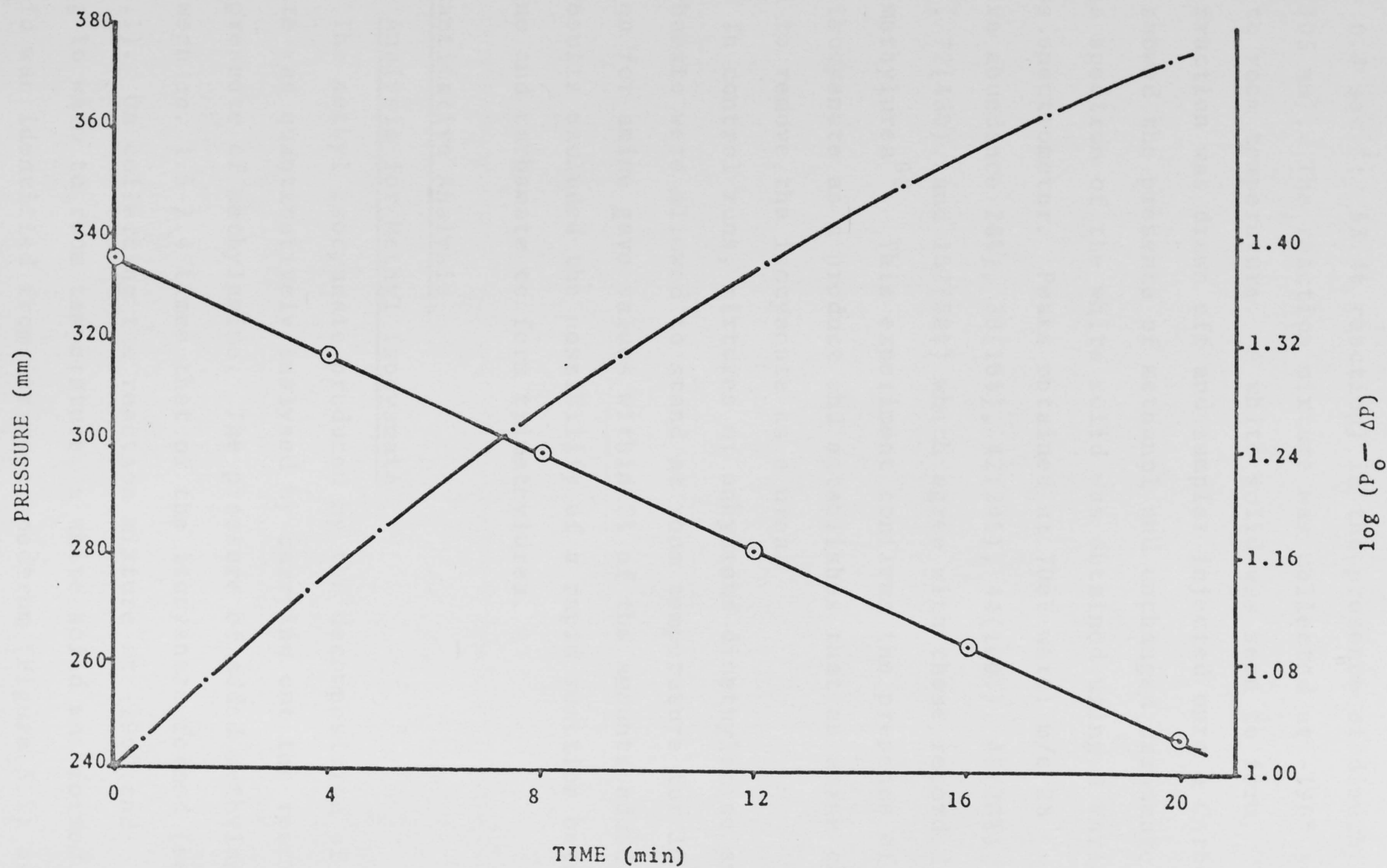
mm) was allowed to react at 401° for 20 min (ΔP = 71.5 mm; $10^4 k_1$ = 6.4 sec^{-1}; 53.4% reaction) in the presence of dimethyl-amine (105 mm). The reaction mixture was collected at -196° and warmed to room temperature. A white solid was seen to form. The liquid fraction was drawn off and samples injected onto a Carbowax column showed the presence of methanol and unchanged carbamate. The mass spectrum of the white solid was obtained using a Varian CH7 mass spectrometer. Peaks obtained at 70eV were: m/e 28 (relative abundance 28%), 30(16%), 42(24%), 44(100%), 45(20%), 58(24%), 72(43%), and 102(58%) which agree with those recorded for trimethylurea[98]. This experiment confirms the presence of methyl isocyanate as a product and establishes that an amine can be used to remove the isocyanate as a urea.

In control runs, mixtures of anhydrous dimethylamine and the carbamate were allowed to stand at room temperature for 10 min. Titration for amine gave values within 2% of the amounts added. These results excluded the possibility of a rapid reaction between the amine and carbamate to form trimethylurea.

(E) Quantitative Analysis

(a) Analysis for Methyl Isocyanate

The methyl isocyanate produced by the decomposition of the carbamate was quantitatively analysed by carrying out the reaction in the presence of methylamine. The pressure of added methylamine was between *ca.* 1.5-2.4 times that of the isocyanate formed (see Table 5.1). On collecting the reaction mixture at -196° and allowing to warm to room temperature, a white solid was formed. The solid was identified from its mass spectrum (Figure 5.2) as *sym*-dimethylurea[98]. The results reported in Table 5.1 show that the isocyanate formed was quantitatively removed as the urea when the products were collected for analysis. The unreacted amine

Figure 5.2

MASS SPECTRUM OF THE WHITE SOLID.
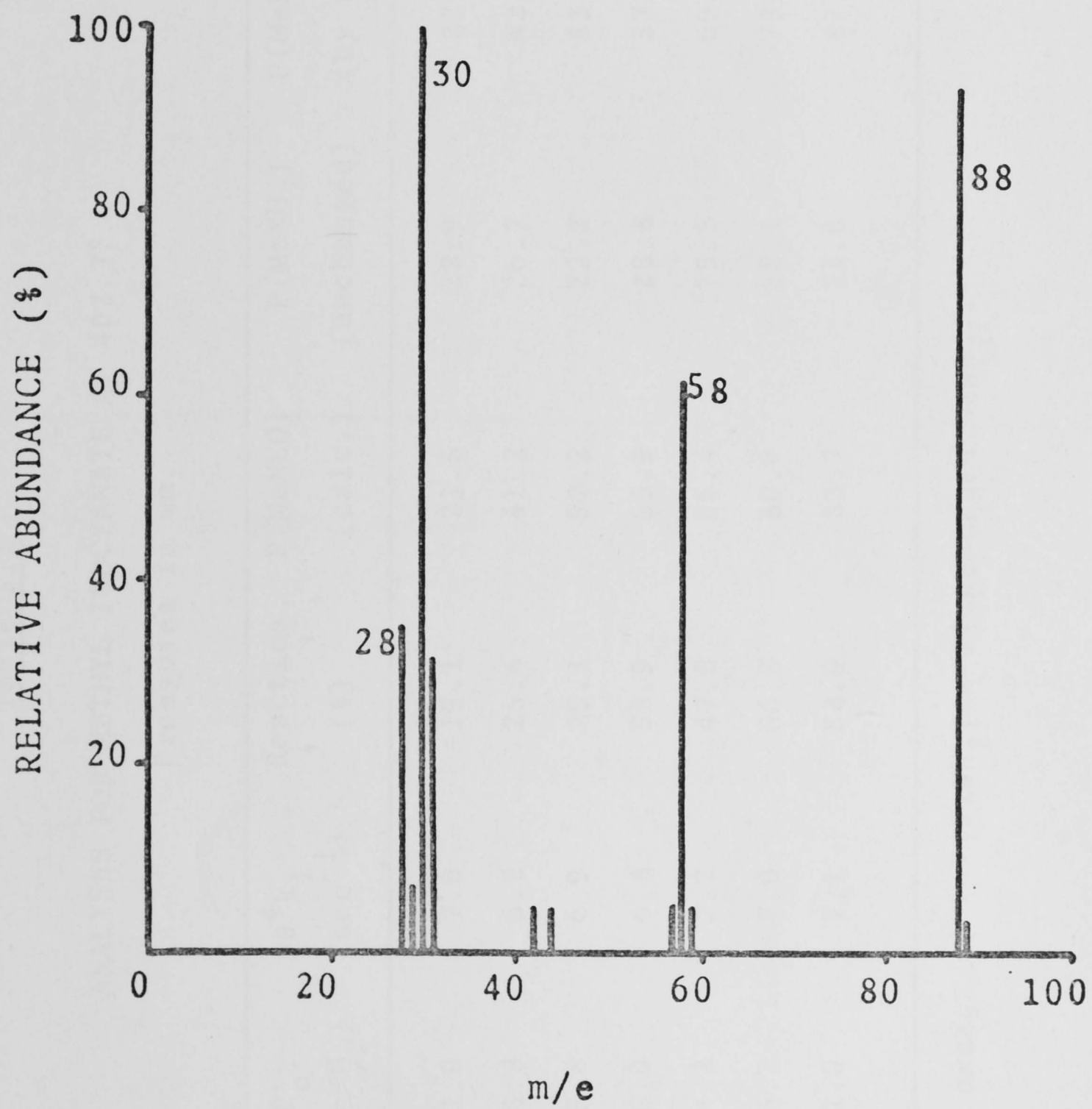
(IDENTIFIED AS SYM-DIMETHYLUREA)

Table 5.1

ANALYSES FOR METHYL ISOCYANATE AT 402.7°

Pressures in mm.

P_o (carbamate)	P_o (MeNH$_2$)	$10^4 k_1$ (sec^{-1})	Reaction (%)	P(MeNCO) (calc.)	P(MeNH$_2$) (unchanged)	P(MeNCO)[a] (by anal.)	Reaction (%) (by anal.)
112.3	51.0	7.0	19.1	21.5	28.9	22.1	19.7
161.0	68.8	6.8	25.6	41.2	26.7	42.1	26.1
179.5	75.8	6.9	29.1	52.2	22.2	53.6	29.9
143.6	86.0	6.8	38.9	55.9	28.8	57.2	39.8
138.8	144.3	7.2	47.8	66.4	75.3	69.0	49.7
140.6	166.3	7.0	56.9	80.0	88.1	78.2	55.6
142.2	161.0	7.1	58.9	83.7	74.0	87.0	61.2

[a] $P(MeNCO)$ (by analysis) = $P(MeNH_2)$ - P(unchanged $MeNH_2$).

was determined by adding an excess of 0.05M HCl solution (through a rubber septum and back titrating with 0.05M NaOH using methyl red indicator. The results show that pressure-time data measure the rate of formation of methyl isocyanate.

Control runs with the carbamate and the urea gave no titre.

(b) Analysis for Methanol

The carbamate was decomposed in the presence of methyl-amine so that the methyl isocyanate was removed as *sym*-dimethylurea when the reaction products were collected. Propanol was added to the reaction mixture as the marker and analyses were carried out as described in Chapter II. Analytical results are reported in Table 5.2 and show that pressure-time data are a measure of the rate of formation of methanol.

(F) Summary of Rate Constants

Methyl N-methylcarbamate decomposes to methyl isocyanate and methanol. The decomposition follows the first-order rate law to *ca*. 40-50% reaction in the temperature range 370-422°. The initial pressure of carbamate was varied by a factor of 5-7 at each temperature and the values for the rate constants showed no dependence on P_o. Table 5.3 summarises runs at 421.6° for a seven fold variation in P_o. The results over the temperature range are presented graphically in Figure 5.3.

Values for the rate constant at various temperatures are reported in Table 5.4. Individual rate constants were reproducible to within 3% of the reported mean values. The plot of $(5 + \log k_1)$ against $10^3/T$ is linear (Figure 5.4) and the Arrhenius parameters were calculated by the method of least squares and are described by the equation:

$$k_1 = 10^{12.39} \exp(-48,060 \pm 600/RT) \text{ sec}^{-1} \qquad (E \text{ in cal. mole}^{-1}).$$

Table 5.2

ANALYSES FOR METHANOL AT 402.7°

P_o^a (carbamate)	P_o (MeNH$_2$)	$10^4 k_1$ (sec^{-1})	Reaction (%)	P(MeOH) calc.	anal.	Reaction(%) (by anal.)
180.1	78.1	7.0	20.6	37.1	38.2	21.2
139.1	96.3	7.0	34.5	48.0	49.5	35.6
135.7	124.2	7.1	45.1	61.2	61.8	45.5
169.7	146.6	7.1	52.0	88.2	90.5	53.3
133.1	147.5	7.0	57.1	76.0	76.1	57.2

a *Pressures are in mm.*

Table 5.3

RATE CONSTANTS OBSERVED AT 421.6° FOR VARIOUS
INITIAL PRESSURES OF CARBAMATE

P_o(carbamate)(mm)	33.1;	49.8;	112.0;	159.0;	232.0.
$10^4 k_1$(sec^{-1})	18.9;	19.1;	18.7;	18.7;	19.1

Mean: $10^4 k_1 = 18.9$ sec^{-1}

Table 5.4

SUMMARY OF OBSERVED RATE CONSTANTS

Temp. (°C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (mm)
421.6	5	18.9 ±0.2[a]	33-232(x 7)[b]
411.3[c]	4	11.6 ±0.2	44-211(x 4.8)
411.2	7	11.2 ±0.2	46-225(x 5)
401.1	6	6.6 ±0.2	44-240(x 5.4)
390.4	5	3.5 ±0.1	41-237(x 5.7)
383.5[c]	3	2.60±0.02	32-197(x 6.1)
380.2	6	2.02±0.03	32-203(x 6.3)
370.2	4	1.21±0.01	40-213(x 5.3)

a *Standard deviation.* b *Factor gives variation in initial pressure.* c *In vessel with S/V ratio 8 cm^{-1}.*

