THE RATE OF THERMAL DISSOCIATION OF DIBENZYL

Iain Munro Thomson Davidson

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THE RATE OF THERMAL DISSOCIATION OF DIBENZYL

being a Thesis
presented by

IAIN MUNRO THOMSON DAVIDSON B.Sc.

to the

UNIVERSITY OF ST.ANDREWS

in application
for the

DEGREE OF DOCTOR OF PHILOSOPHY

May 1958

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 been previously presented in application for a Higher Degree.

The experiments were carried out in the Chemical Research Laboratories of the United College under the direction of Dr. Charles Horrex.

[redacted]

CERTIFICATE

I hereby certify that Mr. Iain Munro Thomson Davidson, 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 United College of the University of St.Andrews in October 1950, and graduated B.Sc. with First Class Honours in Chemistry in June 1954.

The researches described in this Thesis were carried out in the Chemical Research Laboratories of the United College from August 1954 to September 1957, under the direction of Dr. Charles Horrex.

ACKNOWLEDGEMENTS.

I should like to acknowledge my indebtedness to Dr. Charles Horrex for his guidance and assistance in all aspects of this work, and to thank Professor John Read F.R.S. for the provision of research facilities, and the Carnegie Trust for a Research Scholarship.

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INTRODUCTION.

In recent years the gas phase reactions of benzyl compounds have aroused considerable interest, and a reliable value of the heat of formation of the benzyl radical has therefore been sought. This quantity may be derived thermochemically from suitable bond dissociation energies, for example D($PhCH_2$-H) in toluene, but such bond energies have proved surprisingly difficult to determine, and conflicting values have been reported.

Recent experimental work on toluene and other benzyl compounds will be reviewed later in this Introduction and at present only a brief outline of certain work will be given, sufficient to indicate the reasons for undertaking the present investigation.

The problem of the bond dissociation energy of toluene, D($PhCH_2$-H), was first studied by Szwarc(1) who assigned to it a value of 77.5 kcal/mole from his work on the pyrolysis of toluene. In a re-investigation of this reaction Blades, Blades, & Steacie(2) disagreed strongly with his view that the reaction was kinetically simple, and questioned the essential basis of his deductions.

An alternative approach by Anderson, Sheraga, & Van Artsdalen(3) was to study the bromination of toluene; from their results they calculated that D($PhCH_2$-H) was 89.5 kcal. More recently, Benson & Buss(4) have advanced a value of 84 kcal based on a few experiments on the equilibrium constant for the formation of benzyl bromide from toluene and bromine.

Electron impact studies at first confirmed Szwarc's value of 77.5 kcal (5,6), but later work has been in disagreement with this(7,8); to add to the confusion, the $C_7H_7^+$ ion which is the product of electron impact has recently been shown to be the tropylium and not the benzyl ion(19). The interpretation of electron impact studies on toluene is therefore in doubt.

In view of this confused situation, less direct estimates of $D(PhCH_2-H)$ become important, and the evaluation of the central C-C bond dissociation energy in dibenzyl, $PhCH_2CH_2Ph$, should be particularly useful in this connection. The bond energies are related by the heats of formation of dibenzyl, toluene, and the hydrogen atom, thus:-

$$2D(PhCH_2-H) - D(PhCH_2CH_2Ph) = 2\Delta H_f^o(H-) - 2\Delta H_f^o(PhCH_3) + \Delta H_f^o(PhCH_2CH_2Ph)$$

Reliable values of the heats of formation are available, and as $D(PhCH_2-H)$ is doubled in the expression, a moderately accurate value for the dibenzyl bond energy should give a good value of $D(PhCH_2-H)$. Even an inaccurate value of $D(PhCH_2CH_2Ph)$ would be helpful in assessing the relative merits of the values for toluene referred to above, since 77.5 and 89.5 kcal for toluene would correspond to 45 and 69 kcal for dibenzyl.

These considerations prompted Horrex & Miles(9) to study the pyrolysis of dibenzyl with a view to determining the central bond energy. They suggested that the rate-determining step was the dissociation of dibenzyl to benzyl radicals, and that these attacked the parent compound to produce toluene, together with secondary processes leading to benzene, styrene, and stilbene. They concluded that the decomposition was homogeneous and of the first order; their first order rate constants, calculated on the assumption that the toluene was a measure of the benzyl radicals produced, were represented by the equation:-

$$k_{secs^{-1}} = 10^{9.29 \pm 0.22} \exp^{-48000 \pm 1000/RT}$$

They noted that the activation energy of 48 kcal would be anticipated from Szwarc's value for toluene. However, they pointed out that their activation energy would not equal the dissociation energy if an extensive recombination of benzyl radicals occurred, and that their temperature independent factor was abnormally low for a unimolecular reaction.

The pyrolysis was repeated by Pittilo(10) who used a similar reaction system, but had more refined analytical techniques available to him. He found the same products in similar proportions, but his investigation revealed that the product ratios varied both with temperature and with partial pressure of dibenzyl, and that the decomposition,as measured by toluene produced, was not first order, but closely approximated to an order of 1.5, with an energy of activation of 47 kcal. These findings led Pittilo to suggest that an initial equilibrium was rapidly established between dibenzyl molecules and benzyl radicals, and that decomposition then occurred by the attack of radicals on parent molecules. Consequently, the rate-determining step in the decomposition would be the radical attack, and the observed energy of activation would depend on the activation energy for this attack, as well as on the dissociation energy, so that $D(PhCH_2-CH_2Ph)$ could not be calculated from the knowledge of the energy of activation alone.

Pittilo attempted to obtain evidence in support of the idea of an initial equilibrium by synthesising some partly deuterated dibenzyl by the method described later in this Thesis, pyrolysing a mixture of this and normal dibenzyl, and comparing the mass spectrum of the solid products with the mass spectrum of the unpyrolysed mixture. If radical formation and recombination had occurred, the dibenzyl species of intermediate molecular weight would increase at the expense of the heaviest and lightest dibenzyl species in the mixture. The deuterated material prepared by Pittilo was in itself a mixture of at least four dibenzyl species and the resolution of the mass spectrometer was far from adequate, so that he was unable to obtain any quantitative results. A change in the mass spectrum of a mixture after pyrolysis was just detectable and was observed in mixtures which had been pyrolysed at temperatures lower than the decomposition temperatures, which suggested that the dissociation and recombination reactions did occur, and that dissociation was more rapid than decomposition.

Pittilo's work had shown that the value of the energy of activation for the decomposition found by Horrex & Miles was quite accurate, but that they were mistaken in assigning their value to the dissociation energy of the central C-C bond of dibenzyl. It had also indicated a possible way of observing decomposition and dissociation independently, by the use of mixtures of deuterated and undeuterated dibenzyl.

It therefore seemed likely that a quantitative investigation of the pyrolysis of dibenzyl and deuterated dibenzyl would give valuable information. If an isotopically pure, symmetrically deuterated dibenzyl, like 1,2 diphenyl tetradeuteroethane, $PhCD_2CD_2Ph$, could be synthesised, then a mixture of this with an equal amount of dibenzyl, $PhCH_2CH_2Ph$, would give on dissociation $PhCH_2$- and $PhCD_2$- radicals. Recombination of these radicals would give the hybrid, $PhCH_2CD_2Ph$, and the rate of its formation could be measured mass spectrometrically. If the dissociation process proved rate-determining in the formation of $PhCH_2CD_2Ph$, it would be possible to relate the observed energy of activation to the dissociation energy required.

The work described in the subsequent pages of this Thesis carried out the programme outlined above. For its realisation it was necessary:

1) To synthesise $PhCD_2CD_2Ph$ of high isotopic purity.
2) To reconstruct the mass spectrometer used by Pittilo to provide a resolution of 1 in 200.
3) To construct a reaction system which could operate on milligram quantities of mixtures of $PhCH_2CH_2Ph$ and $PhCD_2CD_2Ph$ and permit continuous mass spectrometric observations of the formation of $PhCH_2CD_2Ph$.

Before the description of the experimental work, a brief survey of relevant work on bond dissociation energies is given, with particular reference to methods and reactions which are related to the above problems. A wider survey would be superfluous in view of the number of recent comprehensive publications on the subject(11,12,13).

Bond Dissociation Energies.

Definition: The dissociation energy of the bond $R_1 - R_2$ in the molecule R_1R_2 is the endothermicity of the reaction in which R_1R_2 is dissociated into two fragments, R_1- and R_2- :-

$$R_1R_2 \rightarrow R_1- + R_2- - D(R_1 - R_2)$$

R_1R_2, R_1-, and R_2- should be in the gaseous phase, at zero pressure and at 0°K.

Experimental Methods for the determination of Dissociation Energies.

1) Equilibrium: This method depends on the measurement of the equilibrium constant, K, over a range of temperature for the dissociation:-

$$R_1R_2 = R_1- + R_2-$$

Then from the van't Hoff Isochore, $\frac{d \ln K}{d T} = \frac{\Delta H^o}{RT^2}$, ΔH^o, the change in heat content at the temperature of the investigation, may be obtained. The value of ΔH^o will be close to $D(R_1 - R_2)$, particularly if the temperature is not high. It may be corrected to absolute zero, to give ΔH^o_o, which equals $D(R_1 - R_2)$, if the data for the variation of heat capacity of R_1R_2 with temperature are known.

In order to make use of this method it is necessary either to have sufficient dissociation for the equilibrium pressure of the dissociated fragments, R_1- and R_2-, to be measured accurately, or to use a very sensitive means of analysis based on some suitable physical property related to the concentration of the fragments. Furthermore, R_1- and R_2- must not react in any way other than to re-form R_1R_2.

As a result of these practical limitations few reliable values of dissociation energies have been obtained by the equilibrium method, despite its theoretical simplicity. The method has given good results in the case of iodine, and fair agreement with spectroscopic values has been obtained for some other diatomic molecules; but in general it has been inapplicable to polyatomic molecules, although the central C-C bond energy in hexaphenyl ethane has been evaluated by equilibrium measurements in solution.

The main obstacle is the reactivity of the radicals produced. The benzyl radical, however, is stabilised by resonance, having five main canonical forms, and is as a result much less reactive than simple free radicals. Horrex & Miles$^{(9)}$ therefore attempted to measure the equilibrium constant for the dissociation of dibenzyl:-

$$PhCH_2CH_2Ph \quad = \quad PhCH_2- \; + \; PhCH_2-$$

They conducted their experiments in a static system and measured the pressure with a quartz fibre manometer which had been calibrated against a McLeod gauge for dry air at temperatures up to 1000°K. They used low pressures of dibenzyl, from 4 to 26 microns and found little dissociation up to about 460°C, but a marked increase in pressure thereafter. This pressure change was irreversible, no decrease being observed when the system was cooled below 460°C, which showed that other molecules had been formed by pyrolysis and hence that the dissociation energy of dibenzyl could not be determined by a static manometric method.

2) Kinetic: In the kinetic method the endothermicity of the unimolecular dissociation:- $R_1R_2 \rightarrow R_1- \; + \; R_2-$

is determined. This endothermicity is the difference between the activation energies for the dissociation of R_1R_2 and for the recombination of R_1- and R_2-. The assumption is usually made that the activation energy for the recombination is zero, and that the observed activation energy then equals the bond dissociation energy, $D(R_1 - R_2)$. This is not strictly true, since R_1R_2, R_1-, and R_2- are not in the states stipulated in the Definition of $D(R_1 - R_2)$. The precise relationship between the activation energy and D has been discussed by Szwarc$^{(12)}$, who concluded that the error in identifying the two is less than 2 kcal/mole up to 1000°K. The assumptions made by Szwarc in arriving at his conclusion may not be completely correct, but it is generally accepted that the two quantities are equal within the limits of experimental error of most kinetic measurements, so that no correction is usually made. The assumption that radical recombination reactions have zero activation energy has some theoretical justification, and considerable experimental support: self-consistent values of bond energies in good agreement with those from other sources have been obtained.

The chief limitation of the kinetic method is the difficulty of ensuring that dissociation into radicals does in fact occur and that this dissociation determines the rate of the decomposition. It is rarely possible to measure the rate of formation of radicals directly, and measurement of the radical concentration merely gives the stationary state, i.e. the balance between formation of radicals by dissociation and loss by recombination or reaction. Therefore it is usually necessary to rely on less direct evidence. In order to simplify the decomposition mechanism as much as possible it is best to arrange a system in which the radicals are removed and measured in some way before they have any opportunity to recombine or take part in complicating side reactions. Where this is not possible interpretation of the experimental results is difficult and caution must be exercised in identifying the observed activation energy with the bond dissociation energy.

The pyrolysis of toluene by Szwarc(1) illustrates the use of the kinetic method. He investigated the decomposition in a flow system, between 680° and 850°C, using toluene alone at pressures of 2 to 15 mm. He kept the percentage decomposition between 0.01 and 1 %, so that a large excess of toluene was always present. Under these conditions, Szwarc found methane, hydrogen, and dibenzyl in his products, and no ethane or ethylene. The total ($CH_4 + H_2$) concentration was estimated by pressure measurement in a calibrated volume, and the $CH_4 : H_2$ ratio determined by combustion of the H_2 in a copper oxide furnace. Only the gaseous products were analysed quantitatively. Szwarc proposed the following reaction mechanism:-

$$\mathrm{PhCH_3} \rightarrow \mathrm{PhCH_2-} + \mathrm{H-} \qquad 1)$$

$$\mathrm{PhCH_3} + \mathrm{H-} \rightarrow \mathrm{PhCH_2-} + \mathrm{H_2} \qquad 2)$$

and

$$\mathrm{PhCH_3} + \mathrm{H-} \rightarrow \mathrm{PhH} + \mathrm{CH_3-} \qquad 3)$$

$$\mathrm{PhCH_3} + \mathrm{CH_3-} \rightarrow \mathrm{CH_4} + \mathrm{PhCH_2-} \qquad 4)$$

or

$$\mathrm{PhCH_3} + \mathrm{H-} \rightarrow \mathrm{Ph-} + \mathrm{CH_4} \qquad 5)$$

$$\mathrm{PhCH_3} + \mathrm{Ph-} \rightarrow \mathrm{PhH} + \mathrm{PhCH_2-} \qquad 6)$$

$$2\ \mathrm{PhCH_2-} \rightarrow \mathrm{PhCH_2CH_2Ph} \qquad 7)$$

The decomposition was shown to be homogeneous by packing the reaction vessel with silica wool. The percentage decomposition was calculated from the gas produced, which consisted of CH_4 and H_2 in the ratio 1.5 : 1, on the assumption that one mole of gas corresponded to one mole of primarily decomposed toluene. The decomposition was first order and the rate constants could be expressed by the equation:-

$$k_{\mathrm{secs}^{-1}} = 2 \times 10^{13} \exp^{-77500/RT}$$

On the basis of his reaction scheme, Szwarc proposed 77.5 kcal/mole for $D(PhCH_2-H)$.

In this decomposition a chain reaction was prevented by the rapid reaction of hydrogen atoms and methyl radicals with toluene to form unreactive benzyl radicals, thus greatly simplifying the reaction mechanism. This is an early example of the toluene carrier gas technique. Szwarc & co-workers have pyrolysed a large number of compounds in the presence of toluene and obtained activation energies which they have equated to specific bond dissociation energies. For example, Szwarc(14) pyrolysed ethyl benzene, $PhCH_2CH_3$, in the presence of a 20 to 50 fold excess of toluene and obtained an energy of activation of 63.2 kcal/mole. He concluded from the products, which were largely dibenzyl and methane in approximately equal amounts, that the initial step was the dissociation of ethyl benzene to benzyl and methyl radicals:-

$$PhCH_2CH_3 \rightarrow PhCH_2- + CH_3- \qquad 1)$$

$$PhCH_3 + CH_3- \rightarrow PhCH_2- + CH_4 \qquad 2)$$

and assigned the value of 63 kcal to the dissociation energy, $D(PhCH_2-CH_3)$. From this value, his value of $D(PhCH_2-H)$, and thermochemical data, he calculated $D(CH_3-H)$ to be 102.9 kcal, in excellent agreement with the accepted value for the first bond dissociation energy of methane.

It should be noted, however, that the calculation involved the difference between $D(PhCH_2-H)$ and $D(PhCH_2-CH_3)$, so that if both Szwarc's values were in error by about the same amount, a good value for $D(CH_3-H)$ could still be obtained. The mechanisms on which Szwarc based his calculations are considerably over-simplified, for instance in the case of ethyl benzene, quantities of hydrogen up to 25 % of the methane were formed, so that the toluene had not been effective in suppressing reactions other than 1) and 2) completely. It may be that with two very similar compounds like toluene and ethyl benzene Szwarc's technique introduces a systematic error. In this connection, it is perhaps significant that Szwarc's value of 50.5 kcal for D($PhCH_2$-Br) (15) does not appear to be consistent with his value for toluene (Benson & Buss(4)).

In the case of toluene itself, the re-investigation by Steacie et al.(2) has revealed that the decomposition is considerably more complex than Szwarc had supposed. These workers paid considerable attention to the reaction products, and found the ratio of CH_4 to H_2 to be 2.2, and not 1.5; they identified benzene, in corresponding concentration to the methane, and a small quantity of styrene. UV absorption analysis and chromatography disclosed the presence of dimethyl diphenyls among the solid products, with as little as 50 % dibenzyl. They found that the decomposition was not first order: the rate of (CH_4 + H_2) production increased two-fold as the contact time was increased from 0.068 to 0.568 seconds. Variation of pressure and surface area also affected the rate slightly. Their investigations covered a higher temperature range than Szwarc had used, and in fact there was only an overlap of a few degrees. For a series of experiments at a contact time of 0.068 seconds the temperature dependence of their first order rate constants gave an energy of activation of 90 kcal.

It is unfortunate that Steacie did not carry out his stated intention of repeating Szwarc's work, but used a higher temperature range and a very short contact time in evaluating the activation energy. Nevertheless, his results leave no doubt that Szwarc's interpretation of the mechanism of the thermal decomposition of toluene is incomplete, and his value of $D(PhCH_2-H)$ questionable.

A more elaborate example of the use of kinetic measurements in this field is furnished by the work of Anderson, Sheraga, & van Artsdalen (3) on the thermal and photochemical bromination of toluene. Their results were mainly obtained from photochemical experiments between 82° and 132°C. They showed by infra-red analysis that the reaction was predominantly a side-chain substitution, forming benzyl bromide and hydrogen bromide; the latter strongly inhibited the reaction. They proposed the following scheme:-

$Br_2 \rightarrow 2\ Br-$ 1) photochemical or thermal

$Br- + PhCH_3 \rightarrow PhCH_2- + HBr$ 2)

$PhCH_2- + Br_2 \rightarrow PhCH_2Br + Br-$ 3)

$PhCH_2- + HBr \rightarrow PhCH_3 + Br-$ 4)

$Br- + Br- + M \rightarrow Br_2 + M$ 5)

From the temperature dependence of the rate of the overall reaction they calculated an activation energy of 7.2 kcal/mole, which they took to be the activation energy of the rate-determining step 2). The temperature dependence of the HBr inhibition led to an activation energy of 5 kcal, which they equated to $(E_4 - E_3)$. Hence $D(PhCH_2-H)$ may be calculated:-

Assume $E_3 = 0$, then $E_4 = 5$ kcal. Then:-

$PhCH_3 + Br- \rightarrow PhCH_2- + HBr \quad \Delta H_{381} = E_2 - E_4 = 2.2$ kcal/mole

$HBr \rightarrow H- + Br- \quad \Delta H_{381} = 87.7$ kcal/mole *

$\therefore\ PhCH_3 \rightarrow PhCH_2- + H- \quad \Delta H_{381} = \underline{89.9 \text{ kcal/mole} = D(PhCH_2-H)}$.

(* Selected Values of Chemical Thermodynamic Properties, Nat. Bur. Stds.)

This determination is much less direct than that of Szwarc.

Possible sources of error are: the value of D(H-Br) which was used; the value of the experimentally determined activation energies; and the assumption that $E_3 = 0$. It is quite probable that reaction 3) does require a small activation energy, so that van Artsdalen's value is best regarded as an upper limit. Nevertheless it does suggest that the true value of D($PhCH_2$-H) is appresiably higher than the 77.5 kcal/mole found by Szwarc.

The pyrolysis of dibenzyl illustrated some of the hazards of the kinetic method. Horrex & Miles(9) investigated the decomposition in a flow system with nitrogen as a carrier gas, between 630° and 774°C. They did not have precise means of analysis available to them and were obliged to measure unsaturated products by bromination, and to estimate liquid products by comparison of experimental and synthetic fractional distillation curves. They identified toluene, benzene, styrene, and stilbene among the products, together with very small amounts of hydrogen and hydrocarbon gases. They observed no systematic change in the product ratios, and represented the stoichometry by the equation:-

$$3\ PhCH_2CH_2Ph = 2\ PhCH_3 + PhH + PhCH{:}CH_2 + PhCH{:}CHPh$$

They did not have sufficient evidence to put forward a definite reaction scheme, but suggested the following possible steps:-

$$PhCH_2CH_2Ph \rightarrow 2\ PhCH_2\text{-} \qquad 1)$$

$$PhCH_2CH_2Ph + PhCH_2\text{-} \rightarrow PhCH_3 + PhCH.CH_2Ph \qquad 2)$$

$$PhCH.CH_2Ph \rightarrow PhCH{:}CHPh + H\text{-} \qquad 3)$$

$$PhCH_2CH_2Ph + H\text{-} \rightarrow PhCH_2CH_2\text{-} + PhH \qquad 4)$$

$$PhCH_2CH_2\text{-} \rightarrow PhCH{:}CH_2 + H\text{-} \qquad 5)$$

$PhCH.CH_2Ph \rightarrow PhCH{:}CH_2 + Ph-$ 6)

$PhCH_2CH_2Ph + Ph- \rightarrow PhCH.CH_2Ph + PhH$ 7)

$2\ PhCH.CH_2Ph \rightarrow PhCH{:}CHPh + PhCH_2CH_2Ph$ 8)

They assumed that 1) was the rate-determining step, and that it was followed by 2), then by some or all of the remainder. On this basis, they assigned their value of 48 kcal/mole to D($PhCH_2$-CH_2Ph).

However, the work of Pittilo(10) referred to earlier showed that the rate of the decomposition was determined by steps 1) and 2), as a result of the participation of the reverse of 1) in the mechanism, so that the straightforward application of the kinetic method to dibenzyl is incapable of giving the bond energy.

The bond energy of dibenzyl could be determined kinetically either by measuring the rate of the initial dissociation, the basis of the method to be described in this Thesis, or by carrying out the decomposition in the presence of a compound which would react so rapidly with benzyl radicals that 1) would in fact be the rate-determining step. This is the essential idea of Szwarc's toluene carrier gas technique, but toluene would clearly be ineffective in this case. However, Alexander(16) in a recent investigation pyrolysed dibenzyl in the presence of hydrogen iodide, and found that iodine was produced at a rate which was first order in dibenzyl and independent of hydrogen iodide. The reactions involved are:-

$PhCH_2CH_2Ph \rightarrow 2\ PhCH_2-$ 1)

$PhCH_2- + HI \rightarrow PhCH_3 + I_2$ 2)

Reaction 2) was sufficiently fast for 1) to be the rate-determining step in the formation of iodine. The kinetics were complicated by the occurrence of the reaction :-

$$PhCH_2CH_2Ph + I_2 \rightarrow PhCH{:}CHPh + 2\ HI \qquad 3)$$

Alexander was able to apply a correction for 3) and obtained an activation energy of 61 kcal/mole, which he equated to $D(PhCH_2-CH_2Ph)$.

The results of these three investigations of dibenzyl will be discussed in relation to the findings of this investigation later in this Thesis.

3) Electron Impact: The excitation of molecular energy levels leading to dissociation may be achieved by electron impact.

The molecules of R_1R_2 are bombarded in the ion source of a mass spectrometer by a beam of electrons accelerated across a known potential difference, and the mass to charge ratio and intensity of the ions produced are measured. The energetics of the simple dissociation and ionisation process may be represented by the equation:-

$$A_o(R_1^+) = D(R_1-R_2) + I(R_1) + E(R_1^+) + E(R_2)$$

where $A_o(R_1^+)$ = appearance potential of the ion R_1^+ at rest, i.e. the potential applied to the beam of electrons which is just sufficient to produce R_1^+

$I(R_1)$ = ionisation potential for the process $R_1 \rightarrow R_1^+$

$E(R_1^+)$ & $E(R_2)$ = electronic energy above the ground state of R_1^+ & R_2.

The ionisation potential for atoms is usually known from the atomic spectrum, but for radicals it has to be determined by measurement of the appearance potential when ions are introduced into the mass spectrometer, or from $A_o(R_1^+)$ in R_1R_3, where $D(R_1-R_3)$ is known.

$A_o(R_1^+)$ is determined by plotting the ion current of R_1^+ against the electron accelerating potential for values greater than A_o

and extrapolating to zero ion current. The voltage scale is calibrated by simultaneous measurements on an inert gas of known ionisation potential. The curve obtained, the ionisation efficiency curve, approaches the axis asymptotically, which makes extrapolation difficult, and appearance potential measurements are probably not accurate to more than 0.2 ev. However, Warren(17) has described a method in which the difference of the voltages required to give the same ion current for R_1^+ and the calibrating gas is plotted against ion current and extrapolated to zero. This procedure is said to give values accurate to better than 0.05 ev.

It is usually not possible to determine the values of the E terms in the above equation, so that several values of $D(R_1 - R_2)$ may be derived from appearance potential measurement, depending on the assumed values of the E terms. The assumption is often made that the dissociation and ionisation occurs with the particles in their ground state, so that the E terms are zero. Stevenson(18) has discussed the results obtained by use of this assumption.

By measurement of the appearance potential of the same ion in two different compounds, dissociation energies may be calculated without a knowledge of ionisation potentials, if thermochemical data are available. This indirect method was used by Schissler & Stevenson(5) in their estimation of $D(PhCH_2-H)$ in toluene.

They measured the appearance potential of the $C_7H_7^+$ ion in toluene and dibenzyl as 11.85 ± 0.1 ev and 10.55 ± 0.1 ev respectively. Their calculation was as follows:-

$$PhCH_3 \rightarrow C_7H_7^+ + H- + e \qquad A_1(C_7H_7^+) = D(PhCH_2-H) + I(PhCH_2)_2$$

$$(PhCH_2)_2 \rightarrow C_7H_7^+ + PhCH_2- + e \qquad A_2(C_7H_7^+) = D(PhCH_2-CH_2Ph) + I(PhCH_2)_2$$

Subtracting:-

$$(PhCH_2)_2 + H- \rightarrow PhCH_3 + PhCH_2- \qquad \Delta H = A_2(C_7H_7^+) - A_1(C_7H_7^+) \qquad 3)$$

Take $\Delta H_f^o(PhCH_3) = 11.95$ kcal/mole; $\Delta H_f^o(PhCH_2)_2 = 28.0$ kcal/mole;

$D(H-H) = 4.48$ ev per molecule, then

$$(PhCH_2)_2 + 2H- \rightarrow 2\,PhCH_3 \qquad \Delta H = -4.66 \text{ ev/molecule} \qquad 4)$$

3) - 4) gives:-

$$PhCH_2-H \rightarrow PhCH_2- + H- \qquad D(PhCH_2-H) = 4.66 + A_2(C_7H_7^+) - A_1(C_7H_7^+)$$

$$\therefore D(PhCH_2-H) = 4.66 + 10.53 - 11.85 = 3.34 \pm 0.14 \text{ ev/molecule}$$

$$= \underline{77 \pm 3 \text{ kcal/mole.}}$$

Schissler & Stevenson's result has been criticised by Farmer et al.(7). They show that the former authors' equations may be re-arranged to give the ionisation potential of the benzyl ion purely as a function of observed heats of formation and appearance potentials; the figure obtained is 8.51 ev. Direct measurements of the ionisation potential of benzyl radicals produced thermally from benzyl iodide(20) and from other benzyl compounds all give values close to 7.8 ev, so that Schissler & Stevenson's appearance potentials appear to be incorrect. The errors could arise from the difficulty of extrapolating the ionisation efficiency curves accurately, or from excess energy terms which differed for toluene and dibenzyl, so that they did not cancel out in the subsequent calculations. Farmer et al.(7) investigated the formation of ions from trideuterotoluene, $PhCD_3$. They found that $C_7H_5D_2^+$ and $C_7H_4D_3^+$ ions were produced in the ratio to be expected statistically if all hydrogens were equivalent in the dissociation process. They assumed that these ions were benzyl$^+$ and tolyl$^+$ respectively, and concluded that since the dissociation of toluene under electron impact is obviously not a simple process, the method used by Schissler & Stevenson cannot be applied to the determination of bond energies until inconsistencies in the ionisation and appearance potentials have been resolved.

Recently, Rylander, Meyerson, & Grubb$^{(19)}$ have examined the mass spectra of $PhCH_3$, $PhCH_2D$, and $PhCD_3$. Their results are used later in this Thesis in the analysis of the deuterated toluenes formed in the pyrolysis, and the detailed figures may be found there. They show that the proportions of $C_7H_7^+$ type ions produced in the mass spectra of the deuterated toluenes can only be explained by assuming that all the hydrogens are equivalent, in agreement with the findings of Farmer et al. Unlike these authors, however, they postulate the formation of the tropylium ion, $(CH)_7^+$, which is known to be a stable cation. Since the hydrogen atoms lose their identity in the formation of $C_7H_7^+$ from toluene, the rearrangement to the seven-membered ring must occur before or during bond cleavage.

Rylander et al. show by thermochemical calculation that the tropylium ion will be more stable than the benzyl ion if the resonance energy of the latter is less than 19 kcal. The formation of the tropylium ion may account for the anomalous results of electron impact studies, since the appearance potential observed, that of the tropylium ion, cannot be directly related to the dissociation of toluene to benzyl and hydrogen.

4) Thermochemical: The relationships between bond dissociation energies, thermochemical quantities and thermodynamic quantities have been mentioned, and the use of one bond energy in the determination of another has been illustrated in the specific case of toluene and

dibenzyl. An interesting approach to the benzyl radical problem was used by Benson & Buss(4), who investigated the gas phase reaction:-

$$PhCH_3 + Br_2 = PhCH_2Br + HBr$$

They measured the equilibrium constant at 423°K, from which they calculated the free energy change, $\Delta G^\circ = -RT \ln K$.

Then, having obtained the entropy change, ΔS° from calculated entropies, they were able to calculate the enthalpy change, $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

Their value at 423°K was - 8.0 ± 1.2 kcal/mole.

This is related to the bond energies by the equation:-

$$D(PhCH_2\text{-}H) - D(PhCH_2\text{-}Br) = \Delta H^\circ + D(H\text{-}Br) - D(Br\text{-}Br)$$

When the accepted values of D(HBr) and $D(Br_2)$ have been inserted, the RHS is 33.7 kcal/mole.

$D(PhCH_2\text{-}Br)$ has been evaluated by several workers, and Szwarc's value of 50.5 kcal/mole(15) is generally accepted. Consequently the work of Benson & Buss suggests that $D(PhCH_2\text{-}H)$ is about 84 kcal/mole. They also calculated from their results and the appropriate thermochemical data that the heat of formation of benzyl bromide is 20.0 kcal/mole, and the heat of formation of the benzyl radical, 44.9 kcal/mole.

In this Introduction the methods used to evaluate benzyl-X bond energies have been reviewed. The discrepancies illustrate the need for further investigation by different methods, and this Thesis describes a new variant of the kinetic method, applied to the dissociation of dibenzyl.

THE SYNTHESIS OF TETRADEUTERODIBENZYL.

Preliminary work.

Pittilo(10) attempted to prepare deuterated dibenzyl by shaking a solution of diphenyl acetylene in methanol with Adams catalyst in an atmosphere of deuterium. He prepared the deuterium by the electrolysis of dilute D_2SO_4, formed by adding anhydrous sulphur trioxide to deuterium oxide(99.78%). Identification of his product was hampered by the poor resolution of the mass spectrometer at that time, but he concluded that it consisted of a mixture of four partly deuterated dibenzyls.

When the resolution of the mass spectrometer had been sufficiently improved, the author repeated this preparation. The product was analysed in the mass spectrometer and was found to consist of a mixture of mono-, di-, tri-, and tetra- deutero dibenzyls in the approximate ratios 3 : 5 : 5 : 3. A mass spectrometer analysis of the deuterium used gave its purity as 95.6%, so that it must have been diluted by hydrogen in the course of the reaction, by exchange with either the solvent, the aromatic nuclei, or both.

The extent of the exchange reaction between deuterium and the solvent was studied by shaking methanol with deuterium in the presence of Adams catalyst, drawing off a sample of the gas,, and analysing in the mass spectrometer. After two hours the deuterium content had dropped to 27%. In a similar experiment with n-hexane, the deuterium content dropped to 44% in the same time, thus showing that this particular catalyst could exchange the hydrogen of a hydrocarbon solvent with deuterium.

In order to avoid the use of a solvent, an apparatus was constructed in which diphenyl acetylene could be hydrogenated in the vapour phase. A wide bore pyrex tube, wound with nichrome heating tape, was packed with glass wool coated with Adams catalyst and mounted horizontally in an asbestos jacket. At one end of the tube was a short unheated section, and at the other, a U-tube. The whole assembly was incorporated with a mechanically operated circulating pump$^{(21)}$ and a mercury manometer in a closed circulating system. The system was connected through a tap to high vacuum pumps and could be filled with hydrogen from a storage bulb by means of a Toepler pump. A nickel boat containing diphenyl acetylene was placed in the cold section of the reaction tube and the system evacuated; liquid air was then placed round the U-tube, about 500 mm. of hydrogen admitted to the system, and the boat manoeuvered into the hot zone with a magnet. The hydrogen was circulated through the tube, picking up diphenyl acetylene vapour at the inlet, and depositing the product in the U-tube at the outlet. By adjusting the rate of flow of hydrogen and the temperature of the catalyst-packed region it was possible to obtain in the U-tube a product which was shown by its UV absorption spectrum to be 99% dibenzyl.

An experiment was then performed using deuterium instead of hydrogen. After a time a sample of deuterium was withdrawn and analysed in the mass spectrometer. An appreciable increase in the hydrogen and hydrogen deuteride content was observed, which could only be due to reaction between the deuterium and the hydrogen in the phenyl groups of the diphenyl acetylene.

In view of these findings, no further attempt was made to synthesise tetradeuterodibenzyl, $PhCD_2CD_2Ph$, by direct deuteration.

Substitution reactions.

The possibility of utilising substitution reactions instead of an addition reaction was next considered. Leblanc, Leitch & Renaud(22) have prepared a number of deuterated aliphatic hydrocarbons by the action of zinc and deuterium oxide on alkyl halides. For example, they prepared monodeuteroethane by adding deuterium oxide to a suspension of zinc dust in ethyl iodide, and tetradeuteromethane from carbon tetra-chloride. They carried out the reactions in a vacuum system and reported good yields and high isotopic purity.

As this method seemed capable of wide application, an attempt was made to adapt it directly to the problem of synthesising $PhCD_2CD_2Ph$ by reacting tolan tetrachloride, $PhCCl_2CCl_2Ph$, with zinc and deuterium oxide.

Tolan tetrachloride was synthesised by saturating a solution of diphenyl acetylene in chlorogorm with chlorine at 0°C(23). The tetrachloride was recrystallised from benzene and had a melting point of 161°C.

Several trial experiments were performed to discover if tolan tetrachloride would react with zinc and water to give dibenzyl. 2.5 gm. of zinc dust were added to a solution of 5 gm. of tolan tetrachloride in dioxan, the suspension stirred vigorously, and 0.5 ml. of water added slowly. Stirring was continued for half an hour after the addition of the water, then the solution was filtered, the dioxan distilled off, and the residue examined. It was shown by melting point and a Lassaigne test to be unchanged tolan tetrachloride.

Synthesis of $PhCD_2CD_2Ph$.

Outline of four stage synthesis, showing deuterated products only.

$$CH_3COCl + D_2O \longrightarrow CH_3COOD + DCl_{(\text{collected})} \qquad \text{i)}$$

$$C_6H_5CCl_3 + Zn + 3CH_3COOD \longrightarrow C_6H_5CD_3 \qquad \text{ii)}$$

$$C_6H_5CD_3 + SO_2Cl_2 \xrightarrow{(PhCO_2)_2} C_6H_5CD_2Cl + DCl \qquad \text{iii)}$$

$$2C_6H_5CD_2Cl + 2Mg + 2CuCl_2 \longrightarrow C_6H_5CD_2CD_2C_6H_5 \qquad \text{iv)}$$

Subsequently, more vigorous methods were employed. A mixture of the tetrachloride solution, zinc, and water was refluxed on a water bath for several hours; and similar experiments were carried out in which acetic acid was used in place of water, and ether instead of dioxan. In no case was any reaction observed, and the tolan tetrachloride was invariably recovered unchanged.

The mechanism of this reaction is believed to be similar to that of a Reformatsky reaction, and its failure in this case may be due to the formation of the organo-metallic intermediate being prevented by steric hindrance.

Synthesis from trideuterotoluene, $PhCD_3$.

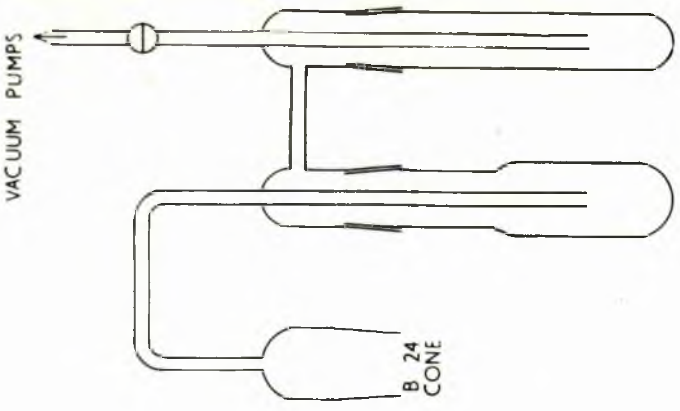
Renaud & Leitch have also described a synthesis of trideuterotoluene from benzotrichloride(24). Their method consisted of adding an ethereal solution of benzotrichloride slowly to a well-stirred mixture of ether, zinc dust, and monodeuteroacetic acid, keeping the temperature at 3°C throughout. They made deuteroacetic acid by adding deuterium oxide to acetyl chloride. They reported a 78% yield of trideuterotoluene, with an isotopic purity of 98%.

