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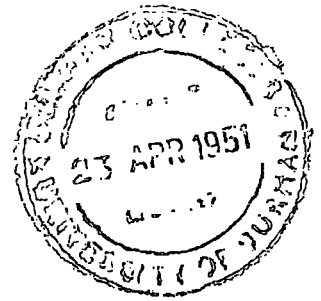
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THESIS

submitted for the degree of

DOCTOR OF PHILOSOPHY

by

R. W. DURHAM, B.Sc., A.R.I.C.

May, 1950

Being an account of research carried out
in the Londonderry Laboratories for
Radiochemistry, Durham University, during
the period 1947 - 1950 under the supervision
of G. R. Martin, B.Sc., A.R.C.S., A.R.I.C.

TITLE

"Radioactive tracer methods applied
to the study of reaction mechanisms."

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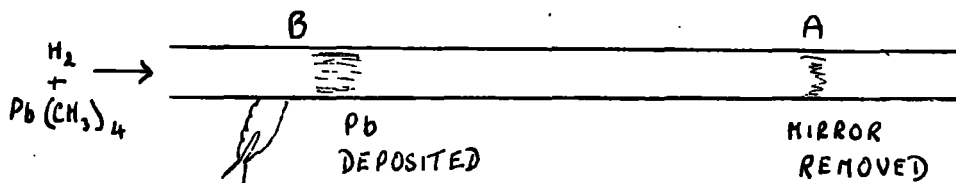
PART I

"An investigation by radioactive
tracer methods of the life period
of free radicals."

INTRODUCTION

The transient existence of so-called "free radicals" was first demonstrated in 1929 by Paneth & Hofeditz (1) and Paneth & Lautsch (2). They investigated the properties of free methyl $\text{CH}_3\cdot$ and free ethyl $\text{C}_2\text{H}_5\cdot$ in various transport gases by using a technique dependent on a high rate of flow of gas at low pressure. The radicals were produced by the thermal decomposition of lead tetramethyl and -ethyl and were found to be extremely reactive. They were detected by their dissolving action on metallic mirrors and this technique has been used by all other investigators due to its sensitivity.

Paneth & Hofeditz made quantitative estimations of the life period of the free radicals by saturating a hydrogen stream with $\text{Pb}(\text{CH}_3)_4$ vapour at about 2 mm. pressure and passing the gas through a quartz tube at about 20 metres/sec. flow rate. This was accomplished by using a mercury diffusion pump backed by rotary oil high vacuum pump.



On heating a point in the quartz tube A with a blow lamp, a mirror of lead was deposited due to the decomposition of the $\text{Pb}(\text{C H}_3)_4$. When next the tube was heated at point B upstream from A a new mirror was deposited but at the same time the mirror at A was gradually removed at a rate proportional to the rate of deposition of the mirror at B. It was found that the presence of small amounts of oxygen in the gas stream stopped removal of the mirror by the radicals probably by coating the metallic mirror with a layer of oxide. In order to overcome this the hydrogen was very carefully purified. This was done by first passing through a bubbler of conc. H_2SO_4 , then over CaCl_2 and P_2O_5 and finally through a charcoal trap cooled in liquid air. Mirrors of Sb, As, and Zn were also removed by the radicals.

In order to investigate the order of the reaction removing the radicals the rate of removal of a standard mirror was taken at various distances along the tube from the point of production of the radicals. This rate of removal of the mirror was found to decrease exponentially with distance point-into to a first order reaction. Paneth & Herzfeld (3) calculated from theoretical grounds that one collision in 1,000 of a free radical with a metal atom in a mirror removed the radical and for a flow rate of 25 metres/sec. in a 5 mm. bore tube, a

lead mirror 1 cm. long removed all radicals reaching it.

Radicals may also disappear by reactions (I) when the transport gas is hydrogen:- $\text{CH}_3 \cdot + \text{H}_2 \rightarrow \text{CH}_4 + \text{H} \cdot$ or

(II) at the walls of the tube:- $2\text{CH}_3 \cdot \rightarrow \text{C}_2\text{H}_6$

(I) will have the appearance of a first order reaction as there is a preponderance of H_2 and also (II) will be of the first order if the radical attaches itself first to the wall becoming deactivated and then sometime later reacts with another $\text{CH}_3 \cdot$ to form ethane. Thus the overall reaction would be first order, although later work showed second order at lower concentrations of radicals. Definite proof that the active particles were in effect free radicals and not activated molecules has been given by chemical investigation of the products of the reaction between the radicals and various metals by Paneth & Loleit (4) and Rice & collaborators (5). Paneth showed the presence of $\text{Zn}(\text{C}_2\text{H}_5)_2$ by freezing out in liquid air the products of reaction of free ethyl with a zinc mirror fractionating the small amounts of condensate and then analysing the $\text{Zn}(\text{C}_2\text{H}_5)_2$. With water the $\text{Zn}(\text{C}_2\text{H}_5)_2$ gave ZnO and ethyl alcohol.