Figure 5.3

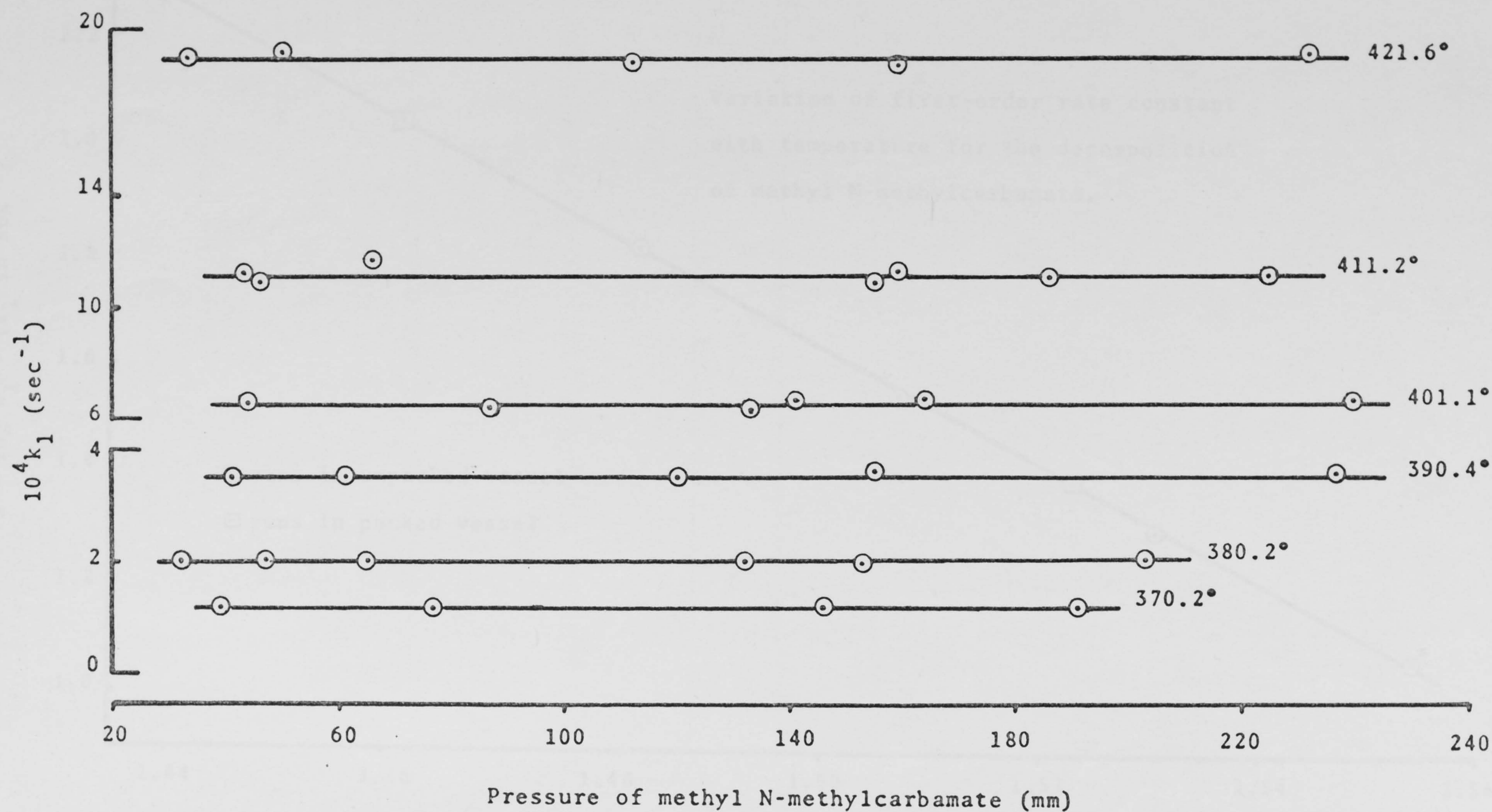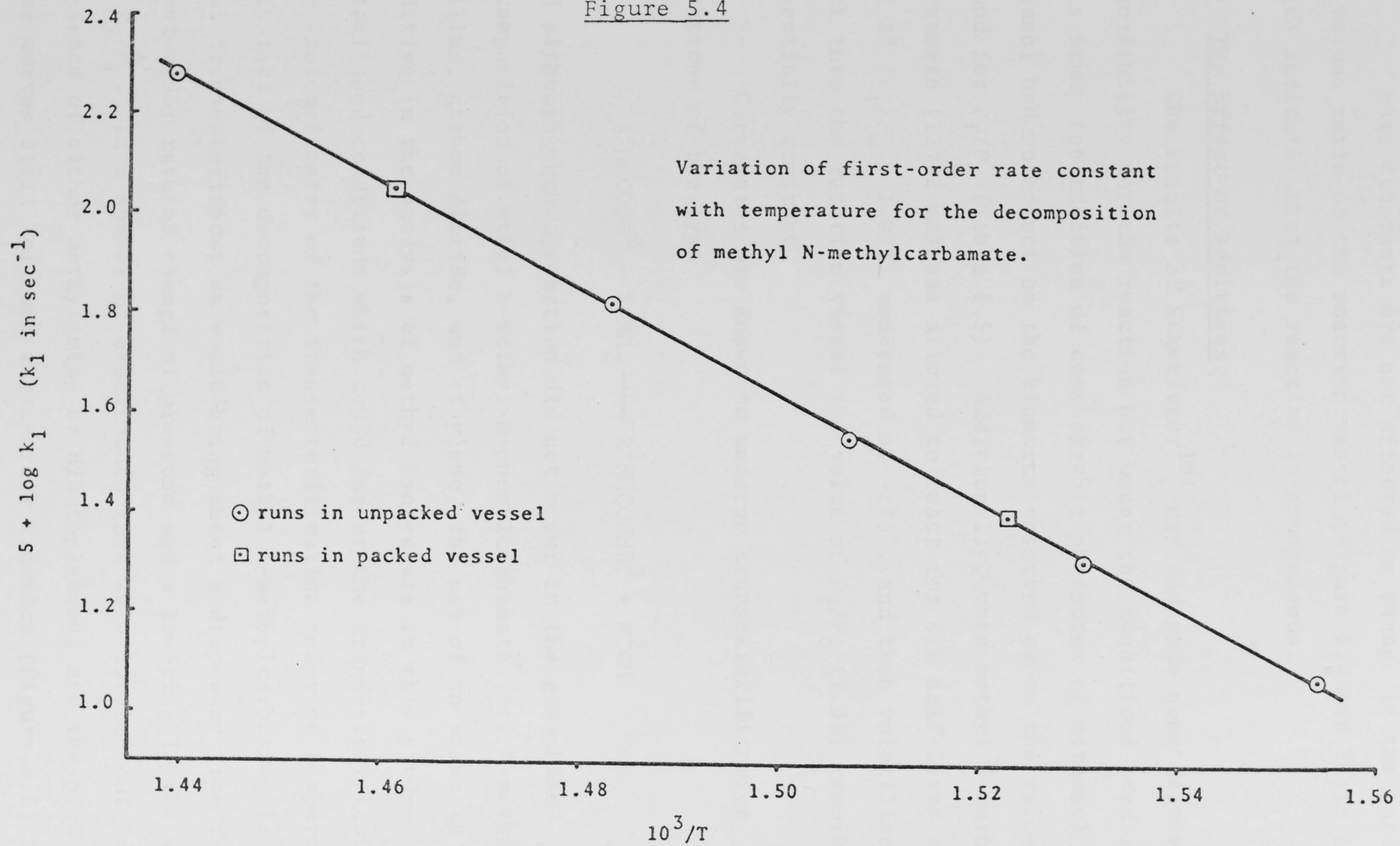Variation of first-order rate constant with initial pressure of methyl N-methylcarbamate.

Figure 5.4

Variation of first-order rate constant
with temperature for the decomposition
of methyl N-methylcarbamate.

⊙ runs in unpacked vessel
⊡ runs in packed vessel

y-axis: $5 + \log k_1$ (k_1 in sec^{-1})

x-axis: $10^3/T$

Rate constants are not affected by change in the surface to volume ratio of the reaction vessel (Figure 5.4 and Table 5.4) which indicates that the reaction is homogeneous.

(G) The Effect of Additives.

The results of Schweitzer[101] may indicate some degree of reversibility for the reaction but under the conditions used in this study the addition of considerable pressures of methanol or ethanol had no effect on the kinetics observed or on the values found for P_f/P_o (Table 5.5). Additionally, when methyl N-methyl-carbamate (127.2 mm) was allowed to react for six half-lives at 411.2° ($P_f/P_o = 1.97$), condensed at -196°, and then volatilised back into the reaction vessel the value of P_f/P_o (1.95) remained essentially constant.

Carbamates are known to undergo transesterification reactions of the type

$$R^1NHCOOR^2 + R^3NH_2 \longrightarrow R^1NHCONHR^3 + R^2OH$$
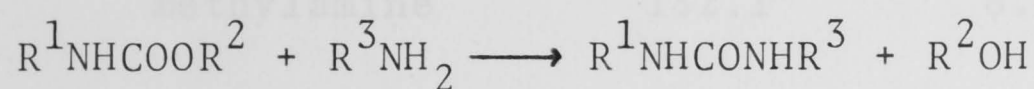
and although such a reaction did not occur in the gas-phase decomposition of ethyl N-methyl-N-phenylcarbamate into N-methyl-aniline, carbon dioxide, and ethylene, the use of an amine as an additive in the analysis of methyl isocyanate in this study established conditions which could favour the transesterification. The stoicheiometry of the transesterification reaction compared with that of the decomposition of methyl N-methylcarbamate is such that transesterification would bring about a drop away from the first-order rate of change of pressure and a lowering in the values of P_f/P_o. In a number of experiments runs were carried out in the presence of either methylamine or dimethylamine, and the pressure-time curves still followed first-order kinetics (Figure 5.5) for 50% reaction; additionally P_f/P_o values were unaffected (Table 5.5)

Table 5.5

EFFECT OF ADDITIVES AT 401.1°

P_o(Carbamate) (mm)	Additive	P(additive) (mm)	$10^4 k_1$ (sec^{-1})	P_f/P_o
87.4	no additive	-	6.4	1.97
240.0	no additive	-	6.8	-
132.8	isobutene	142.7	6.6	-
115.2	isobutene	72.1	6.6	-
67.1	isobutene	187.0	6.4	-
141.0	methylamine	131.7	6.7	-
146.7	methylamine	74.2	6.8	-
87.3	methylamine	152.1	6.6	1.96
87.6	dimethylamine	72.3	6.7	-
132.8	dimethylamine	105.0	6.4	-
73.1	dimethylamine	177.7	6.8	1.97
67.3	methanol	101.1	6.8	-
72.8	methanol	134.0	6.5	-
66.7	ethanol	157.9	6.8	1.96
131.5	ethanol	73.1	6.7	-
72.8	ethanol	131.3	6.6	-

Figure 5.5
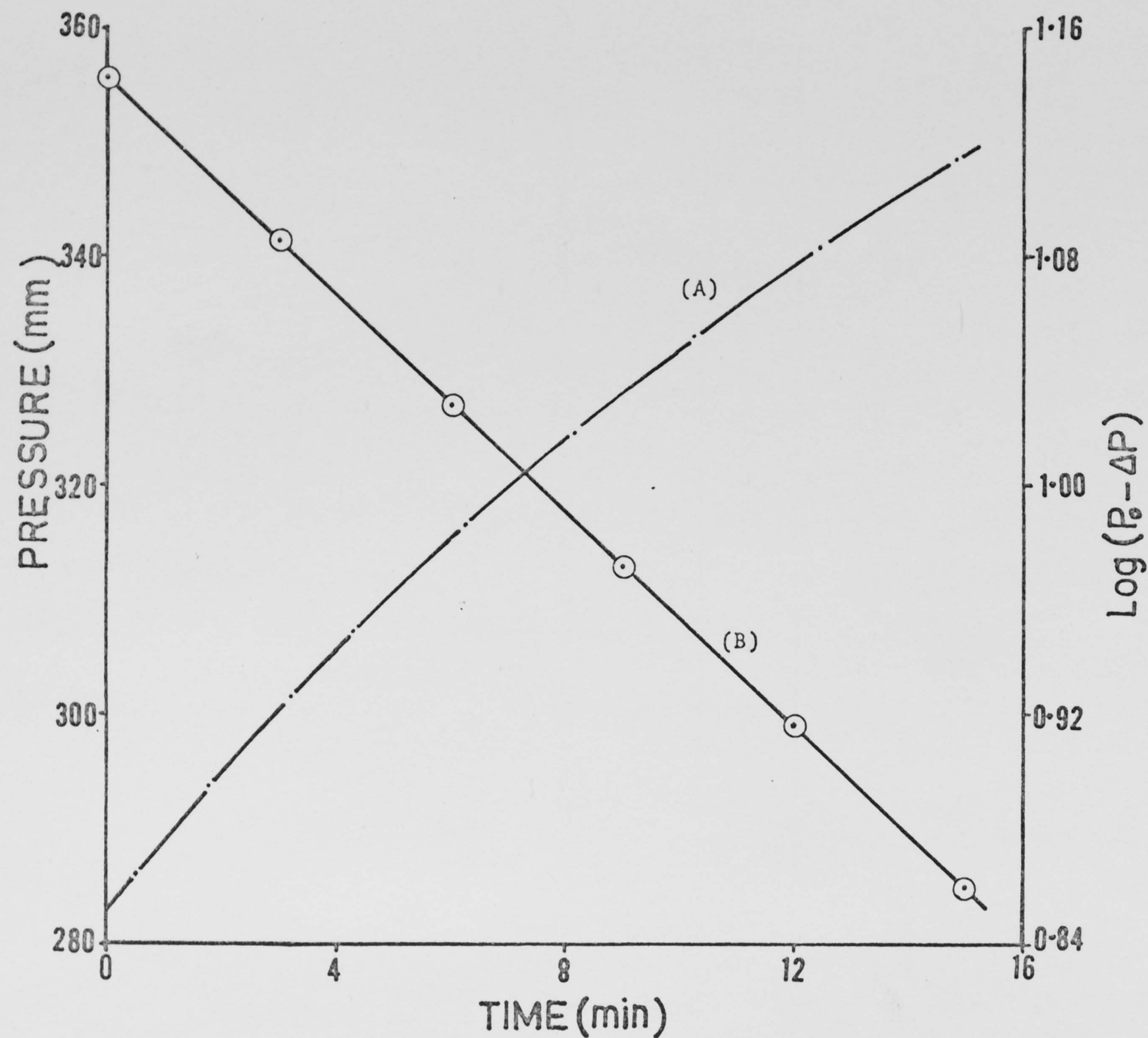
The decomposition of
methyl N-methylcarbamate
in the presence of
methylamine at 402.7°
P(carbamate) 138.8mm
P(MeNH$_2$) 144.3mm
Percent reaction 48%
$10^4 k_1 = 7.2$ sec^{-1}
A,pressure-time curve
B,first-order log-plot.

and it seems that the formation of ureas in the gas phase does not occur. However, when the reaction mixture is removed from the reaction vessel in the presence of an amine, the amine rather than methanol reacts with methyl isocyanate[102] (see Analysis of Methanol, and Table 5.2) which accords with the results of Knorr and Rossler who showed that the reaction of phenyl isocyanate with ethanolamine produces the urea rather than the carbamate[103].

DETAILS OF ALL RUNS

1) <u>Runs in reaction vessel, $S/V = 0.8$ cm^{-1}</u>.

P_o^*(mm)	$10^4 k_1$ (sec^{-1})	P_o(mm)	$10^4 k_1$ (sec^{-1})	P_o(mm)	$10^4 k_1$ (sec^{-1})
Temp. 421.6°		Temp. 411.2°		Temp. 401.1°	
33.1	18.9	43.0	11.2	44.4	6.6
49.8	19.1	46.2	10.9	87.4	6.4
112.0	18.7	66.5	11.7	132.8	6.4
159.0	18.7	154.6	10.9	141.0	6.7
232.0	19.1	158.6	11.3	164.0	6.8
Mean: 18.9		186.4	11.1	240.0	6.8
		225.1	11.2	Mean: 6.6	
		Mean: 11.2			
Temp. 390.4°		Temp. 380.2°		Temp. 370.2°	
41.2	3.5	32.0	2.03	39.1	1.21
61.4	3.5	47.3	2.02	76.7	1.18
119.8	3.5	65.3	2.01	145.8	1.21
154.6	3.6	132.3	2.02	191.3	1.20
236.8	3.6	153.0	1.97	Mean: 1.20	
Mean: 3.5		202.8	2.06		
		Mean: 2.02			

2) <u>Runs in packed reaction, $S/V = 8$ cm^{-1}</u>.

Temp. 411.3°		Temp. 383.5°	
43.6	11.4	32.1	2.60
103.4	11.5	135.7	2.62
137.0	11.8	196.7	2.58
211.4	11.8	Mean: 2.60	
Mean: 11.6			

* P_o *is the initial pressure of methyl N-methylcarbamate.*

CHAPTER VI

THE THERMAL DECOMPOSITION OF

ETHYL N,N-DIMETHYLCARBAMATE.

The thermal decompositions of ethyl N-methyl-N-phenyl-carbamate, isopropyl N,N-dimethylcarbamate and t-butyl N,N-dimethylcarbamate yield amine, carbon dioxide, and alkene, while that of ethyl N-methylcarbamate undergoes the same reaction as the major process. The presence of an N-H bond in the last compound appears to provide the opportunity for isocyanate formation. A preliminary study[104] showed that ethyl N,N-dimethyl-carbamate decomposes into dimethylamine, carbon dioxide, and ethylene, and since this compound is the logical parent compound for making comparisons of substituent effects upon the course of the alkene forming mode of carbamate decomposition, a study was undertaken.

(A) Materials

Ethyl N,N-dimethylcarbamate was prepared from ethyl chloroformate and dimethylamine and after fractionation through a 12-in column of Fenske helices the compound had n_D^{20} 1.4165 (lit. n_D^{20} 1.4163[104]; n_D^{15} 1.4171[105]) (Found: C, 50.98; H, 9.60; N, 11.99. Calc. for $C_5H_{11}NO_2$: C, 51.26; H, 9.46; N, 11.96%).

(B) Reaction Kinetics.