The fact that toluene deuterated only in the side chain can be prepared by this method offers an unambiguous route for the synthesis of $PhCD_2CD_2Ph$: the toluene can readily be chlorinated to benzyl chloride, from which dibenzyl may be prepared by a reaction of the Grignard type.

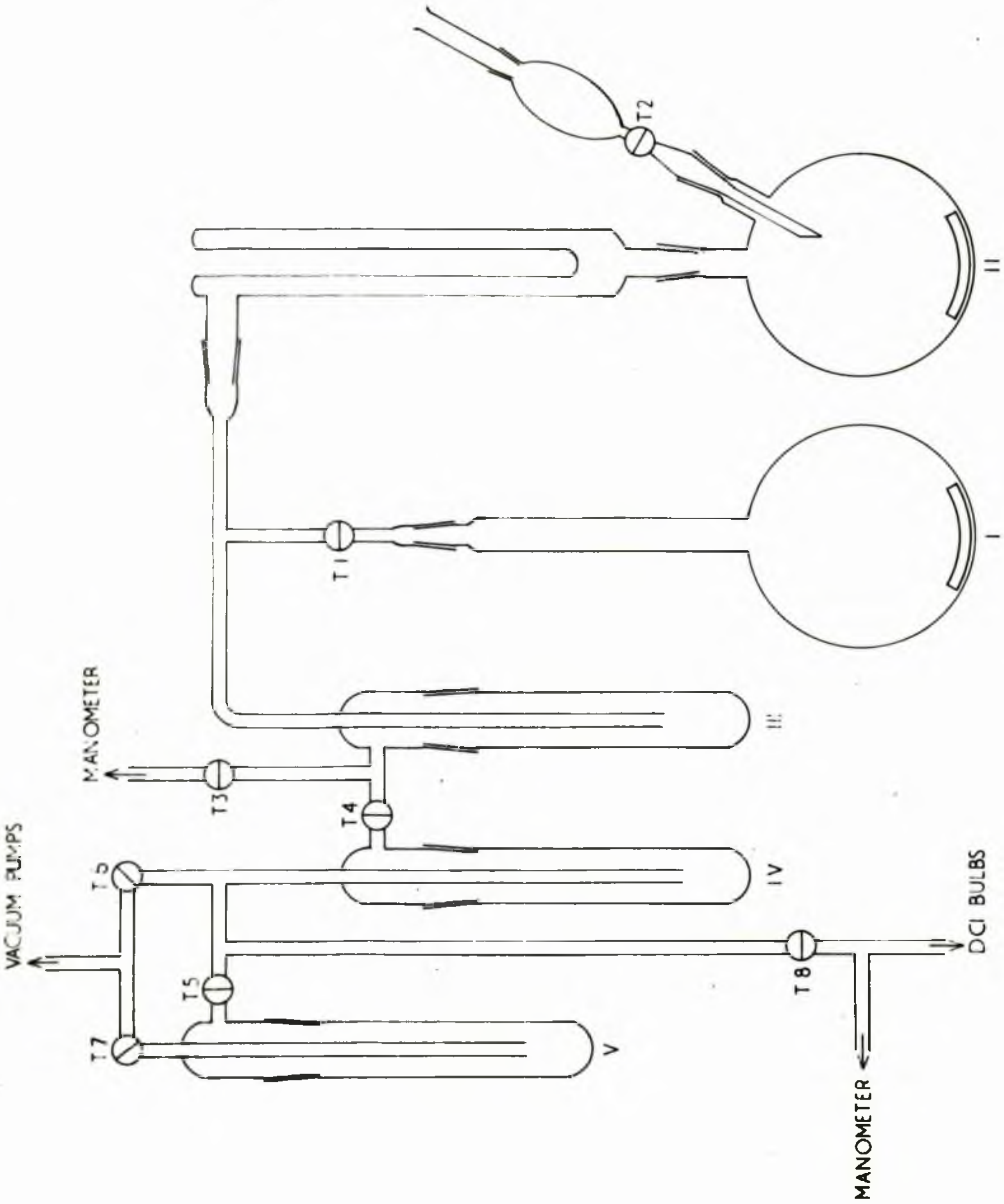
Before this reaction scheme could be applied to the synthesis of $PhCD_2CD_2Ph$, a considerable amount of preliminary work had to be done on most of the steps, in order to develop suitable techniques for

Figures 1 & 2.

BENZYLCHLORIDE DISTILLATION



ACETIC ACID SYNTHESIS



synthesising and collecting the products on the small scale for which the final synthesis was planned. A satisfactory sequence of operations was devised, and it will be convenient to describe the work done at each stage in turn.

i) CH_3COOD from CH_3COCl and D_2O.

This method was used in preference to the more economical reaction between acetic anhydride and deuterium oxide because it gave acetic acid of greater isotopic purity(25). This was the simplest step of the series and presented little difficulty. Following the procedure of Renaud & Leitch, the synthesis was done in a vacuum system, a diagram of which is given in Figure 1. The ground glass joints on the reaction vessel, II, and its cold finger condenser were sealed with Edwards' wax; all other joints and the taps were lubricated with silicone tap grease.

65 ml. of acetyl chloride, which had been distilled over dimethyl aniline to remove dissolved HCl, were placed in the 250 ml. round bottomed vessel, I, along with 5 ml. of freshly distilled dimethyl aniline. This mixture was stirred for two hours by means of a magnetic stirrer, then frozen in liquid air; the system was evacuated and the acetyl chloride degassed four times. Solid carbon dioxide was then placed in the cold finger condenser above the 250 ml. reaction vessel, II, and the purified acetyl chloride allowed to distil into II. 15 gm. of deuterium oxide (99.78%) were pipetted into the small dropping funnel attached to II, using a dried pipette filler, and a small calcium chloride tube was inserted in the neck of the funnel. The acetyl chloride in II was stirred magnetically and the deuterium oxide added slowly; the reaction proceeded smoothly, with evolution of deuterium chloride, which was

allowed to build up to a pressure of about 600 mm. and was periodically collected in trap IV, cooled in liquid air, by opening tap 4. The deuterium oxide was added over a period of two hours and stirring was continued for two hours more; during the latter period the deuterium chloride was allowed to expand slowly into four 5 litre storage bulbs, fitted with constrictions and breakable seals, by replacing the liquid air round trap IV with a bath at -80°C. When all the deuterium chloride had evaporated, about 10 ml. of liquid remained in the trap; this was probably acetyl chloride which had been carried over with the gas. It was distilled into II, and stirring continued for one hour. Trap III was then surrounded by a bath at -50°C, the cold finger condenser warmed, and the contents of II distilled into III, while the system was continuously evacuated through tap 6. Finally, the acetic acid was separated from the small excess of acetyl chloride by placing a bath at -50°C round IV, liquid air round V, and allowing III to warm up, while pumping through tap 7, with tap 6 closed; the deuteroacetic acid collected in IV and the acetyl chloride passed on to V. Dry air was admitted to IV, which was then removed and stoppered. A yield of 45 ml. was obtained.

ii) $PhCD_3$ from $PhCCl_3$, Zn, and CH_3COOD.

The following procedure was devised by Renaud & Leitch:-

200 ml. of anhydrous ether, 45 ml. of CH_3COOD, and 30 gm. of zinc dust were placed in a500 ml. four-necked round bottomed flask fitted with a reflux condenser, thermometer, dropping funnel, and stirrer. The mixture was stirred and kept at 5°C by immersion in a bath of ice water, while a solution of 19.6 gm. of benzotrichloride in 100 ml. of anhydrous

ether was added from the funnel over a period of four hours. Stirring was continued for three hours more, then 200 ml. of water was added and the mixture filtered through glass wool; the ether layer was separated, washed three times with 100 ml. portions of water, once with 10% sodium bicarbonate solution, and finally with water. It was dried over calcium chloride and distilled; the residue was distilled on the vacuum line through a U-tube containing pellets of potassium hydroxide and the distillate fractionated. 7.8 ml. of toluene were obtained.

Before the synthesis of $PhCD_3$ by this method was attempted, about twenty trial experiments using glacial acetic acid instead of monodeuteroacetic acid were performed, and the findings of these experiments will now be summarised:-

Reagents. The following purification methods were used:

Benzotrichloride: BDH benzotrichloride was distilled under vacuum on a water bath through a short Vigreux column; the fraction boiling at 48-49°C at 0.2 mm. was collected, and kept over anhydrous sodium sulphate.

Ether: Macfarlan's anaesthetic grade ether was dried with sodium wire, distilled over sodium, collected in a dry receiver, and sodium wire added; this was replaced by fresh sodium wire two days before use.

Zinc: BDH analar zinc powder was washed with 5% hydrochloric acid, filtered on a Buchner funnel, and washed three times on the funnel with water; this process was repeated, then the zinc was washed twice with methanol and twice with anhydrous ether. Immediately after this treatment it was transferred to the reaction flask.

In the trial experiments the glacial acetic acid was purified by freezing, allowing to melt partly, decanting the liquid, and using the solid acetic acid which remained.

Apparatus and procedure.

Ground glass joints were used throughout, and the stirrer was mercury sealed. Before each experiment all the components were dried in the oven, assembled hot with calcium chloride tubes on the condenser and dropping funnel, and allowed to cool.

It was found that careful control of the experimental conditions was necessary; if the temperature was allowed to rise above 5°C during the addition of benzotrichloride, the ether layer turned yellow, due to the formation of tolan dichloride, PhCCl:CClPh, and as a result the yield of toluene was low. This temperature rise could be prevented by very slow addition of the benzotrichloride, efficient cooling, and thorough stirring.

Slow addition of the benzotrichloride was achieved by drawing the tip of the dropping funnel down to capillary size, so that small drops were formed.

The effect of using an ice and salt bath to cool the system below 5°C was studied; it was found that if the flask was kept below 0°C reaction was incomplete even after nine hours, since some benzotrichloride remained after that time. If the temperature was kept between 0°C and 2°C, however, complete reaction did occur, and this temperature range was used in the final synthesis.

Extremely efficient stirring was necessary to avoid a localised rise of temperature when the benzotrichloride was dropped in, and a paddle stirrer alone was not adequate. The problem was solved by replacing the 500 ml.

flask by a 700 ml. flask with four equally spaced deep dents set vertically in it, so that, viewed from above, the flask had a cross-shaped section. These dents presented an obstruction to the smooth swirling of the liquid by the stirrer, and ensured thorough and rapid mixing of the reactants in the flask.

The reaction procedure, modified in the ways just described, was satisfactory,and the only remaining problems concerned the collection and purification of the products.

The reaction required the use of an excess of CH_3COOD, and it would obviously be advantageous if this excess could be recovered. The problem essentially was that of separating quantitatively about 20 ml. of acetic acid and 7 ml of toluene. Toluene and acetic acid have similar vapour pressure curves and form an azeotropic mixture, so that separation by distillation was impracticable. An attempt was made to take advantage of the considerable difference in melting points (acetic acid, 16.6°C and toluene, -95°C): a vacuum filtration apparatus was constructed which could be immersed in a bath at -80°C. When synthetic mixtures of toluene and acetic acid were filtered, little more than half the toluene passed through the sintered glass disc which formed the filter, the remainder being retained by the mass of solid acetic acid.

Since no convenient way of recovering the acetic acid had been found, the procedure of Renaud & Leitch was adopted, in which it was washed away with water and dilute alkali, the ether solution dried, and the ether distilled off.

For the separation of toluene from the residue of the ether distillation a small fractionating unit was constructed; the boiling flask, of 10 ml capacity, was glass-blown directly to the column, which was packed with glass wool and had a side-arm near the top which acted as an air condenser. The only joint was a B14 socket at the head of the column; this held a Quickfit thermometer, and also provided the means of changing the glass wool packing and filling the boiler. The whole system was inserted in a hole in a steel block which was electrically heated by a nichrome tape winding. Fractions could be collected in small tubes in a rotary collector.

The ether distillation residue was distilled on the vacuum line at room temperature through a tube packed with sodium hydroxide pellets into a trap cooled in liquid air. The vacuum distillate was then fractionated in the small column, but the trial experiments gave poor yields. Another means of purification was therefore sought.

Treatment with concentrated sulphuric acid is a well known purification process for toluene, and the products of several trial experiments were purified in this way; the vacuum distillate was pipetted into a small tube, a few ml. of concentrated sulphuric acid added, allowed to stand, and the organic layer removed with a pipette and transferred to another tube. This process was repeated until the acid layer was no longer yellow (three portions of acid were usually required). Then the toluene was treated in the same way with sodium hydroxide solution and distilled water, and dried over phosphorus pentoxide, which was found to be a more satisfactory drying agent than sodium. The melting point of toluene purified in this way was determined by cooling a sample slowly by immersion in liquid air, and scratching the tube with a pentane thermometer, noting the temperature at which the sample solidified. The products of trial syntheses which had been purified by acid had the same melting point as freshly dried reagent grade toluene. This method of purification was therefore adopted.

In one trial experiment the ether distillation residue was treated directly with sulphuric acid, but a thick yellow emulsion was formed, which dissolved on dilution, and the organic layer was a dark yellow.. It was therefore necessary to retain the drying and vacuum distillation processes used by Renaud & Leitch, in order to separate the toluene from the less volatile reaction products.

As a result of these experiments, $PhCD_5$ was synthesised by the method of Renaud & Leitch, with the small modifications described above. The distillate from the vacuum line distillation was not fractionated, but was purified by treatment with concentrated sulphuric acid. The purified deuterotoluene was finally re-distilled on the vacuum line from phosphorus pentoxide directly into the reaction flask for the next stage of the synthesis.

iii) $PhCD_2Cl$ from $PhCD_5$.

The most efficient and reliable method in the literature for the conversion of toluene to benzyl chloride is that of Kharasch & Brown(26). They refluxed toluene and sulphuryl chloride in the molecular proportions of 2 to 1, together with a small amount of benzoyl peroxide. A brisk reaction occurred, with evolution of hydrogen chloride, and the toluene was converted in high yield to benzyl chloride in about fifteen minutes.

Kharasch & Brown investigated this reaction thoroughly and reported that a negligible amount of benzal chloride was formed; they also observed that the reaction proceeded very slowly in the absence of the peroxide, and suggested that its function was to initiate a chain reaction involving chlorine atoms. They listed a number of compounds which inhibit the reaction.

This specific method of monochlorination was very suitable for the synthesis of $PhCD_2Cl$, and several trial experiments were carried out.

Reagents.

Sulphuryl chloride: BDH sulphuryl chloride was distilled from mercury on a water bath; a large first fraction, which might contain dissolved hydrogen chloride, rejected, and the fraction boiling at 69-70°C collected in a receiver which contained a little clean mercury, and had a phosphorus pentoxide boat suspended in it. The receiver was sealed off and kept in the dark.

Benzoyl peroxide: BDH benzoyl peroxide, which contained 30% of water to minimise the risk of explosion, was used. It was purified by making a concentrated solution in chloroform, drying over sodium sulphate, filtering, and adding dry methanol to the solution until the peroxide was precipitated. It was collected and kept in a vacuum desiccator. Normal recrystallisation is dangerous, because of the explosive nature of the peroxide(27).

In the trial experiments, reagent grade toluene dried over sodium, and toluene synthesised and purified by the method of ii) were used.

Apparatus and procedure.

The quantities of reactants used in the trial experiments were usually the same as in the final synthesis of $PhCD_2Cl$, namely, 5.75 ml. of toluene, 4.42 ml. of sulphuryl chloride, and 0.08 gm. of benzoyl peroxide. The liquids were added by pipette and the peroxide by weight to a 100 ml. round bottomed Quickfit flask. The flask could be surrounded by a small oil bath heated by an electric hot plate controlled by a Simmerstat. The temperature of the bath was usually 130°C. Since hydrogen chloride was evolved in the reaction, an efficient reflux condenser, topped by a cold trap were necessary to prevent some of the reactants and products being carried away by the gas evolved. The condenser used was a double surface and spiral type; it was mounted vertically and had at the top a B19 socket at about 30° to the horizontal; a small U-tube was made, with a B19 drip cone to fit this socket. The trap was surrounded by a bath at -15°C, and liquid which collected in it in the course of the reaction could be returned to the flask by removing the bath and rotating the trap about the ground glass joint. After passing through the trap the hydrogen chloride was bubbled through a wash bottle containing water and was finally absorbed in water.

The progress of the reaction could readily be followed by observing the evolution of hydrogen chloride, which stopped abrubtly when the chlorination was complete.

Kharasch & Brown separated the benzyl chloride from the reaction mixture by fraætionation, and in the earlier experiments the fractionating column described in the toluene synthesis section was used for this purpose. In the course of the fractionation hydrogen chloride was evolved, and an appreciable quantity of a tarry or glassy residue remained at the end of the distillation. Carrying out the distillation in an atmosphere of nitrogen reduced the quantity of residue slightly, but the process was not considered satisfactory and low temperature distillation was therefore considered.

The vapour pressure curve of benzyl chloride diverges quite widely from the vapour pressure curves of toluene and sulphuryl chloride at low temperatures: at -30°C the vapour pressures are:- sulphuryl chloride, 5 mm.; toluene, 1 mm.; benzyl chloride, 5×10^{-2} mm. It should thus be feasible to achieve a good separation of benzyl chloride at low temperature. A vacuum distillation apparatus was constructed, a diagram of which appears in Figure 2. The reaction flask was connected directly to the ground glass cone, a bath at -30°C placed round the first trap, and liquid air round the second. The system was evacuated and a bath of warm water placed round the flask; the benzyl chloride distilled into the first trap and the more volatile compounds, unreacted toluene or sulphuryl chloride, passed on to the liquid air trap. A small involatile residue remained in the flask. This method of distillation was economical and effective and was used in the synthesis of $PhCD_2Cl$.

In several of the trial experiments little evolution of hydrogen chloride occurred and very poor yields of benzyl chloride were obtained. The reaction could be made to proceed normally by adding about four times the stated amount of peroxide, which indicated that the failure of the reaction was due to low peroxide activity.

Benzoyl peroxide may be estimated quantitatively(28) by dissolving a weighed amount in ether and treating this solution with 5% sodium ethoxide below -5°C, which forms sodium perbenzoate; this can be extracted with a known volume of water and used to liberate iodine from potassium iodide in acid solution. By titrating the liberated iodine with sodium thiosulphate solution, the weight of benzoyl peroxide in the original sample may be determined.

The peroxide used in these experiments was analysed in this way and it was found that only 34% of the material was benzoyl peroxide. A fresh supply was therefore obtained, which, after purification by the precipitation process described above, was quite satisfactory.

The $PhCD_3$ was chlorinated by the above method and the $PhCD_2Cl$ collected by high vacuum distillation. It was re-distilled on the vacuum line from anhydrous sodium sulphate just before it was required for the next step in the synthesis. The volume of deuterium chloride evolved in the reaction was small and no attempt was made to recover it.

iv) $PhCD_2CD_2Ph$ from $PhCD_2Cl$.

Benzyl chloride and bromide readily form Grignard reagents, and several methods of forming dibenzyl by Grignard type reactions have been described in the literature; Johnson & Adkins(29) produced diaryls in good yield by the use of a magnesium/copper alloy; and Bert(30) reacted benzyl chloride with ethyl magnesium bromide and reported a good yield of dibenzyl along with ethane and ethylene. Bennet & Turner(31) formed diphenyl in good yield from phenyl magnesium bromide in the presence of chromic chloride, and stated that the method was equally applicable to other diaryls, including dibenzyl. Krizewsky & Turner(32) subsequently reported a similar but more effective and straightforward method in which cupric chloride was used in place of chromic chloride. They represented the reaction by the equation:-

$$2\ CuCl_2 + 2\ ArMgX = Cu_2Cl_2 + 2\ MgClX + Ar.Ar$$

The first trial experiments involved the formation of benzyl magnesium chloride in the presence of excess benzyl chloride(33); poor yields of dibenzyl were obtained, so the more elaborate reactions mentioned above were considered.

The method of Krizewsky & Turner employed a very simple technique; although they had applied it only to the synthesis of diphenyl from phenyl bromide, some experiments were carried out with a view to adapting the method to the synthesis of dibenzyl from benzyl chloride.

Reagents.

Cupric chloride: Hydrated cupric chloride was powdered and heated in an oven at 120°C until it was completely anhydrous.

Magnesium: Grignard reagent grade magnesium turnings were washed with ether to remove grease, and were dried in the oven.

Ether: Macfarlan's anaesthetic grade ether, purified as in ii) above, was used.

Apparatus and procedure.

The apparatus consisted simply of a 100 ml. round bottomed Quickfit flask fitted with a spiral condenser and a calcium chloride tube. Before use, all components were thoroughly cleaned and dried in the oven at 120°C. 1.06 gm. of magnesium and 6.08 gm. of anhydrous cupric chloride were then placed in the flask, the components assembled, and the whole apparatus dried in the oven. After cooling, 5 ml. of benzyl chloride and 35 ml. of ether were added and the mixture was refluxed gently on a water bath for at least twelve hours.

So far, the procedure had been closely modelled on that of Krizewsky & Turner for the synthesis of diphenyl. They worked up their product in the usual way:- The system was cooled, decomposed with ice and water, the precipitated cuprous chloride re-dissolved by treatment with excess concentrated hydrochloric acid, and the ether layer separated. The aqueous layer was extracted repeatedly with ether and the combined ether layers dried and distilled, leaving the product in the residue.

This method was used in the earliest experiments , but the purity and yield of dibenzyl were both unsatisfactory. A simple high vacuum sublimation apparatus was therefore constructed, in which the dibenzyl could be separated from the involatile inorganic products: a ground glass cone to fit the reaction flask was connected to the centre tube of a trap; this centre tube and the length of tubing leading to the cone were electrically heated by windings of nichrome tape. The system could be evacuated through the side-arm of the trap.

The apparatus was used by evaporating off the ether from the reaction mixture and attempting to sublime the dibenzyl away from the mass of inorganic material. This was only moderately successful, but the following satisfactory procedure was devised:-
At the end of the reaction time the ether was distilled off; the flask was cooled in ice, and ice-cold concentrated hydrochloric acid added to dissolve the inorganic material. The contents of the flask were filtered, no attempt being made to remove the crude dibenzyl which adhered to the walls; the residue from the filtration was returned to the flask, after having been washed with water, and the flask was fitted to the sublimation apparatus. The trap was surrounded by a bath at -10°C, the system evacuated and the flask surrounded by a bath of boiling water on an electric hot plate. The dibenzyl was collected in the trap in satisfactory yield and in a good state of purity.

This modified method was applied to the synthesis of $PhCD_2CD_2Ph$.

The yield was lower than that usually obtained in the preliminary experiments, but was quite sufficient for the subsequent kinetic investigations. A sample was analysed in the mass spectrometer and was found to consist almost entirely of dibenzyls of molecular weight 186 and 185 in the ratio 4.5 to 1. If the statistical methods used later in this Thesis are applied to this ratio, the composition of the deuterated dibenzyl may be calculated to be:-

$PhCD_2CD_2Ph$	81 %
$PhCD_2CDHPh$	18 %
$PhCDHCDHPh$	1 %

The overall deuterium content is then $\left\{ 81 + \frac{3}{4}(18) + \frac{1}{2}(1) \right\} = \underline{95\ \%}$ of the theoretical.

In the course of the preliminary experiments described above, a quantity of "ordinary" dibenzyl, $PhCH_2CH_2Ph$, was synthesised, and this was used in the pyrolysis experiments in place of commercially available dibenzyl, which contained about 1% of stilbene.

THE MASS SPECTROMETER.

The mass spectrometer, which had been built in the Department a few years earlier, was a sector field instrument, closely modelled on the design published by Nier in 1947(34). A detailed description will be confined to those parts of the instrument which required reconstruction before it could be used for the present investigation; the remainder will be described very briefly.

The electronic circuits associated with the instrument were quite conventional and resembled those described by Nier, and by Graham, Harkness & Thode(35). They were all supplied from a Westinghouse Stabilistor constant voltage transformer, and comprised the following units:

Extra high tension (EHT) supply.

This had a stabilised output voltage continuously variable in a series of overlapping steps from 800 to 2000 volts DC. It provided the ion accelerating potential in the ion source and the potential for a Phillip s ionisation gauge. The negative lead of the output was earthed.

Emission stabiliser.

The tungsten filament of the electron gun in the source was fed with AC of up to 6 amps. from this unit, which also provided the electron accelerating potential and the potential between the ion source and electron trap. The stabiliser maintained the total electron emission of the filament constant by varying the filament current, and the value of this emission and the electron gun potentials could be varied by manual controls. The unit also contained meters which indicated the filament current in amps.and the electron trap and total emission currents in microamps. The unit was not earthed at any point, but was connected to the output of the EHT supply, so that the whole ion source could be raised to the accelerating potential.

Magnet supply.

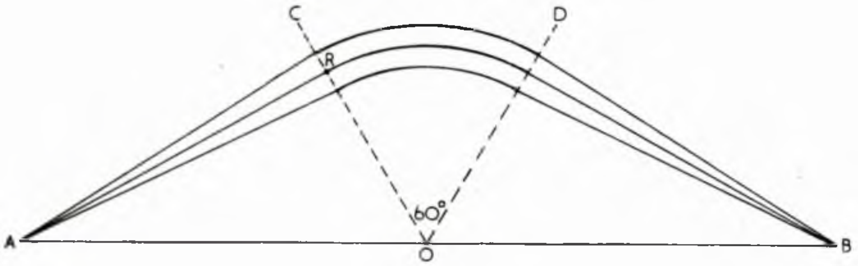
The sector magnetic field of the mass spectrometer consisted of an electromagnet with a narrow pole gap, through which the tube of the mass spectrometer passed. The current for this magnet was supplied by a stabiliser which provided stabilised currents of from 4 to 155 milliamps., continuously variable over four overlapping ranges. In each range, the variation in magnet current was achieved by altering the setting of a potentiometer, and this could be done mechanically by means of a low speed electric motor connected to gears on the potentiometer shaft through a flexible drive.

DC amplifier.

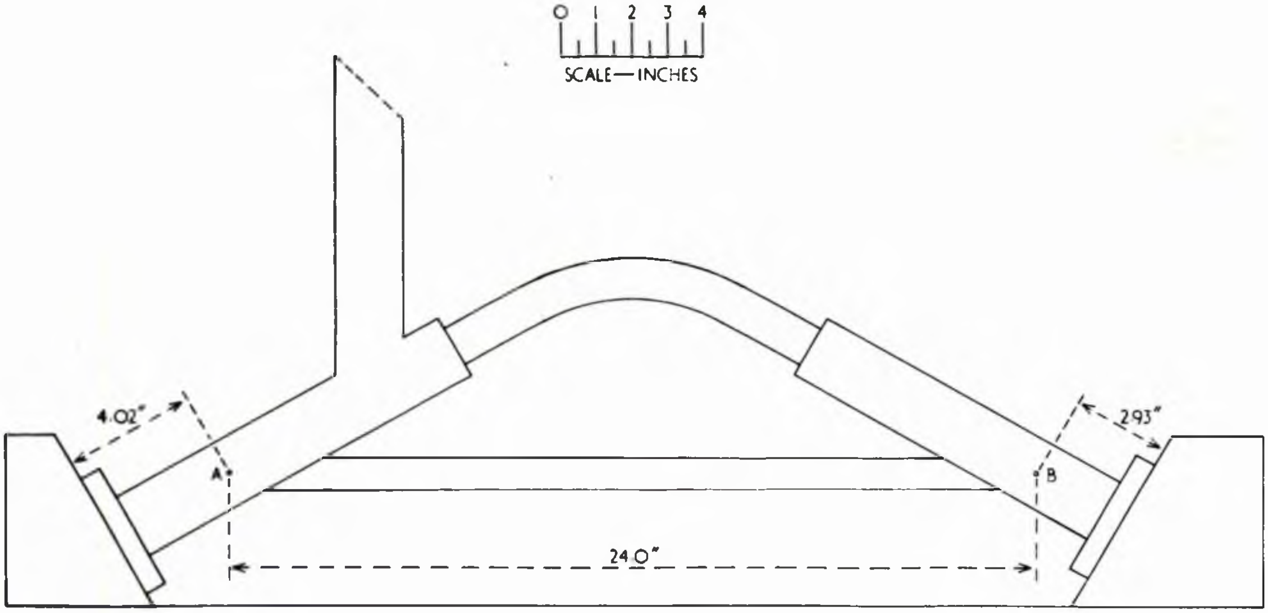
The ion beams fell on a collector plate which was connected through a high value resistor to the grid of an electrometer valve, which was the first stage of a 100% feed-back DC amplifier. The potential developed across the high resistor by the ion current was fed through the amplifier to a Honeywell-Brown 10 millivolt strip chart recorder; the recorder was fitted with a sensitivity unit which enabled signals of up to 30 volts to be measured, and which was capable of either manual or automatic operation. The electrometer valve and two high value resistors, of 10^{10} and 2×10^{11} ohms respectively, were housed in a light-tight, screened, desiccated metal box which was clamped to the mass spectrometer frame close to the end of the tube containing the collector unit. A highly insulated switch enabled either the high grid leak (HGL) or low grid

Figures 3 & 4.

REFOCUSING OF IONS
IN SECTOR MAGNETIC FIELD



ALIGNMENT OF
MASS SPECTROMETER TUBE



leak (LGL) resistor to be selected. The time of response to input signals with the HGL connected was inconveniently long, and the LGL resistor was used whenever possible.

The DC amplifier was very sensitive to small circuit faults, and at one stage it was partly reconstructed and several components were changed in order to improve its stability. Otherwise, only minor alterations and additions to the units were necessary in the course of the investigation.

At a late stage, the EHT supply became unsteady and a stabiliser of more refined design, constructed and kindly loaned by Mr. D. Calvert was used in its place.

Resolution.

If the potentials applied to the ion source are steady and the source itself is free from dirt, badly polished surfaces, and sharp edges, all of which favour the build-up of electrostatic charges which distort the ion beam, then the resolution of a mass spectrometer is determined solely by the geometry of the instrument.

The refocusing of ions in a 60° sector magnetic field is illustrated in Figure 5. If AOD is a straight line, an ion beam diverging from A will converge at B, if the central ray of the beam, AR, is normal to OC; and if OR is the radius of curvature of the ion path in the sector magnetic field. If the resolution is defined as the ability to distinguish between ions of mass to charge ratio m and ions of mass to charge ratio (m+1), then the theoretical maximum value of m is given by $m = \frac{OR}{S_A + S_B}$ where S_A and S_B are the widths of the exit slit at A and the collector slit at B respectively(36).

In practice, this maximum cannot be attained because of several aberrations which prevent perfect refocusing being achieved. Barnard(56) has discussed these aberrations thoroughly and only the practical means of reducing them as much as possible will be considered.

The mass spectrometer tube should be mounted so that point A is vertically above point B; the pole faces of the electromagnet should also lie in a vertical plane, parallel to the plane of symmetry of the tube through A and B. The slits at A and B should be parallel and at right angles to the plane of the magnet pole faces.

The St. Andrews instrument has a radius of curvature of 6 ins. so with exit and collector slits 0.010 inch wide would have a theoretical resolution of 300. In its original form it was fitted with considerably wider slits, and had a resolution of about 80. When it was built the facilities for the construction of a precisely aligned tube and accurately made ion source and collector units were not available, and in any case, the instrument was intended originally for gas analysis, for which high resolution was unnecessary. As a result, in addition to having wide slits, it suffered from most of the possible aberrations, and the desired resolution of 200 could only be attained by re-aligning and stiffening the tube and constructing new ion source and collector units.

The mass spectrometer tube.

The central part of the mass spectrometer tube was made from $1\frac{1}{4}$ inch diameter copper tube, flattened at the curved portion to allow it to pass between the pole faces of the magnet, which were only $\frac{1}{2}$ inch apart. The rest was made from 2 inch diameter inconel tubing; at the lower end the ion collector unit was silver-soldered in, and at the upper, was a

4 inch diameter $\frac{5}{8}$ inch thick inconel flange to which a similar flange carrying the ion source could be fastened by means of six equally spaced 5/16 inch BSF bolts. The removable flange had a circular groove containing a polytetrafluoroethylene (teflon) gasket which mated with a spigot on the fixed flange, forming a vacuum-tight seal. Near the upper end of the tube was the side-arm, also of 2 inch inconel, leading to the cold trap and vacuum pumps.

The fixed ion collector unit was to be replaced by one built on a removable flange, like the ion source, and the alteration of the mass spectrometer tube which this entailed was combined with its realignment.

A pair of 4 inch diameter inconel flanges similar to the pair used for the ion source was made, each flange having six accurately reamed holes so that they could be bolted together with a fixed orientation with respect to each other. The female flange was silver-soldered to a length of 2 inch inconel tube and this assembly was to replace the original inconel tube carrying the collector unit, which was removed.

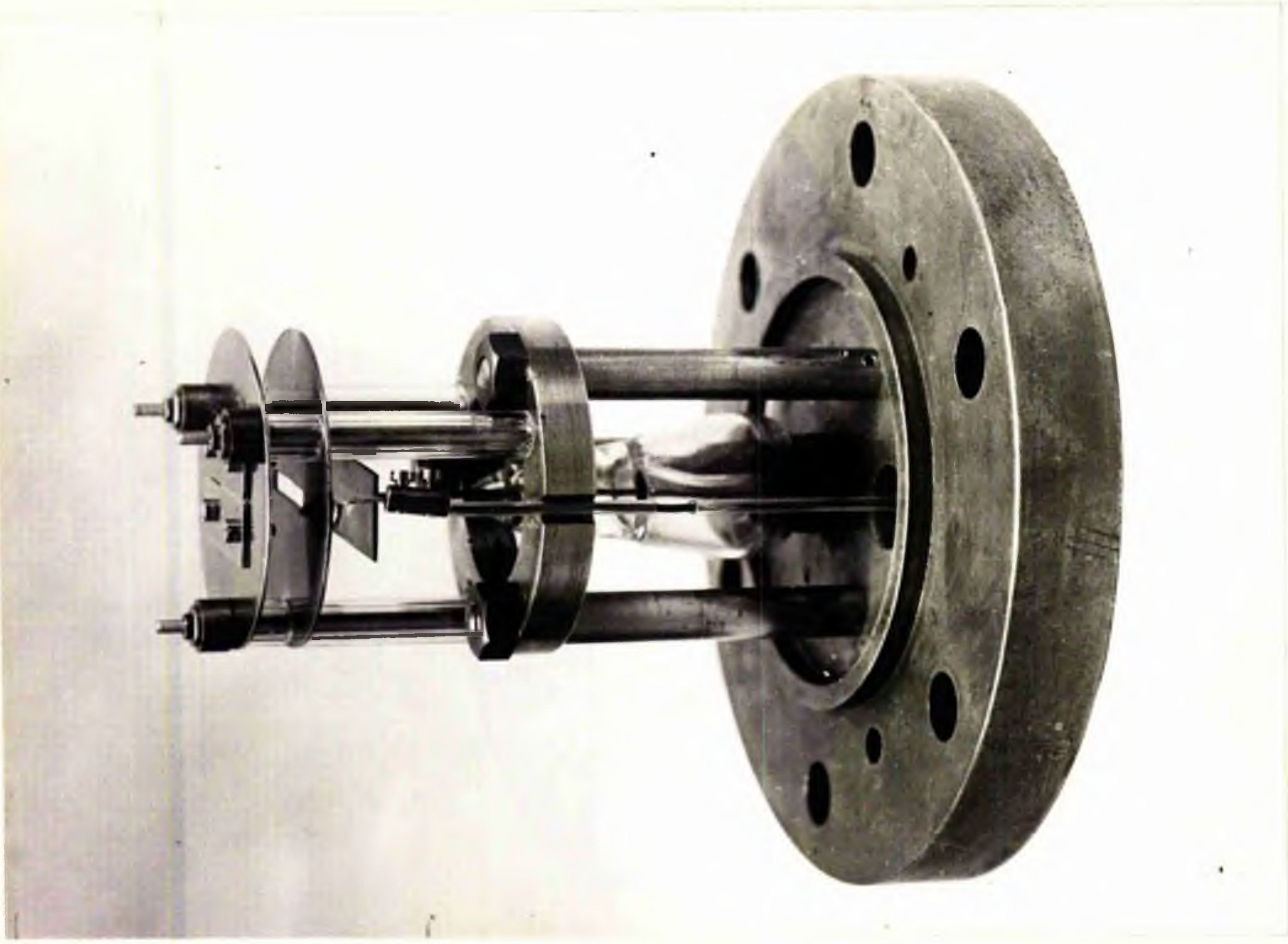
There was in the Department a Universal Milling Machine with a working surface which was flat to 0.0002 inch, and this was used as the reference surface in the reconstruction of the tube. The method is illustrated by Figure 4. Two accurately machined steel blocks, each with a pair of faces enclosing an angle of 60°, were clamped to the table of the milling machine. Each had on its sloping face two pins, lying on a line perpendicular to the table, which fitted diametrically opposite holes in the inconel flanges. The main part of the spectrometer tube, consisting of the upper inconel portion and the copper bend, was bolted by the ion source flange to one block, and the new flange and tube was bolted to the other. As the distance from the exit slit of the ion source to its flange was greater than the corresponding distance at the collector end, the final assembly was not symmetrical, and the distance apart of the blocks and the height of the pins on the block faces were calculated from the lengths of the source and collector units and the requirement that AB had to be horizontal and 24 inches in length (Figure 4).

When the two parts had been set up in this way, the lower end of the copper tube was silver-soldered in situ to the new inconel section, through ah annular inconel adapter. In order to make the whole assembly more rigid a 1 inch diameter brass tube was silver-soldered to the main tube along the line AB. The points at which the line of the slits at A and B would meet the tube were marked on the inconel by means of a scribing block. The tube was then removed and small punch marks made at the two points. All measurements in this work were accurate to 0.005 inch.

An important result of the method of assembly used was the fact that the plane of symmetry of the tube passed through a pair of diametrically opposite holes in each flange. It was thus possible to align the source and collector slits by referring them to these holes, which will be called the "master holes".

The ion collector.