Rice used a different technique in passing the radicals over condensing Hg vapour to form mercury alkyls which then reacted with mercuric halides to give crystalline alkyl mercu-

ric halides with well defined melting points. $\text{CH}_3\cdot$ was identified in the thermal decomposition of acetone. Paneth & Lautsch (6) found that radicals larger than $\text{C}_2\text{H}_5\cdot$ such as propyl and butyl, were broken down to give smaller fragments such as $\text{CH}_3\cdot$ and $\text{C}_2\text{H}_5\cdot$ although later work by Pearson & Purcell (7) has shown the presence of n-propyl in the photolysis of di-n-propyl ketone. It was endeavoured by various workers to increase the accuracy of the "half-life" determination, having obtained clear evidence for the existence of $\text{CH}_3\cdot$ and $\text{C}_2\text{H}_5\cdot$ at low pressures. The half-life period being the time taken for the concentration of radicals to fall to one half of the original value; the value being obtained from $\frac{0.69}{k}$ where k is the first order rate constant for removal of radicals in sec^{-1} . The values of 5.8×10^{-3} sec. for $\text{CH}_3\cdot$ and 3.9×10^{-3} sec. for $\text{C}_2\text{H}_5\cdot$ were obtained by Paneth whilst Rice's figures for $\text{CH}_3\cdot$ vary between 1 and 2×10^{-3} sec. and Pearson (8) quotes a figure of 5.3×10^{-3} secs. Due to the difficult experimental technique results are not always reproducible; Paneth also showed that the half-life increased with the diameter of the reaction tube due to the decrease in removal of radicals at the walls. It was thought that the difficulty in reproducing results was due to the difficulty in producing standard mirrors each time. Pearson therefore used a smoked glass as a standard of compari-

son and distilled the mirror from a pellet of the metal inside the tube (as did Rice and Paneth) until standard and mirror were of similar opacity. Prileshajeva & Terenin (9) used a photometric technique to follow the removal of the mirror.

Leighton and Mortenson (10) were the first to use the radioactive tracer method. (In later work Leighton has returned to the visual control of mirror removal.) They deposited a mirror of RaD in the reaction tube and on freezing out in liquid air the products of the reaction, they were found to have a β -activity due to the growth of RaE. No quantitative results were obtained by this method however, and none either in the work of Burton (11). Burton passed the radicals from cracked CH_3CHO over RaD and then heated the quartz tube downstream from the mirror to deposit the RaD taken up by the radicals. The tube was then cut out at this point, RaD dissolved in HNO_3 , the solution evaporated and then investigated with an electroscope. The present work was made possible by the adaptability of present β -ray counting apparatus and the possibility of access to supplies of radioactive antimony. It was thought that by using mirrors of Sb^{124} and counting the β -particles by placing a Geiger tube over the mirror and outside the reaction tube, a much more accurate estimation of the rate of removal of the mirror would be obtained.