The procedures adopted for carrying out and following runs are the same as for the other studies outlined in this work. During runs pressure increased smoothly with time to values for P_f/P_o of 2.98 ± 0.01 (average of ten values over the temperature range). Rate constants were obtained from plots of the function $\log (P_o - \Delta P/2)$ against time and pressure-time data followed the first-order rate law to *ca.* 60% reaction (Figure 6.1). Rate constants obtained at each temperature are reported in Table 6.1. Plots of first-order rate constant against initial pressure of carbamate are shown in Figure 6.2 and establish that the first-

Figure 6.1 Pressure-time curve and first-order log-plot for the decomposition of ethyl N,N-dimethylcarbamate to 54% reaction at 348.9°.
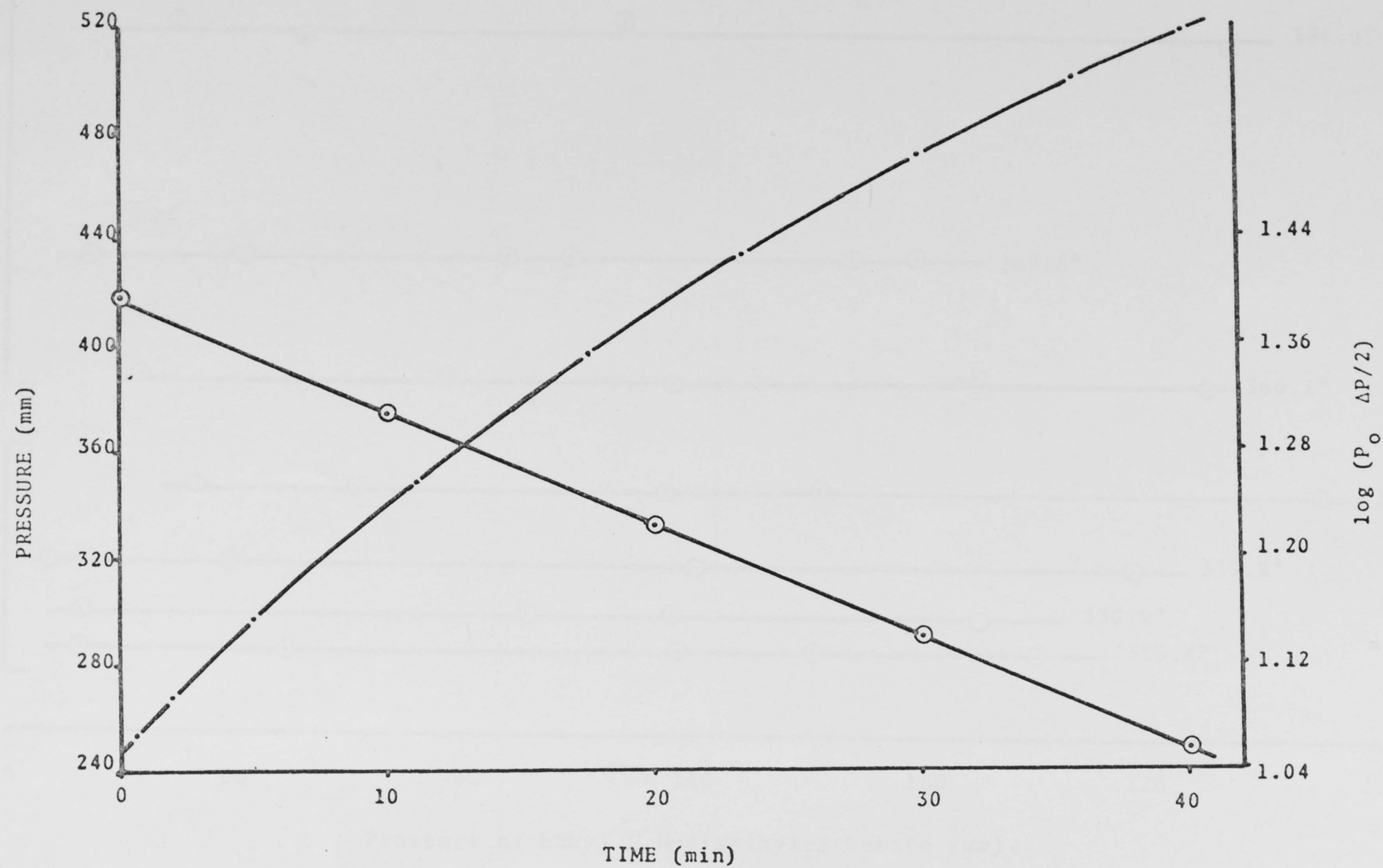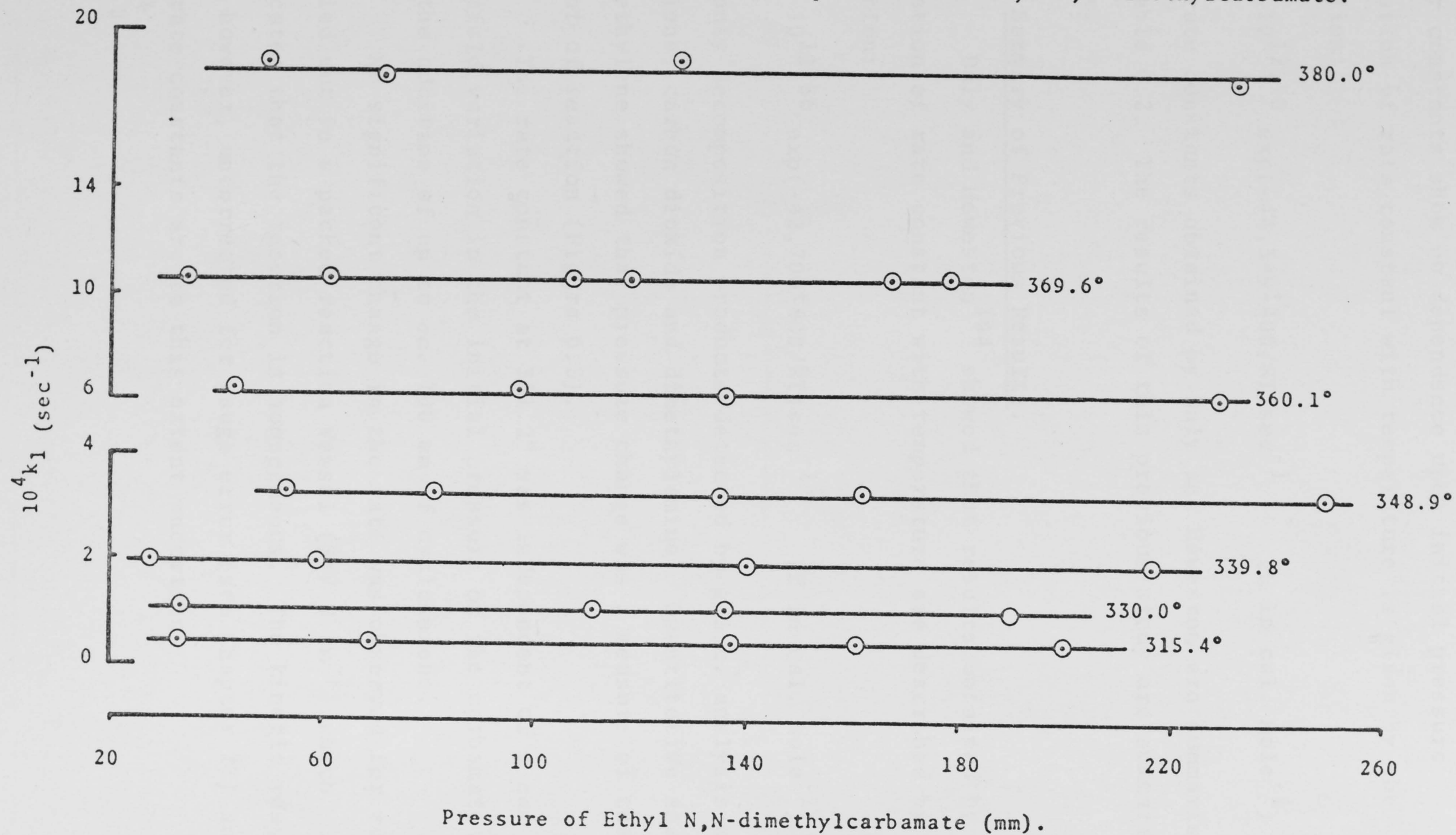
Figure 6.2

Variation of first-order rate constant with initial pressure of ethyl N,N-dimethylcarbamate.

order constants show no dependence upon initial pressure.
Variation of rate constant with temperature is given by the
equation:

$$k_1 = 10^{12.10} \exp(-44,340 \pm 400/RT)\sec^{-1} \qquad (E \text{ in cal. mole}^{-1})$$

The rate constants obtained by Daly and Heweston are summarised
in Table 6.2. The results of this previous study are summarised
below.

(C) Summary of Previous Results.

Daly and Heweston[104] showed that results obtained by the
variation of rate constant with temperature are described by the
equation:

$$k_1 = 10^{11.56} \exp(-42,700 \pm 800/RT)\sec^{-1} \qquad (E \text{ in cal. mole}^{-1})$$

The only decomposition products detected by g.l.c. analysis were
ethylene, carbon dioxide and dimethylamine. Quantitative analysis
for ethylene showed that pressure change was a measure of the
extent of reaction (Figure 6.3).

The rate constant at 351.2° was independent of a $ca.$
eightfold variation in the initial pressure of the carbamate
and the addition of up to $ca.$ 100 mm of cyclohexene.

No significant change in the rate was observed for runs
carried out in a packed reaction vessel (S/V 8 cm^{-1}) which
indicates that the reaction is homogeneous. The kinetic results
are, however, uncorrected for gauge error (see Chapter II) and
the rate constants are to this extent uncertain.

Figure 6.3
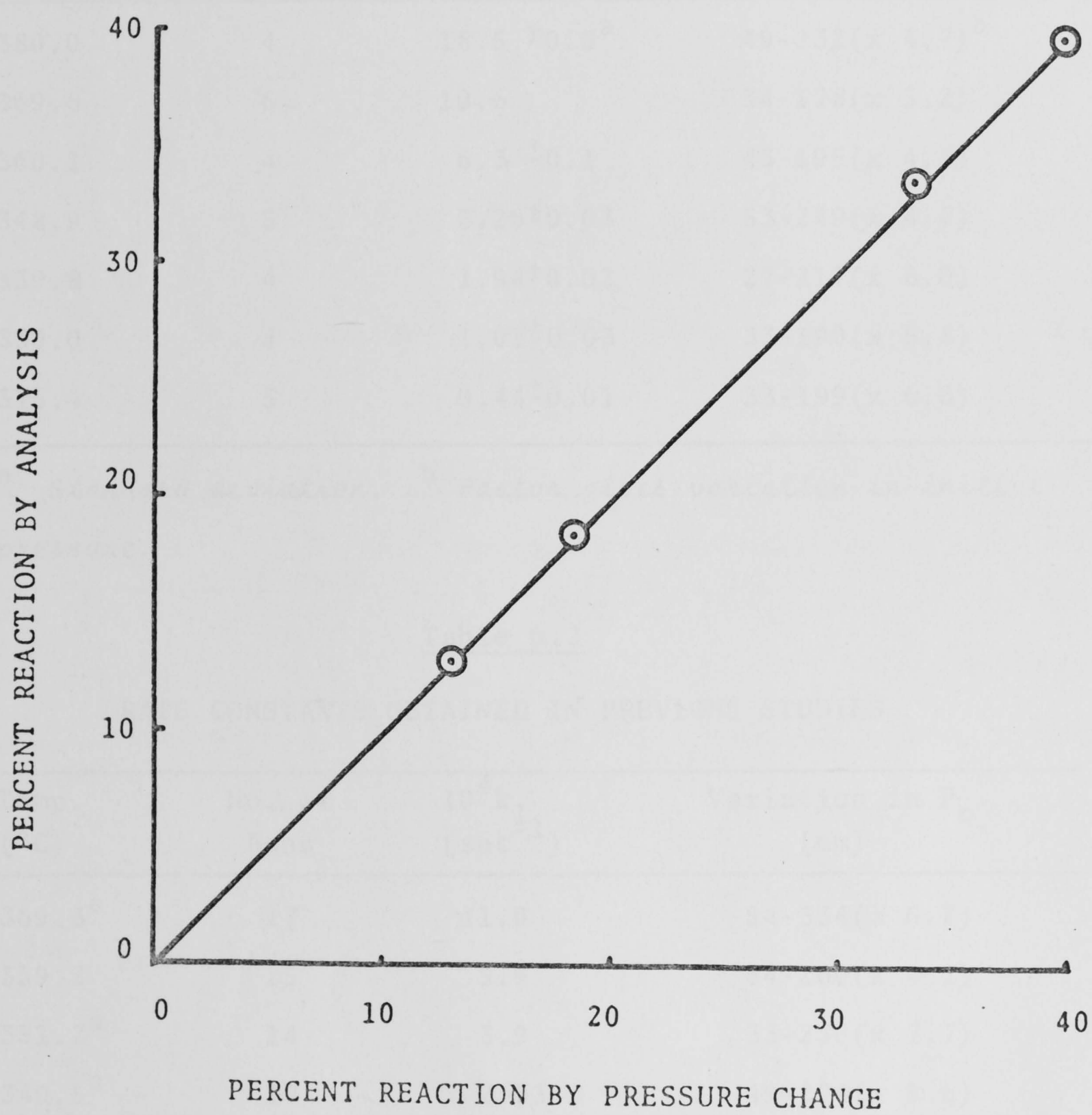
Table 6.1

SUMMARY OF OBSERVED RATE CONSTANTS

Temp. ($^\circ$C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (mm)
380.0	4	18.5 ± 0.3^a	$49-232 (\times 4.7)^b$
369.6	6	10.6	$34-178 (\times 5.2)$
360.1	4	6.3 ± 0.1	$43-195 (\times 4.5)$
348.9	5	3.26 ± 0.03	$53-249 (\times 4.7)$
339.8	4	1.94 ± 0.02	$27-217 (\times 8.0)$
330.0	4	1.07 ± 0.03	$33-190 (\times 5.8)$
315.4	5	0.44 ± 0.01	$33-199 (\times 6.0)$

a *Standard deviation.* b *Factor gives variation in initial pressure.*

Table 6.2

RATE CONSTANTS OBTAINED IN PREVIOUS STUDIES

Temp. ($^\circ$C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (mm)
369.3^a	17	11.0	$54-334 (\times 6.2)$
359.2	25	5.9	$64-266 (\times 4.2)$
351.2^a	14	3.9	$33-256 (\times 7.7)$
340.5^a	17	2.33	$49-274 (\times 5.6)$
329.3	8	1.18	$58-236 (\times 4.1)$
314.4	8	0.45	$54-244 (\times 4.5)$

a *In the presence of 50-180 mm of cyclohexene.*

b *Factor gives variation in initial pressure.*

DETAILS OF ALL RUNS

Runs in reaction vessel, $S/V = 0.8$ cm^{-1}

Temp: 380.0°

P_o(mm)	49.0;	71.2;	127.2;	232.0.
$10^4 k_1 (s^{-1})$	18.8;	18.2;	18.9;	18.2.

Mean: $10^4 k_1 = 18.5$ sec^{-1}

Temp: 369.6°

P_o(mm)	34.4;	60.6;	106.9;	118.5;	166.8;	178.0
$10^4 k_1 (s^{-1})$	10.6;	10.6;	10.6;	10.6;	10.6;	10.7

Mean: $10^4 k_1 = 10.6$ sec^{-1}

Temp: 360.1°

P_o(mm)	43.1;	96.8;	136.4;	228.8
$10^4 k_1 (s^{-1})$	6.5;	6.4;	6.2;	6.2

Mean: $10^4 k_1 = 6.3$ sec^{-1}

Temp: 348.9°

P_o(mm)	53.4;	81.2;	135.4;	162.4;	249.0
$10^4 k_1 (s^{-1})$	3.31;	3.24;	3.21;	3.28;	3.25

Mean: $10^4 k_1 = 3.26$ sec^{-1}

Temp: 339.8°

P_o(mm)	27.5;	58.8;	140.2;	216.6.
$10^4 k_1 (s^{-1})$	1.95;	1.96;	1.92;	1.91.

Mean: $10^4 k_1 = 1.94$ sec^{-1}

Temp: 330.0°

P_o(mm)	33.3;	110.9;	136.0;	189.8.
$10^4 k_1 (s^{-1})$	1.10;	1.07;	1.07;	1.04.

Mean: $10^4 k_1 = 1.07$ sec^{-1}

Temp: 315.4°

P_o(mm)	33.3;	69.5;	137.0;	161.1;	199.6.
$10^4 k_1 (s^{-1})$	0.44;	0.46;	0.44;	0.42;	0.44

Mean: $10^4 k_1 = 0.44$ sec^{-1}

CHAPTER VII

DISCUSSION

(A)   General Considerations

To date, most of the published data on carbamate decompositions is complicated by the occurrence of subsequent reactions. McKay and Vavasour[106] pyrolysed N-benzyl cholesteryl carbamate and obtained the products benzylamine, carbon dioxide and cholest-3,5-diene. They explained the presence of cholesterol and *sym*-dibenzylurea as the subsequent transesterification reaction of benzylamine with unreacted carbamate i.e.

