STUDIES IN THE PYROLYSIS OF SOME BENZYL BROMIDES

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STUDIES IN THE PYROLYSIS OF SOME BENZYL BROMIDES

Being a Thesis presented by Alexander M. Mearns
to the University of St. Andrews in Application for
the Degree of Doctor of Philosophy

DECLARATION

I hereby declare that the following Thesis is a record of results of experiments carried out by me, that it is my own composition, and that it has not previously been presented in application for a Higher Degree.

The experiments were carried out in the Chemical Research Laboratories of St. Salvator's College, St. Andrews under the supervision of Dr. C. Horrex.

[redacted]

CERTIFICATE

I hereby certify that Mr. Alexander Morgan Mearns, B.Sc., has spent thirteen terms at Research Work under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

[redacted]

Director of Research.

UNIVERSITY CAREER

I entered the University of St. Andrews in October 1952 and graduated B.Sc.(Ordinary) in June 1955.

I gained First Class Honours in Chemistry in June 1956.

The work described in this Thesis was carried out during the period August 1956 to September 1959, during the tenure of a Carnegie Scholarship and a supplementary maintenance grant from the Department of Scientific and Industrial Research.

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CONTENTS

INTRODUCTION

AND

SURVEY OF RELATED WORK

INTRODUCTION

The work described in subsequent pages arose from certain difficulties in the current knowledge of the bond dissociation energies (D) of compounds of the type $C_6H_5CH_2-X$. For the reaction

$$C_6H_5CH_2-X \longrightarrow C_6H_5CH_2- + X - D \text{ k.cals.} \quad (1)$$

we can write

$$D(C_6H_5CH_2-X) = \Delta H_f(C_6H_5CH_2-) + \Delta H_f(X-) - \Delta H_f(C_6H_5CH_2-X) \quad (2)$$

where ΔH_f is the heat of formation of a chemical entity. It has been the task of many recent researches to evaluate (D) for different compounds. Since the last two terms in the thermochemical equation are often known, a determination of $D(C_6H_5CH_2-X)$ permits the heat of formation of the benzyl radical to be evaluated. It is obviously necessary that a consistent scheme should produce a single value for $\Delta H_f(C_6H_5CH_2-)$, and one which is independent of the nature of X.

Early work in this field by Szwarc[1] had produced such agreement, but recent more detailed work[2,3] threw doubt on his findings for $D(C_6H_5CH_2-H)$. Since his values were claimed to be cross-checked through (2), it was clear that his work on the determination of $D(C_6H_5CH_2-Br)$[4] might also be in error, for it was claimed to agree with his toluene results.

The pyrolysis of bromides in the presence of excess toluene has been the main kinetic method practised by Szwarc, and benzyl bromide is one of many bromides which have been investigated by him. In theory the method requires that the primary dissociation

$$R\text{-}Br \longrightarrow R\text{-} + Br\text{-} \tag{3}$$

shall be followed by the inhibition of secondary processes by reactions

$$R\text{-} + C_6H_5CH_3 \longrightarrow RH + C_6H_5CH_2\text{-} \tag{4}$$

$$Br\text{-} + C_6H_5CH_3 \longrightarrow HBr + C_6H_5CH_2\text{-} \tag{5}$$

$$2C_6H_5CH_2\text{-} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \tag{6}$$

Szwarc claimed that the method showed the decompositions to have a first order dependence on RBr concentration, and that the temperature dependence of the velocity constant followed an equation

$$\log_{10}k = \log_{10}A - E/4.57T$$

for the most extensively investigated cases. He laid stress on the fact that the values of A he obtained were close to 10^{13} sec.$^{-1}$, which is the expected value for a first order reaction, and hence that he was observing the dissociation process (3). As usual in this field the energy of activation (E) was taken as the bond dissociation energy (D). Justification for this assumption will be considered in the next section.

Benzyl bromide was one of the compounds Szwarc investigated more extensively and the results conformed with the above generalisations. In the case of several other bromides[5] the published results do not justify his assumption that the temperature independent factor would be found to have the value 10^{13} sec.$^{-1}$ under a more exhaustive scrutiny.

These items prompted a re-examination of the whole toluene carrier gas technique as applied to benzyl bromide. In one form of this technique, and probably the most widely used version, a stream of toluene vapour entrains the halide RBr by passage over the surface of the latter. Although temperatures above the dew point of toluene were advocated by Szwarc, elementary considerations suggested that solution of toluene in the RBr could not be prevented by this and uniformity of entrainment would suffer greatly. Varying concentrations of reactant would result and kinetic deductions would be invalidated.

As described in later pages, some simple experiments showed this suspicion about the toluene carrier gas technique to be correct. In view of this and the chemical uncertainties quoted earlier, there seemed a need to re-investigate the pyrolysis of benzyl bromide fairly extensively. In later pages the details of such work are given together with work on the chlorobenzyl bromides. Before dealing with the practical aspects of the work a short survey of the relevant previous investigations and kinetic techniques used is given.

THE CHEMICAL KINETIC METHOD OF MEASURING BOND DISSOCIATION ENERGIES OF ORGANIC MOLECULES

Many reactions of organic molecules which involve the breaking of a single bond have been studied kinetically in the past few years. The kinetic data obtained have been used to compute the energy necessary for this rupture.

The kinetic method is based on a study of the unimolecular dissociation process $R\text{-}X \longrightarrow R\text{-} + X\text{-}$ (1) in which molecule RX splits into R and X, which can be either radicals or atoms.

It is assumed that the experimental energy of activation for this process will equal the dissociation energy of the bond which is broken. This will be valid if the energy of activation for the reverse process of (1), the recombination of radicals R and X, is zero.

The activation energy for the reverse process is difficult to measure because of the uncertainty in estimating the concentrations of radicals. Gomer and Kistiakowsky[6] have estimated the energy required for the recombination of methyl radicals to be -0 ± 0.7k.cals./mole, by a rotating sector method developed by Burnett and Melville[7]. Recombination of ethyl radicals has been studied and the energy required for the process again assessed as zero. The above assumption, made regarding recombination of radicals R and X, would therefore seem to be valid for many cases.

The dissociation energy of the R-X bond in the molecule RX may be defined as the endothermicity of reaction (1) at 0°K.

Thus

$$\begin{aligned}\Delta H(\text{reaction } 1) &= \Delta H_f(R-) + \Delta H_f(X-) - \Delta H_f(R-X)\\ &= D(R-X)\\ &= E_1\end{aligned}$$

where E_1 is energy of activation for reaction (1).
Values are often given which are based on thermochemical data obtained at room temperature rather than at 0°K., but the correction involved is approximately 1 k.cal. which is within the accuracy of the experimental data in most cases.

The problem of finding the bond dissociation energy of RX then resolves itself into the determination of the energy of activation for the forward process (1). Unfortunately the kinetics of such a reaction may be complicated by secondary reactions of the reactive species R and X. For example, the back reaction might well be important, or either R or X might attack the parent molecule RX giving rise to stable secondary products or setting up a chain reaction; almost certainly there will be a significant activation energy involved in any secondary process. In any event, the kinetics will be more complex and the measured activation energy less likely to be assignable to the initial dissociation process.

Because of these uncertainties, many of the bond dissociation energies obtained in recent years must be treated with caution if the kinetics are not well founded. Only those obtained by a method in which the reaction mechanism is well known, and which has been checked by one or more independent researches can be considered reliable.

Methods of eliminating or suppressing side reactions which have been used in kinetic studies of benzyl compounds and which have a bearing on the present research, are considered briefly in this section.

The most straightforward method of obtaining a value for the bond dissociation energy would be to measure the rate of production of radicals directly, but no satisfactory method has yet been devised for measuring the concentrations of radicals as they are produced in a thermal decomposition. If this were possible, the occurrence of any subsequent secondary reactions would be immaterial.

Historically the first kinetic studies which produced values of bond dissociation energies from thermal decomposition work were those of Rice[8]. In this work comparative radical concentrations were obtained at the exit of a fast flow system by the rates of reaction with metallic mirrors outside the furnace. The method was not applicable to sufficient cases of interest and Butler and Polanyi[9] adopted a modified flow technique. In this the initial rates of reaction were studied by ordinary methods of chemical analysis. In order to minimise secondary processes with products they restricted percentage decompositions by adjustment of temperature. By using carrier gas pressures of 0.01 to 0.1mms. all bimolecular processes, such as reaction of radicals with parent compound or products, were decreased and wall destruction of radicals was favoured. Since contact times of the order of 0.1 to 1 second were used the technique is one of fast, rather than very fast, flow and a considerable number of collisions with potential reactants can be made by a reactive fragment. However, such times of contact require high temperatures in order to get even small percentages of decomposition, and at high temperatures heterogeneous processes are diminished in importance compared with homogeneous.

Butler and Polanyi used their technique to study the pyrolysis of many organic iodides including benzyl iodide. It was hoped that secondary reactions would be few, but even under these flow conditions the life-time of an active radical is so short compared with the contact time and one of the products, iodine, is so readily attacked, that various complicating reactions occurred. In the decomposition of benzyl iodide the back reaction was an important feature; this has been confirmed by Gow[10] in the St. Andrews laboratories. It is speculative then to assume that the measured energy of activation is equivalent to the dissociation energy of the R-I bond. The energies of activation for some of these reactions were obtained by measuring the rate at one temperature only, assuming an A factor of 10^{13} sec.$^{-1}$ and calculating the energy of activation from the formula $k = A\ e^{-E/RT}$. The justification for this procedure is not sound and doubt is immediately cast on the reliability of results obtained in this fashion. This will be discussed more fully in a later section.

Many other decompositions have been studied by methods closely similar to that of Butler and Polanyi. In all cases it is necessary to have a full knowledge of the mechanism. Rate constants must be measured over as wide a temperature range as possible to ensure an accurate value for the energy of activation and to obtain a value which does not depend upon making the assumption that the A factor is 10^{13} sec^{-1}.

One method of eliminating side reactions is to 'catch' the radicals from the initial dissociation as soon as they are produced, or, in other words, provide them with an energetically favourable reaction whereby stable, analysable products can result. Many catchers have been used including iodine, nitric oxide, propylene, cyclohexene and toluene, but apart from work with toluene, data obtained through their use have not been employed to determine bond dissociation energies. However Maccoll et al.[11] were able to determine energies of activation for the decomposition of organic bromides using propylene and cyclohexene as radical catchers. Maccoll found that the bromides studied decomposed in one or more of three ways: (1) by a radical non-chain process (2) by a radical chain process (3) by direct unimolecular elimination of hydrogen bromide. The propylene and cyclohexene were used to inhibit chain reactions. In the presence of these unsaturated compounds a marked decrease in rate would be observed compared with the rate of the uninhibited reaction since

$$Br- \; + \; CH_3CH{=}CH_2 \longrightarrow CH_2\overset{\frown}{-CH-}CH_2 \; + \; HBr \qquad (2)$$

is competing with

$$Br- \; + \; RBr \longrightarrow R'Br \; + \; HBr \qquad (3)$$

The 'toluene carrier' method devised by Szwarc[12] has been used, chiefly by Szwarc and collaborators, to catch radicals as they are formed. If a molecule RR' decomposes to give R and R', toluene, which must be present in large excess, will act as a catcher in the following manner:

$$R- + C_6H_5CH_3 \longrightarrow RH + C_6H_5CH_2- \qquad (4)$$

$$R'- + C_6H_5CH_3 \longrightarrow R'H + C_6H_5CH_2- \qquad (5)$$

The benzyl radicals so formed are stabilised by resonance and will not themselves start chain reactions but will dimerise thus

$$2C_6H_5CH_2- \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (6)$$

This method will only be successful if the ruptured bond has a dissociation energy of at least 10 k.cals. less than the C-H side-chain bond dissociation energy of toluene. A further necessity is that the reaction of radicals with toluene shall be rapid compared with the rate of the initial dissociation. Thus in the case of very weak bonds, although the difference in energy between the bond being broken and that of the side-chain C-H bond in toluene is much greater than 10 k.cals., the toluene carrier technique might not be feasible since the temperature of the reaction might be too low for reaction (4) or (5) to take place rapidly. A case in point is the decomposition of diethyl ether by Rebbert and Laidler[13] in which one of the main products was ethane, formed by dimerisation of methyl radicals; methane which would be formed if

$$CH_3- + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2- \qquad (7)$$

was an important reaction, was present in a very small amount. Dimerisation of methyl radicals at a temperature of 200-250°C. was very fast compared with reaction (7).

The toluene carrier technique was a failure in the decomposition of benzyl iodide[1]. Benzyl iodide decomposed to give benzyl radicals and iodine atoms but the reaction between iodine atoms and toluene was very sluggish.

Szwarc[1] has used the toluene carrier technique to obtain bond dissociation energies for a large number of compounds, among them aromatic hydrocarbons, bromides and chlorides. In some cases these bond energies must be regarded with suspicion for the kinetic evidence is meagre; for example, the involatile products of the decomposition of the substituted benzyl bromides were not identified and consequently secondary reactions may have taken place which would render any quantitative results obtained useless.

An interesting use of the toluene carrier technique as an indicator for the presence of free radicals has been made by Blades and Murphy[14]. When ethyl bromide was decomposed in the presence of toluene at 906-970°K., dibenzyl was not one of the products. They concluded that the initial split involved no radical formation but takes place by a molecular elimination process.

Hydrogen iodide, which has a bond strength of 71 k.cals./mole, has been developed as a radical catcher in this department by Downs[15] and Gow[10]. Their researches were carried out on two iodides of low bond strength, trifluoromethyl iodide and benzyl iodide. Alexander[16] had shown that the reaction between a benzyl radical and hydrogen iodide was rapid

$$C_6H_5CH_2\text{-} \; + \; HI \longrightarrow C_6H_5CH_3 \; + \; I\text{-} \qquad (8)$$

In his work with benzyl iodide, Gow showed that a simple dimerisation of iodine atoms was not the only other reaction. Instead a secondary reaction was initiated by the iodine atom

$$I- + C_6H_5CH_2I \longrightarrow C_6H_5CH_2- + I_2 \qquad (9)$$

This became the most important process in some conditions. The energy of activation for reaction (9) could be determined and an estimate for the C-I bond dissociation energy in benzyl iodide obtained from a knowledge of the dissociation energy of the iodine molecule and the energy of activation of the reverse process.

THE HEAT OF FORMATION OF THE BENZYL RADICAL AND THE BOND DISSOCIATION ENERGY OF TOLUENE

General

In this section the results obtained by the experimental methods described in the preceding section and by other methods for the bond dissociation energies of benzyl compounds will be considered.

The value of the dissociation energy of the side-chain C-H bond in toluene has been a disputed quantity for the past ten years. Sswarc[17] carried out a flow kinetic study on toluene and determined the activation energy for the decomposition to be 77.5 ± 1.3 k.cals./mole, which he assigned to the dissociation energy of the weakest C-H bond. Van Artsdalen et al.[2] put forward a value of 89.9 k.cals./mole obtained from a photochemical and thermal investigation of the bromination of toluene while Blades, Blades and Steacie[18], who attempted to repeat the work of Szwarc, gave an estimated value of 90 k.cals./mole for the energy of activation. More recently Smith[3], in the St. Andrews laboratories, suggested a value of 84.7 k.cals./mole but inclined to the view that this activation energy could not definitely be assigned to the bond dissociation energy of the side-chain C-H bond in toluene. Takahasi[19] worked in the range covered by both Sswarc and Steacie and considered that a single value for the activation energy could not be obtained. His values varied between 76.2 and 104.9 k.cals./mole depending on the temperature and the contact time. Two independent determinations by electron impact methods by Schissler and Stevenson[20] and

Lossing et al.[21] gave values of 77 ± 3 and 95 k.cals./mole respectively. The discrepancies between these values have brought forward much discussion in the literature which is dealt with below.

In view of these discrepancies, it is not surprising that independent methods have been sought to find the value of this dissociation energy and of the related heat of formation of the benzyl radical.

As stated in the introduction, if the activation energy for the process

$$C_6H_5CH_2\text{-}X \longrightarrow C_6H_5CH_2\text{-} + X\text{-} \qquad (1)$$

is measured experimentally and if this represents the bond dissociation energy of the C-X bond then

$$\Delta H_f(C_6H_5CH_2\text{-}) = D(C_6H_5CH_2\text{-}X) - \Delta H_f(X\text{-}) + \Delta H_f(C_6H_5CH_2X) \qquad (2)$$

If $\Delta H_f(X\text{-})$ and $\Delta H_f(C_6H_5CH_2X)$ are accurately known, $\Delta H_f(C_6H_5CH_2\text{-})$ may be calculated.

Further $D(C_6H_5CH_2\text{-}H)$ may be calculated from the equation

$$D(C_6H_5CH_2\text{-}H) = \Delta H_f(C_6H_5CH_2\text{-}) + \Delta H_f(H\text{-}) - \Delta H_f(C_6H_5CH_3) \qquad (3)$$

since $\Delta H_f(H\text{-})$ and $\Delta H_f(C_6H_5CH_3)$ are accurately known.

Szwarc's work, referred to in the introduction, using the toluene carrier technique produced values for $\Delta H_f(C_6H_5CH_2\text{-})$ showing agreement among themselves and with $\Delta H_f(C_6H_5CH_2\text{-})$ from his work on the pyrolysis of toluene. Experiments by Alexander[16] on dibenzyl, Davidson[22] on dibenzyl, Gow[10] on benzyl iodide and this work on bensyl bromide have been undertaken in this department to determine independently the value for $\Delta H_f(C_6H_5CH_2\text{-})$.

Details of the work summarised above will be given in this section but a discussion of the data will be postponed until the results of the experimental work of this thesis have been presented.

Flow Kinetic Studies of the Decomposition of Toluene.

Szwarc[17] studied the decomposition of toluene over the temperature range 680-850°C. He attempted to cut down all secondary reactions by using very short contact times (0.235 - 0.905 secs.) and high rates of flow, and also restricted the percentage decomposition to 0.01 - 1.25. The reactant pressure was varied over the range 2 - 15mms.

The reaction rate was measured by the production of hydrogen plus methane, which were produced in the ratio of 60/40 , the assumption being made that one mole of gas formed corresponds to one mole of toluene primarily decomposed.

The number of moles of dibenzyl formed was equal to the moles of hydrogen plus methane. The dibenzyl was characterised by its melting point and by mixed melting point determinations and the amount estimated by weighing. It is doubtful if these methods are of sufficient accuracy to enable one to say definitely that the involatile products consist wholly of dibenzyl. No attempt was made to establish the identity of benzene in the products.

Szwarc stated that the decomposition was a homogeneous gas reaction of the first order with rate constant $k = 2 \times 10^{13} e^{-77,500 \mp 1,300/RT} \text{sec.}^{-1}$. Evidence for first order kinetic behaviour was slight, since the number of experiments was too few and fairly unreliable owing to the fact that the effects of changing contact time and of concentration of reactant were difficult to separate. Six experiments only could be used for this purpose. The results were considered to fit the mechanism:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + H- \qquad (1)$$

$$H- + C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + H_2 \qquad (2)$$

$$H- + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_3- \qquad (3)$$

$$CH_3- + C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + CH_4 \qquad (4)$$

$$2C_6H_5CH_2- \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$

Blades, Blades and Steacie[18] repeated the work of Szwarc using a similar type of apparatus and a range of reaction vessels, the volumes of which varied from a few ccs. to 450 ccs. The products were collected in traps surrounded by acetone-solid carbon dioxide and liquid air, while the non-condensable gases were collected by means of a Toepler pump and measured on a McLeod gauge. These workers agreed with Szwarc that the ratio of hydrogen to methane was independent of temperature of reaction and of contact time, but stated that the ratio was $H_2/CH_4 = 69/31$, which may be compared with 60/40 as determined by Szwarc.

They were able to separate their collected materials into volatile and non-volatile components. The volatile materials were fractionally distilled to give gaseous material, benzene, toluene and a residue which contained styrene. The gaseous material was not present in the products when pre-pyrolysed toluene was used. Chromatographic analysis of the involatile material showed that dibenzyl, dimethyldiphenyls and a small amount of diphenyl were present, the dibenzyl accounting for not more than 50% of the total.

From certain points of view the results of this work were disappointing. The conditions used by Szwarc were not reproduced in at least two instances. For example, it can be deduced from the plot of log k versus 1/T°K. that the temperature range covered was 858-947°C., compared with 738-864°C. used by Szwarc; they do take pains to point out however, that diphenyls were found even at the lowest temperatures. The contact times were varied over the range 0.068-0.568secs., compared with 0.235-0.905secs. in Szwarc's research. The difference may be significant since, in contrast to the conclusions of Szwarc, they deduced that the rate as measured by the rate of formation of hydrogen plus methane varied with contact time and also with reactant concentration, although again the effects of contact time and reactant concentration are not easy to separate. It was also considered that conditioning of the surface of the reactor was necessary before reproducible results could be obtained.

Although the evidence did not suggest a first order reaction, the energy of activation obtained using a contact time of 0.068secs. was 90 k.cals./mole.

While Steacie et al. were conducting their experiments, Smith[3] in the St. Andrews laboratories was also reinvestigating the decomposition of toluene. The reaction was studied over the temperature range 772-880°C., while the variation in contact time was 0.565-2.076secs. and in reactant pressure 0.56-2.34mms. The main difference in the technique was the use of nitrogen carrier gas, while Szwarc used no carrier gas. Smith's results showed that the rate constant at a given temperature, as judged by the hydrogen plus methane rate of formation, was independent of contact time and reactant concentration, thus indicating a first order reaction and disagreeing with the conclusions of Steacie et al. Another noteworthy difference in the results was that the ratio of $H_2/CH_4 = 76.7/23.3$ in contrast to 69/31 (Steacie) and 60/40 (Szwarc). The hydrogen production could be followed continuously by a thermal conductivity gauge measurement. This also showed that the initial hydrogen production was erratic, which supported Steacie's view that seasoning of the reactor was necessary.

Smith examined the products of the reaction by mass spectrometry and agreed with Steacie that methyldiphenyls were important constituents of the products. This was more convincing evidence as the temperature range of the decomposition was of the same order as that of Szwarc. Dibenzyl was thought to constitute 50-60 moles% of the involatile products while dimethyldiphenyls/monomethyldiphenyls = 4/1. The liquid products contained benzene but not in molar amounts equal to those of methane, as suggested by Steacie. The temperature dependence of the first order rate constant was given as $k = 10^{15.1}e^{-84,700/RT}\text{sec.}^{-1}$ but, because of the complexity of the products and the impossibility of deducing a definite reaction scheme, it was not felt possible to ascribe the activation energy to the dissociation energy for the side-chain C-H bond in toluene.

Takahasi[19] examined the toluene pyrolysis over the whole range, 737-953°C., covered by Szwarc and Steacie. He deduced that the Arrhenius plot had a concave curvature and he divided the temperature range rather arbitrarily into three parts each with different gradients and therefore different activation energies and frequency factors. The experimental data indicated that high activation energies (up to 104.9 k.cals./mole) and frequency factors (up to $10^{18.1}$sec.$^{-1}$) are obtained in the highest temperature range (903-956°C.) in experiments carried out with contact times of 0.1-0.3 secs., but in the highest temperature range with contact times from 0.02-0.04 secs. the activation energy remained at a low value of 76.2 k.cals./mole. The failure of Smith and Szwarc to notice any change in rate constant with contact time could be explained by suggesting that the range of contact times used by them (0.235-2.076 secs.) is outwith the range, approximately 0.02-0.1 secs., where such a change would be noticed. It is questionable whether the reactant reached the operating temperature with such low contact times and uncertainty might be introduced because of this. The conclusion reached to explain the change in activation energy with temperature and contact time was that some competitive reaction producing hydrogen and methane was becoming important at higher temperatures and which would be suppressed with lower contact times.

Evidence was produced in the second paper on the pyrolysis of toluene-3-d and toluene-4-d that such a competitive reaction could be the ring abstraction from toluene by hydrogen atom or methyl radical.

Another type of competitive reaction which could be considered is $C_6H_5CH_3 \longrightarrow C_6H_5\text{-} + CH_3\text{-}$. Szwarc considered this reaction unimportant in the pyrolysis of toluene since H_2/CH_4 remained constant over the temperature range considered as it does also in the pyrolysis of n-propylbenzene[23] in toluene. Blades and Steacie[24] repeated the decomposition of n-propylbenzene in toluene-d_3 and found that the methane produced had the isotopic constitution $CH_4 : CD_3H : CD_2H_2 = 1 : 1.5 : 1$ and the $H_2/HD = 1/1$. The ratio of H_2/HD seemed to be evidence that hydrogen atom abstracted from the ring as well as from the side-chain and the production of deuterated methanes indicated that hydrogen atoms produce methane on reaction with toluene and therefore the above reaction is ruled out.

Since C_6H_6/CH_4 was much less than 1/1, Smith did not consider that the evidence ruled out this reaction completely.

Decomposition of $C_6H_5CH_2$-X Compounds using the Toluene Carrier Technique

Szwarc has studied the decomposition of many benzyl compounds in the presence of toluene. The results are summarised in the following table:

Compound	Temp. Range °C.	log A $sec.^{-1}$	E k.cals.	ΔH_f ($C_6H_5CH_2X$) k.cals.	ΔH_f (X-) k.cals.	ΔH_f ($C_6H_5CH_2$-) k.cals.
$C_6H_5CH_2-CH_3$	614-745	13.0	63.2	7.1	32.5	37.8
$C_6H_5CH_2-C_2H_5$	614-743	12.5	57.5	1.9	25.2	34.2
$C_6H_5CH_2-Cl$	649-747	14.8	68.0	5.2	29.0	44.2
$C_6H_5CH_2-Br$	495-599	13.0	50.5	15.6	26.7	39.4
$C_6H_5CH_2-NH_2$	650-800	12.8	59.4	14.0	41.0	32.4
$C_6H_5CH_2-COCH_3$	570-687	16.0	69.0			
$C_6H_5CH_2-CO_2C_6H_5$	635-729	15.3	68.2			
-	-	-	-	-	-	-
$C_6H_5CH_2-H$	680-850	13.3	77.5	11.9	52.0	37.4

The $\Delta H_f(C_6H_5CH_2-)$ in each case has been calculated from the data of Szwarc et al. The heat of formation of the benzyl radical shows a fair degree of constancy if the reactions with high A factors are neglected and considering the errors involved in measuring the thermochemical quantities, but the spread is also wide enough for it to be profitable to look at independent values for the $\Delta H_f(C_6H_5CH_2-)$.

Benzyl Bromide

Since the decomposition of benzyl bromide is of most interest in this research, the results obtained by Szwarc[4] on this compound will be considered more fully. In each of the above compounds the mechanism was considered to be

$$C_6H_5CH_2{-}X \longrightarrow C_6H_5CH_2{-} + X{-} \qquad (1)$$

followed by the fast reaction

$$X{-} + C_6H_5CH_3 \longrightarrow HX + C_6H_5CH_2{-} \qquad (2)$$

and dimerisation of the benzyl radicals. The rate of reaction was measured by the rate of formation of HX. For benzyl bromide then the reaction proceeded by the following route:

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2{-} + Br{-} \qquad (3)$$

$$Br{-} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2{-} + HBr \qquad (4)$$

$$2C_6H_5CH_2{-} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (5)$$

Benzyl bromide, in pressures varying from 0.01 to 0.16mms. (in one instance 2.3mms.), was injected into the toluene stream, the pressures of which varied from 8.7 to 15.2mms. The more involatile products were collected in a trap cooled in ice and the volatile components, including hydrogen bromide, in a trap surrounded by liquid air. The non-condensable gases, hydrogen and methane, were pumped away by two diffusion pumps and analysed by pressure measurements on a McLeod gauge. The hydrogen/methane ratio was 60/40 and the gas was never more than 15 moles% of the total hydrogen bromide (average about 6%), but there did not appear to be any logical trend in the amount of gases obtained. The rate of reaction was measured by titrating the hydrogen bromide formed, and was checked by weighing the 'dibenzyl' which was collected in the trap in ice, and also the amount which appeared in the trap in liquid air. The ratio of HBr/dibenzyl varied from 0.85 to 1.26 but in the great majority of the experiments the ratio was ~1. No method of identification of dibenzyl was given but it was presumed to have been by melting point and mixed melting point determinations similar to the method adopted in the pyrolysis of toluene. In any case the constitution of the involatile products was not investigated.

The partial pressure of bromide was varied from 0.014 to 2.3mms. while the rate constant varied from 0.52 to 0.59sec.$^{-1}$ and the contact time was varied from 0.49 to 1.22secs., the rate constant varying from 0.48 to 0.55sec.$^{-1}$ The reaction was therefore considered to be first order. The rate was independent of toluene partial pressure and the effect of surface change was nil. The reaction was therefore a homogeneous one of the first order. A plot of log k versus $1/T^{o}K$. over the temperature range $768-872^{o}K$. gave an activation energy of 50.5 ± 2 k.cals./mole, while the A factor was 1×10^{13}sec.$^{-1}$.

The mechanism for the formation of hydrogen and methane was not elucidated, but it was pointed out that the H_2/CH_4 ratio was the same as found in the decomposition of toluene (it was also the same as that in the decomposition of n-propylbenzene using toluene as a carrier). The mechanism suggested was

(i) $H- + C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + H_2$ (6)

(ii) $H- + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_3-$ (7)

$CH_3- + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2-$ (8)

Two mechanisms were put forward for the production of hydrogen atoms to start the reaction

$Br- + C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2CHC_6H_5 + HBr$ (9)

$C_6H_5CH_2CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + H-$ (10)

or $C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2CHC_6H_5 + H-$ (11)

$C_6H_5CH_2CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + H-$ (10)

It was pointed out that the first would not change the HBr/dibenzyl ratio but the second would give a small increase in dibenzyl/HBr. Szwarc et al. gave no indication that stilbene or benzene had been formed in the reaction.

Some Decompositions of Other Compounds of Formula $C_6H_5CH_2-X$

Benzyl Chloride[25]

The experimental procedure for the pyrolysis of benzyl chloride was similar. No attempt was made at analysis of involatile products. The energy of activation was 68 k.cals./mole and the A factor $10^{14.8}$ sec.$^{-1}$. No explanation could be given for the magnitude of the A factor which Szwarc et al. considered abnormally high.

Ethyl Benzene[26]

Ethyl benzene was studied over the temperature range 615-745°C.

The collected gas was mainly methane but side reactions were prominent since 15-25% of the gaseous product was hydrogen. The experimental activation energy was 63.2 k.cals./mole and the A factor was 10^{13} sec.$^{-1}$.

Reference may be made to the table above for a comparison of the heats of formation of the benzyl radical from these compounds.

The Decomposition of Dibenzyl

A determination of the dissociation energy of the weak C-C bond in dibenzyl ought to afford valuable information on $\Delta H_f(C_6H_5CH_2-)$, since then the uncertainties in the thermochemical quantities would be reduced from three to two viz. the experimentally determined $D(C_6H_5CH_2-CH_2C_6H_5)$ and $\Delta H_f(C_6H_5CH_2CH_2C_6H_5)$. Horrex and Miles[27] first studied this decomposition in a flow system. They concluded that the stoichiometric equation was

$$3(C_6H_5CH_2CH_2C_6H_5) \longrightarrow 2C_6H_5CH_3 + C_6H_5CH{=}CHC_6H_5 + C_6H_6 + C_6H_5CH{=}CH_2 + (\text{small amount } H_2) \quad (1)$$

The kinetics were obviously extremely difficult to interpret and the rate equation which was deduced was $k = 2 \times 10^9 e^{-48,000/RT}$ sec.$^{-1}$. The A factor for this reaction is much lower than any previously reported for a first order reaction.

Pittilo[28] repeated the work and concluded that the reaction was not first order but was nearer 1.5, which suggested that there was an equilibrium set up for the initial primary dissociation

$$C_6H_5CH_2CH_2C_6H_5 \rightleftharpoons 2C_6H_5CH_2- \quad (2)$$

The reaction then proceeded by the decomposition reaction

$$\begin{gathered} C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_2- \longrightarrow C_6H_5CH_3 + C_6H_5CHCH_2C_6H_5 \\ C_6H_5CH_2CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 + H \end{gathered} \qquad (3)$$

With this knowledge, Davidson[22] studied the rate of formation of $C_6H_5CH_2CD_2C_6H_5$ by mass spectrometry when equal mixtures of $C_6H_5CH_2CH_2C_6H_5$ and $C_6H_5CD_2CD_2C_6H_5$ were reacting at temperatures between 400 and 500°C.

He found that the rate of radical exchange, equivalent to reaction (2), was first order, while the decomposition was 1.5 order at low pressures and tended to first order at high pressures.

At low pressures the decomposition was much slower than the exchange and, by taking into account the slight decomposition, he was able to calculate the activation energy for the exchange reaction and identified it with the $D(C_6H_5CH_2CH_2C_6H_5)$, which he calculated to be 60 k.cals./mole. By thermochemical calculation this led to a value for $\Delta H_f(C_6H_5CH_2-)$ of 44.9 k.cals.

The Bond Dissociation Energy of Toluene obtained by the Photobromination of Toluene

Van Artsdalen[2] has studied the bromination of hydrocarbons including methane, ethane and toluene, the reaction mechanisms being based on that of the classical thermal reaction between hydrogen and bromine, so extensively investigated by Bodenstein and Lind[29].

The basis of the method is to measure ΔH_1 for reaction

$$Br- + C_6H_5CH_3 \underset{E_4}{\overset{E_2}{\rightleftharpoons}} C_6H_5CH_2- + HBr$$

It can be seen that $\Delta H_1 = D(C_6H_5CH_2-H) - D(HBr)$ and $D(HBr)$ being a well established quantity, $D(C_6H_5CH_2-H)$ may readily be deduced. Now $\Delta H_1 = E_2 - E_4$ and therefore E_2 and E_4 must be determined experimentally.

Van Artsdalen studied the reaction photochemically over the temperature range 82-132°C. and thermally at 166°C. in a reaction cell fitted with high vacuum greaseless taps, and using a 1000 watt projection lamp as a source. It was proved that hydrogen bromide and benzyl bromide were the only products, there being no ring substitution of bromine atoms as shown by infra-red analysis.

The complete scheme, based on that of Bodenstein, was:

$$Br_2 + h\nu \longrightarrow 2Br- \quad \text{photochemical} \qquad (1a)$$

$$Br_2 + M \longrightarrow 2Br- + M \quad \text{thermal} \qquad (1b)$$

$$Br- + C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + HBr \qquad (2)$$

$$C_6H_5CH_2- + Br_2 \longrightarrow C_6H_5CH_2Br + Br- \qquad (3)$$

$$C_6H_5CH_2- + HBr \longrightarrow C_6H_5CH_3 + Br- \qquad (4)$$

$$Br- + Br- + M \longrightarrow Br_2 + M \qquad (5)$$

E_2 is obtained by measuring the initial rate of disappearance of bromine from a plot of $[Br_2]$ against time. Under these circumstances there was no inhibition by hydrogen bromide and measurement of the rate constant over the temperature range under these conditions gave the energy of activation for the forward reaction (2).

Van Artsdalen indicated that under these conditions the steady state equation was $-d(Br_2)/dt = k(Br_2)^{\frac{1}{2}}(C_6H_5CH_3)^{\frac{1}{2}}$. The general equation was $-d(Br_2)/dt = k(Br_2)^{\frac{1}{2}}(RH)1/(P)^{\frac{1}{2}}$ but the first equation gave the better results. This was interpreted as meaning that toluene was the only efficient third body in the equation

$$Br\cdot + Br\cdot + M \longrightarrow Br_2 + M \qquad (5)$$

Over a 50°C. range the temperature dependence obeyed the equation $\log k = 1.497 - 1742/T$ which gave an energy of activation of 7.2 ± 0.6 k.cals./mole for reaction (2).

The energy of activation for the reverse reaction (4) was obtained by studying the effect of hydrogen bromide inhibition.

The rate equation for the photochemical decomposition was derived from the previously given complete reaction mechanism as

$$\frac{-d(Br_2)}{dt} = \frac{k_2(C_6H_5CH_3)\left[\frac{\phi Iabs.}{k_5(M)}\right]^{\frac{1}{2}}}{1 + \frac{k_4(HBr)}{k_3(Br_2)}}$$

In this equation $-\frac{d(Br_2)}{dt}$ is the experimentally determined initial rate of the inhibited reaction in presence of HBr,

k_2 is the rate constant for uninhibited reaction at the same temperature,

k_5 and ϕIabs. are temperature independent.

From this equation they were able to deduce k_4/k_3 at three different temperatures, and $\log k_4/k_3 = 3.007 - 1176/T$. This enabled $E_4 - E_3$ to be calculated as 5 k.cals./mole. Arguing from the point of view that

$$H- \; + \; Br_2 \longrightarrow HBr \; + \; Br-$$

and $$CH_3- \; + \; Br_2 \longrightarrow CH_3Br \; + \; Br-$$

had zero energy of activation, they considered that reaction (3) in this research would also have zero activation energy,

$\therefore E_4 = 5$ k.cals./mole. This assumption may well be incorrect.

$$\Delta H_1 = E_2 - E_4$$

$$\therefore \Delta H_1 = 7.2 - 5 = 2.2 \text{ k.cals./mole,}$$

the estimated probable error being ± 1.3 k.cals./mole.

$$\Delta H_1 = D(C_6H_5CH_2-H) - D(HBr)$$

$$\therefore D(C_6H_5CH_2-H) = \Delta H_1 + D(HBr)$$

$$= 2.2 + 87.7 = 89.9 \text{ k.cals./mole.}$$

It can be seen that if (3) does not have zero activation energy, E_4 would be increased, ΔH_1 would be decreased and hence the dissociation energy of the side-chain C-H bond in toluene would be less than 89.9 k.cals./mole. This value may be considered as an upper limit.

Benson and Buss[30] cast doubts on the validity of stating that $Br- + Br- + M \longrightarrow Br_2 + M$ was the only chain ending process. They calculated a large entropy change in

$$Br- \; + \; C_6H_5CH_3 \rightleftharpoons HBr \; + \; C_6H_5CH_2-$$

and considered this favoured a high $C_6H_5CH_2-/Br-$ ratio, so that the chain ending process expected would be

$$2C_6H_5CH_2- \longrightarrow C_6H_5CH_2CH_2C_6H_5,$$

the alternative being to assign collision yields of 10^{-5} to

$$Br\text{-} + C_6H_5CH_2\text{-} \longrightarrow C_6H_5CH_2Br$$

or 10^{-6} to

$$2C_6H_5CH_2\text{-} \longrightarrow (C_6H_5CH_2)_2,$$

both of which they considered to be unreasonable.

Bond Dissociation Energies of Benzyl Compounds from Electron Impact Data

When molecules are bombarded by electrons of controlled and increasing energy, a point is reached when dissociation of certain bonds can be brought about. The dissociations usually produce at least one charged species as in

$$AB + e \longrightarrow A^+ + B + 2e.$$

By performing the process in a mass spectrometer the onset of dissociation can be detected by the appearance of the A^+ ion in the spectrum. The value of the potential through which the bombarding electrons have been accelerated is known as the "appearance potential of A^+ from AB". Ions produced in this manner may have kinetic energy, the value of which is difficult to determine; in the following discussion we shall make the usual assumption that it is negligible or has been allowed for. Such electron impact work may be used to measure the dissociation energy of a molecule AB in two ways, which shall be referred to as the 'direct method' and the 'indirect method'.

(1) The Direct Method

If AB is bombarded to give A^+ we have

$$AB + e \longrightarrow A^{+} + B + 2e \qquad (1)$$

$$A_o(A^{+})_{AB} = D(AB) + I(A)$$

where $A_o(A^{+})_{AB}$ is the appearance potential of A^{+} and I(A) is the ionisation potential of radical A.

If the ionisation potential of radical A, I(A), can be determined directly by electron bombardment of radical A, then D(AB) may be evaluated.

(2) The Indirect Method

If AC is bombarded to give A^{+} we have

$$AC + e \longrightarrow A^{+} + C + 2e \qquad (2)$$

$$A_o(A^{+})_{AC} = D(AC) + I(A)$$

This may be combined with the appearance potential for AB (as deduced in the 'direct method')

$$A_o(A^{+})_{AB} = D(AB) + I(A) \qquad (1)$$

By subtraction

$$A_o(A^{+})_{AC} - A_o(A^{+})_{AB} = D(AC) - D(AB) \qquad (3)$$

If D(AC) is known, D(AB) may be evaluated. This has eliminated the experimentally difficult procedure of measuring the ionisation potential of a radical.

In addition to the possibility that the dissociation products may possess unknown kinetic energy, a great source of error experienced in electron impact work lies in deducing the correct value for the minimum required energy of the bombarding electron. There is a spread of the energy of the electrons because of the normal spread of kinetic energies, depending on the temperature at which the electrons were formed, and for this reason the graph of ion current against electron accelerating potential is curved and the exact point at which it cuts the voltage axis is difficult to ascertain.

Both the direct and indirect methods have been applied to determine the bond dissociation energies of benzyl compounds.

Lossing, Ingold and Henderson[21] applied the direct method to obtain bond dissociation energies for benzyl bromide and benzyl iodide. The benzyl radicals were produced by passing the parent compounds through a furnace and immediately into the mass spectrometer head. Bombardment of the radicals gave I(A) while the appearance potentials of the undissociated compounds were measured by passing them directly into the mass spectrometer without going through the furnace. Values for the bond dissociation energies of benzyl bromide and benzyl iodide of 44.7 ± 3 and 34.6 ± 3 k.cals./mole respectively were measured. These are considerably lower than the values suggested by Szwarc. They calculated the ionisation potential for the benzyl radical to be 7.73 ± 0.08 e.v.

Schissler and Stevenson[20] employed the indirect method to determine $D(C_6H_5CH_2-H)$ using toluene and dibenzyl as reference compounds. The appearance potentials in each case were

$$A_1(C_7H_7^+) = D(C_6H_5CH_2-H) + I(C_6H_5CH_2-) \qquad (4)$$

for $C_6H_5CH_3 + e \longrightarrow C_7H_7^+ + H- + 2e$

and $$A_2(C_7H_7^+) = D(C_6H_5CH_2-CH_2C_6H_5) + I(C_6H_5CH_2-) \qquad (5)$$

for $C_6H_5CH_2CH_2C_6H_5 + e \longrightarrow C_7H_7^+ + C_6H_5CH_2- + 2e$.

Subtracting (4) from (5),

$$A_2(C_7H_7^+) - A_1(C_7H_7^+) = D(C_6H_5CH_2\text{-}CH_2C_6H_5) - D(C_6H_5CH_2\text{-}H) \qquad (6)$$

for $(C_6H_5CH_2)_2 + H\text{-} \longrightarrow C_6H_5CH_3 + C_6H_5CH_2\text{-}$.

Now from

$$(C_6H_5CH_2)_2 + 2H \longrightarrow 2C_6H_5CH_3 \qquad (7)$$

where $\Delta H_f(C_6H_5CH_2)_2$, $\Delta H_f(C_6H_5CH_3)$ and D(H-H) are known, we can calculate ΔH for equation (7).

Subtract (7) from (6), then

$$D(C_6H_5CH_2\text{-}H) = A_2(C_7H_7^+) - A_1(C_7H_7^+) - \Delta H_7$$

for $C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + H\text{-}$. (8)

The bond dissociation energy of toluene was calculated to be 77 ± 3 k.cals./mole. This value depended on the appearance potentials of toluene and dibenzyl. The value for the appearance potential of $C_7H_7^+$ from toluene was checked by thermochemical calculation using an experimentally determined appearance potential of $C_7H_7^+$ from ethyl benzene.

Farmer and Lossing[31] calculated a value for $I(C_6H_5CH_2\text{-})$ from Stevenson's data and thermochemical quantities. The equation they adopted for this procedure is obtained by multiplication of (4) by two and subtracting (5)

$$I(C_6H_5CH_2\text{-}) = 2A_1(C_7H_7^+) - A_2(C_7H_7^+) - 2D(C_6H_5CH_2\text{-}H) + D(C_6H_5CH_2CH_2C_6H_5) \qquad (9)$$

But $D(C_6H_5CH_2\text{-}H) = \Delta H_f(C_6H_5CH_2\text{-}) + \Delta H_f(H\text{-}) - \Delta H_f(C_6H_5CH_3)$

and $D(C_6H_5CH_2)_2 = 2\Delta H_f(C_6H_5CH_2\text{-}) - \Delta H_f(C_6H_5CH_2)_2$

Substituting in equation (9) for $D(C_6H_5CH_2{-}H)$ and $D(C_6H_5CH_2)_2$,

$$I(C_6H_5CH_2-) = 2A_1(C_7H_7^+) - A_2(C_7H_7^+) - 2\Delta H_f(H-) + 2\Delta H_f(C_6H_5CH_3) - \Delta H_f(C_6H_5CH_2)_2 \qquad (10)$$

The value of the ionisation potential calculated by this method was 8.51 e.v. as compared with 7.75 e.v. calculated by the direct method.

Further, if the value for the appearance potential, $A(C_7H_7^+)$, from toluene of Stevenson is combined with the value for $I(C_6H_5CH_2-)$, then for

$$A(C_7H_7^+) = D(C_6H_5CH_2{-}H) + I(C_6H_5CH_2-)$$

$$D(C_6H_5CH_2{-}H) = 11.85 - 7.76 \text{ e.v.}$$

$$= 95 \text{ k.cals./mole.}$$

Hamer[32] in St. Andrews measured the appearance potentials of the benzyl ion from toluene by the direct method and stated it to be 12.34 ± 0.12 e.v., while the ionisation potential of the benzyl radical was 8.05 e.v.

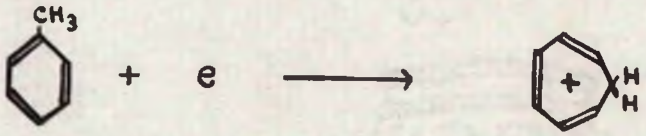
Hence $D(C_6H_5CH_2{-}H) = 12.34 - 8.05 = 4.29$ e.v.

$= 99$ k.cals./mole.

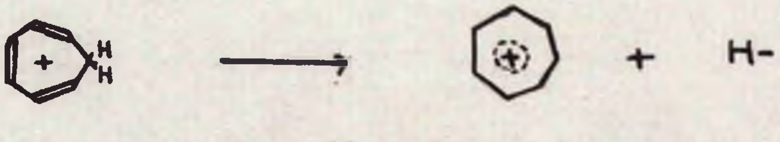
It does appear that these values of 95 and 99 k.cals./mole are excessively high.