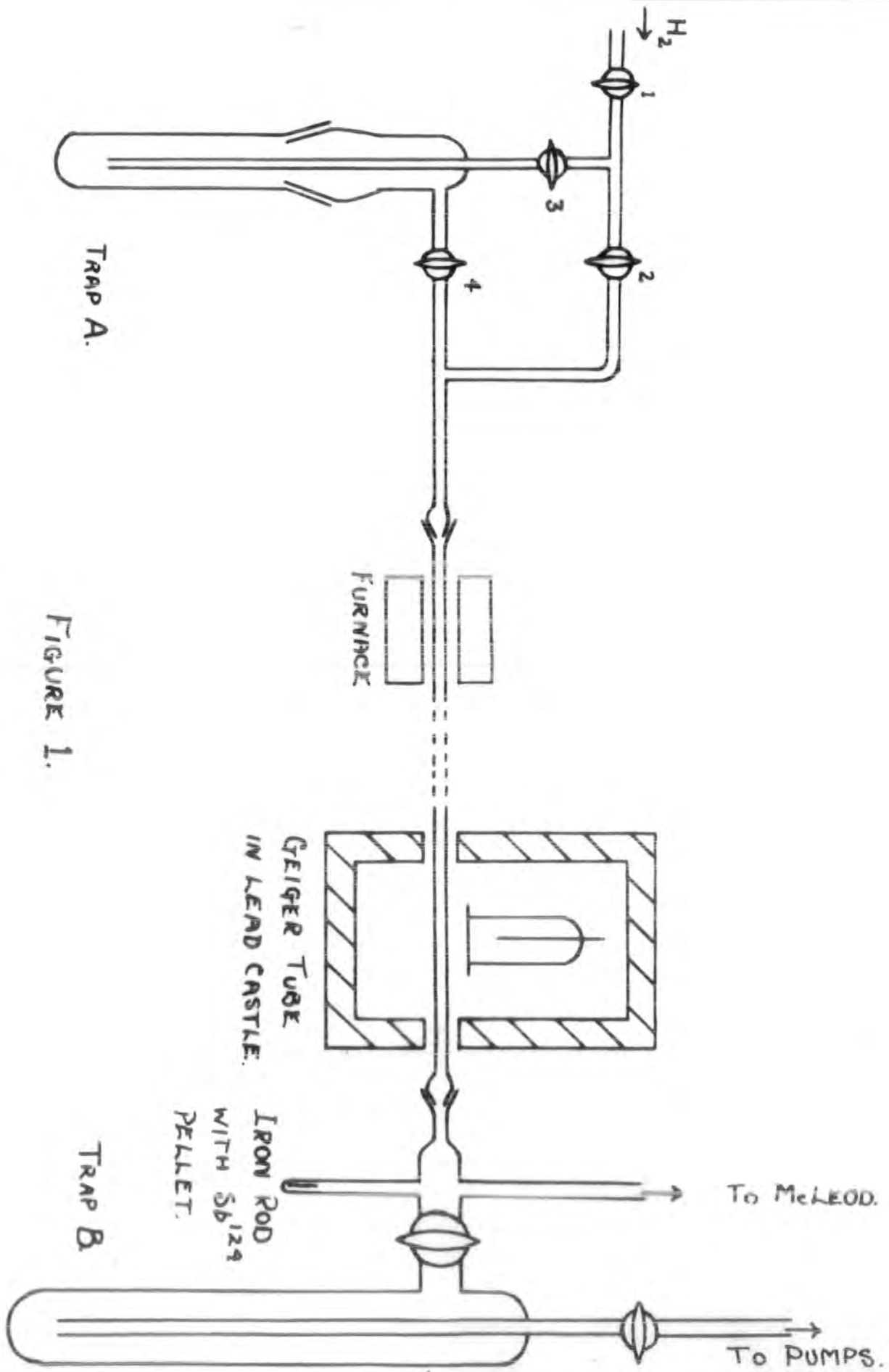


FIGURE 1.

EXPERIMENTS USING INACTIVE MIRRORS

The apparatus used was similar to the original apparatus of Paneth using hydrogen to carry $\text{Pb}(\text{C}_2\text{H}_5)_4$ vapour through the quartz tube. Hydrogen from the action of sulphuric acid on zinc passed through a flowmeter and was purified by bubbling first through $\text{Hg}(\text{NO}_3)_2$ solution, next conc. H_2SO_4 and finally through a charcoal trap cooled in liquid O_2 . $\text{Pb}(\text{C}_2\text{H}_5)_4$ was placed in a trap A; cooled in liquid O_2 , tap 4 opened and the whole apparatus evacuated to remove all traces of oxygen. Trap A was then allowed to warm up and held at -25°C by cooling in a solid CO_2 - acetone bath. By leaving open tap 4 and adjusting taps 1 and 3, a stream of hydrogen could be passed through the apparatus carrying with it $\text{Pb}(\text{C}_2\text{H}_5)_4$ at its vapour pressure at -25°C . The input of hydrogen was adjusted to a rate of about 0.3 ccs. per sec. and the $\text{Pb}(\text{C}_2\text{H}_5)_4$ was frozen out again after passing through the reaction tube by cooling trap B in liquid O_2 . A standard Pb mirror was deposited by heating the point in the tube where the mirror was required for a given length of time with $\text{Pb}(\text{C}_2\text{H}_5)_4$ vapour passing through the tube. Mirrors were about 2 cm. long and opaque in normal lighting.

At the commencement of a run taps 1 and 4 were shut off and the electric furnace which was 3 cms. long was allowed to

reach 500°C, read off from a copper/constantan thermocouple placed in the centre of the furnace between the furnace barrel and the quartz tube. Taps 1 and 4 were then opened together simultaneously with the starting of a stop watch and the time taken for the mirror to disappear completely. The distance between the production and removal of the radicals was taken to be the distance from the end of the furnace to the centre of the mirror. The mirrors were gradually dissolved away from the front edge first in this series of experiments. The time of removal was taken from the instant of introduction of $\text{Pb}(\text{C}_2\text{H}_5)_4$ to the furnace until the last traces of mirror were removed. The time of removal was of the order of several minutes and increased exponentially as the distance of the mirror from the furnace increased.