(R = benzyl)

$$\begin{array}{ccc} & & \\ & + : NH_2R \longrightarrow & \longrightarrow & + RNHCONHR \end{array} \quad (7.1)$$
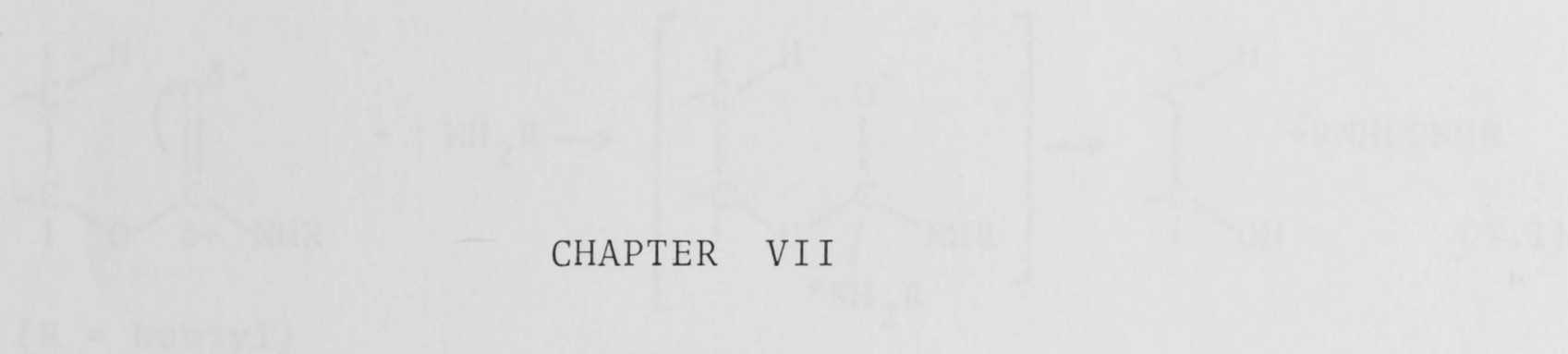
The present work shows that no evidence could be found to support transesterification reactions in the gas-phase (see page 56).
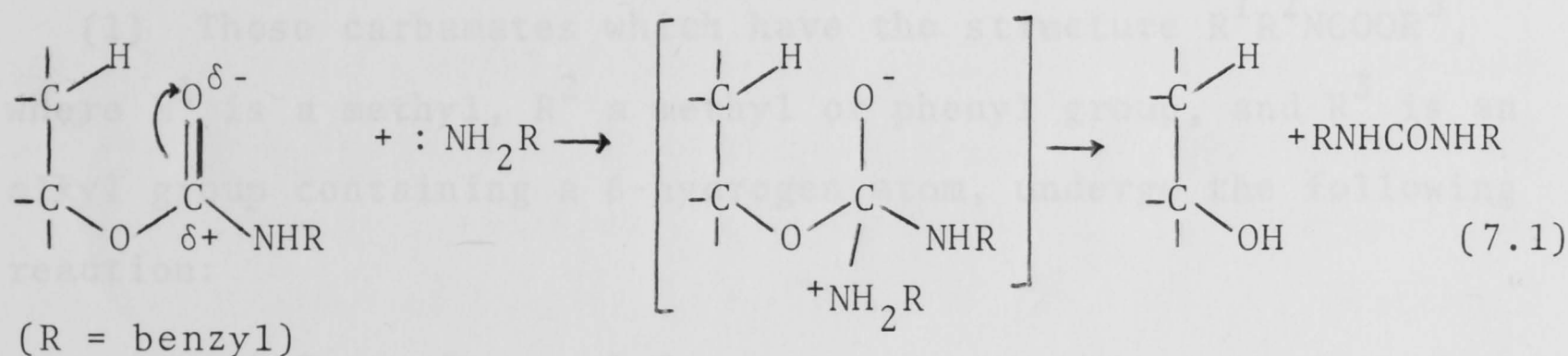
The pyrolysis of N-benzylcholesteryl carbamate was carried out in the liquid phase at 290° and the alcohol and urea may have been formed by a genuine transesterification reaction which are known to occur in solution[107]. However, the possibility exists that the carbamate decomposed by the analogous gas-phase reaction (7.4) to benzyl isocyanate and cholesterol and, under the conditions of the investigation, benzylamine would add instantaneously[108] to the isocyanate to form *sym*-dibenzylurea.

Dyer and Wright[109] studied the decompositions of alkyl N-phenylcarbamates and found products which could not be explained by intramolecular decomposition reactions of the carbamates. The formation of these products were explained in terms of amine displacement reactions on the unreacted carbamates. Again, the decompositions were carried out in the liquid phase and these products can be explained in terms of solution reactions rather

than genuine gas-phase reactions.

In the studies of the gas-phase reactions further reactions between carbon dioxide and amines led to products during the analytical procedures, but these did not occur in the gas-phase.

The following general conclusions can be drawn from the results of this work.

(1) Those carbamates which have the structure $R^1R^2NCOOR^3$, where R^1 is a methyl, R^2 a methyl or phenyl group, and R^3 is an alkyl group containing a β-hydrogen atom, undergo the following reaction:

$$R^1R^2NCOOR^3 \longrightarrow R^1R^2NH + CO_2 + Olefin \qquad (7.2)$$

(2) If R^2 is replaced by a hydrogen atom, another mode of decomposition becomes available. The carbamate can decompose by two simultaneous reactions: one reaction producing an amine, carbon dioxide and an olefin, and the other reaction forming an isocyanate and an alcohol.

$$R^1NHCOOR^3 \longrightarrow \begin{cases} R^1NH_2 + CO_2 + Olefin & (7.3) \\ R^1NCO + R^3OH & (7.4) \end{cases}$$

(3) The olefin-forming reaction can be eliminated if R^3 has no β-hydrogen atoms and the only products are an isocyanate and an alcohol. This mode of decomposition is well illustrated by the gas-phase pyrolysis of methyl N-methylcarbamate:

$$CH_3NHCOOCH_3 \longrightarrow CH_3NCO + CH_3OH \qquad (7.5)$$

At pyrolytic temperatures, no degree of reversibility was found for this reaction.

(4) No evidence was found for the alternative decarboxylation reaction in the gas-phase

$$R^1R^2NCOOR^3 \longrightarrow R^1R^2NR^3 + CO_2 \qquad (7.6)$$
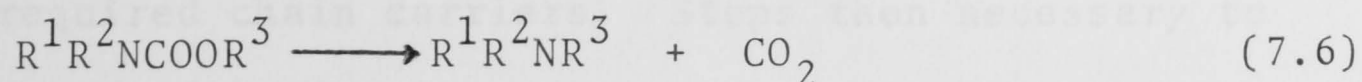
(5) During the decomposition, the amine produced as a product does not react with the unpyrolysed carbamate.
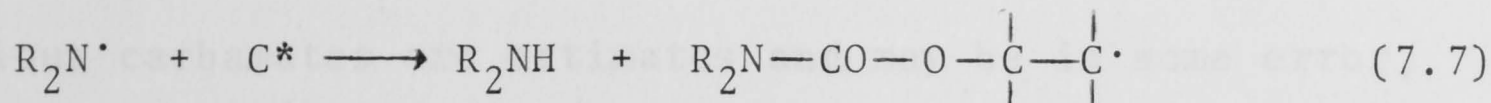
(B) Mechanism of the Gas-Phase Reactions.

In this study, the gas-phase decompositions undergone by ethyl N-methyl-N-phenylcarbamate, isopropyl N,N-dimethylcarbamate, *tert*-butyl N,N-dimethylcarbamate, and ethyl N,N-dimethylcarbamate proceed exclusively according to reaction (7.2); the decomposition of ethyl N-methylcarbamate is in the main (*ca.* 75%) by reaction (7.2) although the minor reaction (*ca.* 25%) occuring (7.4) is important.

In all decompositions the reactions follow first-order kinetics so that if each process is not molecular it seems it ought involve a Rice-Herzfeld chain mechanism. For such large molecules such a chain would be initiated in its first-order region and if the results summarised in Table 1.1 are considered it can be seen that $\beta\beta M$ or $\beta\mu$ termination is required. The products of the reactions are such that any free-radical mechanism would need to be carried by $R_2N^{\cdot}$ radicals.
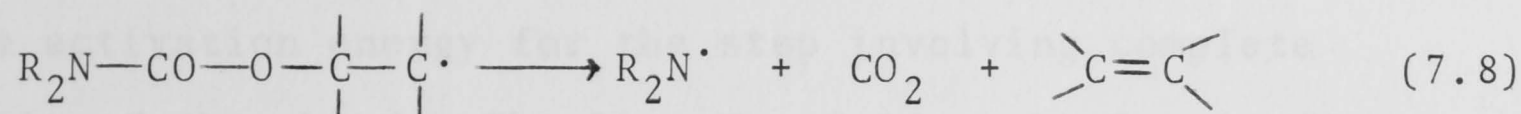
Bond energies estimated from the compilation of Szabo and Berces[110] for ethyl N-methyl-N-phenylcarbamate, ethyl N,N-dimethyl-carbamate, isopropyl N,N-dimethylcarbamate, and t-butyl N,N-dimethylcarbamate show that the N to carbonyl-carbon bond is generally one of the weakest bonds in the molecules and the bond energies are 46 kcal. mole^{-1}; 65 kcal. mole^{-1}; 65 kcal. mole^{-1},
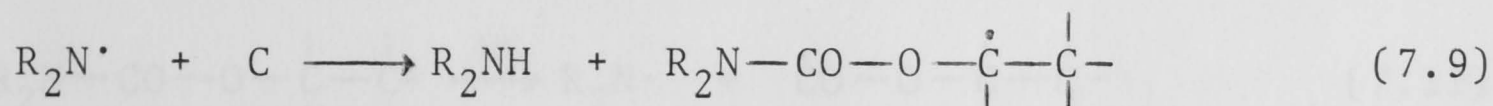
and 65 kcal. mole^{-1} respectively. These values show that first-order initiation by fission of the N-C bond is possible and would produce the required chain carriers. Steps then necessary to lead to the observed products are
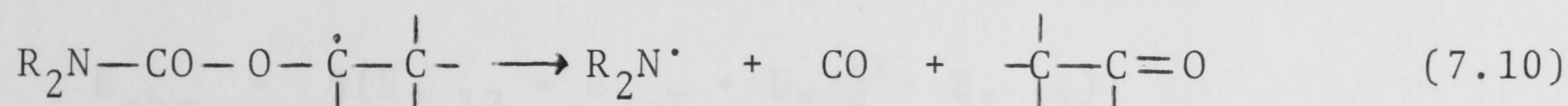
$$R_2N^\cdot \ + \ C^* \longrightarrow R_2NH \ + \ R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^\cdot \qquad (7.7)$$

and

$$R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^\cdot \longrightarrow R_2N^\cdot \ + \ CO_2 \ + \ \underset{/}{\overset{\backslash}{C}}=\underset{\backslash}{\overset{/}{C}} \qquad (7.8)$$

Abstraction reactions of the type

$$R_2N^\cdot \ + \ C \longrightarrow R_2NH \ + \ R_2N-CO-O-\overset{\cdot}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad (7.9)$$

lead to a radical which would seem to have a structure leading to the decompositions

$$R_2N-CO-O-\overset{\cdot}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \longrightarrow R_2N^\cdot \ + \ CO \ + \ -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}=O \qquad (7.10)$$
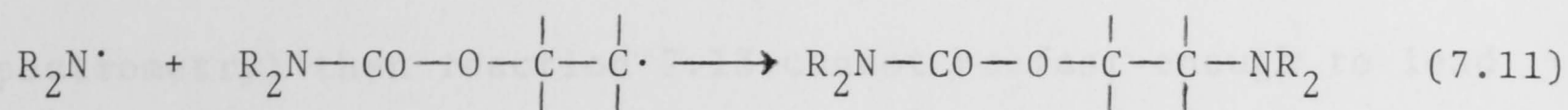
producing carbon monoxide and the appropriate aldehyde rather than a hydrogen shift followed by reaction (7.8). Since abstractions of secondary hydrogens are known to be favoured over those of primary hydrogens, the absence of carbon monoxide and aldehyde as reaction products seem to rule out free-radical chain mechanisms. Reaction (7.9) cannot take place for $Me_2NCOOC(CH_3)_3$ since there are no secondary or tertiary hydrogens available for abstraction by the $R_2N^\cdot$ radical. Thus the radical mechanism could produce exclusively the observed products in this particular case. The $\beta\beta M$ termination required to lead to first-order kinetics seems unlikely for radicals such as $Ph(CH_3)N^\cdot$ or even for $(CH_3)_2N^\cdot$. A third-body would not be required in the recombination of two such complex radicals which have internal degrees of freedom to take care of the excess energy. The alternative $\beta\mu$ termination
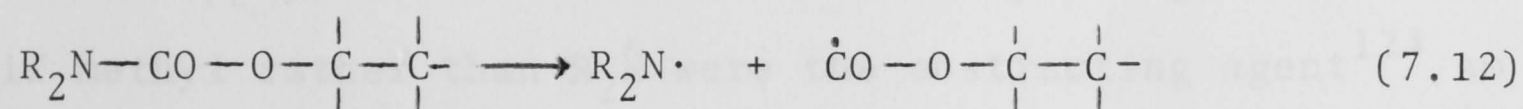
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* C represents $MeN(Ph)COOEt$, $Me_2NCOOEt$, $Me_2NCOOCH(CH_3)_2$ or $Me_2NCOOC(CH_3)_3$ as appropriate.

$$R_2N\cdot \ + \ R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \ \longrightarrow \ R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NR_2 \qquad (7.11)$$

or some appropriate disproportionation seems reasonable.

The bond energies for the N to carbonyl-carbon bonds for the various carbamates are estimates and may be in some error, but are relevant to any homolytic process since they represent the minimum activation energy for the step involving complete homolysis of that bond. The Rice-Herzfeld mechanism leading to the observed kinetics involves initiation by reaction 7.12

$$R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \ \longrightarrow \ R_2N\cdot \ + \ \overset{\bullet}{C}O-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \qquad (7.12)$$

followed by steps (7.7), (7.8) and termination by (7.11). The activation energy for the sequence is
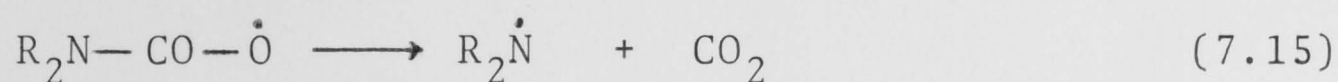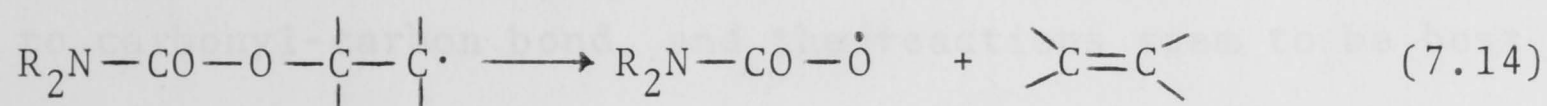
$$E_{obs} \ = \ \tfrac{1}{2}(E_{7.12} \ + \ E_{7.7} \ + \ E_{7.8} \ - \ E_{7.11})$$

if the chains are long. Relevant values are not known so that E_{obs} cannot be calculated. However, for the carbamates the lowest N—C bond energy (46 kcal. mole^{-1}) is observed for ethyl N-methyl-N-phenylcarbamate and if a "normal" pre-exponential term of 10^{13} is assumed then the rate of (7.13)

$$PhN(Me)COOC_2H_5 \ \longrightarrow \ Ph\overset{\bullet}{N}Me \ + \ \overset{\bullet}{C}OOC_2H_5 \qquad (7.13)$$

at 602.5°K is calculated to be 2.07 x 10^{-4} sec^{-1} which is to be compared with the experimentally determined value of 0.95 x 10^{-4} sec^{-1} (Table 3.9) for the overall decomposition. Since ethoxy-carbonyl radicals decompose rapidly yielding carbon dioxide and ethyl[123] and ethyl readily abstracts hydrogen, any process such as a radical non-chain process which occurs and involves fission of the N to carbonyl-carbon bond will lead to ethane as a product. Since ethane is not formed in detectable quantities (even by mass