A possible explanation for the high values obtained by the direct method was put forward by Rylander et al.[33], who carried out electron impact measurements on deuterotoluenes and ethylbenzene-α-β-d_5. By measurement of peak intensities, they were able to show that all the hydrogen atoms in the toluene molecule lose their identity in the process leading to the formation of the $C_7H_7^+$ ion, and can be considered to be equivalent. By studying the secondary dissociation of $C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$ further evidence was obtained for suggesting that the hydrogen atoms in $C_7H_7^+$ were equivalent. They extended their work to study benzyl chloride and benzyl alcohol[34] and again found that when the above secondary dissociation took place, it appeared that there was complete equivalence of seven hydrogen atoms in the $C_7H_7^+$ precursor.

They suggested that this could only be the case if the ion formed was tropylium and not benzyl. They considered that the $A(C_7H_7^+)$ obtained by the direct method was that for the tropylium ion and not for the benzyl ion. They postulated that the higher energy process involved in going to the tropylium ion took place in preference to formation of a benzyl ion, because the process



was faster than formation of benzyl ion. Once this cycloheptatriene ion had been formed, it passed by an activated complex to the tropylium ion, it being impossible for the benzyl ion to be produced from the cycloheptatriene ion.



The experimentally determined $A(C_7H_7^+)$ could not be used then for the calculation of $D(C_6H_5CH_2-H)$ because the appearance potential was that of the tropylium ion and not of the benzyl.

In the case of the benzyl halides, the bond dissociation energies, as measured by the direct method by Lossing et al.[21], were actually lower than the other values from kinetic data. Pylander suggested that the tropylium ion was again a better alternative than the benzyl ion from the electron bombardment of these species. He showed that $\Delta H_f(C_7H_7^+)$ from benzyl bromide, calculated from the directly measured $A(C_7H_7^+)$ and thermochemical data, was 210 k.cals./mole. $\Delta H_f(C_7H_7^+)$ calculated from $\Delta H_f(C_6H_5CH_2-)$, the magnitude of which is of course a disputed quantity, and $I(C_6H_5CH_2-)$ was 216.5 k.cals./mole. The difference of 6.5 k.cals. was considered to be compatible with the idea that the tropylium ion was -5 to 19 k.cals./mole more stable than the benzyl ion.

On the same basis $\Delta H_f(C_7H_7^+)$ from toluene was 231-236 k.cals./mole and it was concluded that the $C_7H_7^+$ ion from the halides, unlike that from the hydrocarbons, was formed from a state of the cycloheptatriene molecule ion with little or no energy beyond the minimum required for dissociation.

It was concluded that it is very hasardous to rely on bond energies obtained by the direct method due to rearrangements. The indirect method would give the correct value only if the energy excess or deficiency of the ions of the two dissociated molecules was the same in each case and disappeared when the difference was taken.

Thermodynamic Study of the Bromination of Toluene

In view of the spread of results obtained for the bond dissociation energy of toluene and for the heat of formation of the benzyl radical by the various kinetic methods and the limitations inherent in the electron impact methods, Benson and Buss[35] decided to obtain independent evidence from a study of the equilibrium

$$C_6H_5CH_3 + Br_2 \rightleftharpoons C_6H_5CH_2Br + HBr \qquad (1)$$

A value for the equilibrium constant for this reaction would enable the free energy change to be calculated by the equation $\Delta F^o = -RT\ln K_p$. Hence the heat of reaction could be expressed as

$$\Delta H^o = -RT\ln K_p + T\Delta S^o$$

The bond dissociation energies of hydrogen bromide and bromine are well established and consequently the difference in bond energies of toluene and benzyl bromide could be calculated from the equation

$$D(C_6H_5CH_3) - D(C_6H_5CH_2Br) = \Delta H^o + D(HBr) - D(Br_2) \qquad (2)$$

The experiments were carried out in sealed, evacuated tubes at 150°C. with a reaction time of 96 hours. The products were separated by isothermal distillation and analysed by standard procedures. Seven experiments only were performed but the equilibrium was approached from both sides.

The equilibrium constant was $7.2 \pm 0.7 \times 10^4$ giving $-\Delta F^o = 9.4 \pm 0.3$ k.cals./mole. The magnitude of the equilibrium constant implies that the equilibrium lies very much to the righthand side of equation (1).

Before obtaining a value for ΔH^o, it was necessary to know the standard entropies for the entities in equation (1). Third law data were available for bromine, hydrogen bromide and toluene but the entropy of benzyl bromide had to be calculated by statistical methods. The entropy change for reaction (1) was given as 3.5 ± 2 cals./mole °K. at 423°K. and 3.3 ± 2 cals./mole °K. at 298°K. giving

$\Delta H^{\circ}_{423^{\circ}K.}$ = −8 ± 0.9 k.cals./mole. $\Delta H_f^{\circ}(C_6H_5CH_2Br)$ was calculated to be 20.0 k.cals./mole.

From equation (2)

$$D(C_6H_5CH_3) - D(C_6H_5CH_2Br) = 34.7 \text{ k.cals./mole}$$

If the bond dissociation energies of Szwarc for benzyl bromide and toluene are used, the difference is 77.5 − 50.5 = 27 k.cals./mole. Benson and Buss concluded that the bond dissociation energy of either toluene or benzyl bromide was incorrect, or perhaps both quantities were in error.

The heat of formation of gaseous benzyl bromide was recalculated by these workers to be 18.4 ± 3 k.cals./mole in contrast to 15.6 ± 3 k.cals./mole determined thermochemically by Gellner and Skinner[36]. Gellner and Skinner measured the heat of the following reactions

$$C_6H_5CH_2Br(\text{liq.}) + AgNO_3(\text{aq.alc.}) + H_2O(\text{aq.alc.}) \longrightarrow$$
$$AgBr(\text{ppt.}) + C_6H_5CH_2OH(\text{aq.alc.}) + HNO_3(\text{aq.alc.}) + q_1 \qquad (3)$$

$$HBr(\text{liq.}) + AgNO_3(\text{aq.alc.}) \longrightarrow$$
$$AgBr(\text{ppt.}) + HNO_3(\text{aq.alc.}) + q_2 \qquad (4)$$

Subtract (4) from (3)

$$C_6H_5CH_2Br(\text{liq.}) + H_2O(\text{aq.alc.}) \longrightarrow$$
$$C_6H_5CH_2OH(\text{aq.alc.}) + HBr(\text{aq.}) + (q_1 - q_2) \qquad (5)$$

Then $\Delta H_f(C_6H_5CH_2Br)$liq. = $\Delta H_f(C_6H_5CH_2OH)$aq.alc. + $\Delta H_f(HBr)$aq.
- $\Delta H_f(H_2O)$aq.alc. - $(q_2 - q_1)$ (6)

The terms on the righthand side are known, so $\Delta H_f(C_6H_5CH_2Br)$liq. could be calculated. The value was given as 6.6 k.cals./mole. The heat of vaporisation of benzyl bromide was estimated to be 9 k.cals./mole, so that $\Delta H_f^o(C_6H_5CH_2Br)$g. = 15.6 k.cals./mole.

In recalculating $\Delta H_f^o(C_6H_5CH_2Br)$g., Benson and Buss stated they used -38.5 k.cals./mole for $\Delta H_f^o(C_6H_5CH_2OH)$aq.alc. suggested by Parks et al.[37] instead of -39 k.cals./mole as used by Skinner. This appears to be an error in the paper, for Skinner indeed used -36 k.cals./mole. A recalculation of $\Delta H_f^o(C_6H_5CH_2Br)$g. employing -38.5 k.cals./mole for the above gives 13.1 k.cals./mole if the estimated heat of vaporisation of 9 k.cals./mole is used. Benson and Buss stated that 11.3 k.cals./mole would be a more accurate heat of vaporisation of benzyl bromide. This would give $\Delta H_f^o(C_6H_5CH_2Br)$g. = 15.4 k.cals./mole (not 18.4 k.cals./mole). The agreement between the $\Delta H_f^o(C_6H_5CH_2Br)$g. of 20 k.cals./mole calculated from their data and 15.4 (or 13.1) k.cals./mole is not very convincing.

Further Thermochemical Data

Ubbelohde et al.[38] had occasion to measure the heat of reaction for

$$C_6H_5CH_2I(g.) + HI(g.) \longrightarrow C_6H_5CH_3(g.) + I_2(g.) \qquad (7)$$

$D(C_6H_5CH_3) - D(C_6H_5CH_2I)$ could be obtained since $D(HI)$ and $D(I_2)$ are well known.

The heat of reaction (7) was obtained by combining the heats of reaction for

$$C_6H_5CH_2MgCl + I_2 \longrightarrow C_6H_5CH_2I + MgICl$$

and

$$C_6H_5CH_2MgCl + HI \longrightarrow C_6H_5CH_3 + MgICl$$

ΔH_7 was calculated to be 1 ± 1.3 k.cals./mole, and

$$D(C_6H_5CH_3) - D(C_6H_5CH_2I) = 34.3 \text{ k.cals./mole} \qquad (8)$$

If we compare equation (8) with equation (2), the disagreement is great

$$D(C_6H_5CH_3) - D(C_6H_5CH_2I) = 34.3 \text{ k.cals./mole} \qquad (8)$$

$$D(C_6H_5CH_3) - D(C_6H_5CH_2Br) = 34.7 \text{ k.cals./mole} \qquad (2)$$

Subtract (2) from (8) then

$$D(C_6H_5CH_2Br) - D(C_6H_5CH_2I) = -0.4 \text{ k.cals./mole}$$

which is clearly impossible.

THE EFFECT OF SUBSTITUTION ON THE ENERGY OF ACTIVATION FOR THE DECOMPOSITION OF AROMATIC BROMIDES IN THE GAS PHASE

Szwarc et al.[5,39] have carried out experiments to decide if the energy of activation for the decomposition of ring substituted benzyl and phenyl bromides show a variation from those of the unsubstituted parent compounds.

The general procedure was to determine the rate constants for the unsubstituted compounds by the toluene carrier technique over a temperature range of approximately 100°C., the rate constants being measured by the rate of production of hydrogen bromide. A few experiments were then carried out on a large number of substituted compounds and the difference in activation energy between the unsubstituted and the substituted compound was calculated for each, assuming that the A factor was constant throughout the series. The difference in activation energies was measured by comparing the rate constants, at the same temperature and determined on the same apparatus, in the two cases when

$$E_u - E_s = RT \ln k_s/k_u \qquad (1)$$

where s refers to substituted compound

and u refers to unsubstituted compound.

The kinetics of the decomposition of the substituted compounds were simply assumed and no attempt was made to analyse the products apart from hydrogen bromide.

By making the usual assumptions that the energy of activation for the decomposition equals the dissociation energy of the ruptured bond, the differences in the bond dissociation energies of the substituted and unsubstituted compounds were calculated.

It is worthwhile examining the assumption that the A factor for the decomposition of organic bromides remains constant. The following table is taken from the paper of Ladacki and Szwarc[40].

Compound	E k.cals./mole	$A \times 10^{13}$ sec.^{-1}
$CH_2{=}CHCH_2{-}Br$	47.5	0.5
$CCl_3{-}Br$	49.0	2.0
$C_6H_5CH_2{-}Br$	50.5	1.0
$C_6H_5CO{-}Br$	57.0	5.0
9-anthracyl-Br	65.6	1.5
$CH_3{-}Br$	67.0	2.0
9-phenanthryl-Br	67.7	1.0
α-naphthyl-Br	70.0	1.5
β-naphthyl-Br	70.9	3.5
phenyl-Br	70.9	2.0

The evidence seems to be in favour of a constant A factor, yet the results obtained from the work on substituted benzyl bromides did not fully conform to the expected pattern. The energies of activation were calculated on the basis of $A = 2 \times 10^{13}\ \text{sec.}^{-1}$ The number of experiments on each compound varied from three to fifteen, and the plot of $\log_{10}k$ against $1/T^{\circ}K.$ was shown against a line obeying the equation

$\log_{10}k = 2 \times 10^{13} - E/RT$. In the case of m-methyl (four experiments), m- and p-chloro, m-bromo (three experiments), p-nitro and p-cyano, the A factors were indeed approximately 2×10^{13} sec.$^{-1}$, but for o- and p-methyl, o-chloro, m-nitro and m-cyano the A factors appear to be less than 2×10^{13} sec.$^{-1}$

On the basis of a constant A factor of 2×10^{13} sec.$^{-1}$, ΔD k.cals./mole, the difference between the energy of activation of the substituted and unsubstituted compounds, was calculated. The table below gives details.

Substituted Benzyl Bromide	ΔD k.cals./mole	Substituted Benzyl Bromide	ΔD k.cals./mole
o-chloro	0.9	m-methyl	0.0
m-chloro	0.1	p-methyl	1.4
p-chloro	0.4	m-nitro	2.1
m-bromo	0.3	p-nitro	1.1
p-bromo	0.3	m-cyano	1.4
o-methyl	2.0	p-cyano	0.7

However, if an energy of activation and A factor are calculated for o-chlorobenzyl bromide and p-methylbenzyl bromide from the results given in the paper, the figures are E = 45.7 and 39.3 k.cals./mole and A = $10^{11.4}$ and $10^{9.75}$ sec.$^{-1}$ respectively. It has to be agreed that these results are very approximate, considering the small number of readings and limited temperature range, but the deviation from

10^{13} sec.$^{-1}$ is marked. Similar deviations would be obtained for o-methyl, m-nitro and m-cyano.

Szwarc does suggest that the ortho effect might be rendering invalid the assumption of constancy of A factor for o-chlorobenzyl bromide, but suitable explanations have not been put forward for the m-nitro and m-cyano differences, for example.

It is noteworthy that Levy, Szwarc and Throssell[41] had occasion to repyrolyse benzyl bromide and p-methylbenzyl bromide. The pyrolysis of benzyl bromide gave similar results to those obtained in the previous investigations, but those for p-methylbenzyl bromide were markedly different. The first order rate constants appeared to be slightly pressure dependent and fell away below 0.05mms. pressure, while the energy of activation was 55 k.cals./mole and the A factor $10^{14.75}$sec.$^{-1}$ It was suggested that slight decomposition of the melted p-methylbenzyl bromide had taken place giving rise to a low energy of activation in the first series of experiments.

Some of these substituted benzyl bromides were of low volatility, and a method of injection was adopted in which toluene carrier gas was passed over the compound to pick it up and carry it into the reaction vessel. It seems rather doubtful whether this technique gave a constant rate of injection. This point will be discussed in the experimental section, but it might be put forward as a contributory factor to the variation of results obtained in the decomposition of these substituted benzyl bromides.

PRELIMINARY EXPERIMENTS

AN INVESTIGATION OF THE METHOD OF INJECTION OF SUBSTITUTED BENZYL BROMIDES USED BY LEIGH, SEHON AND SZWARC

Introduction

A method which has been adopted for the injection of involatile materials into the reaction vessel, when the 'toluene carrier' technique is being used, is to pass the toluene stream through a U-tube containing the involatile material, thus picking up the reactant vapour and carrying it into the reaction vessel. This method was adopted by Leigh, Sehon and Szwarc[5] for the introduction of substituted benzyl bromides of low volatility.

The U-tube containing the bromide was surrounded by a thermostatically controlled heated bath, and the toluene stream was passed through this tube entraining the reactant vapour. The partial pressure of the bromide could be varied by changing the temperature of the bath surrounding the U-tube. The rate of flow of reactant was measured by noting the time taken for a known weight of bromide to disappear from the U-tube, the end of the experiment being signified by the complete removal of bromide from the U-tube.

The partial pressures of bromide were quoted correct to two decimal places, and it was thought that the technique did not justify this, since it was felt that (1) the exposed surface of the material in the U-tube decreases and therefore the quantity of material entrained must also decrease and tend to zero eventually, and (2) since toluene is miscible with the liquid in the U-tube, it will tend to

APPARATUS USED IN PICK-UP EXPERIMENTS

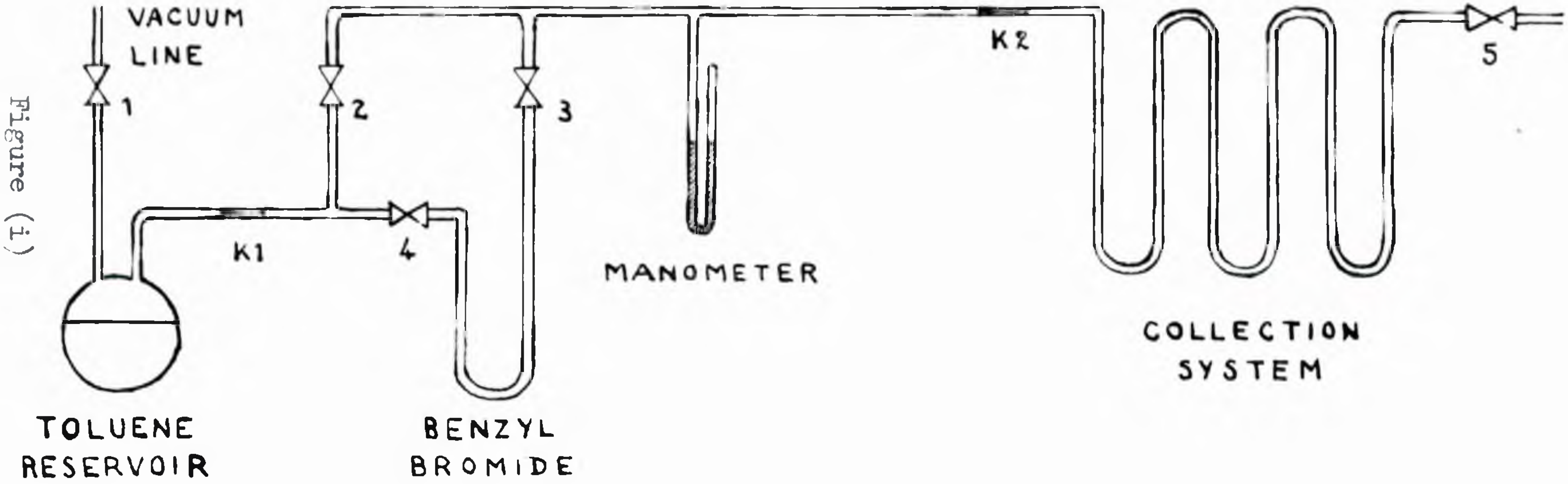


Figure (i)

dissolve in it and cause a change in the partial pressure.

The suggestion implicit in Szwarc's paper that, if the U-tube is at a temperature above the dew point of toluene, there will be no deposition of toluene, cannot be expected to hold if there is a solvent in the U-tube in which the toluene can dissolve.

Apparatus and Experimental Technique

An apparatus was set up to test whether the assumptions made regarding the variation of pick-up of bromide by toluene were valid. The conditions aimed at duplicating the rate of pick-up of reactant in the above work.

Experiments were performed with benzyl bromide and p-bromobenzyl bromide. The apparatus used is shown in Fig.(1). A known weight of the bromide was introduced into the U-tube, which was surrounded by a water bath, the temperature of which was kept constant to ±0.1°C. when a run was in progress. A similar temperature controlled bath was used to surround the toluene reservoir. All tubes from the exit side of the U-tube to the collection system were electrically heated above the temperature of the bath surrounding the U-tube to prevent condensation of the bromide vapour. The manometer was filled with mercury on which was a layer of silicone oil to prevent any evaporation of mercury when heated. K1 and K2 were capillaries chosen to ensure a rate of flow corresponding to that used by the previous workers.

With liquid air surrounding the toluene and bromide reservoirs, the apparatus was evacuated to 5×10^{-5}mms. Taps 1, 3 and 4 were shut and the toluene reservoir was surrounded by the constant temperature bath, the temperature being so chosen that the pressure measured on the manometer was of the order of 10mms. Hg. The benzyl bromide U-tube was immersed in a similar constant temperature bath. The last of the series of U-tubes in the collection system was immersed in liquid air. Taps 3 and 4 were then opened and 2 was closed. When a stable rate of flow was obtained, the next U-tube was immersed in liquid air and collection was carried out over a measured length of time, usually twelve minutes. This procedure was repeated until little or no bromide remained to be picked up.

When a run had been completed, the liquid air traps were removed and the contents allowed to warm up when air was admitted into the apparatus.

In runs with p-bromobenzyl bromide it was found that the bromide tended to condense outside the coldest part of the U-tube. In this case, after the apparatus had been let down to atmospheric pressure, a stream of dry air was drawn through the U-tube system, the U-tubes being once more immersed in liquid air. Gentle heating was sufficient to drive the p-bromobenzyl bromide down into the U-tubes.

The U-tubes were then cut from the apparatus and a sample of the contents of each was examined on an Abbe refractometer, the slide of which was maintained at $23.3^{\circ} \pm 0.1^{\circ}$C. The constitution of any liquid remaining in the U-tube containing the reactant could be similarly examined on the refractometer.

The concentration of benzyl bromide in toluene in each of the collection U-tubes was to be determined by comparing the refractive

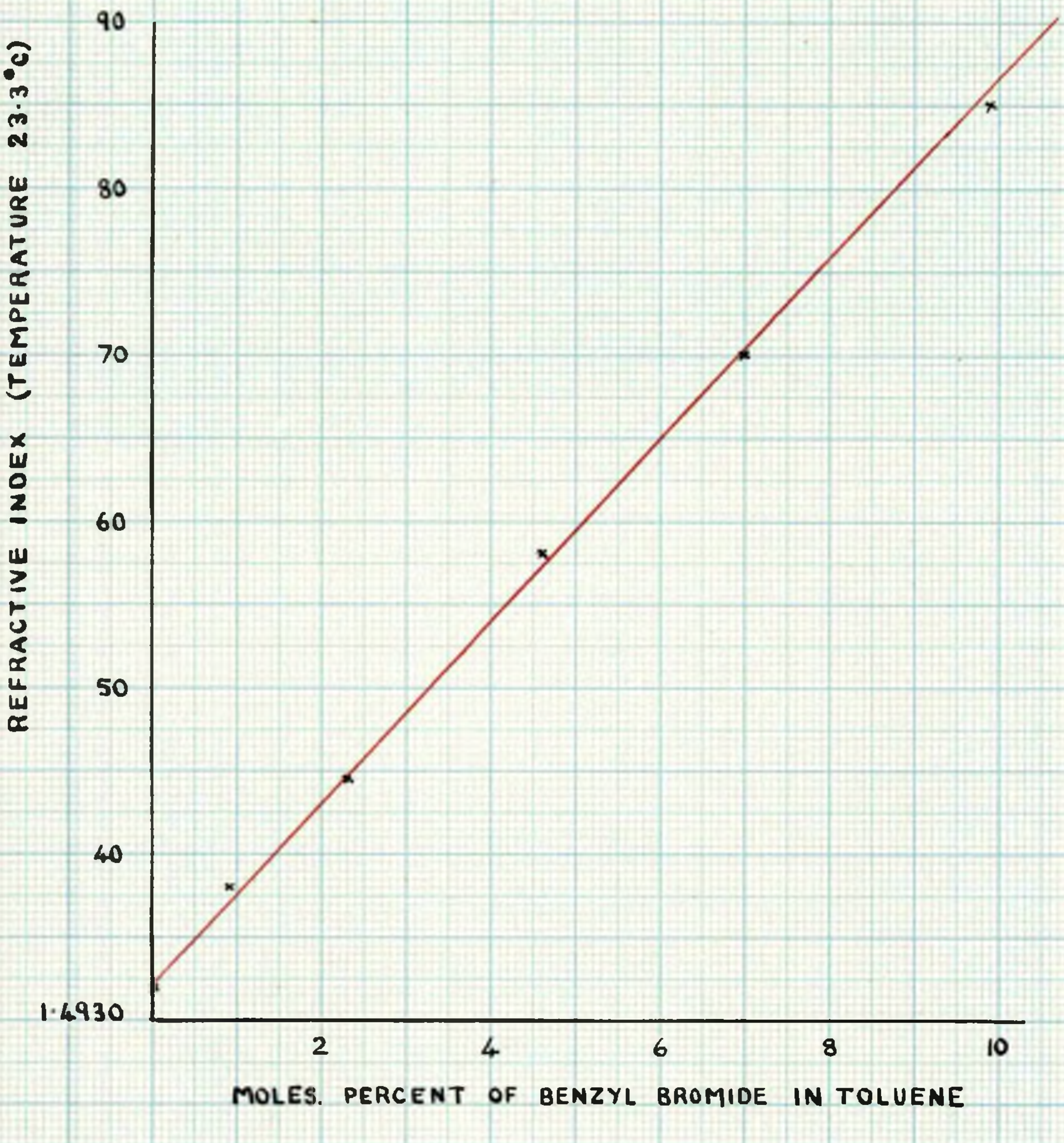

REFRACTIVE INDEX (TEMPERATURE 23·3°C)
90
80
70
60
50
40
1·4930
2
4
6
8
10
MOLES. PERCENT OF BENZYL BROMIDE IN TOLUENE

Figure (ii)

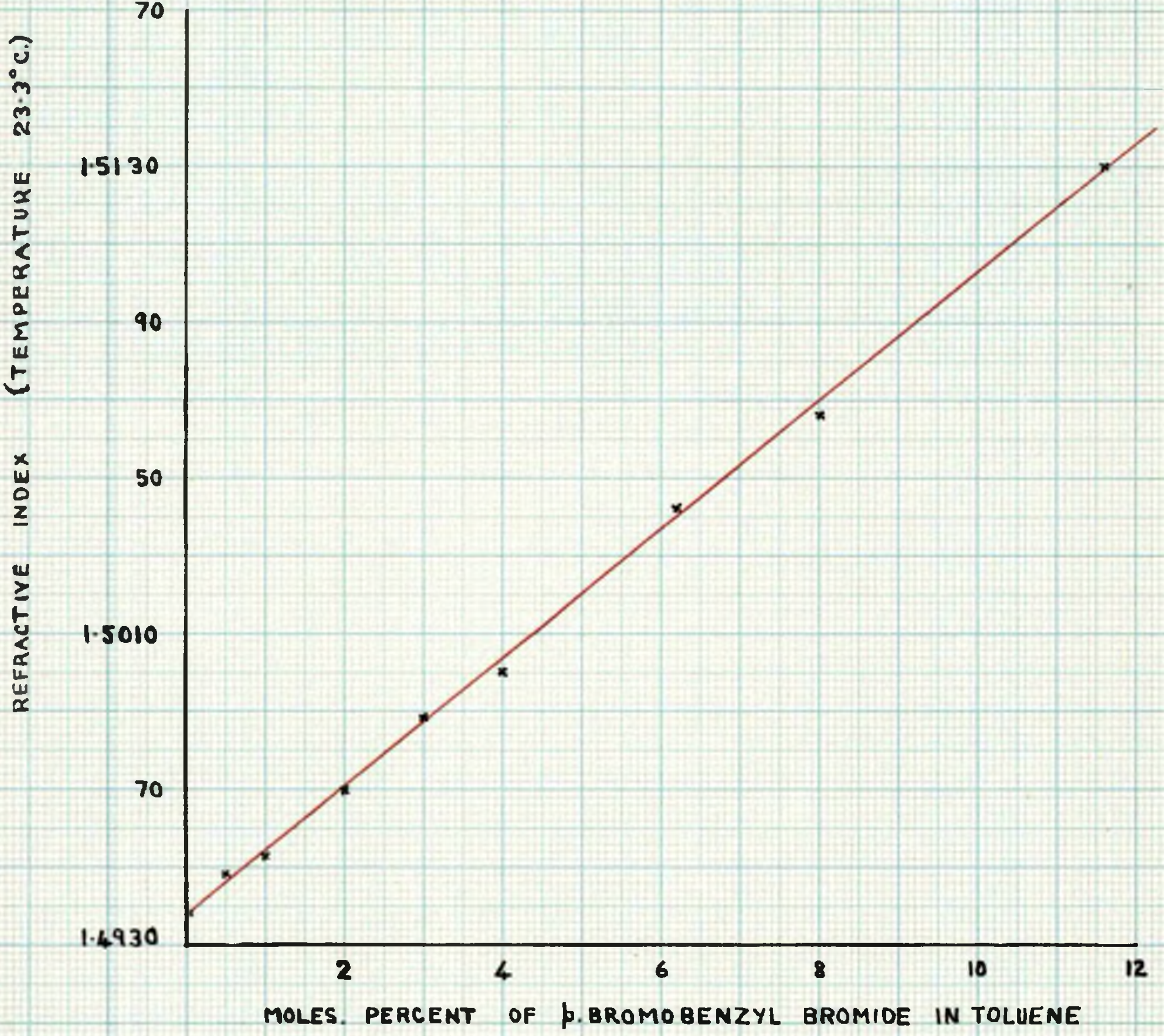

70
1·5130
90
50
1·5010
70
1·4930
REFRACTIVE INDEX (TEMPERATURE 23·3°C.)
2
4
6
8
10
12
MOLES. PERCENT OF p. BROMOBENZYL BROMIDE IN TOLUENE

Figure (iii)

indices of these mixtures with the refractive indices of standard solutions of benzyl bromide in toluene. Synthetic mixtures of benzyl bromide and of p-bromobenzyl bromide in toluene were therefore prepared and examined on the refractometer.

Graphs showing the moles percent of benzyl bromide and p-bromobenzyl bromide in toluene measured against refractive index are given in Fig.(ii) and Fig.(iii) respectively.

Experimental Results and Discussion

(1) Pick-up of benzyl bromide by toluene.

Table (i)

Analysis of U-tubes Refractive Indices at 23.3°C.					Moles% of Benzyl Bromide in Toluene in U-tubes (ex calibration graph)				
1	2	3	4	5	1	2	3	4	5
1.4987	1.4978	1.4973	1.4969	1.4962	10.2	8.5	7.5	6.8	5.5
1.4987	1.4984	1.4980	1.4973	1.4968	10.2	9.6	8.75	7.5	6.6
1.4988	1.4982	1.4979	1.4977	1.4972	10.4	9.25	8.75	8.3	7.4

Residual Liquid

Refractive Index	Moles% Benzyl Bromide in Toluene
1.5280	77
1.5272	74
1.5290	80

(2) Pick-up of p-bromobenzyl bromide by toluene.

Table (ii)

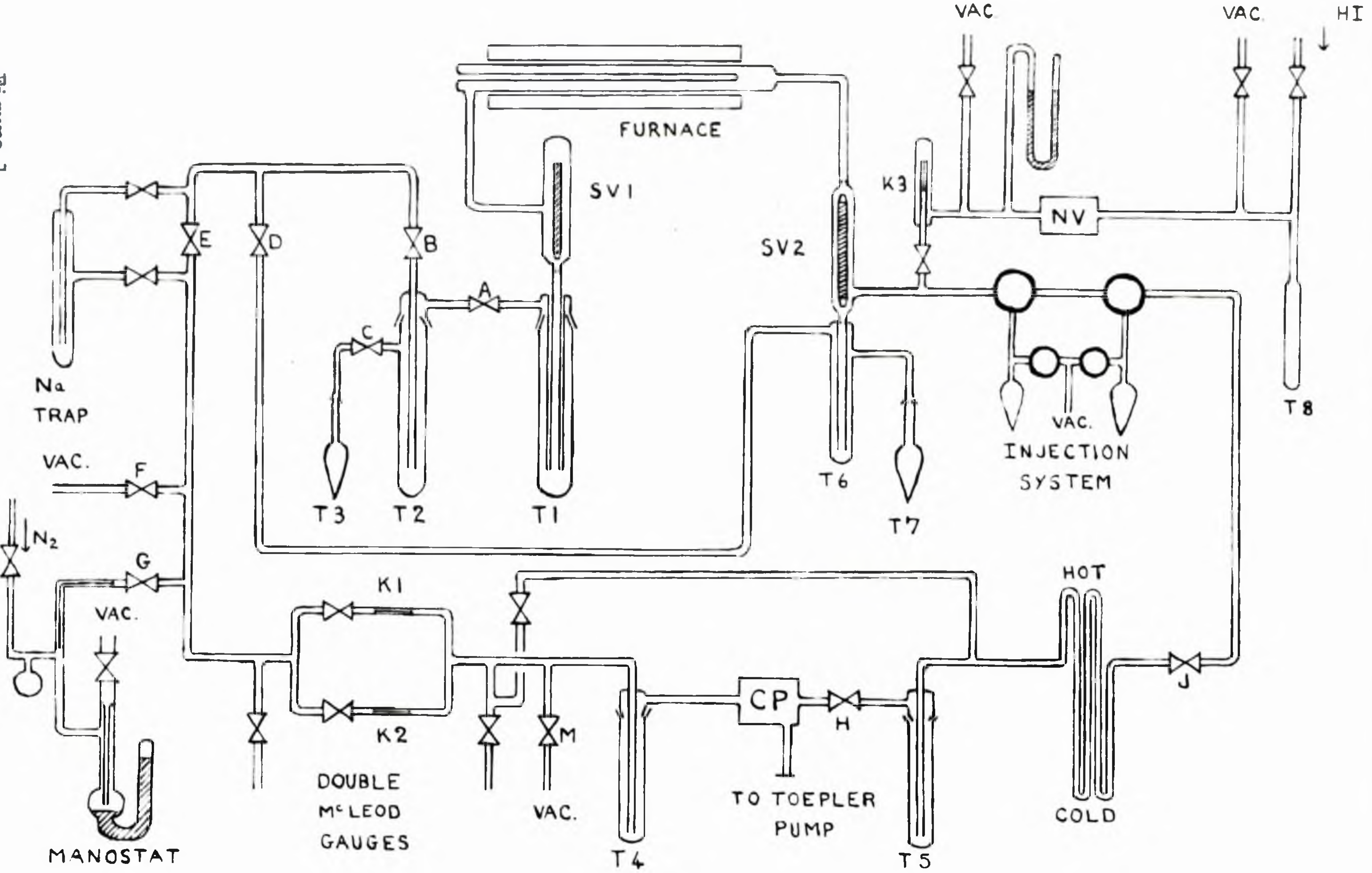
Analysis of U-tubes Refractive Indices at 23.3°C.					Moles% of p-Br Benzyl Bromide in Toluene in U-tubes (ex calibration graph)				
1	2	3	4	5	1	2	3	4	5
1.5088	1.5032	1.4978	1.4940	1.4932	9.1	5.7	2.4	0.2	-
1.5052	1.5030	1.5012	1.4957	1.4932	6.9	5.6	4.5	1.15	-
1.5060	1.5035	1.5010	1.4946	1.4932	7.4	5.9	4.4	0.5	-

These results show that there is a marked decrease in the amount of bromide which is picked up during the period of a run. The experiments with benzyl bromide in which the run was stopped before all the liquid had been removed from the U-tube show also that the liquid remaining in it was not pure benzyl bromide, as was necessary if the method of injection was to give constant delivery of bromide, but was benzyl bromide containing dissolved toluene. If this method of injection were used in an actual flow experiment, it is reasonable to suppose that when the run was nearing completion the percentage of benzyl bromide injected into the circulation line would be very low and much less than at the start.

The partial pressures quoted by Szwarc et al. cannot be regarded as anything other than the mean pressure of reactant for a particular run. No conclusions about the order of reaction could possibly be drawn from data obtained by use of this type of injection system.

APPARATUS AND EXPERIMENTAL RESULTS

Figure 1


VAC
VAC
HI
FURNACE
SV I
K3
NV
SV2
E
D
B
A
C
Na
TRAP
INJECTION
SYSTEM
VAC.
T8
T3
T2
T1
T6
T7
VAC.
F
N2
G
VAC.
K I
K2
M
HOT
J
CP
H
DOUBLE
Mc LEOD
GAUGES
VAC.
TO TOEPLER
PUMP
COLD
MANOSTAT
T4
T5

DESCRIPTION OF APPARATUS USED IN FLOW EXPERIMENTS IN THE THERMAL DECOMPOSITION OF BENZYL BROMIDES

The apparatus was of a type commonly in use for the study of the kinetics of gas-phase reactions at low pressures by the flow technique.

The particular variant of the flow technique used in the experiments on the decomposition of benzyl bromides described here, involved the continuous circulation of nitrogen, as a carrier gas, round a closed path, known as the circulation line, by means of a circulating pump (C.P. in Fig.1) of the mercury diffusion type. The gas was freed from mercury by passing through trap T5, which was cooled in liquid air and also through the demister, one end of which was maintained at a temperature of 150°C. and the other end was immersed in liquid air. Back diffusion of mercury vapour against the gas stream was prevented by trap T4, cooled in liquid air.

The other important features of the apparatus are summarised under the following headings and are described in detail later:-

(1) the injection system which had to be capable of introducing accurately measurable amounts of reactants into the circulation line at a constant rate,

(2) the reaction vessel, of known dimensions, the temperature of which could be maintained constant to within ±0.5°C. and which remained constant along the length of the reaction vessel, and

(3) a unit for the collection of products and unchanged reactants.

A constant rate of flow of gases through the reaction vessel had to be maintained throughout an experiment, in order that the time of reaction was accurately known. Differing rates of flow were obtained by causing the carrier gas to flow through either capillary K1 or K2.

All experiments were carried out under oxygen-free conditions in a vacuum-tight apparatus. Before the introduction of the nitrogen carrier gas, the apparatus was evacuated by means of a single stage mercury diffusion pump, backed by an Edwards Speedivac rotary oil pump. The pressure obtained by this means was 10^{-5}mms. Hg. as measured by a McLeod gauge.

In order to prevent the condensation of reactants or products, the valve injection system and the glass lines between the injection system and the collection unit were wound with Nichrome wire and heated to a sufficiently high temperature.

Description of Apparatus in Detail

The Injection System for Benzyl Bromides and Toluene

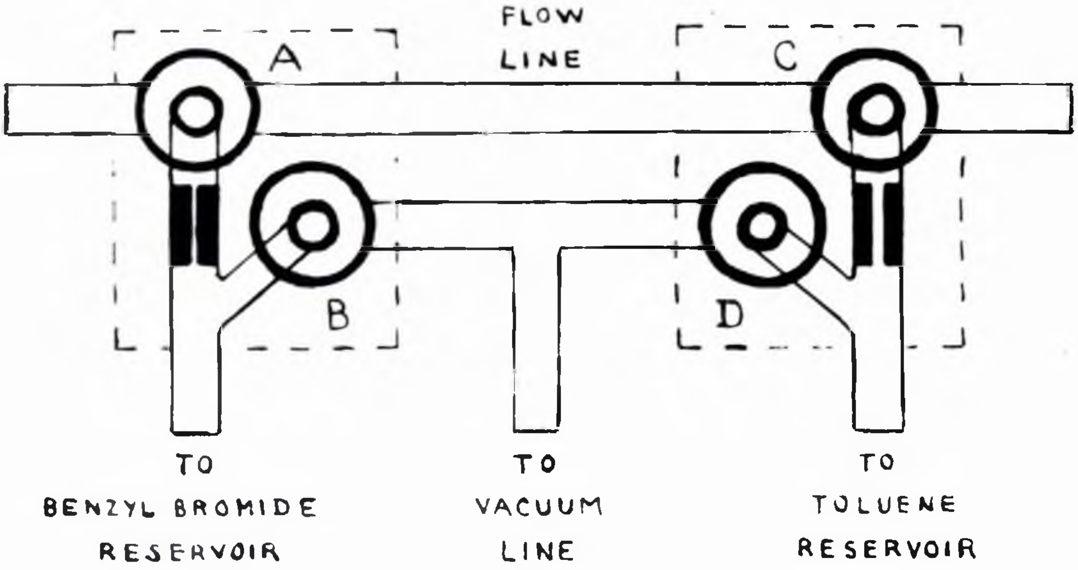
The two main governing factors in the design of an injection system for the benzyl bromides were (1) the relatively involatile nature of the compounds, and (2) the catalytic effect of metals e.g. steel and silver solder on the decomposition of the compounds.

Thus, the valve injection system on the original apparatus, which was constructed of mild steel and embodied brass bellows, was proved to be useless for the present purpose. Trials were carried out in which mild steel, silver solder and brass were put in separate tubes with a few drops of benzyl bromide, such that the bromide vapour but not the liquid would be in direct contact with the metals. The liquid was degassed, the tubes evacuated and sealed off. They were then placed in an oven at 100°C., when metallic materials were in contact with gaseous bromide, at pressures similar to those which would be used in the injection system of the apparatus. It was found that in all cases, and especially in the case of brass, decomposition of benzyl bromide had taken place and large quantities of bromine were produced. Metal valves were then considered to be impracticable.

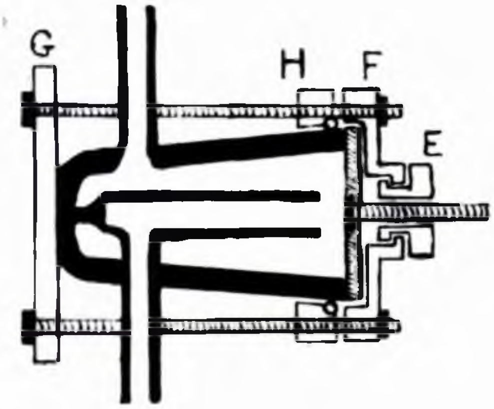
The use of glass valves with non-metallic diaphragms was considered and a glass valve manufactured by Springham with a silicone rubber diaphragm was purchased. Unfortunately, it was shown by experiments similar to those described above that the rubber was badly decomposed in contact with benzyl bromide. Polytetrafluorethylene diaphragms were discarded because they were too inflexible, were not vacuum tight and required excessive pressure on the glass body.

The type of valve and the injection system finally adopted are shown in Fig.2. The valves were of two types; one had three outlets and the other was of a two-way variety. The three-way valve had two connections made through the flow line; the other was to the reactant reservoir, and this could be closed by screwing the rubber diaphragm across the outlet. The two-way valve, which is shown in profile in Fig.2, had one connection to the vacuum line and the other, which could be closed, to the reactant reservoir.

The rubber was GACO, manufactured by G. Angus & Co. Ltd. It was



INJECTION SYSTEM



TWO-WAY VALVE

Figure 2

unaffected by the benzyl bromides and operated successfully up to temperatures of 150°C. The diaphragms were made by sticking together two pieces of rubber about 1/16in. thick, with GACO cement, the rubber having the same diameter as the outer glass wall. The diaphragm was held in place on the outer glass wall of the valve by means of a close-fitting brass cap, F, which was screwed to the base of the structure holding the valve, firmly enough to be vacuum tight. The valve rested on the steel base, G, on a cork cushion. H was a brass ring support fitted with a close-fitting asbestos gasket. The valve was operated by raising or lowering a 4 B.A. screw, the head of which was sunk in the diaphragm. To shut the valve, the knurled nut, E, was twisted in an anti-clockwise direction, when the central portion of the diaphragm was depressed and sealed the central outlet tube. E fitted over the brass cap but was free to rotate in the cap. To open the valve E was rotated in the opposite direction.

The valve body was of an all glass construction, the depth of the concentric central outlet tube to the reservoir being 4mms. below the rim of the outer wall.

The injection system consisted of two identical units, comprising three-way valves A and C and two-way valves B and D (Fig.2). The purpose of B and D was to permit evacuation of the reactant reservoirs without the necessity of having to evacuate through the capillaries.

The capillaries were made by drawing down 9mm. O.D. Pyrex tubing, and were so chosen that the rate of flow of toluene would exceed that of benzyl bromide. The capillaries were selected after a simple and arbitrary intercomparison procedure. The drawn capillaries were allowed to admit air into a fixed volume, (the evacuated vacuum line of the apparatus), and the rate of increase of pressure formed a quick method of assessing their relative resistances to flow. Accurate calibration could be done after building the capillary into the apparatus.

Each valve unit was enclosed in a metal box fitted with heaters and lagged with asbestos cord, and heated above the temperature of the bath surrounding the reservoir.

These valves operated successfully, were vacuum tight and the rubber diaphragms could be readily replaced.

The benzyl bromide reservoir was glass-blown to the valve inlet, and a fresh sample was used for each run. The toluene reservoir was connected to the valve by means of a B. 14 joint which was sealed with Edwards W.6 wax. The glass leads in both cases between the valves and the reservoirs surrounded by hot baths, were wound with Nichrome and heated above the temperature of the surrounding baths.

The Hydrogen Iodide Injection Unit

A number of experiments was carried out in which hydrogen iodide was used as a radical catcher instead of toluene, and another form of injection had to be used for the highly volatile hydrogen iodide.

The hydrogen iodide was stored in two three-litre bulbs, which were painted black to prevent photochemical decomposition taking place. Before an experiment was performed, some hydrogen iodide was condensed in trap T8, which was then surrounded with a bath containing acetone-solid carbon dioxide mixture at -70°C., this giving a suitable backing pressure of hydrogen iodide. The injection valve, NV in Fig.1, was of a type manufactured by Edwards Ltd. with a movable, tapered needle which could be set at any desired position in a valve seat, thus regulating the rate of flow of hydrogen iodide into the circulation line. The low rate of flow required was achieved by inserting a capillary, K3, between the needle valve and the circulation line, the backing pressure being measured with a mercury manometer covered with a layer of silicone oil to prevent attack of the mercury by hydrogen iodide. This injection system could be shut off from the circulation line by a tap, while the lines to the capillary were heated to prevent condensation of benzyl bromide.

Injection of Carrier Gas

The nitrogen carrier gas was stored in a five-litre bulb attached to a manostat by a greased ground joint. One filling of the manostat allowed a constant pressure of 1.4mms. of gas into the circulation line. The manostat was joined to the circulation line through tap G (Fig.1).

Constant Temperature Baths used for Reactant Reservoirs

The constant backing vapour pressures of the benzyl bromide and toluene valves were determined by the temperatures of the hot baths surrounding the reservoirs.

The toluene reservoir was surrounded by a water bath heated by a coil of Nichrome wire, and the temperature of the bath was regulated to ±0.2°C. by a bimetal cartridge thermo-regulator made by Electromethods Ltd. Type 318.