A simple unit, consisting of a plate with narrow slit, negative ion repeller, and ion collector plate was designed. Several more elaborate systems containing metastable ion suppressor plates and electrostatically variable collector slit have been described in the literature(37) and provision was made in this design for these refinements to be added if



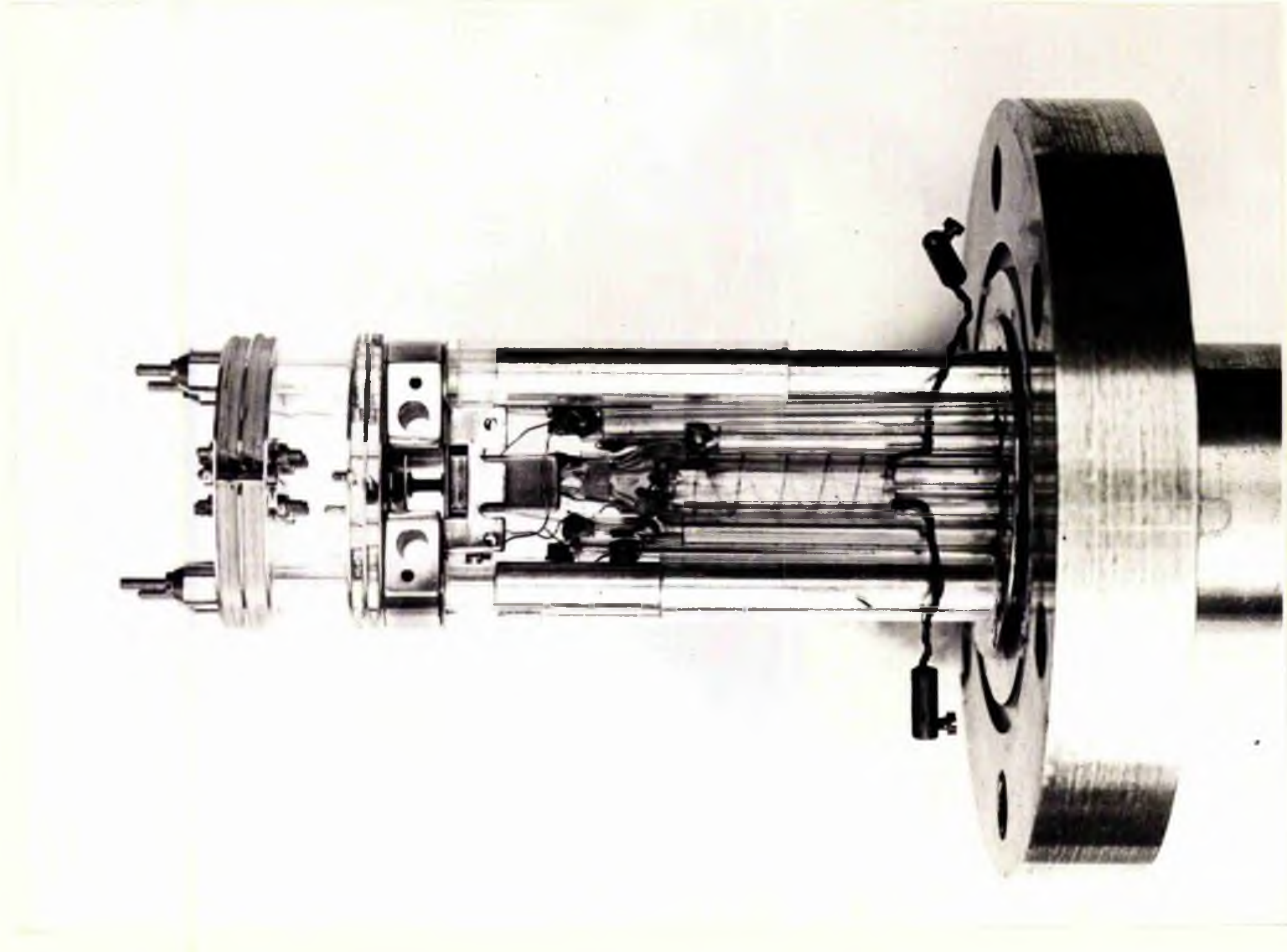


Figure 5.

Ion Collector Unit.

(Actual size.)

Figure 6.

Ion Source.

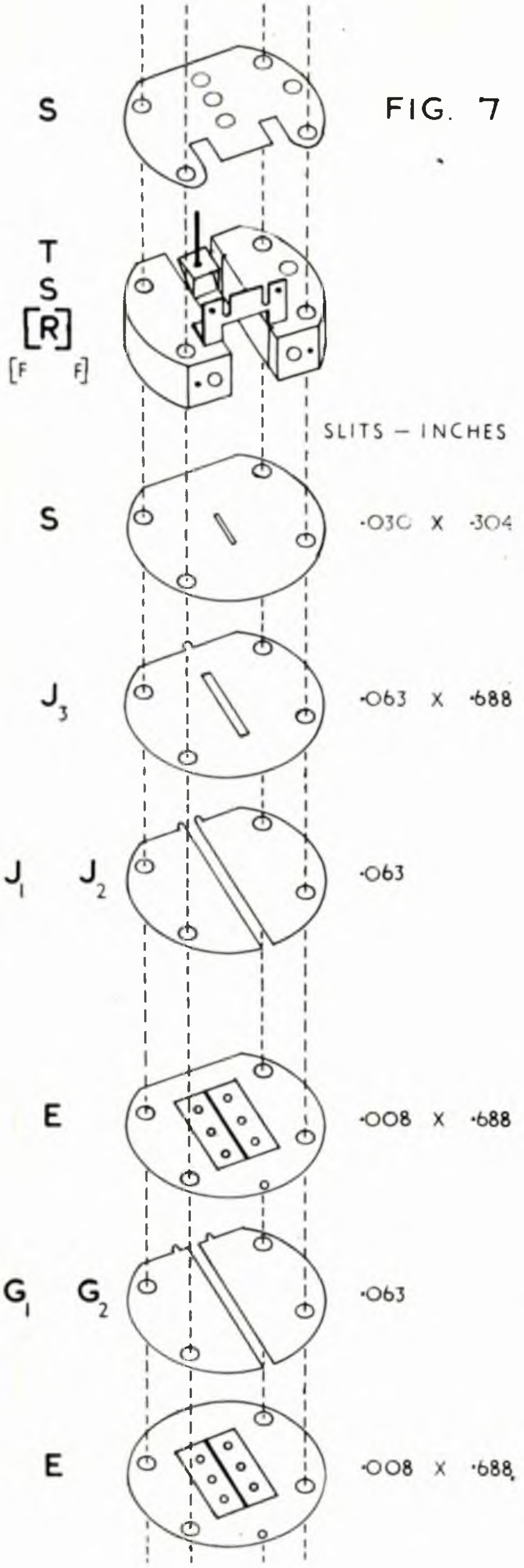
(Actual Size.)

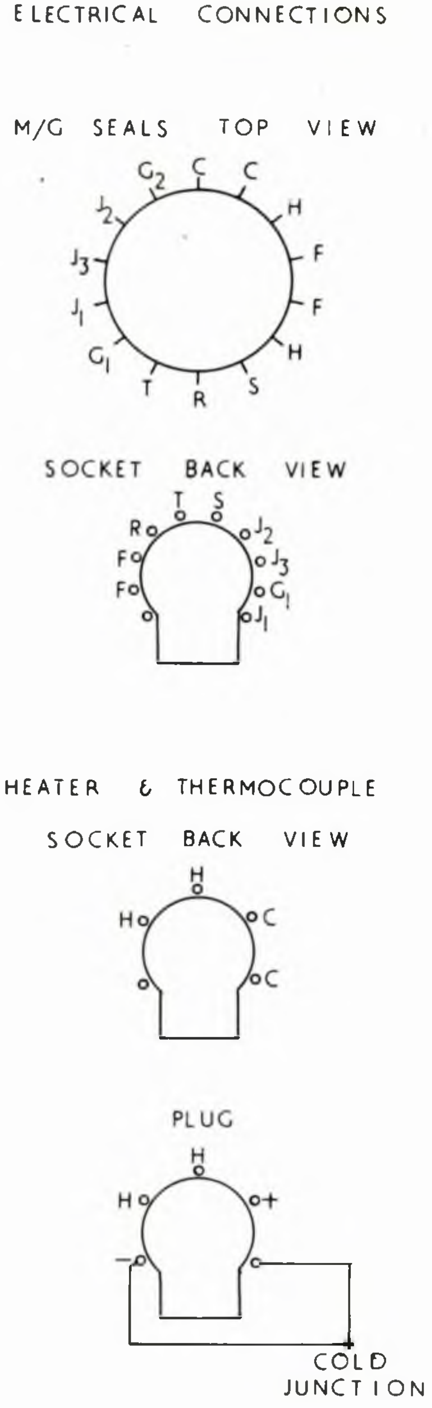
required.

The constructional details may be seen in the photograph, Figure 5. A $\frac{1}{4}$ inch inconel ring was supported on three $1\frac{1}{2}$ inch inconel pillars and inside this space was the specially designed metal/glass seal for the lead from the small rectangular collector plate. The repeller and entrance slit plates were supported on three stems made from non--magnetic stainless steel cycle spokes, sheathed with selected pieces of pyrex tubing. The plates were separated by distance pieces accurately ground from pyrex tubing, the distance between the two plates being 0.25 inch, and the distance from the repeller plate to the ring, 0.95 inch, which allowed room for further plate systems. The plates were cut from 0.025 inch non-magnetic stainless steel sheet and the narrow collector slit was formed by two pieces of knife-edged stainless steel which could be adjusted for width and orientation. The slit in the repeller plate was 0.065 inch wide. The holes in the flange and ring for the pillars and spokes respectively, and the clearance holes in the plates for the glass--sleeved spokes were all drilled in the same specially constructed jig, thus ensuring uniformity. The spokes were silver-soldered to the ring for rigidity and the inconel pillars were screwed into the flange, so that the whole unit could be dismantled.

The repeller lead, which passed through a metal/glass seal in the underside of the flange, was connected to the repeller plate by a small barrel connector so that the plate could be removed for cleaning. The top plate was earthed through the metal spacers and steel spokes. The orientation of the narrow slit with respect to the master holes was done by a similar procedure to that used in aligning the plates of the ion

FIG. 7 ION SOURCE





source, which will be described later.

The collector and repeller leads originally passed from the mass spectrometer tube to the electrometer valve box on the frame through an earthed brass bellows, but it was found that capacity effects caused by vibration disturbed the DC amplifier, and the arrangement was modified by suspending the electrometer box directly from the collector flange by means of a short brass adapter enclosing the two leads.

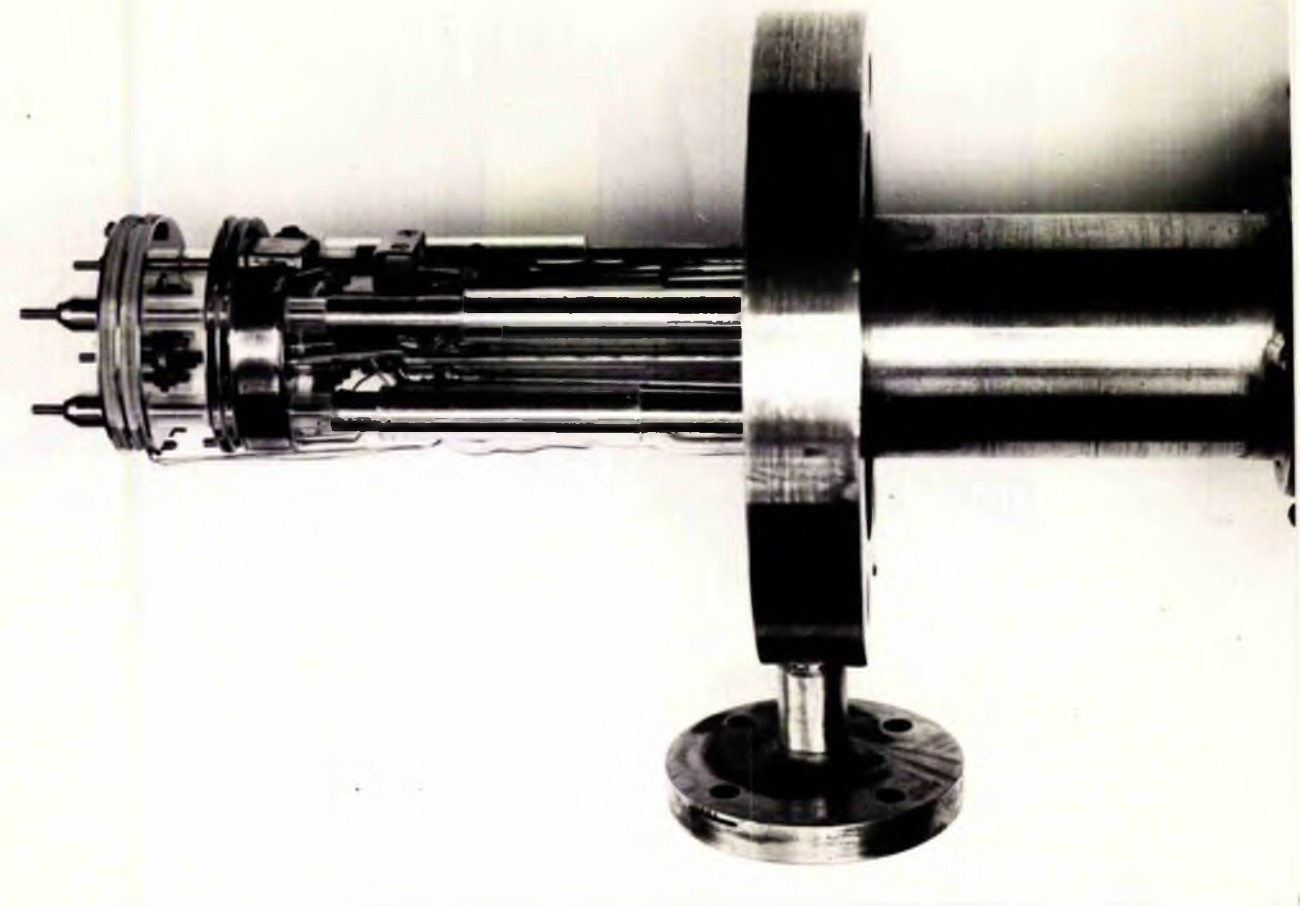
The ion source.

The original ion source was closely modelled on Nier's design and no major departure from this was planned. The overall dimensions of the new source had to be the same as the old, and the main requirements were that the plates of the source should be accurately aligned to avoid distortion of the ion beam; the exit slits should be adjustable for high resolution; the electron gun should be housed in a box fitted with a heater and a thermocouple; and the construction should be so arranged that the whole source could be dismantled completely for cleaning and re-assembled in a reproducible fashion.

Details of the design may be seen in the photographs, Figures 6 and 8, and in the exploded diagram, Figure 7. The plates, 1½ inch in diameter, were cut from 0.025 inch stainless steel and all other metal parts were either non-magnetic stainless steel or inconel. In the construction of the source a tolerance of no more than 0.001 inch was aimed at, and extensive use was made of jigs. The master holes of the flange, corresponding to the master holes of the fixed flange on the tube, were used as the reference points; all the holes in the plates, the electron gun box, and the flange itself were drilled in the same jig, which had been aligned with respect to the master holes of the flange, using the dividing head on the Universal Milling Machine.

For slit cutting, the plates were bolted by their four holes to one face of a small steel block, which had been drilled in the jig. On the other face of the block was a square shaft which had been machined so that the sides of the square were parallel to the sides of the rectangle formed by the four holes. The block was mounted by its square shaft in a small dividing head on a Pultra lathe and the slits cut with rotary cutters. The slit cutting jig was also used in the construction of the electron gun box; the two halves of the box were milled from a disc of stainless steel, 1½ inch diameter and 0.280 inch thick, clamped by the jig in the vice of the milling machine. The upper and lower walls of the box were formed by two plates, the lower having the first ion beam slit. The electron trap and ion repeller plate were suspended from a baked steatite block bolted to the top of the box by lengths of 10 BA threaded rod, which passed through wide clearance holes in the top plate. This plate had a hole in the centre for the single gas inlet tube which was originally installed; subsequently two inlets were necessary and a small stainless steel block with two holes leading to this central hole was silver-soldered to the plate. A thermocouple well and two holes for a U shaped silica tube carrying a tungsten heater were drilled in the box.

The filament assembly slid into two grooves in the sides of the box and was self-aligning. The filament was made from tungsten ribbon, 0.001 x 0.040 inch, spot welded to two stems which were clamped between two pieces of baked steatite. The filament was usually made about 0.22 inch (5.5 mm.) long and a straight filament as close as



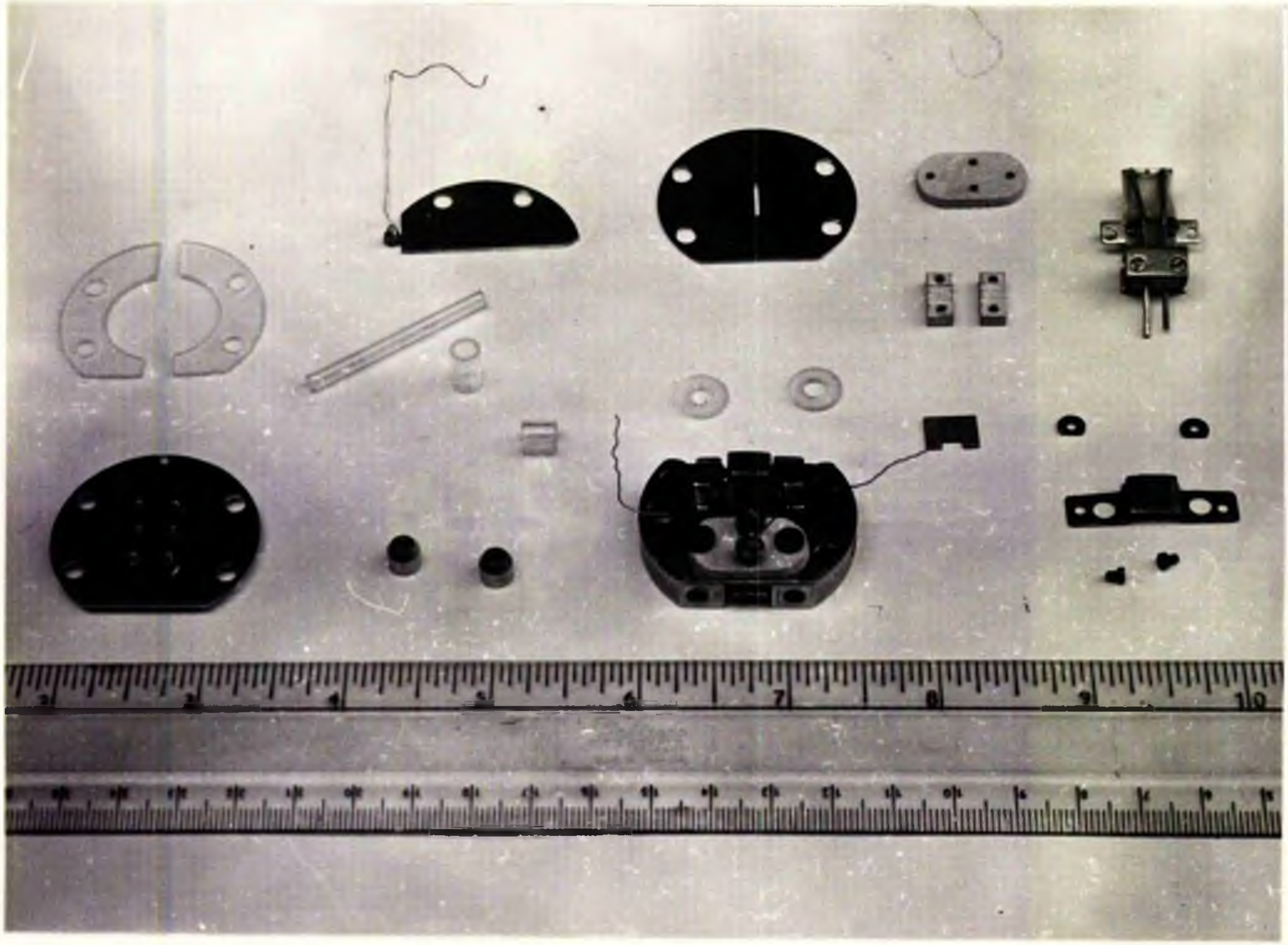


Figure 8.

Ion Source.

Figure 9.

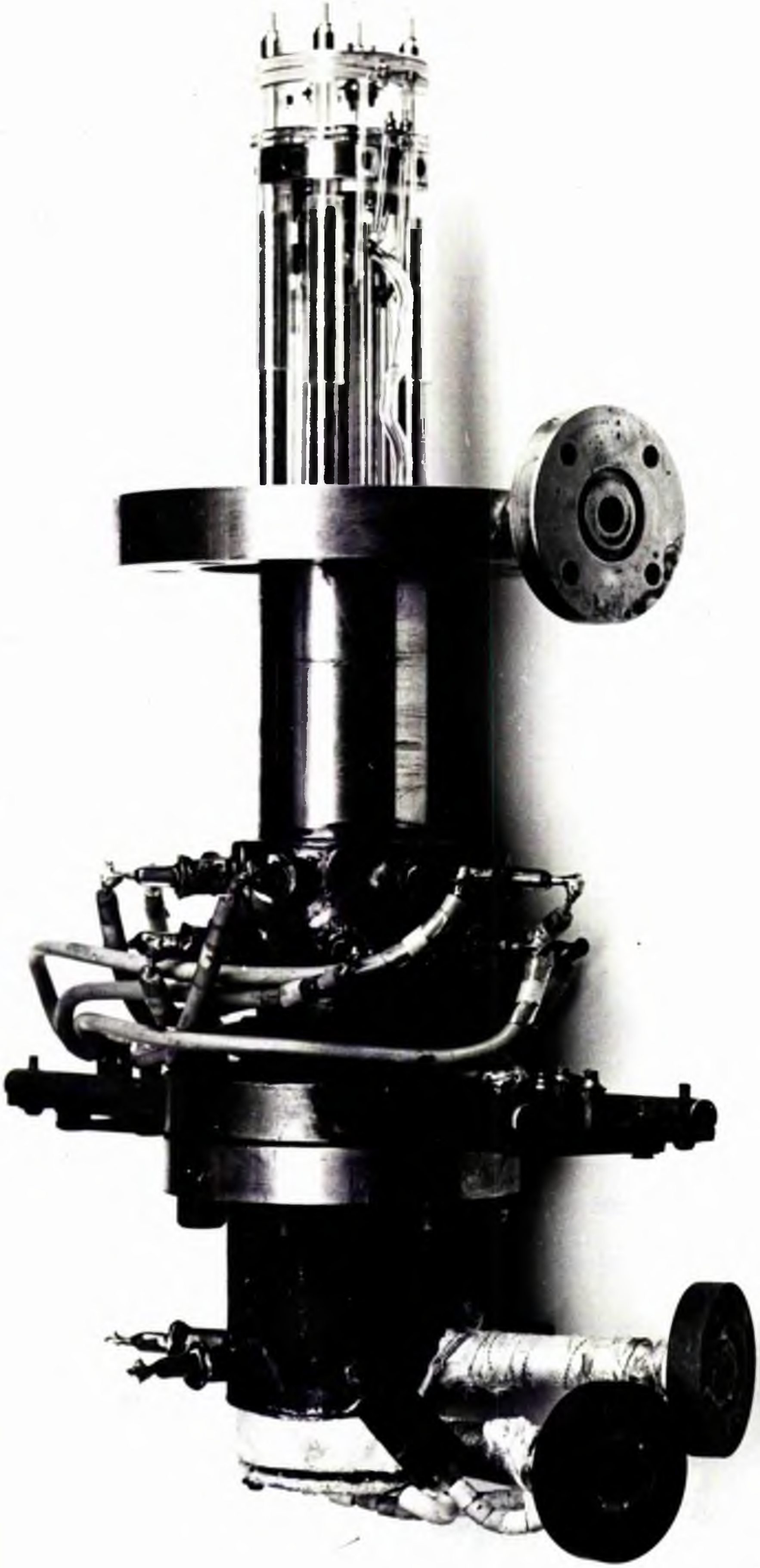
Ion Source Components.

possible to the slit in the filament holder was found to give the most satisfactory electron emission. Originally stems of Nilo K were used, but these tended to vaporise on to the steatite insulators, eventually causing a short circuit between the filament and the box. The insulators were mounted well above the filament to minimise this effect, but trouble was still experienced and the Nilo K was finally replaced by tungsten. The filament was spot welded to the stems through small pieces of nickel, since it was not possible to weld tungsten to tungsten directly.

The electron trap was wedge-shaped and was made from 0.010 inch nichrome sheet. The wall in front of it was cut from a filament holder and slid in and out in two grooves, like the filament unit. A "doorway" type of slit was used. The box and several of its components are included in Figure 9.

The electron gun and the stack of plates were supported on four stainless steel cycle spokes silver-soldered to $\frac{1}{4}$ inch diameter inconel pillars. The spokes were sheathed in selected glass tubing, 0.142 inch in diameter (the holes in the plates were 0.144 inch diameter). The spacers between the inconel pillars and the box, and between the upper and lower parts of the stack were ground from pyrex tubing. All other spacers were originally made from 0.052 inch photographic plates, which were cut to semi-annular shape with brass tools, rotating in a slurry of carborundum in glycerol; clearance holes for the four supports were drilled in the same way. A pair of the completed spacers is illustrated in Figure 9. This type of spacer was used in order to give a large flat bearing surface and thus ensure that the plates in the stack were parallel to each other. These spacers were difficult to make,

Figure 10.



fragile, and, being of soda glass, were not as good insulators as pyrex spacers; consequently they were later replaced by pyrex in the upper part of the stack, where good insulation was essential; but were retained in the lower, where accurate orientation of the exit plates was important. In this lower section they were used in pairs, so that the plates were 0.104 inch apart.

The pyrex spacers were made from specially thickened tubing, of 0.144 inch bore and about $\frac{1}{8}$ inch wall thickness. Slices of this tubing about 0.055 inch thick were cut in the Geology Department with a high speed wheel edged with diamond dust bonded in copper; the assistance of the Geology Department staff is gratefully acknowledged. The slices were ground to the correct thickness on an oil stone. Two of these spacers are included in Figure 9.

The electrical connections to the box, trap, repeller, and plates were made by short lengths of 36 swg nickel wire. The ends were originally silver-soldered to the small projections on the flat edges of the plates, but tended to break off at the join; instead, short pieces of 10 BA threaded rod were silver-soldered to the projections, and the wires secured between 10 BA nuts. The box, trap, and repeller leads were fastened similarly (Figure 9). The two plates carrying the knife-edge narrow slits were connected together by a 10 BA nut and bolt, and the connection to earth made through the bottom plate.

The details of the rest of the source assembly may be seen in the Figure 10. A $1\frac{1}{4}$ inch inconel tube was silver-soldered to the upper surface of the main flange and a stainless steel collar silver-soldered to this tube $2\frac{1}{2}$ inches from the flange. Fourteen holes, arranged in two symmetrical staggered rows of seven, were drilled radially in the collar, and $\frac{3}{4}$ inch lengths of thin-walled cupro-nickel tube silver-soldered into the holes. Each tube was flared out at the end,to hold Edison Swan metal/glass seals, which were soft-soldered in place. This arrangement allowed individual seals to be replaced if required. As a precaution against small leaks and cracks, each seal and soldered joint was painted with silicone varnish. The connections between the seals and the short nickel wire leads were made by lengths of 0.08 inch nickel bronze rod. The rods were bolted to the seals and had 10 BA nuts silver-soldered to their lower ends, to which the nickel leads were fastened by short 10 BA bolts. The rods were alternately long and short, to stagger the terminal connections, and were sheathed in pyrex tubing. The last two inches of the filament leads were braided copper, silver-soldered to the nickel bronze rods, as they had to be flexible to allow the filament to be changed without dismantling the stack. The connection to the filament stems was made by small stainless steel barrel connectors.

At the top of the $1\frac{1}{4}$ inch tube, 1 inch above the seal collar, was a 3 inch diameter inconel flange. Originally the flange which mated with this carried a single steel inlet tube, which was connected through a brass bellows inside to the single glass inlet to the ionisation box. Subsequently the more elaborate system shown in Figure 10 was built, and will be described later.

Alignment.

The accurate alignment of the source exit slits was done with the aid of a travelling microscope. The sample inlet flange was removed and the source clamped by the upper flange in the chuck of the milling machine dividing head. A dial gauge was arranged to bear on the edge of the main flange and the position of the source in the chuck adjusted by gentle tapping until rotation of the chuck caused deflections of less than 0.001 inch. The line of the master holes was made vertical by inserting two accurately machined pointed pins in the holes and adjusting the chuck until both pins coincided with a fixed point on the milling machine as the milling table was racked vertically. The travelling microscope was placed on the table and its horizontal hair line set against the horizontal surface of a square block; the slits could then be checked against the hair line. By racking the microscope forward, both narrow slits could be examined in turn, and any adjustments were made by slackening the knife-edges one at a time and re-setting them with feeler gauges. A 0.008 inch feeler gauge was used to set the slit width. The position of the two slits with respect to the rest of the stack was determined by passing the 0.008 inch feeler gauge through both slits and into the box; if it did not pass centrally through the upper slits the height of the exit slits above the table was adjusted.

The ion collector slit was set perpendicular to the line of the master holes in its flange by a similar procedure; a slit width of 0.010 inch was used.

The mass spectrometer tube was held in the frame by a large clamp attached to the horizontal pumping tube and by a bolt passing through the new brass stiffening tube. A plumb line was suspended from the upper flange and the tube adjusted until the thread just touched it at the punch marks A and B (Figure 4). The pole faces of the magnet were also set vertically with the aid of a plumb line and the best position of the magnet relative to the tube found by trial and error(36).

Focusing.

The mechanical alterations necessary for high resolution were now completed, but alterations were also required in the electrical focusing arrangement. The original ion source had a very simple focusing system: the disposition of the plates below the box was slightly different, J_3 being below J_1 and J_2, while J_1 and J_3 were connected together. The ions were drawn out of the box by applying a potential rather lower than the box potential to J_1J_3 and this potential could be varied in small steps. The beam was focused by adjusting the potential of J_2 relative to J_1J_3, which was done by a single potentiometer.

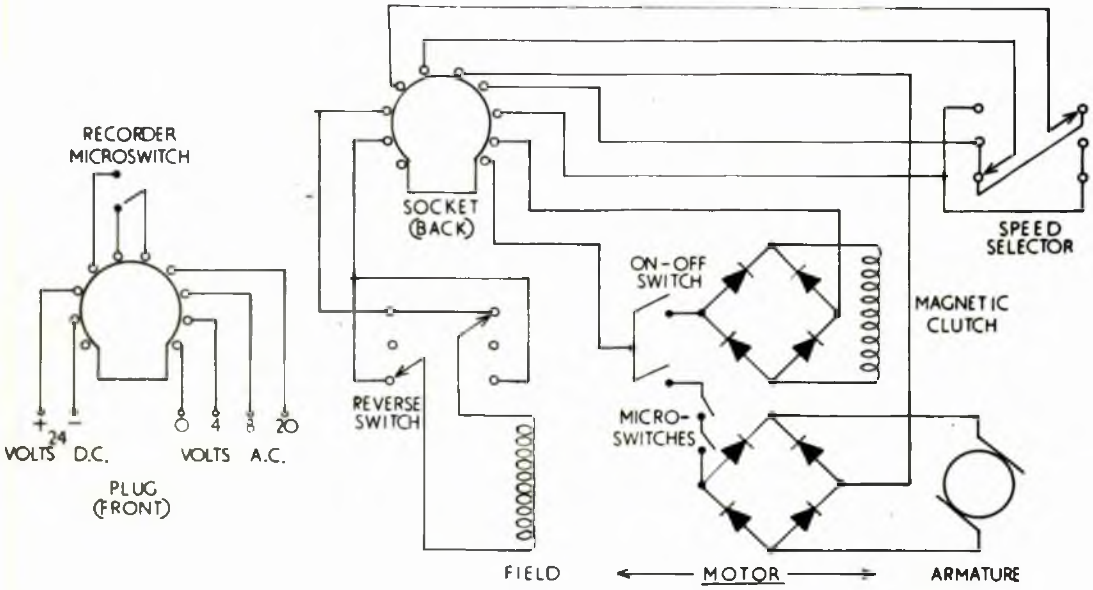
The J plate arrangement was altered in the new source (Figure 7), as it was thought that the presence of two half plates at different potentials just below the box might cause distortion. A commercial instrument of similar design uses this second arrangement and in it the potential of the focusing plates is only about 200 volts above earth, so that the ions are accelerated across the narrow gap between the J plates, and not across the wider gap, as in the original Nier source.

Accordingly, a new focus unit was constructed which could be adapted to provide potentials for either system, and which had provision for varying the repeller potential relative to the box and for applying a potential to G_1, to suppress the ion beam. The circuit of this unit was based on a design developed by Hamer(38).

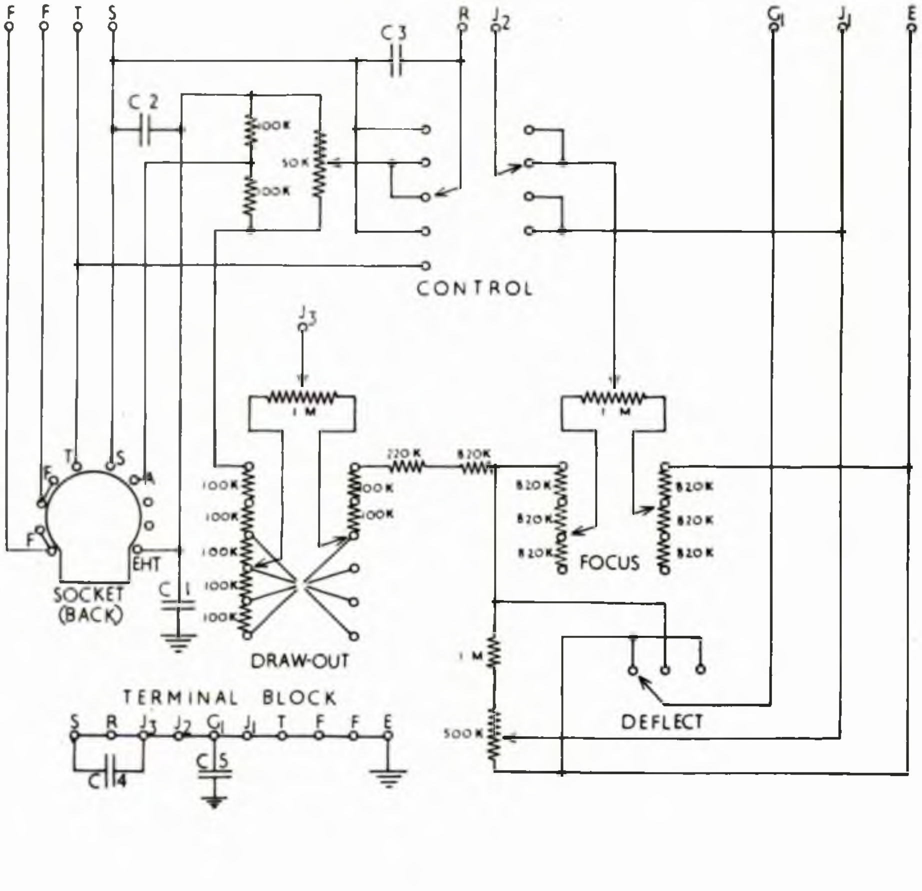
It was found that slightly better sensitivity and resolution were obtained when the ions were accelerated across the gap between the J plates, and the circuit diagram in Figure 11 shows the unit arranged

Figures 11 & 12.

SCANNING MOTOR CIRCUIT



FOCUS UNIT CIRCUIT



C1	1·5 μF	3KV
C2	2 μF	100V
C3	1 μF	400V
C4	1 μF	400V
C5	·02 μF	700V

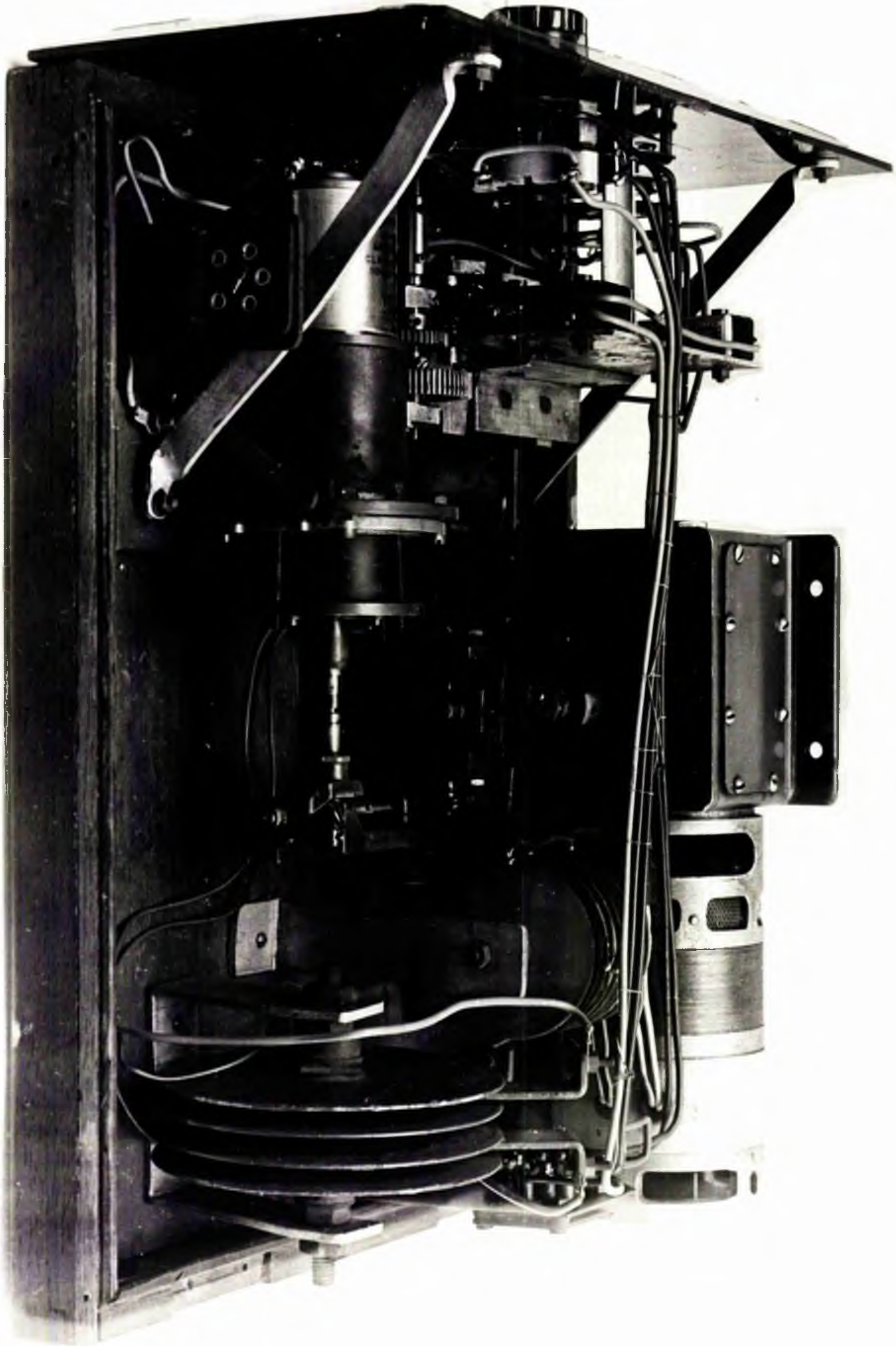
in this way. With an EHT of 1520 volts supplied to the resistor chain, the potential of J_1 could be varied from 0 to 200 volts; J_2 from 0 to 600 volts; J_3 from 1200 to 1500 volts; and R from 1500 to 1520 volts above earth. By means of the Control switch it was possible to connect the repeller, R, to the box, S; and J_1 to J_2 either independently or simultaneously. In the focusing procedure the potential of J_3 was adjusted to give maximum peak height with R = S and $J_1 = J_2$, then the repeller and J_2 were freed and set to maximum peak height in turn. J_1 was usually at 150 volts. The switch could also connect the repeller to the trap potential, which enabled the total number of electrons entering the box to be measured on the trap current meter.