spectrometry) then reaction 7.13 cannot be fast enough to lead
to products and $E_{7.13} = 46$ kcal. mole^{-1} is an underestimate. A
value of $E \approx 56$ kcal. mole^{-1} is necessary to preclude ethane.
This appears reasonable and requires an activation energy of about
10 kcal. mole^{-1} for the reversal of reaction (7.13). The Rice-
Herzfeld chain can be initiated by (7.13) and does not require
ethane as a product if the value for the chain length is moderately
large. Activation energies for the propagation steps are not known
but may be roughly estimated by analogy. A value about 9 kcal.
mole^{-1} would apply for the abstraction corresponding to reaction
(7.7) if methyl rather than $R_2\dot{N}$ were the abstracting agent[124] so
that a value for $R_2\dot{N}$ would probably be a little higher. Reaction
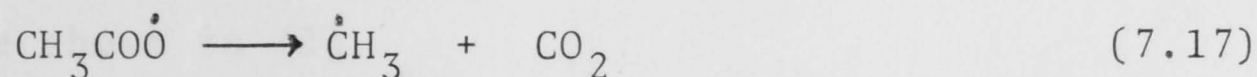7.8 is a decomposition of a μ-radical and may take place in the
steps

$$R_2N-CO-O-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \longrightarrow R_2N-CO-\dot{O} \ + \ \overset{}{\underset{}{>}}C=C\overset{}{\underset{}{<}} \tag{7.14}$$

$$R_2N-CO-\dot{O} \longrightarrow R_2\dot{N} \ + \ CO_2 \tag{7.15}$$

In the analogous reaction[125]

$$CH_3-CO-O-CH_2-\dot{C}H-CH_2-C_2H_5 \longrightarrow C_5H_{10} \ + \ CH_3C\dot{O}_2 \tag{7.16}$$
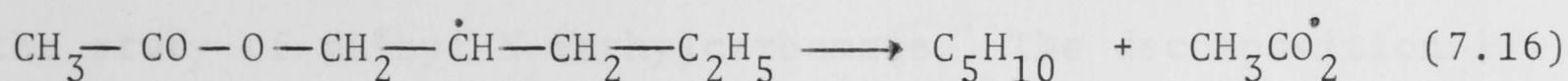
the decomposition has an activation energy of 16 kcal. mole^{-1}.
The decomposition

$$CH_3CO\dot{O} \longrightarrow \dot{C}H_3 \ + \ CO_2 \tag{7.17}$$

has an activation energy for which estimates[126] are as low as
1-2 kcal. mole^{-1} although higher values have been proposed. The
effect of the electronegative NR_2 group ought to be to confer added
stability on the radical so that the energy for reaction (7.17)
may be in the region of 4-5 kcal. mole^{-1}. Overall, a value of
$E_{obs} \approx 45$ kcal. mole^{-1} can be rationalised for the case of ethyl

N-methyl-N-phenylcarbamate, but since the N—C bond in the remaining carbamates is 19 kcal. mole^{-1} higher, E_{obs} so calculated would be higher although experimentally (Table 7.1) this is not the case. So that even if a Rice-Herzfeld chain is feasible for ethyl N-methyl-N-phenylcarbamate, it does not seem likely in the remaining carbamates.

In all studies, no induction periods in the rate of pressure change were observable and the addition of chain inhibitors such as cyclohexene and isobutene had no effect on rates, nor did the production of propene or isobutene throughout the course of a reaction have an effect, so that the case in support of a radical chain mechanism is weak. Additionally, neither the activation energies (Table 7.1) nor the relative rate constants at 400° (Table 7.2) correlate with the homolytic bond energies of the N to carbonyl-carbon bond, and the reactions seem to be best described as molecular processes.

The existence of a thermal reaction producing isocyanate according to (7.5) is characterised as first-order by the results of the study of methyl N-methylcarbamate. The decomposition is homogeneous and rate constants are unaffected by the addition of significant quantities of isobutene, and seem well described as a molecular process proceeding through a four-centred transition state of the type shown in (1)

$$
\text{Me} - \text{N} \text{---} \text{C} = \text{O}
$$
$$
\text{H} \text{----} \text{O} - \text{Me}
$$

(1)
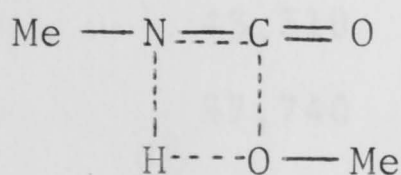
The rate constant for the process is given by the equation

$$
k_1 = 10^{12.39} \exp(-48{,}060/RT) \text{ sec}^{-1} \qquad (E \text{ in cal. mole}^{-1})
$$

The compound was chosen since its structure does not permit elimination to form olefin, carbon dioxide and amine. Of the carbamates studied that do have a structure enabling elimination of olefin, only ethyl N-methylcarbamate produces isocyanate. Thus although the rate constant for decomposition of methyl N-methyl-carbamate relative to that of ethyl N-methyl-N-phenylcarbamate is 0.11 at 380°, the latter compound produces no isocyanate so that it seems that a N—H bond is necessary for the process, and that ether formation (7.14) is not as facile.

$$R_2NCOOR^1 \longrightarrow RNCO + ROR^1 \qquad (7.14)$$

The competing reactions observed for ethyl N-methylcarbamate whereby not only methylamine, carbon dioxide, and ethylene but also methyl isocyanate and ethanol are formed seem reasonable in view of the relative rates quoted above. The Arrhenius parameters for the carbamates studied in this work are summarised in Table 7.1.

Table 7.1

SUMMARY OF ARRHENIUS PARAMETERS FOR CARBAMATE PYROLYSES.

Compound	Alkene forming reaction		Isocyanate forming reaction	
	log A (A in sec^{-1})	E (cal.mole^{-1})	log A (A in sec^{-1})	E (cal.mole^{-1})
MeN(Ph)COOEt	12.44	45,380		
Me$_2$NCOOEt	12.10	44,340		
Me$_2$NCOOi-Pr	13.04	43,310		
Me$_2$NCOOt-Bu	12.87	37,740		
MeNHCOOMe			12.39	48,060
MeNHCOOEt	12.47	46,020	10.91	43,070

(C) <u>Nature of the Transition State</u>.

The evidence from the studies is that the reactions occur by molecular processes.

There are two simple transition states [(2) and (3)] for the olefin-forming decompositions of carbamates which lead to the observed products.

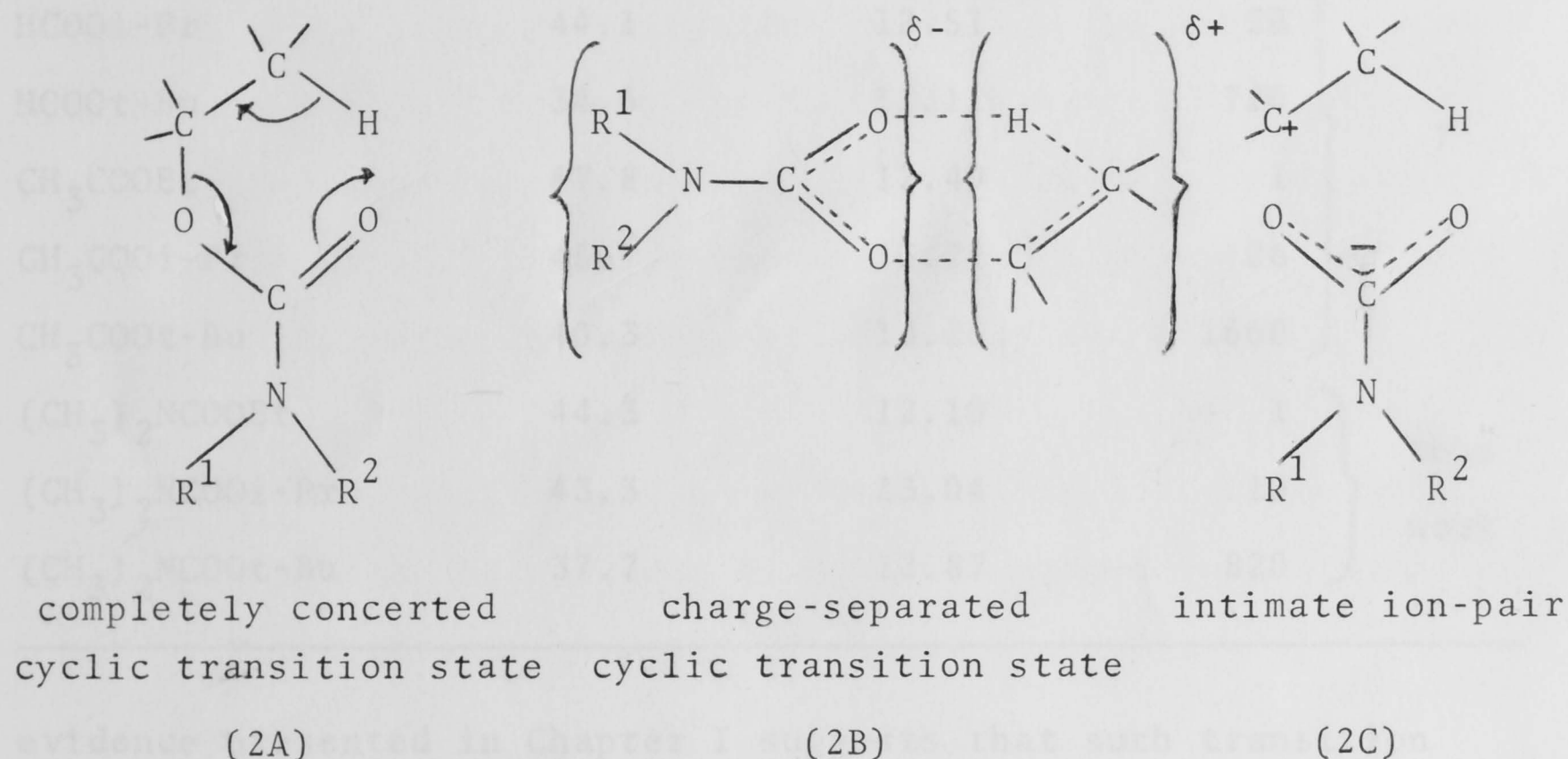   (2)   (3)
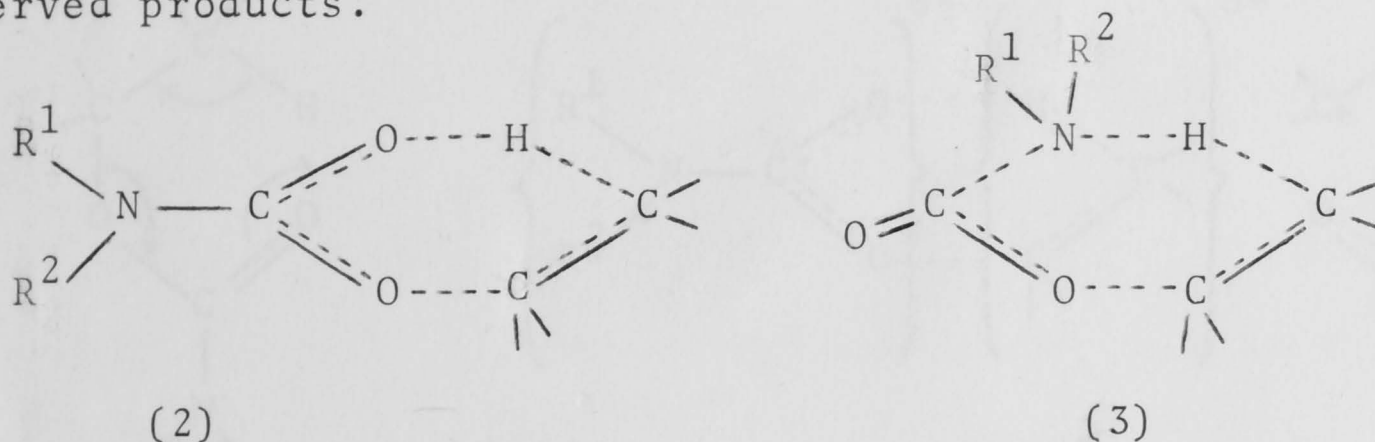
Transition state (2) leads to formation of an olefin and the unstable carbamic acid which presumably decomposes spontaneously to carbon dioxide and an amine. Transition state (3) leads to direct formation of the observed products. Such cyclic transition states can result from either homolytic or heterolytic partial fission of bonds.

The Arrhenius parameters for the olefin-producing eliminations of carbamates are listed in Table 7.2 together with those obtained for the corresponding reactions of formates and acetates. The similarity suggests that the slow step in each of the systems is of a similar nature. Transition state (2) is generally accepted as appropriate for the pyrolyses of formates and acetates[57]. Xanthates also undergo a reaction analogous to the carbamates and decompose to mercaptan, olefin, and carbon oxysulphide. Bader and Bourns[84] measured the kinetic isotope effect on the thio-ether sulphur atom, the thion sulphur atom, and the carbonyl-carbonatom in the decomposition of S-methyl-*trans*-2-methyl-1-indanyl xanthate and concluded that the

transition state belongs to the class of type (2) but not of type (3). Thus if carbamates belong to the family of reactions formed by formates, acetates and xanthates, transition state (2) is favoured.

Three different structures have been proposed for transition state (2):

completely concerted   charge-separated   intimate ion-pair
cyclic transition state   cyclic transition state

(2A)   (2B)   (2C)

The results of this work show that the ease of pyrolysis of carbamates is affected by methyl substitution at the α-carbon of the alkyl group and is similar to that observed for acetates and formates. Relative rates at 400° are reported in Table 7.2 and support the conclusion that heterolysis of the alkyl-carbon to oxygen bond is important in the rate-determining step for carbamate pyrolysis. Comparison of the effects of α-methyl substitution in Table 7.2 with those in Table 1.2 (Table 1.2 is on page 3) shows that like esters the pyrolyses of carbamates exhibit less heterolytic character than the pyrolysis of alkyl halides.

It is difficult to rationalise the effect of α-methyl substitution in carbamate pyrolysis by the completely concerted cyclic transition state (2A), nor is evidence provided in this work which rejects the ion-pair two step mechanism (2C), but the

Table 7.2

COMPARISON OF ARRHENIUS PARAMETERS

| Compound	E (kcal. mole^{-1})	log A (A in sec^{-1})	Rel. rate at 400°	Ref.
HCOOEt	44.1	11.33	1	
HCOOi-Pr	44.1	12.51	20	
HCOOt-Bu	34.6	11.11	720	7
CH$_3$COOEt	47.8	12.49	1	
CH$_3$COOi-Pr	45.7	13.21	26	
CH$_3$COOt-Bu	40.3	13.25	1660	
(CH$_3$)$_2$NCOOEt	44.3	12.10	1	
(CH$_3$)$_2$NCOOi-Pr	43.3	13.04	19	this work
(CH$_3$)$_2$NCOOt-Bu	37.7	12.87	820	

evidence presented in Chapter I suggests that such transition
states are not favoured for ester pyrolysis. The charged
separated cyclic transition state (2B) seems to represent
reasonably the transition state which satisfactorily explains the
data for the olefin-forming reactions of carbamates.

Varying the substituent on the N atom of the carbamate has
little effect on the rate of pyrolysis. This may be compared with
the effect of varying the nature of the acyl group in esters where
little effect upon the rate of pyrolysis is observed. Thus
varying R in RCOOEt from methyl to *tert*-butyl[49] increases the rate
by only *ca*.10%. In this study, the relative rates of pyrolyses
of MeNHCOOEt: Me$_2$NCOOEt: Me$_2$N(Ph)COOEt at 400° are 1 : 1.5 : 1.5
which correspond with the ester cases.

Transition state (3) appears likely to be less favourable
than transition state (2) because ring formation to form transition
state (3) requires the additional loss of free rotation about the

N — C bond which leads to a less favourable entropy of activation.

Further, greater steric hindrance may result from the approach of

a β-hydrogen atom to a substituted N atom than to the isolated

carbonyl-carbon atom. It also appears likely that there would be

less electrostatic attraction of the β-hydrogen to the N atom

than to the carbonyl-oxygen atom. Resonance structures for the

$\overset{\displaystyle\searrow}{N}-\underset{\displaystyle|}{C}=0$ group place more negative charge on the carbonyl-oxygen

than on the N atom. However, the main case against transition

state (3) seems to be the analogy with the xanthate pyrolyses

where the results of the measurements of kinetic isotope effects

provide strong evidence in support of transition state (2).