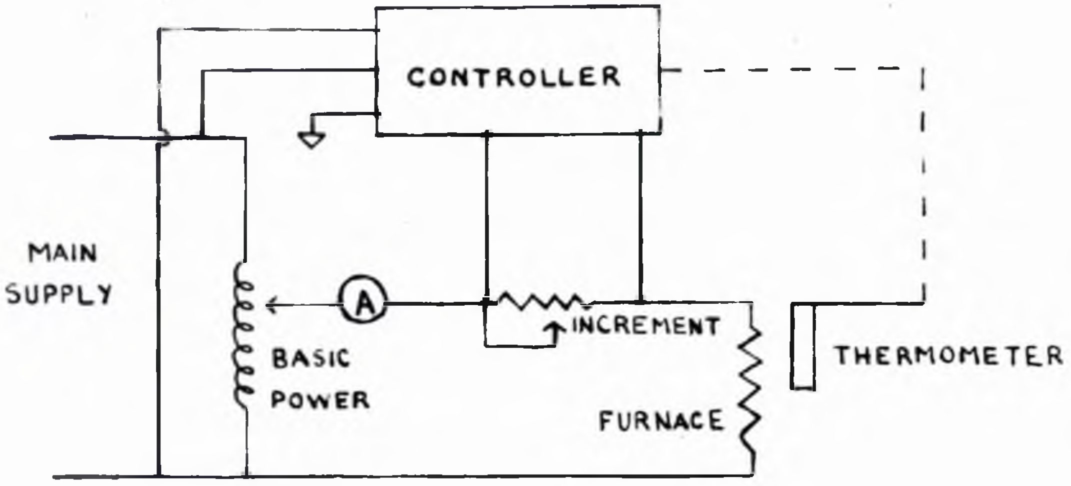
The bromide reservoir bath was oil filled and regulated by a Sunvic Controller Type T.S. 1. Both baths were stirred vigorously during use.

Reaction Vessel and Furnace

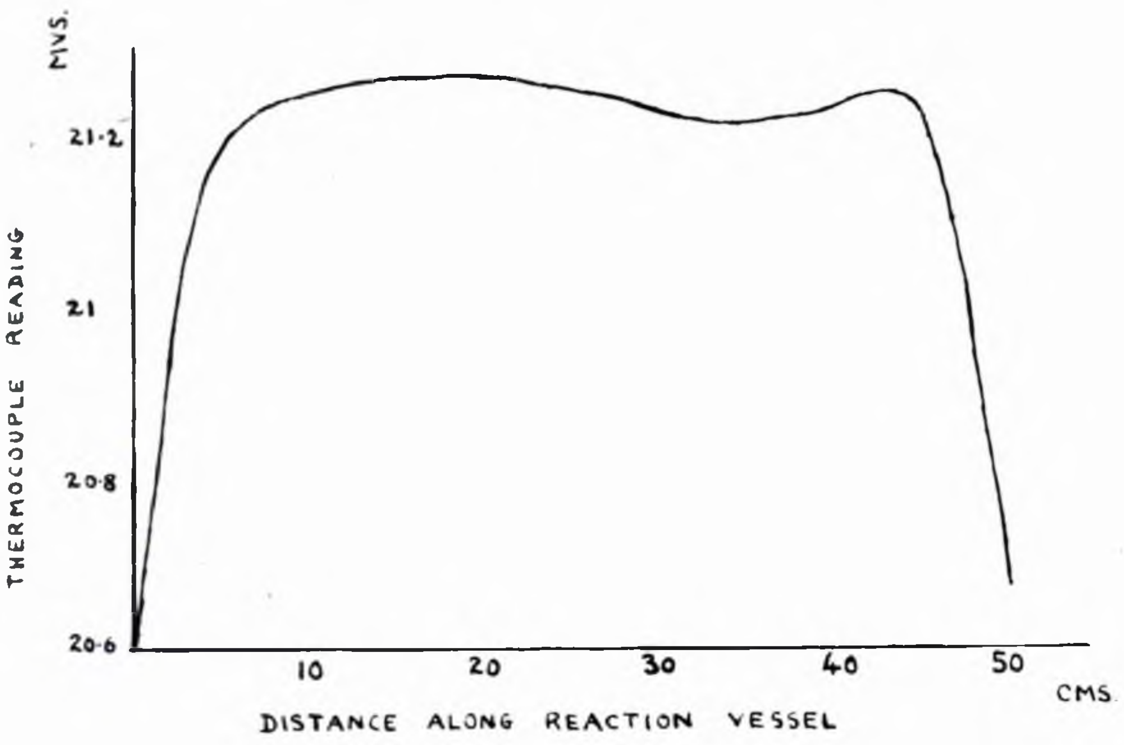
The reaction vessel was a silica cylinder of length 57cms. and diameter 3.2cms., with a concentric thermocouple well of diameter 0.9cms. Connections were made to the Pyrex flow line by means of graded silica to Pyrex seals. The volume of the hot zone of the reaction vessel was calculated to be 312ccs.

The furnace consisted of an inconel cylinder of length 68cms. and outer diameter 2.7cms. This was coated with alundum cement as insulator, and wound with Nichrome tape in five sections with tappings taken off at each section. The windings were coated with another layer of alundun cement and the whole encased in an asbestos jacket to minimize the heat loss to the atmosphere.

It was essential that the temperature throughout the reaction vessel should be constant, and it is obvious that the heat loss from the ends of the furnace would be much greater than the loss from the central portion, if the same electric current were flowing through the Nichrome windings. To offset the drop at the ends of the furnace, the ends were well packed with asbestos fibre, while the temperature profile along the length of the furnace was made 'smooth' by tapping



FURNACE CONTROLLER
BASIC CIRCUIT



FURNACE TEMPERATURE PROFILE

Figure 3

the Nichrome windings at intervals along the length and including variable resistors in parallel with the heating element. This is shown in Fig.3. Suitable adjustments of resistors brought about a 'smooth' temperature profile. It was also essential to have a steep temperature gradient at each end. In the furnace used in this series of experiments the effective length of the reaction vessel was 42cms., while the temperature over this length was constant to ±1.5°C., and the gradient was 5°C. per cm. over the first three cms.

Temperature Control and Measurement

Temperatures were measured by means of a chromel-alumel thermocouple which had been calibrated against the cooling curve standardisations using aluminium, silver and zinc. The thermocouple was set at a particular distance along the thermocouple well, corresponding to the mid-point of the temperature range along the reaction vessel. The thermocouple voltage was fed to a Pye 35mV. Junior potentiometer and the galvanometer used was a Pye Scalamp, giving voltages accurate to 0.01mV. The millivolt to °C. temperature conversions were those of Roeser, Dahl and Gowens.[42]

The furnace was controlled by means of a Sunvic Controller Type RT 2, which provided accurate proportional control and which employed a platinum resistance thermometer, whose resistance changed with temperature, as the active element. This instrument was designed to control furnaces in which a proportion of the load was controlled and for this reason a variable resistor was included in the circuit to act as the 'increment' (see Fig.3). Another variable resistor was used to control the basic power input to the furnace, the power being supplied at mains voltage.

The Collection System

The collection system was arranged in triplicate, thus making it possible for three experiments to be carried out before air was allowed into the apparatus. Each of these collecting units consisted of two traps connected in series (traps T1 and T2 in Fig.1). T1 was specially designed for the collection of relatively involatile materials, with its central stem heated to prevent condensation of products outside the trap. T1 was normally cooled in solid carbon dioxide-acetone mixture, while T2 was cooled in liquid air and was used for the collection of volatile materials. T3 was a small trap connected to T2, and contained degassed water into which hydrogen bromide was distilled.

Collection of products was made into each of the three units in turn with an electro-magnetic solenoid type valve being open over the first unit but shut over the other two. The electro-magnetic solenoid valve consisted of a piece of soft iron in a glass envelope with an acutely tapered cone, which fitted into a mating socket. The valve could be opened by activating a solenoid which pulled the soft iron rod in its envelope out of the socket into the magnetic field. The solenoid was made from insulated copper wire of 18Ω resistance, wound on a former of depth 5cms. and with an outer diameter of 7.5cms. The coil was fed from a 24 volt. D.C. rectifier through a 110Ω dropping resistor. Decreasing the current through the solenoid by increasing the variable resistance produced a slow and gradual return of the cone into its socket, thus preventing any damage which might be caused by a sudden entry. By connecting each of the three solenoids in parallel and associating a switch with each, it was possible to use only one source of power and one dropping resistor. By use of this method, change over from one trap unit to another occupied about three seconds only.

In addition to the collection system just described, a flow line which by-passed the reaction vessel and collection system was incorporated in the apparatus. This by-pass included traps T6 and T7, normally cooled in liquid air, and re-entered the main flow line through tap D. Flow could be directed through the by-pass by lifting the electro-magnetic type valve out of its socket into a similar seat which closed the path through the reaction vessel. Decreasing the current through this solenoid, SV2, returned the valve to its seating over trap T6. This by-pass was used to collect undecomposed reactant thus facilitating a direct method of analysis for amount of reactant flowing per second.

Circulating Pump and Rate of Flow Measurements for Carrier Gas

(1) Circulating Pump

The circulating pump was a three nozzle mercury diffusion pump. The mercury was heated by means of a Woods metal bath fed from a

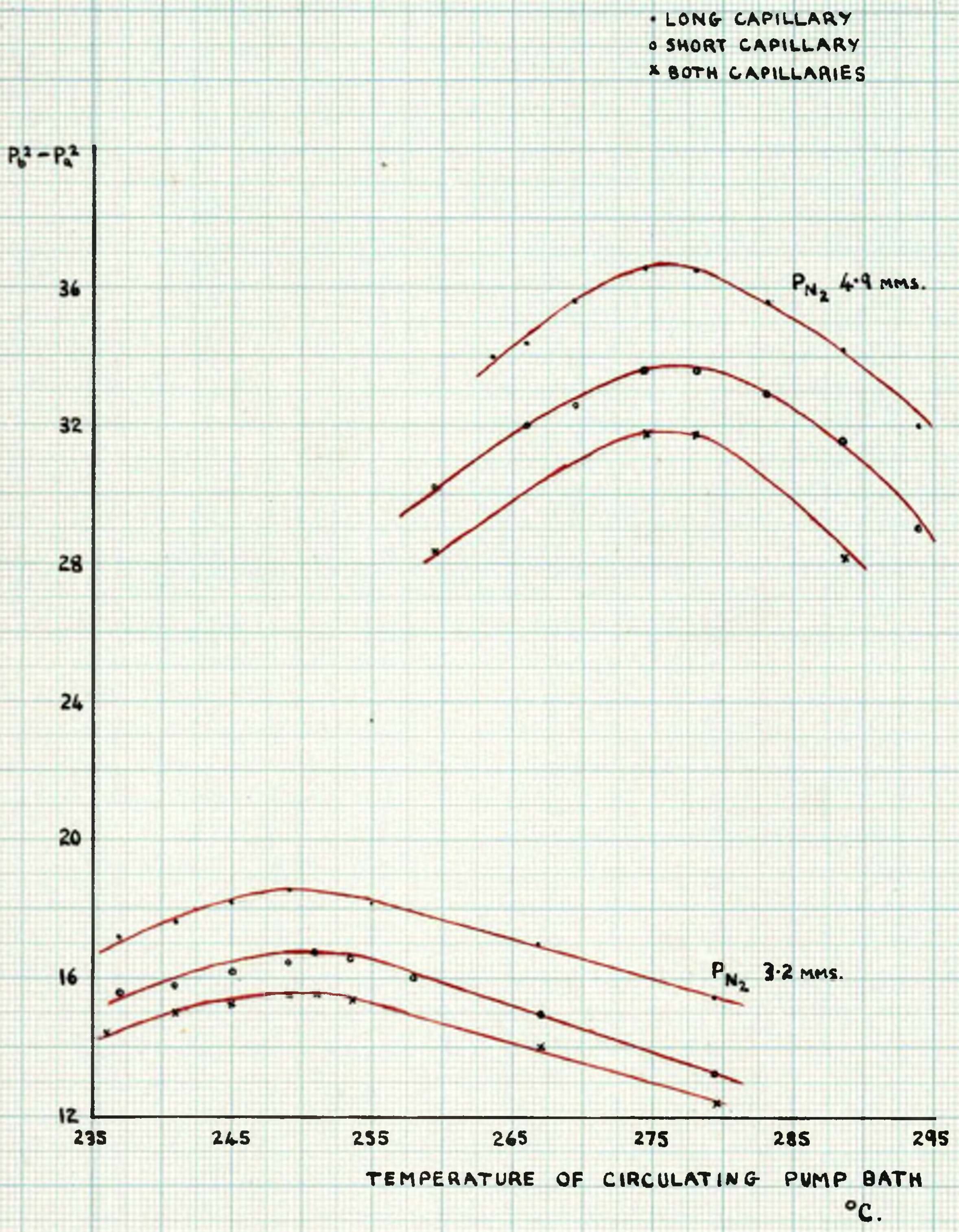

• LONG CAPILLARY
o SHORT CAPILLARY
x BOTH CAPILLARIES
$P_b^2 - P_a^2$
36
32
28
24
20
16
12
P_{N_2} 4·9 mms.
P_{N_2} 3·2 mms.
235
245
255
265
275
285
295
TEMPERATURE OF CIRCULATING PUMP BATH
°C.

Figure 4

Sunvic energy controller, with an auxiliary heater, fed from a fixed power supply, heating the sides of the bath. The column of the circulating pump was heated to a temperature of approximately 300°C.

It had been shown by Moore[43] that there was an optimum pumping speed for a particular static pressure of carrier gas in the circulation line. For the particular apparatus used, graphs were produced of temperature of circulating pump bath against the difference of squares of the pressures of carrier gas across one of the flow capillaries, as measured by the double McLeod gauges. This latter measurement was proportional to the rate of flow of gas. A series of graphs was constructed for each static pressure of carrier gas used. These are shown in Fig.4. It is seen from any of the graphs that the rate of flow increases with temperature to a certain point, there is a spread of temperature when maximum pumping speed is maintained and then the pumping speed decreases with a further rise in temperature. As Moore had observed, this pumping speed depended on the static pressure of carrier gas in the line. Both capillaries were used for determinations with a particular static pressure and, as the graphs show, this optimum circulating pump bath temperature does not depend on the capillary constants.

Experiments were always carried out with optimum pumping conditions being attained for the particular static pressure of carrier gas. The rate of flow was then constant when the variation of the circulating pump bath temperature was ±1°C.

A graph of the temperature of the circulating pump bath against

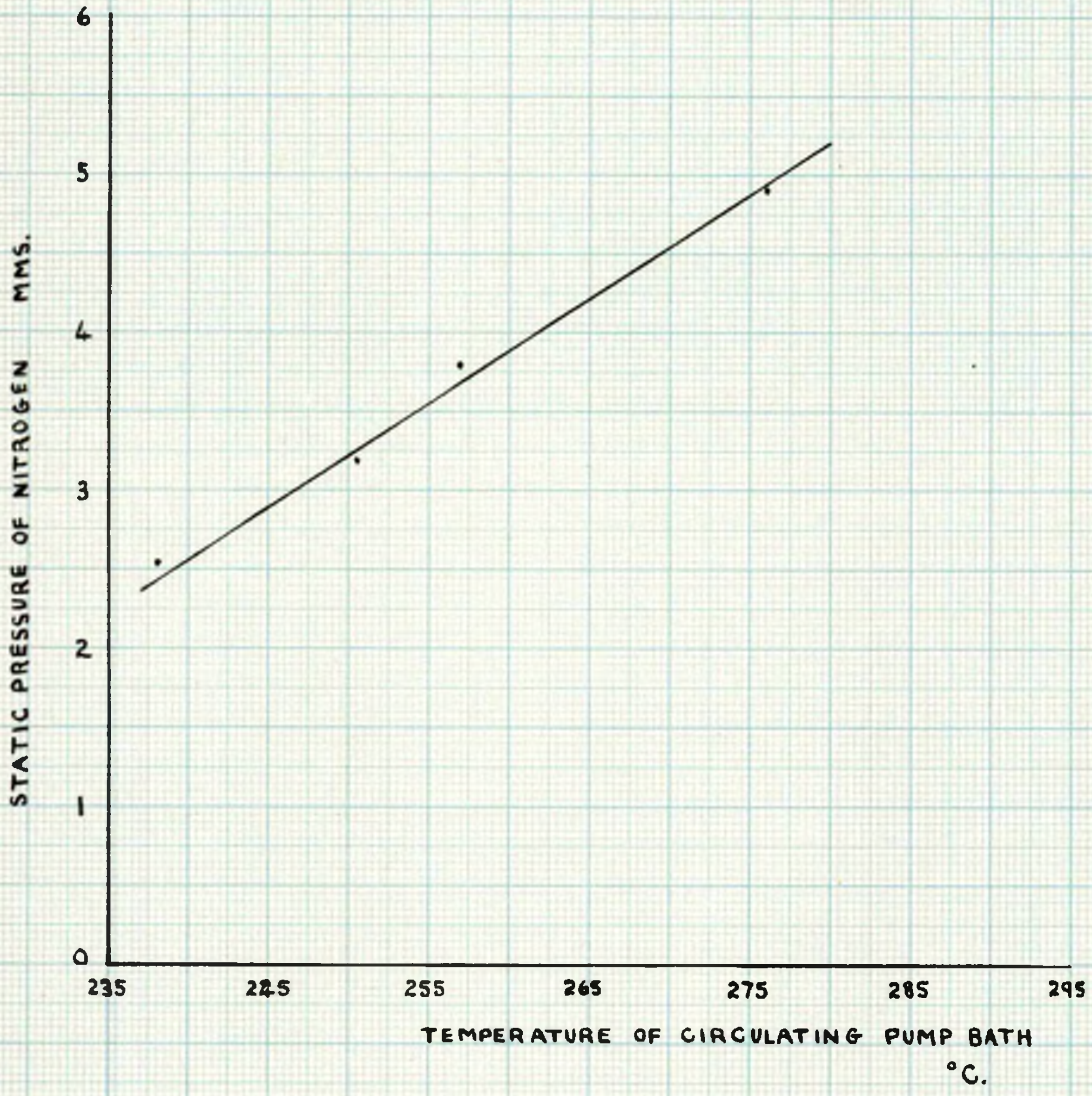

STATIC PRESSURE OF NITROGEN MMS.
6
5
4
3
2
1
0
235
245
255
265
275
285
295
TEMPERATURE OF CIRCULATING PUMP BATH °C.

Figure 5

the static pressure of carrier gas at optimum pumping speed is also shown (Fig.5).

(2) Measurement of Carrier Gas Flow

The rate of flow of gas was measured by the pressure drop across the calibrated capillaries K1 and K2, the pressure being read on double McLeod gauges.

Theoretically, if the dimensions of the capillary are known one can calculate the rate of flow by applying Meyer's modification of Poiseuille's Law:

Number of moles of gas flowing per sec. $n = \frac{\pi r^4}{16 l R T \eta}(P_b^2 - P_a^2)$

r = radius of capillary in cms.

P_b = pressure of gas entering capillary in dynes per cm^2.

P_a = pressure of gas emerging from capillary in dynes per cm^2.

l = length of the capillary in cms.

η = coefficient of viscosity for the gas

R = gas constant $\qquad$ T = absolute temperature

It may be written that $n = k(P_b^2 - P_a^2)$ where $k = \frac{\pi r^4}{16 l R T \eta}$

k is the capillary constant.

It has been shown, in actual fact, that deviation from ideal behaviour does occur and calibrations musy be carried out for each capillary.

The capillaries were constructed from a piece of uniform capillary tubing, the radius of which was determined by weighing an accurately measured length of mercury in the capillary. The radius

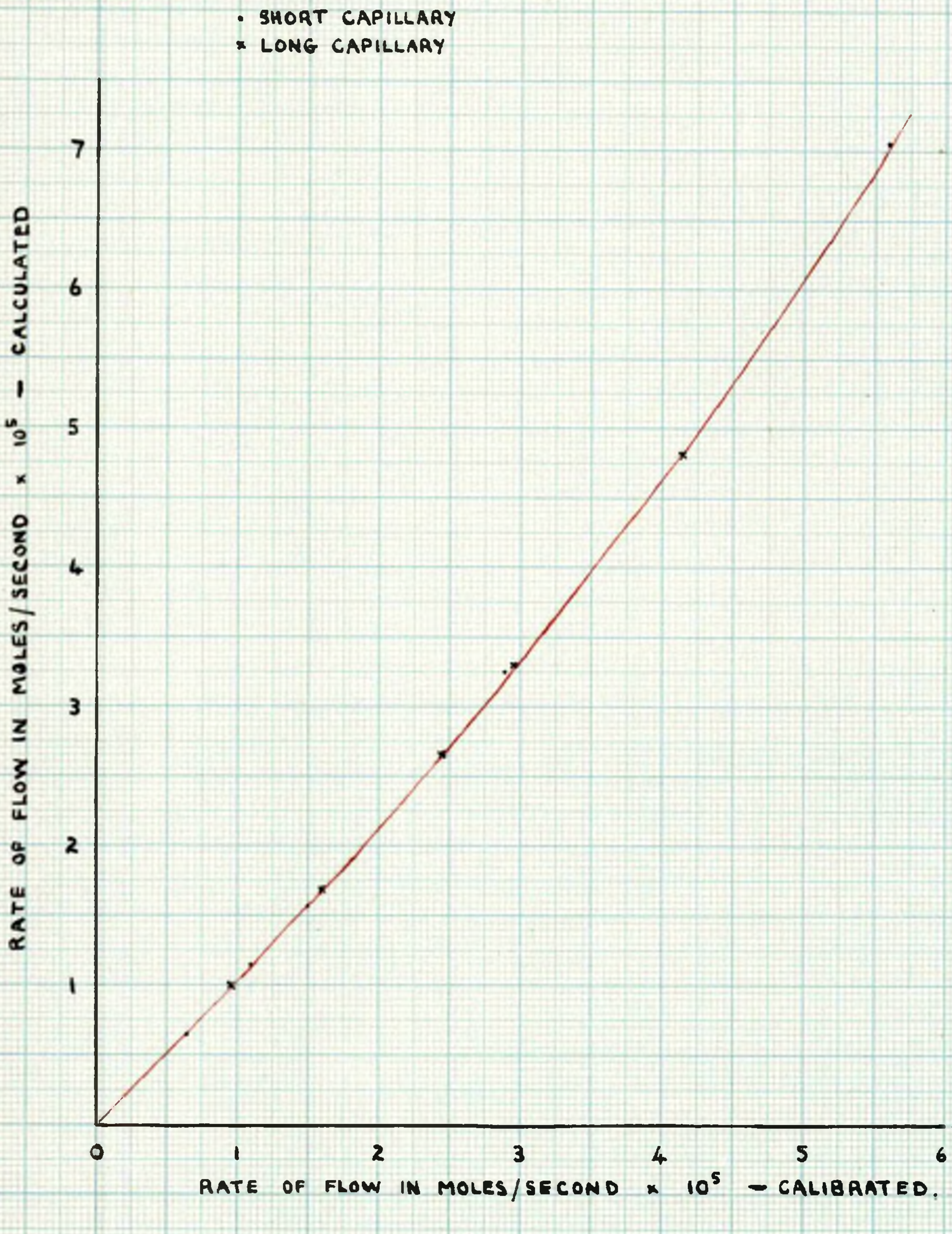

• SHORT CAPILLARY
× LONG CAPILLARY
RATE OF FLOW IN MOLES/SECOND × 10^5 — CALCULATED
RATE OF FLOW IN MOLES/SECOND × 10^5 — CALIBRATED.
0
1
2
3
4
5
6
7

Figure 6

was 0.08979cms. and the lengths of K1 and K2 were 5.0 and 12.55cms. respectively. The theoretical capillary constant k was calculated for nitrogen from the above formula to be :

$$k \text{ for K1} \quad 10.58 \times 10^{-7}$$

$$k \text{ for K2} \quad 4.22 \times 10^{-7}$$

Calibrations for each capillary were carried out by noting the rate of flow of a known volume of air through the capillary, when the time taken for the volume to pass through was measured. The pressure difference on the double McLeod gauges was measured at the same time and the calculated rate of flow computed.

Fig.6 shows a graph of calculated rate of flow against calibrated rate of flow. Deviations due to the use of air instead of nitrogen in the calibration were not considered large, and observed calibrations for air were merely corrected for viscosity differences of the gases. Values for viscosities were taken from Partington's Treatise on Physical Chemistry Vol.1.

The calibrated rate of flow of gases from the calibration graph was used in all calculations for the time of contact.

The rate of flow round the circulation line could be varied by operating a tap, H in Fig.1, at the exit of the circulating pump such that the gas flow was strangled to any required degree and a wide variation in the rate of flow of the carrier gas effected.

Measurements Required for the Calculation of Time of Contact

The contact or reaction time in the flow apparatus just described,

$$t, \text{ is given as } \frac{\text{volume of the reaction vessel in ccs.}}{\text{rate of flow of gas in ccs. per sec.}}$$

$$= \frac{\text{volume of reaction vessel in ccs.}}{\text{rate of flow in moles per sec. at the temperature and pressure in the reaction vessel}}$$

$$= \frac{\text{volume} \times 273 \times P_r}{\text{total rate of flow in moles per sec.} \times 22400 \times 760 \times T}$$

where P_r is pressure in the reaction vessel in mms.

T is absolute temperature.

It is therefore necessary to derive values for P_r and the total rate of flow at a given temperature T^oK.

Calculation of Pressure in the Reaction Vessel

In these experiments no attempt was made to measure the average pressure in the reaction vessel directly because of trouble with mercury contamination of products or contamination of the McLeod gauges. Instead calibrations were performed with gases at room temperature and an equation produced which related the pressures at various points in the circulation path and enabled calculation of the pressure in the reaction vessel to be made.

The pressure in the circulation line was obviously greatest at the exit of the pump and there were drops in the pressure of carrier gas at points of greatest resistance to flow. In the apparatus described above, these were at the entrance to the reaction vessel, where there was a jet to prevent back diffusion of gas from the reaction vessel, and at the capillaries K1 and K2. There were much smaller drops in pressure at the injection unit and at the collection system.

Leads were taken from each end of the capillary K1 or K2, from the exit of the circulating pump and from the reaction vessel to the double McLeod gauges. Nitrogen carrier gas was circulated in the line, the circulating pump operating under the optimum conditions described previously. A series of readings was taken for P_r (pressure of reaction vessel), P_c (pressure at circulating pump), P_b (pressure before capillary) and P_a (pressure behind capillary) for each capillary and for various pressures of carrier gas.

It was possible to obtain an equation for the pressure in the reaction vessel

$$P_r = P_b + (P_c - P_b)\,k'$$

where k' is a constant.

k' did not vary by more than 10% for each capillary or for the two capillaries connected in parallel. Toluene, at pressures of the same order as those to be used in experiment, was injected, and a slightly different value of k' was obtained. For a static pressure of nitrogen of 4.2mms., the value of k' was 0.2 and this was adopted for future calculations for pressure in the reaction vessel, using equation $P_r = P_b + (P_c - P_b)\,k'$, where P_b and P_c are measurable quantities.

The pressure in the reaction vessel is the sum of the partial

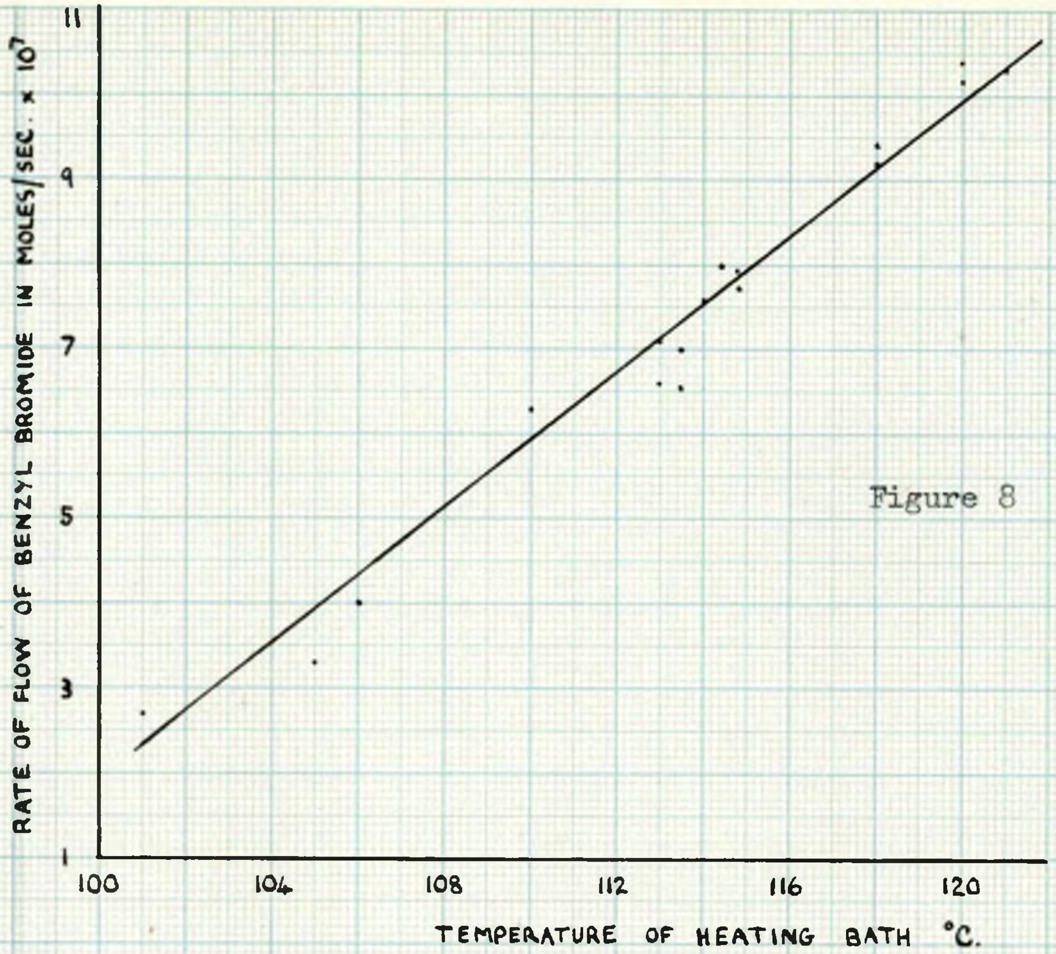


Figure 8

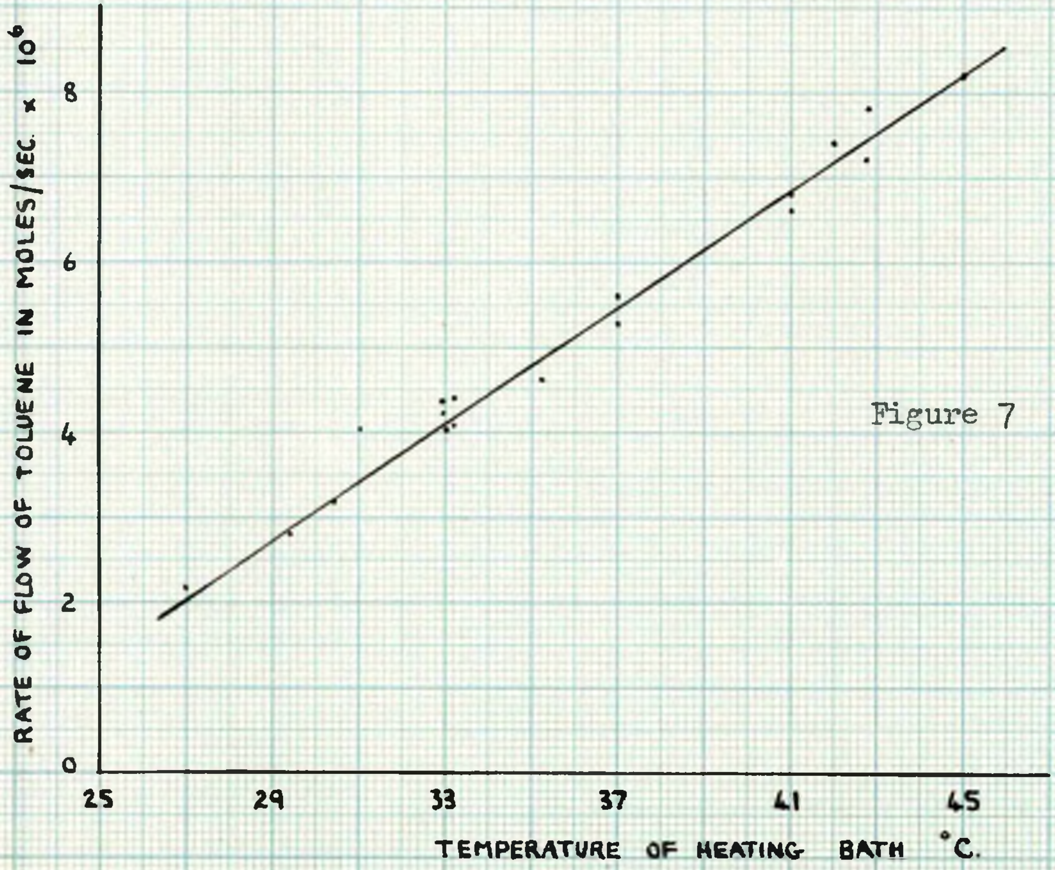


Figure 7

pressures of all the gases in the reaction vessel.

Calculation of Rate of Flow of Gases through Reaction Vessel

The total rate of flow of gas through the reaction vessel was equal to the rate of flow of nitrogen carrier gas, plus the rate of flow of toluene, plus the rate of flow of benzyl bromide, all quantities being measured in moles per second, when benzyl bromide was being decomposed in presence of toluene.

Measurement of the rate of flow of nitrogen has been described in a previous section.

The rate of flow of benzyl bromide and toluene was measured by analysis of the amount of material collected in a given time. This was normally done by collecting toluene and benzyl bromide in trap T6 in the by-pass line before commencing a decomposition experiment. The contents of T6 were distilled into T7 and weighed. The amount of benzyl bromide was determined by titration and, by subtraction, the amount of toluene collected was ascertained.

Calibration graphs were produced for the rate of flow of toluene and of benzyl bromide against temperatures of the baths surrounding the reservoirs.(Fig.7 and Fig.8). It was thus possible to produce a required rate of flow for either reactant or catcher easily.

The partial pressure of any substance in the reaction vessel can be written as

$$\frac{\text{moles of substance flowing per sec.}}{\text{total no. of moles flowing per sec.}} \times P_r.$$

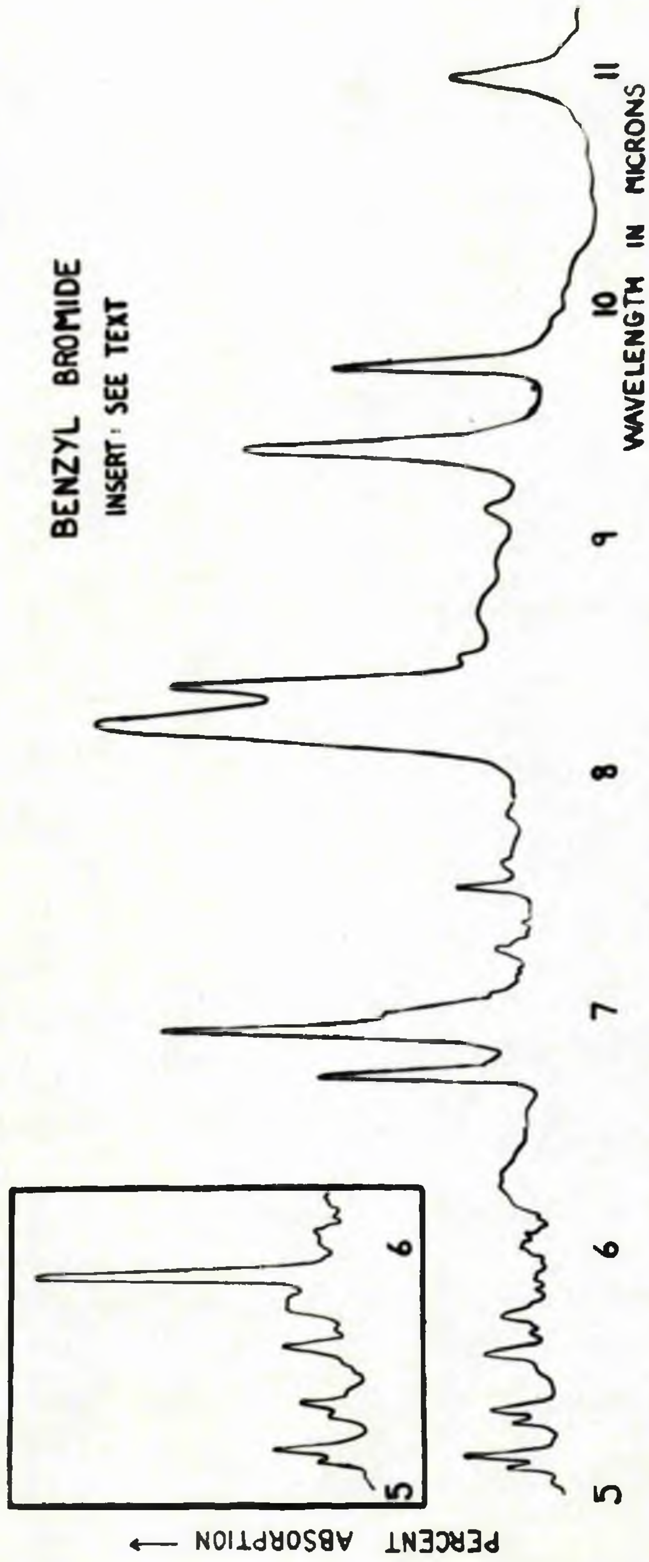

BENZYL BROMIDE
INSERT: SEE TEXT
PERCENT ABSORPTION ←
5
6
5
6
7
8
9
10
11
WAVELENGTH IN MICRONS

Figure 9

PREPARATION AND PURIFICATION OF MATERIALS

Benzyl Bromide

The benzyl bromide was a commercial sample supplied by British Drug Houses Ltd. It was dried over potassium carbonate and distilled at atmospheric pressure, b. pt. 196-197°C.

An infra-red analysis indicated the presence of a strongly absorbing peak at 5.85μ which was certainly due to some impurity. The peak was thought to be that of a C=O stretching vibration and the presence of benzaldehyde, which exhibits a vapour pressure versus temperature graph very similar to that of benzyl bromide, was thought likely. If this were the case it would be impossible to purify the bromide by fractional distillation. Consequently, the bromide was shaken with a saturated solution of sodium bisulphite, washed with water and dried over potassium carbonate.

The benzyl bromide was then distilled under reduced pressure and the middle fraction, boiling at 89.5°C. at 35mms. pressure, collected and stored with a drop of mercury in a dark glass bottle.

The infra-red spectrum of this sample indicated that the carbonyl grouping was absent (Fig.9). The insert shows the spectrum between 5μ and 6μ before purification.

o- and m-chlorobenzyl bromides

These were commercial samples from L. Light & Co. Ltd. These showed no carbonyl grouping. They were purified by distillation under reduced pressure, the middle fraction being collected and further distilled under reduced pressure using a 10in. Vigreux type distillation column. They were stored in dark bottles over a drop of mercury.

p-chlorobenzyl bromide[44]

This material was prepared by the bromination of p-chlorotoluene under the action of ultra-violet light.

42gms. of p-chlorotoluene in a three-necked flask, fitted with a mercury filled stirrer, dropping funnel and reflux condenser together with gas trap, were heated in an oil bath at 120°C. and exposed to the light of a 100 watt ultra-violet lamp. 26.7gms. of bromine were added over a period of two hours with constant stirring. The stirring was continued until the hydrogen bromide evolution had stopped.

On cooling, the mixture solidified to a brownish mass and was filtered and washed with 40-60°C. petroleum ether. On standing, another crop of crystals was obtained from the mother liquors, and the whole was recrystallised twice from 40-60°C. petroleum ether. The melting point of the crystals was 50.5°C. The material still had a cream colouration, and pure white crystals were obtained by distilling in vacuo (10^{-4}mms.).

The yield was low at 24% when 16.2gms. of p-chlorobenzyl bromide were obtained.

p-bromobenzyl bromide[44]

This was prepared from p-bromotoluene by the method described above. The crystals produced after two recrystallisations were needle-shaped and pure white; no further purification was carried out.

20.2gms. of p-bromotoluene gave 13gms. of p-bromobenzyl bromide, m. pt. 61°C. The yield was 45%.

Toluene

Szwarc[17] had shown that in order to obtain reproducible results for the pyrolysis of toluene, it was necessary to pre-pyrolyse the starting material. Although here toluene was being used simply as a catcher, it was thought desirable to adopt this procedure.

After being scrubbed with sulphuric acid, washed with water and dried over calcium chloride, toluene, supplied by Petrochemicals Ltd., was partially pyrolysed at 825°C. The toluene was degassed and pumped through the reaction vessel from a reservoir maintained at 1°C. above room temperature, the time spent in the hot zone being of the order of one second. The more condensable materials were collected in a trap at room temperature, while the toluene was collected in a trap surrounded by an acetone-solid carbon dioxide bath.

The partially pyrolysed toluene was shaken with one-tenth of its volume of concentrated sulphuric acid until no yellow colouration persisted. It was then shaken with water and with N/10 potassium permanganate until all the unsaturated materials had been removed, shaken with sodium bicarbonate and with water and dried over calcium chloride.

The dried material was distilled from sodium on a three foot long fractionating column packed with Fenske rings, the reflux ratio being 100/4. The material boiling in the range 110.5-110.7°C.

was collected.

Hydrogen Iodide

Hydrogen iodide was prepared by the dehydration of 55% aqueous hydriodic acid.

Phosphorus pentoxide was contained in a 500cc. flask, fitted with a dropping funnel containing aqueous hydriodic acid, and having an outlet to the purification and collection system. The acid was dropped slowly on to the phosphorus pentoxide, when dense white clouds of gaseous hydrogen iodide were given off. This was drawn through the purification system, consisting of a phosphorus pentoxide boat, a trap cooled in ice to remove iodine and another phosphorus pentoxide boat, by a water pump. The hydrogen iodide was collected under liquid air. It was purified by trap-to-trap distillation in vacuo from acetone-solid carbon dioxide mixture to liquid air. After three distillations the end product was practically colourless and the less volatile iodine had been pumped off. The hydrogen iodide was stored in two three-litre bulbs, painted black to eliminate photochemical decomposition.

Nitrogen

The nitrogen used was supplied by The British Oxygen Company, and was stripped of any oxygen by passing it through two traps, connected in series, containing molten sodium at 240°C. The nitrogen was stored in a three-litre glass bulb.

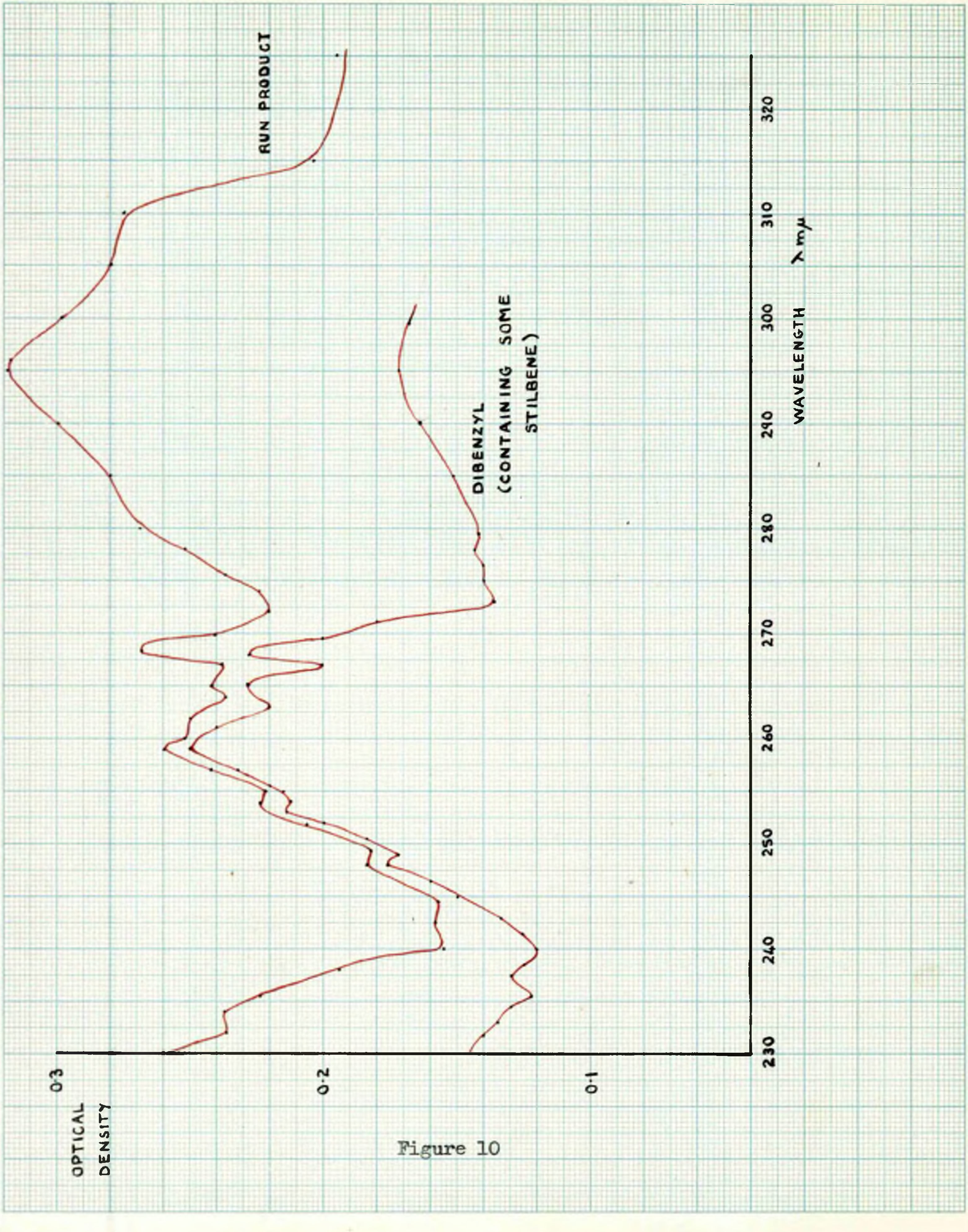

OPTICAL DENSITY
0·3
0·2
0·1
230
240
250
260
270
280
290
300
310
320
WAVELENGTH λ mμ
RUN PRODUCT
DIBENZYL (CONTAINING SOME STILBENE)

Figure 10

To be quite certain that all traces of oxygen had been removed from the nitrogen, in admitting nitrogen from the manostat into the circulation line of the apparatus, the carrier gas was once more passed through a trap containing molten sodium (Fig.1).