The total pressure in the tube was read off on a McLeod gauge. During a run it was possible to keep the flow rate reasonably constant by adjusting the input rate of hydrogen. The linear flow rate through the reaction tube was estimated by converting the volume of hydrogen entering at atmospheric pressure as measured on the flow meter to the pressure obtaining in the tube and dividing by the cross-sectional area of the tube. Knowing the linear flow rate of gas through the tube, the time for a radical to traverse it can be calculated.

CALCULATION OF RESULTS

Rate of flow in reaction tube

$$\begin{aligned}
 \text{H}_2 \text{ input at S.T.P.} &= 0.3 \text{ cc./sec.} \\
 \text{Pressure in tube} &= 0.20 \text{ mm. Hg} \\
 \text{Radius of tube} &= 4 \text{ mms.} \\
 \text{Rate of flow} &= \frac{0.3 \times 760}{0.167 \times 0.2 \times 100} \text{ metres/sec.} \\
 &= \underline{22.7 \text{ m/sec}}
 \end{aligned}$$

Half-life period

Dist. "D"	Time radicals take to travel dist. "d"	Time "t" of removal of mirror	Activity "A" = 1/t	100 Log ₁₀ A
6 cms.	2.6 x 10 ⁻³ secss.	2 mins	0.5	1.7
9	4.0	4	0.25	1.4
18	7.9	10	0.10	1.0
22	9.7	16	0.06	0.8

For a reaction of the first order

$$k = \frac{2.3}{d} \log \frac{A_1}{A_2}$$

By plotting values of log A against "d" a graph can be obtained from the slope of which "k", the first order reaction constant, can be calculated. Then, $T_{\frac{1}{2}} = \frac{.69}{k}$

DEPENDENCE OF HALF LIFE ON TUBE DIAMETER

Prior adsorption of free radicals on the walls of the reaction tube would cause first order removal of radicals from the gas stream through a heterogeneous process. The recombination activation energy for two radicals is almost certainly zero and in the presence of an acceptor (i.e. the tube wall) for the excess energy, the reaction would be extremely rapid. This would lead to the removal of a radical at almost each collision with an adsorbed one and depending on the amount of adsorption, could be a prime factor affecting the life period of the radicals.

An estimate of the importance of this effect can be made by observing the half life of the free radical under conditions in which the surface to volume ratio of the reaction tube is altered. In Graph I are plotted results for the half life of free ethyl obtained by the classical mirror technique, first in a quartz tube of radius 4 mms. and then in one of radius 2 mms. The ratio of surface to volume for a cylinder is given by:-

$$\frac{2\pi rL}{\pi r^2 L} = \frac{2}{r}$$

This means that the ratio for the 4 mms. tube is half

I

○ TUBE RADIUS 4 mm.

□ TUBE RADIUS 2 mm.