The decomposition of a carbamate to an isocyanate and an

alcohol appears to be a molecular reaction proceeding through

a four-centred transition state of the type shown in (4).

$$R^1 — N ---- C = 0$$
$$H ---- 0 — R^2$$
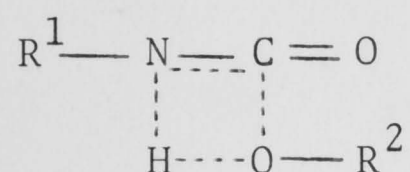
(4)

Kinetic data are reported in Table 7.1 and show that the

relative rates at 400° are:

MeNHCOOMe : MeNHCOOEt = 1 : 1.4

The available results do not allow speculations on the

homolycity or heterolycity of the transition state.

CHAPTER VIII

THE THERMAL DECOMPOSITION OF
CITRACONIC ANHYDRIDE.

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28-35%) pressure data is a good measure (verified by quantitative analysis) of the decomposition of one mole of anhydride to three moles of products. Beyond $ca.$ 35% reaction, the decrease in pressure caused by the polymerisation of one of the products, propyne, becomes significant such that pressure data becomes a progressively worse measure of the extent of reaction. The polymerisation reaction explains the values observed for $\Delta P/P_o$ (e.g., after 6 half-lives at 480°, $\Delta P/P_o = 1.65$).

Rate constants were obtained from plots of $\log(P_o - \Delta P/2)$ against time (Figure 8.1) for up to $ca.$ 30% reaction.

(C) Product Identification

(a) Gas-liquid Chromatography

Two columns were used: Column A (Porapak Q; 42 x ¼ in; helium flow rate: 65 ml.min^{-1}) was programmed from 35° with temperature increasing at a rate of 11°/min and column B (Carbowax; 72 x ¼ in; helium flow rate: 120 ml.min^{-1}) at 160°.

Citraconic anhydride (107.2 mm) was allowed to react for 40 min at 449.3° ($10^4 k_1 = 1.65$; $\Delta P = 70.0$ mm; 32.6% reaction) and the reaction mixture collected in a tap-vessel at -196° and allowed to warm to ambient temperature. A sample of the gaseous fraction of the reaction mixture injected onto column A separated into carbon dioxide (retention time 96 sec) and propyne (540 sec). A sample of the liquid fraction injected onto column B gave a peak corresponding to that for an authentic sample of citraconic anhydride (365 sec).

(b) Mass Spectrometry

Mass spectra were recorded on an AEI MS10 mass spectrometer using an ionization potential of 70eV and an emission current of 50μA. The mass spectrum of the gaseous fraction of the reaction mixture is shown in Figure 8.2. The peak at m/e 44 is the parent

Figure 8.1
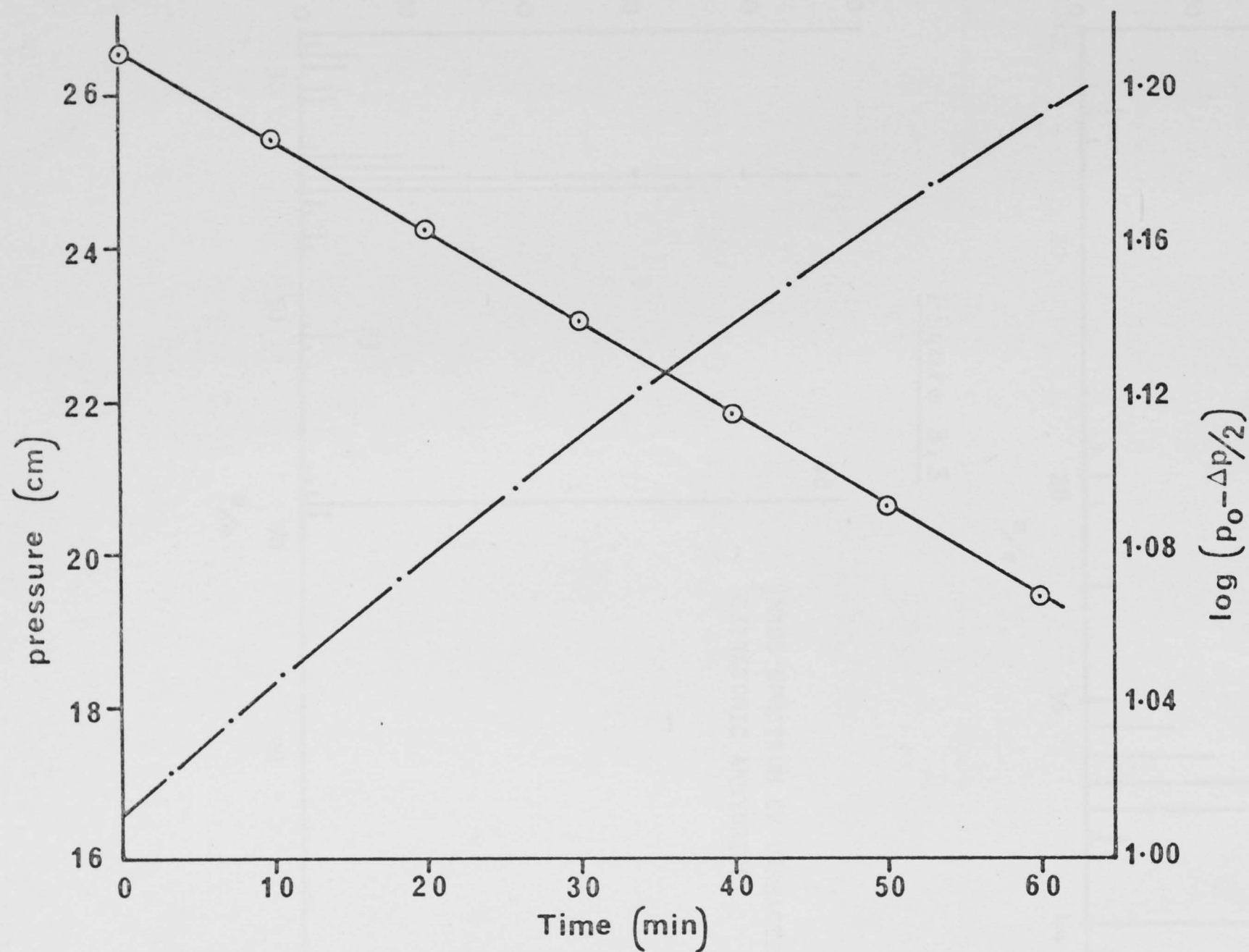
Typical run at 440.5°
to 28% reaction
P_0(anhydride)= 16.26 cm
$10^4 k_1 = 0.91$ sec^{-1}

Figure 8.2

MASS SPECTRUM OF GASEOUS FRACTION

Figure 8.3

MASS SPECTRUM OF UNREACTED
CITRACONIC ANHYDRIDE
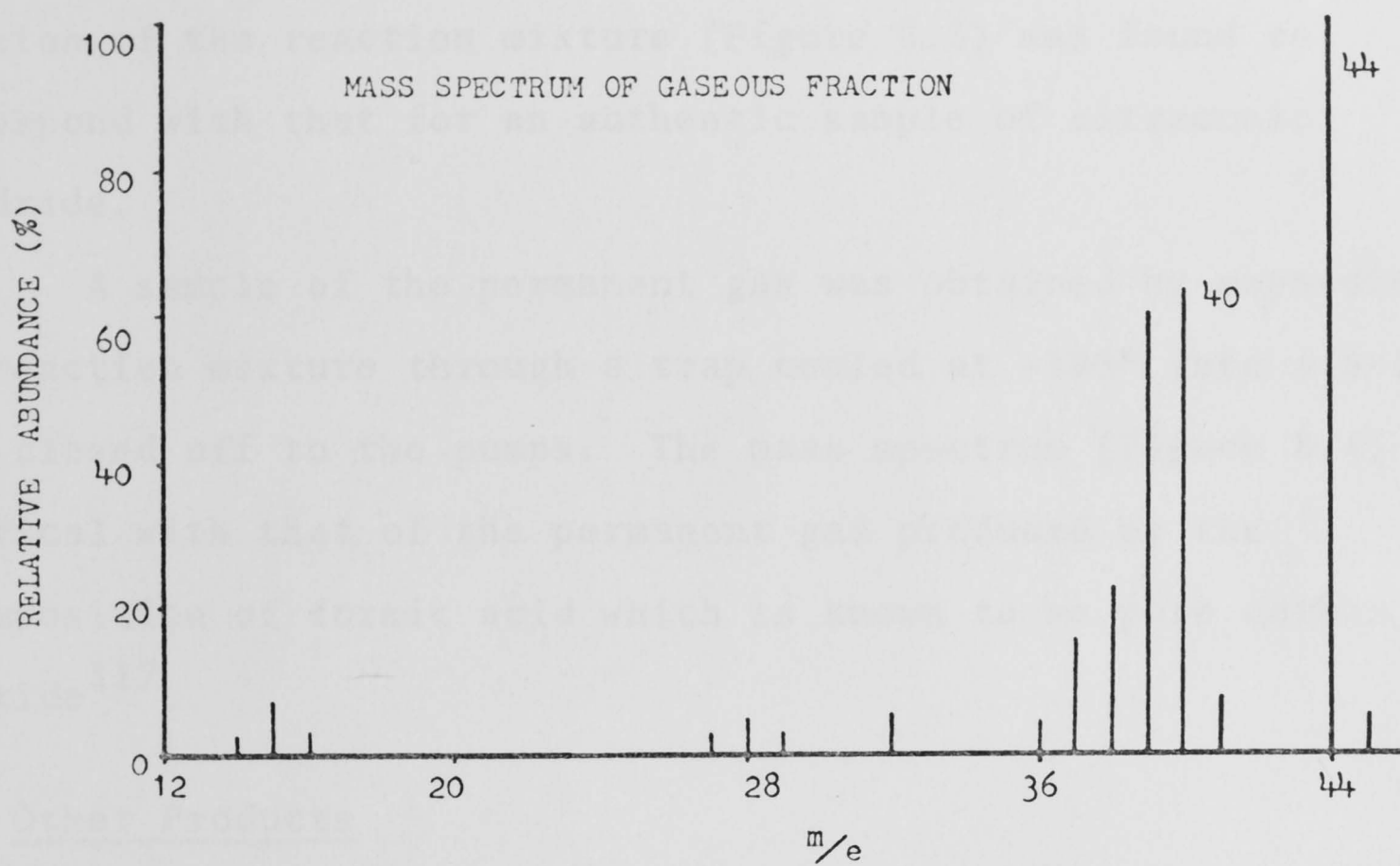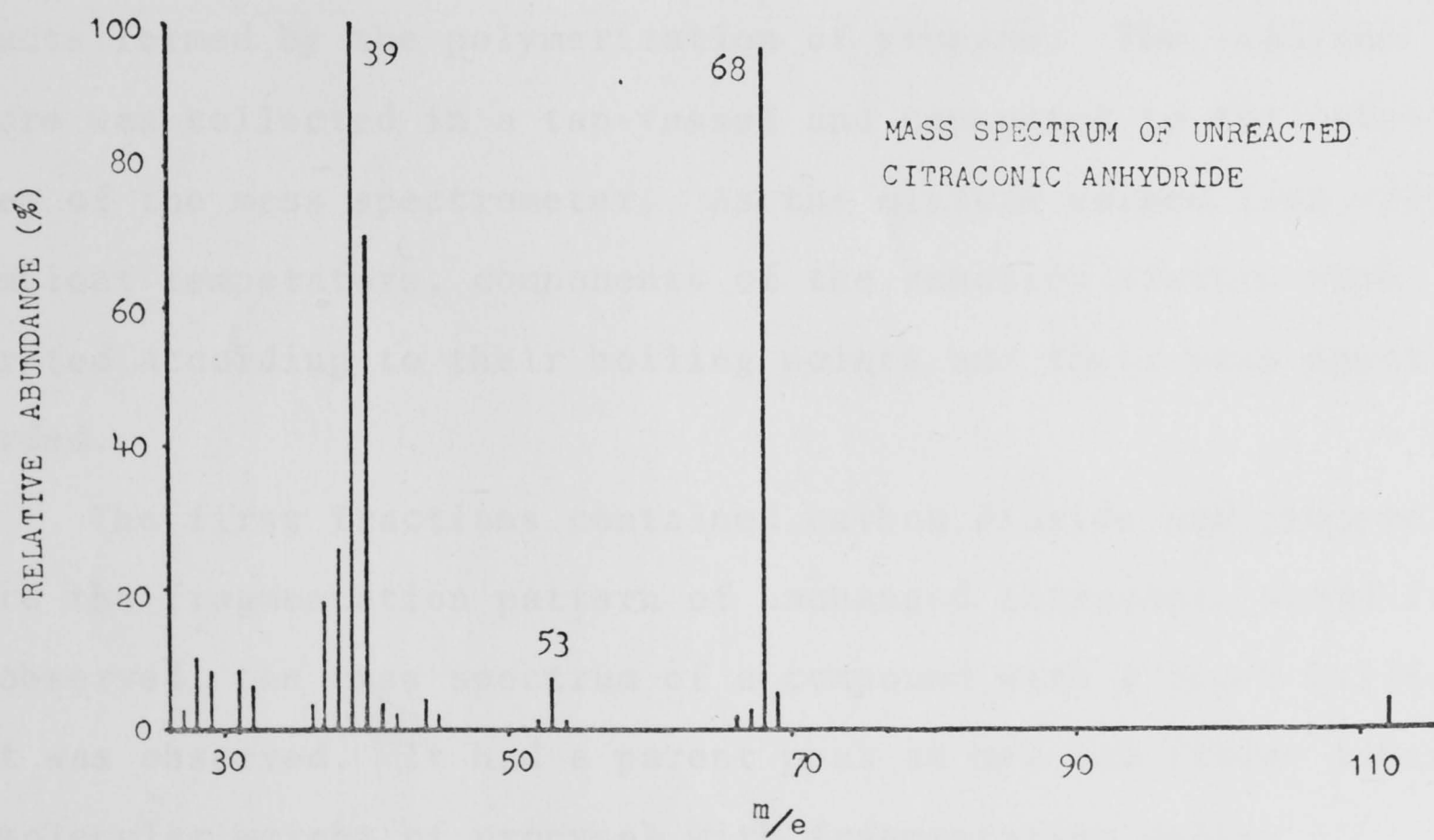
peak for carbon dioxide and the remainder of the spectrum corresponds to the fragmentation pattern for an authentic sample of propyne (parent peak: m/e 40). The mass spectrum of the liquid fraction of the reaction mixture (Figure 8.3) was found to correspond with that for an authentic sample of citraconic anhydride.

A sample of the permanent gas was obtained by expanding the reaction mixture through a trap cooled at -196° into a 5-litre bulb closed off to the pumps. The mass spectrum (Figure 8.4) is identical with that of the permanent gas produced by the decomposition of formic acid which is known to be pure carbon monoxide[117].

(D) Other Products

The anhydride (154.6 mm) was allowed to react for *ca.* three half-lives at 479.7° in order to increase the amount of products formed by the polymerization of propyne. The reaction mixture was collected in a tap-vessel and connected to the inlet system of the mass spectrometer. As the mixture warmed from -196° to ambient temperature, components of the reaction mixture were separated according to their boiling points and their mass spectra recorded.

The first fractions contained carbon dioxide and propyne. Before the fragmentation pattern of unchanged citraconic anhydride was observed, the mass spectrum of a compound with a lower boiling point was observed. It had a parent peak at m/e 120 (three times the molecular weight of propyne) with fragmentation peaks corresponding to that recorded for the trimethylbenzenes[118](Figure 8.5).