The following substances were prepared as standard materials used in the analysis of involatile products of decomposition:

Dibenzyl

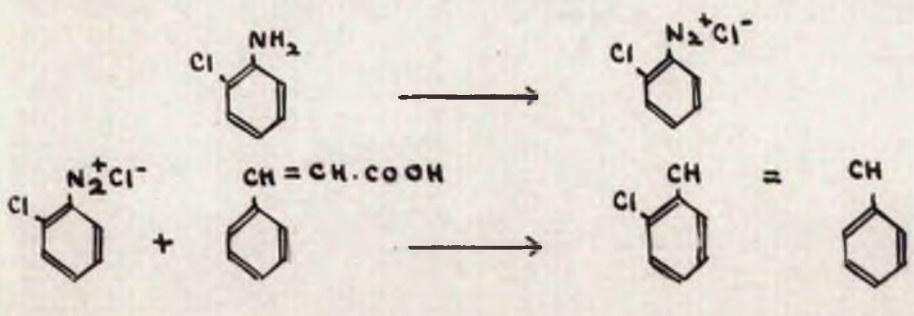
This was a commercial sample which had been purified by recrystallisation and reduced to eliminate stilbene. It was shown to be almost free of stilbene by ultra-violet spectrophotometry (Fig.10). The melting point was 52.5°C.

Stilbene (trans)

The stilbene was a commercial sample purified by recrystallisation and having a melting point of 124°C.

o-chlorostilbene and o-chlorodibenzyl[45]

A solution of o-chloroaniline(26gms.) in water(100ccs.) and hydrochloric acid(80ccs.) was diazotised at 0°C. with a solution of sodium nitrite(15gms.) in water. The diazo compound was reacted with cinnamic acid in a Meerwein reaction, and carbon dioxide and nitrogen were eliminated, the CO_2 being replaced by the aryl group.



The clear diazo solution was added to a cooled solution of cinnamic acid(30gms.) in acetone(250ccs.). After addition and solution of sodium acetate(44gms.), a solution of cupric chloride(8.5gms.) in water was added. The temperature was allowed to rise slowly to 20°C. when gas evolution began. Stirring was continued at 23-24°C. for three hours. At the end of the coupling reaction two layers had formed. The material was steam distilled and the oil collected was dissolved in benzene and washed with 3N. ammonium hydroxide and water. A red oil was obtained on distillation. This was converted into the dibromide by treatment with excess bromine in carbon tetrachloride, and the dibromide was recrystallised from petroleum ether(130°C.). The melting point was 181-182°C.

The dibromide was dissolved in ether(15ccs.) and acetic acid(7ccs.) and zinc were added and refluxed for one hour. The solution was decanted from the zinc, washed with water, 2N. sodium hydroxide and water and dried over sodium sulphate. The ether was distilled off and the o-chlorostilbene crystallised on standing in ice. It was recrystallised from ethyl alcohol and had a melting point of 39°C.

The o-chlorostilbene was reduced to o-chlorodibenzyl with palladium-barium sulphate catalyst in ethanol, the product being an oil which boiled at 142°C. at 4mms. pressure.

ANALYSIS OF PRODUCTS AND REACTANTS

Hydrogen Bromide

Hydrogen bromide was determined as an acid which liberated iodine from standard potassium iodate in the presence of excess potassium iodide according to the equation:

$$KIO_3 + 5KI + 6HBr \longrightarrow 6KBr + 3I_2 + 3H_2O$$

The hydrogen bromide was made up to 100ccs. in distilled water and a few crystals of 'Analar' potassium iodide was added to 20ccs. of this solution. If any bromine was present in the hydrogen bromide this would liberate iodine from the potassium iodide. Thus a check was kept on the production of bromine. At no time was any bromine detected.

An excess volume of standard potassium iodate was added and the liberated iodine was titrated using standard sodium thiosulphate and starch indicator.

The strengths of iodate and thiosulphate used varied from 0.002 to 0.01N. When the weakest solutions were employed it was found desirable to carry out the titrations in the presence of nitrogen to eliminate liberation of iodine by atmospheric oxidation.

The thiosulphate used was standardised against potassium iodate using hydrochloric acid to liberate the iodine.

Benzyl Bromides

The benzyl bromides were determined by reaction with silver nitrate in aqueous-alcoholic solution and titration of the excess silver nitrate with potassium thiocyanate solution using ferric alum as the indicator.

$$C_6H_5CH_2Br + AgNO_3 + H_2O \longrightarrow AgBr + C_6H_5CH_2OH + HNO_3$$

$$AgNO_3 + KCNS \longrightarrow AgCNS + KNO_3$$

It was proved by analysis of weighed samples of benzyl bromide that this method gave quantitative results for the determination of benzyl bromide.

The procedure adopted was to heat the mixture of benzyl bromide and silver nitrate on a water bath at 60°C. for fifteen minutes, when reaction was complete. In the case of the substituted bromides, the reaction was complete after about half an hour. On cooling, the excess silver nitrate was then determined by titration with the thiocyanate.

The benzyl bromide collected in the heater traps was usually made up to 100ccs. in methanol and 20ccs. portions used for analysis, the strengths of the silver nitrate and potassium thiocyanate solutions being 0.02 or 0.04N. Because the unchanged benzyl bromide in each trap could be analysed in addition to the bromide collected in the calibration trap T6 (Fig.1), a good check was kept on the rate of flow of bromide during an entire run.

The Involatile Products

Three methods were applied in the qualitative analysis of the products which remained in the heater trap after the unchanged bromide and toluene were distilled away: (1) ultra-violet spectrophotometry,

(2) infra-red spectrophotometry and (3) mass spectrometry.

(1) Ultra-violet Spectrophotometry

The products were dissolved in methanol, which had been purified by refluxing with activated charcoal for three hours and then distilling. The optical density of methanol purified in this way was insignificant below 230mμ, which was outwith the wavelength range used in the present analyses.

The products were diluted further if necessary until they gave reasonable optical density measurements on a Unicam S. P. 500 spectrophotometer, 1cm. silica cells being used.

(2) Infra-red Spectrophotometry

The products were washed out of the heater traps with carbon tetrachloride, which was dried over calcium chloride. The carbon tetrachloride was distilled off until the remaining solution was concentrated enough to give measurable absorption in the infra-red region.

The absorption of the solutions was measured on a Grubb-Parsons Double Beam Spectrophotometer. 0.8mm. or 2mm. cells were used, in which the liquid was contained between two rock salt plates separated by a lead spacer. Two methods were employed in obtaining a spectrum; one in which carbon tetrachloride was placed in the reference beam and the unknown solution in carbon tetrachloride in the sample beam, and the other in which the absorption due to the solution in carbon tetrachloride was measured, and the absorption due to pure carbon tetrachloride recorded on the same scale immediately afterwards, the reference beam being empty in each case.

It should also be mentioned that the contents of the heater traps in experiments with hydrogen iodide were analysed without removal of the benzyl bromide by distillation.

The infra-red spectrophotometer was also used to analyse mixtures of hydrogen bromide and iodide. The experimental procedure for this will be described in a later section.

(3) Mass Spectrometry

The mass spectrometer was constructed in the St. Andrews laboratories, the design being of the Nier type with a 60° sector magnet. The resolution obtained was 1 in 200 so that it was eminently suitable for analysis in the mass region 180-260. The masses were scanned by magnetic field variation and the ion-accelerating voltages employed were in the range 1140-1500.

In conjunction with the mass spectrometer there was a handling system with a lead into the head. This handling system was used to inject the more involatile products of decomposition which collected in the heater traps, as described previously.

The handling system consisted of three metal valves in series, which allowed the sample holder to be connected up to the mass spectrometer, to the vacuum line or to be shut off from the rest of the apparatus. The inlet line to the mass spectrometer led through a Metrosil 4F porous plug by way of a two-litre bulb and a circulating pump. The two-litre bulb was used as a reaction vessel in other work in this department and was contained in a furnace. The pump was of a positive displacement type of metal construction with polytetrafluorethylene piston rings. It was capable of working at high temperatures and circulating very low pressures of material. (A fuller description of the mass spectrometer will be found in the thesis of Davidson[22] and of the circulating pump in that of Smith[3])

The lines leading into the mass spectrometer, the mass spectrometer head, the valves and the reaction vessel were kept at a temperature of about 100°C., to prevent condensation of the material under analysis but not so high as to induce decomposition of the material.

For some of the more involatile substances, a period of time of up to three hours elapsed before any peaks appeared. This may have been due to adsorption of the injected materials on to the ionisation chamber of the mass spectrometer and surrounding metal work. The slow decay of the peaks on pumping out was probably the reverse effect of slow desorption from these parts. There may also have been a cold spot in the line between the valves and the head of the mass spectrometer.

The procedure for analysis on the mass spectrometer was as follows: the heaters of the handling system and circulating pump were switched on, and the material under analysis, contained in a 50ccs. flask, was attached to the lead from the injection valve with Edwards W.6 wax. The whole apparatus was evacuated, the sample flask being cooled in liquid air. Background scans in the relevant mass region were recorded. The liquid air bath was removed from the sample flask and replaced with an air heater at a temperature which would volatilise all the material. The sample flask was opened to the mass spectrometer and scans were recorded over the appropriate regions.

The following compounds had to be analysed when hydrogen iodide was used as a radical catcher:

Hydrogen Iodide

This was collected with hydrogen bromide in the trap surrounded by liquid air. The method used was a modification of that of Leipert[46], which is described in Belcher and Godbert[47]. The basis of the method was the oxidation of iodide to iodate with bromine, and estimation of the iodate by liberation of iodine in presence of excess acid and potassium iodate. This method had the advantage that 1/6(gm.equiv. of original iodide) = 1 gm. mole. of sodium thiosulphate used in the titration of iodine liberated.

$$I_2 + 5Br_2 + 6H_2O \longrightarrow 2HIO_3 + 10HBr$$

$$HIO_3 + 5HCl + 5KI \longrightarrow 5KCl + 3I_2 + 3H_2O$$

Experimentally 5ccs. of the iodide solution were added to 10ccs. of sodium acetate in acetic acid (10%). Five drops of 'Analar' bromine and 25ccs. of 20% sodium acetate were added to complete the oxidation mixture in its buffered medium. The flask was stoppered and left to stand in the dark for thirty minutes until the reaction was complete. Excess bromine was destroyed by adding 'Analar' formic acid. A red colouration obtained with methyl red indicated that all the bromine had been destroyed. Solid potassium iodide and acid were added in the manner described for the analysis of hydrogen bromide and the iodine liberated titrated in the usual way.

This method of analysis was unaffected by the presence of hydrogen bromide.

Iodine

The iodine produced in the decomposition was analysed by direct titration with sodium thiosulphate using starch indicator. The thiosulphate was standardised against potassium iodate before each analysis, and solutions of strengths 0.004-0.05N. were used.

Total Iodide

The total iodide collected in the heater traps was analysed by the method used for the determination of hydrogen iodide.

GENERAL DESCRIPTION OF FLOW EXPERIMENTS

Prior to carrying out an experiment all liquids had to be degassed. The toluene, benzyl bromide and distilled water, contained in the pear-shaped vessels T3 and used for dissolving the hydrogen bromide produced, were degassed three times by successively freezing in liquid air, warming up and pumping out the air evolved.

The power to the furnace was time-controlled by a Venner switch, which was set to switch on the current to the furnace about five hours before a run was due to commence, so that the furnace temperature was approximately the correct setting on arrival in the morning and a run could proceed without delay.

The apparatus was pumped as hard as possible (to 10^{-5} mms.) for two to three hours while the constant temperature baths surrounding the reservoirs, the circulating pump heaters, the line heaters, the valve box heaters, the sodium trap heater, the mercury demister heater and the copper oxide furnace (used on two occasions), were attaining their operating temperatures.

The heater traps, T1 in Fig.1, were immersed in acetone-solid carbon dioxide mixture while traps T2, T4, T5, T6 were immersed in liquid air. If hydrogen iodide was being used in the experiment, some hydrogen iodide was distilled from the storage bulbs into trap T8, which was then immersed in an acetone- solid carbon dioxide bath.

Taps F and M were shut isolating the circulation line from the vacuum line. The required static pressure of nitrogen was allowed into the circulating line by shutting tap E and directing the rate of flow through the sodium trap, to remove any oxygen.

The circulating pump bath was then raised round the mercury reservoir, and the temperature allowed to attain the optimum value. The strangling tap, H, was adjusted for the required rate of flow and the circulation of carrier gas prolonged for about half an hour, to achieve stability in rate of flow and in the temperature of the heating baths.

Tap E was opened and those to the sodium trap shut, so that now the path of the gas was through the reaction vessel, through one of the three collection units, through either capillary K1 or K2 to the circulating pump and injection system.

The heating baths to the benzyl bromide and toluene reservoirs were raised and the stirring started. The trap heaters were also switched on.

When stable conditions had been reached, the benzyl bromide and toluene valves were opened. The first of the set of three collection units served as a collector of material not required for analysis, since the flow of reactants initially was not constant, owing to the fact that a substantial amount of material had collected between the capillary and the diaphragm when the valve was shut; this meant that a large pulse of material surged out in the first few seconds of the experiment. Any volatile materials present in either reservoir were collected in this trap also.

Flow of reactant through the by-pass system was achieved by closing the electro-magnetic valve across the path to the reaction vessel, and by closing the electro-magnetic valve to the first collection unit.

The first quantitative experiment was started by opening the electro-magnetic valve in the second collection unit and closing the by-pass, thereby opening the line to the reaction vessel again, the operation taking about three seconds. The time was noted and collection of products was made for a period of time, depending on the temperature of decomposition or the contact time, but usually from ten to thirty minutes. During this period, pressure readings across the capillary and at the circulating pump were taken, and the temperatures of the furnace and of the various baths noted.

Collection was made in the same manner into the third unit. During the experiment it was essential to keep all the cooling baths topped up to maintain constancy of flow rate.

Flow was then directed into the first unit again for a few minutes. The injection valves were closed, flow was continued for a few minutes longer to clean the lines and the reservoir heating baths were removed.

When the hydrogen iodide was used as a catcher the procedure was slightly different. Then the order of events was

(1) flow of benzyl bromide and hydrogen iodide into unit 1,

(2) flow of benzyl bromide and hydrogen iodide into unit 2, then unit 3,

(3) flow of benzyl bromide and hydrogen iodide into unit 1 when hydrogen iodide flow was stopped,

(4) flow of benzyl bromide alone into by-pass trap, and

(5) flow of benzyl bromide into unit 1.

On the completion of a run, the circulation line was opened to the vacuum line and the carrier gas pumped out. If the carrier gas was to be examined on the mass spectrometer, tap H was shut and the gas collected in a 100ccs. storage flask by means of the circulating pump and a Toepler pump.

The collection system, comprising three identical units, was isolated by closing taps A and B. The pear-shaped vessels T3 were frozen in liquid air and the hydrogen bromide, collected in traps T2, distilled into T3 when taps C were opened. When distillation was complete, the water was allowed to warm up and the hydrogen bromide went into solution. The hydrogen bromide solution was again frozen in liquid air. Taps C were shut and, on warming up, the aqueous solution was collected in standard flasks ready for analysis. For runs in which hydrogen iodide was used, the procedure was similar, in which case unchanged hydrogen iodide was also collected.

Involatile products, unchanged benzyl bromide and toluene were collected in the heater traps under acetone-solid carbon dioxide. If isolation of the involatile products was required, the toluene and unchanged benzyl bromide were distilled off into traps T2, and the remaining materials were dissolved in solvent and collected when the apparatus was let down to atmospheric pressure. Solvents used were spectroscopic methanol, if analysis was to be performed on the ultra-violet spectrophotometer, or carbon tetrachloride for determinations by infra-red or mass spectrometry.

If collection of involatile materials was not desired, the unchanged benzyl bromide, toluene and products were dissolved in methanol and the amount of unchanged benzyl bromide determined.

While the hydrogen bromide was distilling into the distilled water, the benzyl bromide and toluene to be used for calibration of rate of flow of these materials were distilled into T7, which was then detached, when the apparatus was at atmospheric pressure, sealed with a ground glass stopper and weighed.

In runs with hydrogen iodide, iodine was collected in T1 and was dissolved in methanol and collected in standard flasks for analysis.

THE THERMAL DECOMPOSITION OF BENZYL BROMIDE USING TOLUENE AS A RADICAL CATCHER

Method of Calculation of Rate Constants

In all the experiments noted in this section, the rate constants are of the first order calculated by the integrated form of the equation

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

where k is the rate constant in $\sec.^{-1}$

t is the time of contact in sec.

a and a-x are the initial and final concentrations of benzyl bromide in gm. moles/l. In practice the quantities inserted in the ratio (a/a-x) were for a, the rate of flow of benzyl bromide in gm. moles/sec., and for x, the rate of production of product in gm. moles/sec., where the product is hydrogen bromide.

Effect of Variation of Partial Pressure of Toluene

In using the toluene carrier technique, it is essential that all the bromide atoms produced by the thermal fission of the C-Br bond in benzyl bromide shall react with the toluene.

To investigate the effect of varying the partial pressure of toluene, experiments were carried out at a fixed temperature with a constant partial pressure of benzyl bromide and using the same contact time in each experiment.

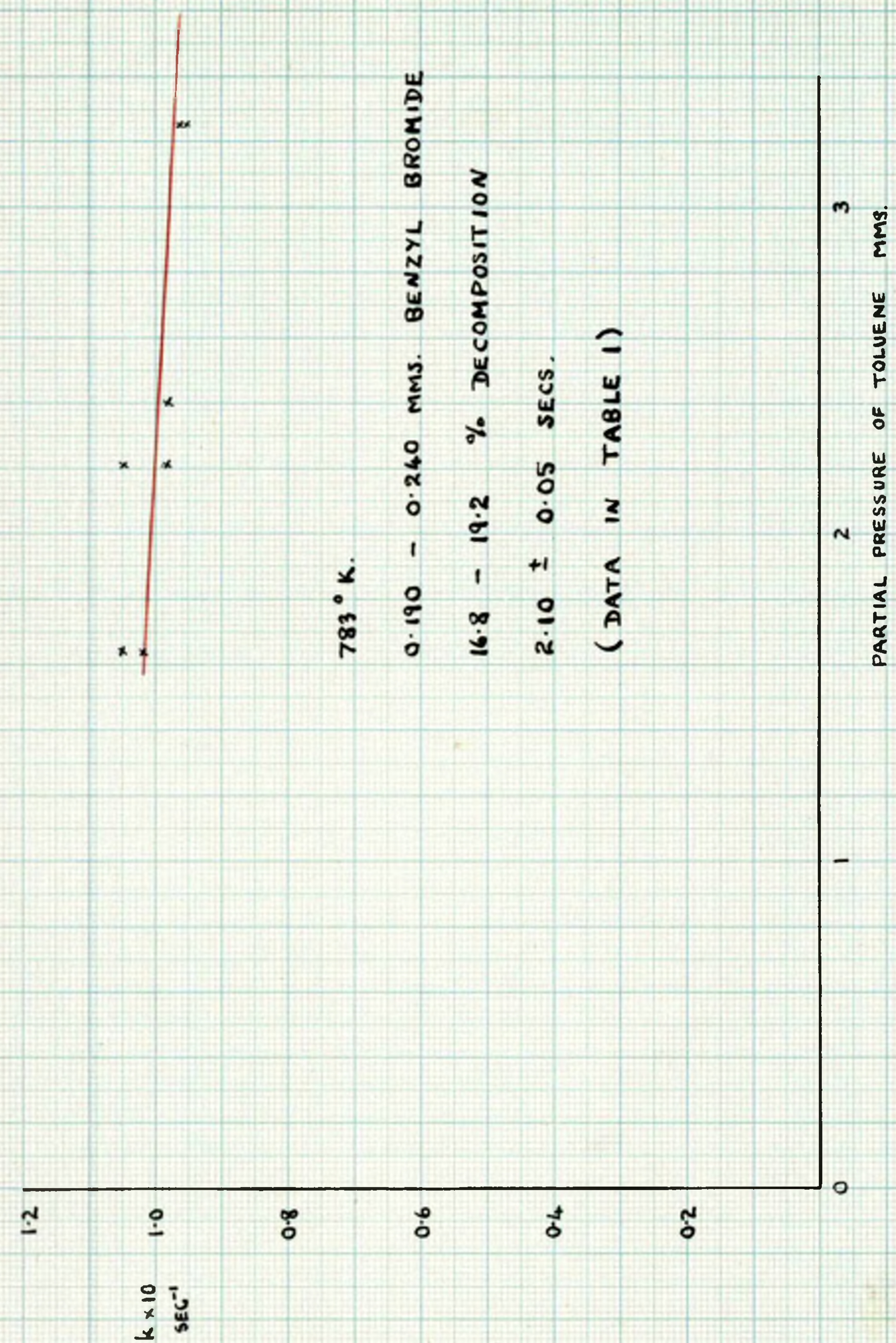

k × 10
SEC⁻¹
1·2
1·0
0·8
0·6
0·4
0·2
0
1
2
3
PARTIAL PRESSURE OF TOLUENE MMS.
783° K.
0·190 – 0·240 MMS. BENZYL BROMIDE
16·8 – 19·2 % DECOMPOSITION
2·10 ± 0·05 SECS.
(DATA IN TABLE I)

Figure 11

Fig.11 illustrates the results tabulated below for this investigation.

Table 1

Temperature of reaction - 783°K.

Time of contact - 2.10 ± 0.05secs.

Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	$\frac{\text{P.p. Toluene}}{\text{P.p. 'Bromine Atom'}}$	% Decomp.	k sec.$^{-1}$
0.235	1.64	37.8	18.5	0.102
0.240	1.64	35.6	19.2	0.105
0.200	2.21	61.4	18.0	0.105
0.199	2.21	65.7	16.8	0.098
0.228	2.40	57.8	18.25	0.098
0.229	2.40	58.3	18.05	0.098
0.190	3.25	95.5	17.95	0.095
0.194	3.25	93.7	18.5	0.096

Using the flow technique and keeping the other factors constant, it was difficult to obtain a partial pressure of toluene greater than 3.25mms.

The ratio given in the third column is calculated assuming all the bromine atoms found as hydrogen bromide had existed at the same time. Since these atoms are being progressively formed and removed, the actual relative concentrations would be much higher than the data

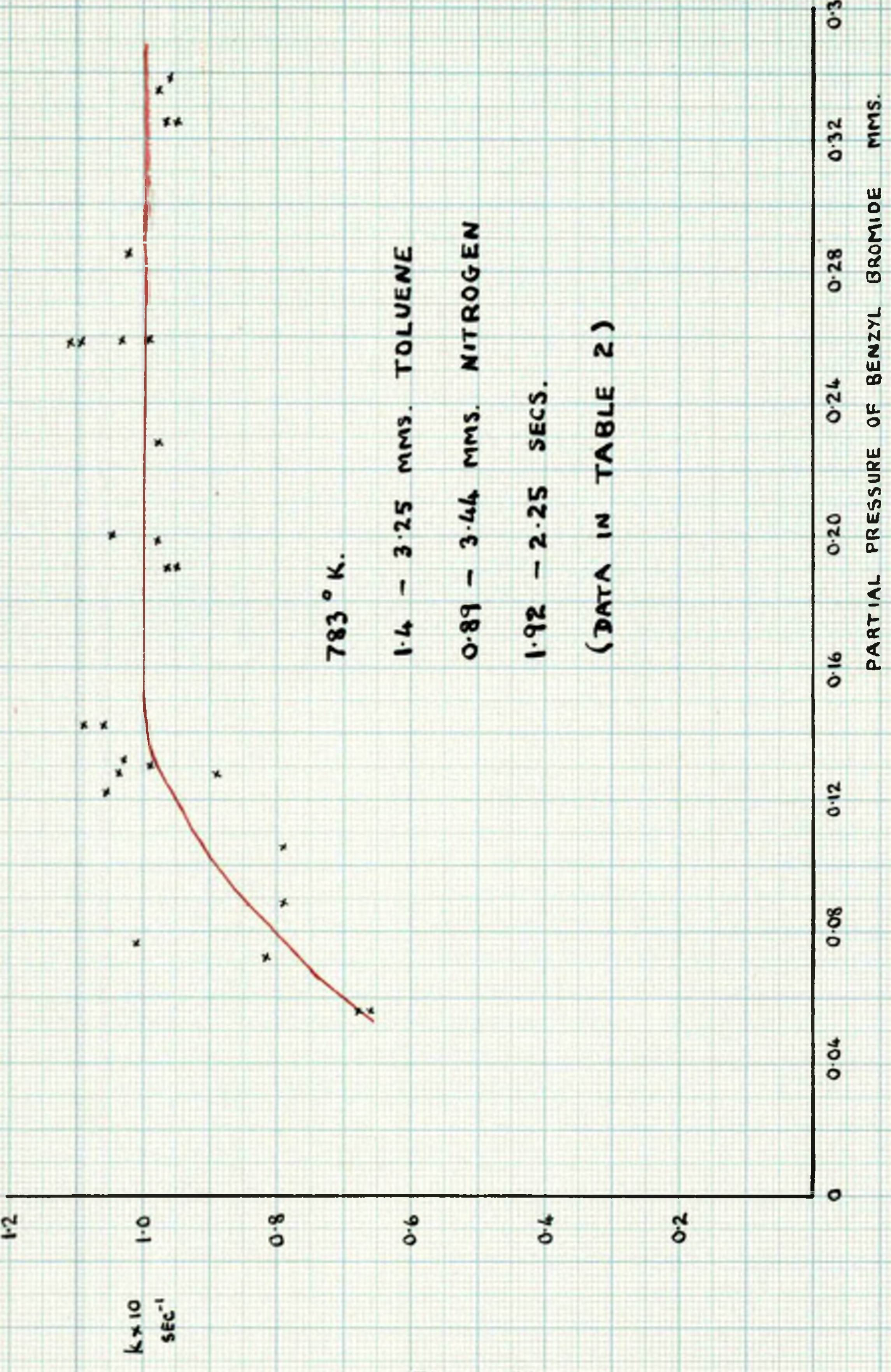

783 °K.
1·4 – 3·25 MMS. TOLUENE
0·89 – 3·44 MMS. NITROGEN
1·92 – 2·25 SECS.
(DATA IN TABLE 2)
k×10 SEC⁻¹
1·2
1·0
0·8
0·6
0·4
0·2
0
0·04
0·08
0·12
0·16
0·20
0·24
0·28
0·32
0·36
PARTIAL PRESSURE OF BENZYL BROMIDE MMS.

Figure 12

of column 3, and the latter must be taken for comparative purposes only. From the point of view of capture of bromine atoms, this quantity should be significant. In Fig.11 the velocity constant is plotted against the partial pressure of toluene.

It could be inferred from this series of experiments that, with partial pressure of toluene/partial pressure of bromine atoms > 35.6, toluene will capture all the bromine atoms produced.

The following experiments were carried out with this condition being fulfilled.

Determination of the Order of the Reaction

Two methods were used to study the order of reaction: (1) variation of partial pressure of benzyl bromide, and (2) variation of contact time.

(1) Effect of Variation of Partial Pressure of Benzyl Bromide

Experiments were performed at a temperature of 783°K., and the time of contact was held constant to 2.1 ± 0.15secs. over the series of experiments. The partial pressure of benzyl bromide could be varied by changing the temperature of the heater bath surrounding the bromide reservoir.

Twenty-six experiments were carried out over the range of partial pressures from 0.056 to 0.339mms. of benzyl bromide. Fig.12 illustrates the relationship between the partial pressure of benzyl bromide and the first order rate constant k.

Table 2

Expt. No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.^{-1}
35	0.056	1.51	3.17	2.25	13.2	0.066
36	0.057	1.51	3.17	2.25	13.8	0.068
39	0.072	1.62	3.09	2.17	16.7	0.082
40	0.072	1.62	3.09	2.17	16.6	0.082
25	0.076	2.46	1.97	1.97	19.2	0.101
30	0.089	1.88	2.82	2.21	16.1	0.079
29	0.106	1.88	2.82	2.21	16.1	0.079
33	0.122	1.52	3.34	2.11	20.0	0.106
34	0.128	1.52	3.34	2.11	19.7	0.104
27	0.128	2.57	1.97	2.10	17.0	0.089
23	0.130	1.75	2.91	2.15	19.1	0.099
24	0.131	1.77	2.91	2.15	19.1	0.099
21	0.142	1.43	3.30	2.25	21.4	0.107
22	0.142	1.43	3.30	2.24	21.7	0.109
43	0.190	3.25	0.89	2.10	17.95	0.095
44	0.194	3.25	0.89	2.10	18.5	0.096
13	0.199	2.21	2.36	1.92	16.8	0.098
12	0.200	2.21	2.36	1.92	18.0	0.105
10	0.228	2.40	1.97	2.06	18.25	0.098
11	0.229	2.40	1.97	2.06	18.05	0.098

Table 2 (cont.)

Expt. No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k $sec.^{-1}$
41	0.259	1.84	2.67	2.05	20.2	0.110
42	0.262	1.84	2.67	2.05	20.5	0.112
79	0.329	2.79	1.43	1.93	17.6	0.097
80	0.329	2.79	1.43	1.93	15.9	0.093
18	0.335	1.40	3.40	2.11	18.25	0.097
17	0.339	1.43	3.44	2.11	17.95	0.096

The above results seem to indicate that the reaction obeys the first order rate equation over the range of partial pressures from 0.14 to 0.339mms. of benzyl bromide. The reason for the fall-off in the rate constant in the low pressure region is not clear.

One possible reason that could be put forward is that a change from first to second order could be taking place. If this were the case, increasing the partial pressure of toluene for a given partial pressure of benzyl bromide might be expected to raise the value of the rate constant, since toluene has been proved to be a very efficient third body in the transference of energy . The evidence obtained in these experiments is not extensive enough for a definite opinion to be given. If experiments 39-40 and 25 are compared, increasing the toluene partial pressure from 1.62 to 2.46mms.

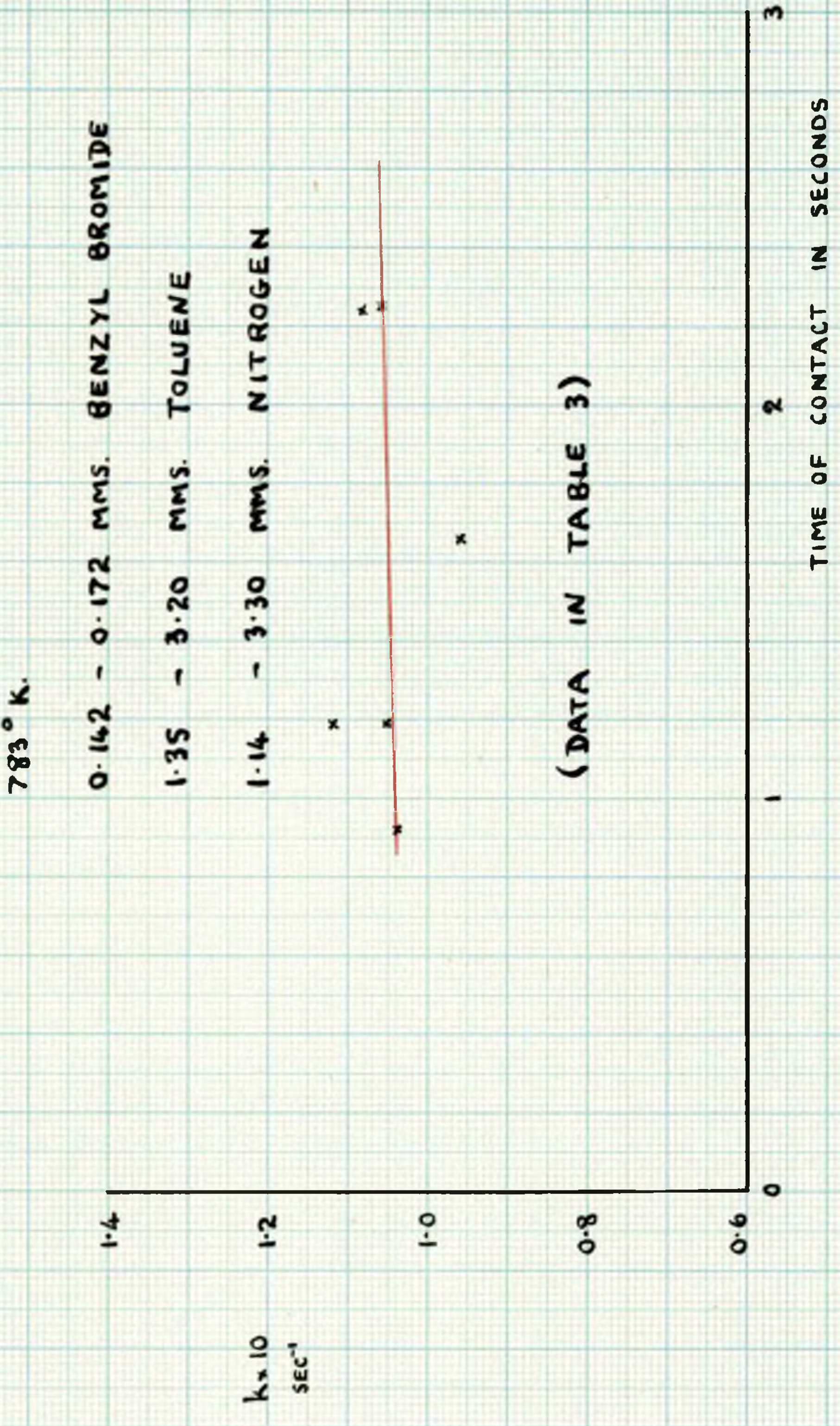

783° K.
0·142 – 0·172 MMS. BENZYL BROMIDE
1·35 – 3·20 MMS. TOLUENE
1·14 – 3·30 MMS. NITROGEN
(DATA IN TABLE 3)
k×10
SEC⁻¹
1·4
1·2
1·0
0·8
0·6
0
1
2
3
TIME OF CONTACT IN SECONDS

Figure 13

increases the first order rate constant from 0.082 to 0.101 sec.$^{-1}$, but on the other hand, if a comparison is made between experiments 23-24 and 27, where the toluene partial pressure increases from 1.75 to 2.57mms., the first order rate constant decreases from 0.099 to 0.089 sec.$^{-1}$

Further work on this problem was not pursued, but it was hoped to gain some more evidence from a study of the decomposition using hydrogen iodide, which would be expected to be a much less efficient third body, as the radical catcher. It was considered that in any subsequent work in determination of the energy of activation of the decomposition, first order rate constants could justly be calculated, provided the work was carried out using partial pressures of benzyl bromide of the order of 0.2 - 0.3mms.

(2) Effect of Variation of Contact Time

The effect on the first order rate constant produced by varying the contact time could be determined most readily by altering the rate of flow of nitrogen carrier gas through the system, and adjusting the temperature of the bath surrounding the bromide reservoir so that the partial pressure of bromide in each experiment was constant.

A plot of the results is shown in Fig.13 and tabulated below.

Table 3

Temperature - 783°K.

Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$
0.150	1.45	2.84	0.92	9.10	0.104
0.144	1.35	2.27	1.19	12.45	0.112
0.144	1.35	2.27	1.19	11.75	0.105
0.172	3.20	1.14	1.65	14.10	0.096
0.142	1.43	3.30	2.24	21.70	0.109
0.142	1.43	3.30	2.25	21.40	0.107

These results indicate that the first order rate constant is not influenced by any change in the contact time of the reaction when the variation extends over the range 0.92 to 2.25secs. It was experimentally difficult to obtain data at lower contact times, with the capillaries in the apparatus used in this work.

The results of Szwarc et al.[4], who carried out rather fewer experiments on the effect of changing the bromide partial pressure and contact time, are in agreement with those quoted above. The other workers did not indicate any fall-off in the rate constant at pressures of benzyl bromide less than 0.12mms. The main difference in the technique of the two sets of experiments lies in the type of carrier gas used. Szwarc used toluene as a carrier gas as well as a radical catcher, while, in the present investigation, nitrogen was used as a carrier gas and toluene as the catcher. Thus the amount of toluene used in the previous investigation was much greater than in the present one, and this may account for the difference in the results at low partial pressures of benzyl bromide.

Szwarc had shown that changing the surface/volume ratio by four to five times had no effect on the rate constant. These results were assumed and no experiments were performed to verify this in the present investigation.

The thermal decomposition of benzyl bromide was therefore considered to be a homogeneous gas reaction of the first order, as measured by the formation of hydrogen bromide.

The Effect of Temperature on the First Order Rate Constant

Experiments were performed over the range 731 - 816°K. The lowest partial pressure of benzyl bromide used was 0.125mms., while the toluene partial pressure was adequate to ensure that all the bromine atoms produced were caught.

Fig.14 shows the plot of $\log_{10}$ (first order rate constant) against $1/T^{o}K$. The energy of activation and the A factor have been calculated by the method of least squares.

Values for the parameters in the equation

$$\log_{10} k = \frac{-E}{2.303RT} + \log_{10} A$$

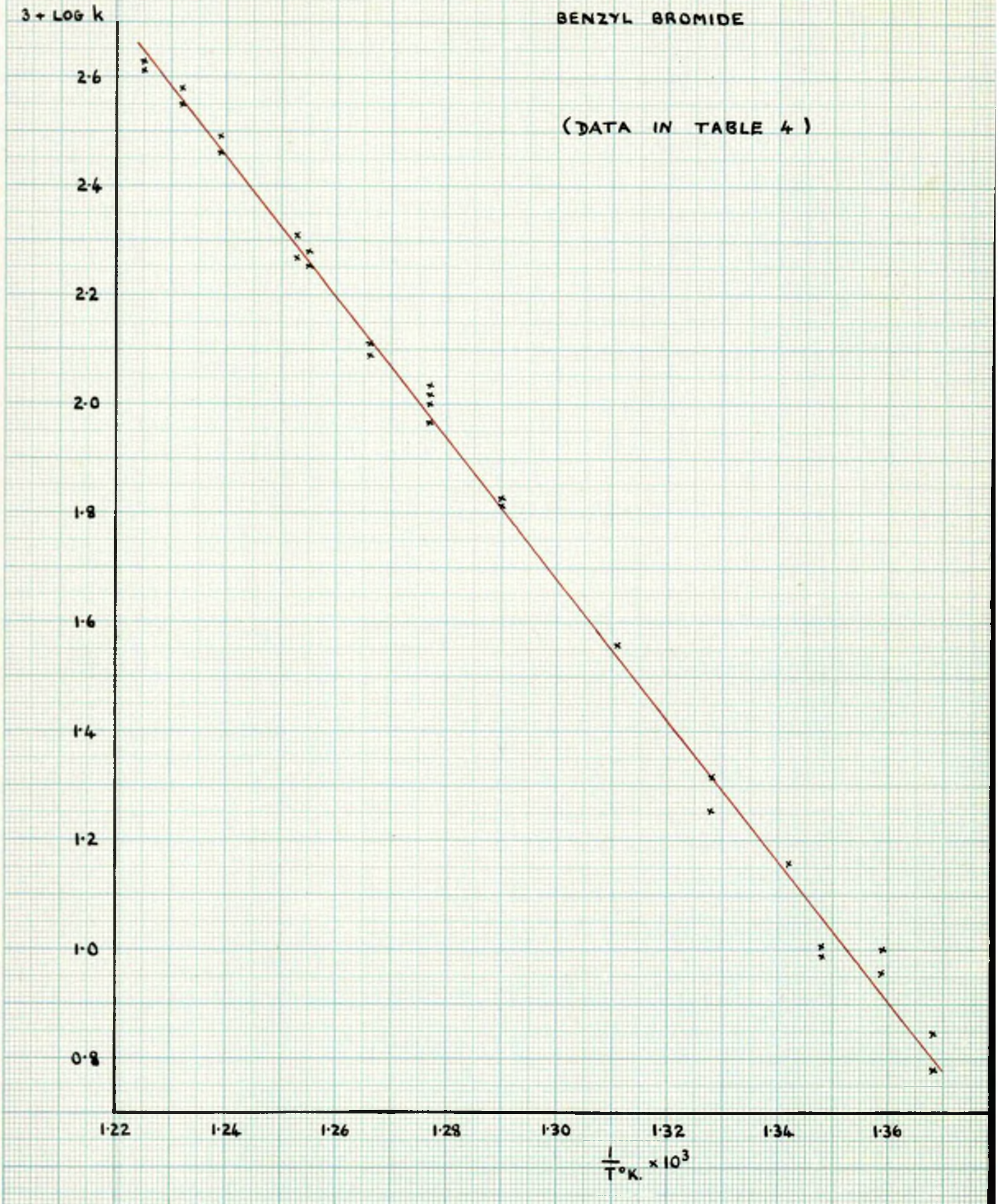

3 + LOG k
BENZYL BROMIDE
(DATA IN TABLE 4)
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
1·22
1·24
1·26
1·28
1·30
1·32
1·34
1·36
$\frac{1}{T°K.} \times 10^3$

Figure 14

were calculated to be $E = 58.02 \pm 0.68$ k.cals./mole

$$\log_{10} A = 15.22 \text{ sec.}^{-1}$$

The table below shows the results of experiments used in the determination of the above parameters.

Table 4

Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.^{-1}	Temp. °K
0.276	1.88	2.42	2.11	1.5	0.0073	731
0.276	1.88	2.42	2.11	1.3	0.0062	731
0.20	2.59	1.625	2.12	2.1	0.01	736
0.182	2.59	1.625	2.13	1.9	0.009	736
0.274	2.31	1.98	2.20	2.25	0.0098	742
0.274	2.31	1.98	2.20	2.02	0.0103	742
0.316	2.60	1.58	2.0	3.08	0.0155	745
0.329	2.60	1.58	2.0	2.85	0.0151	745
0.258	2.30	1.845	2.24	4.48	0.0206	753
0.257	2.30	1.845	2.24	3.88	0.0177	753
0.258	2.38	1.72	2.2	4.24	0.0198	753
0.26	2.41	1.82	2.03	7.3	0.036	763
0.26	2.41	1.82	2.03	7.1	0.036	763
0.201	1.38	2.67	1.38	8.8	0.067	775
0.205	1.38	2.67	1.38	8.75	0.067	775
0.159	2.24	1.885	0.98	11.85	0.128	790

Table 4 (cont.)

Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
0.162	2.24	1.885	0.98	11.4	0.123	790
0.161	1.60	2.75	1.08	17.2	0.178	797
0.150	1.60	2.75	1.08	17.6	0.190	797
0.132	1.35	3.24	1.13	18.95	0.186	798
0.125	1.35	3.24	1.13	20.5	0.204	798
0.156	1.14	3.41	1.14	27.6	0.306	807
0.148	1.14	3.41	1.14	27.9	0.289	807
0.176	2.40	1.76	1.01	32.5	0.388	812
0.186	2.40	1.76	1.01	30.5	0.359	812
0.182	2.31	1.84	0.95	32.0	0.406	816
0.189	2.31	1.84	0.95	32.9	0.414	816

Experiments 23, 24, 21, 22, 43,44,13, 12, 10, 11, 41, 42, 79, 80, 18, and 17 of Table 2, which were performed at 783°K, were also used in computation of the parameters.

Six months after the completion of work on the decomposition of benzyl bromide with toluene catcher, a new sample of benzyl bromide was purified as previously described and three experiments performed in order to obtain the involatile products for analysis by the mass spectrometer.

These experiments were carried out at 783°K. The results are shown below.

Table 5

Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k $sec.^{-1}$
0.258	3.27	1.59	1.42	13.8	0.104
0.258	3.27	1.51	1.42	13.0	0.0985
2.285	3.17	2.15	1.45	13.9	0.103
0.133	3.43	1.28	1.27	10.6	0.088

These results are in distinct agreement with the first order rate constants calculated previously at this temperature, the arithmetic mean of these determinations being 0.102 $sec.^{-1}$

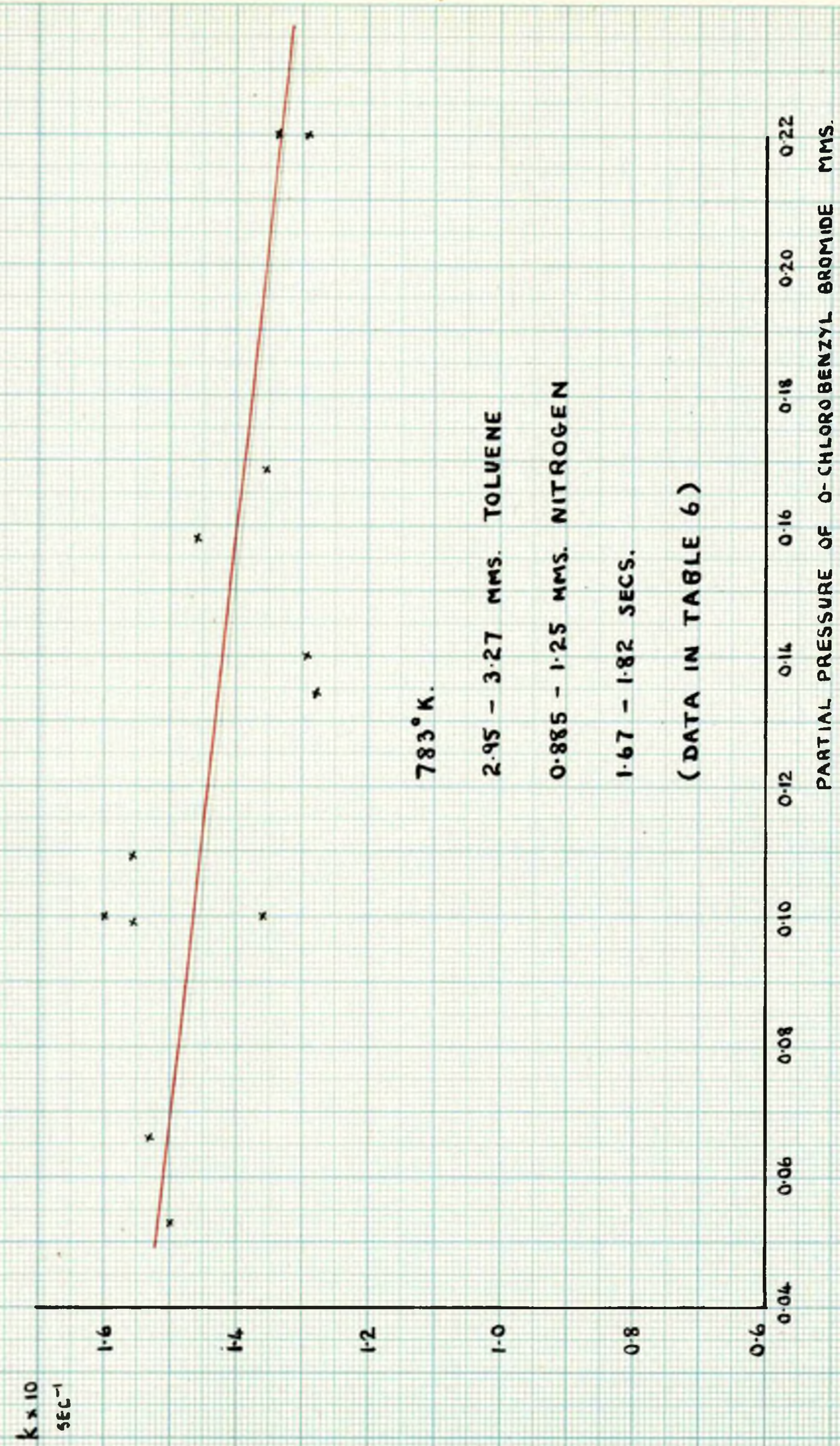

k × 10
SEC⁻¹
1·6
1·4
1·2
1·0
0·8
0·6
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
0·20
0·22
PARTIAL PRESSURE OF O-CHLOROBENZYL BROMIDE MMS.
783° K.
2·95 – 3·27 MMS. TOLUENE
0·885 – 1·25 MMS. NITROGEN
1·67 – 1·82 SECS.
(DATA IN TABLE 6)

Figure 15

THE THERMAL DECOMPOSITION OF O-CHLOROBENZYL BROMIDE USING TOLUENE AS A RADICAL CATCHER

Effect of Variation of Partial Pressure of Toluene

An extensive series of experiments to determine the effect of varying the partial pressure of toluene was not performed.