There was no room for the focus unit in the existing EHT deck, so it was housed in a separate steel box with an ebonite front on which all the components were mounted; the knobs were linked to the potentio-meters and switches through tufnol adapters and the metal casing was earthed.

Scanning.

The improved mass spectrometer was tested by examining the mercury background spectrum, which revealed a further shortcoming in the original instrument; the background was scanned by varying the magnet current mechanically and it was found that the successive ion beams were moved across the narrow collector slit too fast for the recorder, which failed to reach the top of each peak or the bottom of each valley between peaks. As a result, the peak heights were too low, and the apparent resolution, as judged by the recorder chart, less than the actual resolution of the instrument.

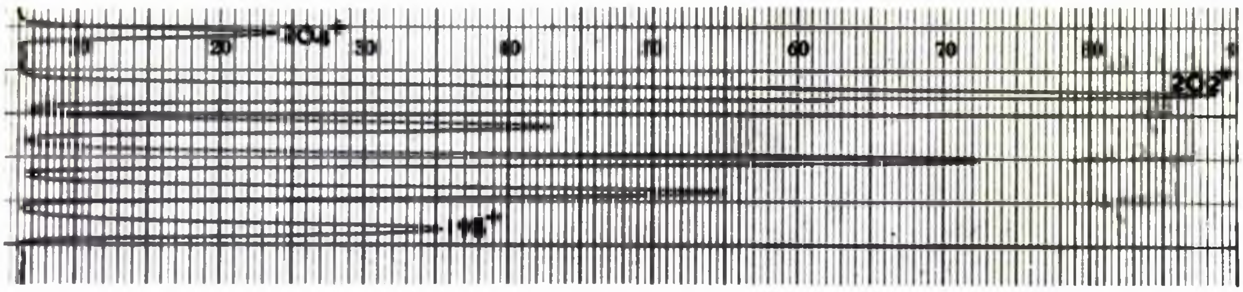
Figure 13.



A new scanning mechanism was therefore constructed; it had a ten turn 100 K ohm helipot in place of the single potentiometer in the original circuit, driven directly through a train of gears by a 24 volt DC shunt wound motor. The field of the motor was supplied with 24 volts DC and either 8 or 20 volts could be supplied to the armature, which gave the motor two speeds, 0.1 and 0.8 RPM. The slow speed allowed the recorder time to reach a peak height close to the real value, but as a full scan of the helipot range took 100 minutes, the fast speed was provided to save time between peaks. A micro-switch in the recorder automatically made the change from fast to slow when the pointer passed 20 on the scale. Manual selection of the speeds was also possible and the circuit included a safety device which switched the motor off when the helipot reached either end of its range. A change-over switch in the magnet supply panel allowed either the original or the new mechanism to be used, and the circuit details may be seen in the circuit diagram, Figure 12 and the photograph, Figure 13.

After all these modifications the instrument was capable of resolving the singly charged mercury isotopes completely, and a photograph of a strip chart record of the mass region 198^+ to 204^+ is given in Figure 14. The resolution deteriorated slowly with use, due to contamination of the source, but could be restored by cleaning.

At one stage of the work the resolution deteriorated very rapidly and the instrument could not be used. Cleaning of the source and a thorough check of the electronic circuits caused no improvement, and it was eventually established that the trouble was caused by the



10
20
30
40
50
60
70
80
204+
202+
196+

Figure 14.

Resolution of Mercury Isotopes.

build-up of charge on the plates of the source, whose surfaces had lost their original high polish. A more elaborate cleaning procedure was devised which was successful in restoring the resolution; it entailed first rubbing any carbon deposits and metal burn marks off the plates with fine emery paper, then polishing all metal parts of the stack with a high speed cloth wheel and very fine rouge; the components were cleaned with carbon tetrachloride, boiled in distilled water and a little Teepol, boiled twice in distilled water and dried by evacuation in a warmed flask. The glass components were boiled in concentrated nitric acid, boiled in distilled water, and vacuum dried.

Use of the Mass Spectrometer.

For analysis, the pressure of a gas or vapour in the ionisation box of the mass spectrometer source should be about 10^{-4} mm., and as sample pressures would normally be 1 mm. or more, some form of fine leak is necessary between the sample handling system and the ion source.

All leaks in this investigation were made from "Metrosil". This material is semi-porous and will fuse to pyrex; leaks were made by fusing small pieces of 4 F metrosil rod into narrowed pyrex tube. The porosity of the leaks depended on the length of the piece of metrosil and on the temperature it reached when being fused in; each was calibrated by allowing air to leak through it into an evacuated fixed volume of about 1 litre and measuring the rate of the pressure rise on a mercury manometer. The porosity of each leak was then expressed in minutes per cm.

Hydrocarbon molecules break up on electron bombardment in a mass spectrometer source into fragments, and consequently each hydrocarbon gives rise to a number of peaks of different mass to charge ratio. The relative heights of these peaks constitute the 'cracking pattern' of the hydrocarbon, which remains constant for a fixed electron accelerating voltage. The cracking patterns of many compounds have been published(39), but because of their dependence on source conditions it was necessary to determine the cracking patterns of compounds to be analysed in this investigation.

Table 1 lists the main peaks of interest in the cracking pattern of dibenzyl, relative to the 91^+ peak as 100.

Table 1.

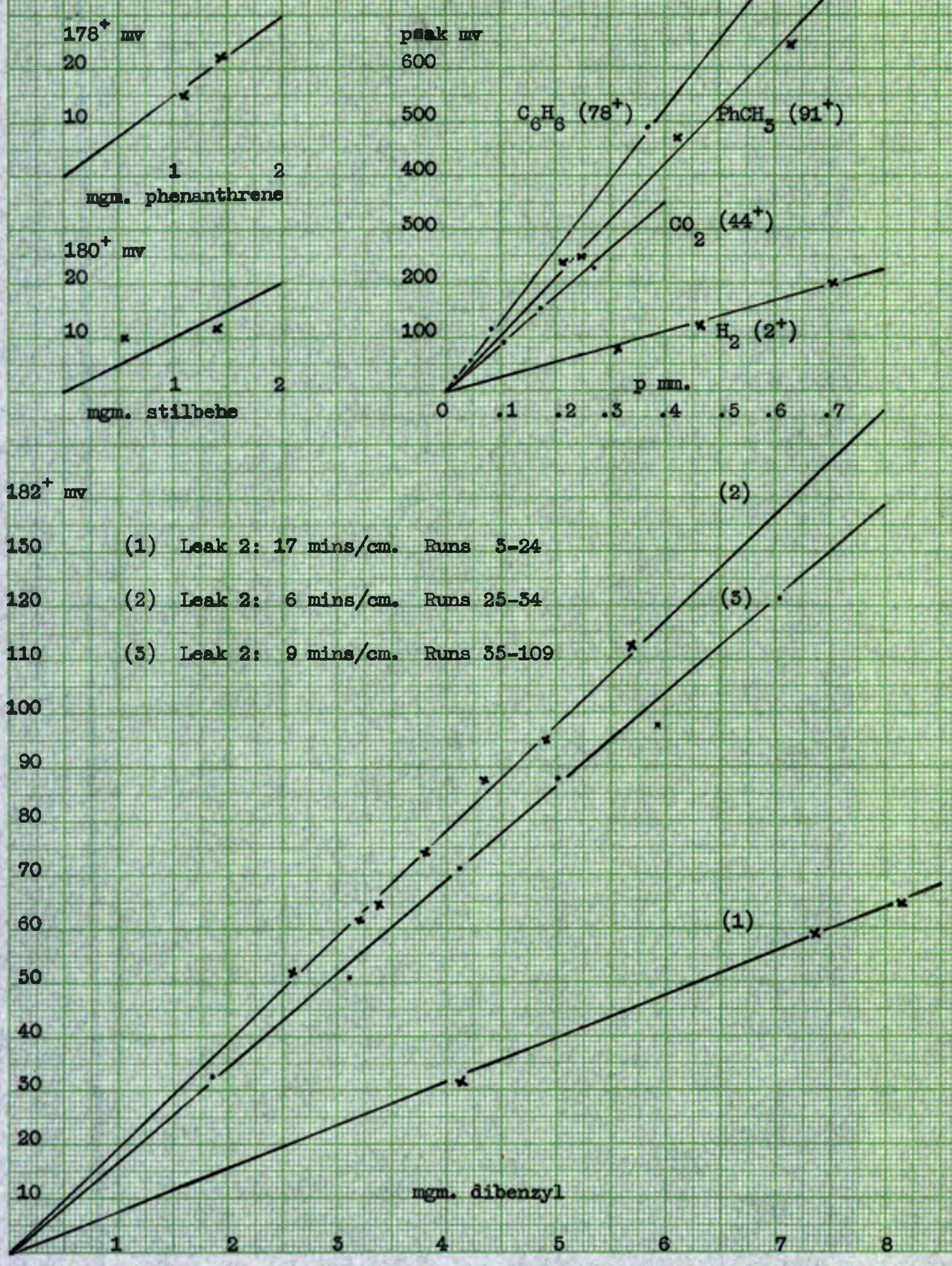
Mass no.	2	77	78	91	92	178	179	180	182	183
Intensity	2.60	3.16	1.76	100.00	8.49	1.52	1.11	0.56	22.42	3.38

The parent ion, 182^+, was used as a measure of the dibenzyl concentration, but the value of 182^+ would depend both on the pressure of dibenzyl in the inlet system and on the sensitivity of the mass spectrometer, which varied from day to day and even altered slowly in the course of analysis. A comparative method of quantitative analysis was therefore employed, in which the instrument was first calibrated for dibenzyl.

The sample inlet system had two metrosil leaks and a weighed quantity of dibenzyl was admitted round one leak while argon at a known pressure, measured on a McLeod gauge, was admitted round the other. The 182^+ dibenzyl peak and 40^+ argon peak were then measured, keeping the electron trap current constant by manual adjustment, since the peak heights varied with the trap current and the emission stabiliser operated to keep the total emission and not the trap current constant. The sensitivity of the mass spectrometer to argon was expressed in volts/mm. and the 182^+ peak height corrected to correspond to a sensitivity of 2.00 volts/mm. for argon, by multiplying by 2 and dividing by the observed argon sensitivity. This procedure was repeated for different weights of dibenzyl and a graph of mgm. dibenzyl against corrected peak height plotted. A straight line was obtained and unknown samples of dibenzyl could then be analysed by comparison of their corrected peak heights with the calibration line.

The mass spectrometer was calibrated for stilbene and

Figure 17.


178+ mv
20
10
1
2
mgm. phenanthrene
180+ mv
20
10
1
2
mgm. stilbene
peak mv
600
500
400
300
200
100
C_6H_6 (78+)
$PhCH_3$ (91+)
CO_2 (44+)
H_2 (2+)
p mm.
0
.1
.2
.3
.4
.5
.6
.7
182+ mv
130
120
110
100
90
80
70
60
50
40
30
20
10
(1) Leak 2: 17 mins/cm. Runs 3-24
(2) Leak 2: 6 mins/cm. Runs 25-34
(3) Leak 2: 9 mins/cm. Runs 35-109
(2)
(3)
(1)
mgm. dibenzyl
1
2
3
4
5
6
7
8

phenanthrene in the same way, and for toluene and benzene by admitting vapour from a bath at known temperatures to the inlet system. It was also calibrated for hydrogen and carbon dioxide, the inlet pressures of these gases being measured on a McLeod gauge.

This calibration method assumes that if the sensitivity of the mass spectrometer to argon changes, the sensitivity to dibenzyl, or to any peak under consideration, will change in proportion. The validity of this assumption was established by admitting argon to the system and measuring the 40^+ peak and 202^+ mercury background peak at different settings of the focus controls, which altered the sensitivity. The ratio of the two peaks remained constant.

The dibenzyl calibration lines for the three different leak 2 metrosils used in the course of the investigation are plotted in Figure 17, along with the calibration lines for other substances studied, determined with the leak 2 used for Runs 35 to 109.

REACTION & GAS HANDLING SYSTEM

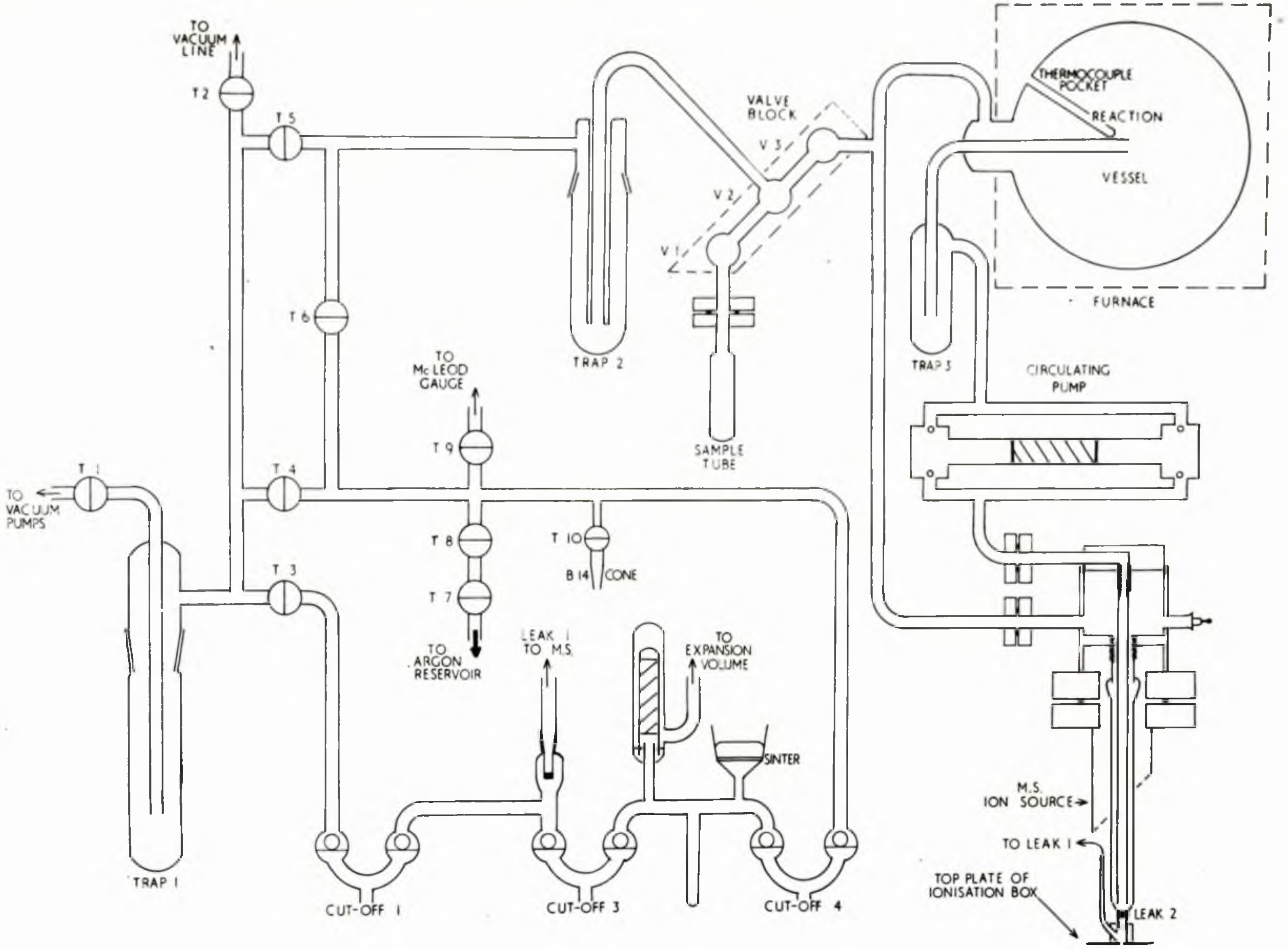


Figure 15.

THE REACTION AND INLET SYSTEM.

For its use as an analytical instrument the mass spectrometer had associated with it a gas handling system and a simple heated inlet for the analysis of volatile solids. For the present investigation the former was modified and the latter replaced by a reaction system, in which the thermal dissociation and decomposition of dibenzyl could be observed continuously in the mass spectrometer. In the course of the work several modifications were made, and Figure 15 shows the reaction system in its final form, with the relevant parts of the gas handling system.

The whole apparatus except the valve block and circulating pump was constructed of pyrex glass.

Vacuum pumps.

The apparatus could be evacuated by a single stage mercury diffusion pump, backed by a single stage rotary oil pump; with liquid air on Trap 1 a pressure of 10^{-5} mm., measured with a McLeod gauge, could be attained.

Gas handling system.

Mercury sealed cut-offs, designed by Pittilo(10), were used in the gas handling system instead of greased taps. Each had two ½ inch stainless steel balls which could be raised into ground seatings by raising a mercury reservoir attached to the centre tube of the cut-off; when the reservoir was lowered, to open the cut-off, the balls rested on tungsten wires sealed into the glass.

The metrosil leak 1 was attached to the system through a B14 joint, sealed with Edwards' wax. Gases and liquids could be injected round the leak by touching a fine jet or pipette on to the mercury-sealed 4 F sintered glass disc; gases could also be admitted from bulbs attached to the B14 cone below Tap 10. A finger trap was provided between Cut-offs 3 and 4 for condensable substances.

The expansion volume consisted of a 5 litre bulb connected through a mercury sealed cut-off, which was opened and closed by a glass plunger with an iron core, actuated by a solenoid.

The argon used for calibration was contained in a 3 litre bulb attached to Tap 7. It was filled in a separate system, in which cylinder argon at one atmosphere pressure passed through a long capillary, then through a liquid air trap to remove condensable impurities, two traps containing sodium at 300°C to remove oxygen, another liquid air trap, and finally into the previously evacuated bulb.

The gas handling system could be evacuated on either side of Cut-off 3 through Taps 3 or 4.

Solids injection valves.

All parts of the apparatus in which dibenzyl was to be used had to be heated to prevent condensation, and consequently glass taps could not be used. Instead, there was a system of three valves, machined from a single mild steel block. Each of the three tubes leading from the block originated from a hole in the centre of a seating which could be closed by a steel rod; the rods were mounted from metal bellows, to give the necessary degree of movement, and the upper ends were threaded 5/16 BSF. Each had a nut on the threaded part, set in a bush so that it could only be rotated and not moved up or down. The rods could therefore be moved off and on the seats by turning the nuts, rotation of the rods and bellows being prevented by guide screws running in slots. The three seats were connected by a hole running the length of the block, so that any combination of the three tubes could be connected together.

This valve was designed by Pittilo(10) for use in the original solids inlet system. In its original form the valve rods were tipped with teflon discs and the bellows were seamed stainless steel; both gave trouble, the teflon shredded with use and the bellows developed leaks at the seams. The valve unit was completely dismantled and rebuilt, using copper seating discs on the valve rods and seamless brass bellows, which proved satisfactory. A further modification involved the sample tube, the flange of which was originally bolted directly to the valve block. The threads in the fixing holes in the block began to strip, and the ring in the block which mated with the groove in the flange carrying the teflon sealing gasket was not a good fit, so that leaks developed. The arrangement shown in the diagram was therefore adopted, in which a fixed flange was suspended from the block by a short length of steel tube. Two flanges to mate with this were made, so that two interchangeable sample holders were available.

The valve block was mounted on the mass spectrometer frame and connected to the glass apparatus by metal/glass seals; the sample tubes were pyrex, connected directly to their flanges by metal/glass seals. The block was heated by hot plates made from nichrome tape wound on mica formers, and by nichrome tape windings on the cylindrical casings round the bellows.

The glass leads to the reaction vessel and to trap 2 were heated by wrappings of asbestos tape with nichrome tape threaded through them;

the glass tubes were also lagged with broad asbestos tape.

The connection to the vacuum pumps was made through Trap 2, which had a re-entrant centre tube heated by a nichrome winding, to allow the condensable products of a run in the reaction vessel to be collected.

Tap 6 connected the gas and solid handling systems directly, and enabled argon or other gases to be admitted to the latter.

Reaction system.

The reaction vessel was a 2 litre bulb, mounted in a furnace on top of the mass spectrometer frame and fitted with a thermocouple pocket, centre tube, and side-arm. The system linking the reaction vessel to the mass spectrometer underwent several changes.

At first, a very simple system was built, in which Valve 5 was connected to the side-arm of the reaction vessel and the solids leak 2 sealed into the end of the centre tube, which was connected to the tube from leak 1. The mass spectrometer inlet consisted of a single tube from the upper flange to the ionisation box and this was connected to a lead from the tube joining the two leaks. All tubes down to the upper flange were wrapped with heating tape, except a few inches above leak 1, since the mercury cut-off could not be heated. All the inconel parts of the mass spectrometer tube were also heated electrically to about 80°C, to cut down 'memory' effects due to adsorption. The metrosil leaks had the following porosities:- leak 1, 7 minutes/cm.; leak 2, 19 minutes/cm.

The arrangement was unsatisfactory: if dibenzyl was injected into the reaction vessel, 10 to 20 minutes elapsed before maximum peak height was attained, and when the dibenzyl was pumped away, the peak persisted in the mass spectrometer for at least one hour. Benzene could be admitted and removed quite rapidly, and the difference was clearly due to adsorption of dibenzyl on the leads between the leaks and the ion gun. A slight improvement was obtained by raising the temperature of the heated parts from 80°C to 120°C, and by installing a new leak 2, of porosity 6 minutes/cm., but the system was still unsuitable.

A more elaborate system was therefore constructed in which the leak 2 was mounted in the vertical arm of a Y-shaped tube just outside the main flange of the ion source. The two upper arms of the Y were connected through a circulating pump to the side-arm and centre tube of the reaction vessel, so that the contents could be circulated past the leak. The arm of the Y carrying the leak was connected through a flange to the side-arm on the main flange which may be seen in Figure 8; this was connected to the inlet on the top plate of the ionisation box by a length of quill tubing. The original inlet tube was still used for leak 1, so that there were two separated inlets which only met at the ionisation box.

The circulating pump was not constructed by the author and a full description of it has been given by Miss F.G. Smith(40). The piston in the centre tube was of steel, with two teflon piston rings, and the remainder of the pump was brass. The piston was operated by two solenoids placed round the centre tube and energised alternately. At each end of the pump was an exhaust valve and an inlet valve consisting of steel ball bearings on brass seats; these could be raised, to open the valves, by solenoids, and were so arranged that each exhaust valve opened as the piston moved towards it, the inlet valve at the opposite end opening at the same time. The timing of the piston and valves was controlled by two microswitches operated by eccentric cams on a shaft driven by a low speed electric motor. The pump was capable of circulating vapour at pressures down to a fraction of 1 mm. and was heated by windings of nichrome tape.

This arrangement shortened the path between leak 2 and the ionisation box substantially and the response of the instrument to dibenzyl was more rapid, as maximum peak height was reached in just over 5 minutes. When the dibenzyl was pumped away from the leak, the peak dropped rapidly although a small residual peak persisted for some time, probably because the short quill tube inside the source was unheated.

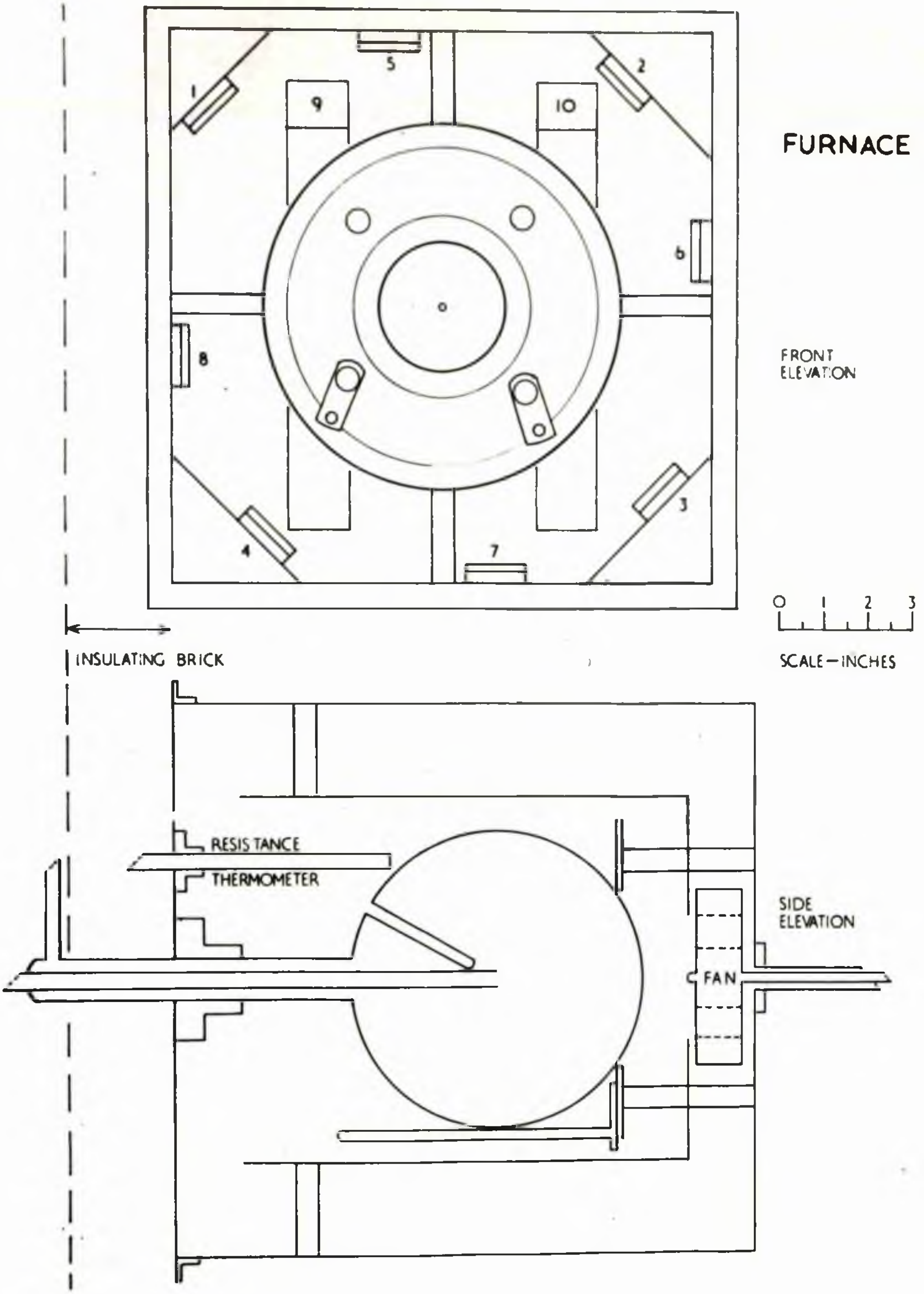
The earlier Runs were done using this system, Runs 3 to 24 with a leak 2 of 17 minutes/cm., and Runs 25 to 34 with a leak 2 of 6 minutes/cm.

Although fairly satisfactory results had been obtained, the uncertainty caused by the small delay in response made it desirable to attempt to reduce this time lag further. The obvious solution was to have the metrosil leak 2 just above the ionisation box, which required that the heated circulation system be extended inside the mass spectrometer source, where very little space was available. After some re-arrangement of the source it was possible to install such a system, details of which may be seen in Figures 6 and 10.

The former solids inlet, comprising the side-arm on the main flange and the quill tube to the box, was connected to leak 1, to form the gas inlet; and the upper flange carrying the former gas inlet was removed and replaced by a new flange supporting the circulating system.

All parts above the flange were made of mild steel, the main cylindrical casing being machined from a single piece of steel rod. The outer glass tube carrying leak 2 was connected to the casing through a metal/glass seal and a length of brass bellows for flexibility. The inner tube fitted inside a piece of brass bellows fastened to the disc-shaped top cap. Nichrome heating wire was wound round the outside of the inner tube from the top and was returned up the centre of the tube, passing through a hole drilled in the glass and the brass bellows, where it was insulated by a small porcelain bead and cemented by silver chloride. Four metal/glass seals were attached to the casing in the same way as the seals on the source, two for the heating winding and the others for a chromel/alumel thermocouple with its junction halfway down the concentric tubes. The leads were insulated by glass fibre sleeving and tape. The side-arm flanges mated with flanges attached to the circulating system through bellows which allowed sufficient movement for the removal of the ion source. All metal joints were silver-soldered, except the top cap, which was soft-soldered. The whole of the casing and the flanges were heated by nichrome hot plates and windings.

When this system was tested it was found to give inconsistent results, even with argon; the peak height fluctuated and depended on the rate of operation of the circulating pump, indicating that the concentric tubes constituted sufficient of a constriction for the circulating pump to compress gas in the region of leak 2. The inlet was dismantled and the electrical leads in the source re-arranged to allow room for wider bore tubes. Tubes of 10 mm. and 6 mm. bore were fitted and the thermocouple omitted, as there was no longer space for it. With these modifications the inlet gave reproducible results. A leak of 9 mins./cm.



FURNACE

1
5
2
9
10
6
8
3
4
7
FRONT ELEVATION
0 1 2 3
SCALE—INCHES
INSULATING BRICK
RESISTANCE
THERMOMETER
SIDE ELEVATION
FAN

FURNACE CIRCUIT

3 HEAT SWITCH

POSITION	CONTACTS	OHMS
1	LR—3G L—M	22
2	L—3G L—M	34
3	L—3G	48
4	—	80

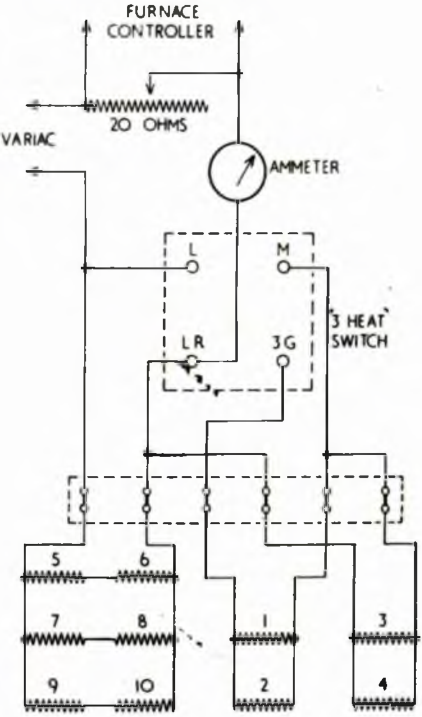


Figure 16.

was used, and maximum peak height for dibenzyl could be reached 2 minutes after injection, which was about the same as the time required for benzene. The drop of the peak after pumping out was also rapid.

The apparatus in this form was used for Runs 35 to 82.

The final modification to the reaction system was the installation of Trap 3. The heating tapes on the glass leads of the system were wound round the top third of the trap only; the rest was normally heated by a detachable metal tube with a nichrome winding on it, but the reaction products could be condensed selectively in the trap by surrounding it with a suitable cold bath.

The apparatus in its final form, as illustrated in Figure 15, was available for Runs 83 to 109.

Furnace.

The furnace and reaction vessel are only illustrated diagrammatically in Figure 15, scale drawings of both are given in Figure 16.

The furnace was constructed of 18 swg sheet iron, bent and riveted to form a box 12 x 12 x 15 inches. It was insulated by K.I.P. furnace bricks, $2\frac{1}{2}$ inches thick, and was mounted on a metal tray on top of the mass spectrometer frame. The heaters, which were totally enclosed in steel and had a resistance of 120 ohms each, were mounted on the five walls of the box and on diagonally placed plates on the corners, as shown in the Front Elevation in Figure 16. They were held off the walls by $\frac{1}{4}$ inch asbestos washers. Uniform heating was achieved by running the heaters below their rated wattage; surrounding the reaction vessel with a cylindrical shield to protect it from direct radiation; and providing a circulating system in which the air in the furnace was drawn through a hole in the end of the cylindrical shield by a small fan and circulated round the walls of the box. The fan shaft passed through two water-cooled ball races outside the furnace and was driven by a 24 volt DC motor.

The reaction vessel was supported inside the shield by a vertical asbestos ring and two horizontal steel rods wrapped with asbestos string. Its neck passed through a gland block in the front face, which was in two vertically divided halves, bolted to an angle iron flange, to enable the reaction vessel to be removed. The chromel/alumel thermocouple leads passed through a small hole in the face, to which was also attached a block holding the platinum resistance thermometer that formed the temperature-sensitive element of the furnace controller.

At first the heating tapes on the glass tubes from the reaction vessel were taken right up to the furnace wall, but it was found that the part of the neck inside the insulating brick became so hot that the pyrex tubing softened and collapsed. Therefore this part of the neck was wrapped with nickel foil and the heating windings stopped at the face of the brick, the rest being heated by conduction along the nickel.

The ten furnace heaters were connected as shown in the diagram; the connections inside the furnace and to the 6-way terminal block outside were made by thick nickel wire insulated with porcelain beads. A three heat switch was modified to give four different arrangements of the three groups of heaters, to enable the furnace to be used over a wide temperature range. For this investigation it was possible to use position 3 only, in which all ten heaters were equally loaded, being connected in pairs in series across the voltage supply so that they ran at not more than one quarter their rated wattage. The circuit also included a 20 ohm variable resistance, which could be switched in and out by the furnace controller, and an ammeter. Power was supplied from the mains through a Variac auto transformer.

Furnace controller.

Since the furnace was to be used for experiments which might last several hours, the temperature had to be controlled accurately and a furnace controller of conventional design was built for this purpose.

The controller switched in and out a relay across the resistance in the furnace circuit, so that the furnace current was alternately high ahd low. The frequency of the cycling of this relay was affected by the amplified output from an AC bridge which had as one of its arms the platinum resistance thermometer in the furnace. The bridge could be set to be balanced at specific values of thermometer resistance, corresponding to temperatures between 30°C and 1100°C, and the circuit was so arranged that if the temperature of the furnace was below the value corresponding to the chosen resistance the relay was closed for longer than usual, so that the furnace temperature rose. If the temperature was too high, the resistance was switched into the circuit for longer. When properly adjusted, the controller maintained the temperature constant to about $\frac{1}{4}^{\circ}$ at 400°C.

The temperature inside the cylindrical shield in the furnace was checked for uniformity with a probe thermocouple. No significant variation was found.

The chromel/alumel thermocouple itself was checked by direct comparison with a similar thermocouple which had been calibrated by plott-

-ing the cooling curves of analar metals. The two thermocouples agreed within 1° up to 600°C, measured on the Pye direct reading potentiometer which was used in all experimental work.

The furnace required several hours to reach its working temperature and its mains supply was controlled by a Venner Time Switch, which also switched the power to the controller and to a transformer and rectifier which provided 24 volts DC for the furnace fan motor.

Heaters.

All heaters on the apparatus and the mass spectrometer tube were supplied with AC from a 2.5 Kw multi-tap transformer, which also provided power for the variable speed scanning motor. The mass spectrometer tube was heated continuously and the other heaters could be switched on as required.

Mass spectrometer vacuum pumps.

The 2 inch diameter inconel pumping tube of the mass spectrometer was connected through a wide bore brass bellows to a 80 mm. diameter pyrex trap, then to a three stage mercury diffusion pump, backed by a two stage rotary oil pump. Between the two pumps was a section, isolable by taps, containing a trap like Trap 1 of the handling system, a single stage mercury diffusion pump, and a 2 litre backing volume. When the mass spectrometer had to be evacuated from atmospheric pressure it was pumped for four hours by the rotary oil pump and small diffusion pump, with liquid air on the small trap to freeze out all condensable vapour (the handling system had to be evacuated at the same time, since the two were linked by leaks 1 and 2). The section was then isolated, the trap removed and cleaned, and pumping continued using the three stage diffusion pump, with a -80°C bath round the large trap. Several more hours' pump-

-ing were required to reach the operating pressure of 10^{-6} to 10^{-7} mm. An uncalibrated Phillips cold cathode ionisation gauge was used to estimate the pressure. It was mounted on the inconel tube just above the trap. When in use the mass spectrometer was pumped continuously; the rotary oil pump was switched off overnight and the 2 litre backing volume opened to the diffusion pump, which had a relay in its heater circuit arranged to switch off if the cooling water supply failed.

Vacuum line.

The vacuum line could be connected directly or through a capillary to a side-arm in the mass spectrometer tube beside the Phillips gauge; this arrangement enabled the mass spectrometer to be used for leak testing apparatus attached to the vacuum line with a hydrogen probe.

USE OF THE APPARATUS.

The apparatus was used both for following reactions in the reaction vessel and for the analysis of the products of experiments in sealed tubes, to supplement the data obtained from the reaction vessel Runs. The procedure in each case will be described.

Procedure for a Run in the reaction vessel.

The furnace was switched on several hours before the Run was due to start by the Venner Time Switch, which also operated a relay to switch on the heaters for the valve block, since these took longer to warm up than the rest. One hour before the start of the Run the electronic circuits of the mass spectrometer and the remaining heaters were switched on.

The large -80°C bath on the mass spectrometer pumping trap was filled up with solid carbon dioxide, a liquid air bath was put round Trap 1, and the mass spectrometer rotary oil pump and the handling system pumps were started. The whole of the handling and reaction system was opened to the pumps (it was kept evacuated between Runs since it was connected directly to the mass spectrometer) and pumped to 10^{-5} mm.