A control run was carried out with 213.0 mm of propyne which was allowed to react for 120 min at 449.3°. The reaction

Figure 8.4

MASS SPECTRUM OF
PERMANENT GAS

Figure 8.6

PRODUCTS FROM HEATING 21•3 cm OF
PROPYNE FOR 2 HOURS AT 449•3°

PEAK S — SOLVENT: DIETHYL ETHER
PEAKS A to H — REACTION PRODUCTS

RETENTION TIME (sec)
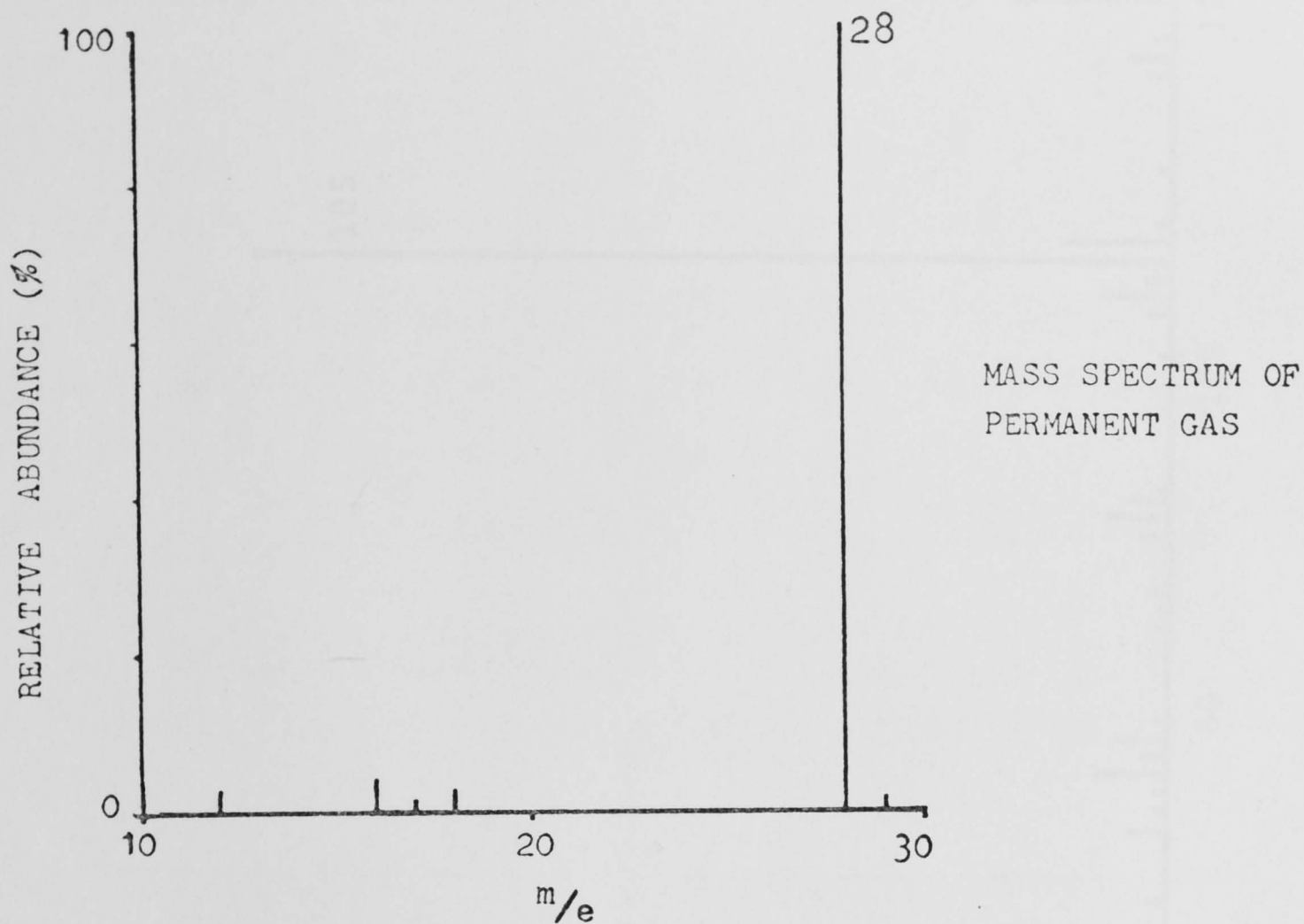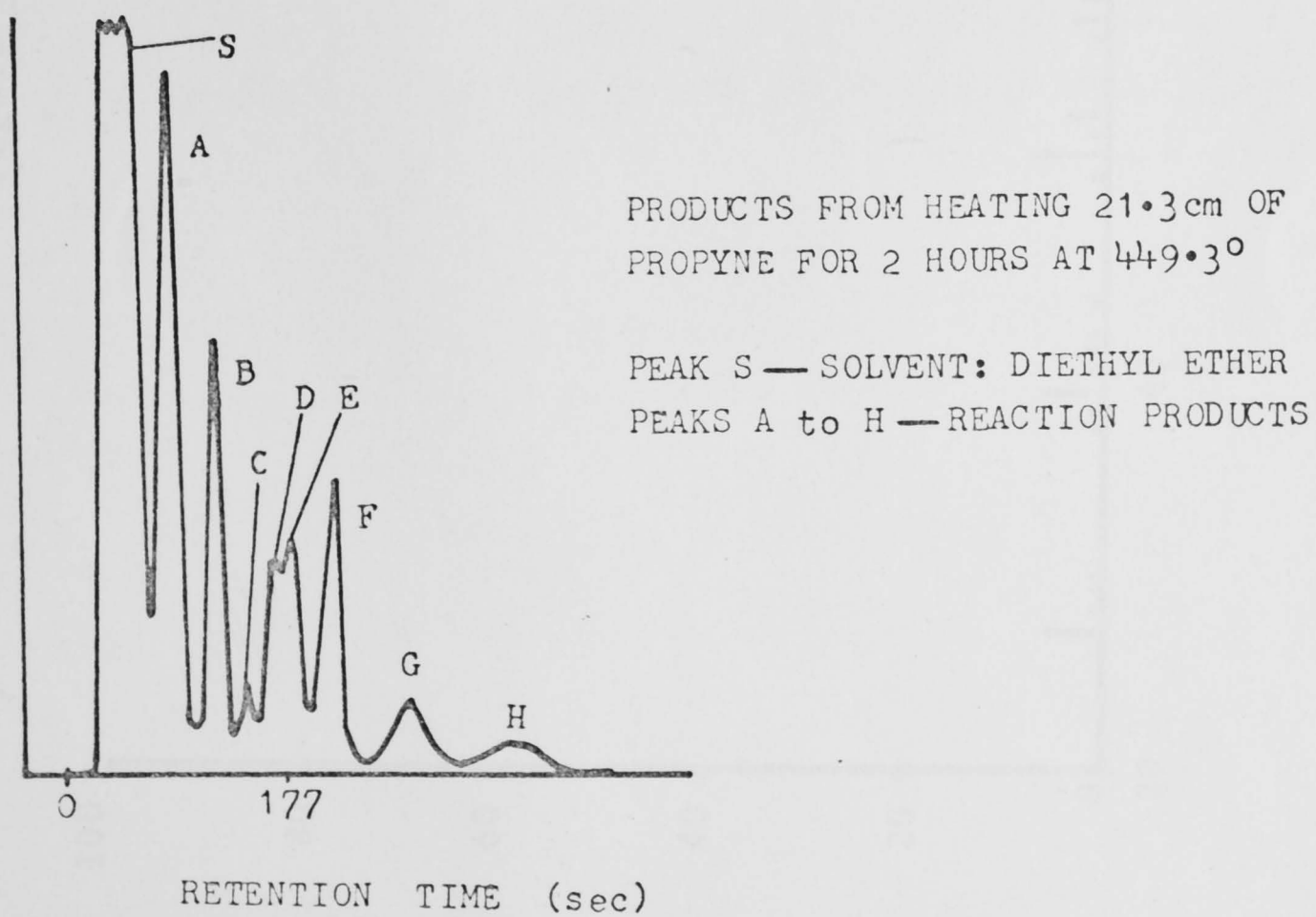
Figure 8.5
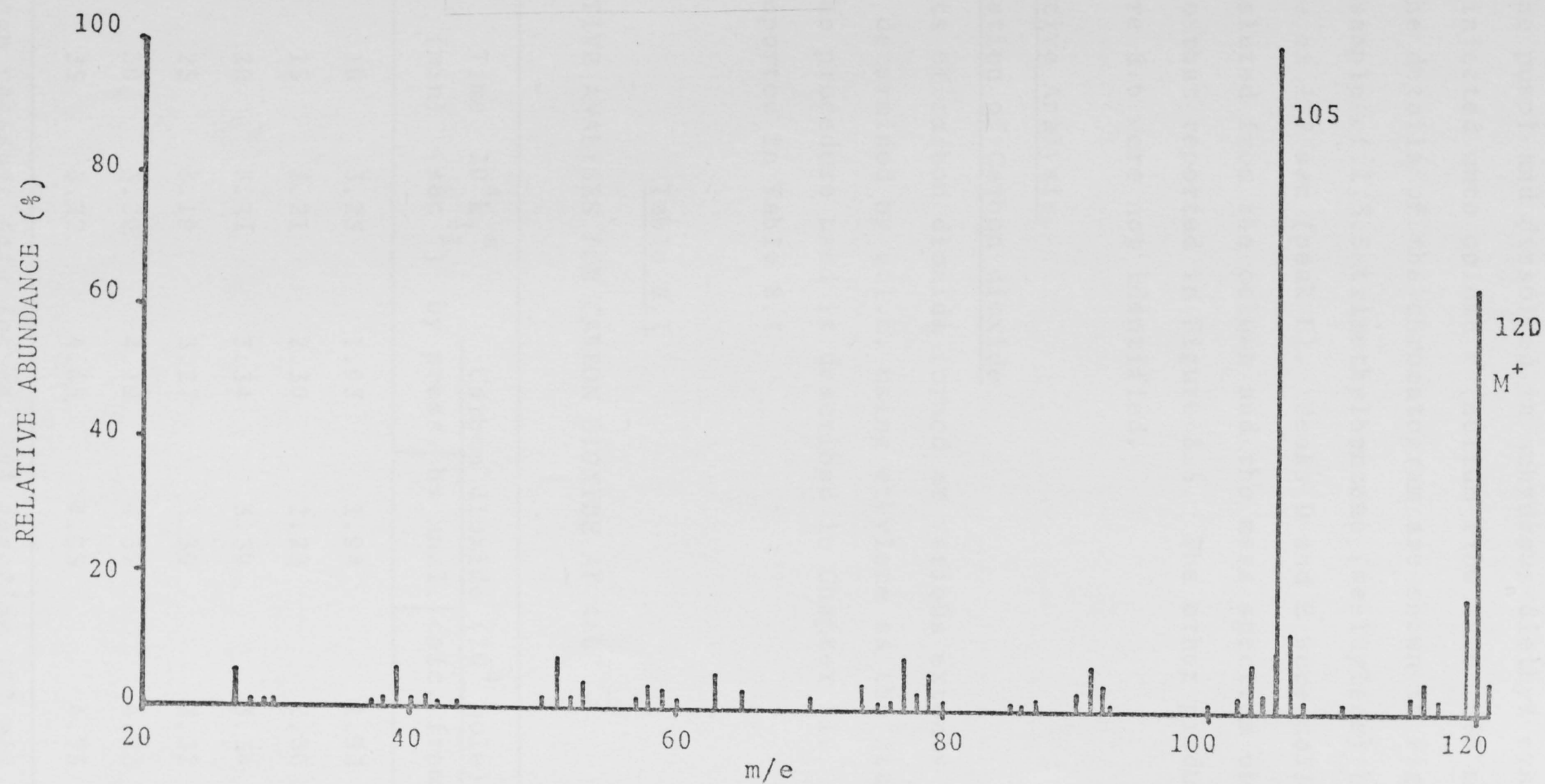
mixture was collected at -196° (a trace of permanent gas was detected at the pump) and dissolved in anhydrous diethyl ether. Samples were injected onto column B (helium flow rate: 85 ml.min^{-1}) at 125° and the details of the chromatogram are shown in Figure 8.6. An authentic sample of 1,3,5-trimethylbenzene (mesitylene) had a retention time of 177 sec (peak E). Peaks D and E were collected as they were eluted from the column and the mass spectrum obtained was similar to that reported in Figure 8.5. The other products shown in Figure 8.6 were not identified.

(E) Quantitative Analysis.

(a) Estimation of Carbon dioxide.

Amounts of carbon dioxide formed at various extents of reaction were determined by g.l.c. using ethylene as the standard reference. The procedure used is described in Chapter II. Results are reported in Table 8.1

Table 8.1

QUANTITATIVE ANALYSES FOR CARBON DIOXIDE AT 460°

P_0(anhydride) (mm)	Time (min)	$10^4 k_1^a$ (sec^{-1})	Carbon dioxide (10^4 mole)		
			by press.	by anal.	calc. from k_1^a
167.6	10	3.23	1.93	1.94	1.93
141.2	15	3.21	2.30	2.23	2.30
160.4	20	3.21	3.34	3.39	3.34
133.6	25	3.19	3.27	3.39	3.32
148.4	30	3.20	4.19	4.37	4.23
148.4	35	3.22	4.65	4.95	4.75

a k_1 calc. from pressure data for ca. 30% reaction (20 min run).

(b) Estimation of Citraconic anhydride.

The -80° condensables of the reaction mixture were
collected, distilled water added, and the solution boiled to
increase the rate of hydrolysis of the unpyrolysed anhydride to
the dibasic acid and to remove the last traces of carbon dioxide.
The dibasic acid was titrated with standard barium hydroxide
solution and the amount of unpyrolysed anhydride determined.
Results are reported in Table 8.2.

Table 8.2

QUANTITATIVE ANALYSES FOR CITRACONIC ANHYDRIDE AT 460°.

P_o(anhydride) (mm)	Time of run (min)	$10^4 k_1{}^a$ (sec^{-1})	Anhydride (10^4 mole) by anal.	calc. from $k_1{}^a$
145.9	15	3.0	7.40	7.23
161.5	20	3.2	7.21	7.15
158.6	25	3.3	6.33	6.32
148.0	25	3.3	6.07	5.92
150.4	30	3.1	5.59	5.59
153.2	35	3.4	4.95	4.84

^{a} *k_1 calc. from pressure data for ca. 30% reaction (20 min run).*

(F) Discussion

Citraconic anhydride decomposes in the temperature range
440-490° to give carbon dioxide, carbon monoxide and propyne. All
products have been confirmed by the mass spectrometric and gas
chromatographic results. These observations are interpreted in
terms of the decomposition reaction.

$$C_5H_4O_3 \longrightarrow CO_2 + CO + CH_3C\equiv CH$$
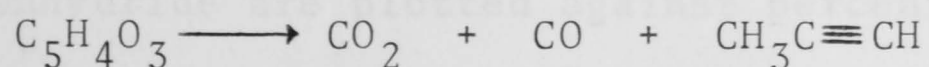
which is followed by the slower polymerization of propyne to form

mainly trimethylbenzenes. The polymerization explains the values observed for $\Delta P/P_o$ rather than the theoretical value 2.0 required by the stoicheiometry of the decomposition. The k_1 values were plotted against the initial pressures of anhydride and show (Figure 8.7) that k_1 is independent of a sixfold variation of pressure. Rate constants are listed in Table 8.3. The variation of rate constant with temperature is given by the equation

$$k_1 = 10^{15.64} \exp(-64,230 \pm 500/RT) \sec^{-1} \qquad (E \text{ in cal. mole}^{-1}).$$

Table 8.3

SUMMARY OF OBSERVED RATE CONSTANTS

T (°C)	No. of Runs	$10^4 k_1$ (sec^{-1})	Variation in P_o (mm)
440.5	8	0.90	42-243 (x 5.8)[a]
440.5[b]	5	0.89	38-211 (x 5.6)
447.7[c]	6	1.49	33-198 (x 6.0)
449.3	6	1.63	47-161 (x 3.4)
459.8	5	3.12	74-217 (x 3.0)
459.8[b]	3	3.02	50-227 (x 4.5)
469.0	7	5.29	51-272 (x 5.3)
469.0[b]	4	5.40	46-201 (x 4.4)
473.9[c]	5	7.0	41-173 (x 4.2)
479.7	6	9.74	50-199 (x 4.0)
490.0	7	17.3	57-257 (x 4.5)

[a] *Factor gives the variation in initial pressure.*
[b] *In presence of isobutene (50-182 mm).*
[c] *In vessel with S/V ratio 8 cm^{-1}.*