Two experiments were conducted in which the partial pressure of bromide was 0.169 and 0.163mms. respectively and the contact time was 1.67secs. The toluene pressures were 1.52 and 2.95mms. and the rate constants 0.136 and 0.140 sec.$^{-1}$ respectively.

Together with the evidence provided by varying the partial pressure of toluene in the decomposition of benzyl bromide, it was thought that the data were sufficient to show that there was an amount of toluene adequate to catch all the bromine atoms produced.

Determination of the Order of Reaction

Effect of Varying the Partial Pressure of o-Chlorobenzyl Bromide

A series of experiments similar to that on benzyl bromide, was carried out. The partial pressure of the substituted benzyl bromide was varied by altering the temperature of the bath surrounding the reservoir. The toluene partial pressure varied over the small range from 2.95 to 3.27mms. while the contact time was 1.75 ± 0.08secs. The experiments were performed at a temperature of 783°K.

A plot of the results is shown in Fig.13 and tabulated below.

Table 6

Partial Pressure o-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$
0.053	3.18	1.03	1.69	22.4	0.150
0.066	3.18	1.03	1.70	22.75	0.153
0.099	3.24	0.93	1.71	23.4	0.156
0.100	3.27	0.885	1.82	22.0	0.137
0.100	3.24	0.93	1.71	23.8	0.160
0.109	3.27	0.885	1.82	24.7	0.156
0.134	3.10	1.25	1.78	20.3	0.128
0.140	3.10	1.25	1.78	20.4	0.129
0.158	2.95	1.16	1.67	21.7	0.147
0.169	2.95	1.16	1.67	20.4	0.136
0.220	3.03	1.00	1.73	19.5	0.129
0.220	3.03	1.00	1.73	20.6	0.134

It is seen that for a four-fold variation in the partial pressure of the bromide from 0.053 to 0.22mms., the first order rate constant shows a variation of 17%. Although there does appear from the data to be a slight diminution in the rate constant for increasing bromide partial pressure, the magnitude of this drift would not seem to be sufficient to warrant any other conclusion than that the decomposition is first order with respect to o-chlorobenzyl bromide.

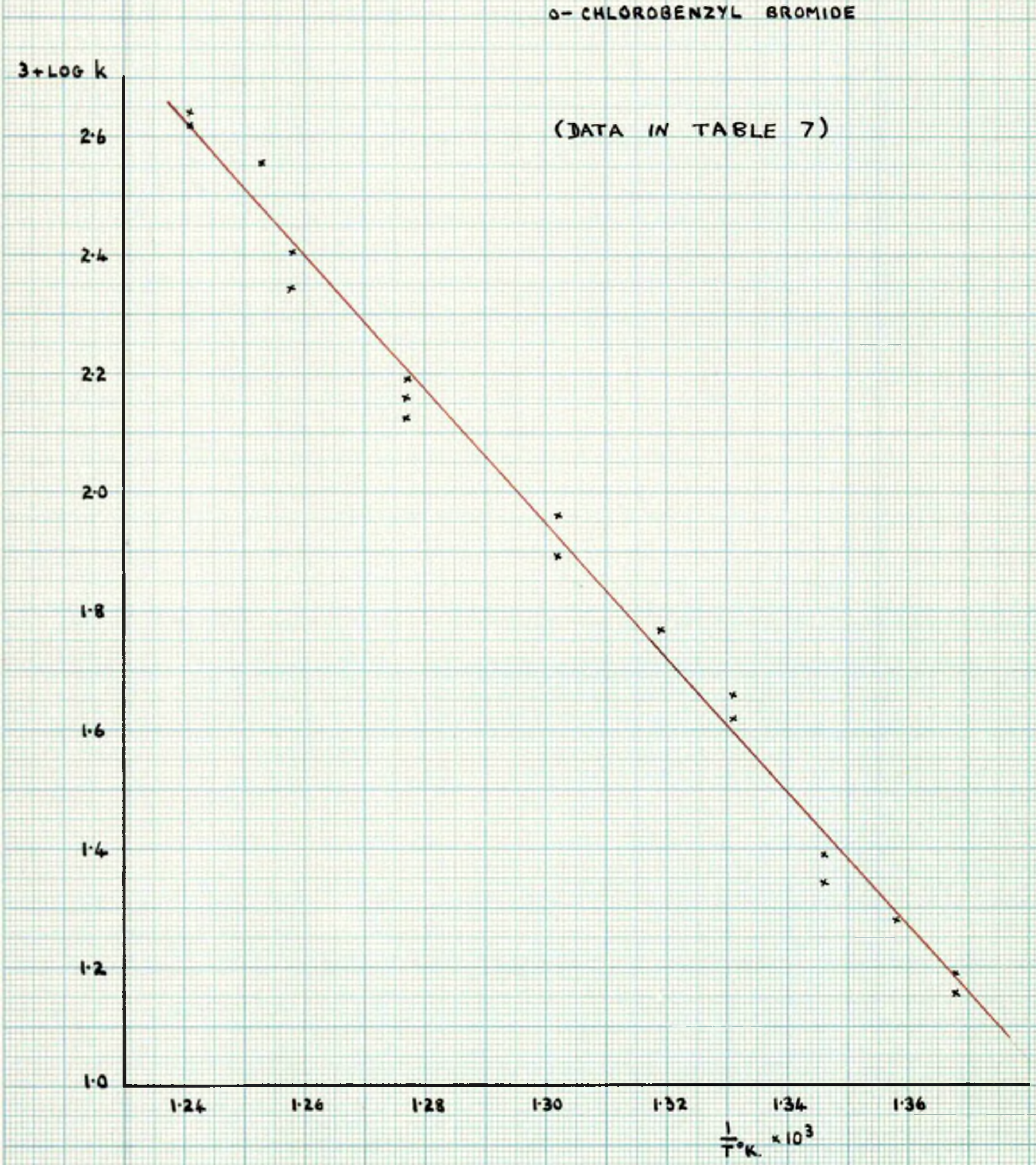

o- CHLOROBENZYL BROMIDE
(DATA IN TABLE 7)
3 + LOG k
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
1·24
1·26
1·28
1·30
1·32
1·34
1·36
$\frac{1}{T\,°K} \times 10^3$

Figure 16

The Effect of Temperature on the Rate Constant

When the order of the reaction had been established, and analysis of the products obtained in the decomposition had shown that there were no complicating factors to the kinetics, experiments were carried out to determine the energy of activation and A factor for the decomposition. It was hoped to carry out similar experiments with the other two isomeric chlorobenzyl bromides and compare the parameters with those obtained for benzyl bromide.

In the case of o-chlorobenzyl bromide, the rate constants were determined over the temperature range 731° - 805°K.

Limitations were set on the higher end of the temperature scale, firstly by the magnitude of the decomposition and secondly by the temperature needed on the bromide injection valve. In order to achieve a low contact time and a sufficient partial pressure of bromide, the temperature of the bath surrounding the bromide reservoir had to be raised to a degree which might have affected the GACO diaphragms in the valve on lengthy exposure.

The data obtained from the experiments are shown in Fig.16 and tabulated below.

The following rate equation was calculated by the method of least squares from the available data:

$$k = 10^{13.45} \exp^{-(51.21 \pm 1.45) \times 10^3/RT} \sec.^{-1}$$

Table 7

Partial Pressure o-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
0.214	2.53	1.72	2.08	2.95	0.0144	731
0.217	2.53	1.72	2.08	3.35	0.0157	731
0.216	2.43	1.67	2.10	3.9	0.0190	736
0.206	2.63	1.60	2.32	5.1	0.0225	743
0.208	2.63	1.60	2.32	5.7	0.0249	743
0.173	2.19	2.36	1.92	7.9	0.047	751.5
0.178	2.19	2.36	1.92	7.7	0.043	751.5
0.140	2.55	1.50	1.65	9.4	0.060	758
0.124	2.21	2.06	1.17	10.5	0.095	768
0.140	2.21	2.06	1.17	8.8	0.077	768
0.100	3.27	0.885	1.82	22.0	0.137	783
0.109	3.27	0.885	1.82	24.7	0.156	783
0.158	2.95	1.16	1.67	21.4	0.147	783
0.220	3.03	1.0	1.73	19.5	0.129	783
0.110	2.02	2.40	1.04	23.0	0.256	795
0.110	2.02	2.40	1.04	20.0	0.217	795
0.029	1.87	3.0	1.0	31.2	0.375	798
0.030	1.87	3.0	1.0	31.1	0.373	798
0.084	1.98	2.62	0.932	33.0	0.427	805
0.084	1.94	2.62	0.932	34.0	0.446	805

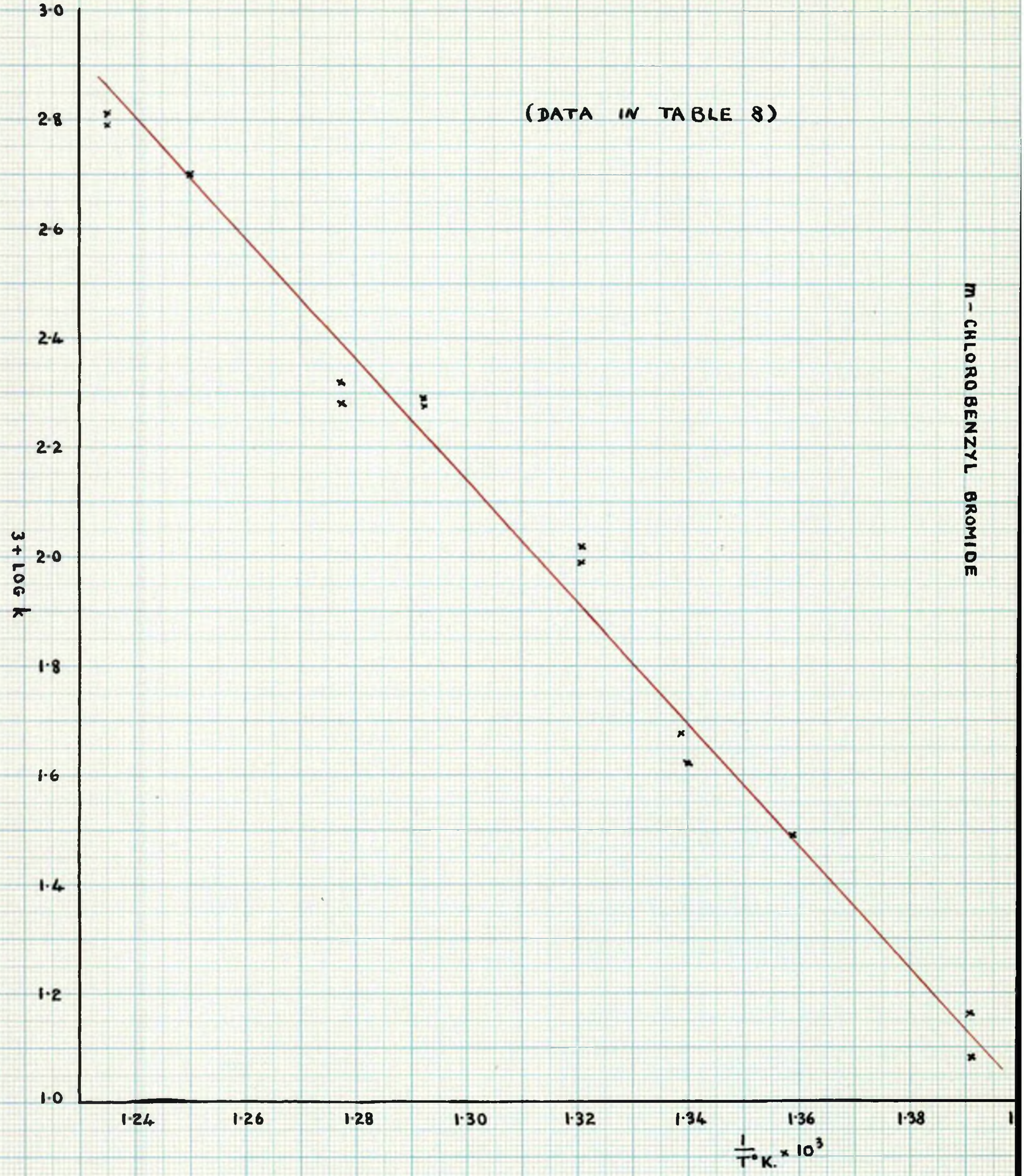

(DATA IN TABLE 8)
m-CHLOROBENZYL BROMIDE
3 + LOG k
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
1·24
1·26
1·28
1·30
1·32
1·34
1·36
1·38
1
1/T°K. × 10³

Figure 17

THE THERMAL DECOMPOSITION OF M-CHLOROBENZYL BROMIDE AND OF P-CHLOROBENZYL BROMIDE USING TOLUENE AS A RADICAL CATCHER

The Effect of Temperature on the Rate Constant

(1) m- Chlorobenzyl Bromide

Because of lack of time to carry out the experimental work, the decomposition of this compound and of p-chlorobenzyl bromide were assumed to be first order, by analogy with the decomposition of o-chlorobenzyl bromide.

The experimental procedure adopted for the study of the decomposition of m-chlorobenzyl bromide was similar to that for the ortho compound.

The temperature range covered was 91°C. from 719 - 810°K. The plot of $\log_{10}k$ against $1/T$°K. is shown in Fig.17 and the data used appears in Table 8 below.

The following rate equation was calculated by the method of least squares from the available data:

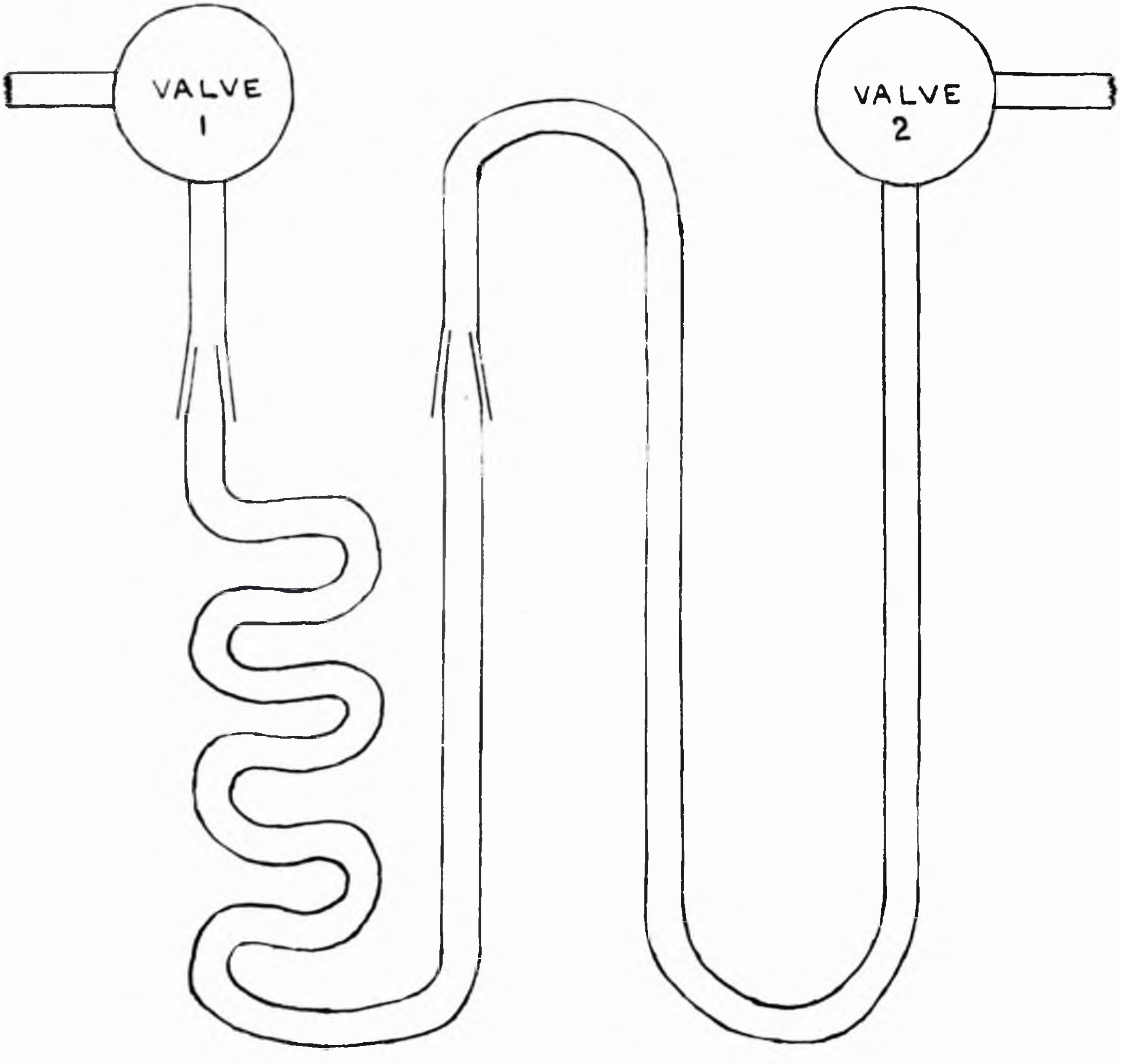
$$k = 10^{12.39} \exp^{-(48.50 \pm 1.72) \times 10^3/RT} \text{ sec.}^{-1}$$

Table 8

Partial Pressure m-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k $sec.^{-1}$	Temp. $^{\circ}K$
0.194	3.50	1.40	1.95	2.33	0.012	719
0.199	3.50	1.48	1.94	2.95	0.015	719
0.248	3.39	1.74	1.87	5.15	0.031	736
0.234	3.39	1.74	1.85	7.0	0.042	746
0.215	2.62	2.29	1.79	7.3	0.048	747
0.237	3.33	2.32	1.48	14.6	0.106	757
0.196	3.30	2.32	1.48	13.6	0.099	757
0.248	1.89	3.38	1.0	17.3	0.191	774
0.243	1.89	3.38	1.0	17.7	0.194	774
0.294	3.06	2.01	1.53	26.4	0.189	783
0.304	3.06	2.01	1.53	29.6	0.210	783
0.041	2.26	3.29	1.19	44.7	0.501	800
0.237	1.88	3.75	0.86	42.3	0.644	810
0.237	1.88	3.75	0.86	41.9	0.630	810

(2) p- Chlorobenzyl Bromide

p-Chlorobenzyl bromide differed from the other compounds in that it was a white solid of m.pt. 50.5°C., the preparation of which has been described. The relationship between the vapour pressure and



SATURATOR SYSTEM

Figure 18

temperature was unknown, but it was felt that the vapour pressure at a given temperature might be somewhat similar to that of the liquid chloro substituted benzyl bromides, and consequently, the form of injection system to be used could remain the same as for the other bromides.

The first experiment was conducted at 758°K. and the rate constant of 0.090 $sec.^{-1}$ appeared to have the value expected, since it was close to that obtained for o- and m-chlorobenzyl bromides at the same temperature. It was noticed that the colour of the material remaining in the reservoir had darkened, which could be explained by the production of bromine.

A second experiment with a fresh sample of p-chlorobenzyl bromide was carried out. This time there was a large production of hydrogen bromide corresponding to almost 100% decomposition of the material. The substance remaining in the reservoir was examined closely. On cooling, it resinified to a hard polymeric mass which had no lacrymatory effect and was insoluble in common solvents, including benzene, carbon tetrachloride and ether. It was sparingly soluble in 40-60°C. petroleum ether, from which it could be recovered as a white solid melting over a range from 90-105°C.

The nature of the compound was not investigated further; it was obvious that a method of injecting the material must be used in which high temperatures were avoided.

The valve injection system was therefore replaced by a saturator system (Fig.18). This consisted of a detachable spiral in the form of a U which was in series with another U-tube of conventional design. Two two-way valves of the type described earlier were used to isolate the saturator from the rest of the apparatus. The valves were enclosed in a heated box and all leads could be heated if necessary.

The spiral was kept at a temperature of 10-15°C. above that of the U-tube, which was controlled to ±0.2°C. The p-chlorobenzyl bromide was distributed over the coils of the spiral. The principle of the method was that the carrier gas should draw the material over from the spiral into the U-tube, which was at a lower temperature. The carrier gas would then be saturated with p-chlorobenzyl bromide at that temperature and a constant partial pressure of bromide would be carried into the reaction vessel.

The main disadvantage of the method is that the partial pressure depends on the rate of flow of carrier gas and the variation of partial pressures of reactants and carrier gas is more difficult to obtain. But in dealing with the variation of reaction rate with temperature we are not interested in maintaining strictly constant values of partial pressures over a series of experiments.

In the experiments tabulated below, the temperatures of the U-tube were in the range 40-45°C. All the experimental results used in the determination of the activation energy and A factor for the decomposition of p-chlorobenzyl bromide were obtained using the saturator system.

The reaction was studied over the temperature range 719 - 808°K. The following rate equation was calculated by the method of least

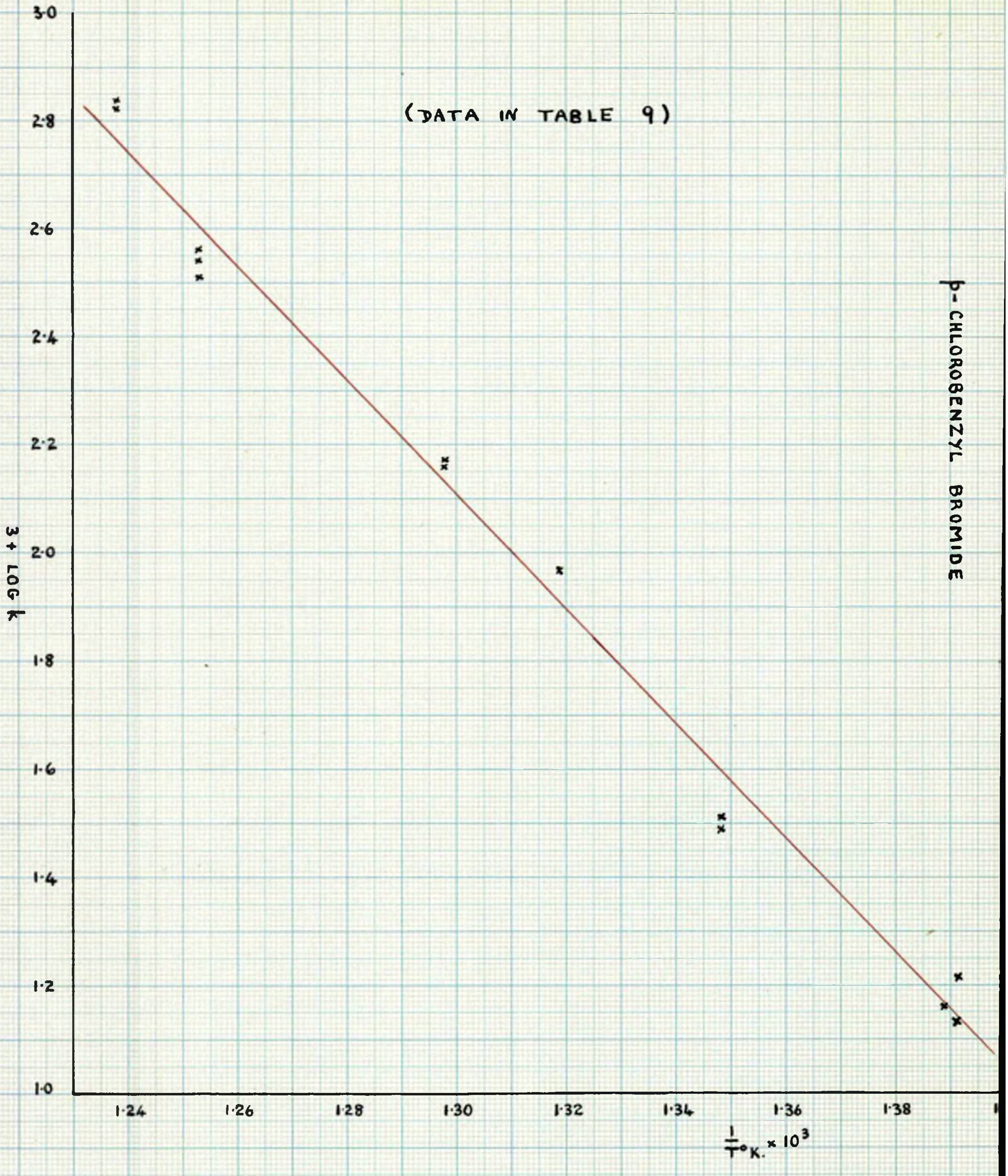

(DATA IN TABLE 9)
p- CHLOROBENZYL BROMIDE
3 + LOG k
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
1·24
1·26
1·28
1·30
1·32
1·34
1·36
1·38
$\frac{1}{T°K.} \times 10^3$

Figure 19

squares from the available data:

$$k = 10^{12.78} \exp^{-(48.05 \pm 1.57) \times 10^3/RT} \text{ sec.}^{-1}$$

The plot of $\log_{10}k$ against $1/T^{\circ}K.$ is shown in Fig. 19 and the results are tabulated below.

Table 9

Partial Pressure p-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.^{-1}	Temp. °K.
0.175	2.97	2.52	2.01	2.75	0.0138	719
0.166	2.97	2.52	2.01	3.9	0.0170	719
0.087	4.26	1.27	1.97	2.65	0.0140	720
0.263	2.78	3.03	1.84	6.5	0.0363	742
0.266	2.78	3.03	1.84	6.2	0.0350	742
0.168	2.99	2.81	1.72	15.0	0.0940	758
0.108	3.16	1.63	1.96	25.1	0.147	770.5
0.114	3.16	1.63	1.96	25.4	0.149	770.5
0.162	2.95	2.45	1.03	28.6	0.327	798
0.154	2.95	2.45	1.03	30.0	0.347	798
0.129	3.45	2.03	0.94	29.4	0.370	798
0.124	3.45	2.03	0.935	29.6	0.375	798
0.280	2.48	3.19	1.10	56.8	0.762	808
0.290	2.48	3.19	1.10	58.4	0.790	808

EXAMINATION OF THE INVOLATILE PRODUCTS OF THE PYROLYSIS OF BENZYL BROMIDE USING TOLUENE AS A RADICAL CATCHER

In the paper by Ghosh, Sehon and Szwarc[4], there was no proof given that dibenzyl was the only involatile product. The method of identification of dibenzyl was not described and it must be inferred that the solid products obtained were weighed and assumed to consist wholly of dibenzyl.

In view of the fact that Smith[3] had found that methyl diphenyls were important constituents of the products of the pyrolysis of toluene, it was felt that the nature of products of the pyrolysis of benzyl bromide ought to be examined more thoroughly. A preliminary investigation was carried out by ultra-violet spectrophotometry.

Pure dibenzyl shows maxima at 248, 253, 255, 259, 265 and 268mμ while trans-stilbene shows a fairly broad absorption band at 296mμ. If comparison is made between the spectrum of the sample (Fig.10) and the spectrum of dibenzyl and stilbene (Fig.10), it is seen that the sample shows maxima at 248, 254, 259, 265, 268 and 296mμ, which indicates that dibenzyl and stilbene are important constituents. The fact that the 268mμ peak is of greater intensity than the 259mμ peak in the product spectrum, is due to the contribution made by the stilbene absorption to the dibenzyl spectrum.

The relative extinction coefficients of stilbene at 296mμ and dibenzyl at 259mμ are 27,000/479, so that the amount of stilbene in the products is small.

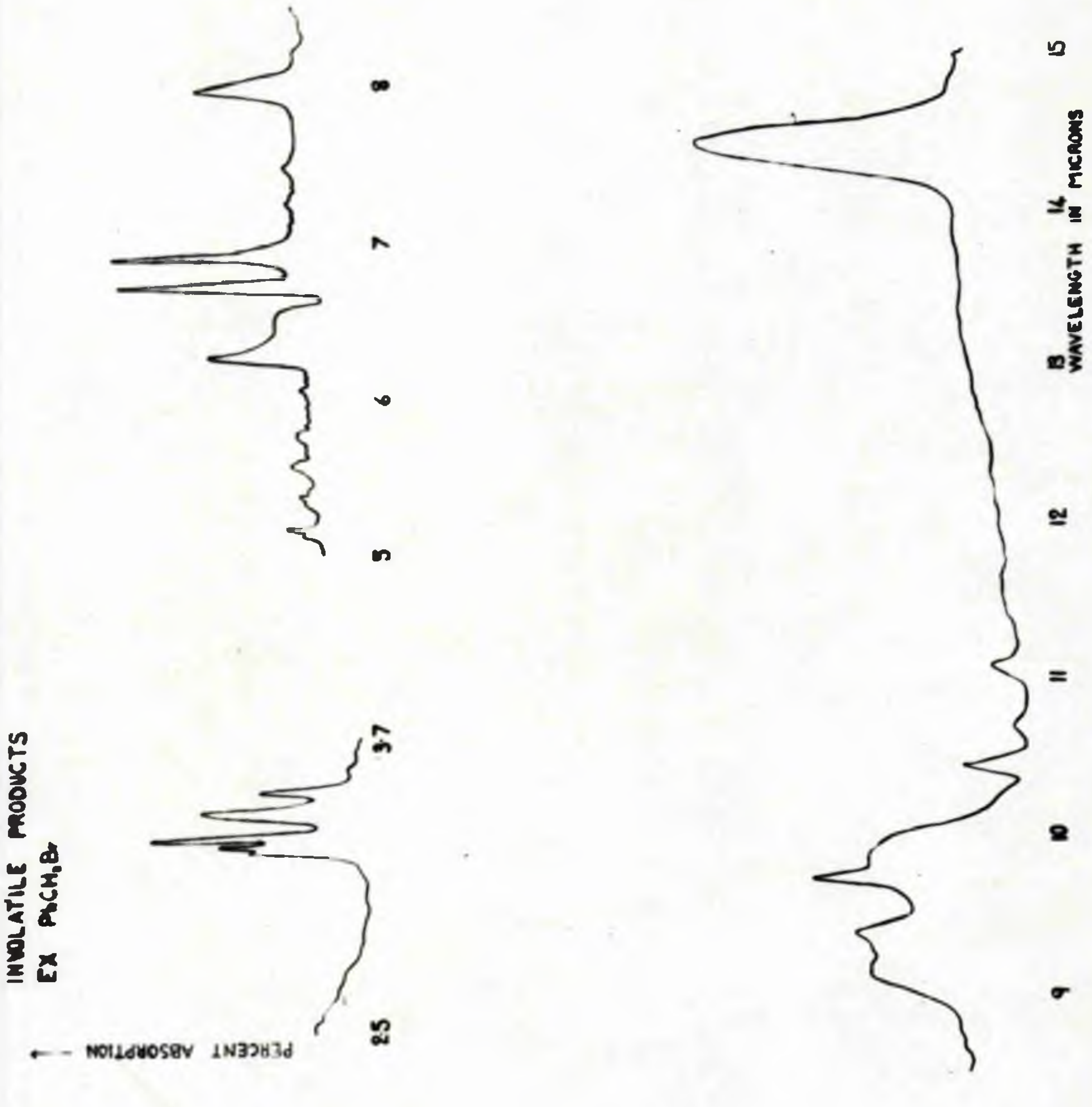

INVOLATILE PRODUCTS
EX PhCH$_2$Br
PERCENT ABSORPTION
2.5
3.7
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH IN MICRONS

Figure 20

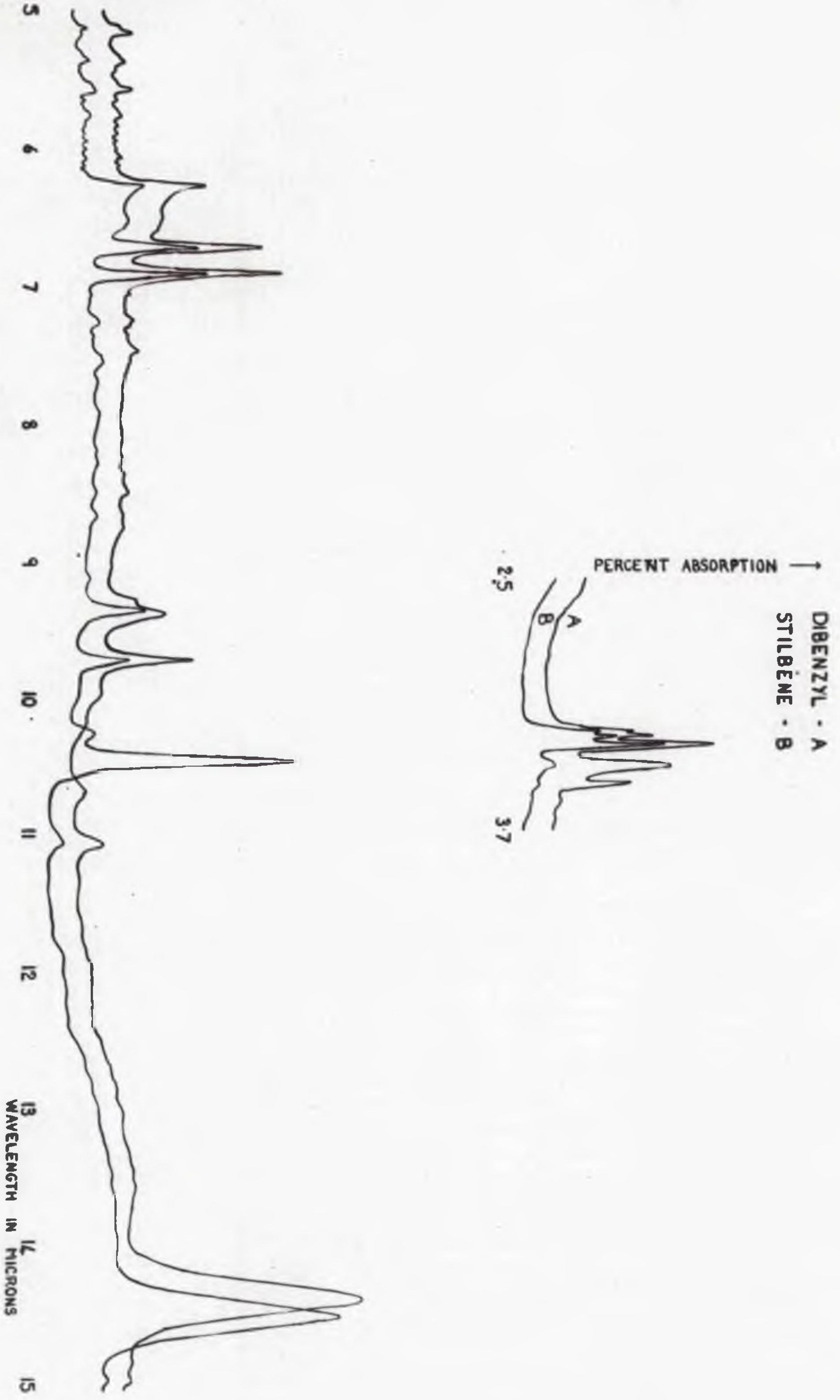

DIBENZYL - A
STILBENE - B
PERCENT ABSORPTION →
A
B
2.5
3.7
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH IN MICRONS

Figure 21

The absorption band from 230-240mμ shown in the product spectrum is probably due to a small amount of benzyl bromide still present, the benzyl bromide showing a maximum at 224mμ and decreasing to zero at 300mμ.

The extinction coefficients for diphenyl and the substituted diphenyls are of the order of those of stilbene, and the maxima occur at a slightly shorter wavelength than that of dibenzyl. If these compounds are present, the amounts must be very small, since there are no pronounced bands of absorption which cannot be assigned to dibenzyl or stilbene.

Two analytical techniques could be used in a further investigation: (1) infra-red spectrophotometry and (2) mass spectrometry.

(1) Examination of the Products by Infra-red Spectrophotometry

Of the products considered possible, diphenyl had a strong absorption peak at 12.8μ, methyl diphenyls at 12.2 and 9.9μ while diphenylmethane had a peak at 13.6μ. If these were present in sufficient quantity, they could be identified since there would be no interference between their absorption peaks and those of stilbene and dibenzyl.

The infra-red spectrum of the products of a particular experiment is shown in Fig.20, and comparison can be made between this and the spectra of pure stilbene and dibenzyl(Fig.21). The spectra were recorded in carbon tetrachloride solution, with pure carbon tetrachloride in the reference cell. The standard spectra show that stilbene in dibenzyl could be identified by the peak at 10.45μ.

Examination of the spectrum shows that stilbene is present in small quantity. There are no peaks at the wavelengths indicated above, so that diphenyl type compounds were proved to be absent or present in such small amounts that they were unidentifiable by infra-red spectroscopy.

There are certain peaks present, at 7.95μ and 9-10μ, in the product spectrum which are not present in the spectra of pure dibenzyl or stilbene. An explanation for their presence could not be given for quite some time. It was noticed that these peaks also occurred in the spectrum of the involatile products of o-chlorobenzyl bromide, and later work on the products of the decomposition of benzyl bromide using hydrogen iodide as a radical catcher again provided spectra with these peaks prominent. The intensity of these peaks varied in a random fashion and sometimes they were completely absent. It seemed apparent that such peaks were not due to any decomposition product, dependent on the nature of the catcher. One possibility was that oxygen was present during an experiment, although the apparatus was considered to be free of leaks. The sodium trap, used in the final de-oxygenation of the nitrogen carrier gas, had been in operation for four years and it was thought that the sodium might have been spent. The sodium was renewed but the effect on the nature of the spectra was nil. The spectra of many oxygenated benzyl type compounds were recorded but no clues were obtained.

Edwards' Silicone High Vacuum Tap Grease was used on the joints of the heater traps and it was thought desirable to examine a sample

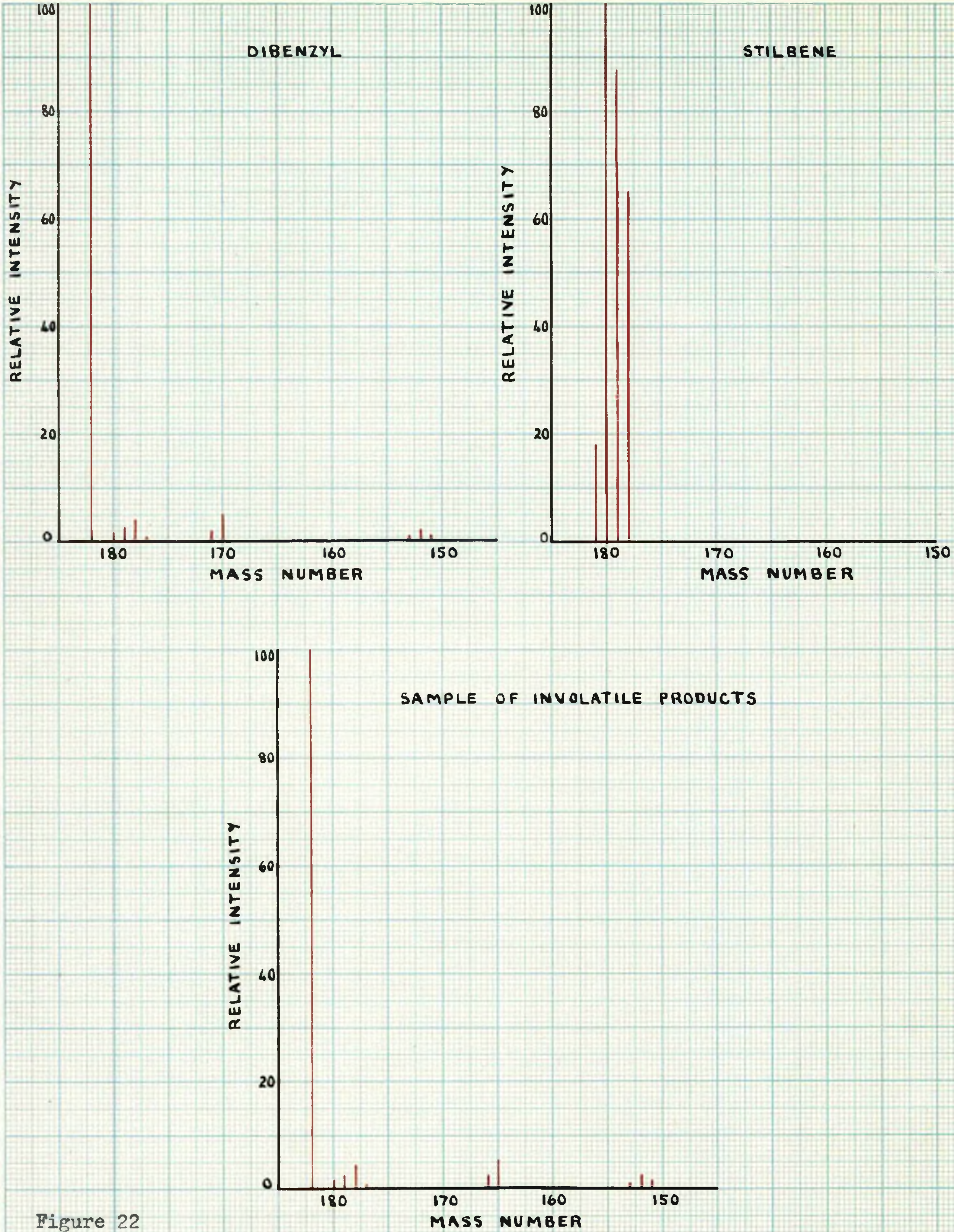

DIBENZYL
RELATIVE INTENSITY
100
80
60
40
20
0
180
170
160
150
MASS NUMBER
STILBENE
RELATIVE INTENSITY
100
80
60
40
20
0
180
170
160
150
MASS NUMBER
SAMPLE OF INVOLATILE PRODUCTS
RELATIVE INTENSITY
100
80
60
40
20
0
180
170
160
150
MASS NUMBER

Figure 22

of this in carbon tetrachloride solution. Strong absorption was noted in the regions indicated above. Reasonable care had been exercised in the removal of the tap grease from the cones of the traps, but during a run, these were kept fairly hot, and the silicone grease may have flowed and dissolved in the unchanged reactant or toluene. The broad band occurring at 9-10μ may be assigned to an Si - 0 - Si stretching frequency, and the peak at 7.95μ may be due to an $-Si(CH_3)_3$ rocking vibration[48].

(2) Examination of the Products by Mass Spectrometry

This method had the advantage that small amounts of material could be identified readily, provided that it had a sufficient vapour pressure to allow some of it into the 'head' of the mass spectrometer. For this reason the lines leading into the mass spectrometer were heated to 100°C.

Smith identified the solid products formed in the thermal decomposition of toluene. In the course of the investigation, she measured standard spectra of dibenzyl, stilbene, diphenyl, diphenylmethane and methyl diphenyls on the St. Andrews mass spectrometer. Dibenzyl and stilbene are reproduced in Fig.22. These are shown in the form of relative intensities of the peak heights at various values of m/e, the most prominent peak being assigned the value 100.

In the present analysis, 4.4mgm. of dibenzyl was injected as a reference marker. The region scanned covered the mass range from 138 to 185 . The peaks due to dibenzyl were well known and were easily identified. The relative intensities agreed well with those obtained by Smith.

A sample of solid product from a run was examined using the same accelerating potential and scanning over the same mass range as for the dibenzyl marker. The product spectrum is shown in diagrammatic form in Fig.22 and the relative intensities may be compared with those of pure dibenzyl and stilbene. The relative intensities of peaks of pure dibenzyl and run products are tabulated below. Again the convention adopted is to assign the value 100 to the most prominent peak.

Table 10

Mass No.	Relative Intensity Pure Dibenzyl	Relative Intensity Run Products
182	100	100
180	1.37	1.62
178	3.97	4.12
165	4.66	5.30
152	1.92	2.03

It can be seen that the relative intensities in two columns of the table are very similar. The 180^+ peak is of great interest, since this is the most intense peak in the stilbene spectrum. The fact that the relative intensity of this peak in the product spectrum is not greater than in the dibenzyl spectrum means that little stilbene is present. A further factor which would affect the intensity of the 180^+ peak is that stilbene is much more involatile than dibenzyl, and consequently a longer time would elapse before the maximum intensity of the 180^+ peak due to stilbene would be reached.