← $\log_{10} A$

0.5

1.0

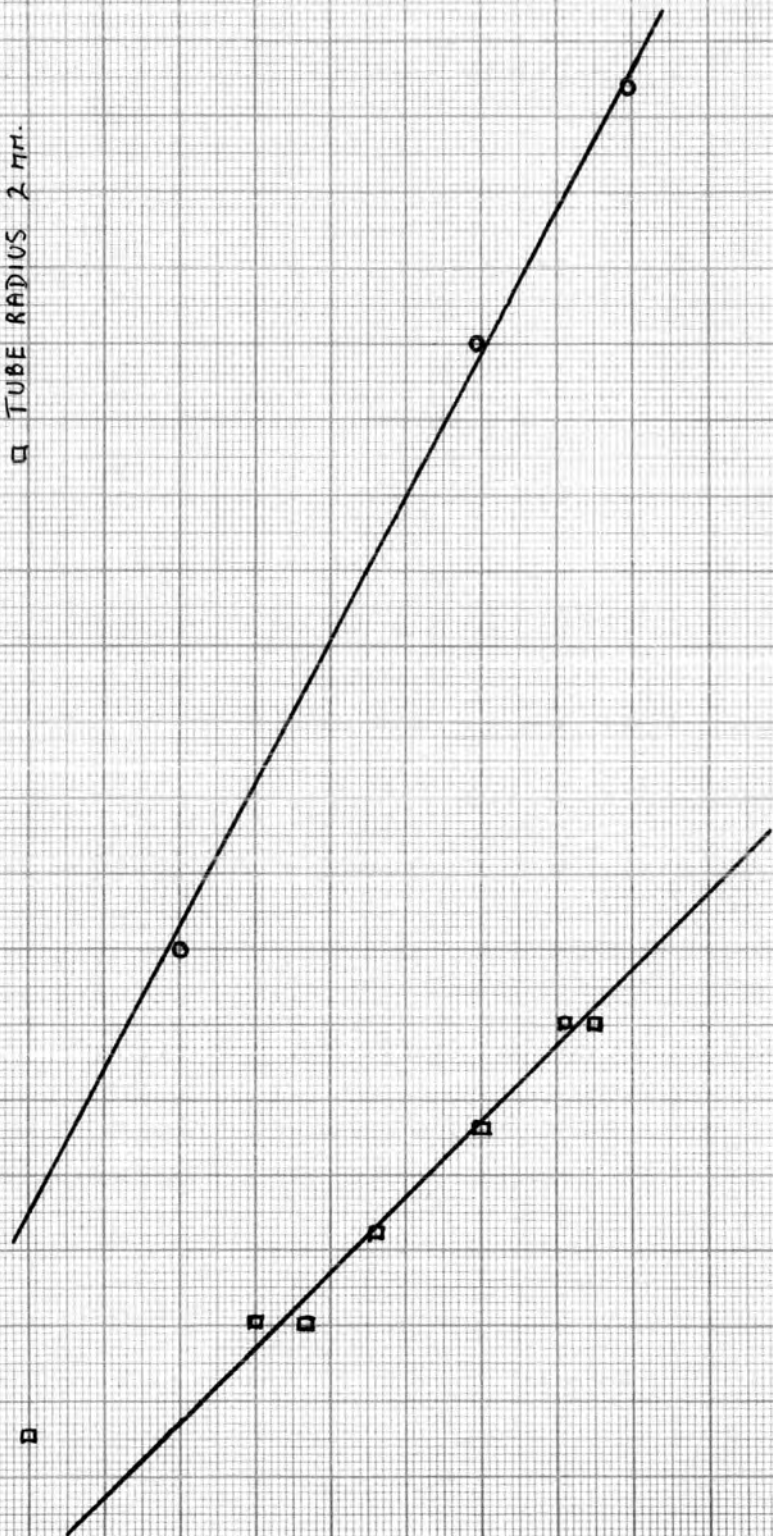
1.5

5

d'

→

10×10^{-8} sec.



that of the 2mms. one.

We now obtain from the slope of the Graph I for the 4 mms. tube

$$\begin{aligned} T_{\frac{1}{2}} &= \frac{0.69}{2.3 \times 1.1 \times 10^2} \\ &= \underline{2.7 \times 10^{-3} \text{ secs.}} \end{aligned}$$

and for the 2mms. one

$$T_{\frac{1}{2}} = \underline{1.5 \times 10^{-3} \text{ secs.}}$$

Thus almost a two fold increase in life time is obtained by halving the surface to volume ratio. Substitution of nitrogen for hydrogen as a carrier gas was found by Paneth and co-workers to have little effect on the half life whereas heating the walls of the tube which would tend to decrease adsorption of radicals, increased it appreciably. These results show that by far the greater number of radicals in the gas stream disappear by a first order recombination or disproportionation reaction at the walls of the tube.