At 460°, up to 50% reaction, the percentages of reaction calculated from quantitative analyses for carbon dioxide and citraconic anhydride are plotted against percentages calculated from the first-order rate constant. The excellent correlation
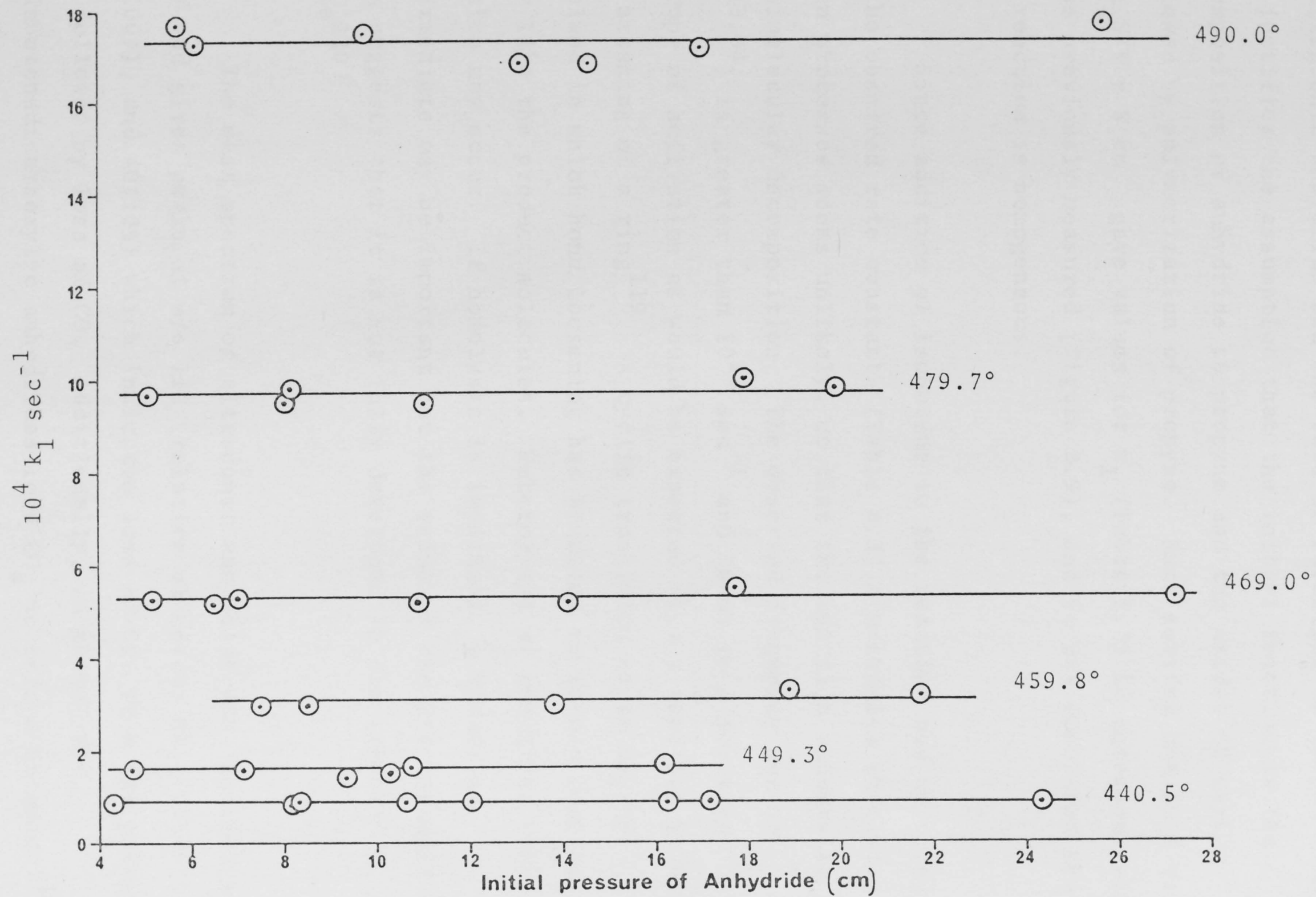
Figure 8.7

(Figure 8.8) shows that k_1 measures both the rate of consumption of citraconic anhydride and the rate of formation of carbon dioxide, and justifies the assumption that the initial reaction is the decomposition of anhydride to propyne and the oxides of carbon followed by polymerization of propyne. Runs carried out in a vessel with $S/V = 8$ cm^{-1} gave values for k_1 (Table 8.3) in agreement with those previously measured (Figure 8.9), and it was concluded that the reaction is homogeneous.

Since addition of isobutene to the reaction had no effect on the observed rate constants (Table 8.3) a mechanism involving chain processes seems unlikely, so that the reaction appears to be a unimolecular decomposition. The observed frequency factor ($10^{15.64}$) is greater than 10^{13} sec^{-1} and leads to a positive entropy of activation as would be expected from a reaction involving the breaking of a ring[119]. A cyclic transition state may be involved in which bond loosening has occurred to form a complex very like the product molecules. Heterolytic or homolytic bond fission may occur. If homolysis is important, a biradical intermediate may be important but the value of the pre-exponential term suggests that it is not fully developed in the transition state[120].

The mass spectrum of citraconic anhydride was recorded at 15eV and gives peaks at m/e 112 (relative abundance 6%), 69(4%), 68(100%), and 40(10%) which indicates loss of CO_2 from the parent ion followed by loss of CO. Additionally, on photolysis, cyclobutenedicarboxylic anhydrides lose CO_2 to form a biradical[121] which subsequently loses CO. Thus the thermal reaction of the anhydride has similarities to the photolytic and mass spectral fragmentations although the dimerizations observed in the photolytic reactions are not seen thermally.[122]

Figure 8.8

PERCENTAGE OF REACTION BY ANALYSIS
AGAINST PERCENTAGE CALCULATED FROM k_1
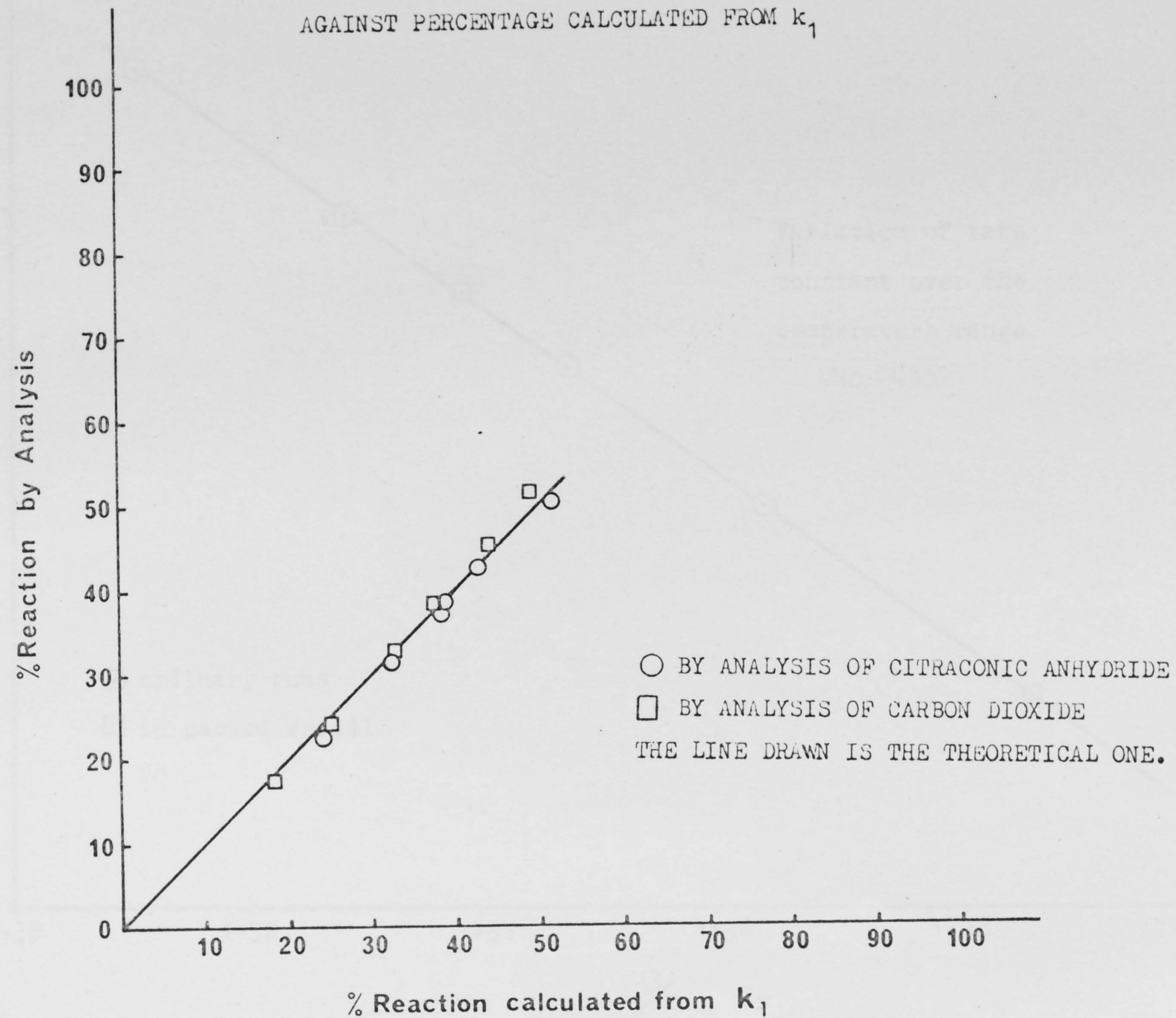
○ BY ANALYSIS OF CITRACONIC ANHYDRIDE
□ BY ANALYSIS OF CARBON DIOXIDE
THE LINE DRAWN IS THE THEORETICAL ONE.

% Reaction by Analysis

% Reaction calculated from k_1

Figure 8.9
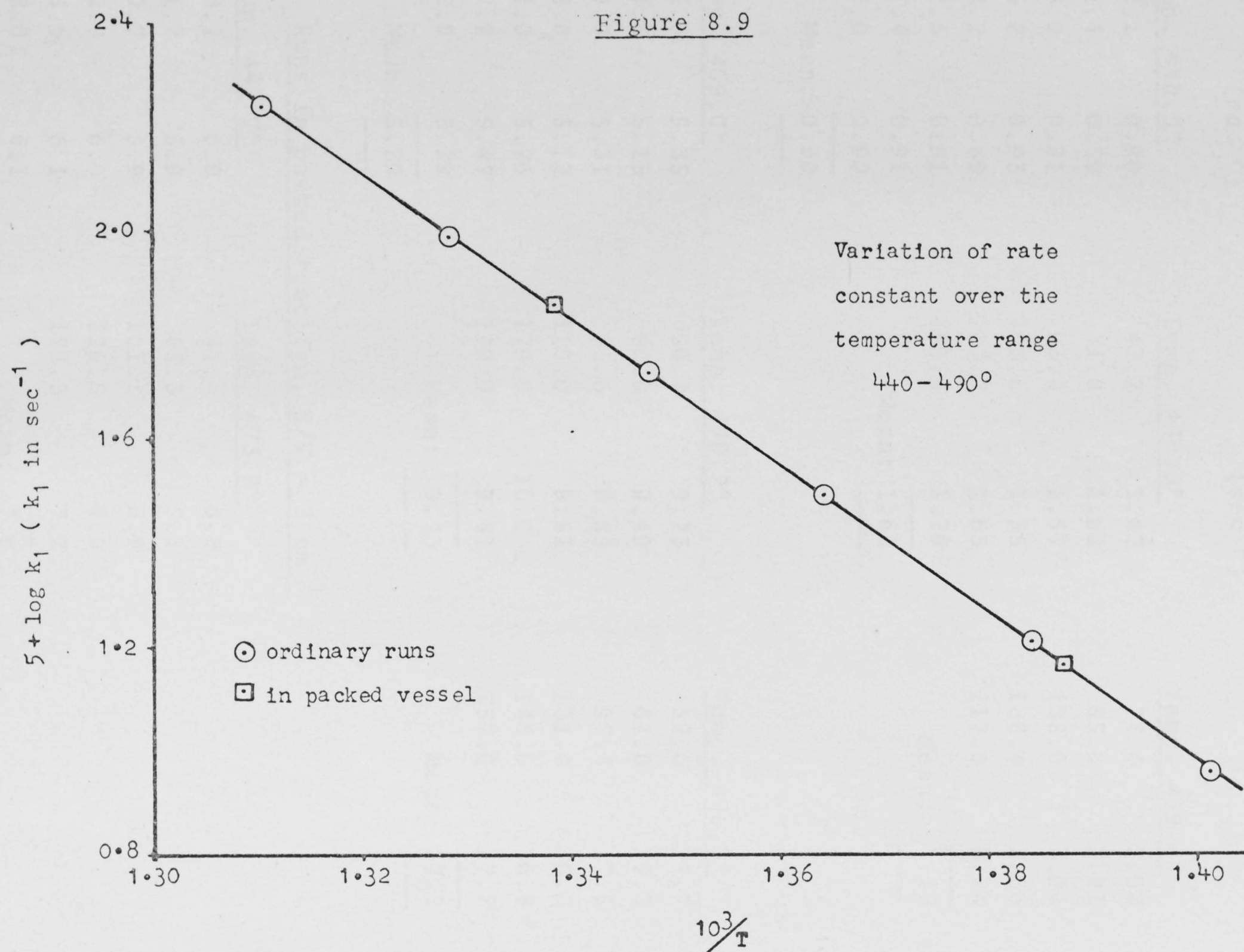
Variation of rate constant over the temperature range 440 – 490°

DETAILS OF ALL RUNS

1) <u>Runs in reaction vessel, S/V = 0.8 cm^{-1}.</u>

P_o^*(mm)	$10^4 k_{1_1}$ (sec^{-1})	P_o(mm)	$10^4 k_{1_1}$ (sec^{-1})	P_o(mm)	$10^4 k_{1_1}$ (sec^{-1})
<u>Temp. 440.5°</u>		<u>Temp. 449.3°</u>		<u>Temp. 459.8°</u>	
42.1	0.90	47.2	1.67	74.4	3.02
81.4	0.89	71.0	1.62	85.0	3.01
83.0	0.91	93.4	1.57	138.0	3.04
106.2	0.93	103.0	1.55	188.4	3.26
120.2	0.89	107.2	1.65	217.0	3.24
162.6	0.91	161.4	1.70	Mean:	3.12
171.4	0.91	Mean:	1.63		
243.0	0.90				
Mean:	0.90				

<u>Temp. 469.0°</u>		<u>Temp. 479.7°</u>		<u>Temp. 490.0°</u>	
51.0	5.35	50.2	9.73	57.0	17.7
64.5	5.18	80.0	9.49	61.0	17.3
70.0	5.31	81.6	9.85	97.4	17.5
108.8	5.17	110.0	9.51	131.0	16.8
141.0	5.26	179.0	10.0	146.0	16.8
177.2	5.47	199.0	9.81	257.0	17.7
272.0	5.29	Mean:	9.73	Mean:	17.3
Mean:	5.29				

2) <u>Runs in packed reaction, S/V = 8 cm^{-1}.</u>

<u>Temp. 447.7°</u>		<u>Temp. 473.9°</u>	
33.1	6.0	41.4	6.8
41.2	5.9	65.3	7.1
50.7	5.9	101.1	6.9
79.9	6.0	126.5	7.0
135.6	6.1	173.3	7.2
198.0	6.1	Mean:	7.0
Mean:	6.0		

---

* P_o is the initial pressure of citraconic anhydride.

APPENDIX I

Least Squares Analysis

Suppose the data consists of n points, the co-ordinates of which are $(x_1y_1, x_2y_2\ldots\ldots x_iy_i\ldots\ldots x_ny_n)$. Let the equation of the "true" line be:

$$Y = a + bx,$$

where a and b are constants. At the plotted point (x_i,y_i) the ordinate of the straight line is Y_i. The sum of the squares of deviations of the plotted points (x_i,y_i) from this line is:

$$SS = \Sigma(y_i - Y_i)^2 = \Sigma(y_i - a - bx_i)^2$$

To obtain the values of a and b which minimise SS the simultaneous equations $\delta(SS)/\delta a = 0$, $\delta(SS)/\delta b = 0$ are solved. The solution is:

$$b = \frac{n\Sigma xy - \Sigma x\Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

and
$$a = \frac{1}{n}(\Sigma y - b\Sigma x)$$

The variance of a (S_a^2) and b (S_b^2) may be estimated by

$$S_a^2 = \frac{\Sigma x^2}{n\Sigma x^2 - (\Sigma x)^2} \cdot S_y^2$$

$$S_b^2 = \frac{n}{n\Sigma x^2 - (\Sigma x)^2} \cdot S_y^2$$

where
$$S_y^2 = \frac{n\Sigma y^2 - (\Sigma y)^2 - b^2[n\Sigma x^2 - (\Sigma x)^2]}{n(n-2)}$$

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ADDENDUM

and column C (72 x ¼ in; Carbowax ; helium flow rate: 110 ml.min^{-1}.
The column temperature was programmed for operation from 40°
with a temperature rise of 30° min^{-1}).