The peaks at mass number 168 for diphenylmethane and 4-methyldiphenyl, and at 167 for 4-4'-dimethyldiphenyl do not occur. The volatility of these compounds is of the same order as that of dibenzyl and they could be identified if they were present.

There are no other peaks in the spectrum which do not belong to the dibenzyl pattern.

Conclusion

The conclusion reached from the evidence provided by ultra-violet and infra-red spectrophotometry and by mass spectrometry is that the solid products of the decomposition of benzyl bromide, using toluene as a radical catcher, consist entirely of dibenzyl with a small amount of stilbene present there also.

Examination of the Gaseous Products

At the end of an experiment the nitrogen carrier gas was collected by means of a Toepler pump into a 100ccs. flask. The flask was removed and its contents examined on the mass spectrometer. I am indebted to Mr. J. Rhind for carrying out these analyses. A small amount of gas in the bulb was allowed to diffuse through a Metrosil porous plug into the mass spectrometer and its spectrum examined.

Before the gas from the bulb was injected into the system, the background had to be scanned over the region of interest, since the 2^+ peak from hydrogen, the 14^+ peak from nitrogen and the 16^+ peak from oxygen are always present to a slight extent. The background from 27^+ to 32^+ was also examined.

Hydrogen present in the carrier gas could be detected simply by the increase in intensity of the 2^+ peak.

The standard spectrum of methane shows peaks at 12^+, 13^+, 14^+, 15^+, in addition to 16^+, the relative intensities being in the ratio 2.41 : 7.86 : 16.98 : 85.5 : 100. The 12^+ and 13^+ peaks are too small to examine and the 14^+ peak is seriously affected by the presence of the large amount of nitrogen carrier gas, since nitrogen contributes to the peak height in the form of N_2^{++}. Methane could most readily be identified and its amount measured by reference to the 15^+ and 16^+ peaks.

Table 11 shows the intensities of the 2^+, 15^+ and 16^+ peaks in millivolts in the two determinations.

Table 11

Experiment No.	Intensities in millivolts		
	$H_2^+(2^+)$	$CH_3^+(15^+)$	$CH_4^+(16^+)$
1	27	16	18
2	48	35	32

If the ratio of the H_2^+ and CH_4^+ intensities are compared in the two cases, then $H_2^+/CH_4^+ = 27/18 = 48/32$ i.e. $H_2^+/CH_4^+ = 60/40$. But the ratio of the sensitivities of H_2/CH_4 was 45.1/39.6, so that the real ratio of $H_2/CH_4 = 57/43$.

Szwarc et al.[4] indicate that the ratio of $H_2/CH_4 = 60/40$.

Examination of the Liquid Products

The appearance of methane as a secondary product of the reaction prompted a search for benzene in the product mixture, since methane probably arose from an induced split of the toluene molecule, and therefore phenyl radicals might be expected to be present. These might ultimately give rise to benzene.

It was considered that benzene would be collected in the trap cooled in acetone-solid carbon dioxide mixture together with toluene, unchanged benzyl bromide and the solid products. Distillation under suitable conditions would separate the benzene-toluene mixture from the other components of the mixture. Benzene has a strongly absorbing peak at 14.9μ in the infra-red region, which is due to the out-of-plane bending vibration of the aromatic C – H bond. In toluene this band appears at a lower wavelength.

The first attempt at isolating benzene was made by distilling the more volatile products at a temperature of -10°C. into a trap contained in an acetone-solid carbon dioxide bath at -70°C. The volatile products were dissolved in carbon tetrachloride and examined on the infra-red spectrophotometer. The spectrum obtained was that of toluene alone and no benzene absorption was found at 14.9μ.

BENZENE
IN PRODUCTS

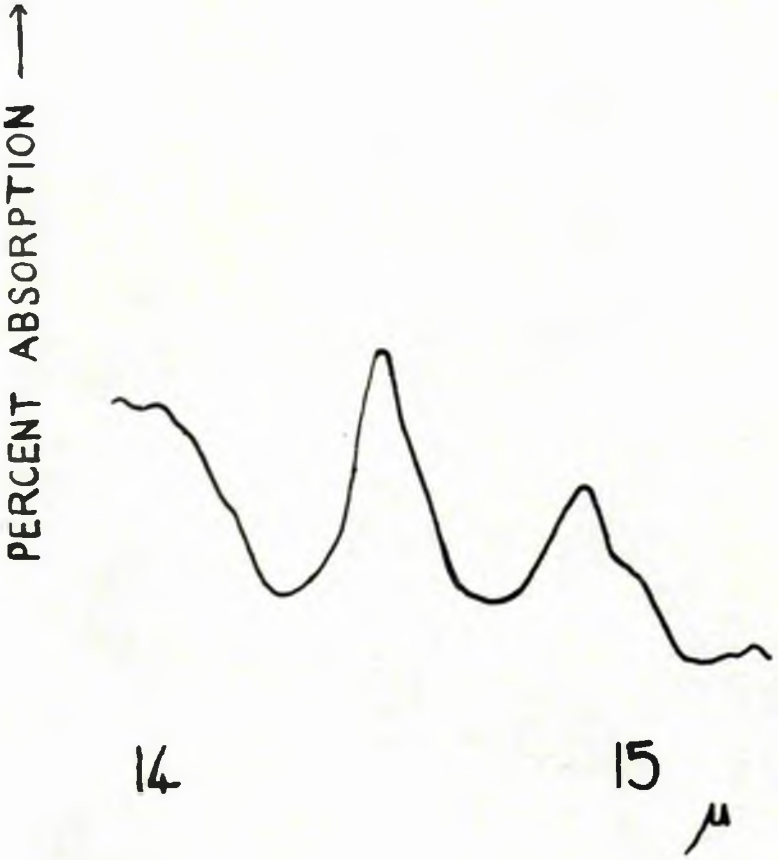


Figure 23

On further consideration, it was felt that the benzene would be produced in such small amounts that it would probably pass through the heater trap and be collected under liquid air. Consequently, experiments were performed in which the products appearing in the colder trap were distilled into vessels containing degassed carbon tetrachloride and examined as before on the infra-red spectrophotometer. The spectrum indicated that a small amount of toluene had been collected, but a peak was evident at 14.9μ (Fig.23), proving that benzene was indeed a constituent of the products.

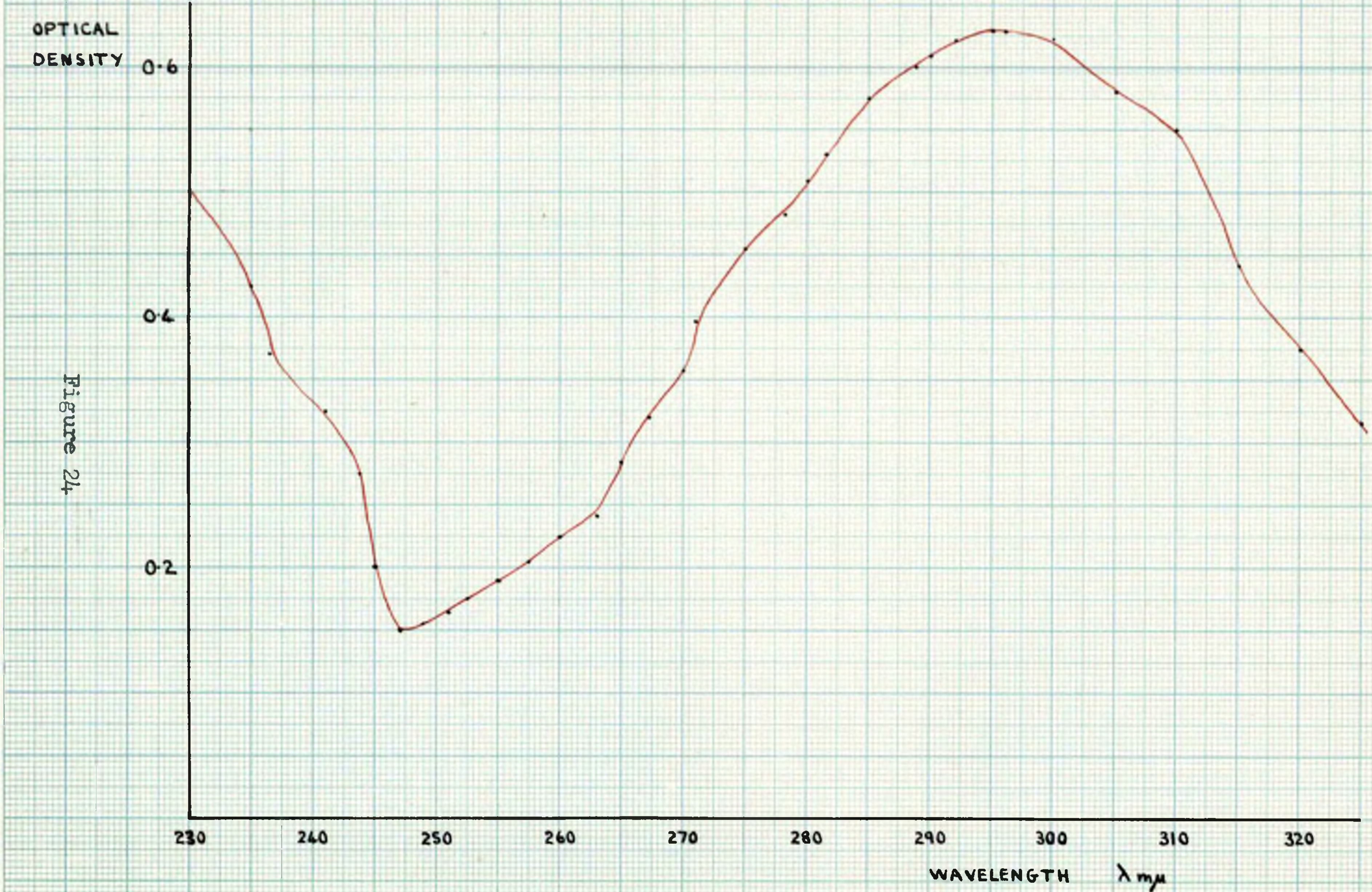

OPTICAL
DENSITY
0·6
0·4
0·2
230
240
250
260
270
280
290
300
310
320
WAVELENGTH λ mμ

Figure 24

EXAMINATION OF THE INVOLATILE PRODUCTS OF THE PYROLYSIS OF THE CHLOROBENZYL BROMIDES USING TOLUENE AS A RADICAL CATCHER

o-Chlorobenzyl Bromide

The products remaining after the removal of toluene and unchanged bromide were not entirely solid, but seemed to be a mixture of solid and liquid constituents. Since o-chlorodibenzyl is a liquid at room temperature, the indications were that this might be one of the expected products.

A preliminary examination by ultra-violet spectroscopy showed a large band of absorption at 296mμ indicating the presence of stilbene but the dibenzyl pattern was not at all evident (Fig.24). The strongly absorbing stilbene had obliterated the pattern of the weakly absorbing dibenzyl.

The two methods employed in the analysis of the products of the pyrolysis of benzyl bromide were again used here.

(1) Observations from Infra-red Spectrophotometer Studies

Standard spectra were not available in the literature for the possible involatile products of o-chlorodibenzyl, o-chlorostilbene, o-o'-dichlorodibenzyl and o-o'-dichlorostilbene.

Pure o-chlorostilbene and o-chlorodibenzyl were prepared (see previous section) and their spectra were recorded in carbon tetrachloride solution. For o-chlorostilbene the reference cell contained carbon tetrachloride solvent, but in the case of

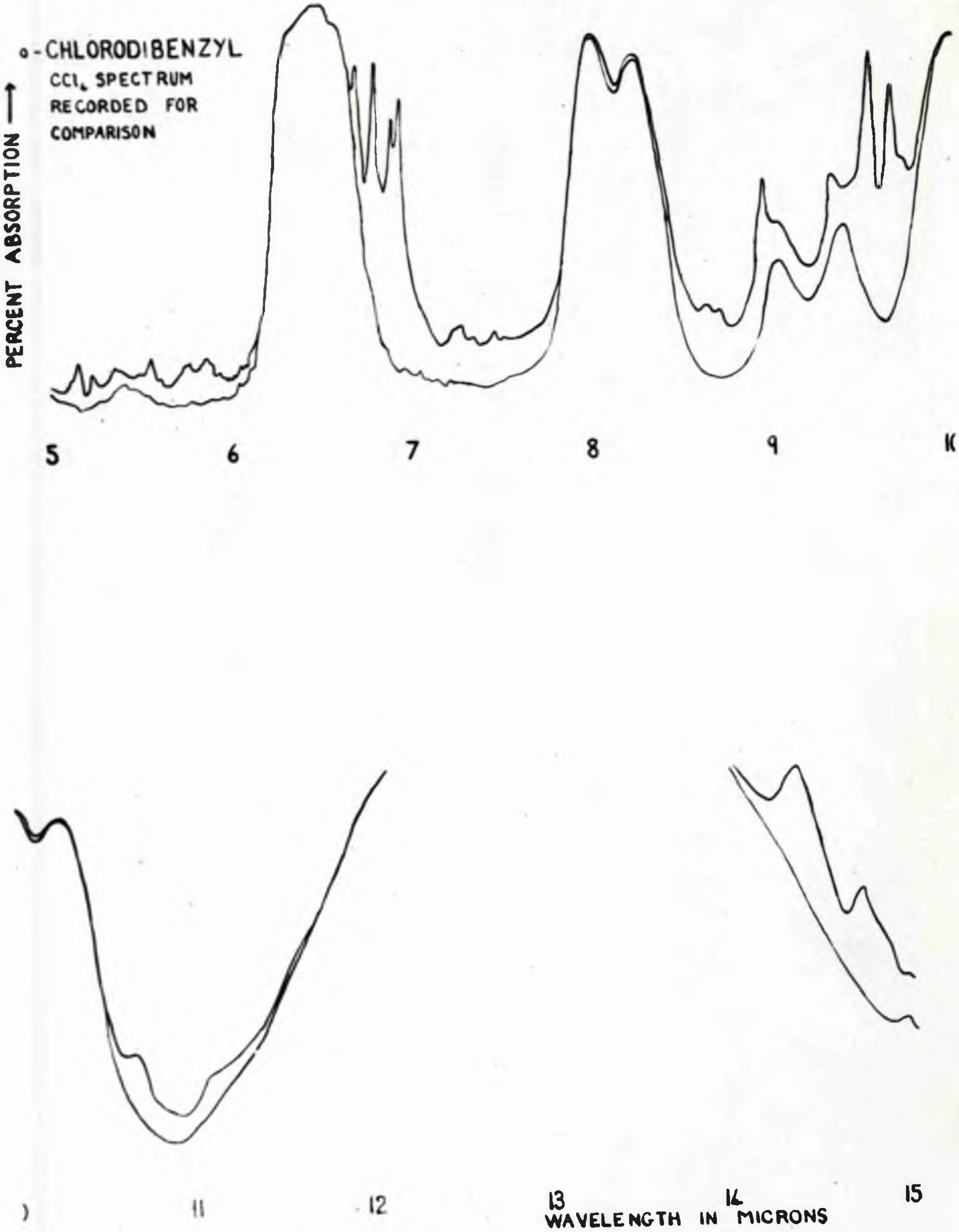

o-CHLORODIBENZYL
CCl₄ SPECTRUM RECORDED FOR COMPARISON
PERCENT ABSORPTION
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH IN MICRONS

Figure 25

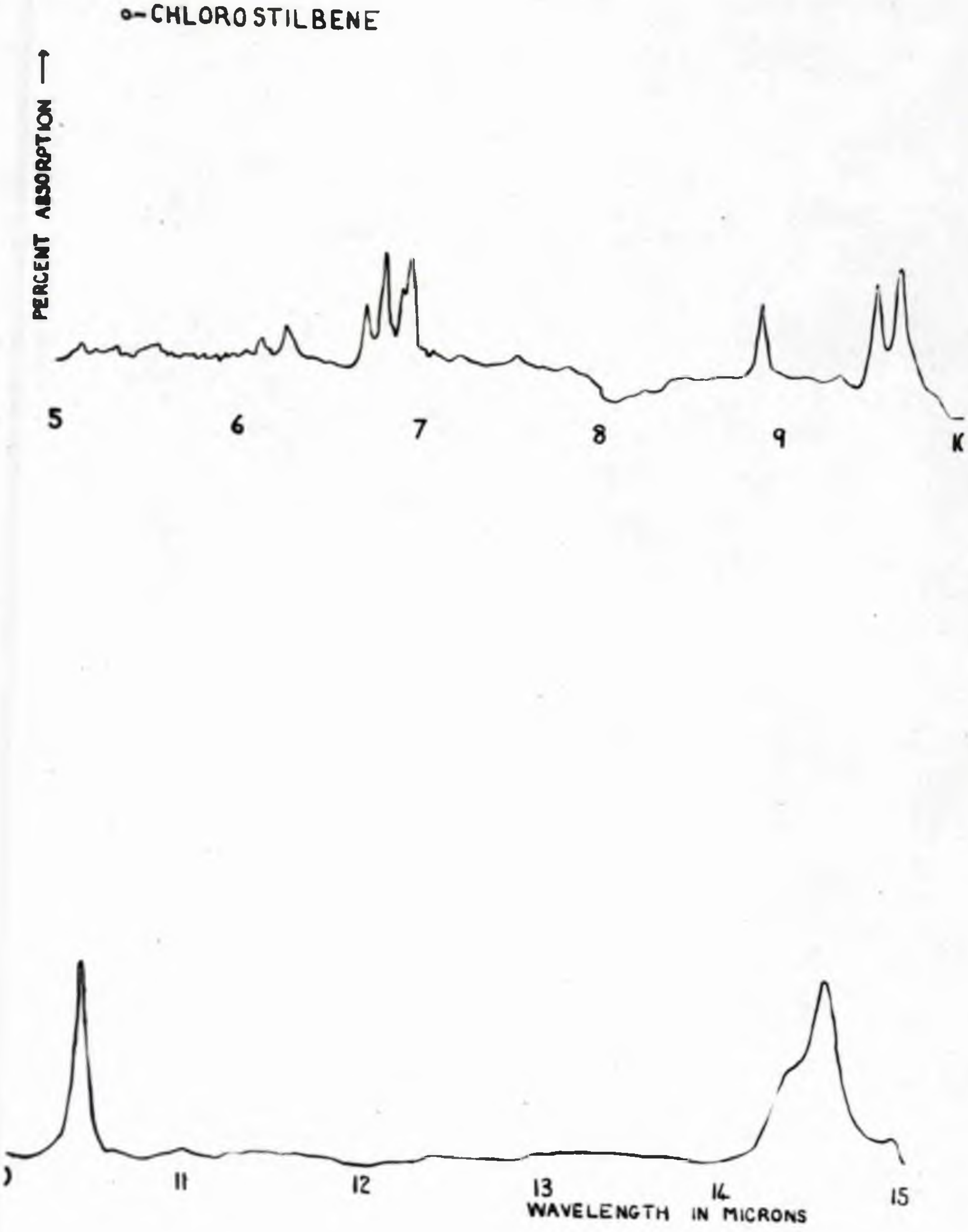

o-CHLOROSTILBENE
PERCENT ABSORPTION →
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH IN MICRONS

Figure 26

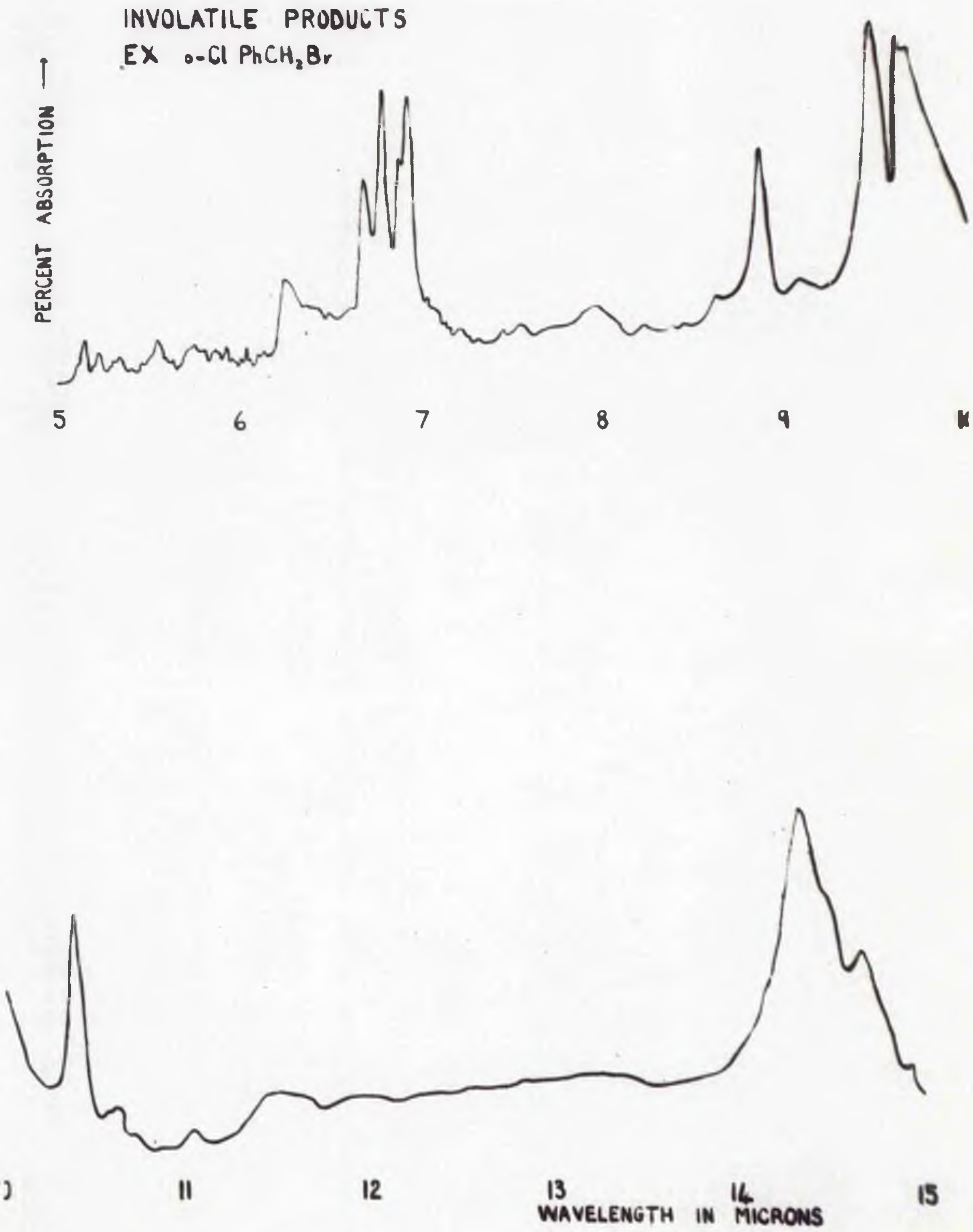

INVOLATILE PRODUCTS
EX o-Cl PhCH$_2$Br
PERCENT ABSORPTION →
5
6
7
8
9
11
12
13
14
15
WAVELENGTH IN MICRONS

Figure 27

o-chlorodibenzyl the reference cell was blank and the spectrum of pure carbon tetrachloride was recorded for comparison.

The main difference in the spectra of the chloro substituted compounds from those of the unsubstituted was the presence of a peak at 8.9μ which did not occur in dibenzyl or stilbene, while the unsubstituted compounds had identifiable peaks at 9.35μ and 9.725μ which did not occur in the substituted compound spectra. The spectra of o-chlorodibenzyl and o-chlorostilbene are shown in Fig.25 and Fig.26.

The spectrum of the involatile products (Fig.27) indicated the presence of peaks at 9.35μ and 9.725μ which was evidence for the presence of unsubstituted compounds, but it was not possible to say whether these were dibenzyl or stilbene or both. There was however a prominent peak at 10.425μ which signified the presence of stilbenes, but, once again, it was not possible to say whether this was indicative of o-chlorostilbene or of stilbene itself or of both. The prominent peak at 8.9μ proved that chloro substituted compounds were components of the products.

The conclusion reached from a study of the infra-red spectra of the products is that there are both chloro substituted and unsubstituted compounds in the mixture, that these compounds consist of dibenzyls and stilbenes but it is not possible to say from the evidence whether the dibenzyls and stilbenes consist of the unsubstituted or substituted compounds or both.

Because of the similarity of the spectra of the unsubstituted and

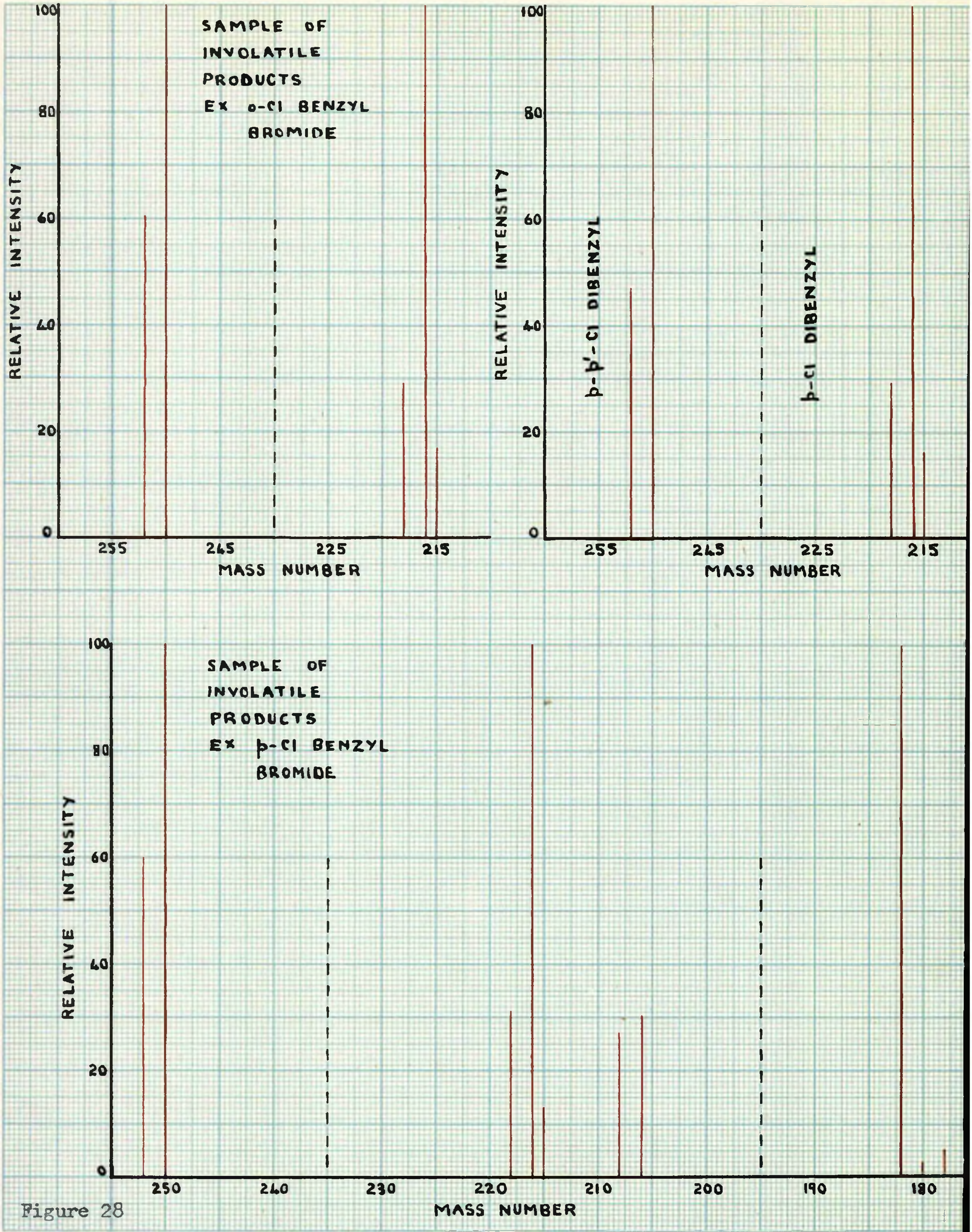

SAMPLE OF INVOLATILE PRODUCTS EX o-Cl BENZYL BROMIDE
RELATIVE INTENSITY
100
80
60
40
20
0
255
245
225
215
MASS NUMBER
p-p'-Cl DIBENZYL
p-Cl DIBENZYL
RELATIVE INTENSITY
100
80
60
40
20
0
255
245
225
215
MASS NUMBER
SAMPLE OF INVOLATILE PRODUCTS EX p-Cl BENZYL BROMIDE
RELATIVE INTENSITY
100
80
60
40
20
0
250
240
230
220
210
200
190
180
MASS NUMBER

Figure 28

monosubstituted chloro compounds, the preparation and spectral examination of the disubstituted chloro compounds was not pursued.

(2) Observations from Mass Spectrometer Studies

The products which were expected from this decomposition were dibenzyl, o-chlorodibenzyl, o-o'-dichlorodibenzyl and the corresponding stilbenes. These covered the mass range from 178 to 252. It was important to be able to assign to the various peaks appearing on the scan the correct mass numbers. For this reason, dibenzyl, which had an easily identifiable spectrum, and the mercury peaks, which were always evident in a background scan, were used as markers.

Calvert[49] examined the spectra of samples of p-chlorodibenzyl and p-p'-dichlorodibenzyl and measured the relative intensities of the peaks. It was assumed that the ortho compounds would display the same peaks of the same relative intensity.

The sample was admitted into the mass spectrometer and after about fifteen minutes, the spectrum was examined. The dibenzyl pattern was prominent and a single peak was apparent in the region expected for o-chlorodibenzyl but there were no peaks in the 250-255 mass region.

The occurrence of a cold spot in the lines into the mass spectrometer explained the incomplete nature of the spectrum. The temperature of these lines was therefore increased.

The spectrum over the mass range was therefore re-examined. The mass spectra obtained by Calvert and the product spectrum are shown in diagrammatic form in Fig.28. The pattern of the product spectrum in the 215-220 mass region closely resembled that obtained for p-chlorodibenzyl, although the resolution in the present case was not as good. Two peaks also occurred at mass numbers 250 and 252, but their intensity was rather low.

Table 12 gives a comparison between the relative intensities of the peaks obtained in the present work and the standard peaks obtained by Calvert.

Table 12

Mass No.	Relative Intensities Sample	Relative Intensities (Calvert's Data)	
		p-Cl dibenzyl	p-p'-diCl dibenzyl
215	17	15.3	-
216	100	100	-
218	29.3	29.4	-
250	100	-	100
252	60	-	47.2

The fact that the relative intensities of the peaks in the two mass regions are in agreement with those obtained for the standard spectra of p-chlorodibenzyl and p-p'-dichlorodibenzyl seems to be good evidence for suggesting that o-chlorodibenzyl and o-o'-dichlorodibenzyl appear in the products.

A comparison of intensities of peaks from dibenzyl with those from o-chlorodibenzyl and o-o'-dichlorodibenzyl cannot be made since we have no knowledge of the relative volatilities of these compounds, and the maximum intensities for the substituted dibenzyls may not have been reached.

The qualitative conclusions which may be drawn about the nature of the involatile products of the decomposition of o-chlorobenzyl bromide, using toluene as a radical catcher, are that dibenzyl, o-chlorodibenzyl and o-o'-dichlorodibenzyl are present; that there are small amounts of stilbene also, but whether all three stilbenes are there, it is not possible to say. There is no evidence from any of the methods of analysis used, to suggest that there are any involatile compounds other than dibenzyls and stilbenes produced in the decomposition.

p-Chlorobenzyl Bromide

The nature of the involatile products of the decomposition of p-chlorobenzyl bromide was examined by mass spectrometry in a similar fashion to that adopted for the o-chloro compound.

The pattern obtained for the spectra was similar, although a much longer time elapsed before the peaks in the 250-255 mass region became evident, which might suggest a rather greater involatility than for the ortho substituted compounds. In actual fact, it was four hours after the sample was injected into the mass spectrometer before the peaks became noticeable.

The spectra of the products are shown in diagrammatical form of relative intensity against mass number in Fig.28.

The table gives a comparison between the intensities of the peaks obtained in the present work and the standard peaks obtained by Calvert on p-chlorodibenzyl and p-p'-dichlorodibenzyl.

Table 13

Mass No.	Relative Intensities Sample	Relative Intensities Dibenzyl	Relative Intensities (Calvert's Data)	
			p-Cl dibenzyl	p-p'-diCl dibenzyl
178	5.0	3.97	-	-
180	2.8	1.37	-	-
182	100	100	-	-
215	13.4	-	15.3	-
216	100	-	100	-
218	31.3	-	29.4	-
250	100	-	-	100
252	60	-	-	47.2

The similarity in the intensities of the peaks in the mass regions 215-218 and 250-252 supports the conclusion that p-chlorodibenzyl and p-p'-dichlorodibenzyl are two of the main constituents of the products.

The increase in intensity of the 180^+ and 178^+ peaks in comparison with those of the standard dibenzyl is probably due to the contribution made by stilbene, which has its most intense peak in this region at mass number 180, and a peak of 65% intensity at 178 (see Fig.22).

It is deduced that the products of decomposition are composed of dibenzyl, p-chlorodibenzyl, p-p'-dichlorodibenzyl and a small amount of stilbene. Proof of the occurrence of substituted stilbenes cannot be obtained from this mass spectral study.

It is noticeable in the diagrammatic representation of the spectrum of the products in Fig.28 that two peaks appear at mass numbers 206 and 208. These most likely arise from the parent p-chlorobenzyl bromide, a small amount of which might still have been present with the products. p-Chlorobenzyl bromide would be expected to give three peaks at mass numbers 204, 206 and 208, originating from the bromine isotopes 79 and 81 and the chlorine isotopes 35 and 37. The 204^+ peak would of course be masked by the mercury isotopic peak occurring at that mass number.

THE THERMAL DECOMPOSITION OF BENZYL BROMIDE USING HYDROGEN IODIDE AS A RADICAL CATCHER

It was thought that an independent value for the energy of activation for the decomposition of benzyl bromide might be obtained by using hydrogen iodide as a radical catcher instead of toluene. The bond strength in hydrogen iodide is 71 k.cals./mole and distinctly less than the estimates for the side-chain C - H bond in toluene, and it ought to be a more efficient radical acceptor. Although the thermal decomposition of hydrogen iodide has the low energy of activation of 44 k.cals./mole, the process is bimolecular and at the concentrations used in the low pressure flow systems of this work the rate of decomposition is low.

Hydrogen iodide was also used in the hope that some further evidence might be obtained for the presence of a change from first to second order reaction at low pressures of benzyl bromide. Since hydrogen iodide is a much less complex molecule than toluene, it might be expected to be much less efficient as a third body in energy transfer.

By analogy with the mechanism for the primary decomposition of benzyl bromide using toluene as a catcher, it was considered that the reaction might proceed as follows:

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2- + -Br$$

$$Br- + HI \longrightarrow HBr + I-$$

$$C_6H_5CH_2- + HI \longrightarrow C_6H_5CH_3 + I-$$

$$I- + I- \rightleftharpoons I_2$$

The rate of reaction might then be followed by measurement of the rate of production of hydrogen bromide, toluene or iodine. For practical reasons it was best to analyse for iodine, since hydrogen bromide would be produced in quantities which were very small compared with the amount of hydrogen iodide catcher present. These would of course be collected together in the trap surrounded by liquid air, and the analysis of hydrogen bromide would be difficult. It would also be difficult to analyse quantitatively for toluene since it would be distributed between the acetone-solid carbon dioxide trap and the liquid air trap.

Preliminary Experiments

The first experiment was carried out at a temperature of 775°K. The aim was to reproduce the conditions for partial pressure of benzyl bromide, partial pressure of radical acceptor and contact time, as used in the decomposition at this temperature with toluene as the acceptor. The percentage decomposition then was 9%, but on analysis of iodine in this experiment, the percentage decomposition was calculated to be 71%.

The temperature was lowered in succeeding experiments, as shown in the table, until a reasonable percentage decomposition was obtained. The results using toluene as a catcher at similar temperatures are shown for comparison.

Table 14

Partial Pressure Benzyl Bromide mms.	Partial Pressure Hydrogen Iodide mms.	Contact Time secs.	% Decomp.	Temp. °K
With added Hydrogen Iodide				
0.243	1.49	1.46	71	775
0.252	1.62	1.66	57	737.5
0.176	1.31	2.08	22.1	704.5
With added Toluene				
0.201	1.38	1.38	8.8	775
0.200	2.59	2.12	2.1	736

At the time, two explanations seemed possible for the marked increase in reaction rate using hydrogen iodide as a radical catcher instead of toluene. Hydrogen iodide was either very much more reactive than toluene or the supposed reaction mechanism was very incorrect. The first possibility was considered to be extremely unlikely, since at no time had bromine been obtained as one of the products in the decomposition using toluene. This would have been the case if free bromine atoms were not being caught by the toluene.

The high percentage decomposition made it seem most unlikely that all the radicals produced in the initial split of benzyl bromide were captured by the hydrogen iodide. It seemed desirable therefore to examine the variation of percentage decomposition with

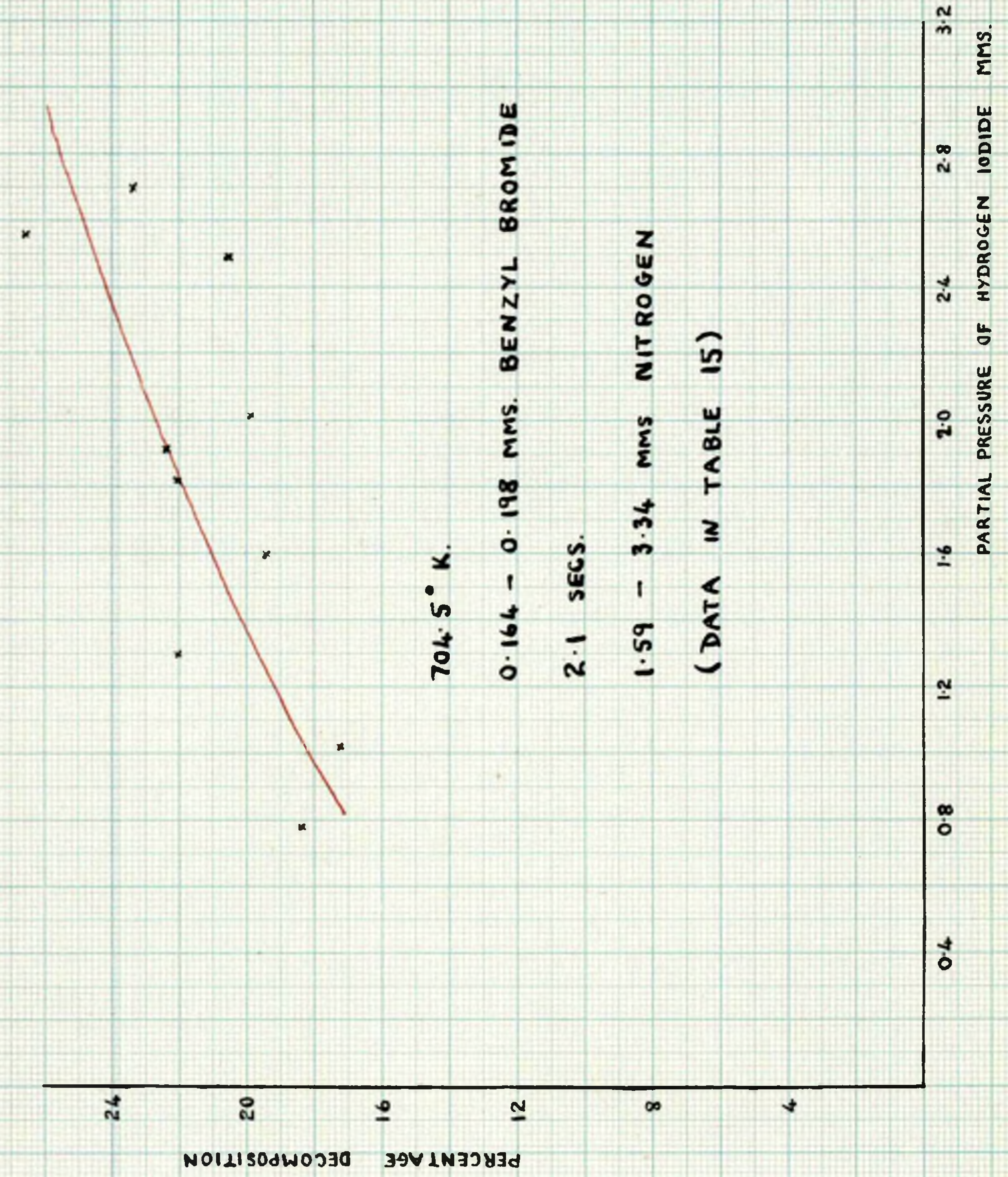

704·5° K.
0·164 – 0·198 MMS. BENZYL BROMIDE
2·1 SECS.
1·59 – 3·34 MMS NITROGEN
(DATA IN TABLE 15)
PERCENTAGE DECOMPOSITION
4
8
12
16
20
24
PARTIAL PRESSURE OF HYDROGEN IODIDE MMS.
0·4
0·8
1·2
1·6
2·0
2·4
2·8
3·2

Figure 29

partial pressure of hydrogen iodide.

If part or all of the suggested decomposition mechanism were incorrect, independent analyses of the other products of decomposition, toluene and hydrogen bromide, would be necessary.

Effect of Variation of Partial Pressure of Hydrogen Iodide

An attempt was made to produce conditions similar to those obtaining in the decomposition using toluene as a catcher, but also such that the radicals would be captured by the hydrogen iodide. The partial pressure of benzyl bromide was approximately 0.18mms., the contact time 2.1secs. The temperature was 704.5°K while the hydrogen iodide partial pressure was varied between 0.78 and 2.70mms. It can be seen from Fig.29, the data for which appear in Table 15 overleaf, that the percentage decomposition increased with increasing partial pressure of hydrogen iodide.

It seemed therefore that hydrogen iodide was not acting as a completely efficient catcher. An alternative possibility was that the reaction $C_6H_5CH_2- + HI \longrightarrow C_6H_5CH_3 + I-$ was not complete and that, at the decomposition rate involved, there was a competing reaction $C_6H_5CH_2- + I_2 \longrightarrow C_6H_5CH_2I + I-$. The latter is an exothermic reaction and would be feasible.

Because of these possibilities it was decided to examine the products of the decomposition for benzyl iodide, and to estimate quantitatively the amount of iodide formed, other than molecular iodine.

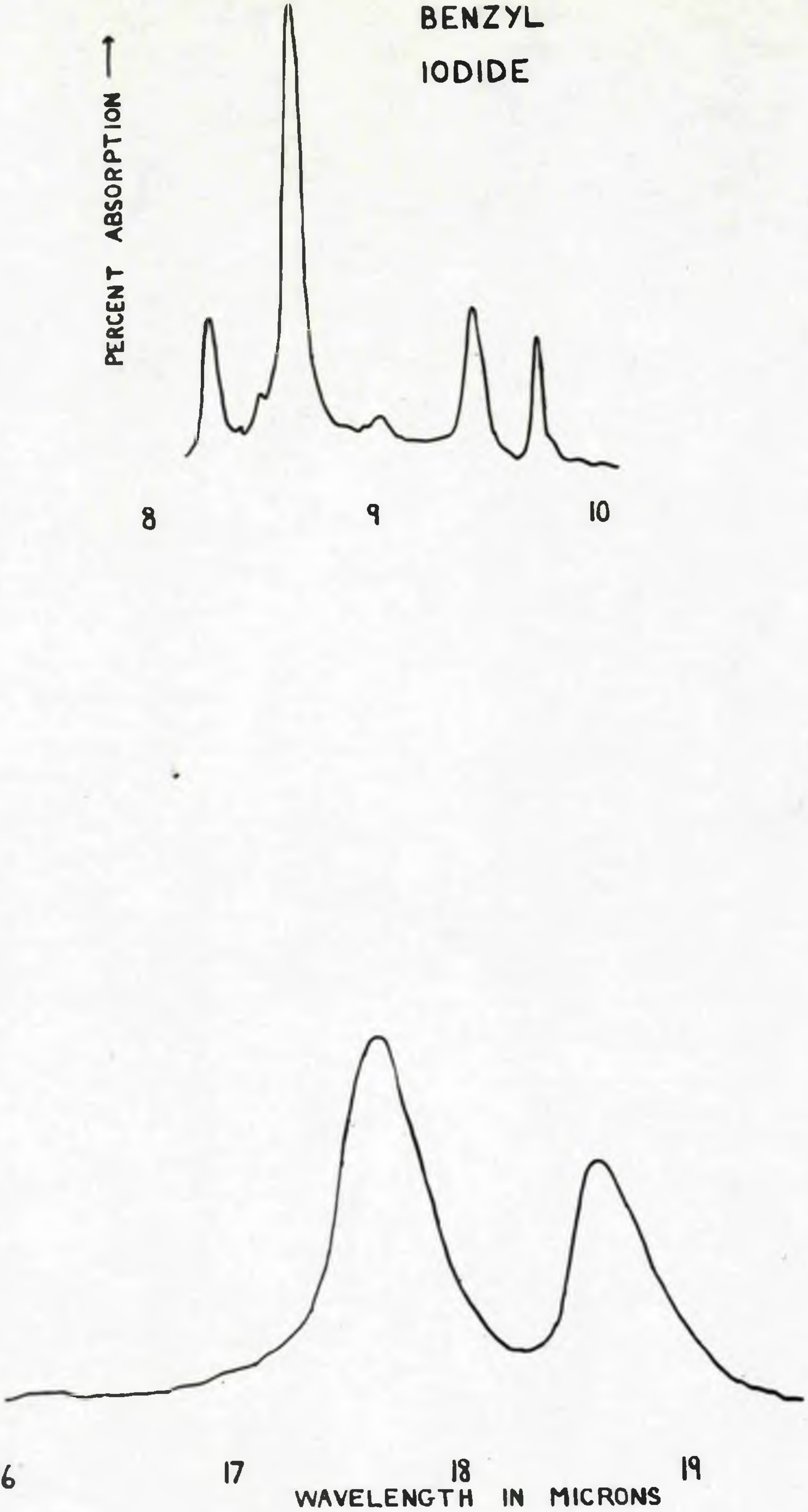

BENZYL
IODIDE
PERCENT ABSORPTION →
8
9
10
16
17
18
19
WAVELENGTH IN MICRONS

Figure 30

Table 15

Partial Pressure Benzyl Bromide mms.	Partial Pressure Hydrogen Iodide mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$
0.198	0.785	3.34	2.14	18.6	0.087
0.164	1.025	3.16	2.08	17.0	0.090
0.164	1.025	3.16	2.08	17.1	0.090
0.176	1.306	2.82	2.08	22.1	0.120
0.180	1.590	2.52	2.16	19.35	0.100
0.175	1.820	2.20	2.11	22.0	0.119
0.172	1.910	2.20	2.08	22.4	0.122
0.177	2.020	2.23	2.14	19.8	0.108
0.185	2.490	1.77	2.24	20.6	0.103
0.170	2.560	1.59	2.13	26.7	0.146
0.166	2.700	1.59	2.13	23.4	0.134

In the above table, k sec.$^{-1}$ is the calculated first order rate constant based on the amount of iodine produced.