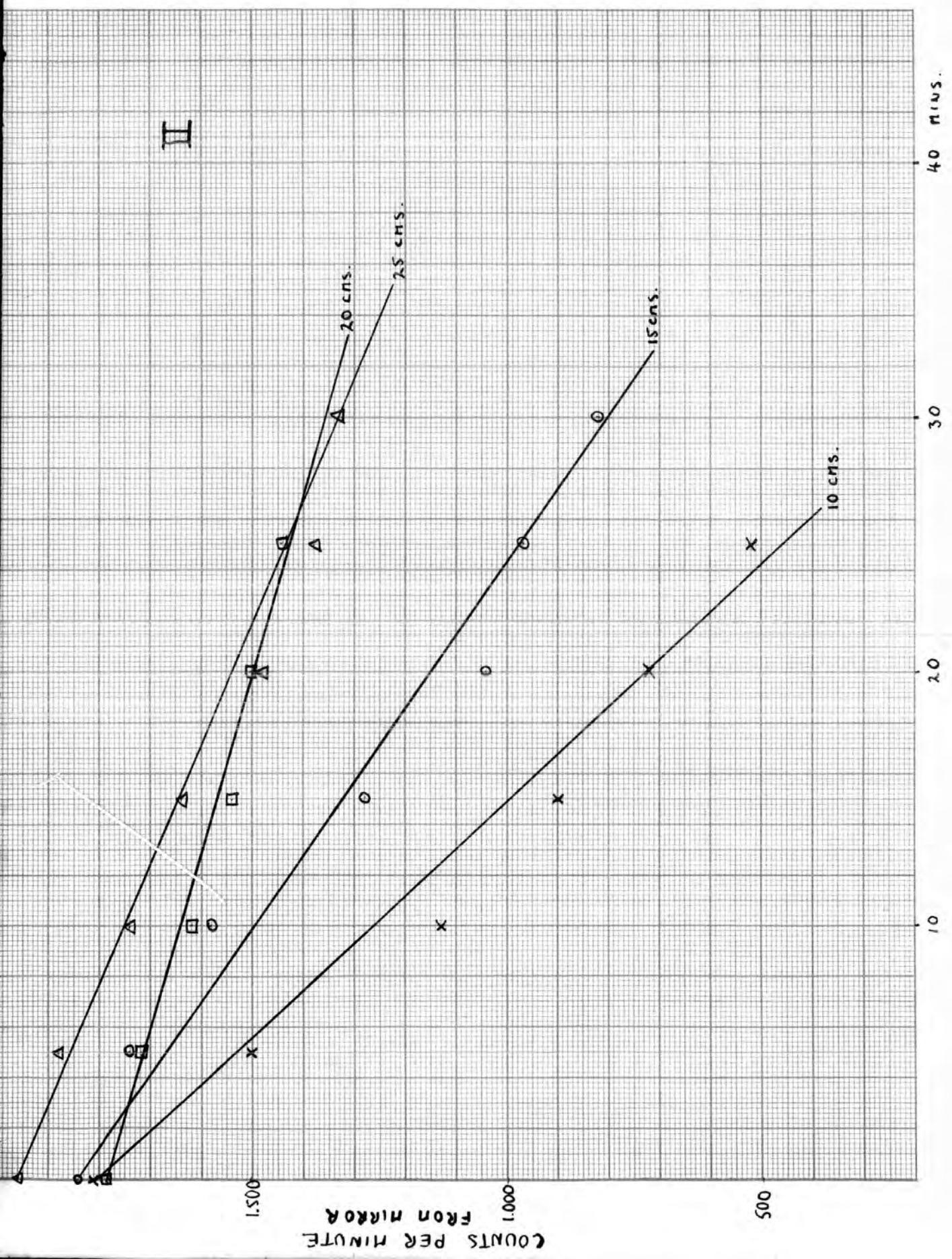
EXPERIMENTS USING RADIOACTIVE MIRRORS

A similar apparatus was used for the tracer experiments, having a quartz reaction tube, 2 mm. in radius, the main difference being the portable counter used to investigate the rate of removal of the active mirror. A sidearm also was attached to the apparatus in which rested a small tube, open at one end, which contained a pellet of Sb^{124} and which had a steel nail sealed into it. This was moved into the reaction tube by means of an external magnet and by heating the tube at this point with a blow torch, a mirror of Sb^{124} could be deposited. The antimony pellet was then moved back to the sidearm and the Sb^{124} mirror distilled down the tube in a stream of H_2 to the desired position. It was found that the mirrors were unreactive unless distilled along the tube previously in the H_2 stream, probably because of a film of oxide on the mirror surface. The Geiger tube was mounted above the mirror and at right angles to the axis of the reaction tube and at first the only attempt at standardization of the mirrors was to obtain a similar total count each time. The Geiger tube and reaction tube were surrounded by a lead castle and two minute counts were taken every five minutes with the radical stream passing. The count being plotted against the time, the slope of the graph gave the rate of removal of the mirror and hence the activity "A" X

distilling Sb^{124} down the tube has a thick leading edge, gradually decreasing in thickness to the edge farther away from the furnace. When this thin section is removed the mirror does not remove all the radicals and hence the rate of removal decreases. This effect showed that the mirror was no longer being attacked from the leading edge first. The high flow rate of gas in these experiments must enable some of the radicals to traverse the mirror without reacting.

High pumping speeds were used here so that the rate of decay of radicals could be investigated over as small a range of concentration change as possible. This is necessary because it has been shown that for low concentrations of radicals the first order kinetics break down and second order removal of radicals is important. Thus it was found by Paneth, Hofeditz and Wunch (30) and also by Norrish and Porter (31) that for distances corresponding to more than a half life the first order decay plot fell off and approached that of a second order reaction. Porter's reason for this was that the no. of radicals absorbed on the walls decreased below a certain critical concn. in the gas phase and the rate of combination of radicals became dependent on the square of the concentration in the gas phase.