When the solids inlet heaters had reached temperature (about 130°C for the valve and 100°C for the rest) all pumping taps except Tap 5 were shut, Valves 1 and 3 closed, and the sample tube removed and replaced by the other containing the quantity of dibenzyl to be injected. The quantities used ranged from 1 to 8 mgm. and in most runs aliquots of a solution of dibenzyl in carbon tetrachloride were evaporated in the sample tube by attaching it through an adapter to another vacuum system where it was pumped from ice and water by a rotary oil pump alone until a Tesla coil discharge no longer showed the characteristic green colour of carbon tetrachloride vapour. This method was checked for loss by analysing samples in the mass spectrometer and comparing the weight derived from the calibration graph with the weight calculated from the volume of solution evaporated. These weights agreed within 2 %. In some cases the dibenzyl was weighed directly into small tubes which were dropped into the sample tube. When the sample tube containing the dibenzyl had been bolted in place it was surrounded by a -80°C bath and was evacuated.

With Cut-offs 3 and 4 open, the cut-off to the expansion volume up, and Cut-off 1 and Tap 4 closed, argon from the reservoir was admitted to the space between Taps 7 and 8, then this volume was expanded into the 5 litre bulb and round leak 1, to give about $\frac{1}{2}$ mm. of argon in the system.

The background peaks of the mass spectrometer in the mass regions to be studied were scanned; all valves were then closed and a hot air bath consisting of an electrically heated iron tube was put round the sample tube. The circulating pump was started and liquid air was put round Trap 3. Valves 1 and 3 were opened and the dibenzyl distilled into Trap 3. After about three minutes Valves 1 and 3 were closed and the liquid air round Trap 3 replaced by the hot air bath; the time of this change was taken as the zero time for the Run.

The peaks of interest were scanned in the mass spectrometer and the heights of the important ones measured accurately by manual adjustment of the magnet current. The 40^+ argon peak was measured as soon as possible after each scan and the argon pressure read off the McLeod gauge. In the Runs done with a mixture of dibenzyl and deuterated dibenzyl mostt of the readings were taken in the mass region 180^+ to 186^+; the three peaks 182^+, 184^+, and 186^+ could be hand-scanned and the 40^+ peak measured in two minutes. The time of measuring 184^+ was taken as the time of the reading. If strip chart records were made readings could be made at about 7 minute intervals; for some runs at high temperature the strip chart record was dispensed with, and hand-scanned readings only made, at intervals of about 3 minutes.

At the end of the Run the quantities of toluene and benzene produced could be measured by collecting all the contents of the reaction vessel in liquid air in Trap 3, then replacing the liquid air by ice and water which retained the dibenzyl and solid products and enabled the volatile products to be measured in the mass spectrometer. Trap 3 was then warmed and the system pumped out with a -80°C bath round Trap 2 to collect the products for UV analysis.

For Runs in the presence of argon the dibenzyl was distilled into Trap 3 before any argon was admitted to the system. Then, with Taps 4 and 5 and Cut-off 4 closed, the volume of argon between Taps 7 and 8 was expandäd into the reaction vessel by opening Tap 6 and Valve 2. The argon was allowed to equilibrate and its pressure measured, then all valves and Tap 6 were closed, keeping the same pressure of argon on each side of the valves in case they leaked slightly. The argon could then be pumped away from the rest of the system. In these Runs the argon in the reaction vessel was used as the calibrating gas.

Nitrogen or deuterium could be admitted from a bulb attached to the cone below Tap 10 by a similar procedure; once the pressure of gas in the reaction vessel had been recorded the gas handling system could be pumped out and argon admitted round leak 1 in the normal way.

In the Runs done before Trap 3 was available the zero time for the reaction was taken as the time of opening Valve 3, and the reaction products were pumped directly into Trap 2 at the end of the Run.

Procedure for a sealed tube Run.

Runs in the reaction vessel could only be done over a limited pressure range and it was not convenient to vary the surface to volume ratio; therefore several Runs were done in sealed tubes to extend the pressure range of the investigation and to observe the effect of changing the surface to volume ratio.

The tubes used were made of pyrex which had been cleaned in aqua regia and thoroughly washed. They ranged from 5 to 320 ml. in volume; each had a breakable seal in the neck and a side-arm with a constriction below the seal. An aliquot of the carbon tetrachloride solution of dibenzyl was pipetted into the tube by the side-arm, washed in with a little carbon tetrachloride, and evaporated through the side-arm in the way described. When the carbon tetrachloride had been removed the tube was surrounded by a -80°C bath, pumped to 10^{-5} mm., and sealed off at the constriction under vacuum.

The tube was heated for a known time in a furnace consisting of a 4 inch diameter iron tube wrapped with nichrome tape and insulated with alundum and asbestos. The temperature was measured by a chromel/ /alumel thermocouple and was controlled by a platinum resistance thermometer controller.

One of the sample tubes for the valve block was cut below the metal/glass seal and the sealed tube glass-blown on above the break seal. A short piece of steel rod was gently lowered on to the tip of the seal and the modified sample tube was bolted to the valve and evacuated.

For all analyses the reaction vessel furnace was set at 170°C, which was the temperature used in the calibration experiments. Otherwise the mass spectrometer procedure was the same as before.

Before the seal was broken the background was scanned, with argon round leak 1. The piece of steel rod, manipulated with a magnet, was used to break the seal, and the tube was heated to distil the contents into Trap 3, cooled in liquid air.

A thorough survey of the reaction products could then be done by surrounding Trap 3 with a series of baths so that the products were vaporised in turn: with liquid air on the trap the hydrogen region of the mass spectrum was scanned; with a -80°C bath, C_2 to C_4 hydrocarbons; with ice and water, benzene and toluene; and with hot air, dibenzyl and solid products.

Before Trap 3 was fitted a similar procedure was used in which the succession of baths was put round the reaction tube itself, so that the products were vaporised in turn into the circulating system. It was difficult to get quantitative results for the solids, since the volatile substances present impeded their flow into the circulating system, and Trap 3 was in fact included in the system to overcome this difficulty.

A direct comparison of the sensitivity of each leak to argon was done periodically as a check on the metrosils. Starting with an evacuated system with no dibenzyl present, argon was admitted round leak 1 in the normal way and its pressure and peak height measured; Cut-off 3 was raised, Cut-off 1 lowered and the argon pumped away from leak 1 through

Tap 3 until the 40^+ peak was negligible. With Tap 5 closed and all valves open, Tap 6 was then opened, thus admitting argon through the reaction system to leak 2; the pressure and peak height were recorded and the sequence of measurements could be repeated by closing Taps 3 and 6 and pumping out the reaction vessel through Tap 5, then re-admitting argon round leak 1, and so on.

The relative sensitivity of the leaks to argon was necessary in order to compare the results of Runs in the presence of argon with other reaction vessel Runs, and was also useful in checking that the porosities of the metrosil leaks did not change.

EXPERIMENTAL RESULTS.

The experiments performed in the course of the investigation may conveniently be classified into three groups, thus:-

I. Preliminary.

Mixtures of pure dibenzyl (diB_h) and the deuterated mixture (diB_d*) prepared by the deuteration of diphenyl acetylene were heated in the reaction vessel at temperatures between 410°C and 480°C and changes in the mass spectrum in the region of the parent peaks observed (Runs 1 - 11). Because of the complicated nature of the mass spectrum of diB_d* the results were difficult to interpret and no calculations were attempted. Nevertheless two qualitative observations could be made: some of the lower mass peaks in diB_d* did rise at the expense of the higher mass peaks and of the main peak of diB_h, indicating that dissociation into radicals and recombination to form a randomised mixture did occur; and peaks appeared just below the parent peak of diB_h, suggesting that decomposition of dibenzyl to stilbene also occurred.

II. Investigation of the decomposition of diB_h alone.

In view of the results of the preliminary experiments, a series of Runs (12 - 18 & 21 - 26) in the reaction vessel using diB_h only was carried out. The decomposition was studied between 455°C and 495°C, in the presence of pressures of nitrogen ranging from 0 to 14.5 mm. The main purpose of these experiments was to determine the rate of disappearance of dibenzyl, but some information as to the nature of the decomposition products was also obtained, both by mass spectrometry and by ultraviolet absorption measurements on the solid products of certain Runs.

The pressure range of this investigation was extended by two series of Runs in sealed tubes. The first consisted of Runs 46 - 64, for which the low temperature of 384°C was selected to enable the reaction to be studied at low percentage decomposition. A range of dibenzyl pressures was obtained by using different weights of diB_h and different volumes of tubes; tubes packed with lengths of pyrex quill tubing were used in some Runs to vary the surface to volume ratio. These Runs were done before Trap 3 had been installed, and the results were rather inconsistent both for dibenzyl lost and for products formed.

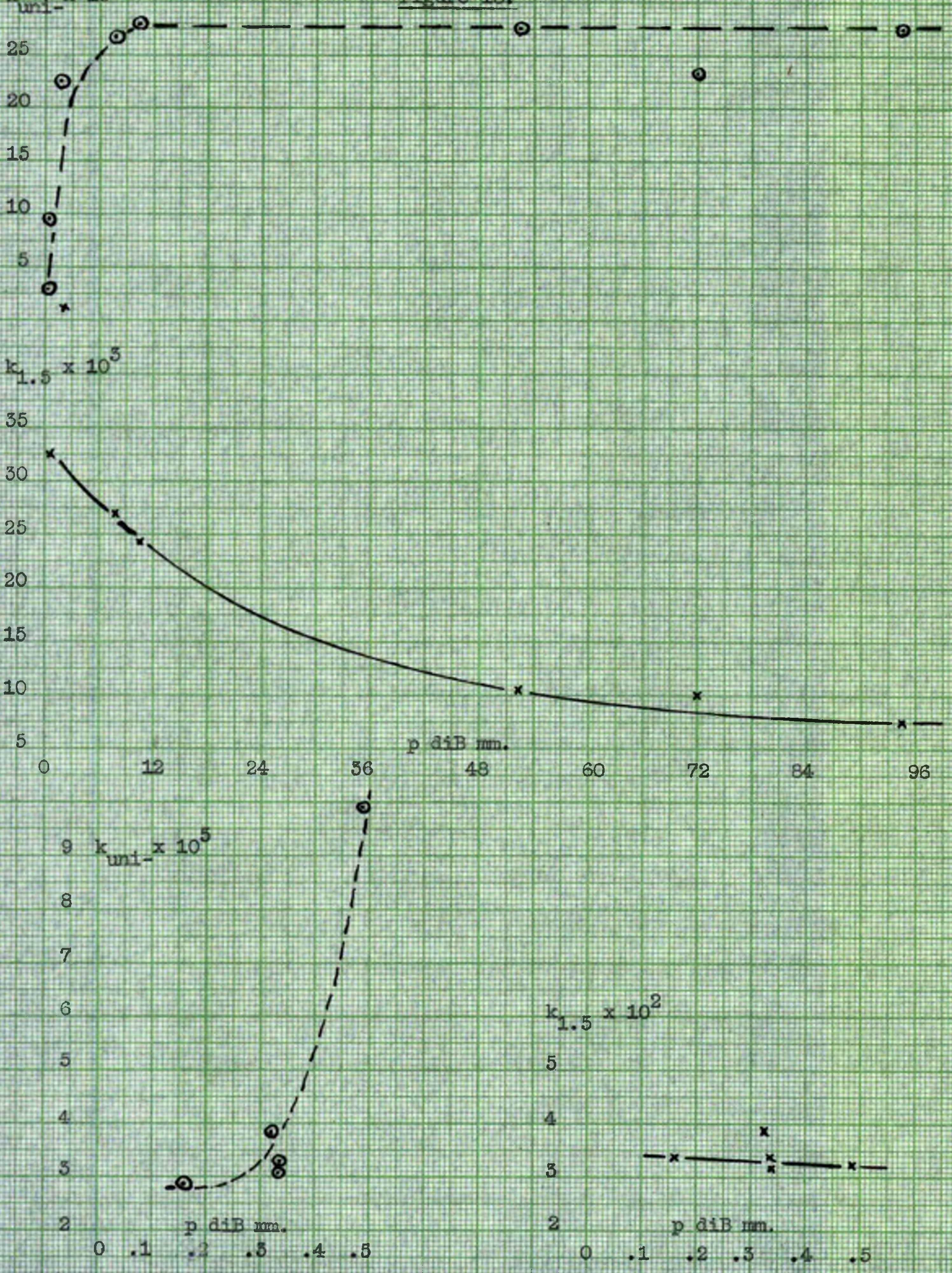
After Trap 3 had been included in the system a further series was therefore carried out (Runs 85 - 91). These Runs were all done at 462°C over a range of dibenzyl pressure and were analysed for products of different volatility with the aid of Trap 3. The UV absorption spectra of the solid products of five of the Runs were measured.

When the pure tetradeuterodibenzyl (diB_d) became available, one sealed tube decomposition experiment (Run 67) using it alone was done. All other experiments may be placed in the third group.

III. Investigation of the reaction between DiB_h and DiB_d.

Most of the Runs in this group were done in the reaction vessel between 400°C and 500°C, usually with equal weight mixtures of diB_h and diB_d. Some Runs were done in the presence of nitrogen, argon, deuterium, or oxygen. In all Runs in the reaction vessel the rate of forming $PhCH_2CD_2Ph$ (diB_{hd}) was measured, and so was the rate of loss of total dibenzyl, to supplement the decomposition data obtained from Group II. In addition a few Runs in sealed tubes were used to investigate the formation of diB_{hd}

Figure 18.


$k_{uni-} \times 10^5$
25
20
15
10
5
$k_{1.5} \times 10^3$
35
30
25
20
15
10
5
p diB mm.
0
12
24
36
48
60
72
84
96
9
$k_{uni-} \times 10^5$
8
7
6
5
4
3
2
p diB mm.
0
.1
.2
.3
.4
.5
$k_{1.5} \times 10^2$
5
4
3
2
p diB mm.
0
.1
.2
.3
.4
.5

at higher pressures; in these Runs the partially deuterated decomposition products as well as the dibenzyl were analysed by mass spectrometry.

Decomposition of dibenzyl.

The experiments of Group II had shown that the rate of decomposition of dibenzyl was pressure dependent, and therefore in the Group III experiments low dibenzyl pressures (0.08 to 0.68 mm.) were used so that the study of the dissociation would be complicated as little as possible by decomposition.

As a result, most of the Runs done in the course of this investigation were in this low pressure range, using dibenzyl concentrations of about 10^{-5} gm. moles per litre in the reaction vessel. The concentrations of the decomposition products were rather low for accurate mass spectrometer analysis, and consequently the decomposition calculations cannot be of high accuracy.

Pittilo(10) investigated the decomposition of dibenzyl in a flow system in which sufficient products for accurate analysis could be accumulated. He showed that the decomposition closely approximated to 1.5 order, with an energy of activation of 47 kcals per mole.

In this investigation good evidence for a 1.5 order decomposition is provided by the results of the Runs at 462°C, both in sealed tubes and in the reaction vessel, which covered a range of dibenzyl pressure from 0.08 to 94.5 mm. and which included Runs in the presence of argon and deuterium. IH Figure 18 calculated 1st and 1.5 order rate constants for these Runs are plotted against dibenzyl pressure;

Figure 19.

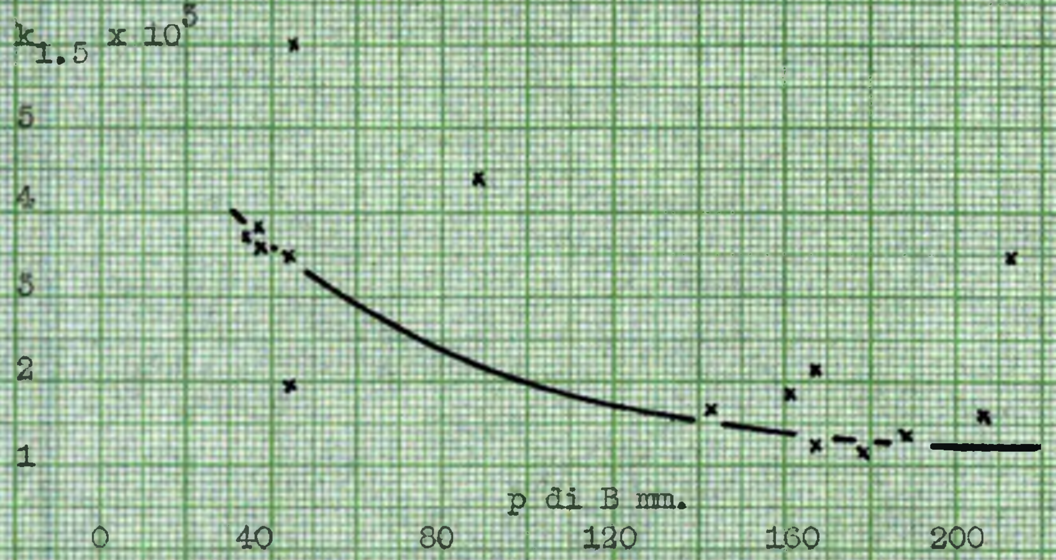


Figure 20.

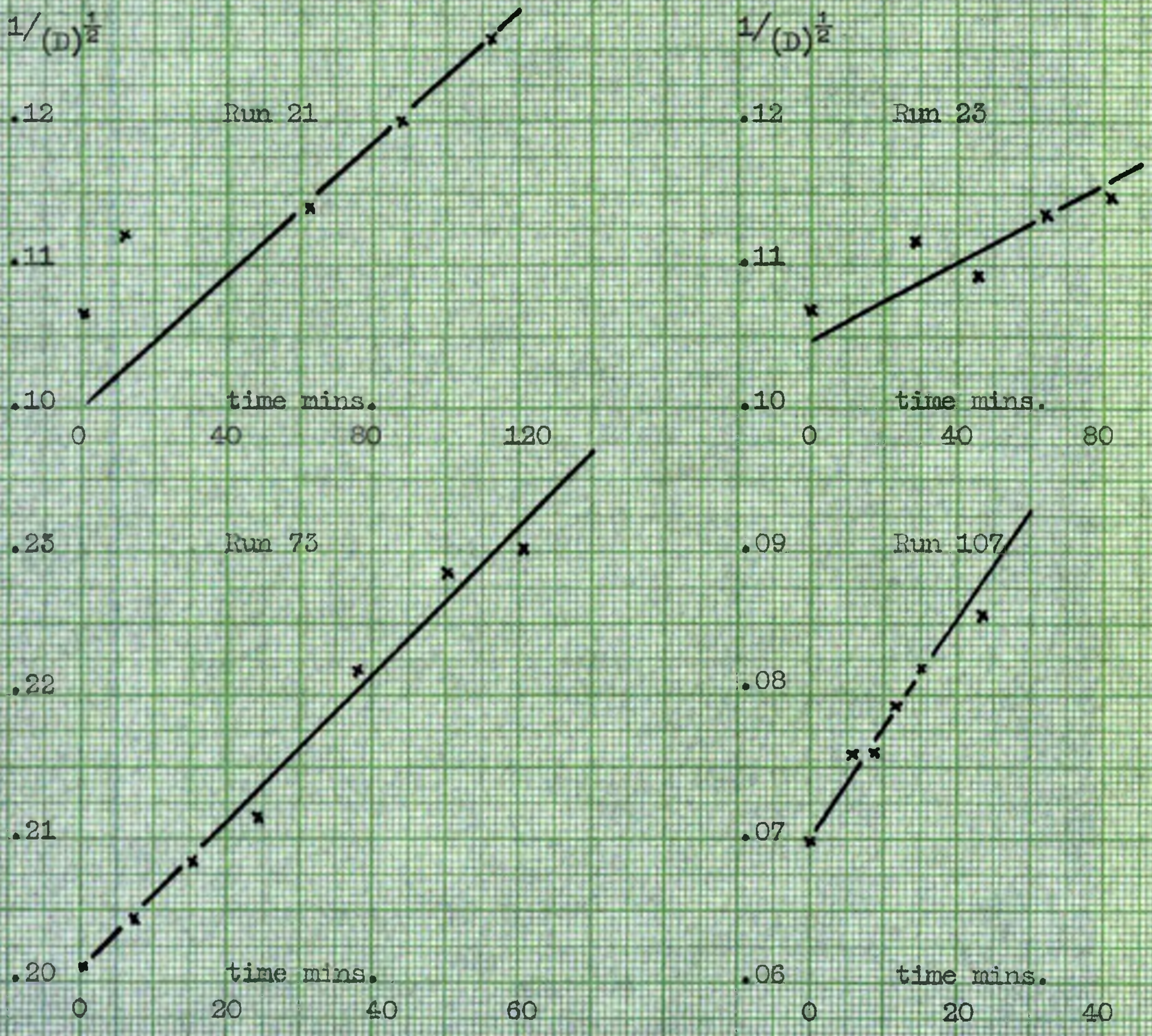
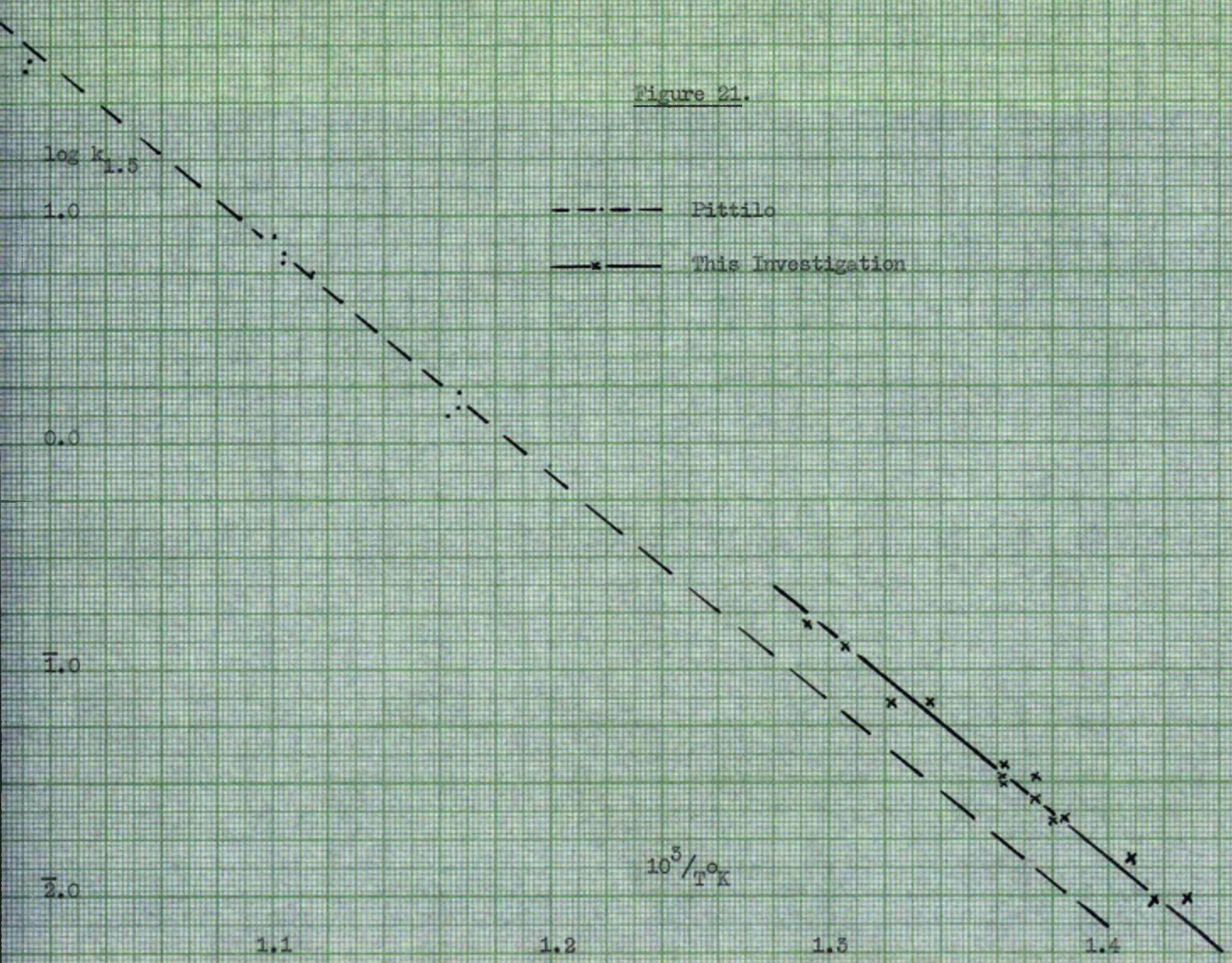


Figure 21.


log $k_{1.5}$
1.0
0.0
$\bar{1}.0$
$\bar{2}.0$
1.1
1.2
1.3
1.4
$10^3/T°K$
Pittilo
This Investigation

the decomposition closely obeys the 1.5 order law over the pressure range used in the reaction vessel, but becomes 1st order at higher pressures. The presence of argon (Runs 102 & 105) had no effect on the rate of the decomposition.

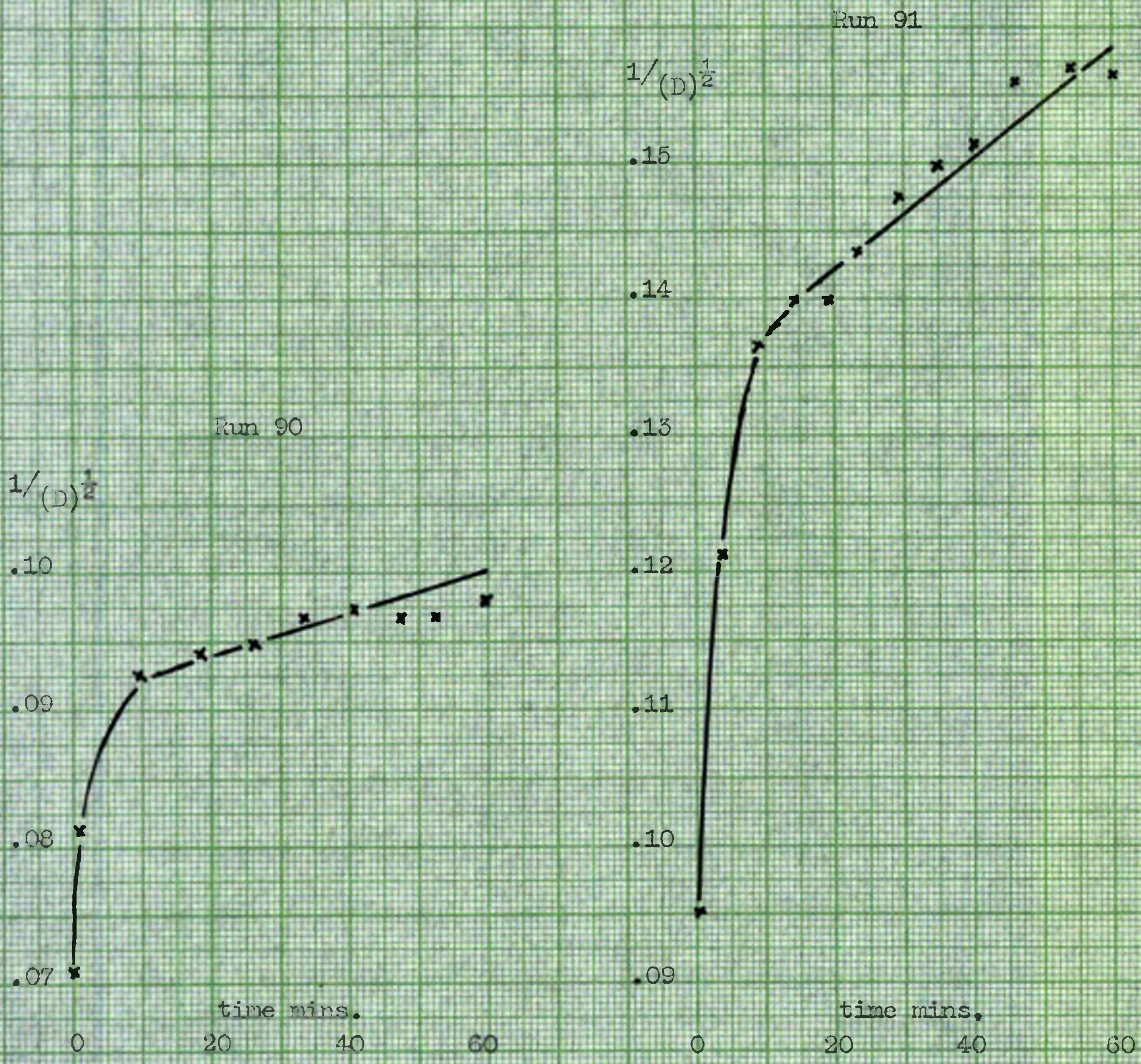
The sealed tube experiments at 384°C did not cover the low pressure region, but show similar behaviour at higher pressures to the 462°C experiments (Figure 19).

The results obtained by measuring the rate of loss of dibenzyl in the reaction vessel were plotted according to the integrated form of the 1.5 order rate equation and rate constants calculated from the slope of the best straight line in each case. In several experiments, the earlier ones in particular, the time required for dibenzyl to enter the reaction system on injection made the first few points unreliable, and they were ignored in drawing the line. Some typical rate plots are given in Figure 20. (List of symbols etc on p. 125)

The variation of rate constant with temperature is shown in the Arrhenius plot, Figure 21. The earlier, less reliable experiments were omitted, as were Runs in the presence of added gases. The results obtained by Pittilo for dibenzyl partial pressures between 0.25 and 0.38 mm. are also included in Figure 21, and the two series of experiments are clearly in agreement.

Therefore the results of this investigation support Pittilo's value of 47 kcals per mole for the decomposition of dibenzyl.

Figure 22.


Run 90
1/(D)^½
.10
.09
.08
.07
time mins.
0
20
40
60
Run 91
1/(D)^½
.15
.14
.13
.12
.11
.10
.09
time mins.
0
20
40
60

Surface effects.

Surface / Volume ratio. In the 584°C experiments, Runs in tubes packed to increase their surface area $6\frac{1}{2}$ - fold had the same rate of decomposition as Runs in similar unpacked tubes with the same pressure of dibenzyl. (Figure 19, Runs 58 & 60 and 49 & 51)

In the 462°C experiments, the surface / volume ratio of the sealed tubes varied from 0.7 to 2.4 $cm.^{-1}$ and the surface / volume ratio of the reaction vessel was 0.36 $cm.^{-1}$. The effect of surface / volume ratio at fixed dibenzyl pressure was not studied, but no systematic change in rate due to variation of surface / volume ratio was observed.

Nature of Surface. In some Runs in the reaction vessel the rate of decomposition was high initially, then settled to about the expected value. The rate plots of Runs 90 and 91 show this effect well (Figure 22). Consistent results were probably obtained when the reaction vessel had a surface coating of carbon, and if this coating were to be removed, rapid decomposition on the clean surface would occur until it was restored. Such a coating was quite likely to be removed from time to time, since it was sometimes necessary to admit air to the reaction vessel while the furnace was still hot.

This hypothesis was tested by admitting about 4 mm. of oxygen to the reaction vessel with the furnace at 462°C, and observing the carbon dioxide and water peaks in the mass spectrometer. The water peak did not rise appreciably, but a substantial increase in carbon dioxide was observed, confirming that a surface coating, largely carbon, had existed.

Immediately after this treatment, an experiment was done in the

Figure 23.


log o.d.
$\bar{1}.5$
$\bar{1}.4$
$\bar{1}.3$
Solid Products, Run 17.
wavelength mu
230
240
250
260
270
280
290
300
log e
4.6
4.4
4.2
4.0
3.8
3.6
Phenanthrene.
wavelength mu
230
240
250
260
270
280
290
300

reaction vessel (Run 108); the rate constant for decomposition was 31 % higher than the expected value.

The sealed tube reactions were done in clean tubes, and the rapid surface reaction would therefore occur initially. In the Runs with high dibenzyl pressures the effect on the rate would probably be insignificant, but in the case of Run 86 with a pressure of 1.7 mm. of dibenzyl the surface reaction might account for the high value of the rate constant observed (Figure 18).

Nature and Proportions of reaction products.

Pittilo identified by mass spectrometer and UV absorption analysis the following decomposition products: toluene, stilbene, benzene, and styrene. He found that the product ratios were not constant, but varied with both temperature and partial pressure of dibenzyl; toluene was the major product and the proportions of toluene to each other product decreased as the partial pressure was increased and as the temperature was lowered.

In this investigation mass spectrometer analysis revealed the presence of toluene, stilbene, and benzene, together with small amounts of hydrogen and possibly traces of aliphatic hydrocarbons up to C_5. No styrene was found.

The UV absorption spectra of the solid products differed from those observed by Pittilo, as peaks due to phenanthrene were prominent (Figure 23). The high extinction coefficients of stilbene and phenanthrene, and the overlapping UV spectra of these compounds and of dibenzyl made reliable UV analysis of the solid products impossible.

Quantitative analysis of the reaction products by mass spectrometry is complicated by overlapping cracking patterns; the 180^+ peak consists of stilbene parent and a contribution from dibenzyl; both dibenzyl and stilbene contribute to 178^+, the phenanthrene parent; and the main peak of toluene, 91^+, is also the main peak in the dibenzyl cracking pattern. Dibenzyl peaks are also present at 92^+, 77^+, 78^+, and 2^+.

Toluene and benzene could be analysed satisfactorily after Trap 3 had been installed, but the solid products could not be separated and analytical figures for stilbene and phenanthrene are therefore less accurate. The ratios of the products in gm. moles obtained by mass spectrometer analysis of five sealed tube Runs at 462°C in which diB_h alone was decomposed are collected in Table II.

Table II.

Run	p_{diB} mm.	$\frac{\text{toluene}}{\text{benzene}}$	$\frac{\text{toluene}}{\text{stilbene}}$	$\frac{\text{toluene}}{\text{phenanthrene}}$	$\frac{\text{diB decomposed}}{\text{toluene}}$	Carbon balance %
83	7.5	2.4	1.7	4.5	1.3	118
87	10.3	3.3	1.6	5.8	1.7	87
84	52.0	4.5	2.3	4.4	1.2	103
88	72.0	5.3	1.8	4.6	1.4	96
89	94.5	5.9	2.0	4.0	1.4	95

Pittilo observed the variation of product ratios in the pressure range 0.1 to 1.0 mm. of dibenzyl. From about 0.5 to 1.0 mm. the ratios showed little variation, and his values for Toluene/ Benzene and Toluene/ Stilbene were both 2 at 1.0 mm. The results given in Table II suggest that in the case of the Toluene/ Stilbene ratio this constancy is maintained in the higher pressure region covered in this investigation, and the Dibenzyl decomposed / Toluene and Toluene / Phenanthrene ratios also appear constant over this pressure range. These results would therefore support Pittilo's finding that the ratios approached constant values at pressures above 0.5 mm. The formation of phenanthrene instead of styrene is presumably the result of the very different reaction conditions: lower temperature and much longer contact time than Pittilo's experiments.

In the case of the Toluene / Benzene ratio, however, the approach to constancy observed by Pittilo is not maintained. The ratio shows a steady rise from 2 at 1 mm. (Pittilo) to 6 at 94.5 mm.

The significance of these findings in relation to the mechanism of the decomposition will be discussed later in this Thesis.

Formation of deuterated toluenes in Runs with diB_h and diB_d.

The products of several Runs in sealed tubes with mixtures of diB_h and diB_d were analysed for deuterated toluenes, in order to obtain some information about the mechanism of toluene formation, and if possible to evaluate the deuterium isotope effect in this reaction.

The deuterium isotope effect has been thoroughly reviewed recently by Wiberg$^{(41)}$ and no theoretical discussion of it will be given; it is sufficient for the present purpose to note that bonds to deuterium are found to be stronger than the corresponding bonds to hydrogen. This effect is due to a difference in zero-point energy, so that the deuterium isotope effect diminishes as the temperature of the reaction system is raised.

The most probable mechanism for the formation of toluene in the decomposition of dibenzyl is the abstraction of hydrogen from dibenzyl by benzyl radicals. This abstraction would probably occur at the central carbon atoms of the dibenzyl, but the presence of phenanthrene among the products might be due to some abstraction from the phenyl groups also occurring. A knowledge of the proportions of the side-chain deuterated toluenes would therefore be helpful in deciding on the main mechanism for the formation of toluene.

In order to analyse the deuterated toluenes by mass spectrometry the cracking patterns of all species were required; pure samples were not available and it was therefore necessary to calculate the cracking patterns from figures published in the literature.

The work of Rylander, Meyerson, & Grubb$^{(19)}$ has been referred to in earlier pages in connection with the formation of the tropylium

Table III.

Toluene	91^+	92^+	93^+	94^+	95^+
$PhCH_3$	100	67.7			
$PhCH_2D$	13.3	100	77.4		
$PhCD_3$			50.8	96.3	100

Table IV.

Toluene	91^+	92^+	93^+	94^+	95^+
$PhCH_3$	148	100			
$PhCH_2D$	17.2	129	100		
$PhCD_2H$		33.6	113.5	100	
$PhCD_3$			50.8	96.3	100

Table V.

Toluene	91^+	92^+	93^+	94^+	95^+
$PhCH_3$	139	100			
$PhCH_2D$	16.4	123	100		
$PhCD_2H$		32	108	100	
$PhCD_3$			48.5	91.6	100

ion and not the benzyl ion by electron bombardment of toluene in a mass spectrometer. These authors determined the cracking patterns of $PhCH_2D$ and $PhCD_3$, and their figures for the parent and tropylium peaks are given in Table III. If these figures are rearranged so that the parent ion intensity is 100 in each case, then the sum of the tropylium ion intensities is between 146 and 148, and the tropylium ions formed are proportional to the H/D ratio in the toluene molecule. Hence the cracking pattern of $PhCD_2H$ may be calculated by analogy (Table IV). In the St. Andrews mass spectrometer, $91^+/92^+$ in $PhCH_3$ was 1.59, not 1.48 as in Table IV. Therefore all intensities were altered to correspond with the former value. The figures then obtained are given in Table V, and were used in this work as the cracking patterns of the deuterated toluenes. If the sensitivity of the mass spectrometer to each toluene species is assumed to be the same, and if the relative amounts of $PhCH_3$, $PhCH_2D$, $PhCD_2H$, and $PhCD_3$ are a, b, c, and d respectively, then the following simultaneous equations may be written:-

$$\begin{aligned}
159\,a + 16.4\,b &= 91^+ \\
100\,a + 125\,b + 32\,c &= 92^+ \\
100\,b + 108\,c + 48.4\,d &= 93^+ \\
100\,c + 91.6\,d &= 94^+ \\
100\,d &= 95^+
\end{aligned}$$

The proportions of toluene species formed in each Run was calculated from the last four equations, and the values obtained substituted in the first equation as a check of accuracy. Agreement was poor in several cases, but in ten experiments the first equation was satisfied to within 4 %, and the results of these experiments were used in the calculations.