The Qualitative and Quantitative Analysis for Benzyl Iodide

The infra-red spectrum of a sample of pure benzyl iodide (Fig.30) showed that it had a very strong absorption peak at 8.65μ. There was no interference from the absorption peaks of benzyl bromide, and the presence of this peak in the product sample spectrum seemed good

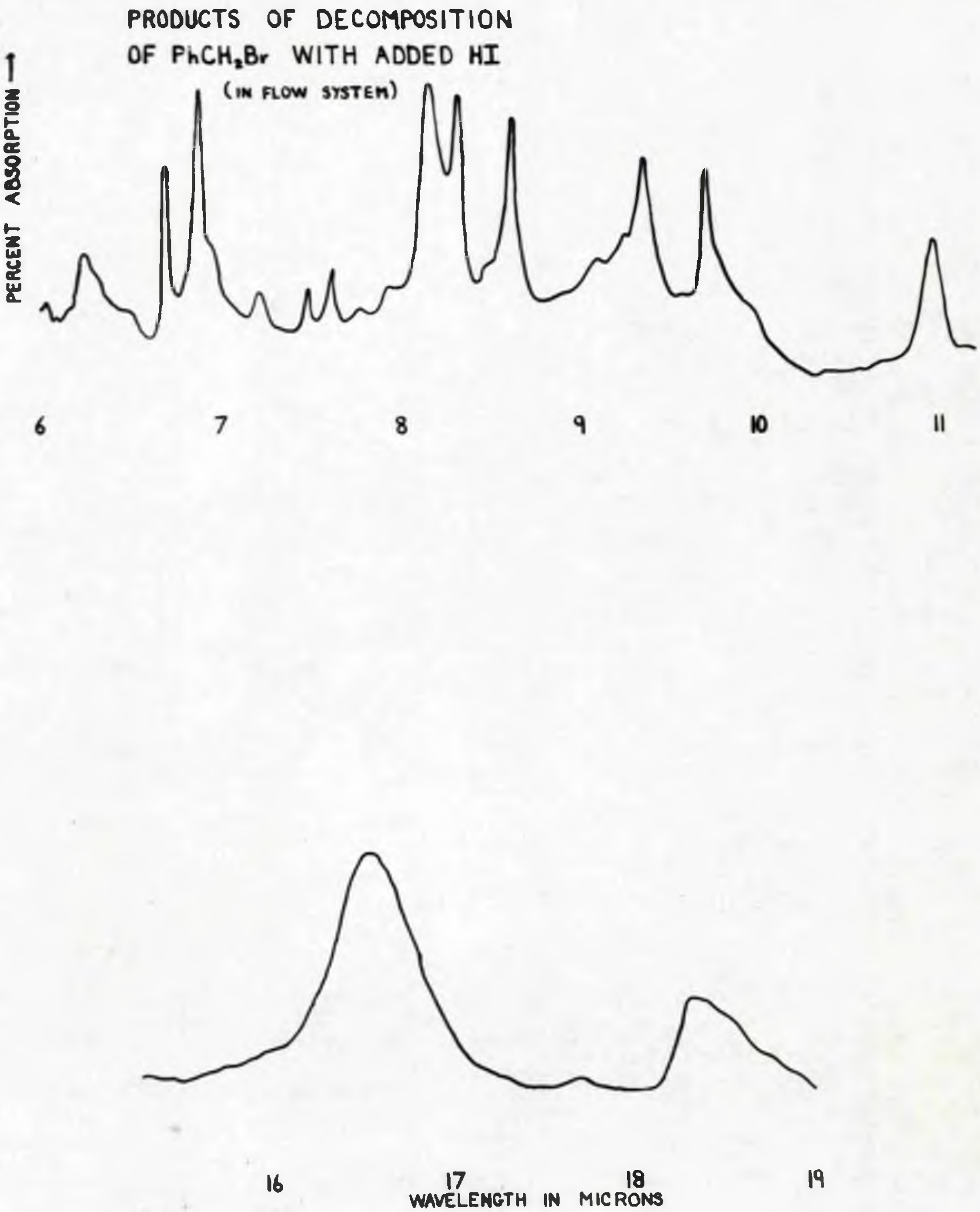

PRODUCTS OF DECOMPOSITION
OF PhCH₂Br WITH ADDED HI
(IN FLOW SYSTEM)
PERCENT ABSORPTION →
6
7
8
9
10
11
16
17
18
19
WAVELENGTH IN MICRONS

Figure 31

evidence for the presence of benzyl iodide. The spectrum was measured using a 0.8mm. cell fitted with KBr plates, in an attempt to pick up the C - I vibration for benzyl iodide. This band occurs at 17.65μ.

An analysis of products of the heater trap showed the peak at 8.65μ clearly, while the peak at 17.65μ could just be detected in the solution of low concentration of benzyl iodide in benzyl bromide (Fig.31).

Over a series of runs at different temperatures the total 'iodide', which consisted of iodine plus benzyl iodide, collected in the heater trap was measured by the method used for the analysis of hydrogen iodide (see 'Analysis of Products and Reactants').

The table gives the number of moles of total 'iodide' and the number of moles of molecular iodine measured in a series of runs.

Table 16

Temp. ^{o}K	Partial Pressure Benzyl Bromide mms.	Partial Pressure Hydrogen Iodide mms.	Contact Time secs.	Total 'Iodide' Moles/sec.$x10^{8}$	Iodine Moles/sec.$x10^{8}$
679.5	0.123	1.23	1.81	13.19	8.02
686	0.236	1.685	2.46	16.94	10.96
714	0.246	1.52	1.94	38.38	29.4
724	0.210	1.51	1.45	32.60	24.65
724.5	0.213	1.61	1.55	29.53	20.2

The data are not extensive enough and there are too many variables, notably contact time and benzyl bromide partial pressure, but it does seem that the percentage of benzyl iodide in the total 'iodide' is greater at lower temperatures than it is at higher temperatures. If a comparison is made between the first and fourth examples in Table 16, the percentage of iodine present as benzyl iodide in relation to the total 'iodide' in forms other than hydrogen iodide is 39.2 at the lower temperature and 24.4 at the higher.

It is reasonable to expect less benzyl iodide at high temperatures than at low, since at temperatures involved in the decomposition, benzyl iodide would not be expected to be stable.

The Analysis of Other Products of Decomposition of Benzyl Bromide Using Hydrogen Iodide as Radical Catcher

Toluene

The identification of toluene in the products was attempted by use of infra-red spectroscopy.

Synthetic mixtures of toluene in benzyl bromide were prepared and examined on the infra-red spectrophotometer to try to decide which were the best peaks in the toluene spectrum to use for identification when small quantities of toluene were present in large amounts of benzyl bromide. Four mixtures were prepared containing 8.5, 11.3, 20.3 and 34 moles percent of toluene in benzyl bromide. From the spectra, it was considered that solutions containing more than 20.3 moles percent of toluene in benzyl bromide gave spectra in which

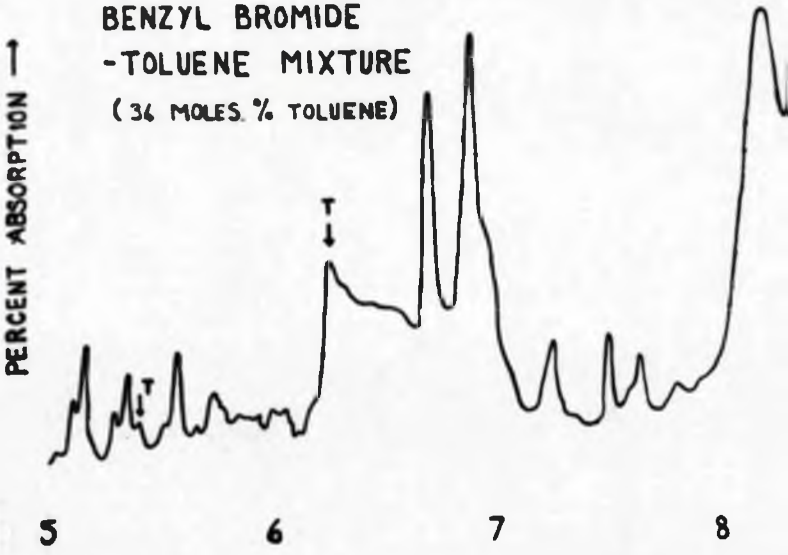
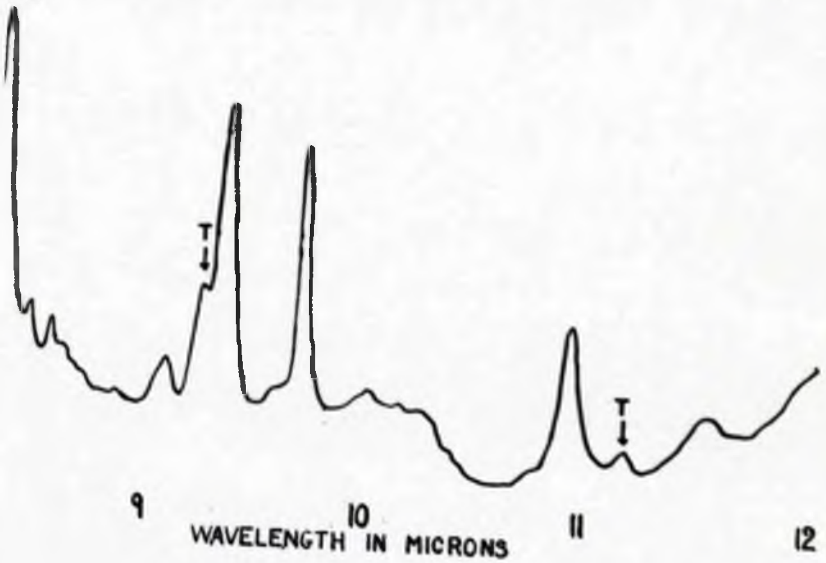

BENZYL BROMIDE
-TOLUENE MIXTURE
(36 MOLES % TOLUENE)
PERCENT ABSORPTION
T
T
5
6
7
8

Figure 32


T
T
9
10
11
12
WAVELENGTH IN MICRONS

toluene could be readily detected by the presence of peaks at 11.175, 9.25, 6.25 and 5.4μ. These peaks are indicated by the letter T in the spectrum of benzyl bromide containing 34% toluene in Fig.32

An experiment was performed at 704.5°C. in which collection of products was prolonged for thirty minutes to ensure collection of a sufficient amount of toluene. No separation of the products was undertaken and the total products and unchanged reactants were collected in a trap immersed in liquid air. The contents were dissolved in carbon tetrachloride, which was distilled off until a solution of suitable concentration for examination on the infra-red spectrometer was obtained. The moles percent of iodine was 20.6 of the benzyl bromide so that toluene was likely to be there in sufficient quantity for detection.

A spectrum of the products indicated the presence of small peaks at 5.4 and 11.2μ, a shoulder on the benzyl bromide peak at 9.25μ and an increase in intensity of the peak at 6.25μ. These features were present in some other spectra recorded in this investigation. Because of the low intensity of the peaks, no attempt was made at a quantitative estimation of toluene. The intensities could have been increased of course, but then the degree of dissociation of the benzyl bromide would have been too great, and the chances of secondary reactions, due to insufficient hydrogen iodide, would have been increased.

Hydrogen Bromide

Any hydrogen bromide produced in the reaction was collected under liquid air together with the much larger amount of hydrogen iodide. In theory it seemed possible to estimate the total acid produced and to determine the iodide independently; hence, by subtraction, the bromide became calculable. But , because of the relative proportions of bromide and iodide, the method would have been most inaccurate and it was discarded as a possibility. Other procedures which were tried are given below.

(1) Colorimetric method of Kolthoff[50].

The principle of the method is as follows:

Phenol red reacts with very dilute hypobromite in weakly alkaline solution to form an indicator of the bromphenol blue type which changes from yellow to blue-violet over the pH range 3.2 - 4.6. By comparing the colours at pH 5 - 5.4 of a series of standards with that of the sample, the amount of bromide can be assessed.

The bromide present in the sample is oxidised to the hypobromite with bleaching powder in a borax buffer.

Experimentally, the method requires a solution containing 3 - 18μgms. of bromide in 10ccs. 0.2ccs. of phenol red and 2ccs. of borax solution are added. 0.2ccs. of 0.1N. hypochlorite are added as oxidising agent and the mixture allowed to stand for four minutes. Then 0.5ccs. of 0.1N. sodium arsenite is added to destroy the hypochlorite. After the addition of 1.5ccs. of sodium acetate buffer, the solution is compared in colour with the standards and an assessment of the bromide present made.

In the actual experimental samples, hydrogen iodide was also present and had to be removed. This was done by boiling the original solution of hydrogen bromide and hydrogen iodide with 1N. sulphuric acid and 0.5N. sodium nitrite until colourless.

It was estimated that this method would have an accuracy of 10%. The standard solutions were prepared from 'Analar' potassium bromide.

The following table shows the estimated number of moles of hydrogen bromide and is compared with the moles of iodine and of total 'iodide', which consists of iodine and benzyl iodide, as determined by titration.

Table 17

Hydrogen Bromide moles/sec. x 10^8	Iodine moles/sec. x 10^8	Total 'Iodide' moles/sec. x 10^8
6.25	9.5	-
14.75	10.96	16.94
16.1	12.07	-
24.8	20.2	29.53
26.0	21.0	-

These results indicate that the rate of production of hydrogen bromide was rather greater than the rate of production of iodine. In only two of the five examples shown in the above table was it possible to compare the rate of production of total 'iodide' with the rate of production of hydrogen bromide but the latter approached that of the former. (The above two results are the second and fifth examples of Table 16). A more precise relationship would not be justified because of the degree of accuracy of the results. It was apparent that an independent method of determination of the amount of hydrogen bromide would be useful.

(2) Infra-red analysis for Hydrogen Bromide in Hydrogen Iodide.

The vibrational-rotational spectra of hydrogen bromide and hydrogen iodide were quite distinct, and there was no overlapping of the 'P' branch of hydrogen bromide with the 'R' branch of hydrogen iodide in the region of interest from 3.6 to 5μ. It was thought that quantitative measurements of the intensities of the hydrogen bromide peaks could give a better estimate of the rate of production of hydrogen bromide.

A 10cms. infra-red gas cell, fitted with potassium bromide end plates and a narrow diameter tube for freezing down contents of the cell, was connected to the collection system of the apparatus replacing trap T3 in Fig.1. On the completion of a run, the hydrogen bromide and hydrogen iodide which had been collected were distilled into the small tube attachment and the cell isolated. On gaining room temperature, the gas was examined on the infra-red spectrophotometer.

An initial qualitative run showed that the vibrational-rotational spectrum obtained for hydrogen bromide was quite measurable, and that the intensity of peaks for hydrogen iodide was smaller than for the bromide even although the HI/HBr ratio was large. This was explained by the decrease in polar nature of the hydrogen iodide molecule compared with the hydrogen bromide. The positions of the peaks in

SPECTRUM OF GASEOUS

HYDROGEN BROMIDE

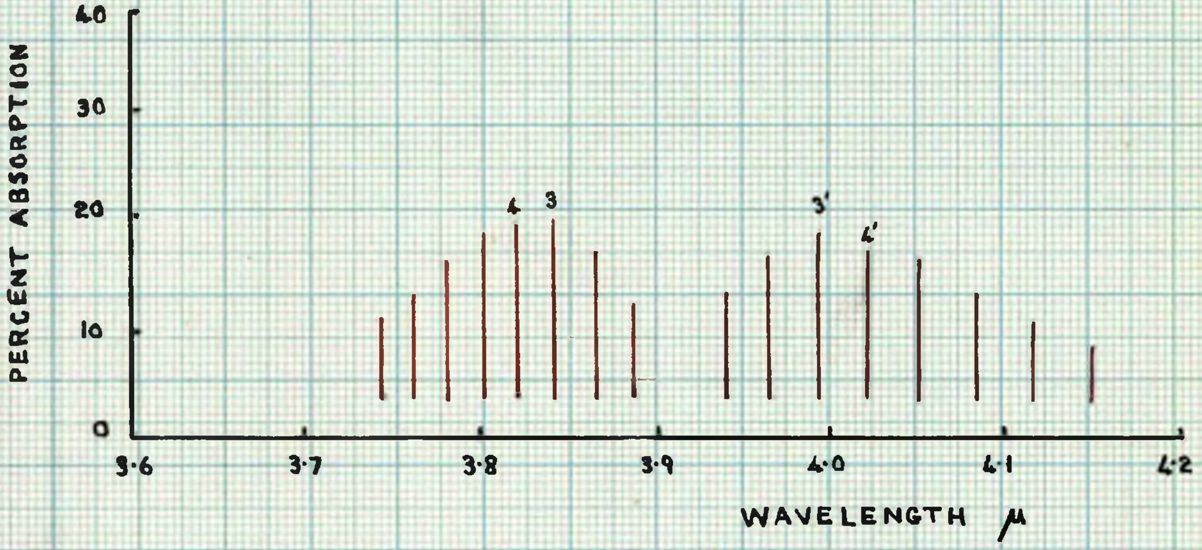


Figure 33

this qualitative run agreed with those given in the literature[51,52].

For a quantitative estimation of the hydrogen bromide, the intensity of peaks had to be compared with the peak heights for synthetic mixtures of hydrogen bromide and hydrogen iodide, containing known amounts of hydrogen bromide. Synthetic mixtures of hydrogen bromide and hydrogen iodide were therefore prepared. The hydrogen bromide was prepared by the bromination of tetrahydronaphthalene[53], collected under liquid air and transferred to a three-litre bulb, painted black, which was attached to the same injection system as used for hydrogen iodide. The cell was filled by flowing hydrogen iodide and hydrogen bromide in turn through this injection system and collecting the gases in the small tube attached to the gas cell. A measure of the amount of hydrogen iodide and hydrogen bromide was obtained by collection and analysis of control runs using similar flow conditions. A check for the total acid could also be made by analysis of the cell contents after the infra-red analysis had been carried out.

An infra-red determination of hydrogen iodide alone showed that there was no hydrogen bromide present in the hydrogen iodide.

The conditions used in analysis in each case were a slit width of 0.035ins., an amplifier gain of 12/65 and single beam filter. The infra-red spectrum of hydrogen bromide from a synthetic mixture is shown in Fig.33. Calculation of amounts of hydrogen bromide is shown in the Appendix.

Four estimations of the hydrogen bromide produced were made for each run by comparing the intensities of four of the peaks in the spectrum with the corresponding peaks of the standard spectrum of a mixture containing a known amount of hydrogen bromide.

In Table 18 the rate of production of hydrogen bromide, as measured by this method, is compared with the rate of production of total 'iodide' (iodine plus benzyl iodide). The two runs labelled 1 and 3 are the first and third examples of Table 16.

Table 18

Run No.	Hydrogen Bromide moles/sec. x 10^8		Total 'iodide' moles/sec. x 10^8
3	34.7		
	31.3	Mean	38.38
	33.6	33.92	
	36.1		
1	14.6		
	14.3	Mean	13.19
	14.6	14.52	
	14.6		

It was not possible to determine the amounts of bromide by the two independent methods on a particular run, but the evidence from both sources on separate runs indicates that the production of hydrogen bromide approximates to that of total 'iodide'.

Reactions in a Static System

Using Hydrogen Iodide as a Radical Catcher

The initial experiments using hydrogen iodide as a radical catcher in the flow series of runs had shown that the rate of decomposition of benzyl bromide was much faster than when toluene was used as a catcher.

It was thought that the reason for this might be the existence of an iodine catalysed chain reaction. Gow[10] had carried out similar work with benzyl iodide using a hydrogen iodide catcher. He postulated that the rate determining step in the reaction was

$$I- + C_6H_5CH_2I \longrightarrow I_2 + C_6H_5CH_2-.$$

By analogy it might be expected that the rate determining step in the benzyl bromide case would be

$$I- + C_6H_5CH_2Br \longrightarrow IBr + C_6H_5CH_2-.$$

A series of experiments was performed to test this theory, and also to attempt to form some idea of the magnitude of the energy of activation for this reaction, if indeed it did occur.

Since it was necessary to test the above theory by injecting iodine into the system, and because the simultaneous injection of three reactants into a flow system was technically very difficult, it was decided to carry out the experiments in a static form of apparatus.

Apparatus used in Static Experiments

The reaction vessel was a Pyrex glass cylinder of diameter 10cms.

and volume 680ccs. It narrowed at both ends to a diameter of 1.3cms. The narrow tube attached to one end of the cylinder could be immersed in liquid air to freeze any reactants or products. The other end was glass-blown to the injection system for filling, and had a constriction which could be sealed off when filling had been completed.

Benzyl bromide and iodine were weighed out in small glass vials and placed in the reaction vessel, before attachment to the system used for injection of hydrogen iodide. The reaction vessel was glass-blown on to the hydrogen iodide injection unit and evacuated, the narrow closed end being immersed in liquid air to prevent benzyl bromide and iodine being pumped away. The method of filling with hydrogen iodide was that adopted for filling the infra-red gas cell. The hydrogen iodide entered through the Edwards' needle valve, while a measure of the amount of hydrogen iodide in the reaction vessel could be obtained by collecting the hydrogen iodide in one of the traps T2 (Fig.1) for a known length of time. Distillation into degassed water in T3 and analysis by the usual method enabled the rate of flow of hydrogen iodide to be determined. The same rate of flow was used for filling the reaction vessel and thus the amount of hydrogen iodide in it could be determined.

Two forms of heater were used in this series of experiments. The first was a furnace, similar to that described in the section 'Description of Apparatus used in Flow Experiments'. This furnace had a 'smooth' temperature profile while the temperature was controlled by a Sunvic Controller Type RT2, similar to the one previously

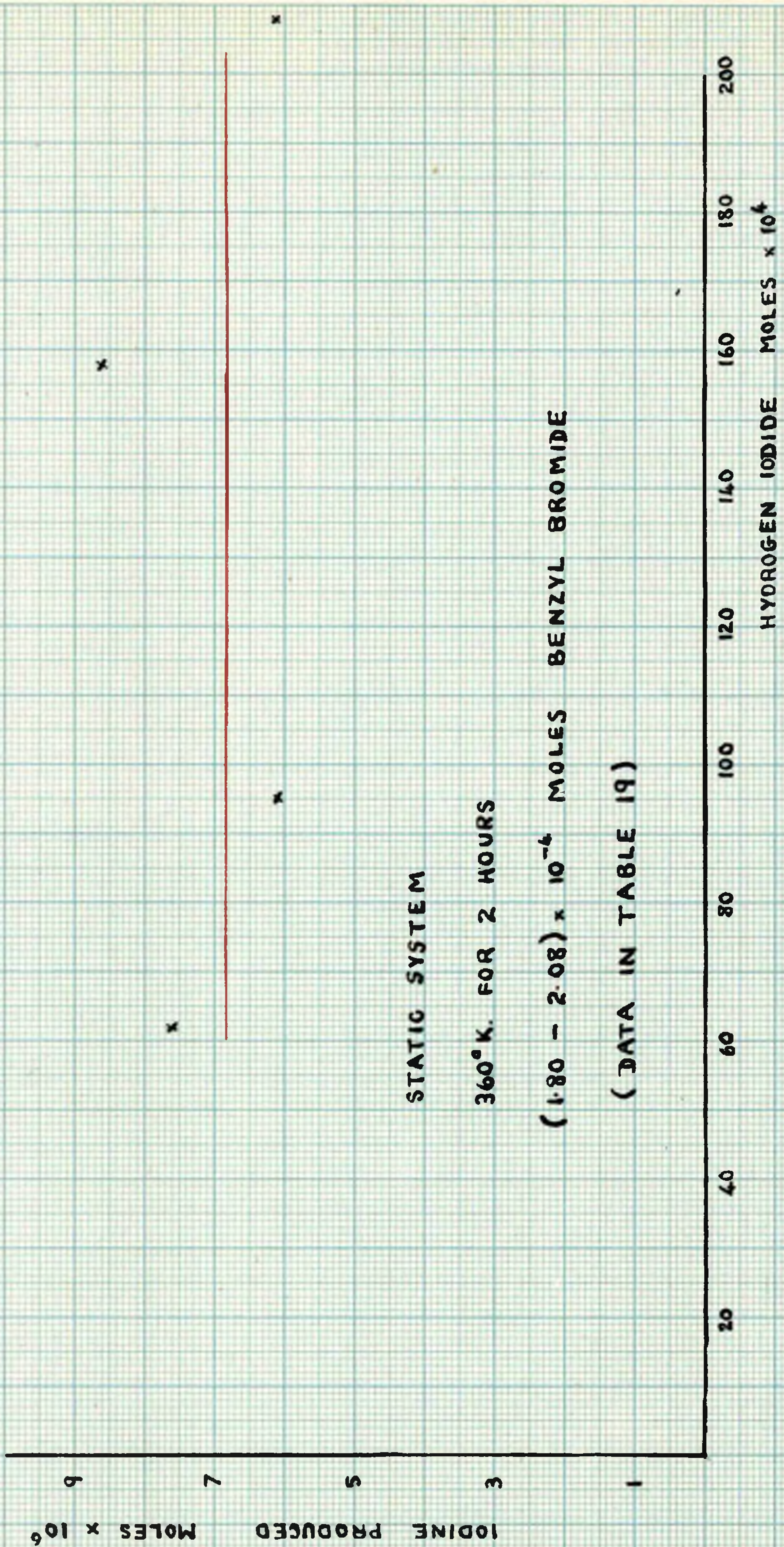

STATIC SYSTEM
360°K. FOR 2 HOURS
(1·80 – 2·08) × 10⁻⁴ MOLES BENZYL BROMIDE
(DATA IN TABLE 19)
IODINE PRODUCED MOLES × 10⁶
1
3
5
7
9
HYDROGEN IODIDE MOLES × 10⁴
20
40
60
80
100
120
140
160
180
200

Figure 34

described. The second type of heater which was used in the greater part of the experiments was simply a bath of boiling water, the level of the water being maintained by constant flow.

To carry out an experiment, the reaction vessel was sealed under vacuo and inserted in the heating vessel, the time of insertion being noted. In experiments using the air heater the minimum time of reaction was two hours, since immediately on insertion of the reaction vessel the temperature of the furnace dropped, and to keep the error in the temperature reading at a safe minimum, two hours was thought to be the shortest time of reaction possible.

The reaction was stopped by removing the reaction vessel from the heater and freezing the contents in liquid air. The vessel was then cut open and the contents dissolved in aqueous-alcoholic solvent. The iodine produced in the reaction was analysed in the usual manner with standard thiosulphate solution.

Variation of Iodine Production With Hydrogen Iodide Concentration

The concentration of benzyl bromide, the time of reaction and temperature of the decomposition were kept constant. The amount of hydrogen iodide was varied.

The moles of iodine produced for moles of hydrogen iodide used is tabulated below and shown graphically in Fig.34.

Table 19

Temperature of reaction - 360°K.

Time of reaction - 2 hours

Benzyl Bromide moles x 10^4	Hydrogen Iodide moles x 10^4	Iodine Produced moles x 10^6	% Decomposition (measured on moles I_2)
1.80	61.0	7.56	4.2
2.04	94.8	6.09	2.86
1.88	158.0	8.65	4.6
2.08	208.0	6.09	3.0

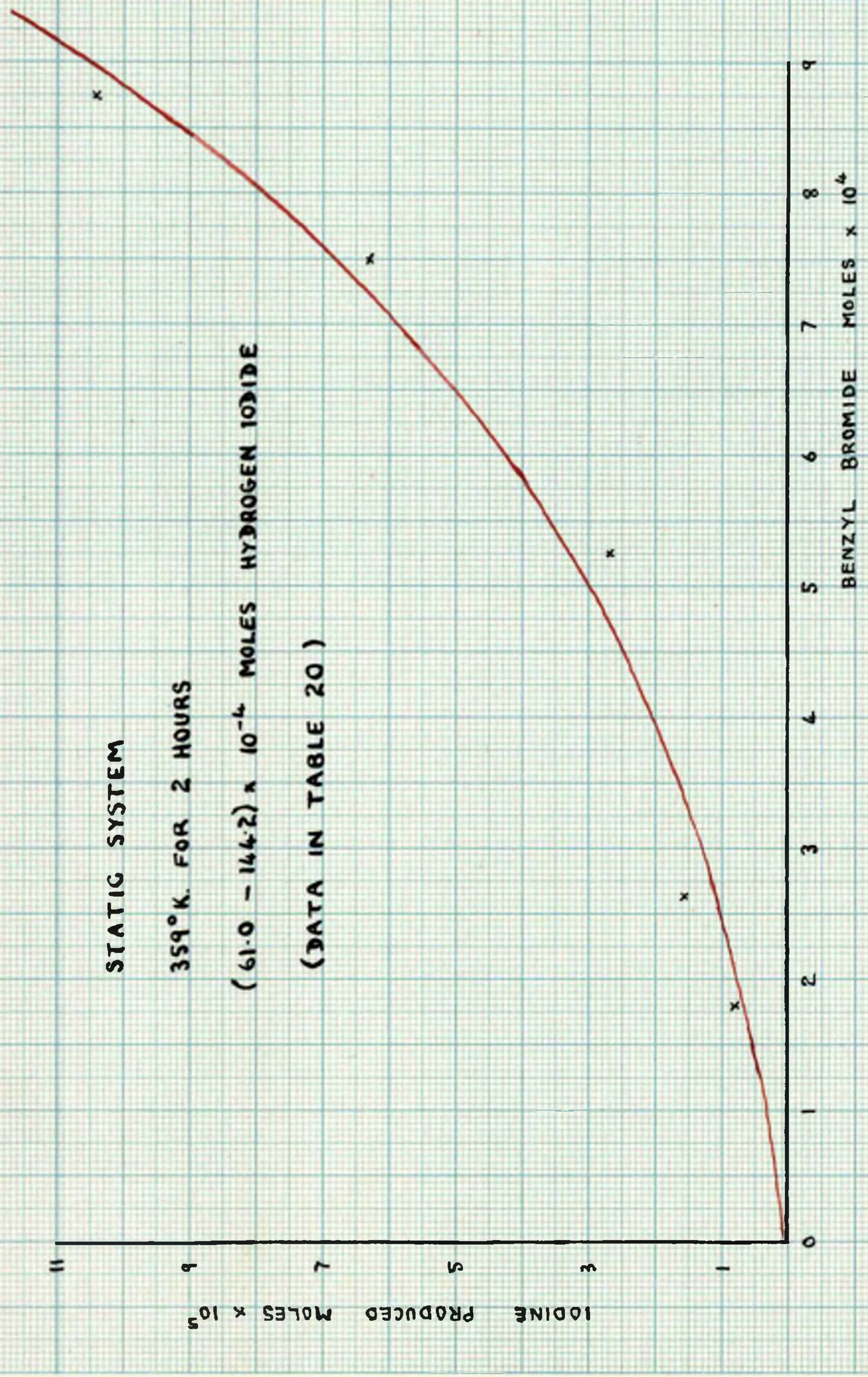
The spread of points is fairly large, but there does not appear to be a systematic increase in the amount of iodine produced for increasing concentration of hydrogen iodide catcher when the amount is increased from 61.5 to 208 x 10^{-4} moles.

It should be pointed out that an experiment was conducted with hydrogen iodide alone. The moles of hydrogen iodide used were 98.4 x 10^{-4} and the moles of iodine produced were 1.2 x 10^{-6}. If 2 x 10^{-4} moles of benzyl bromide had been used, this would have been evaluated as 0.6% decomposition. The decomposition for a blank sample of hydrogen iodide is small in comparison with the decomposition when benzyl bromide is present.

Variation of Iodine Production with Benzyl Bromide Concentration

The amount of benzyl bromide was varied from 1.8 x 10^{-4}

Figure 35


STATIC SYSTEM
359°K. FOR 2 HOURS
(61.0 – 144.2) x 10^{-4} MOLES HYDROGEN IODIDE
(DATA IN TABLE 20)
IODINE PRODUCED MOLES x 10^5
11
9
7
5
3
1
BENZYL BROMIDE MOLES x 10^4
0
1
2
3
4
5
6
7
8
9

to 8.76 x 10^{-4} gram moles. There was an upper limit to the amount of benzyl bromide which could be used. It was necessary to have the reactants in the vapour phase; it was calculated that with a vessel of 680ccs. capacity and the vapour pressure of benzyl bromide at the temperature of the reaction being known, the maximum amount of benzyl bromide which would be present in the gaseous phase was 9.16 x 10^{-4} gram moles.

The results tabulated below, are shown in Fig. 35 with moles of iodine produced plotted against benzyl bromide concentration.

Table 20

Temperature of reaction - 359°K.

Time of reaction - 2 hours

Benzyl Bromide moles x 10^4	Hydrogen Iodide moles x 10^4	Iodine Produced moles x 10^5	% Decomposition (measured on moles I_2)
1.80	61.0	0.756	4.2
2.64	142.8	1.58	6.0
5.25	93.0	2.68	5.1
7.50	144.2	6.30	8.4
8.76	141.4	10.40	11.8

The spread of results is again fairly large, but an examination of the data in the above table does indicate that the percentage decomposition increased with increasing concentration of benzyl bromide.

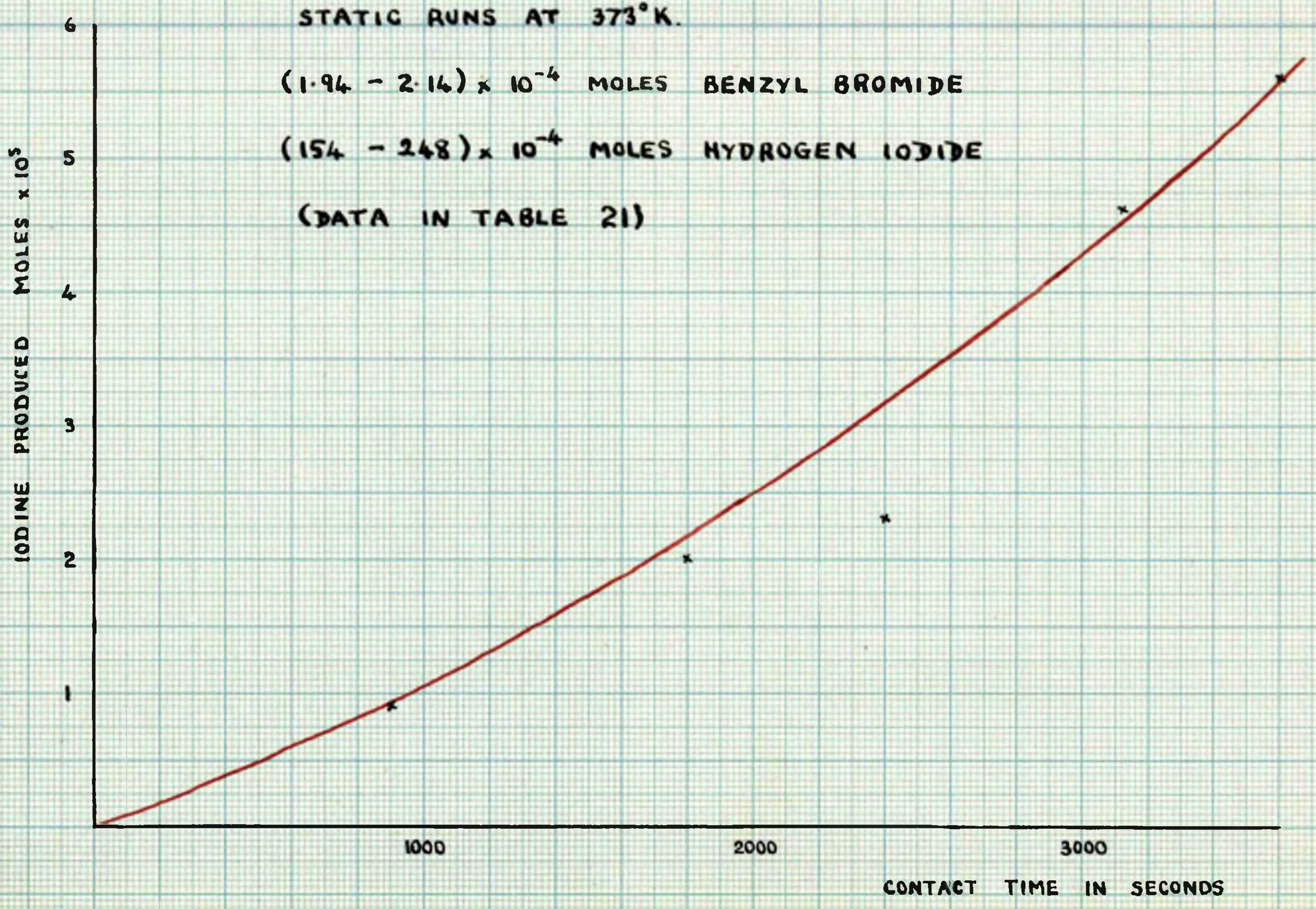

STATIC RUNS AT 373°K.
(1·94 - 2·14) x 10^{-4} MOLES BENZYL BROMIDE
(154 - 248) x 10^{-4} MOLES HYDROGEN IODIDE
(DATA IN TABLE 21)
IODINE PRODUCED MOLES x 10^5
6
5
4
3
2
1
1000
2000
3000
CONTACT TIME IN SECONDS

Figure 36

Examination of the Iodine Catalysed Reaction

If the reaction I- + $C_6H_5CH_2Br \longrightarrow IBr + C_6H_5CH_2$- did occur, then it would be expected that the rate of reaction would increase with increasing contact time since more iodine would be produced at longer contact times. The addition of iodine should also have an accelerating effect on the rate of the above reaction.

(1) The Effect of Contact Time on the Rate of Reaction

The reaction vessel was heated in a boiling water bath in this series of experiments. The plot of moles of iodine produced against contact time is shown in Fig.36.

Table 21

Benzyl Bromide moles x 10^4	Hydrogen Iodide moles x 10^4	Iodine Produced moles x 10^5	Contact Time secs.	% Decomp. (measured on moles I_2)
1.94	173.6	0.902	900	4.6
2.0	157.7	2.00	1800	10.0
1.93	188.0	2.30	2400	11.9
2.14	248.0	4.63	3120	21.6
1.95	154.1	5.60	3600	28.7

The rate of production of iodine is seen to be increasing at longer contact times, which is in accordance with expectation if the above iodine catalysed reaction is the rate determining step.

(2) The Effect of Added Iodine on the Rate of Reaction

The iodine was weighed in small vials and put in the reaction

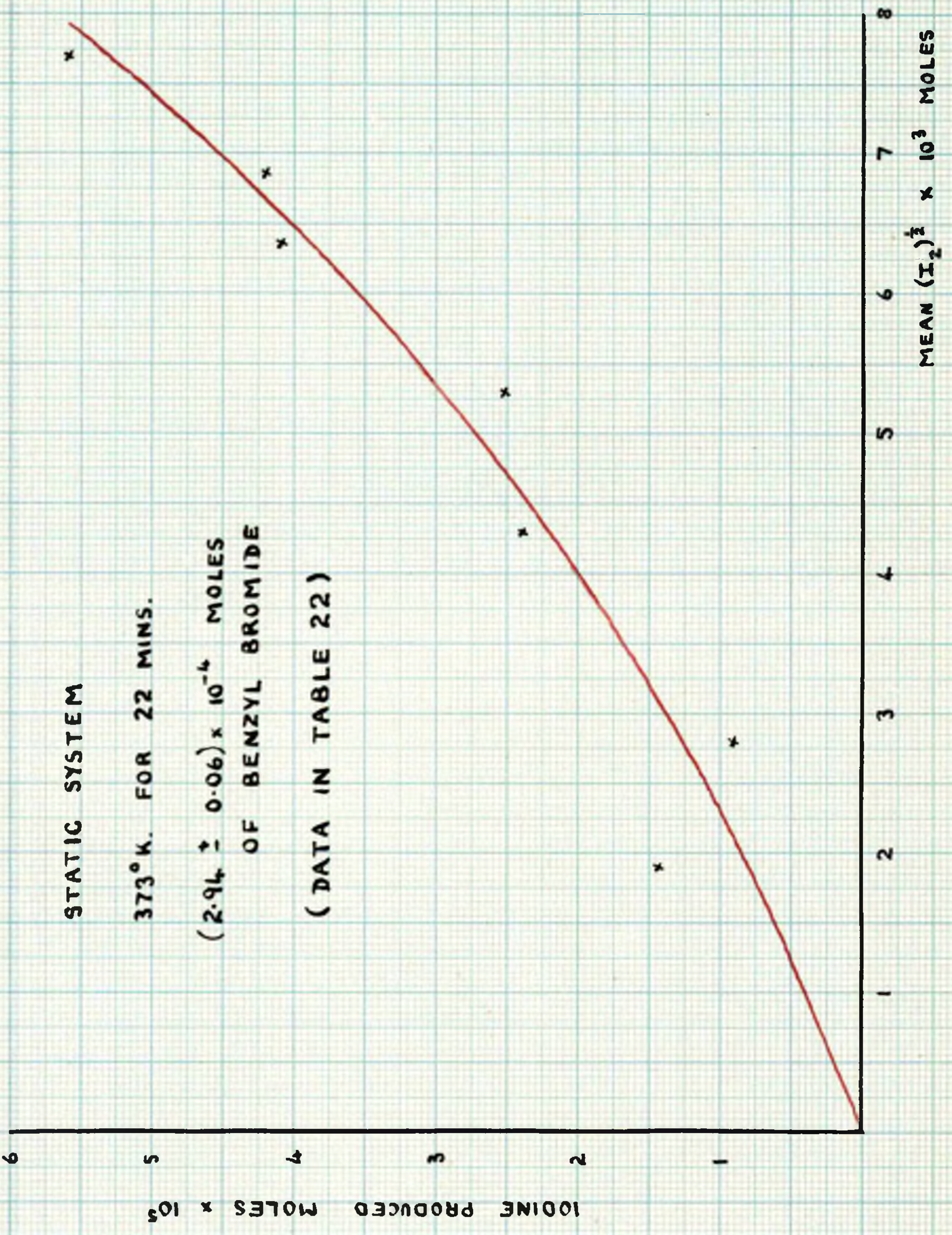

STATIC SYSTEM
373°K. FOR 22 MINS.
(2·94 ± 0·06) × 10⁻⁴ MOLES
OF BENZYL BROMIDE
(DATA IN TABLE 22)
IODINE PRODUCED MOLES × 10⁵
1
2
3
4
5
6
MEAN (I₂)½ × 10³ MOLES
1
2
3
4
5
6
7
8

Figure 37

vessel at the same time as the benzyl bromide.

Fig.37 is a graph of moles of iodine produced against mean value of (moles iodine)$^{\frac{1}{2}}$. The mean is the arithmetic mean of iodine atom concentration initially and the iodine atom concentration finally.

Table 22

Benzyl Bromide - 2.94 ± 0.06 x 10^{-4} gram moles

Temperature of Reaction - 373°K.

Time of Reaction - 22 minutes

Iodine Added moles x 10^5	Iodine Finally moles x 10^5	Iodine Produced moles x 10^5	Mean Value $(I_2)^{\frac{1}{2}}$ x 10^3	% Decomp. (measured on moles I_2)
-	1.44	1.44	1.892	4.9
0.393	1.334	0.941	2.815	3.2
0.866	3.270	2.404	4.33	8.1
1.69	4.205	2.515	5.295	8.4
2.24	6.36	4.12	6.352	13.8
2.83	7.01	4.18	6.845	14.6
3.48	9.076	5.596	7.715	18.9

The increase in the rate of production of iodine with increasing additions of iodine again justifies the conclusion that the iodine catalysed chain reaction is the dominant process in the decomposition of benzyl bromide in presence of hydrogen iodide.

More extensive work would be needed to establish whether the rate of reaction was proportional to $(I_2)^{\frac{1}{2}}$.