II



LOG₁₀ A

0.25

0.50

0.75

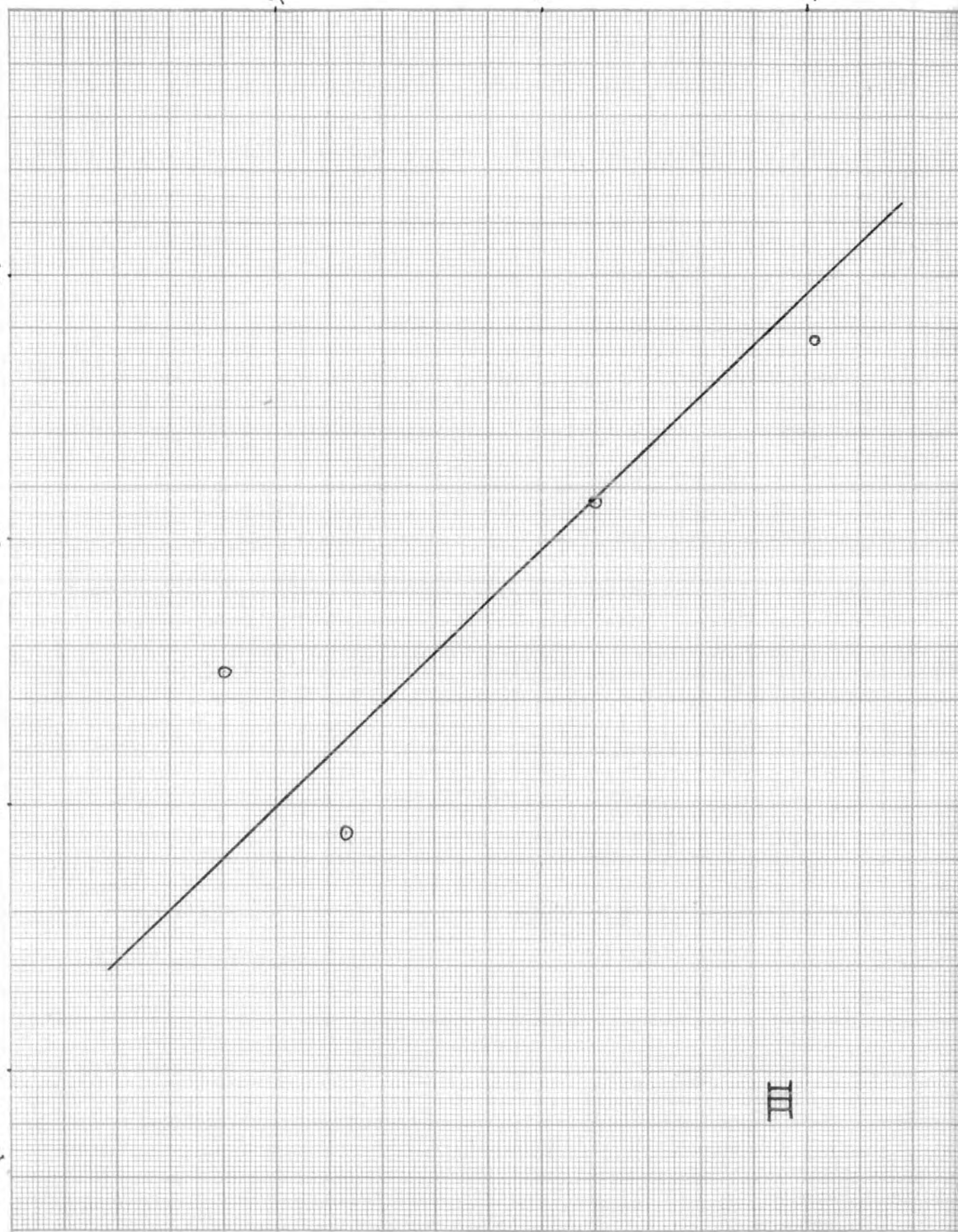
1.0

2.0

3.0

4.0 x 10⁻⁵ sec.

III



Contrary to the work of Prileshajeva & Terenin (9) no induction period was noticed before the mirror began to be removed on first passing the radicals.

From Graph II the rate of removal of the mirror at different distances was obtained and on Graph III the logarithms of the removal rates were plotted against the time for the radicals to traverse the distance from the furnace to the mirror. The point on Graph III representing the rate of removal of the mirror at 20 cms. is much too low and is probably caused by the mirror being impure. The production of clean mirrors was very difficult even when extremely pure antimony was used. Possibly the Sb¹²⁴ mirror was contaminated by carbon or other decomposition products of $Pb(C_2H_5)_4$ picked up from the walls of the reaction tube because it was found that a clean mirror was more easily obtained after several mirrors had been distilled down the tube.

The slope of this graph gave a value of $6.45 \times 10^2 \text{ sec}^{-1}$ for "k", the monomolecular rateconstant, from which the "half-life period" is seen to be 1.1×10^{-3} secs.