Calculations.

An equal weight mixture of diB_h and diB_d was used in these Runs, i.e. $PhCH_2CH_2Ph : PhCDHCDHPh : PhCDHCD_2PH : PhCD_2CD_2Ph = 100 : 1 : 18 : 81$. Then the proportions of benzyl radicals formed by dissociation, if all dibenzyl species dissociate at equal rates are:- $PhCH_2- \mid PhCDH- \mid PhCD_2-$

$$= \left[2(PhCH_2CH_2Ph)\right] \Big| \left[2(PhCDHCDHPh) + PhCDHCD_2Ph\right] \Big| \left[PhCDHCDHPh + 2(PhCD_2CD_2Ph)\right]$$

$= 10 : 1 : 9$.

If the hydrogen on the central carbon atoms of dibenzyl is denoted by the subscript $_c$, then $H_c/D_c = 21 / 19 = 1.105$.

If the benzyl radicals form toluene by abstracting hydrogen from dibenzyl, then the number of C-H and C-D bonds broken in this way will depend on the isotope effect as well as on the number of C-H and C-D bonds available.

In the case of reactions involving methyl radicals, the reactivity of CH_3- and CD_3- in attacking the same bond is considered to be the same (Dainton$^{(42)}$), and this view is supported by the work of McNesby & Gordon$^{(45)}$, who photolysed CD_3COCD_3 and $CH_3CD_2CD_2CH_3$ mixtures under conditions where the $CH_3CD.CD_2CH_3$ radical, formed by abstraction of hydrogen by photolytically produced CD_3- radicals, decomposed to CH_3- and $CH_3CD{:}CD_2$. Hence the butane was attacked by CH_3- and CD_3- radicals, and from analysis of the deuterated methanes formed the rate of attack of methyl radicals of both kinds on the primary and secondary carbon atoms of the butane could be determined. They found CH_3- and CD_3- to be equally effective.

If the benzyl radicals of each kind are assumed to be equally reactive in this system, two reactions forming toluene may be considered:

TABLE VI.

Run	$T^{\circ}C$	P_{diB}^{mm}	a	b	c	d	n_1	n_2	$\frac{a+b}{c+d}$
38	450	76.3	1.07	0.87	1.00	0.34	1.34	1.40	1.45
41	397	55.3	1.37	0.81	1.00	0.51	1.46	2.04	1.45
42	430	74.6	1.32	0.61	1.00	0.22	2.09	2.77	1.58
43	450	74.4	1.19	0.72	1.00	0.21	1.70	1.98	1.58
66	414	97.2	1.32	0.63	1.00	0.36	2.01	2.66	1.45
69	435	3.2	1.46	0.42	1.00	0.22	3.45	5.34	1.54
78	461	5.2	1.37	0.37	1.00	0.16	4.13	5.77	1.50
79	461	142.5	1.23	0.68	1.00	0.26	1.82	2.21	1.52
81	461	4.8	0.95	0.40	1.00	0.29	3.69	3.12	1.05
82	461	101.5	1.13	0.63	1.00	0.39	2.00	2.20	1.27

Notes: a, b, c, & d represent ($PhCH_3$), ($PhCH_2D$), ($PhCD_2H$), & ($PhCD_3$) respectively. (relative molar proportions)

$$n_1 = \frac{10 - b}{9b - 1} \qquad n_2 = \frac{10\ a/b}{10 - a/b}$$

1) All three types of benzyl radical abstracting H

2) All three types of benzyl radical abstracting D

i.e. $\mathrm{PhCH_2}- + \mathrm{RH} \rightarrow \mathrm{PhCH_3} + \mathrm{R}-$

$\mathrm{PhCDH}- + \mathrm{RH} \rightarrow \mathrm{PhCH_2D} + \mathrm{R}- \leftarrow \mathrm{PhCH_2}- + \mathrm{RD}$

$\mathrm{PhCD_2}- + \mathrm{RH} \rightarrow \mathrm{PhCD_2H} + \mathrm{R}- \leftarrow \mathrm{PhCDH}- + \mathrm{RD}$

$\mathrm{PhCD_3} + \mathrm{R}- \leftarrow \mathrm{PhCD_2}- + \mathrm{RD}$

If, by virtue of the isotope effect, and of the number of H and D atoms available, reaction 1) occurs n times more frequently than reaction 2), the proportions of toluene species formed will depend on n and on the statistical composition of the benzyl radical mixture, thus:-

Toluene	reaction 1)		reaction 2)
$\mathrm{PhCH_3}$	10 n	+	0
$\mathrm{PhCH_2D}$	n	+	10
$\mathrm{PhCD_2H}$	9 n	+	1
$\mathrm{PhCD_3}$	0	+	9

These identities were applied to the experimental ratios, and n was evaluated from the ratio of $\mathrm{PhCD_2H}$ to $\mathrm{PhCH_2D}$ and from the ratio of $\mathrm{PhCH_3}$ to $\mathrm{PhCH_2D}$. The results are given in Table VI.

These results were not sufficiently accurate for any reliable conclusions to be drawn from the experiments, but several noteworthy points may be made:-

The two values of n obtained in each experiment show poor agreement in most cases, which may be due to inaccuracies in measuring the mass spectral peak heights, errors in the cracking patterns and hence in the simultaneous equations used, or invalid assumptions in the setting up of the functions of n given above.

Furthermore, the values of n over the ten experiments vary widely; n has been defined so that the isotope effect equals n divided by the ratio of H to D available. Theoretically, the value of the isotope effect should range from 2.3 at 410°C to 2.1 at 500°C(41); if toluene was formed only by the attack of radicals on the central carbon atoms of dibenzyl the isotope effect would be n / 1.105. Most of the values of n in Table VI are low enough to support the idea that only the central carbon atoms are attacked; but Runs 69, 78, & 81 give considerably higher values of n, which would imply that a higher proportion of H was available, presumably from the phenyl groups of dibenzyl. These anomalous Runs had much lower pressures of dibenzyl than the others, but there is no evidence in the product ratios of a rise in the proportions of phenanthrene at low pressures, and phenanthrene would presumably result from the combination of ring hydrogen with benzyl radicals. Also, about 40 % of the total hydrogen abstracted would have to come from the phenyl groups in order to give values of n as high as 4, which seems most unreasonable.

Hence the bulk of the evidence would support the assumption that benzyl radicals attacked the hydrogen on the central carbon atoms of dibenzyl only in forming toluene; no explanation of the three results which do not agree with this assumption can be offered, because of the large number of uncertainties in the calculation and the results. Also, the majority of the results would point to an isotope effect of two or less in this reaction.

One further point of interest is the value of the ratio $\frac{a + b}{c + d}$ in Table VI. This ratio should be largely independent of n, since it represents the attack of all benzyl radicals on the same number of C-H and C-D bonds. In terms of the simple scheme developed above, it equals $\frac{11\,n + 10}{9\,n + 10}$ and should depend mainly on the ratio $PhCH_2$- : $PhCD_2$- (1.11); e.g. if n = 2, $\frac{a + b}{c + d}$ = 1.14, while if n = 4, it is 1.17. The value of $\frac{a + b}{c + d}$ calculated from the experimental results are quite constant, since with two exceptions they fall between 1.43 and 1.58. It is difficult to see any other explanation for these high values than that the benzyl radicals do in fact differ in reactivity in the sense that $PhCH_2$- is more effective in hydrogen abstraction than $PhCD_2$-. For example, if $PhCH_2$- is 1.3 times as reactive as $PhCD_2$-, and PhCDH- is of intermediate reactivity, the value of $\frac{a + b}{c + d}$, assuming n = 2, is 1.47, which is within the experimentally observed range. This conclusion is in disagreement with the findings on methyl radicals referred to earlier, and further work would be necessary. If the benzyl radicals do differ in reactivity the values of n would be slightly higher than those in Table VI, but the general situation would remain the same.

Run 107.

In this Run the reaction was carried out in the reaction vessel in the presence of 1.15 mm. of deuterium and the diB_h and diB_d were in the ratio 1 : 1.12 by weight. The composition of the deuterium used was determined mass spectrometrically as D_2: 96.31 %; HD: 3.05 %; H_2: 0.64 %
The proportions of the toluene species formed differed appreciably from those in Table VI; they were: a : b : c : d = 0.90 : 0.92 : 1.00 : 0.65
It is obvious that benzyl radicals have reacted with deuterium to form toluene, but the uncertainties discussed above prevent an accurate assessment of the contribution of this reaction to the overall formation of toluene; it would appear from a rough estimate that benzyl radicals

react with deuterium at about $\frac{3}{4}$ of the rate at which they react with C-D bonds in dibenzyl. The reaction of benzyl radicals with deuterium is confirmed by the observed 1.5 order rate constant for the decomposition of dibenzyl in this Run, which was well over twice the expected value.

All the experimental results of the study of the decomposition of dibenzyl, and the analyses of the products, are collected in Appendix II, which also contains details of the calculation of concentrations from mass spectrometer peak heights.

Dissociation of dibenzyl.

The basic information from which the rate of dissociation of dibenzyl in the reaction between diB_h and diB_d may be calculated is the rate of formation of the mixed dibenzyl, diB_{hd} ($PhCH_2CD_2Ph$). However, the rate equation used was derived in terms, not of the absolute rate of formation of diB_{hd}, but of the rate of increase of the ratio of diB_{hd} to total dibenzyl concentration. The use of this ratio had the advantage that the observed mass spectrometer peak heights could be used without conversion to concentrations, so that any inaccuracies in the mass spectrometer calibration, and errors introduced by the short delay between the measurement of the dibenzyl peaks and the argon peak, were avoided. Also, it was easier to apply a correction for the small amount of decomposition of dibenzyl which occurred in the course of the reaction.

Derivation of the rate equation.

The derivation of the rate equation can best be explained by beginning with the simplest, ideal case, and progressively introducing the complicating features found in practice.

1) Equal weight mixture of $PhCH_2CH_2Ph$ and pure $PhCD_2CD_2Ph$, with no decomposition.

Dissociation into benzyl radicals will form $PhCH_2$- and $PhCD_2$-. It is reasonable to consider that the presence of deuterium on some of the central carbon atoms of dibenzyl does not affect the strength of the central bond, so that all dibenzyl species will dissociate at the same rate. In this case, therefore, the dissociated radicals will consist of equal numbers of $PhCH_2$- and $PhCD_2$-. Each $PhCH_2$- radical makes an equal number of collisions with $PhCH_2$- and $PhCD_2$-, resulting in the formation of equal amounts of $PhCH_2CH_2Ph$ and $PhCH_2CD_2Ph$; similarly, equal amounts of $PhCD_2CD_2Ph$ and $PhCH_2CD_2Ph$ result from the collisions of $PhCD_2$- radicals with $PhCH_2$- and $PhCD_2$-. Hence recombination of benzyl radicals forms dibenzyl species in the proportions:-

$$PhCH_2CH_2Ph : PhCH_2CD_2Ph : PhCD_2CD_2Ph = 1 : 2 : 1.$$

Denote $(PhCH_2CH_2Ph + PhCD_2CD_2Ph)$ by A

$(PhCH_2CD_2Ph)$ by C

and $(PhCH_2- + PhCD_2-)$ by B

Then let the dissociation of dibenzyl be a unimolecular reaction, with rate constant k_f, defined by:-

$$-\frac{d(A+C)}{dt} \text{ by dissociation} = k_f(A+C) = \tfrac{1}{2}\frac{d(B)}{dt}$$

Let the recombination of radicals be a bimolecular reaction, with rate constant k_r, defined by:-

$$\frac{d(A+C)}{dt} \text{ by recombination} = k_r(B)^2 = \tfrac{1}{2}\left\{-\frac{d(B)}{dt}\right\}$$

Then the following rate equations may be written:-

$$-\frac{d(A)}{dt} = k_f(A) - \tfrac{1}{2}k_r(B)^2 \qquad (1)$$

$$\frac{d(C)}{dt} = \tfrac{1}{2}k_r(B)^2 - k_f(C) \qquad (2)$$

$$-\frac{d(A+C)}{dt} = k_f(A+C) - k_r(B)^2 \qquad (3)$$

$$\frac{d(B)}{dt} = 2\,k_f(A+C) - 2\,k_r(B)^2 \qquad (4)$$

Now,

$$\frac{d\,\frac{(C)}{(A+C)}}{dt} = \frac{(A+C)\frac{d(C)}{dt} - (C)\frac{d(A+C)}{dt}}{(A+C)^2}$$

$$= \frac{\tfrac{1}{2}k_r(B)^2 - k_f(C)}{(A+C)} + \frac{k_f(C) - k_r(B)^2\frac{(C)}{(A+C)}}{(A+C)}$$

$$= \frac{\frac{1}{2} k_r (B)^2}{(A+C)} \left\{ 1 - \frac{2\,(C)}{(A+C)} \right\} \qquad (5)$$

If the concentration of benzyl radicals is low, and steady state conditions exist, $\frac{d(B)}{dt} = 0$, and then, from (4):-

$$2\,k_r (B)^2 = 2\,k_f (A+C) \qquad (6)$$

Substitute (6) in (5):-

$$-\frac{d(A+C)}{dt} = 0 \qquad (7)$$

i.e. the dissociation and recombination reactions do not alter the total dibenzyl concentration. If (6) is substituted in (5),

$$\underline{\frac{d\,\frac{(C)}{(A+C)}}{dt} = \tfrac{1}{2} k_f \left\{ 1 - \frac{2\,(C)}{(A+C)} \right\}} \qquad (8)$$

2) Equal weight mixture of $PhCH_2CH_2Ph$ and pure $PhCD_2CD_2Ph$, with decomposition.

The reaction step leading to decomposition is almost certainly of the type $PhCH_2CH_2Ph + PhCH_2\text{-} \text{ --- } PhCH.CH_2Ph + PhCH_3$ followed by rapid decomposition of the $PhCH.CH_2Ph$ radical.

Let the decomposition rate be determined by the bimolecular reaction between dibenzyl and benzyl radicals, with the rate constant k_a, defined by:-

$$-\frac{d(B)}{dt} \text{ by decomposition } = k_a (A+C)(B)$$

Every radical attack may lead, depending on the decomposition mechanism, to the loss of further molecules of dibenzyl, and in order to take account of this possibility, L is defined as the number of dibenzyl molecules decomposed by one benzyl radical attack on dibenzyl.

Then, $$-\frac{d(A+C)}{dt} \text{ by decomposition} = L\,k_a(A+C)(B)$$

Then the rate equations of Case 1) are modified by the addition of terms to take decomposition into account:-

$$-\frac{d(A)}{dt} = k_f(A) - \tfrac{1}{2}\,k_r(B)^2 + L\,k_a(A)(B) \qquad (1)$$

$$\frac{d(C)}{dt} = \tfrac{1}{2}\,k_r(B)^2 - k_f(C) - L\,k_a(C)(B) \qquad (2)$$

$$-\frac{d(A+C)}{dt} = k_f(A+C) - k_r(B)^2 + L\,k_a(A+C)(B) \qquad (3)$$

$$\frac{d(B)}{dt} = 2\,k_f(A+C) - 2\,k_r(B)^2 - k_a(A+C)(B) \qquad (4)$$

Then, using the same identity as in Case 1):-

$$\frac{d\frac{(C)}{(A+C)}}{dt} = \frac{\frac{1}{2}k_r(B)^2 - k_f(C) - Lk_a(C)(B)}{(A+C)} + \frac{k_f(C) - k_r(B)^2\frac{2\,(C)}{(A+C)} + Lk_a(C)(B)}{(A+C)}$$

$$= \frac{\frac{1}{2}\,k_r(B)^2}{(A+C)}\left\{1 - \frac{2\,(C)}{(A+C)}\right\} \qquad (5)$$

Equation (5) is the same as (5) in Case 1), but $k_r(B)^2$ now has a different value. Applying the steady state condition that $\frac{d(B)}{dt} = 0$,

$$2\,k_r(B)^2 = 2\,k_f(A+C) - k_a(A+C)(B) \qquad (6)$$

Substitute (6) in (3):-

$$-\frac{d(A+C)}{dt} = (L+\tfrac{1}{2})\,k_a(A+C)(B) \qquad (7)$$

It is interesting at this stage to consider the two extreme cases possible in equation (6):-

i) If $k_a(A+C)(B)$ is much greater than $2\,k_r(B)^2$ i.e. decomposition much faster than radical recombination.

Then $2\,k_f(A+C) = k_a(A+C)(B)$ approximately. Substitute in (7):-

$$\underline{-\frac{d(A+C)}{dt} = 2(L+\tfrac{1}{2})\,k_f(A+C)}$$ i.e. first order in (A+C).

ii) If $2\,k_r(B)^2$ is much greater than $k_a(A+C)(B)$ i.e. radical recombination much faster than decomposition.

Then $2\,k_r(B)^2 \;=\; 2\,k_f(A+C)$ approximately. Substitute in (7):-

$$-\frac{d(A+C)}{dt} \;=\; (L+\tfrac{1}{2})\,k_a k_f^{\frac{1}{2}} k_r^{-\frac{1}{2}}(A+C)^{1\frac{1}{2}}$$ i.e. 1.5 order in (A+C).

The experimental results reported in the previous part of the Thesis have shown that under the low pressure conditions used for the study of the dissociation the decomposition order was close to 1.5. On this basis a correction for decomposition may be applied:-

$$-\frac{d(A+C)}{dt} \;=\; k_{1.5}(A+C)^{1\frac{1}{2}} \quad \text{from experimental results} \qquad (8)$$

$$\therefore\; k_{1.5}(A+C)^{\frac{1}{2}} \;=\; (L+\tfrac{1}{2})\,k_a(B) \quad \text{from comparison of (7) and (8)} \qquad (9)$$

Substitute (9) in (6):-

$$\frac{k_r(B)^2}{(A+C)} \;=\; k_f - \frac{1}{2\,(L+\frac{1}{2})}\,k_{1.5}(A+C)^{\frac{1}{2}} \qquad (10)$$

The integrated form of the 1.5 order rate law is:-

$$k_{1.5}t \;=\; 2\left\{\frac{1}{(A+C)^{\frac{1}{2}}} - \frac{1}{(A_o)^{\frac{1}{2}}}\right\}$$ where A_o = total dibenzyl concentration at t = 0.

$$\therefore\; (A+C)^{\frac{1}{2}} \;=\; \frac{(A_o)^{\frac{1}{2}}}{1 + \frac{1}{2}\,k_{1.5}(A_o)^{\frac{1}{2}}\,t} \qquad (11)$$

Substitute the value of $(A+C)^{\frac{1}{2}}$ from (11) in (10), and substitute the expression obtained in equation (5):-

$$\therefore\; \frac{d\,\frac{(C)}{(A+C)}}{dt} \;=\; \tfrac{1}{2}\left\{k_f - \frac{\frac{1}{2}\,k_{1.5}\,(A_o)^{\frac{1}{2}}}{(L+\frac{1}{2})(1 + \frac{1}{2}k_{1.5}(A_o)^{\frac{1}{2}}t)}\right\}\left\{1 - \frac{2\,(C)}{(A+C)}\right\} \qquad (12)$$

Comparison of this expression with equation (8) of Case 1) shows that the effect of the decomposition is to reduce the rate of increase of the ratio by an amount which is a function of the initial dibenzyl concentration, the rate constant for decomposition at the temperature of the experiment, and time.

By putting $\frac{(C)}{(A+C)} = r$ and $\frac{1}{2}\, k_{1.5}(A_o)^{\frac{1}{2}} = n$, equation (12) may be simplified, thus:-

$$\frac{dr}{dt} = \frac{1}{2}\left\{ k_f - \frac{n}{(L+\frac{1}{2})(1+nt)} \right\}\left\{ 1 - 2r \right\} \qquad (13)$$

3) Equal weight mixture of $PhCH_2CH_2Ph$ and impure $PhCD_2CD_2Ph$, with decomposition.

It is difficult to prepare deuterated compounds of high isotopic purity, particularly if syntheses of more than one stage are used. In this work diB_d was prepared by a four stage synthesis and its isotopic purity was 95 %. The composition was:-

PhCDHCDHPh	M.W.	184	1 %
$PhCDHCD_2Ph$	M.W.	185	18 %
$PhCD_2CD_2Ph$	M.W.	186	81 %

Then the composition of an equal weight mixture of diB_h and diB_d, denoting the different dibenzyl species by their molecular weights, is:-

182 : 183 : 184 : 185 : 186 = 1.00 : 0 : 0.01 : 0.18 : 0.81

The composition of radicals produced by dissociation of this mixture is: $PhCH_2$- (91) proportional to [2 (182)]; PhCDH- (92) proportional to [2 (184) + (185)]; and $PhCD_2$- (93) proportional to [2 (186) + (185)]. If these proportions are (91) = p_1; (92) = p_2; (93) = p_3, and $p_1 + p_2 + p_3 = 1$, then they have the values 0.50, 0.05, and 0.45 respectively in this case.

If statistical recombination of radicals is assumed, the proportions of dibenzyl species so formed are given by:-

182	p_1^2	0.2500
183	$2\, p_1p_2$	0.0500

184	$2\,p_1p_3 + p_2^2$	0.4525
185	$2\,p_2p_3$	0.0450
186	p_3^2	0.2025

The rate equations of Case 2) must now be modified since the benzyl radicals are no longer equally divided between $\bar{A}$ and $\bar{C}$ on recombination:

$$-\frac{d(A)}{dt} = k_f(A) - 0.5475\,k_r(B)^2 + L\,k_a(A)(B) \qquad (1)$$

$$\frac{d(C)}{dt} = 0.4525\,k_r(B)^2 - k_f(C) - L\,k_a(C)(B) \qquad (2)$$

Equations (3) and (4) are the same as in Case 2) and the subsequent steps are identical, so that the equation corresponding to equation (5) is:-

$$\frac{d\,\frac{(C)}{(A+C)}}{dt} = \frac{0.4525\,k_r(B)^2}{(A+C)}\left\{1 - \frac{2.210\,(C)}{(A+C)}\right\} \qquad (5)$$

Then, as in Case 2),

$$\underline{\frac{dr}{dt} = 0.4525\left\{k_f - \frac{n}{(L+\frac{1}{2})(1+nt)}\right\}\left\{1 - 2.210\,r\right\}}$$

<u>Integration:</u> Separate the variables, and integrate with respect to r & t:-

$$-\frac{1}{2.210}\ln(1-2.210r) = 0.4525k_f t - \frac{0.4525n}{(L+\frac{1}{2})n}\ln(1+nt) + \text{integration const.}$$

$$-\log(1-2.210r) = \frac{k_f t}{2.303} - \frac{1}{(L+\frac{1}{2})}\log(1+nt) + \text{constant}$$

When $t = 0$, $r = 0.005$ (from initial composition of diB_h + diB_d mixture)

$$\therefore \text{constant} = -\log(1-2.210r) = -\log 0.989 = +0.005$$

$$\underline{\therefore \frac{k_f t}{2.303} + 0.005 = \frac{1}{(L+\frac{1}{2})}\log(1+nt) - \log(1-2.210r)}$$

In the above derivation it has been assumed that all dibenzyl and benzyl radical species have the same reactivity, and that there is therefore no isotopic discrimination due to decomposition.

The assumption of equal reactivity is not strictly true, since by virtue of the deuterium isotope effect C-H bonds are more easily broken than the corresponding C-D bonds, and therefore $PhCH_2CH_2Ph$ will be decomposed at a faster rate than $PhCD_2CD_2Ph$. The investigation of the composition of deuterated toluenes formed in the decomposition did not furnish an accurate value of the isotope effect, but the effect is not large, and since dissociation is about ten times faster than decomposition under the reaction conditions used, no significant error is introduced by the neglect of the isotope effect in the calculations.

The postulated rate-determining reaction leading to decomposition, attack of benzyl radicals on dibenzyl molecules, does not cause any isotopic discrimination if the deuterium isotope effect is ignored, since the choice of radical is purely statistical. This may be demonstrated mathematically:-

Consider the loss of $PhCH_2CH_2Ph$ (182) and $PhCD_2CD_2Ph$ (186) by decomposition:

$$-\frac{d(182)}{dt} = L\,k_a(182)(B)$$

$$-\frac{d(186)}{dt} = L\,k_a(186)(B)$$

$$\therefore \quad \frac{d\,\frac{(182)}{(186)}}{dt} = \frac{(186)\frac{d(182)}{dt} - (182)\frac{d(186)}{dt}}{(186)^2} = 0$$

So that there is no change in the ratio of 182 to 186 as a result of decomposition. Similarly it may be shown that none of the dibenzyl species ratios is altered by decomposition.

Evaluation of r from mass spectral peaks.

Only the peak heights of 182^+, 184^+, and 186^+ were recorded, since 183^+ and 185^+ were too small for accurate measurement. Also, since some stilbene was formed during the experiments, the 182^+ peak was not a reliable measure of $PhCH_2CH_2Ph$ because of the interference of PhCD:CDPh. Consequently the most satisfactory way of using the mass spectral data was to derive an expression for r in terms of 184^+ and 186^+ only. This may be done from the statistical distribution in the following way:-

Initially, 182 : 183 : 184 : 185 : 186 = 1.00 : 0.00 : 0.01 : 0.18 : 0.81

The proportions formed by statistical recombination of the radicals are:-

182 : 183 : 184 : 185 : 186 = 1.00 : 0.20 : 1.81 : 0.18 : 0.81

I.e. 182, 185, and 186 are reformed in their original proportions, and since the decomposition causes no change in ratio, it may be concluded that 182 : 185 : 186 remains constant during an experiment, and that 183 : 184 also remains constant, since these are formed in a statistically fixed ratio (this neglects the small amount of 184 present initially, but the error is negligible).

Then from the original composition of the mixture, 182 : 186 = 1.235

and 185 : 186 = 0.222

From the recombination distribution, 183 : 184 = 0.110

$$\therefore \quad (A+C) = 1.110\,(184) + 2.457\,(186)$$

In the cracking pattern of $PhCH_2CH_2Ph$, $183^+ : 182^+ = 0.15$. This is due to the presence of ^{13}C in the dibenzyl and therefore the same ratio will apply to the other dibenzyl species.

If θ is defined as the factor relating peak heights to dibenzyl concentration, the following equations may be written:-

$$186^+ = \theta \left\{ (186) + 0.15(185) \right\} = \theta\, 1.033\,(186)$$

$$\therefore (186) = 1/\theta\; 0.968\,(186^+)$$

$$184^+ = \theta \left\{ (184) + 0.15(183) \right\} = \theta\, 1.017\,(184)$$

$$\therefore (184) = 1/\theta\; 0.983\,(184^+)$$

$$\therefore \underline{\frac{(C)}{(A+C)}} = \frac{(184)}{1.110\ (184) + 2.457\ (186)} = \underline{\frac{0.90\ (184^{+})}{(184^{+}) + 2.18\ (186^{+})}}$$

4) Mixture of $PhCH_2CH_2Ph$ and impure $PhCD_2CD_2Ph$ in the ratio 1 : 1.12 by weight, with decomposition.

In the last ten Runs of this investigation an unequal weight mixture of dibenzyl species was used, with the intention of compensating for the impurity of the deuterated dibenzyl. The derivation of the rate equation only differs numerically from Case 3).

The initial composition of the dibenzyl mixture is:-

182 : 183 : 184 : 185 : 186 = 0.893 : 0 : 0.01 : 0.18 : 0.81

The composition of benzyl radicals formed by dissociation is:-

91 : 92 : 93 = 1.786 : 0.20 : 1.80 = 0.472 : 0.053 : 0.475

Then the proportions of dibenzyl species formed by statistical recombination of the radicals are:-

182 : 183 : 184 : 185 : 186 = 0.2227:0.0500:0.4512:0.0504:0.2256

$$\text{Then} -\frac{d(A)}{dt} = k_f(A) - 0.5488\ k_r(B)^2 + L\ k_a(A)(B) \qquad (1)$$

$$\frac{d(C)}{dt} = 0.4512\ k_r(B)^2 - k_f(C) - L\ k_a(C)(B) \qquad (2)$$

All subsequent steps are similar to Case 3), and the integrated form of the equation is:-

$$\underline{\frac{k_f t}{2.303} + 0.005 = \frac{1}{(L+\frac{1}{2})}\ \log\ (1 + nt) - \log\ (1 - 2.216r)}$$

<u>Evaluation of r from mass spectral peaks.</u>

Initially 182 : 183 : 184 : 185 : 186 = 0.89 : 0.00 : 0.01 : 0.18 : 0.81

The proportions formed by statistical recombination of the radicals are:-

182 : 183 : 184 : 185 : 186 = 0.80 : 0.18 : 1.62 : 0.18 : 0.81

So that the use of unequal weights has been successful in giving a symmetrical recombination distribution, but introduces the complicating feature that 182 : 186 does not remain constant during an experiment.

From the original composition, 185 : 186 = 0.222

From the recombination 183 : 184 = 0.110

But 182 : 186 varies from 1.10 at t = 0, to 0.99 at equilibrium, when all the molecules have been through the processes of dissociation and recombination. Let 182 : 186 = 1.0 approximately

$\therefore$ (A+C) = 1.11 (184) + 2.22 (186) and (184) & (186) have the same values as in Case 3)

$$\therefore \underline{\frac{(C)}{(A+C)}} = \frac{(184)}{1.11\ (184) + 2.22\ (186)} = \underline{\frac{0.90\ (184^{+})}{(184^{+}) + 1.97\ (186^{+})}}$$

The value of L.

Before the integrated rate equation could be used, it was necessary to evaluate L. The value of L depends on the mechanism of the decomposition and two pieces of experimental evidence are available, the product ratios and the results of the experiments in which deuterated toluenes were formed.

i) Product ratios: In Table II the ratio of dibenzyl decomposed to toluene formed is given as 1.3, 1.7, 1.2, 1.4, & 1.4 for the five Runs calculated. Hence dibenzyl decomposed / toluene may be taken to be 3 / 2.

If toluene is formed only by the attack of benzyl radicals on dibenzyl, then the toluene formed is a measure of the benzyl radicals which attacked dibenzyl; while the decomposed dibenzyl is the sum of the dibenzyl dissociated to form the radicals which attack, the dibenzyl attacked, and the dibenzyl subsequently lost. Then in the terms used in the rate equation, $\frac{\text{dibenzyl decomposed}}{\text{toluene}} = (L + \frac{1}{2}) = \frac{3}{2}$

$\therefore L = 1.$

ii) Deuterated toluenes: The composition of the deuterated toluene mixtures formed is largely consistent with the attack of benzyl radicals on the central atoms of dibenzyl being the only source of toluene. Therefore this evidence supports the assumption made in i) above, and confirms the value of L = 1.

Hence the forms of the rate equation used in calculating the results of the Runs of Group III in the reaction vessel were:-

i) Runs 19 to 99 with equal weight mixture of diB_h and diB_d.

$$\frac{k_f t}{2.303} + 0.005 = 0.667 \log (1 + nt) - \log \left\{1 - \frac{1.989\ (184^+)}{(184^+) + 2.18(186^+)}\right\}$$

ii) Runs 102 to 109 with unequal weight mixture of diB_h and diB_d.

$$\frac{k_f t}{2.303} + 0.005 = 0.667 \log (1 + nt) - \log \left\{1 - \frac{1.994\ (184^+)}{(184^+) + 1.97(186^+)}\right\}$$

Where $n = \frac{1}{2} k_{1.5}(A_o)^{\frac{1}{2}}$.

Figure 25.

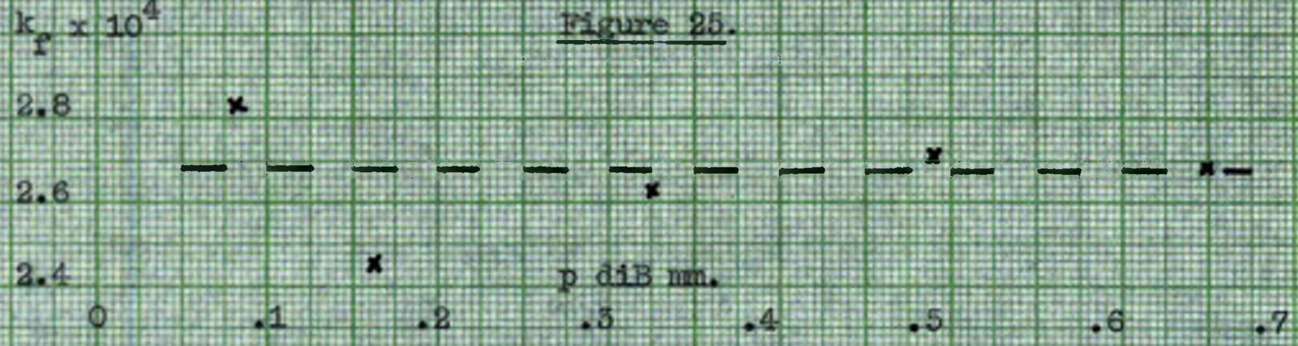
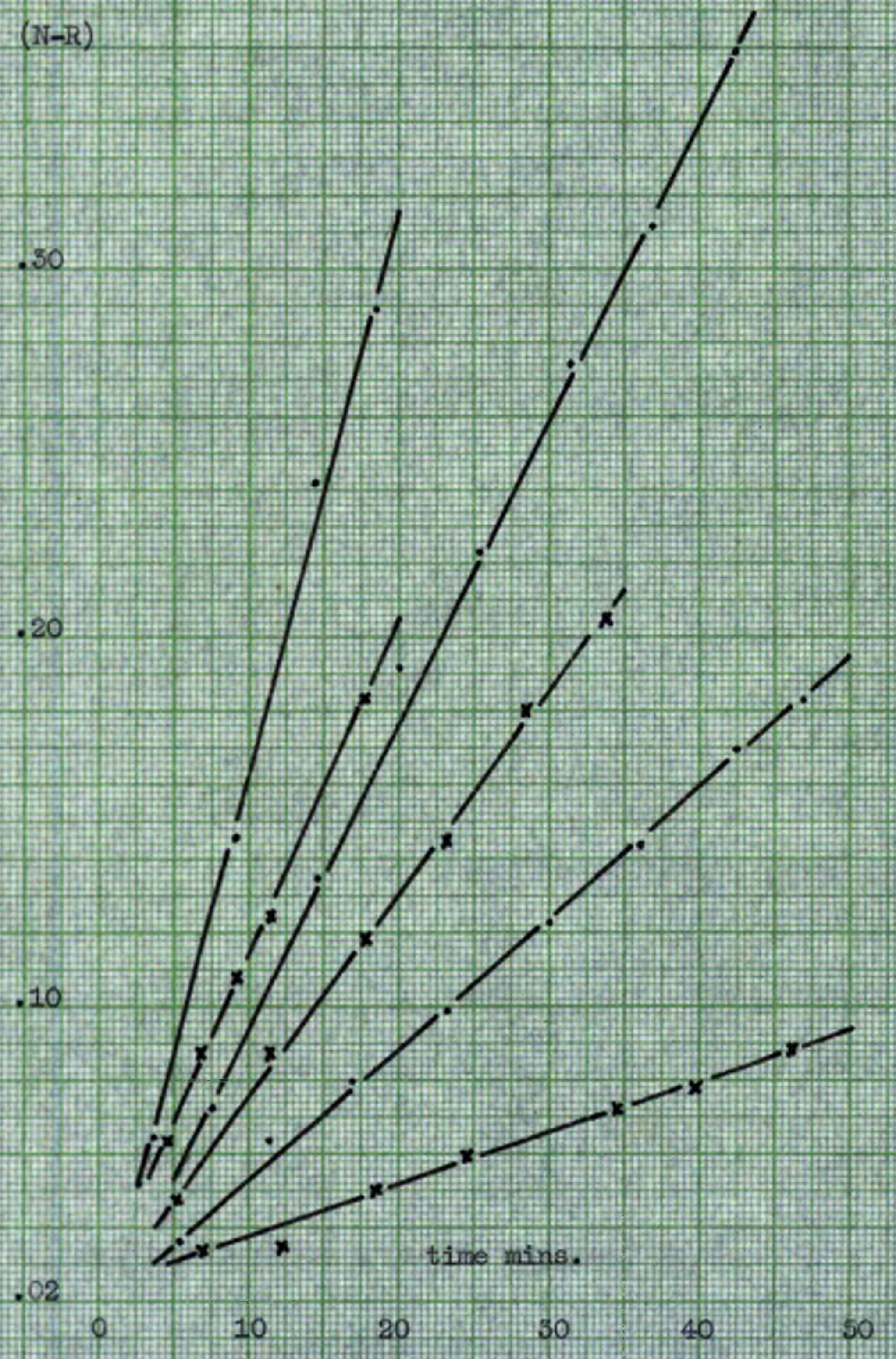


Figure 24.



Results.

In the Runs of Group III in the reaction vessel the times at which readings of peak heights were taken in each experiment were corrected by division by a factor to take into account the time spent by the dibenzyl vapour in the circulating system outside the furnace, and these "corrected times" were used in the calculations, in which the RHS of the appropriate equation derived above was evaluated for each time interval and the values obtained plotted against time. The details of the calculation are given, with the tabulated results, in Appendix III. From the slopes of the straight line graphs, values of k_f were obtained. Because of the use of the peak height ratios in the equation, more accurate results were obtained than in the case of the decomposition study, and most Runs gave good straight line plots, a series of which at different temperatures feature in Figure 24. The ordinate (N-R) represents the RHS of the equation. The failure of most of the lines to cut the ordinate at 0.005 is probably due to a short delay in the dibenzyl reaching the temperature of the furnace after the opening of Valve 3 or the heating of Trap 3, which was taken as the start of the Run. This error in zero time does not affect the accuracy of the results, since the subsequent time intervals, and hence the slopes, are correct.

Order of Reaction.