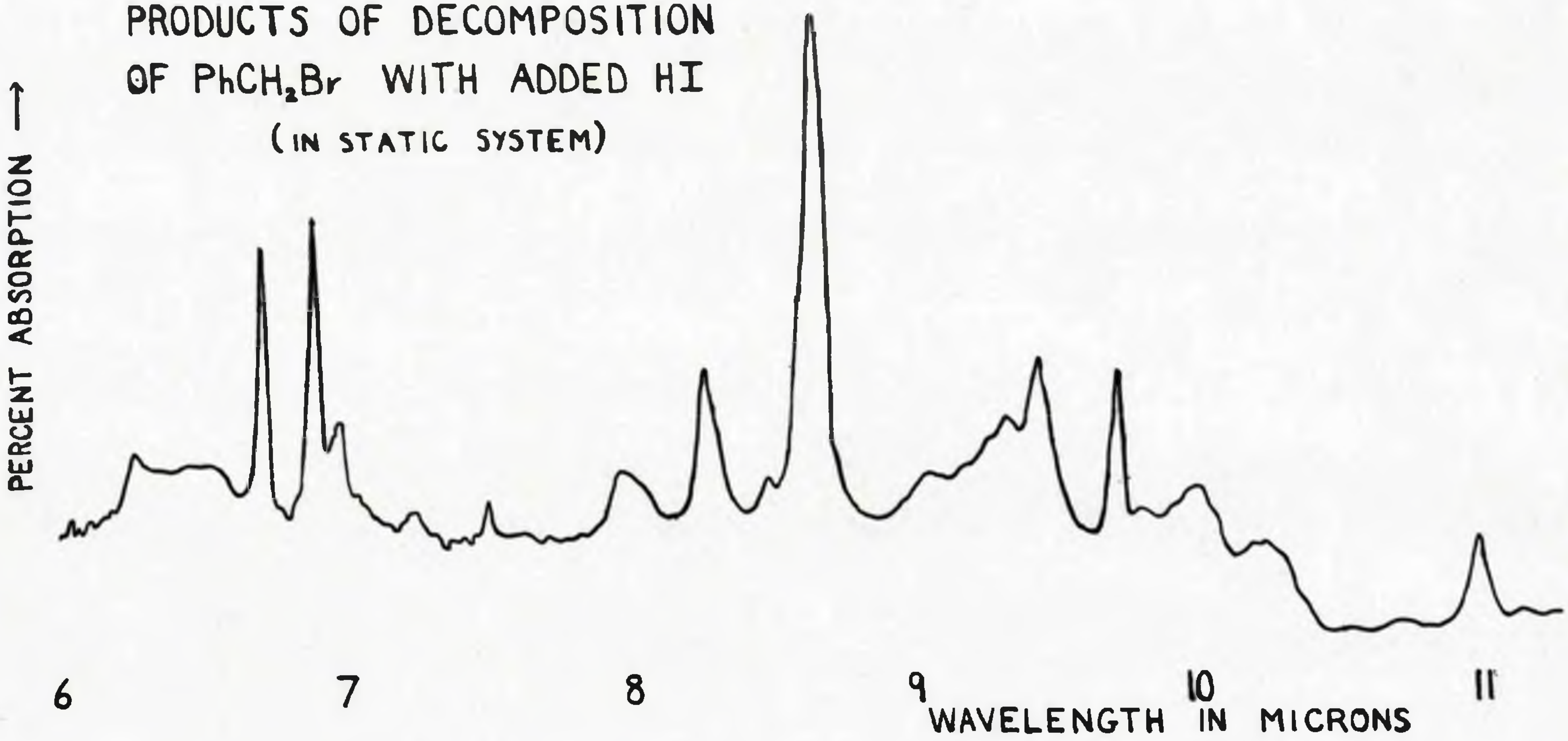

PRODUCTS OF DECOMPOSITION
OF $PhCH_2Br$ WITH ADDED HI
(IN STATIC SYSTEM)
PERCENT ABSORPTION →
6
7
8
9
10
11
WAVELENGTH IN MICRONS

Figure 38

Examination of the Products of the Static Decomposition of Benzyl Bromide using Hydrogen Iodide as Radical Catcher

In view of the fact that benzyl iodide had been identified as one of the products of decomposition in flow runs at much higher temperatures, it was thought desirable to look for benzyl iodide in the products of these static runs at lower temperatures.

The products of decomposition and unreacted bromide were dissolved in carbon tetrachloride and examined by infra-red spectroscopy. The spectrum of the products (Fig.38) was very similar to that of benzyl iodide (Fig.30), and the main distinguishing features of the spectrum of benzyl bromide, viz. a band of absorption with peaks at 8.2 and 8.35μ, had disappeared. It seemed that the proportion of benzyl iodide in the products was very large, and it was therefore desirable to be able to analyse quantitatively for the amount of benzyl iodide produced.

For this reason an attempt was made to separate the volatile unchanged hydrogen iodide from the mixture and to analyse for total iodide in the products remaining. For these experiments the reaction vessel was fitted with a break seal. When a run had been completed, the vessel was glass-blown on to a system which was used for the collection of the volatile hydrogen iodide. This consisted of a 250ccs. bulb with a lead to the vacuum line and one to the reaction vessel via the break seal. The bulb was also fitted with a tap to isolate it from the rest of the apparatus. Attached to the bulb was a narrow diameter tube, into which any gas collected could be frozen down under liquid air. The collection system was evacuated and then shut off from the vacuum line. The seal was then broken and the hydrogen iodide distilled from the reaction vessel in acetone-solid carbon dioxide, to the flask in liquid air. The 250ccs. bulb was then isolated and air allowed into the apparatus.

The products remaining in the reaction vessel were dissolved in aqueous-alcoholic solvent, collected in standard flasks and analysed for 'total iodide' (benzyl iodide and iodine) and iodine, as described in a previous section.

Results of Experiment

Initial amounts:

Benzyl bromide - 0.02775gms. = 1.62 x 10^{-4}gm.moles

Hydrogen iodide =132.2 x 10^{-4}gm.moles

Iodine added - 0.00390gms. = 1.54 x 10^{-5}gm.moles

Final amounts:

Total iodine - 0.007874gms. = 3.10 x 10^{-5}gm.moles

∴ iodine produced - 0.003974gms. = 1.56 x 10^{-5}gm.moles

Total 'iodide' - 0.02621gms.

∴ 'iodide' as benzyl iodide - 0.02621 - 0.007874

= 0.018336gms. = 1.44 x 10^{-4}gm.moles

It appears from the above result that the exchange of bromine atoms for iodine atoms by the benzyl radical has been almost complete.

This result is contrary to any expectations on the basis of estimations of ΔH and ΔS for such processes, but it might be explained if the benzyl iodide was formed in the liquid phase at the temperature of reaction and the system was heterogeneous and not homogeneous.

It was not desirable to carry out the reaction at a temperature of sufficient magnitude to prevent the condensation of benzyl iodide, because then the amount of iodine produced would be too great. A reaction was carried out at 494°K. with 2.225×10^{-4} gm.moles of benzyl bromide. The contact time was two hours and 1.63×10^{-4} gm.moles of iodine was produced, corresponding to 73% decomposition.

General Conclusions on the use of Hydrogen Iodide as a Radical Catcher

In this particular problem the experiments described above show fairly clearly that there is one major disadvantage in using hydrogen iodide as a radical catcher. This is the occurrence of a decomposition catalysed by iodine, presumably $I\text{-} + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2\text{-} + IBr$, which becomes the dominant process in a short time. As a result further work on this was suspended.

DISCUSSION

Mechanism and Products

The results obtained for the decomposition of benzyl bromide using toluene as a radical catcher have shown that the reaction can be regarded as first order at partial pressures of bromide greater than 0.14 mms., and, in the determination of the energy of activation care was taken to ensure that all work was performed with pressures above this limit.

It has been emphasised that before any deductions regarding bond energies can be made the kinetics of the reaction must be fully understood and this demands a thorough examination of the products. Evidence was produced for the presence of hydrogen bromide and dibenzyl as the main products of the decomposition, but stilbene, benzene, hydrogen and methane were also present in small amount.

The main products would seem to be consistent with the following scheme of decomposition

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2- \ + \ Br- \qquad (1)$$

$$Br- \ + \ C_6H_5CH_3 \longrightarrow C_6H_5CH_2- \ + \ HBr \qquad (2)$$

$$C_6H_5CH_2- \ + \ C_6H_5CH_2- \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (3)$$

The fact that no molecular bromine was detected in the reaction products is evidence against any recombination of bromine atoms. Since there was no detectable increase of rate of production of hydrogen bromide when the toluene pressure was varied over a two-fold range, it can be concluded that the bromine atoms reacted completely with the toluene.

It is necessary to account for the small amount of stilbene which is produced. This could arise in two possible ways (1) by thermal decomposition of dibenzyl or (2) by the attack of a bromine atom on dibenzyl.

Data are available from the thesis of Davidson[22] to enable the rate of decomposition of dibenzyl to be calculated, and the mechanism for this decomposition is fairly well established.

Dibenzyl decomposes by a split of the central C-C bond to produce two benzyl radicals. There is much recombination of these radicals but attack of a benzyl radical on the parent molecule initiates the next stage of decomposition.

$$C_6H_5CH_2- \;+\; C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH_3 \;+\; C_6H_5CH_2CHC_6H_5 \qquad (4)$$

$$C_6H_5CH_2CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 \;+\; H- \qquad (5)$$

Davidson deduced the rate equation for the decomposition to be $k = 10^{14.3}\exp^{-60,000/RT}$ sec.$^{-1}$. At a temperature of 773°K. the rate constant is computed to be 0.0021 sec.$^{-1}$. This rate constant is very low and, since the chance of a collision between a benzyl radical and a dibenzyl molecule is also small, it does not seem that this mechanism would be feasible for the production of the stilbene in our work.

The other possible scheme of formation of stilbene is the attack of a bromine atom on dibenzyl

$$Br- \;+\; C_6H_5CH_2CH_2C_6H_5 \longrightarrow HBr \;+\; C_6H_5CH_2CHC_6H_5 \qquad (6)$$

$$C_6H_5CH_2CHC_6H_5 \longrightarrow C_6H_5CH{=}CHC_6H_5 \;+\; H- \qquad (5)$$

Reaction (6) is exothermic to the extent of 27 k.cals. and would be expected to be very rapid. This reaction seems a distinct possibility for the formation of stilbene, but it does mean that not all the bromine atoms produced in the primary split react with toluene. The number reacting in reaction (6) would be very small and the fact that the effect of changing the partial pressure of toluene on the rate was seemingly negligible, can well be understood. In any event the method of formation of hydrogen bromide does not alter the kinetic deduction of a first order decomposition, and dibenzyl would be functioning as an alternative free atom acceptor.

Either of the above schemes of formation of stilbene produces a hydrogen atom, and the formation of small amounts of hydrogen and methane probably arises from reaction of this atom.

It must be noted that the ratio of hydrogen/methane was 57/43 in each of the experiments in which this was measured. This is in general accord with the results of Szwarc et al.[17] It is significant that Szwarc, Steacie et al.[18] and Smith[3] each found that the hydrogen/methane ratio was unchanged under differing conditions in the decomposition of toluene, although they disagreed about the numerical value of the ratio. The determinations of this hydrogen/methane ratio were less extensive in our work than in the work of some of the others, but it is of distinct interest that the ratio obtained was of the same order as that in the decomposition of toluene.

Two mechanisms were put forward to explain the production of hydrogen and methane in toluene:

$$(1)\qquad H\text{-} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + H_2 \qquad (7)$$

$$H\text{-} + C_6H_5CH_3 \longrightarrow C_6H_6 + CH_3\text{-} \qquad (8)$$

$$CH_3\text{-} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + CH_4 \qquad (9)$$

$$(2)\qquad C_6H_5CH_3 \longrightarrow C_6H_5\text{-} + CH_3\text{-} \qquad (10)$$

$$CH_3\text{-} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + CH_4 \qquad (9)$$

If the value of 84.7 k.cals./mole of Smith[3] is accepted for the energy of activation for the decomposition of toluene, this energy of activation being assigned to the step $C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + H\text{-}$, the rate constant at a temperature of 773°K., which is the mid-point of the temperature range used in the decomposition of benzyl bromide, may be calculated to be 1.35×10^{-9} sec.$^{-1}$ from her rate equation $k = 10^{15.1} \exp^{-84{,}700/R \times 773}\,\text{sec.}^{-1}$. The decomposition of toluene is therefore negligible. If the first step in the decomposition of toluene proceeds by reaction (10), the rate of this reaction cannot be faster than the rate for $C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + H\text{-}$ so that it seems improbable that methane could be formed by the second scheme.

The first reaction scheme would therefore seem to be the more probable and fits the experimental findings.

The suggested scheme of decomposition of o-chlorobenzyl bromide and p-chlorobenzyl bromide, the products of which have been studied in some detail, is analagous to that for benzyl bromide:

$$o\text{-Cl}\ C_6H_4CH_2Br \longrightarrow o\text{-Cl}\ C_6H_4CH_2\text{-} + Br \qquad (11)$$

$$Br\text{-} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2\text{-} + HBr \qquad (2)$$

$$\text{o-Cl } C_6H_4CH_2\text{-} + C_6H_5CH_2\text{-} \longrightarrow \text{o-Cl } C_6H_4CH_2CH_2C_6H_5 \qquad (12)$$

$$\text{o-Cl } C_6H_4CH_2\text{-} + \text{o-Cl } C_6H_4CH_2\text{-} \longrightarrow \text{o-Cl } C_6H_4CH_2CH_2 \text{ o-Cl } C_6H_4 \qquad (13)$$

$$C_6H_5CH_2\text{-} + C_6H_5CH_2\text{-} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (3)$$

The Rate Constant and its Variation with Temperature

Perhaps the most interesting fact produced by our work is that the A factor for the decomposition of benzyl bromide is $10^{15.2}$sec.$^{-1}$, the complete equation being $k = 10^{15.2}\exp^{-(58.02 \pm 0.68) \times 10^3/RT}$sec.$^{-1}$. This A factor is higher than the more normally accepted value of 10^{13}sec.$^{-1}$ for first order reactions and higher than the value of 1×10^{13}sec.$^{-1}$ used by Ghosh, Sehon and Szwarc[4].

The rate equations obtained in this work for the decompositions of the chloro substituted benzyl bromides are:

o-chloro $k = 10^{13.4}\exp^{-(51.2 \pm 1.45) \times 10^3/RT}$sec.$^{-1}$

m-chloro $k = 10^{12.4}\exp^{-(48.5 \pm 1.72) \times 10^3/RT}$sec.$^{-1}$

p-chloro $k = 10^{12.8}\exp^{-(48.05 \pm 1.57) \times 10^3/RT}$sec.$^{-1}$

Here again there are note-worthy features. The A factors for these compounds are all near the 'normal' value while the activation energies are approximately 9 k.cals./mole less than the value for the unsubstituted compound.

The question of the magnitude of normal A factors is an interesting one and has been discussed in many places. One recent review by Gowenlock[54] attempts to classify reactions where A differs from 10^{13}sec.$^{-1}$ in terms of the type of reaction and the magnitude of the deviation. He considers rather arbitrarily that we should take a thousand fold range of A factors as representing 'normal' behaviour. This range is taken as $(10^{11.5} - 10^{14.5})$sec.$^{-1}$ and some known cases lying outside this range are examined in terms of a possible entropy of activation in the transition state. Explanations are summarised for reactions with high A factors in terms of a 'loose' transition state or a three or four fragment decomposition.

In a rather more detailed paper Steel and Laidler[55] have discussed reasons for high A factors i.e. those lying above $10^{14.5}$sec.$^{-1}$. They use the idea that high frequency factors are related to positive entropies of activation and try to relate these in terms of vibration of a molecule and passage over the energy barrier. The Kassel[56], Rice-Ramsperger[57], Slater[58] theories of unimolecular reactions all predict in their simplest forms that $k_\infty = A_\infty \exp^{-\epsilon/kT}$ for the first order rate constant at high pressures where A_∞ is related to the vibrational frequency of the molecule and has the value of about 10^{13}sec.$^{-1}$. Eyring's[59] transition state theory states that $k_\infty = kT/h\exp^{\Delta S^*/R}\exp^{-\Delta H^*/RT}$ and from this it can be seen that if ΔS^* is large and positive high A factors will result since kT/h is approximately equal to 10^{13}sec.$^{-1}$. These are the two theories which Steel and Laidler try to reconcile.

For many reactions with high A factors they consider that the activated complex corresponds to the top of the free energy barrier, not the dissociation energy barrier and according to KRRS theory, the system crosses this barrier with a frequency of 10^{13}sec.$^{-1}$. Therefore if the thermodynamic equation $D_0 - T\Delta S = \Delta F$, where D_0 is the dissociation energy, ΔS is entropy of activation and ΔF is the free energy, is applied and if the increase in entropy occurs at an early stage in the dissociation process then ΔF will rise to a limiting value as the bond is broken. The free energy is less than the dissociation energy in this case. This means that the normal modes of vibration in the unimolecular rate theory should actually be worked out in terms of free energy instead of total energy. The molecule would still cross the barrier with a frequency of 10^{13} sec.$^{-1}$ but the barrier is lower since it is the free energy rather than total energy barrier which must be considered. They have further analysed what sort of entropy of activation is involved and have come to the conclusion that 'softening' of the vibrations in the activated state and these 'loose' vibrations eventually becoming translational and rotational is the important feature. If in the breaking of a single bond in a molecule to give two free radicals there is a softening of the torsional vibrations and the bending modes become loose, then the A factors will go higher. This would seem to be possible with most polyatomic molecules and high A factors are readily understood. In the case of benzyl bromide, which is a complicated molecule and exhibits complex vibrational patterns, this softening could quite conceivably occur.

The early work of Polanyi and Wigner[60] identified 10^{13} sec.$^{-1}$ with a critical vibration frequency in a molecule but the cases they cited are known now to be complicated kinetically. It is perhaps unfortunate that too much emphasis for too long has been placed on 10^{13} sec.$^{-1}$ as proposed in unimolecular rate theory and kT/h in transition state theory and that any reaction not giving an A factor of about 10^{13} sec.$^{-1}$

has been considered abnormal.

Szwarc's[1] work suggested that he had obtained the necessary experimental conditions for simple bond fission studies and the bulk of his data gave A factors close to 10^{13}sec.$^{-1}$. We have discussed earlier the inadequacy of some of his kinetic evidence, and the difficulties now arising in the interpretation of his energy of activation values. A series of researches in St. Andrews have produced data on reactions of relevance to the present work where the temperature independent factors have deviated considerably from 10^{13}sec.$^{-1}$. For example, Smith[3] deduced an A factor of $10^{15.1}$sec.$^{-1}$ for toluene and in two independent researches A factors of $10^{14.3}$sec.$^{-1}$ and $10^{15.4}$sec.$^{-1}$ were computed for the decomposition of dibenzyl by Davidson[22] and Alexander[16]. Szwarc and Taylor[25] published the A factor for the benzyl chloride decomposition as $10^{14.8}$sec.$^{-1}$.

Whereas the interpretation of A factors is in a relatively weak quantitative position that of E values for bond fission studies has shown marked strides in building up a picture which can be self-checking. As detailed earlier the identification of energies of activation with bond dissociation energies can lead to heats of formation of radicals. Thus the bond energy of benzyl bromide obtained from this present work was 58 k.cals./mole. Knowing $\Delta H_f(Br-)$ and $\Delta H_f(C_6H_5CH_2Br)g$, $\Delta H_f(C_6H_5CH_2-)$ may be calculated from the equation

$$\Delta H_f(C_6H_5CH_2-) \quad = \quad D(C_6H_5CH_2Br) \quad + \quad \Delta H_f(C_6H_5CH_2Br)g \quad - \quad \Delta H_f(Br-) \qquad (1)$$

As discussed in the survey at the beginning of this thesis in the section dealing with the thermodynamic study of the bromination of toluene, $\Delta H_f(C_6H_5CH_2Br)g.$ may be calculated from Skinner's[36] data and a more recent value for $\Delta H_f(C_6H_5CH_2OH)$[37] to be 13.1 k.cals./mole. If the value of 11.3 k.cals./mole. of Benson and Buss[35] for the heat of vaporisation of benzyl bromide is used instead of Skinner's estimated value of 9 k.cals., $\Delta H_f(C_6H_5CH_2Br)g.$ is computed to be 15.4 k.cals./mole. If these values are inserted in equation (1) above then

$$\Delta H_f(C_6H_5CH_2-) = 58 + 15.4 - 26.7 = 46.7 \text{ k.cals.}$$
$$\text{or} = 58 + 13.1 - 26.7 = 44.4 \text{ k.cals.}$$

If the value of 13.1 k.cals./mole is accepted for $\Delta H_f(C_6H_5CH_2Br)$ we obtain a value for the side chain C-H bond dissociation energy in toluene of 84.5 k.cals./mole by use of equation:

$$D(C_6H_5CH_2-H) = \Delta H_f(C_6H_5CH_2-) + \Delta H_f(H-) - \Delta H_f(C_6H_5CH_3) \qquad (2)$$
$$= 44.4 + 52 - 11.9$$
$$= 84.5 \text{ k.cals./mole.}$$

This value may be compared with those obtained from other sources.

Source	$\Delta H_f(C_6H_5CH_2-)$ k.cals.	$D(C_6H_5CH_2-H)$ k.cals./mole
Szwarc[17]	37.5	77.5
Van Artsdalen[2]	49.5	89.5
Benson and Buss[35]	44.9	84-85
Alexander[16]	45.4	85.4
Davidson[22]	44.9	84.9
Smith[3]	44.6	84.7
This thesis	44.4	84.5

The agreement in the results in the latter five determinations is striking. The result obtained in this research does of course depend on the accuracy of the value for the heat of formation of benzyl bromide, but the method is independent of data used in the other calculations. It is concluded that the value of 58 k.cals./mole for the energy of activation in the decomposition of benzyl bromide is entirely reasonable.

Some comment can be made regarding the results obtained by Benson and Buss. It must be pointed out that if their results are combined with ours then $D(C_6H_5CH_3) - D(C_6H_5CH_2Br) = 84.5 - 58 = 26.5$ k.cals. If however the data produced by Szwarc is inserted,

$$D(C_6H_5CH_3) - D(C_6H_5CH_2Br) = 77.5 - 50.5 = 27 \text{ k.cals.}$$

Benson and Buss considered that the difference ought to have been 34 k.cals. The results obtained in this thesis do not agree with their findings any better than did Szwarc's. Their calculation for the heat of formation of benzyl bromide of 20 k.cals./mole is not in agreement with that used in this thesis of 13.1 k.cals. This has been discussed in the survey early in the thesis.

The study of benzyl bromide was much more extensive than the work on the chlorobenzyl bromides, and in assessing the results this has to be borne in mind. It must be admitted that the change in the A and E values on passing from the unsubstituted to the substituted benzene ring is surprising. It is possible that the less exhaustive investigations of the chloro compounds failed to establish the kinetics adequately. If this were the case and there proved to be a substantial error, we consider it could only be in the absence of true first order behaviour. Modern views on the effects of substituents on bond dissociation energies are largely based on Szwarc's[5,17,39,61] work and we consider his proofs of first order behaviour to be very inadequate indeed. Our data would suggest a lowering of bond strength by some 9 k.cals. due to the chlorine substitution, in contrast to his values of less than 1 k.cal. Unfortunately there are no data with which cross-checking can be done and further investigation in this and related fields is needed.

The small spread in the activation energies for the three chloro substituted compounds seems to indicate that the position of substitution of a chlorine atom on the benzene ring has no effect on the C-Br bond energy.

Work with Hydrogen Iodide as Radical Acceptor

The most significant feature about the decomposition of benzyl bromide in presence of hydrogen iodide was that the reaction was much faster than in the case where toluene was used as a radical acceptor. Although deductions made from experiments in the static system are not proved beyond all doubt because of the high concentration of benzyl iodide formed by a heterogeneous process, the sets of experiments in which the contact time was varied, the partial pressure of benzyl bromide was varied and differing amounts of iodine were added, almost certainly indicate a marked auto-catalytic action of iodine atoms. In each of the three cases, the rate of production of iodine increased because there was an increase in iodine atom concentration.

The primary dissociation process could again be regarded as

$$C_6H_5CH_2Br \longrightarrow C_6H_5\dot{C}H_2- + Br- \qquad (1)$$

The reactive particles produced reacted with hydrogen iodide thus

$$C_6H_5CH_2- + HI \longrightarrow C_6H_5CH_3 + I- \qquad (2)$$

$$Br- + HI \longrightarrow HBr + I- \qquad (3)$$

The presence of toluene and hydrogen bromide in the reaction products has been adequately proved.

Benson and O'Neal[62] have recently reinterpreted data of Ogg[63] on the reactions of alkyl iodides with hydrogen iodide. They regard the chain propagating step to be $I- + RI \longrightarrow R- + I_2$. Gow[10] and Downs[15] offer a similar step in the interpretation of the reactions of benzyl iodide and trifluoromethyl iodide respectively. It is suggested that the experimental evidence from the present work summarised above strongly indicates that a similar autocatalytic process becomes the rate determining step in the reaction of benzyl bromide with hydrogen iodide as carrier

$$I- + C_6H_5CH_2Br \longrightarrow IBr + C_6H_5CH_2- \qquad (4)$$

The iodine atoms and benzyl radicals acted as chain carriers in reactions (4) and (2) and it can readily be seen why the decomposition was apparently faster than in the toluene case. In flow experiments the iodine monobromide would have been dissociated to a substantial extent and the bromine atoms would also have acted as chain carriers in accordance with reaction (3).

To explain the occurence of all the products, it is necessary to adopt some further reaction steps. In the flow experiments there was evidence to suggest that the moles of hydrogen bromide was approximately equal to the moles of iodine plus the moles of benzyl iodide. Flow experiments in which increasing amounts of hydrogen iodide were used showed that hydrogen iodide was not capturing all the radicals produced. Since this was the case, benzyl radicals were probably reacting with iodine or iodine atoms

$$C_6H_5CH_2- + I_2 \longrightarrow C_6H_5CH_2I + I- \qquad (5)$$

$$C_6H_5CH_2- + I- \longrightarrow C_6H_5CH_2I \qquad (6)$$

Reaction (5) is exothermic to about 8 k.cals. and would be expected to take place.

The following series of reactions might explain the occurence of the various reaction products

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2- + Br- \qquad (1)$$

$$C_6H_5CH_2- + HI \longrightarrow C_6H_5CH_3 + I- \qquad (2)$$

$$Br- + HI \longrightarrow HBr + I- \qquad (3)$$

$$I- + C_6H_5CH_2Br \longrightarrow IBr + C_6H_5CH_2- \qquad (4)$$

$$IBr \longrightarrow I- + Br- \qquad (7)$$

$$C_6H_5CH_2- + I_2 \longrightarrow C_6H_5CH_2I + I- \qquad (5)$$

$$C_6H_5CH_2- + I- \rightleftharpoons C_6H_5CH_2I \qquad (6)$$

$$I- + I- \rightleftharpoons I_2 \qquad (8)$$

The catalysis of the decomposition of iodides by free iodine atoms certainly occurs even with iodides with high bond strengths as methyl[62] iodide (D = 53 k.cals./mole) and trifluoromethyl[15] iodide (D = 54 k.cals./mole). The catalysed decomposition of bromides clearly offers a field of further investigation and it could contribute values of activation energies which would be useful in assessing bond energies.

SUMMARY

(1) With the accumulation of data on the bond dissociation energies of benzyl type compounds, certain major disagreements in the values obtained by various workers have become apparent.

(2) In the first part of the thesis a critical survey is made of these bond dissociation energies and the experimental techniques employed, especially for results obtained by flow kinetic methods, is discussed. Conclusions reached from a previous study on the effect of ring substitution on benzyl bromides are analysed.

(3) Benzyl bromide was studied with the idea of getting a value for the heat of formation of the benzyl radical which would fit better with the values obtained from work on other benzyl compounds.

(4) Preliminary experiments showed that the method of introducing substituted benzyl bromides into the reaction system employed by Szwarc et al.[5] did not give a constant rate of flow, which was necessary if quantitative conclusions were to be drawn.

The type of injection system used in the present series of experiments is fully described and other features of the apparatus are set forth in detail.

(5) The decomposition of benzyl bromide has been studied with this improved experimental technique and, by using nitrogen as a carrier gas in the toluene stream, it has been possible to study the effects of changing the contact time and the partial pressure of the bromide independently, thereby proving quite definitely that the reaction was of the first order. The energy of activation for the decomposition was computed from experiments over the temperature

range 731-816°K to be 58.02 ± 0.68 k.cals./mole and the temperature independent factor to be $10^{15.22}$ sec.$^{-1}$

(6) The products of the decomposition were studied in detail and consisted of hydrogen bromide and dibenzyl with small amounts of hydrogen, methane, benzene and stilbene. The main reaction scheme is well founded:

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2- + Br-$$

$$Br- + C_6H_5CH_3 \longrightarrow C_6H_5CH_2- + HBr$$

$$2(C_6H_5CH_2-) \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

The mechanism of formation of the minor products is examined in the final section of the thesis.

(7) The kinetics of the decomposition of o-chlorobenzyl bromide in the presence of toluene was studied in less detail, and the effect of temperature on the rate of decomposition for m- and p-chlorobenzyl bromides was measured. Assuming a first order dependence for these bromides, the bond energies for o-, m- and p-chlorobenzyl bromides were calculated to be 51.2, 48.5 and 48.05 k.cals./mole respectively.

(8) The composition of the involatile products obtained in the decomposition of o- and p-chlorobenzyl bromides was examined by infra-red spectrophotometry and mass spectrometry and found to consist of substituted and unsubstituted dibenzyls with smaller amounts of stilbenes.

(9) The decomposition of benzyl bromide in the presence of hydrogen iodide was also studied. It was hoped to produce a value for the bond energy by this method but it became apparent that the reaction

was more complicated than had been expected. The reaction rate was faster than in the presence of toluene and experiments in a static system and analysis of products for both flow and static experiments showed that an iodine catalysed reaction was an important feature.

(10) The result of 58 k.cals./mole for the C-Br bond energy in benzyl bromide, by thermochemical calculation, gives a value for the heat of formation of the benzyl radical which is consistent with values obtained in independent researches on benzyl compounds. This value is considered to be in better agreement than the previously reported one of 51 k.cals./mole.

(11) The value of the A factor, $10^{15.2}$ sec.$^{-1}$, is higher than the commonly accepted 'normal' value and its magnitude is discussed in the light of recent theory and the suggestion is made that it might not at all be abnormal.

(12) The difference in the activation energies of about 9 k.cals/mole between the unsubstituted benzyl bromide and the chloro substituted ones is surprising, but the small difference in the activation energies for the three substituted cases is not large enough to indicate that the point of substitution has any effect on the C-Br bond dissociation energy.

Calculation of Amounts of Hydrogen Bromide Produced in the Decomposition of Benzyl Bromide using Hydrogen Iodide as Radical Catcher by Quantitative Infra-red Analysis

By Lambert-Beer Law

$$\log_{10} \frac{Io}{I} = k\,c\,l \tag{1}$$

where Io = incident light intensity

I = transmitted light intensity

k = extinction coefficient

c = concentration of absorbing material

l = path length.

Samples of hydrogen bromide in hydrogen iodide, where the concentration, C, of hydrogen bromide was known, were examined in the region from 3.6 to 5 and $\log_{10}$ Io/I evaluated from measurements of the peak heights.

The spectrum of hydrogen bromide from a synthetic mixture of hydrogen bromide in hydrogen iodide is shown in Fig.33. The vertical axis depicts percentage absorption but figures for Io and I are simply (100 - percent absorption).

If a sample of hydrogen bromide produced in a reaction, the concentration of which is unknown, is examined under identical conditions, i.e. in the same cell and under the same spectral conditions, we may write

$$\log_{10} \frac{Io'}{I'} = k\,c'\,l \tag{2}$$

where c' is an unknown concentration.

Combining (1) and (2), we may write

$$\frac{\log_{10} \frac{Io}{I}}{\log_{10} \frac{Io'}{I'}} = \frac{k\,c\,l}{k\,c'\,l} = \frac{c}{c'} \qquad (3)$$

Since c is known, c' may be evaluated.

Io' and I' were measured for the four sample peaks corresponding to the four synthetic mixture peaks measured. Thus four values for the unknown concentration, c', were obtained. The average of these was taken as the value of the unknown hydrogen bromide concentration.

The spectrum of each sample and synthetic mixture was recorded three times so that any random errors were reduced.

HBr - HI Synthetic Mixture No. 1

(c = 15.5 x 10^{-8} g.moles of HBr/sec.)

Peak 4		Peak 3		Peak 4'		Peak 3'	
Io	I	Io	I	Io	I	Io	I
91.5	78.5	92.0	79	91.5	80.5	91.5	79
91.5	77.5	92.0	77	92	79	91.5	79
91.5	76.5	92.0	77	91.5	78.5	91	77

HBr - HI Synthetic Mixture No. 2

(c = 7.5×10^{-8} g.moles of HBr/sec.)

Peak 4		Peak 3		Peak 4'		Peak 3'	
Io	I	Io	I	Io	I	Io	I
92	82.5	91.5	83	92.5	84.5	92.5	83.5
91.5	83	91.5	83	92.5	84.5	92	83

Sample 1

Peak 4		Peak 3		Peak 4'		Peak 3'	
Io	I	Io	I	Io	I	Io	I
94	85.25	93.5	85.5	94	87	94	86.5
93	85.25	94.5	84.5	94	86.75	93.5	86
93.5	84.75	94	85	94	86	94	86

Sample 3

Peak 4		Peak 3		Peak 4'		Peak 3'	
Io	I	Io	I	Io	I	Io	I
87.5	70	87.5	70.5	87.5	72.5	88	71
87.5	70.5	87.5	70.5	-		-	

The values of c' which have been obtained by use of equation 3 for the samples 1 and 3 are shown in the text of this thesis.

COMPLETE LIST OF EXPERIMENTS

(1) Decomposition of Benzyl Bromide with Toluene as Radical Catcher.

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
10	0.228	2.40	1.97	2.06	18.25	0.098	783
11	0.229	2.40	1.97	2.06	18.05	0.098	783
12	0.200	2.21	2.60	1.98	18.00	0.105	783
13	0.199	2.21	2.36	1.98	16.8	0.098	783
14	0.235	1.64	2.71	2.04	18.5	0.102	783
15	0.240	1.64	2.71	2.04	19.2	0.105	783
17	0.339	1.43	3.44	2.11	17.95	0.096	783
18	0.335	1.40	3.40	2.11	18.25	0.097	783
19	0.106	1.47	3.20	2.195	26.3	0.143	787
20	0.106	1.47	3.20	2.195	26.9	0.143	787
21	0.142	1.43	3.30	2.25	21.4	0.107	783
22	0.142	1.43	3.30	2.24	21.7	0.109	783
23	0.130	1.75	2.91	2.15	19.1	0.099	783
24	0.131	1.77	2.91	2.15	19.1	0.099	783
25	0.076	2.46	1.97	1.97	19.2	0.100	783
27	0.128	2.57	1.97	2.10	17.0	0.089	783
29	0.106	1.88	2.12	2.21	16.1	0.079	783
30	0.089	1.88	2.82	2.21	16.1	0.079	783

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
31	0.037	1.81	2.96	2.23	12.6	0.058	783
32	0.041	1.81	2.96	2.24	14.6	0.070	783
33	0.122	1.52	3.34	2.11	20.0	0.106	783
34	0.128	1.52	3.34	2.11	19.7	0.104	783
35	0.056	1.51	3.17	2.25	13.2	0.066	783
36	0.057	1.51	3.17	2.25	13.8	0.068	783
37	0.144	1.35	2.27	1.19	12.45	0.112	783
38	0.144	1.35	2.27	1.19	11.75	0.105	783
39	0.072	1.62	3.09	2.17	16.7	0.082	783
40	0.072	1.62	3.09	2.17	16.6	0.082	783
41	0.259	1.84	2.67	2.05	20.2	0.110	783
42	0.262	1.84	2.67	2.05	20.5	0.112	783
43	0.190	3.25	0.89	2.10	17.95	0.095	783
44	0.194	3.25	0.89	2.10	18.5	0.096	783
45	0.150	1.45	2.84	0.92	9.1	0.104	783
46	0.260	2.41	1.82	2.03	7.3	0.036	763
47	0.260	2.41	1.82	2.03	7.1	0.036	763
48	0.274	2.31	1.98	2.20	2.25	0.0098	742
49	0.274	2.31	1.98	2.20	2.02	0.0103	742
50	0.156	1.14	3.41	1.14	27.6	0.306	807
51	0.148	1.14	3.41	1.14	27.9	0.289	807
52	0.132	1.35	3.24	1.13	18.95	0.186	798

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. ^{o}K
53	0.125	1.35	3.24	1.13	20.5	0.204	798
54	0.258	2.3	1.845	2.24	4.48	0.0206	753
55	0.257	2.3	1.845	2.24	3.88	0.0177	753
56	0.258	2.38	1.72	2.20	4.24	0.0198	753
57	0.161	1.60	2.75	1.08	17.2	0.178	797
58	0.150	1.60	2.75	1.08	17.6	0.190	797
59	0.172	3.20	1.14	1.65	14.1	0.096	783
61	0.098	1.45	2.84	1.10	7.15	0.070	783
62	0.098	1.45	2.84	1.10	8.6	0.083	783
63	0.201	1.38	2.67	1.38	8.8	0.067	775
64	0.205	1.38	2.67	1.38	8.75	0.066	775
65	0.276	1.88	2.42	2.11	1.5	0.0013	731
66	0.276	1.88	2.42	2.11	1.3	0.0662	731
67	0.182	2.31	1.84	0.95	32.0	0.406	816
68	1.189	2.31	1.84	0.95	32.9	0.414	816
69	0.176	2.40	1.76	1.01	32.5	0.388	812
70	0.186	2.40	1.84	1.11	30.5	0.359	812
71	0.159	2.24	1.885	0.98	11.85	0.128	790
72	0.162	2.24	1.885	0.98	11.4	0.123	790
73	0.316	2.6	1.58	2.0	3.08	0.0155	745
74	0.329	2.6	1.58	2.0	2.85	0.0151	745
75	0.20	2.59	1.625	2.12	2.1	0.010	736

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
76	0.182	2.59	1.625	2.13	1.9	0.009	736
79	0.329	2.79	1.43	1.93	17.6	0.097	783
80	0.329	2.79	1.43	1.93	15.9	0.093	783
192	0.258	3.27	1.59	1.42	13.8	0.104	783
193	0.258	3.27	1.51	1.42	13.0	0.0985	783
194	0.285	3.17	2.15	1.45	13.9	0.103	783
195	0.133	3.43	1.28	1.27	10.6	0.088	783

(2) Decomposition of o-Chlorobenzyl Bromide with Toluene as Radical Catcher.

No.	Partial Pressure o-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
87	0.12	3.03	0.92	1.96	21.1	0.121	783
88	0.12	3.03	0.92	1.97	21.7	0.125	783
89	0.134	3.1	1.25	1.78	20.3	0.128	783
90	0.140	3.1	1.25	1.78	20.4	0.129	783
91	0.109	3.27	0.885	1.82	22.0	0.137	783
92	0.10	3.27	0.885	1.82	24.7	0.156	783
93	0.10	3.24	0.93	1.71	23.8	0.160	783
94	0.099	3.24	0.93	1.71	23.4	0.156	783
95	0.066	3.18	1.03	1.70	22.75	0.153	783

No.	Partial Pressure o-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
96	0.053	3.18	1.03	1.69	22.4	0.150	783
97	0.169	2.95	1.16	1.67	20.4	0.136	783
98	0.158	2.95	1.16	1.67	21.7	0.147	783
99	0.220	3.03	1.0	1.73	19.5	0.128	783
100	0.220	3.03	1.0	1.73	20.6	0.134	783
103	0.140	2.55	1.50	1.65	9.4	0.060	758
104	0.206	2.63	1.60	2.32	5.1	0.0225	743
105	0.208	2.63	1.60	2.32	5.7	0.0249	743
106	0.110	2.02	2.40	1.04	23.0	0.256	795
107	0.110	2.02	2.40	1.04	20.0	0.217	795
108	0.084	1.98	2.62	0.932	33.0	0.427	805
109	0.084	1.94	2.62	0.932	34.0	0.446	805
110	0.029	1.87	3.0	1.0	31.2	0.375	798
111	0.030	1.87	3.0	1.0	31.1	0.373	798
112	0.124	2.21	2.06	1.17	10.5	0.095	768
113	0.140	2.21	2.06	1.17	8.8	0.077	768
114	0.173	2.19	2.36	1.92	8.7	0.047	751.5
115	0.178	2.19	2.36	1.92	7.9	0.043	751.5
116	0.214	2.53	1.72	2.08	2.95	0.0144	731
117	0.217	2.53	1.72	2.08	3.35	0.0157	731
118	0.216	2.43	1.67	2.10	3.9	0.0190	736

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Hydrogen Iodide mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp. (calc. from moles I_2)	k sec.^{-1}	Temp. °K
119	0.243	1.49	2.77	1.46	71.2		775
120	0.243	1.49	2.77	1.46	71.0		775
121	0.252	1.62	2.57	1.66	57.0		737.5
122	0.252	1.62	2.57	1.67	54.0		737.5
123	0.176	1.31	2.82	2.08	22.1	0.120	704.5
125	0.166	2.70	1.59	2.13	23.4	0.134	704.5
126	0.170	2.56	1.59	2.13	26.7	0.146	704.5
127	0.198	0.785	3.34	2.14	18.6	0.087	704.5
128	0.198	0.785	3.34	2.14	17.9	0.084	704.5
129	0.180	1.59	2.52	2.16	19.35	0.100	704.5
130	0.192	1.36	2.77	2.31	20.3	0.099	704.5
131	0.177	2.02	2.33	2.14	19.8	0.108	703.5
133	0.164	1.025	3.16	2.08	17.0	0.090	704.5
134	0.164	1.025	3.16	2.08	17.1	0.090	704.5
135	0.175	1.82	2.20	2.11	22.0	0.119	704.5
136	0.172	1.91	2.20	2.08	22.4	0.122	704.5
137	0.185	2.49	1.77	2.24	20.6	0.103	704.5
140	0.187	3.26	1.07	2.93	46.4	0.213	704.5
141	0.298	1.15	3.0	1.74	15.2		699
142	0.298	1.15	3.0	1.75	13.2		699
148	0.170	1.65	2.68	2.04	20.8		705.5

No.	Partial Pressure Benzyl Bromide mms.	Partial Pressure Hydrogen Iodide mms.	Contact Time secs.	Total 'Iodide' moles/sec. x 10^8	Iodine moles/sec. x 10^8	Temp. °K
151	0.236	1.685	2.46	16.94	10.96	686
152	0.236	1.685	2.46	-	11.1	686
153	0.216	1.64	1.59	-	19.7	724.5
154	0.213	1.61	1.55	29.53	20.2	724.5
155	0.211	1.52	1.46	-	26.9	724
156	0.210	1.51	1.45	32.6	24.65	724
157	0.246	1.52	1.94	-	-	714
158	0.246	1.52	1.94	38.38	29.4	714
159	0.123	1.23	1.81	-	-	679.5
160	0.123	1.23	1.81	13.19	8.02	679.5

The Decomposition of Benzyl Bromide using Hydrogen Iodide as Radical Catcher in Static System.

No.	Benzyl Bromide moles x 10^4	Hydrogen Iodide moles x 10^4	Iodine Produced moles x 10^6	% Decomp. (calc. from moles I_2)	Contact Time secs.	Temp. °K
166	-	104	5.3	-	7200	492
167	2.225	74.1	176	73	7200	494
168	1.80	61.0	7.56	4.2	7200	359
169	2.04	94.8	6.09	2.86	7200	360

No.	Benzyl Bromide moles x 10^4	Hydrogen Iodide moles x 10^4	Iodine Produced moles x 10^6	% Decomp. (calc. from moles I_2)	Contact Time secs.	Temp. °K
170	1.88	158.0	8.65	4.6	7200	360
171	5.25	93.0	2.68	5.1	7200	359
172	2.08	208.0	6.09	3.0	7200	301
173	-	98.4	1.2	-	7200	360
174	2.64	142.8	1.58	6.0	7200	359
175	8.76	141.4	10.40	11.8	7200	359
176	7.50	144.2	6.30	8.4	7200	359
177	1.94	154.1	5.6	28.7	3600	373
178	2.0	157.7	2.0	10	1800	373
179	1.94	173.6	0.902	4.6	900	373
180	1.93	188.0	2.3	11.9	2400	373
181	2.41	248.0	4.63	21.6	3120	373

			Iodine Added moles x 10^5	Iodine Finally moles x 10^5			
183	2.94	163	-	1.44	4.9	1320	373
184	2.99	148	2.24	6.36	13.8	1320	373
185	2.95	148	0.866	3.27	8.1	1320	373
186	2.98	179	0.393	1.334	3.2	1320	373
187	2.96	244	3.48	9.076	18.9	1320	373
188	2.00	213	1.69	4.205	8.4	1320	373
189	2.88	125	2.83	7.01	14.6	1320	373

(4) Decomposition of m-Chlorobenzyl Bromide using Toluene as Radical Catcher.

No.	Partial Pressure m-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k sec.$^{-1}$	Temp. °K
198	0.294	3.06	2.01	1.53	26.4	0.189	783
199	0.304	3.06	2.01	1.53	29.6	0.210	783
200	0.215	2.62	2.29	1.79	7.3	0.048	747
202	0.234	3.39	1.74	1.85	7.0	0.042	746
203	0.248	3.39	1.74	1.87	5.15	0.031	736
204	0.194	3.50	1.40	1.95	2.33	0.012	719
205	0.199	3.50	1.48	1.94	2.95	0.015	719
206	0.041	2.26	3.29	1.19	44.7	0.501	800
208	0.048	1.97	3.34	1.04	9.3	0.094	767
212	0.248	1.89	3.38	1.0	17.3	0.191	774
213	0.243	1.89	3.38	1.0	17.7	0.194	774
214	0.237	1.88	3.75	0.86	42.3	0.644	810
215	0.237	1.88	3.75	0.86	41.9	0.630	810
216	0.237	3.33	2.32	1.48	14.6	0.106	757
217	0.196	3.30	2.32	1.48	13.6	0.099	757

(5) Decomposition of p-Chlorobenzyl Bromide with Toluene as Radical Catcher.

No.	Partial Pressure p-Cl Benzyl Bromide mms.	Partial Pressure Toluene mms.	Partial Pressure Nitrogen mms.	Contact Time secs.	% Decomp.	k $sec.^{-1}$	Temp. °K
223	0.168	2.99	2.81	1.72	15.0	0.094	758
224	0.175	2.99	2.81	1.72	14.2	0.090	758
229	0.108	3.16	1.63	1.96	25.1	0.147	770.5
230	0.114	3.16	1.63	1.96	25.4	0.149	770.5
231	0.162	2.95	2.45	1.03	28.6	0.327	798
232	0.154	2.95	2.45	1.03	30.0	0.347	798
233	0.129	3.45	2.03	0.94	29.4	0.370	798
234	0.124	3.45	2.03	0.935	29.6	0.375	798
235	0.087	4.26	1.27	1.97	2.65	0.014	720
237	0.280	2.48	3.19	1.10	56.8	0.762	808
238	0.290	2.48	3.19	1.10	58.4	0.790	808
241	0.175	2.97	2.52	2.01	2.75	0.0138	719
242	0.166	2.97	2.52	2.01	3.9	0.0170	719
243	0.263	2.78	3.03	1.84	6.5	0.0363	742
244	0.266	2.78	3.03	1.84	6.2	0.0350	742

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