In a series of Runs at 461°C the pressure of dibenzyl was changed over an eight-fold range, and a plot of first order rate constant, k_f secs^{-1}, against dibenzyl pressure is given in Figure 25. In the two lowest pressure experiments the low peak heights reduced the accuracy of the rate measurement, but there is clearly no significant deviation, and it

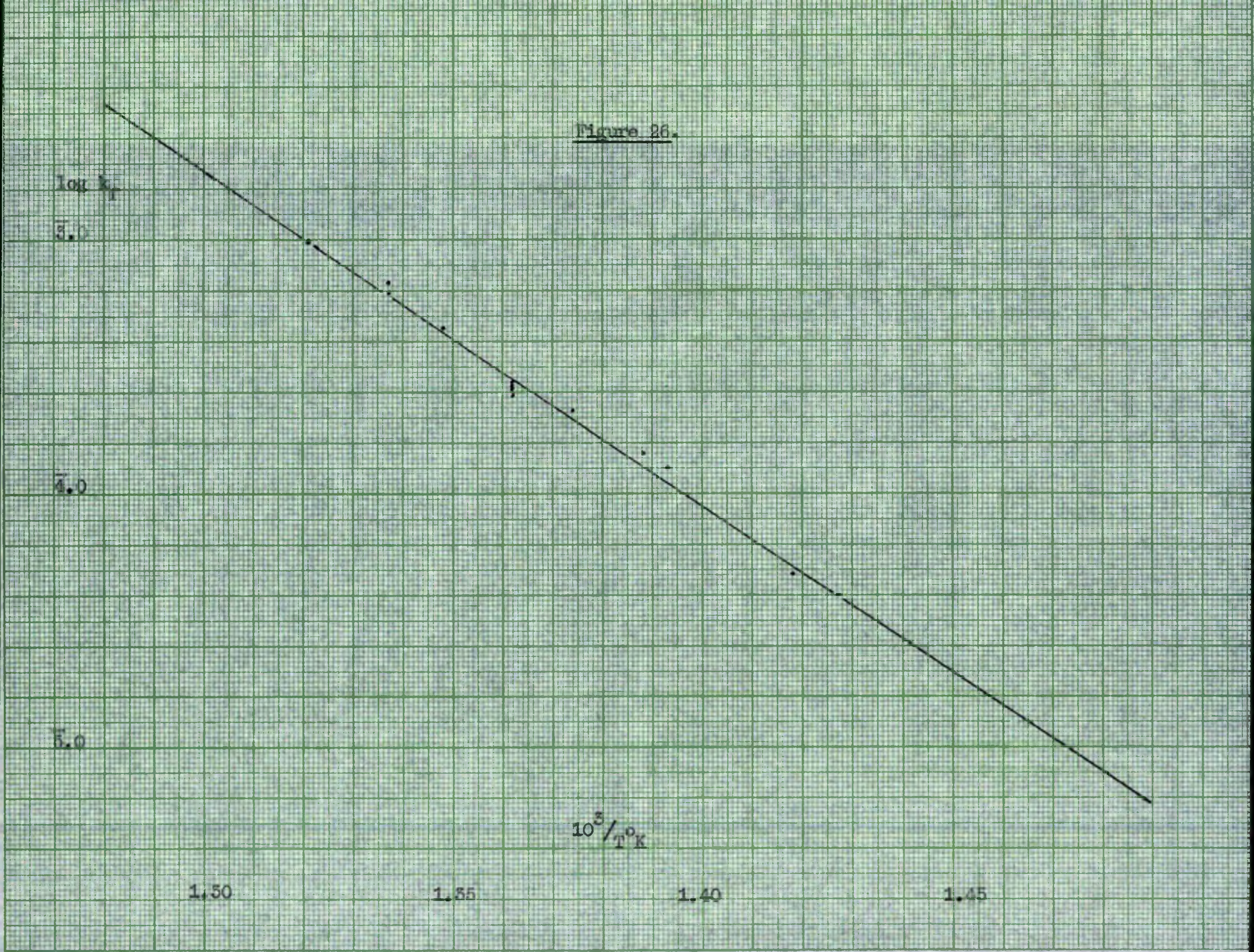


Figure 26.

may be concluded that the formation of diB_{hd} is first order over the range of dibenzyl pressure used.

Temperature dependence.

The reaction was studied in the reaction vessel between 402° and 501°C. This was the largest temperature range possible, since at the high temperatures the rate equation failed to compensate adequately for decomposition, while at the low, the small changes in peak heights were difficult to measure.

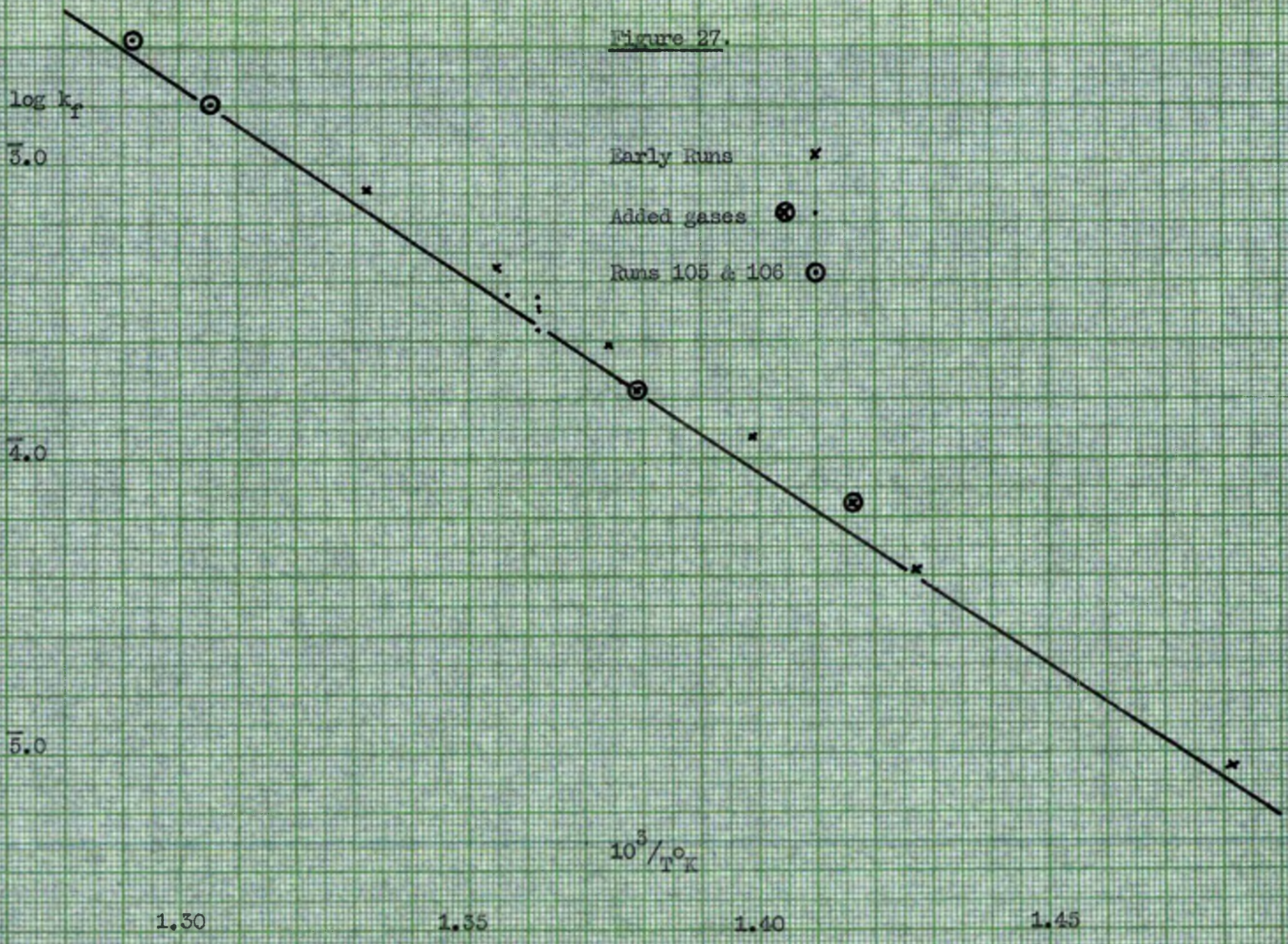
In the calculation of the temperature coefficient of the reaction the results of the following experiments were not used:-

1) All Runs done before the metrosil leak 2 was fitted directly above the mass spectrometer ion source (Nos. 19 - 33).
2) All Runs in the presence of added gases or in the reaction vessel immediately after surface cleaning (Nos. 102, 103, 107, 108, 109).
3) The two highest temperature Runs, 105 & 106, in which the contribution of the decomposition was large, and the equation gave curved plots, from which k_f had to be estimated by drawing initial tangents.

The remaining thirteen experiments were plotted according to the Arrhenius equation and the best straight line calculated by the method of least squares. The line and the points used to obtain it are given in Figure 26.

In addition to the statistical error in the temperature independent factor there is a possibility of error in the correction made to the reaction times, which was based on the volumes of the reaction vessel and the circulating system. The overall error of the temperature

Figure 27.


log k_f
$\bar{3}.0$
$\bar{4}.0$
$\bar{5}.0$
Early Runs ×
Added gases ⊗ ·
Runs 105 & 106 ⊙
$10^3/T^oK$
1.30
1.35
1.40
1.45

independent factor was therefore estimated and not calculated by the least squares method.

The results of these experiments on the rate of formation of $PhCH_2CD_2Ph$ from mixtures of $PhCH_2CH_2Ph$ and $PhCD_2CD_2Ph$ give the following expression for the unimolecular dissociation of dibenzyl:-

$$k_f \ \mathrm{secs}^{-1} = 10^{14.5 \pm 0.5} \exp - (60 \pm 1) \times 10^3 / RT$$

Other Runs.

The results of the experiments not used in evaluating the best line are compared with the line in Figure 27.

The earlier experiments would lie on a parallel, slightly higher line; the small difference may arise from the different shape and volume of the circulating system, or from the longer time lag in the earlier system.

The high temperature Runs, 105 & 106, give rate constants in agreement with the line, although, as pointed out above, these constants were calculated from tangents.

Added gases.

The following experiments with added gases were carried out:-

Runs 102 & 103 in argon; Run 107 in deuterium; Run 109 in oxygen; and in the earlier series, Runs 19 & 20 in nitrogen.

It can be seen from Figure 27 that in no case was there a significant change in the rate in the presence of these gases.

Effect of Surface.

The Surface / Volume ratio of the reaction vessel was not varied, so no accurate data on the effect of this paramater are available. The rate

TABLE VII.

Run	T^{o}C	diB$_h$ mgm.	diB$_d$ mgm.	p diB mm.	184$^+$ obs.	186$^+$ obs.	r	low p r
40	384	2.04	2.04	69.6	4	59	.03	.03
41	397	2.04	2.04	53.3	5	39	.05	.03
65	414	2.65	2.65	91.2	3	13	.08	.06
66	414	2.65	2.65	97.2	2	15.5	.05	.06
68	453	2.04	2.04	3.2	2.5	15	.06	.08
69	453	2.04	2.04	3.2	2	10	.08	.08
78	461	3.06	3.06	5.2	4.5	12	.13	.25
79	461	3.06	3.06	142.5	4	9	.15	.25
81	461	3.06	3.06	4.8	13	18	.22	.25
82	461	3.06	3.06	101.5	10	16.5	.20	.25
100	463	5.2	5.3	8.5	9	6	.36	.28
101	463	5.0	5.5	8.6	16	23	.21	.28

Notes: All Runs of 60 minutes duration.

Last column gives approximate value of r after 60 minutes for low pressure Runs at similar temperatures.

constant of Run 108 in the reaction vessel immediately after the surface had been cleaned with oxygen was normal, so that the formation of diB_{hd} was independent of the presence of a carbon coating. This is good evidence for the reaction being homogeneous.

Sealed tube Runs.

Some of the sealed tube Runs which provided information about the composition of the deuterated toluenes were also analysed for dibenzyl. The results are collected in Table VII; because of the high percentage decomposition, and because it was difficult to admit solids quantitatively from the tubes in the presence of toluene and other volatile substances before Trap 3 was installed, the dibenzyl peaks were very small, and the accuracy of the measurements was poor.

Also, since the decomposition under these high pressure conditions did not obey the 1.5 order law, the assumptions made in deriving the rate equation were invalid and k_f could not be calculated from these results. Consequently only the values of r are given in Table VII.

It can be seen from the Table that the results, although scattered for the reasons just given, show that the formation of diB_{hd} continues at high pressures, at about the same rate as at low.

DISCUSSION.

The aims of this Discussion are:-

i) To compare the results of this investigation with the results of the previous work on the pyrolysis of dibenzyl by Horrex & Miles(9) and by Pittilo(10).

ii) To derive a value for the heat of formation of the benzyl radical from the experimental results, and to compare it with the other available values.

In general, the major findings of Pittilo have been confirmed; the quantitative development of the exchange reaction between dibenzyl and deuterated dibenzyl has been entirely successful and it has been established beyond doubt that dibenzyl dissociates to form benzyl radicals, which recombine to re-form dibenzyl. At low pressures this dissociation and recombination is about ten times faster than the loss of dibenzyl by decomposition in the temperature region studied. This rapid radical equilibration does not of itself mean that the subsequent decomposition rate is determined by the attack of radicals on dibenzyl, although the 1.5 order decomposition rate found by Pittilo and confirmed by this investigation (Figure 18) strongly supports this view. The results of the analyses of the side-chain deuterated toluenes formed provide further convincing support (Table VI pp. 84-89). Hence there appears to be no doubt that the initial stages of the decomposition may be represented by the equations:-

$$PhCH_2CH_2Ph \quad \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \quad 2\ PhCH_2- \qquad (1)$$

$$PhCH_2CH_2Ph + PhCH_2- \quad \xrightarrow[k_a]{} \quad PhCH_3 + PhCH.CH_2Ph \qquad (2)$$

The data provided by the exchange reaction between diB_h and diB_d afford the opportunity of discussing equation (1), which is the most significant theoretically since it alone can lead to a value of $D(PhCH_2\text{-}CH_2Ph)$, the major interest of this work. The results described in the previous section have shown that the formation of $PhCH_2CD_2Ph$ from mixtures of $PhCH_2CH_2Ph$ and $PhCD_2CD_2Ph$ is a homogeneous,first order reaction, occurring much more rapidly than decomposition under the low pressure conditions used. It has been assumed in the derivation of the rate equation that the concentration of benzyl radicals in the system is low, and the validity of this assumption is supported by the approximate thermodynamic calculation of the equilibrium constant for equation (1) given in Appendix I. If the usual assumption that the recombination of radicals requires no activation energy is made, then the rate of formation of $PhCH_2CD_2Ph$ is determined by the rate of dissociation of dibenzyl. It is a necessary consequence of this conclusion that the energy of activation of the radical exchange reaction would measure the endothermicity of the dissociation, i.e. $D(PhCH_2\text{-}CH_2Ph)$.

All these considerations are implicit in the mathematical treatment of the rate equation derived on pp.91-102, in which k_f is expressed in terms of the ratio of $PhCH_2CD_2Ph$ to total dibenzyl. The expression:-

$$k_f\ \sec^{-1} = 10^{14.3} \exp {}^{-60000}/_{RT}$$

therefore refers to the dissociation of dibenzyl, i.e. the forward reaction of equation (1).

Before the magnitude of D($PhCH_2$-CH_2Ph) is discussed, it is relevant at this stage to note that a first order gaseous reaction of this type would be expected, on the Lindemann theory and all its modern developments, to show a gradual change from first to second order behaviour as the pressure is lowered. The pressures used in this work were of necessity low, in order to minimise the contribution of the 1.5 order decomposition reaction, but no falling off of first order rate constant was observed (Figure 25) and the addition of nitrogen, argon, deuterium, and oxygen did not increase the rate significantly (Figure 27). It was not part of the aim of this work to determine where any decrease of first order rate constant would occur and the matter was not pursued; in any case, the lowest pressure, 0.08 mm., is very low for a static experiment. The theories are not sufficiently developed to predict where the fall-off would be expected to occur in the case of a molecule of the complexity of dibenzyl; the results obtained suggest that even as far as 0.08 mm. the full quota of activated dibenzyl molecules is maintained by collisional processes.

The temperature independent factor of $10^{14.3}$ sec^{-1} which was observed is about the upper limit of "normal" values for unimolecular reactions, and in the present state of knowledge its magnitude does not appear to be unreasonable for a unimolecular dissociation. The data certainly identify it with such a process and this radical exchange is clearly one of the simplest conceivable reactions; many of the reactions said to have A factors with a "normal" value of about 10^{13} are in fact processes of some kinetic complexity. Explanations for A factors of

Table VIII.

Source	$\Delta H_f^o(PhCH_2-)$	$D(PhCH_2-H)$	Method
Szwarc	37.5	77.5	Pyrolysis of toluene
Van Artsdalen	49.5	89.5	Photobromination of toluene
Benson & Buss	44.9	84-85	Equilibrium constant of $PhCH_3+Br_2 = PhCH_2Br+HBr$
Alexander	45.4	85.4	Pyrolysis of dibenzyl + HI
This Thesis	44.9	84.9	Thermal dissociation of $(PhCH_2)_2 + (PhCD_2)_2$

10^{15} to 10^{17} have been advanced by Pritchard$^{(44)}$ for the dissociation of diketones and compounds of the type $Hg.R_2$, which involve the simultaneous dissociation of two bonds; it is quite obvious that the reactions of equation (1) cannot be considered in this way.

The energy of activation for the dissociation is of more chemical significance. If it is accepted as equalling $D(PhCH_2{-}CH_2Ph)$, the following derivations may be made:-

$$\begin{aligned}
&PhCH_2CH_2Ph && \longrightarrow && 2\,PhCH_2{-} \;-\; D(PhCH_2{-}CH_2Ph) \\
&\therefore\; D(PhCH_2{-}CH_2Ph) && = && 2\,\Delta H_f^o(PhCH_2{-}) - \Delta H_f^o(PhCH_2CH_2Ph) \\
&\therefore\; 60 && = && 2\,\Delta H_f^o(PhCH_2{-}) - 29.7 \\
&\underline{\therefore\; \Delta H_f^o(PhCH_2{-}) \quad = \quad 44.9 \text{ kcal.}}
\end{aligned}$$

$$\begin{aligned}
&2\,D(PhCH_2{-}H) - D(PhCH_2CH_2Ph) = 2\,\Delta H_f^o(H{-}) - 2\,\Delta H_f^o(PhCH_3) + \Delta H_f^o(PhCH_2CH_2Ph) \\
&2\,D(PhCH_2{-}H) - 60 = 104 - 23.9 + 29.7 \\
&\underline{\therefore\; D(PhCH_2{-}H) \quad = \quad 84.9 \text{ kcal/mole.}}
\end{aligned}$$

Other existing values for these quantities have been reviewed in the Introduction and are collected in Table VIII.

The results of this investigation are in excellent agreement with those of Alexander and of Benson & Buss; the method used by Alexander and the method used in this work are two variants of the kinetic approach, differing appreciably in technique. Their agreement and the agreement with the results obtained by a totally different approach by Benson & Buss would seem to constitute very strong evidence that the value of 44.9 kcal for the heat of formation of the benzyl radical is in fact correct. It is interesting to note that Roberts & Skinner(45) derived a value of 44.7 kcal for the heat of formation of the benzyl radical from calculated resonance energies.

It has been maintained in support of Szwarc's values in Table VIII that they are consistent with the bond energies and heats of formation of a variety of related compounds of the type $PhCH_2$-X. Some comments on this point have been made in the Introduction: the evident complexity of the decomposition of toluene casts doubt on Szwarc's value for D($PhCH_2$-H) and the experimental work on other $PhCH_2$-X compounds has not yet been repeated by any other workers.

Finally, it may be noted that even if the A factor of this work was substantially in error and in fact had the value of 10^{15} sec^{-1} the observed temperature dependence of the rate of dissociation would lead to a value of the activation energy of 55.8 kcal/mole at 700°K; this would reduce D($PhCH_2$-H) by only 2 kcal/mole, so that the agreement with Alexander and with Benson & Buss would not be destroyed.

Pittilo has calculated the thermochemistry of the postulated reaction steps in the decomposition of dibenzyl. He used Szwarc's value for the heat of formation of the benzyl radical, and these calculations have been repeated in Appendix I using the value of 44.9 kcal. References to the sources of the thermochemical data used above are also included in Appendix I.

Although the main aim of this work was to investigate the dissociation of dibenzyl under conditions in which the decomposition reaction was insignificant, some further comments on the latter can be made from the results available.

Pittilo's conclusion that the decomposition obeyed a 1.5 order law for low pressures of dibenzyl has been confirmed, and the results of this work may be expressed by the equation:-

$$k_{1.5} = 10^{12.5} \exp^{-47000/RT}$$

The 1.5 order kinetics are readily explicable in terms of the mathematical treatment developed in earlier pages. There it was shown that if radical recombination was much more rapid than decomposition by reaction (2) above, the rate of loss of dibenzyl could be expressed as:-

$$-\frac{d(diB)}{dt} = (L+\tfrac{1}{2})\, k_a\, k_f^{\frac{1}{2}}\, k_r^{-\frac{1}{2}}\, (diB)^{1\frac{1}{2}} = k_{1.5}(diB)^{1\frac{1}{2}}$$

If the approximation implicit in the above expression is accepted, E_a, the energy of activation of reaction (2) may be calculated:-

$$k_{1.5} = (L+\tfrac{1}{2})\, k_a\, k_f^{\frac{1}{2}}\, k_r^{-\frac{1}{2}}$$

Now, $k_{1.5} = A_{1.5}\exp^{-E_{1.5}/RT}$ and k_a, k_f, and k_r have similar identities. Substitute these in the above equation, and equate the powers of e:

$$\therefore E_{1.5} = E_a + \tfrac{1}{2}E_f - \tfrac{1}{2}E_r$$

$$47 = E_a + \tfrac{1}{2}(60) - 0$$

$$\therefore \underline{E_a = 17 \text{ kcal.}}$$

At first sight this value seems rather high for a hydrogen abstraction reaction by a free radical. No data for such reactions by the benzyl radical are available for comparison, but in the aliphatic series Heller & Gordon(46) report that the abstraction of hydrogen from C_6H_{14} by the iso-propyl radical requires an activation energy of 8.5 kcal, and Hoey & Le Roy(47) ascribe an energy of activation of 12.5 kcal to the attack of propyl radicals on hydrogen. Similar reactions involving the benzyl radical would be expected to require higher activation energies because of the greater stability of the radical.

The value of E_a depends on the ease of breaking the secondary C-H bond in dibenzyl as well as on the reactivity of the benzyl radical, and an interesting calculation can be made, following an argument originated by Szwarc$^{(48)}$.

The results of this investigation lead to a value of 85 kcal/mole for $D(PhCH_2-H)$, and if $D(CH_3-H)$ is accepted as 102 kcal/mole, the resonance energy of the benzyl radical, in the sense used by Szwarc, is (102 - 85) = 17 kcal. If $D(CH_3-CH_3)$ is taken to be 83 kcal/mole, the value of $D(PhCH_2-CH_2Ph)$ would be expected to be (83 - 2 x 17) = 49 kcal, which is 11 kcal less than the value found experimentally. The strengthening of the central bond in dibenzyl by 11 kcal should manifest itself in a shorter bond length, and there is evidence for this being the case$^{(49)}$. Szwarc$^{(48)}$ has suggested that the effect is due to hyperconjugation of the central bond to form a completely conjugated system. The formation of the $PhCH.CH_2Ph$ would disturb this conjugation, and would therefore be an energetically unfavourable process, so that a high value of E_a would be expected.

The value of the pre-exponential factor is of interest in relation to the results of Horrex & Miles, who calculated first order rate constants, represented by the equation:-

$$k_{uni-}\ sec^{-1} = 10^{9.3} \exp - {}^{48000}/_{RT}$$

Since the decomposition is in fact 1.5 order, there is the relation:

$$k_{uni-} = k_{1.5}(\text{diB})^{\frac{1}{2}} \qquad \text{and hence:}$$

$$A_{uni-} = A_{1.5}(\text{diB})^{\frac{1}{2}}$$

In Horrex & Miles' work, and in this investigation, (diB) was about 10^{-6} gm. moles per litre,

$$\therefore 10^{9.3} = A_{1.5}\,(10^{-6})^{\frac{1}{2}}$$

$$\therefore \underline{A_{1.5} = 10^{12.3}\ \text{moles}^{-\frac{1}{2}}\ \text{litres}^{\frac{1}{2}}\ \text{secs}^{-1}}$$

Hence the true pre-exponential term of Horrex & Miles' experiments agrees well with the results of this investigation.

The mathematical treatment of this system given earlier predicted that if the decomposition by reaction (2) became much more important than recombination, the loss of dibenzyl would be given by:-

$$-\frac{d(\text{diB})}{dt} = 2(L+\tfrac{1}{2})\,k_f\,(\text{diB}) = 3\,k_f\,(\text{diB}) \quad \text{if } L = 1.$$

This is first order in dibenzyl and the coefficient 3 has a simple physical significance: when one dibenzyl molecule dissociates it forms two radicals, each of which attacks a further dibenzyl molecule by reaction (2), so that three molecules are lost per dissociation.

The results of the study of the decomposition show a change to first order behaviour at higher pressures (Figure 18), but although the first order rate constant appears to have reached a steady value, this does not represent the situation implied in the above equation, where practically no recombination occurs. In the first place, the results in Table VII show that the formation of diB_{hd} continues at high pressure, which implies recombination; and the value of the first order rate constant for decomposition at 461°C is only about the same as k_f for that temperature, not $3\,k_f$. Hence at the higher pressures used in this work, reaction (2) was competing with recombination sufficiently to give first order kinetics for the decomposition, but not sufficiently for all the benzyl radicals formed to be lost by attack on dibenzyl.

The nature and proportions of the decomposition products were similar to Pittilo's, except that phenanthrene was formed instead of styrene. The results of early work on the pyrolysis of dibenzyl, toluene, and stilbene in red hot tubes are conflicting and seem to depend strongly on the conditions used, but Graebe(50) has reported the formation of phenanthrene and much toluene from the decomposition of stilbene, and some phenanthrene from the pyrolysis of dibenzyl; Graebe also obtained phananthrene from the decomposition of toluene(51). The formation of phenanthrene is therefore not surprising, nor is the absence of styrene, which was likely to have polymerised under the reaction conditions used in this investigation.

The results of this work were much less accurate and comprehensive than Pittilo's as far as the study of the products is concerned, since this was one of the major aspects of Pittilo's investigation, and little fresh information has been obtained. Pittilo found that his product ratios approached constant values at the upper end of his pressure range, about 1 mm. With one exception, the product ratios determined in this work have the same value as Pittilo's high pressure limit up to 94.5 mm., thus confirming his idea that the stoichiometry becomes simpler and more constant at high pressures. The exception is the Toluene / Benzene ratio, which decreases steadily in benzene as the pressure is raised. The loss of benzene was probably consistent with the carbon balance of about 95 % found in the highest pressure experiments (Table II), but no other products formed at the expense of the benzene were identified.

SUMMARY.

1) The most recent work on the pyrolysis of dibenzyl suggested that a thermal equilibrium:- $PhCH_2CH_2Ph \rightleftharpoons 2\ PhCH_2$- was set up as a preliminary to decomposition.

The aim of this research was to test this idea by heating mixtures of $PhCH_2CH_2Ph$ (M.W. 182) and $PhCD_2CD_2Ph$ (M.W. 186) and following mass spectrometrically the growth of $PhCH_2CD_2Ph$ (M.W. 184) formed by radical recombination.

2) A four stage synthesis of deuterated dibenzyl was developed and used to prepare dibenzyl of 95% isotopic purity with the composition:-

$PhCD_2CD_2Ph$, 81 %; $PhCD_2CDHPh$, 18 %; PhCDHCDHPh, 1 %.

$PhCH_2CH_2Ph$ was synthesised by the same sequence of reactions.

3) In order to provide the necessary experimental equipment, the following items have been developed and constructed and descriptions of them are given in this Thesis:-

a) a 2 litre reaction vessel with an electronically controlled furnace was arranged with a gas circulating system feeding the inlet of a mass spectrometer;

b) an existing mass spectrometer was extensively modified in order to give resolution of 1 in 200:-

i) the spectrometer tube was stiffened and accurately re-aligned;

ii) the ion collector unit was made detachable and its construction improved;

iii) a new ion source was designed and built to the required high accuracy;

iv) a new scanning unit was built for variation of the magnetic field.

4) The rate of formation of $PhCH_2CD_2Ph$ was followed in mixtures of $PhCH_2CH_2Ph$ and $PhCD_2CD_2Ph$ at pressures of 0.08 to 0.66 mm. in the reaction vessel, and at pressures up to 142 mm. in sealed tubes, using temperatures between 400° and 500°C. Data were also obtained on the rate of decomposition of $PhCH_2CH_2Ph$ alone in similar systems.

5) The rate of radical exchange was found to be first order, independent of surface and of pressures of added A, N_2, D_2, and O_2.

The decomposition reaction was shown to be 1.5 order at low pressures, and tended to first order at high pressures. At lower pressures it was much slower than the radical exchange.

6) A rate equation for radical exchange in terms of the rate of dissociation of dibenzyl, making due allowance for the simultaneous decomposition of dibenzyl has been developed and applied in the lower pressure region where exchange was of major importance. It gives:-

$$k_r \text{ sec}^{-1} = 10^{14.3} \exp - 60000/_{RT}$$

7) The energy of activation in 6) has been identified with $D(PhCH_2\text{-}CH_2Ph)$ in dibenzyl. This value has been discussed in relation to current data on the heat of formation of the benzyl radical and bond dissociation energies in benzyl compounds, notably $D(PhCH_2\text{-}H)$ in toluene.

8) The energy of activation for the decomposition was found to be 47 kcal and the nature and proportions of the reaction products were established and compared with previous work. The proportions of side-chain deuterated toluenes formed were consistent with a deuterium isotope effect of 2 or less, and with toluene being made by the abstraction of hydrogen from the central carbon atoms of dibenzyl by benzyl radicals. Benzyl radicals were also shown to react with deuterium to form toluene.

APPENDIX I.

1) Calculation of equilibrium constant at 450°C for dissociation of diB.

2) Thermochemical calculations.

1) Calculation of equilibrium constant at 450°C for dissociation of diB.

Entropies and specific heats from the Handbook of Chemistry & Physics **37** 1753 (1956).

$S^{o}_{(PhCH_2)_2}$ unknown, so calculated from the empirical relation for compounds in the gas phase:- $S^{o}_{AB} = \frac{1}{2}(S^{o}_{A_2} + S^{o}_{B_2})$

i) $S^{o}_{H_2} = 31.21$ e.u. $S^{o}_{PhCH_3} = 76.42$ e.u. $\therefore S^{o}_{(PhCH_2)_2} = 121.63$ e.

ii) $S^{o}_{PhCH_2CH_3} = 86.15$ e.u. $S^{o}_{C_2H_6} = 58.45$ e.u. $\therefore S^{o}_{(PhCH_2)_2} = 117.2$ e.u

Hence take $S^{o}_{(PhCH_2)_2} = 120$ e.u.

Assume $S^{o}_{(PhCH_2-)} = S^{o}_{(PhCH_3)} + 1.4$ e.u. $= 76.42 + 1.4 = 77.82$ e.u.

Then for $PhCH_2CH_2Ph == 2\,PhCH_2-$ $\Delta S^{o} = 2(77.82) - 120 = 35.64$ e.u.

At 25°C(298°K) $C_p(PhCH_2)_2 = 66.1$ cal. and $C_p(PhCH_2-) = C_p(PhCH_3)$
$= 37.05$ cal.

$\therefore \Delta C_p = 8$ cal.

$\therefore \Delta S^{T_2}_{T_1} = \Delta C_p \ln T_2/T_1 = 8 \times 2.3 \log \frac{723}{298} = 7.1$ e.u. at 450°C

$\therefore \Delta S^{o}_{723} = (35.64 + 7.1) = 42.74$ e.u.

$\therefore T\Delta S^{o} = 30{,}900$ cal. If $\Delta H^{o} = 60$ kcal,

$\Delta H^{o} - T\Delta S^{o} = 29.1$ kcal $= \Delta G^{o}$ & $\ln K_p = \frac{-\Delta G^{o}}{RT}$

$\therefore \log K_p = -\frac{29.1 \times 10^{3}}{4.57 \times 723} = -8.8$

and $\log K_c = \log K_p - \log RT = -8.8 - 3.16 = \underline{-11.96}$

$\therefore$The equilibrium constant in terms of concentration, $K_c = 10^{-11.96}$

Hence if dibenzyl concentration is 10^{-6} gm. moles per litre, the benzyl radical concentration is 10^{-9} gm. moles per litre, which justifies assumption in derivation of rate equation that benzyl radical concentration is low.

2) Thermochemical calculations. (All data for gaseous substances)

The thermochemistry of the possible steps in the decomposition of dibenzyl may be calculated from the molecule and radical heats of formation. This was done by Pittilo(10) using Szwarc's value for the heat of formation of the benzyl radical. His calculations are repeated below using the value obtained in this investigation.

Molecules.	ΔH_f^o	calculated from:
$PhCH_2CH_2Ph$	29.70 kcal/mole	heat of combustion(s)(52); heat of fusion(53) vapour pressure (54)
$PhCH_3$	11.95	heats of combustion(l) & vaporisation(55)
PhCH:CHPh	54.31	heats of combustion(s)(56) & fusion(53); v.p.(54)
PhH	19.82	heats of combustion(l) & vaporisation(55)
$PhCH:CH_2$	35.11	heats of combustion(l) & vaporisation(55)

Radicals. Direct determinations not possible; calculated as follows:-

$PhCH.CH_2Ph$ assume secondary C-H bond 7 kcal weaker than primary C-H and take $D(PhCH_2\text{-}H) = 84.9$ kcal/mole.

Then $D(PhCH_2CH\text{-}HPh) = 77.9$ kcal/mole.

$$PhCH_2CH_2Ph \rightarrow PhCH.CH_2Ph + H\text{-} \quad - \quad D(PhCH\text{-}HCH_2Ph)$$

$$\therefore \Delta H_f^o(PhCH.CH_2Ph) = \Delta H_f^o(PhCH_2CH_2Ph) - \Delta H_f^o(H\text{-}) + D(PhCH\text{-}HCH_2Ph)$$

$$= 29.7 - 52 + 77.9$$

$$\therefore \Delta H_f^o(PhCH.CH_2Ph) = 55.6 \text{ kcal}$$

$PhCH_2CH_2$. take $D(CH_3CH_2\text{-}H) = 96$ kcal/mole(11) $= D(PhCH_2CH_2\text{-}H)$ approx.

$$PhCH_2CH_3 \rightarrow PhCH_2CH_2. + H\text{-}$$

$$\therefore \Delta H_f^o(PhCH_2CH_2.) = \Delta H_f^o(PhCH_2CH_3) - \Delta H_f^o(H\text{-}) + D(PhCH_2CH_2\text{-}H)$$

$$= 7.12^{(55)} - 52 + 96$$

$$\therefore \Delta H_f^o(PhCH_2CH_2.) = 51.1 \text{ kcal.}$$

$PhCH_2$. $\Delta H_f^o = 44.9$ kcal, as calculated in text from $D(PhCH_2\text{-}CH_2Ph)$

Ph. available data give poor agreement; use $\Delta H_f^o = 72.4$ kcal.

From the heats of formation on the previous page, the thermochemistry of the reaction steps postulated by Pittilo & by Horrex & Miles can be calculated:-

				This Thesis	Pittilo
1)	$PhCH_2CH_2Ph$	$\rightarrow$	$PhCH_2- + PhCH_2-$	-60	-47
2)	$PhCH_2CH_2Ph + PhCH_2-$	$\rightarrow$	$PhCH_3 + PhCH.CH_2Ph$	+ 7	+ 7
3)	$PhCH.CH_2Ph$	$\rightarrow$	$PhCH:CHPh + H-$	-30.7	-38.1
4)	$PhCH_2CH_2Ph + H-$	$\rightarrow$	$PhCH_2CH_2. + PhH$	+10.8	+10.8
5)	$PhCH_2CH_2.$	$\rightarrow$	$PhCH:CH_2 + H-$	-36.0	-36.0
6)	$PhCH.CH_2Ph$	$\rightarrow$	$PhCH:CH_2 + Ph-$	-51.9	-66.7
7)	$PhCH_2CH_2Ph + Ph-$	$\rightarrow$	$PhH + PhCH.CH_2Ph$	+26.7	+30.7
8)	$2\ PhCH.CH_2Ph$	$\rightarrow$	$PhCH:CHPh + PhCH_2CH_2Ph$	+27.2	+12.4
9)	$PhCH_2CH_2Ph + H-$	$\rightarrow$	$PhCH.CH_2Ph + H_2$	+26.1	+33.5
10)	$PhCH_2CH_2Ph + H-$	$\rightarrow$	$PhCH_3 + PhCH_2.$	+24.8	+32.3

(values in kcal.)

APPENDIX II.

Calculation of dibenzyl concentration.

Symbols and conversion factors used in Decomposition calculations.

Correction for loss of dibenzyl through leak 2.

Tabulated Results; decomposition of dibenzyl:-

1) Runs in the reaction vessel; diB_h alone
2) Runs in sealed tubes at 384°C; diB_h alone
3) Runs in sealed tubes at 462°C; diB_h alone
4) Runs in the reaction vessel at 461°C; $diB_h + diB_d$
5) Runs in the reaction vessel at other temperatures; $diB_h + diB_d$
6) Products of Runs in sealed tubes at 462°C; diB_h alone
7) Runs in sealed tubes; $diB_h + diB_d$; analysis for deuterated toluenes.

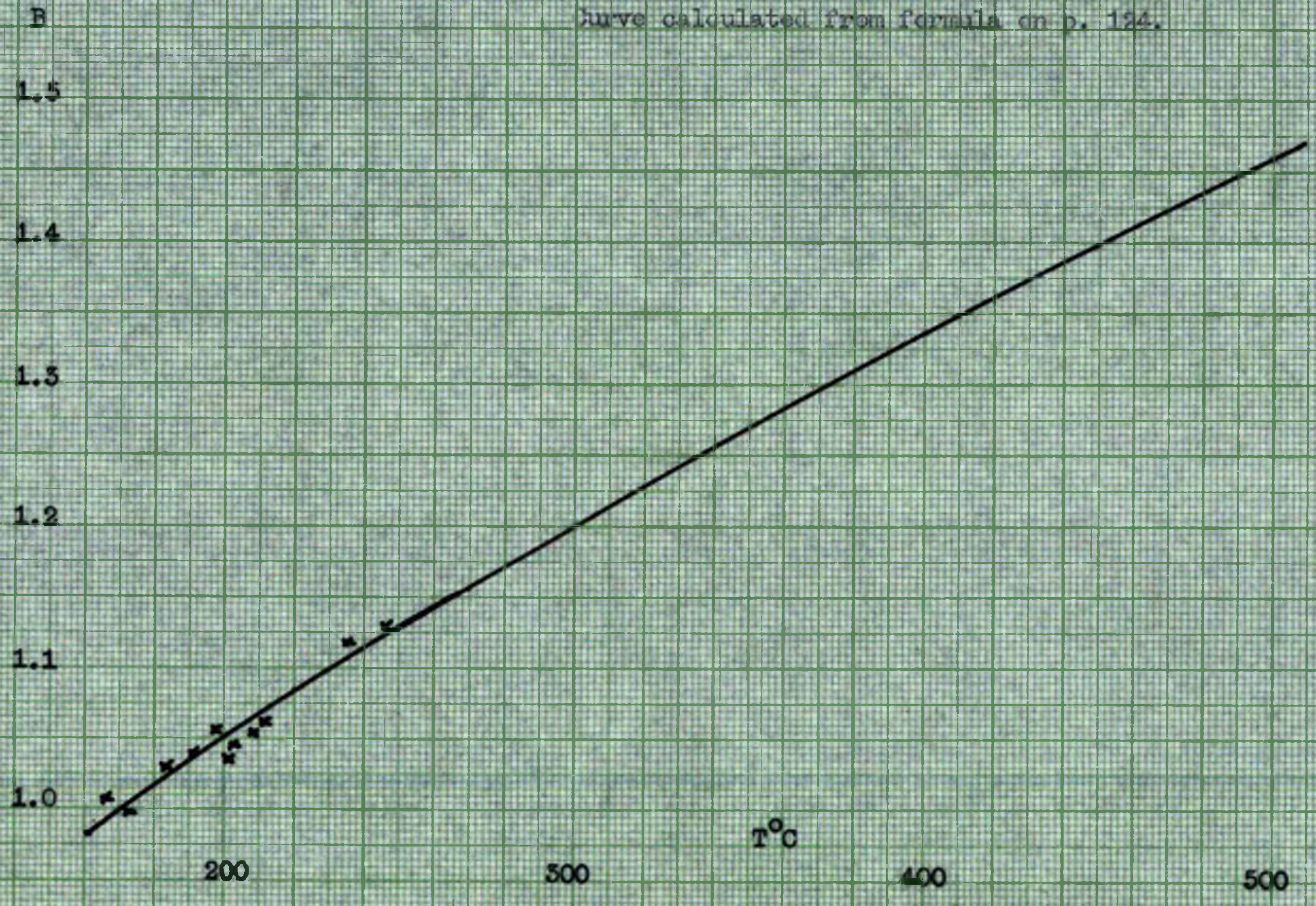


Figure 28.

Curve calculated from formula on p. 124.

Calculation of dibenzyl concentration.

Since the mass spectrometer was calibrated for dibenzyl by weight, allowance had to be made for the effect of the furnace temperature on the pressure of dibenzyl in the reaction system when calculating the concentration of dibenzyl from peak heights in the reaction vessel Runs.

In the calibration, the furnace temperature was set at 170°C, (445°K) and the temperature of the valve and circulating system was about 100°C (375°K).

The total volume of the reaction system, from the valve to the mass spectrometer was found by expansion of a known volume of dry air and pressure measurement to be 2.6 litres, and the reaction vessel volume was 2 litres.

Then under calibration conditions, there were 2 litres at 445°K and 0.6 litre at 375°K; under reaction conditions, with the furnace at T°K, 2 litres at T°K and 0.6 litre at 375°K.

Then the ratio of the pressures exerted by a fixed weight of dibenzyl is:-

$$\frac{p_T}{p_{445}} = \frac{\frac{0.6}{375} + \frac{2.0}{445}}{\frac{0.6}{375} + \frac{2.0}{T}} = \frac{0.00611}{0.0016 + \frac{2.0}{T}}$$

Since the dibenzyl peak in the mass spectrometer is proportional to the pressure of dibenzyl, this pressure ratio equals the sensitivity ratio of the mass spectrometer to dibenzyl in millivolts per milligram, denoted by B. The curve of B against T plotted in Figure 28 was obtained from the formula derived above. The points on the curve were experimentally obtained by injecting a quantity of dibenzyl into the system with the furnace at 170°C, raising the furnace current, and measuring the 182^+ peak at short temperature intervals over the temperature range where decomposition was inappreciable.

Symbols and conversion factors used in Decomposition calculations.

DB = sensitivity of mass spectrometer to dibenzyl in millivolts (parent $)^{+}$ corrected, per mgm. dibenzyl.

B = ratio of DB at $T^{o}K$ to DB at $443^{o}K$ (solids calibration temperature).

D = 182^{+} or (total dibenzyl parent$)^{+}$ in millivolts, corrected.

D_{60} = D after 60 minutes of reaction.

D_{o}' = D at zero time, calculated for $443^{o}K$ from mgm. dibenzyl and calibration line.

D_{o} = D_{o}' corrected to $T^{o}K$. i.e. $D_{o} = D_{o}' \times B$.

(diB) = concentration of dibenzyl in gm. moles per litre.

M = gm. molecular weight of dibenzyl.

V = volume of reaction system in litres.

v = volume of sealed reaction tubes in ml.

X = correction for time spent by vapour in circulating system attached to reaction vessel. Taken to be ratio of total reaction system volume to reaction vessel volume. i.e. V/2.

g' = slope of plot of $\frac{1}{D^{\frac{1}{2}}}$ or log D against time in minutes.

g = g' corrected for loss of dibenzyl through metrosil leak 2.

$k_{1.5}$ = 1.5 order rate constant in moles$^{-\frac{1}{2}}$ litres$^{\frac{1}{2}}$ seconds^{-1}.

k_{uni-} = 1st order rate constant in seconds^{-1}.

Calculation of $k_{1.5}$

$$(diB) = \frac{D \times 10^{-3}}{B \times DB \times M \times V} \qquad \therefore \frac{1}{(diB)^{\frac{1}{2}}} = \frac{1}{D^{\frac{1}{2}}} \times (B.\ DB.\ M.\ V.\ 10^{3})^{\frac{1}{2}}$$

$$\therefore k_{1.5} = g \times (B.\ DB.\ M.\ V.\ 10^{3})^{\frac{1}{2}} \times X \times \frac{2}{60}$$

B = 1.537 at $673^{o}K$, and 1.458 at $773^{o}K$. If B put equal to 1.4 for all Runs, maximum error in $k_{1.5}$ as a result of this approximation is 1.4 % (Run 106).

Run	DB	M	V	X	$k_{1.5}$
12- 24	8.0	182	2.4	1.2	92 g
25- 34	19.6	184	2.6	1.3	158 g
35-109	17.3	184	2.6	1.3	147 g

Runs in sealed tubes.

$$(\text{diB}) = \frac{D \times 10^{-3} \times 10^{3}}{DB \times M \times v} \qquad \therefore \frac{1}{(\text{diB})^{\frac{1}{2}}} = \frac{1}{D^{\frac{1}{2}}} \times v^{\frac{1}{2}} \times 56.125 \text{ for Runs } 35 - 109.$$

$$\therefore k_{1.5} = \left(\frac{1}{D_{60}^{\frac{1}{2}}} - \frac{1}{D_{o}^{\frac{1}{2}}} \right) \times v^{\frac{1}{2}} \times 56.125 \times \frac{2}{60 \times 60} \qquad \text{for Runs of 60 minutes.}$$

$$\therefore k_{1.5} = 0.0312\, v^{\frac{1}{2}} \left(\frac{1}{D_{60}^{\frac{1}{2}}} - \frac{1}{D_{o}^{\frac{1}{2}}} \right)$$

Calculation of k_{uni-}

$\log_{10} D$ plotted against time, mins: line of slope g' drawn.

$$k_{uni-} = g \times \frac{2.303 \times X}{60} = 0.05\, g \quad \text{for Runs } 35 - 109.$$

Runs in sealed tubes.

$$k_{uni-} = \log_{10} \frac{D_o}{D_{60}} \times \frac{2.303}{60 \times 60} \quad \text{for Runs of 60 minutes.}$$

$$\therefore k_{uni-} = \log \frac{D_o}{D_{60}} \times 6.4 \times 10^{-4}$$

Calculation of dibenzyl pressure, p_{diB}, in reaction vessel.

If G gm. moles dibenzyl exert a pressure of p mm. at T°K,

$$p = \frac{22.4 \times 760 \times G}{\left\{ \frac{0.6}{375} + \frac{2.0}{T} \right\} 273} = \frac{22.4 \times 760 \times B \times 10^{-3}}{273 \times 0.00611 \times 184} \times (\text{ mgm. diB }).$$

$$\therefore p = 0.0561 \times B \times (\text{ mgm. diB }).$$

Correction for loss of dibenzyl through leak 2.

For each leak 2 used, the rate of loss of dibenzyl from the reaction system with the furnace at 170°C was observed, and plotted according to 1st order and 1.5 order laws. Since the rate of loss was small, both plots were linear and the slopes were subtracted from the slopes of the corresponding decomposition plots to give the net slope due to decomposition, from which k_{uni-} or $k_{1.5}$ was calculated.

1) Runs 12 - 24; leak 2: 17 mins/cm.

Time mins.	19	65	105	122	770	no loss
D mv	58	60	58	61	61	no correction

2) Runs 25 - 34; leak 2: 6 mins/cm.

Time mins	10	15	16	85	154	slope uni- = 0.00028
D mv	103.5	104	103.3	99.2	97.4	slope 1.5 = 0.000034

3) Runs 35 - 109; leak 2: 9 mins/cm.

Time mins.	0	154	220	262	slope uni- = 0.00046
D mv	106	90.7	82.7	80.6	slope 1.5 = 0.000057

Hence the following corrections were made:-

Runs 12- 24	1st order	g = g'	1.5 order	g = g'
Runs 25- 34	1st order	g = g' - 0.0005	1.5 order	g = g' - 0.00005
Runs 35-109	1st order	g = g' - 0.0005	1.5 order	g = g' - 0.00006

1) Runs in the reaction vessel; diB_h alone.

Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv
Run 12		Run 15		Run 16		Run 17		Run 18		Run 91	
10	71.5	37	70	20	65.5	27	35	31	54	4	68
25	73	92	66	46	62	45	26	45	61	9	53.5
40	68.4	120	65	70	62	65	21	67	52	14	51
52	68.4	207	54	90	59			80	49	19	51
65	63.5			100	61	Run 90		94	48	23	48.5
79	65	Run 22		120	59	2	152	106	45	29	46
105	61.1	20	77.4	145	57	10	116			35	44.5
120	52.2	36	80.4	175	49	19	113	Run 24		40	43.5
170	51.3	48	74.3			26	111.5	16	73.5	46	41.5
205	38.7	74	64.1	Run 23		34	107	32	79	54	40.5
Run 21		88	67.3	29	80.4	41	106	46	75.9	60	40.8
12	67.6	105	61.7	45	84.4	48	107	60	80.3		
62	77			64	78.1	53	107	74	68.6		
87	69.6			81	76.4	60	105	135	51.4		
112	63.4										

Run	T°C	p_{N_2} mm.	mgm. diB	p_{diB} mm.	$k_{1.5}$
12	435	-	8.0	0.62	0.0176
15	435	10.2	8.2	0.64	0.0137
16	435	13.5	8.1	0.63	0.0168
17	495	14.5	8.1	0.66	0.1193
18	452	13.5	7.8	0.615	0.0306
21	452	7.4	7.8	0.615	0.0221
22	452	5.0	7.8	0.615	0.0208
23	452	9.4	7.8	0.615	0.0158
24	452	-	7.8	0.615	0.0215
90	462	-	8.1	0.645	--
91	462	-	4.8	0.38	--

2) Runs in sealed tubes at 384°C (657°K); diB_h alone.

Run	mgm.diB	v ml.	p_{diB} mm.	D_{60} mv	$k_{1.5}$	
46	4.08	5.7	161.1	47.8	0.00187	
47	4.08	20.6	44.6	38.0	0.00604	
48	4.08	5.5	167.0	52.6	0.00208	
49	4.08	20.9	43.9	48.2	0.00349	
50	4.08	6.4	143.5	50.4	0.00169	
51	4.08	24.6	37.3	49.0	0.00362	
52	8.16	21.0	87.6	75.2	0.00443	
53	4.08	4.5	204.8	49.0	0.00155	
54	4.08	4.9	187.9	52.1	0.00132	
55	4.08	5.5	167.0	54.3	0.00119	
56	2.04	10.8	42.6	28.2	0.00198	
57	10.20	10.85	211.8	83,7	0.00346	
58	4.08	24.6*	37.3	48.4	0.00374	* packed tube
60	4.08	24.9*	36.9	48.3	0.00380	* packed tube
63	8.16	10.3	178.5	109.4	0.00113	

3) Runs in sealed tubes at 462°C (735°K); diB_h alone.

Run	mgm.diB	v ml.	p_{diB} mm.	D_{60} mv	$k_{1.5}$	k_{uni-}
83	2.1	70.8	7.5	13.8	0.0269	2.67×10^{-4}
84	4.2	20.2	52.0	26.5	0.0107	2.77
86	2.1	310.0	1.7	15.9	0.0461	2.27
87	3.1	75.1	10.3	19.4	0.0244	2.82
88	4.3	15.0	72.0	32.2	0.0102	2.32
89	8.1	21.4	94.5	52.0	0.0078	2.75

4) Runs in the reaction vessel at 461-462°C (735°K); $diB_h + diB_d$.

Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv
Run 70		Run 71		Run 72		Run 73		Run 77		Run 103	
12	71.5	5	86.7	9	42.9	7	24.0	6	51.6	9	122.5
25	69.7	15	91.9	18	41.6	15	23.0	20	54.4	16	103.2
30	70.5	25	107.0	30	40.6	24	22.4	28	54.7	22	98.9
40	63.7	34	112.9	39	38.4	38	20.3	37	55.3	29	93.8
48	66.5	42	113.2	54	36.0	50	19.2	46	56.0	36	93.4
57	68.3	54	115.9	66	35.8	62	18.9	65	53.1	42	91.9
95	58.4	62	115.7	76	36.7			72	52.7	48	91.8
112	63.1	74	116.6	92	35.5	Run 102		79	52.5	55	91.3
		88	109.7	Run 80		10	99.7	86	51.8	61	82.7
Run 107				5	250.1	19	87.5	92	53.1		
6	173.3	Run 108		18	212.8	26	83.5				
9	172.5	5	78.5	30	100.4	33	81.8				
12	160.3	12	79.6	40	99.1	41	80.6				
15	149.5	18	73.7	51	101.8	48	79.1				
23	136.2	26	73.2	60	95.6	55	79.2				
		34	70.3	70	110.0	61	77.0				
				82	91.6						

Run	mgm. diB	p_{diB} mm.	$k_{1.5}$	k_{uni-}	
70	4.08	0.325	0.0391	0.385 x 10^{-4}	
72	2.04	0.162	0.0341	0.290 "	
73	1.02	0.081	0.0620	0.730 "	
80	6.12	0.486	0.0330	0.990 "	
102	4.24	0.337	0.0324	0.330 "	in 1.92 mm. of argon
103	4.24	0.337	0.0338	0.310 "	in 5.75 mm. of argon
107	8.48	0.675	0.0964	3.325 "	in 1.15 mm. deuterium
108	4.24	0.337	0.0426	1.125 "	in clean reaction vessel.

5) Runs in the reaction vessel at other temperatures; $diB_h + diB_d$.

Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv	Time mins	D mv
Run 19		Run 25		Run 27		Run 30		Run 32		Run 33	
25	47.5	12	251	20	102.2	30	89.6	16	100.2	22	116.7
50	47.5	17	209	24	99.8	37	96.8	22	108.1	26	120.1
62	47	22	228	29	98.2	50	94.3	28	106.4	30	117.1
97	46	27	216	32	96.9	60	89.0	35	102.4	39	106.6
108	48.6	32	213	40	93.5	86	89.1	46	102.0	48	104.6
121	43	37	216	46	89.5	95	85.6	56	88.8	65	94.4
144	38	42	216	54	90.2	115	79.6	72	93.7	71	94.7
169	40	46	210	65	88.3	125	81.6	94	95.3	88	91.1
175	38	50	210	70	89.3	144	78.4	115	90.7		
225	35	55	206	75	86.1	157	82.2	130	91.8	Run 34	
278	29.5	59	208	85	83.2	168	81.1	150	85.7	22	242.2
		63	201	100	78.8	185	75.9			27	230.8
Run 20		68	205			259	75.1	Run 35		43	214.3
15	95	72	197	Run 28				10	83.5	50	203.7
25	83.5	77	194	16	70.2	Run 31		16	74	60	191
42	76.5	82	197	20	70.3	11	100.8	22	75.9		
60	75	87	195	26	71.6	15	104.3	28	79.5	Run 75	
77	74	92	191	35	72.4	18	107.6	33	77	5	40.4
124	75	98	189	54	68.5	22	104.6	44	74.9	12	37.3
175	74	102	191	116	67.2	30	99.6	54	95.5	30	36.1
227	68	107	185	145	63	35	97.7	63	68.2	47	36.1
275	61	112	182	178	61.7	47	88.8	69	66.6	97	33.1
313	58	116	178			127	85.3	78	64	123	34.9
		200	167			160	66.2	90	69.8	148	33.6
		241	129								
		292	128								
		300	110								

Time mins	Dmv
Run 36	
6	98.1
12	97.1
17	92.1
24	81.9
32	90.1
37	90.1
45	90.4
68	92.5
75	87.2
102	90.5
Run 96	
7	62.8
15	60.9
22	60.5
31	59.1
40	59.9
48	62.8
55	62.8
60	63
68	61.9

Time mins	D mv
Run 74	
7	44
15	35.6
27	33.8
37	33.8
57	31.7
65	32.7
81	32.2
98	33.5
137	38
144	36.8
160	36.4
170	34.7
184	35.3
Run 105	
5	76.8
7	73.7
10	73.2
12	69.7
14	66.9
16	66.9
19	66.7
25	68.6

Time mins	D mv
Run 76	
6	33.8
21	26.3
38	25.9
49	26.5
100	30.0
121	27.8
140	28.6
146	28.9
175	27.0
192	25.5
Run 98	
6	66.9
12	66.6
18	65.7
24	62.8
32	61.9
Run 99	
5	39.6
12	37.7
19	37.8
24	36.6

Time mins	D mv
Run 92	
6	62.4
14	61.7
22	65.2
30	65.4
37	64.2
45	65.6
52	66.4
60	64.9
Run 93	
7	67
15	68.3
22	66.9
30	68
39	66.9
47	66.9
55	67.9
61	65.8
Run 94	
7	64.8
15	72.1
23	67.5
30	66.4
37	62.2
44	64.1

Time mins	D mv
Run 95	
7	61.6
16	61.2
24	60.4
32	59.3
45	61.6
52	61.3
60	58.8
Run 97	
7	68.7
14	65.2
20	64.1
27	62.6
41	59.7
47	60.1
Run 106	
5	71.5
8	69.1
10	69.8
12	66
14	66.8
17	65.6
24	63.8

Time mins	D mv
Run 104	
5	72.9
9	72
11	72.6
14	73.5
16	72.3
20	72.9
23	71.5
30	69.3
37	67.1
45	64.9
52	62.6
60	61.2
70	58.7
81	57.1
93	55.5
106	54.1
120	54
135	51.2
145	49
158	42.9
175	42.4

Run	T°C	mgm.diB	p_{diB}mm.	$k_{1.5}$	
19	452	7.0	0.551	0.0224	in 13.0mm. of nitrogen
20	433	9.0	0.697	0.0101	in 7.7mm. of nitrogen
25	450	mgm.diB unknown		0.0118	
27	450	4.08	0.321	0.0228	
28	402	4.08	0.308	0.0065	
30	428	4.08	0.315	0.0101	
31	478	4.08	0.326	0.0380	
32	443	4.08	0.319	0.0076	
33	465	4.08	0.325	0.0136	
34	455	8.16	0.322	0.0275	
35	450	8.16	0.639	--	
36	450	8.16	0.639	--	
74	440	4.08	0.318	0.0093	
75	440	4.08	0.318	0.0103	
76	440	4.08	0.318	0.0103	
92	445	4.10	0.321	--	
93	447	4.08	0.320	--	
94	455	4.08	0.322	0.0346	
95	432	4.08	0.316	0.0150	
96	428	4.08	0.315	--	
97	469	4.08	0.326	0.0750	
98	475	4.08	0.328	0.1072	
99	475	2.04	0.164	0.0721	
104	484	4.24	0.343	0.0721	
105	493	4.24	0.345	0.1308	
106	501	4.24	0.348	0.1633	
109	464	4.24	0.337	0.0559	in 6.52 mm. of oxygen

6) Products of Runs in sealed tubes at 462°C; diB_h alone.

Run number	83	84	86	87	88	89
Initial diB pressure, mm.	7.5	52	1.7	10.3	72	94.5
Initial mgm. diB	2.1	4.2	2.1	3.1	4.3	8.1
78^+ peak, corrected, mv	33.1	38	17	28.6	24.9	49.2
91^+ peak, corrected, mv	60.2	131.5	30.1	70.2	100.5	229.5
180^+peak, corrected, mv	6.6	10	-	8	10.3	19.5
180^+ from stilbene (- diB)	6.18	9.2	-	7.41	9.31	17.9
178^+peak, corrected, mv	7.7	13.7	-	8.4	12.4	25.1
178^+ from phenanthrene (- diB & stilbene)	3.36	6.8	-	2.98	5.04	11.62
182^+peak, corrected, mv	13.8	26.5	15.9	19.4	32.2	52.0
Toluene / Benzene	2.4	4.5	2.4	3.3	5.3	5.6
Toluene / Stilbene	1.7	2.3	-	1.6	1.8	2.0
Toluene / Phenanthrene	4.5	4.4	-	5.8	4.6	4.0
diB decomposed / Toluene	1.3	1.2	2.3	1.7	1.4	1.4
Carbon balance, %	118	103	-	87	96	95

Notes: Toluene and benzene pressures; and stilbene, phenanthrene, and dibenzyl weights read off mass spectrometer calibration lines (Figure 17).

For toluene and benzene,

$$\text{gm. moles} = p \times \left\{ \frac{0.6}{375} + \frac{2.0}{443} \right\} \times \frac{273}{22.4 \times 760}$$

$$= p \times 97.97 \times 10^{-6}$$

Corrections to 180^+ and 178^+ peaks from cracking pattern ratios:-

Stilbene:- $\frac{178^+}{180^+} = 0.545$. Dibenzyl:- $\frac{178^+}{182^+} = 0.07$; and $\frac{180^+}{182^+} = 0.03$.

Product ratios are in gm. moles.

7) Runs in sealed tubes; diB_h + diB_d; analysis for deuterated toluenes.

Run	Time mins	T^oC	91^+	92^+	93^+	94^+	95^+	$PhCH_3$	$PhCH_2D$	$PhCD_2H$	$PhCD_3$
			---- relative peak heights----								
38	60	450	77.3	116	100	62.2	16.3	1.07	0.87	1.00	0.34
41	60	397	131.5	126	100	68.5	23.7	1.37	0.81	1.00	0.51
42	60	450	112	133	100	66.7	12.1	1.32	0.61	1.00	0.22
43	30	450	96.3	126	100	62.6	10.7	1.19	0.72	1.00	0.21
44	60	418	135	146	100	66.3	10.8	1.53	0.60	1.00	0.19
65	60	414	125	137	100	69.5	15.7	1.43	0.60	1.00	0.28
66	60	414	105	128	100	70.5	19.0	1.32	0.63	1.00	0.36
67	60	414	9.8	34.2	100	110	80.5	0	0.60	1.00	2.22
68	60	433	141	125	100	72	18.5	1.25	0.57	1.00	0.34
69	180	433	127	143	100	74.6	13.4	1.46	0.42	1.00	0.22
78	60	461	134.5	140.5	100	75	10.6	1.37	0.37	1.00	0.16
79	60	461	100	126.5	100	65.6	13.6	1.23	0.68	1.00	0.26
81	60	461	87	109	100	78	17.8	0.95	0.40	1.00	0.29
82	60	461	90	117	100	71.5	20.6	1.13	0.63	1.00	0.39
100	60	465	197	184.5	100	56.5	12.5	2.54	1.00	1.00	0.28
101	60	464	-	117	100	69.5	25	1.20	0.80	1.00	0.54

Run in reaction vessel in 1.15 mm. deuterium.

107	87	461	86.4	102	100	68.3	27.3	0.90	0.92	1.00	0.63

Notes: Run 67: diB_d alone.

Runs 100, 101: diB_h : diB_d = 1 : 1.12 by weight.

All other Runs with equal weight mixture of diB_h + diB_d

'$PhCH_3$' etc. refer to relative molar proportions of toluenes, calculated from the simultaneous equations derived on p. 85.

APPENDIX III.

Dissociation of dibenzyl: calculation of k_f.

Tabulated Results; dissociation of dibenzyl:-

1) Runs in the reaction vessel; equal weights of diB_h and diB_d
2) Runs in the reaction vessel; unequal weights of diB_h and diB_d
3) k_f for all Runs in reaction vessel.

Dissociation of dibenzyl; calculation of k_f.

The equations used have been derived in the text of the Thesis.

For Runs 19 to 99:

$$\frac{k_f t}{2.303} + 0.005 = 0.667 \log (1 + nt) - \log \left\{ 1 - \frac{1.989\,(184^+)}{(184^+) + 2.18(186^+)} \right\}$$

For Runs 102 to 109:

$$\frac{k_f t}{2.303} + 0.005 = 0.667 \log (1 + nt) - \log \left\{ 1 - \frac{1.994\,(184^+)}{(184^+) + 1.97(186^+)} \right\}$$

$$\text{where } n = \tfrac{1}{2} k_{1.5} (A_o)^{\frac{1}{2}}$$

$$\text{Let } R = \log \left\{ 1 - \frac{1.989\,(184^+)}{(184^+) + 2.18(186^+)} \right\} \text{ Or } \log \left\{ 1 - \frac{1.994\,(184^+)}{(184^+) + 1.97(186^+)} \right\}$$

$$\text{and } N = 0.667 \log (1+nt)$$

Then from the observed peak heights of 184^+ and 186^+, R was calculated.

(A_o) was calculated in gm. moles/litre from the initial total mgm. of diB and $k_{1.5}$ from the decomposition results in Appendix II.
Hence n was evaluated.

$$t = \text{time in minutes} = \frac{\text{observed time}}{X} \quad \text{(Appendix II).}$$

From n & t, N was calculated.

The tables of results give the observed peak heights necessary; (- R), which is the expression uncorrected for decomposition; and (N - R), which is the fully corrected expression. There is no need to allow for loss through leak 2 (Appendix II) in the evaluation of R, because of the use of a ratio of peak heights.

(N - R) was plotted against t (corrected time) and straight line of slope g drawn; then since $\log_{10}$ was used in calculations, and t was in minutes,

$$k_f \text{ sec}^{-1} = \frac{2.303}{60} g$$

$$\therefore \log k_f = \log g + \bar{2}.585$$

1) Runs in reaction vessel; equal weights of diB_h and diB_d

Run	Time mins.	184^+ obs.	186^+ obs.	- R	N - R
19	25	4	16	.100	.115
	50	6	13.5	.179	.208
	62	7.5	14.5	.209	.245
	97	7.5	10	.309	.364
	108	9.5	11	.322	.382
	121	8.5	9.5	.375	.442
	144	9	9.5	.400	.478
	169	10	8.5	.520	.609
	175	9.5	9	.456	.548
	225	12	11	.476	.590
	278	9.5	7.5	.570	.705
20	15	4	44	.036	.041
	25	5.5	37	.059	.067
	42	6	30.5	.078	.091
	60	6.5	28	.092	.111
	77	6.5	25	.103	.126
	124	9.5	24	.159	.196
	175	12	22	.221	.272
	227	12	24	.202	.266
	275	14	19	.304	.380
	313	14	19	.304	.389
28	16	4.5	100.5	.0178	.0185
	20	5	103.5	.0191	.0200
	26	5	103	.0194	.0205
	35	5.5	104	.0211	.0226
	54	6	102	.0231	.0255
	116	6.5	97.5	.0264	.0313
	145	5	88.5	.0225	.0291
	178	9	87	.0380	.0461

,Run	Time mins.	184^+ obs.	186^+ obs.	- R	N - R
27	22	22.5	132	.068	.078
	26	24.3	126	.076	.087
	30	27.5	120	.091	.104
	34	30	116.5	.103	.118
	41	39.5	109.5	.144	.162
	48	42	100.5	.167	.188
	55	50	98.5	.205	.229
	66	56.5	91.5	.252	.281
	72	60.5	89	.278	.309
	77	61.5	84	.302	.335
	86	66	81	.340	.376
	101	69	72	.407	.449
30	30	8.5	118.5	.029	.035
	37	10.5	110.5	.039	.046
	50	12	97.5	.049	.059
	60	12.5	84.5	.059	.071
	86	16	84	.076	.093
	95	17.5	83.5	.084	.103
	115	19	75	.101	.123
	125	20	76	.105	.129
	144	24	76.5	.125	.152
	157	26.5	76	.139	.168
	168	27	73.5	.148	.180
	185	25.5	63	.162	.197
	259	40.5	73.5	.223	.270

Run	Time mins	184^+ obs.	186^+ obs.	- R	N - R
31	11	20	96	.084	.092
	15	35	96	.148	.159
	18	45.5	90.5	.205	.216
	22	52.5	85	.253	.269
	30	64.5	72.5	.375	.394
	35	72	62	.511	.536
	47	74	52.5	.658	.691
	127	114	60.5	1.125	1.207
	160	75	38	1.268	1.368
32	16	8	104	.031	.036
	22	11.5	104.5	.043	.050
	28	13.5	97	.055	.063
	35	15.5	88	.070	.080
	46	19	79	.096	.109
	56	19.5	70.5	.111	.127
	72	26	70	.149	.170
	94	34	69	.199	.226
	115	38	61	.254	.286
	130	43.5	60	.298	.334
	150	47.5	55	.362	.403
33	22	39.5	114	.138	.144
	26	45.5	106.5	.171	.178
	30	48.5	96.5	.203	.211
	39	57	84	.278	.289
	48	72	81	.373	.386
	65	80	67.5	.526	.543
	71	81.5	64.5	.572	.591
	88	87	58.5	.712	.734

Run	Time mins	184^+ obs.	186^+ obs.	- R	N - R
70	12	2.5	16	.062	.071
	25	4.5	15	.119	.138
	30	5.5	15	.146	.168
	40	6	13	.186	.215
	48	6.5	13.5	.194	.229
	57	7.5	13.5	.225	.266
	95	8.5	10	.366	.431
	112	12	10	.526	.601
71	5	2	21	.038	.043
	15	4.5	22	.081	.096
	25	7.5	25	.120	.146
	34	11	25.5	.174	.209
	42	10.5	24.5	.173	.215
	54	13	24.5	.216	.269
	62	15.5	24	.264	.324
	74	17.5	22.5	.323	.394
	88	17	21	.336	.418
72	9	5	61.5	.032	.036
	18	14	57	.097	.105
	30	15.5	53.5	.116	.130
	39	21	48.5	.174	.192
	54	25.5	44	.234	.258
	66	28.5	41	.285	.314
	76	32	44	.300	.333
	92	33	35.5	.391	.432
73	7	3	35	.036	.041
	15	6	31	.077	.086
	24	9	29	.123	.137
	38	12	23	.218	.240
	50	14	21.5	.267	.296
	62	15	20	.311	.346

Run	Time mins	184^+ obs.	186^+ obs.	- R	N - R
80	5	5	63	.032	.036
	18	12.5	50	.100	.114
	30	8.5	21.5	.159	.182
	40	9.5	20	.191	.221
	51	10	19	.213	.251
	60	11.5	17	.237	.281
	70	13	16	.338	.389
	82	11	12.5	.370	.429
92	6	5	55	.036	.039
	14	6	53	.049	.054
	22	8.5	54	.067	.075
	30	10	51.5	.077	.088
	37	10.5	49	.086	.099
	45	12	48	.100	.116
	52	13	46.5	.112	.131
	60	13.5	43.5	.124	.145
93	7	5	62.5	.032	.035
	15	8	57	.056	.063
	22	9	51	.070	.079
	30	10.5	49	.086	.098
	39	12.5	46.5	.107	.123
	47	14	44.5	.125	.144
	55	16	43.5	.148	.169
	61	16	40.5	.159	.183
94	7	6.5	62.5	.042	.047
	15	11	56.5	.077	.087
	23	13	50	.103	.118
	30	14.5	46	.126	.145
	37	16	41	.156	.180
	44	17.5	39.5	.178	.206

Run	Time mins	184^+ obs.	186^+ obs.	- R	N - R
95	7	4	52.5	.031	.033
	16	4	50.5	.032	.037
	24	5	47	.043	.050
	32	5.5	43.5	.050	.059
	45	6.5	43.5	.059	.072
	52	7	44	.063	.078
	60	7.5	42	.071	.088
96	7	3.5	52	.027	.028
	15	4	48	.033	.036
	22	4	45	.035	.039
	31	4.5	42	.042	.047
	40	5	40	.050	.057
	48	5.5	41	.053	.062
	55	5.5	39	.056	.066
	60	5	37.5	.053	.064
	68	5	37	.054	.067
97	7	6	58	.041	.051
	14	12.5	46.5	.107	.127
	20	15	40	.150	.178
	27	17	36	.190	.227
	41	19.5	29	.275	.330
	47	21	27	.323	.385
98	6	9.5	45	.084	.097
	12	15	40	.150	.174
	18	18.5	33.5	.210	.246
	24	21	31	.278	.325
	32	22.5	28.5	.328	.389
99	5	5	34	.058	.063
	12	9.5	28.5	.133	.145
	19	14	25.5	.222	.241
	24	15	23	.265	.288

2) Runs in reaction vessel; unequal weights of diB_h and diB_d

Run	Time mins.	184^+ obs.	186^+ obs.	- R	N - R
102	10	10.5	72	.065	.072
	19	14.5	53	.122	.134
	26	18	46	.175	.191
	33	18.5	41	.202	.223
	41	20.5	37.5	.249	.274
	48	21	34	.282	.311
	55	22.5	32	.326	.359
	61	22.5	30	.348	.385
103	9	9	53	.075	.082
	16	11	39	.125	.136
	22	13	34	.172	.187
	29	14.5	29.5	.222	.241
	36	16	27.5	.265	.288
	42	16.5	26	.291	.318
	48	17	24	.326	.357
	55	17.5	21.5	.381	.416
	61	16	20	.377	.416
106	5	28.5	57	.226	.242
	8	33	49	.310	.336
	10	34.5	45.5	.353	.385
	12	34.5	42	.385	.422
	14	39	40.5	.463	.506
	17	40	37.5	.526	.577
	24	42	33	.670	.741
107	6	12	114	.047	.063
	9	15	104	.064	.087
	12	17	99	.076	.107
	15	18	94	.086	.124
	23	22.5	79.5	.126	.183
108	5	5.5	53	.046	.050
	12	8.5	48	.078	.088
	18	10	41.5	.107	.122
	26	12.5	38.5	.145	.166
	34	13	34	.171	.198

Run	Time mins.	184^+ obs.	186^+ obs.	- R	N - R
104	5	21	64	.147	.156
	9	26	57	.205	.221
	11	28	54	.234	.253
	14	32	51	.287	.311
	16	34.5	48.5	.330	.357
	20	37	46.5	.373	.406
	23	40	42.5	.454	.493
	30	41	38	.535	.584
	37	42	33	.666	.725
	45	40.5	29	.770	.841
	52	38.5	27	.796	.876
	60	38	25	.892	.983
	70	36.5	22.5	1.018	1.121
	81	35.5	21	1.119	1.236
	93	34	19.5	1.222	1.353
	106	32	18	1.301	1.446
	120	31	17.5	1.284	1.444
	135	28	16	1.237	1.412
	145	27	15	1.319	1.503
	158	25.5	13.5	1.699	1.895
	175	22	13	1.120	1.331
105	5	13	70	.082	.095
	7	21	56	.168	.187
	10	25	53	.212	.237
	12	26	47	.251	.281
	14	29	43	.310	.345
	16	31	40	.361	.400
	19	33	39.5	.394	.440
	25	37	35	.520	.579
109	10	8	43	.083	.094
	17	10.5	38	.123	.141
	22	14	37.5	.166	.190
	29	14	32	.198	.228

3) k_f for all Runs in reaction vessel.

Run	T°C	mgm. diB_h	mgm. diB_d	log k_f	
19	452	3.50	3.50	$\bar{4}.222$	in 13.0 mm. of nitrogen
20	433	4.50	4.50	$\bar{5}.840$	in 7.7 mm. of nitrogen
27	455	2.04	2.04	$\bar{4}.380$	
28	402	2.04	2.04	$\bar{6}.943$	
30	428	2.04	2.04	$\bar{5}.619$	
31	478	2.04	2.04	$\bar{4}.912$	
32	443	2.04	2.04	$\bar{4}.064$	
33	465	2.04	2.04	$\bar{4}.657$	
70	461	2.04	2.04	$\bar{4}.420$	
71	461	4.08	4.08	$\bar{4}.428$	
72	461	1.02	1.02	$\bar{4}.391$	
73	461	0.51	0.51	$\bar{4}.452$	
80	461	3.06	3.06	$\bar{4}.436$	
92	445	2.05	2.05	$\bar{4}.104$	
93	447	2.04	2.04	$\bar{4}.162$	
94	455	2.04	2.04	$\bar{4}.332$	
95	432	2.04	2.04	$\bar{5}.685$	
96	428	2.04	2.04	$\bar{5}.602$	
97	469	2.04	2.04	$\bar{4}.654$	
98	475	2.04	2.04	$\bar{4}.853$	
99	475	1.02	1.02	$\bar{4}.789$	
102	461	2.00	2.24	$\bar{4}.506$	in 1.92 mm. of argon
103	461	2.00	2.24	$\bar{4}.514$	in 5.75 mm. of argon
104	484	2.00	2.24	$\bar{4}.990$	
105	493	2.00	2,24	$\bar{3}.201$	
106	501	2.00	2.24	$\bar{3}.425$	
107	461	4.00	4.48	$\bar{4}.544$	in 1.15 mm. of deuterium
108	461	2.00	2.24	$\bar{4}.439$	in oxygen-cleaned R.V.
109	464	2.00	2.24	4.553	in 0.52 mm. of oxygen

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