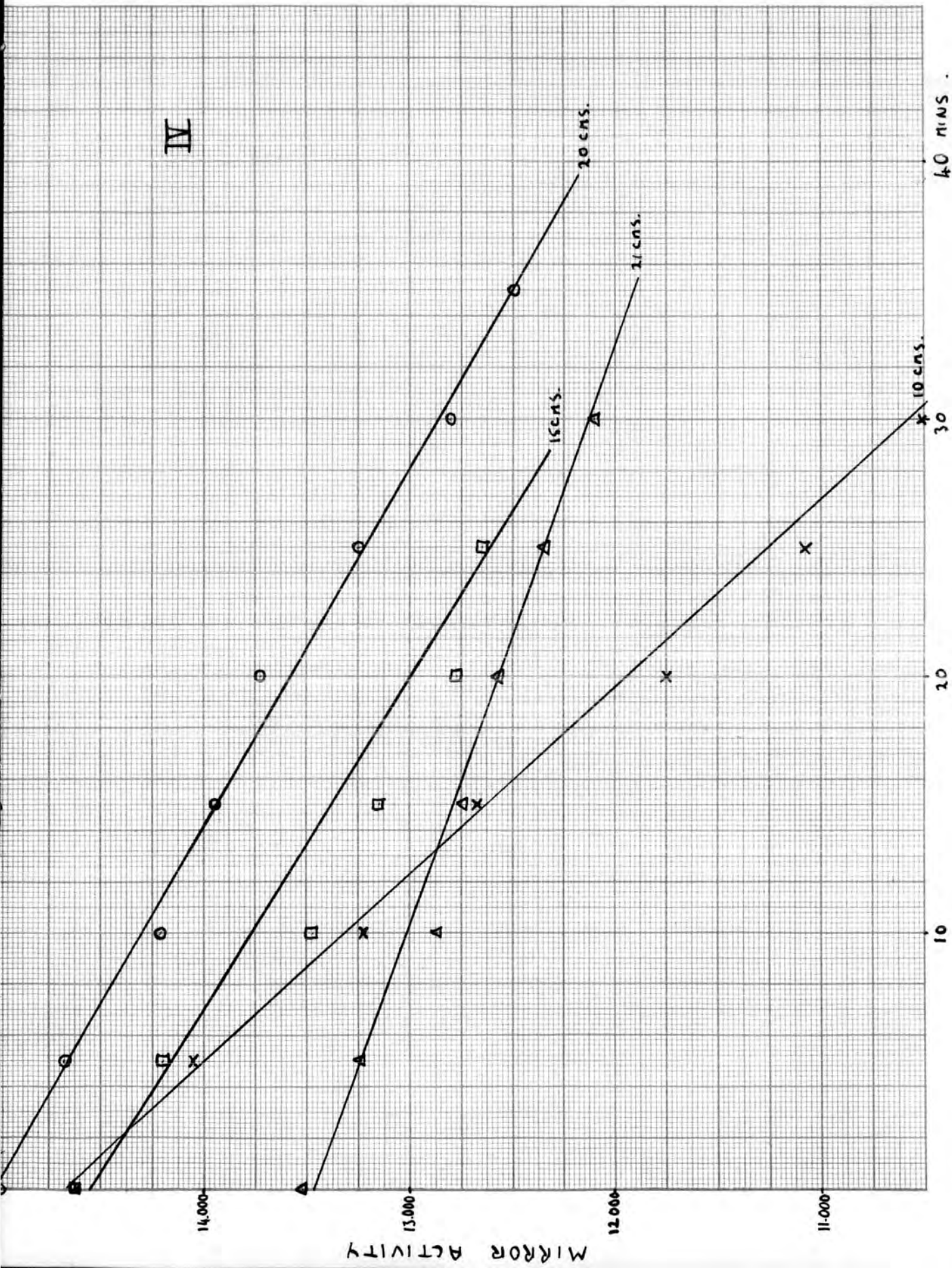
SECTION B

Experiments were next carried out in order to obtain a constant rate of removal of the mirror; in previous experiments it was noticed that with thin long mirrors, the counting rate decreased exponentially instead of linearly as would be expected.

First of all a longitudinal Geiger tube was used in place of the end window type used in previous experiments. With this type of tube the counting efficiency would not alter with a decrease in size of the mirror as long as the β -ray sensitive section of the tube was larger than the mirror. Several runs were tried using this counter but due to the lower sensitivity of this type of counter, the low count obtained from the mirror decreased the counting accuracy so much that the results could not be relied on.

In a paper by Paneth & Herzfeld (3) it was shown from theoretical considerations that a mirror 1 cm. in length was sufficient to remove all radicals passing over it. It was decided therefore to produce a standard mirror each time of this length and of uniform thickness. This was done by distilling a mirror rather longer than 1cm. into the required position in the tube with H_2 passing through, then cutting off the H_2 supply and heating the trailing edge of the mirror

IV



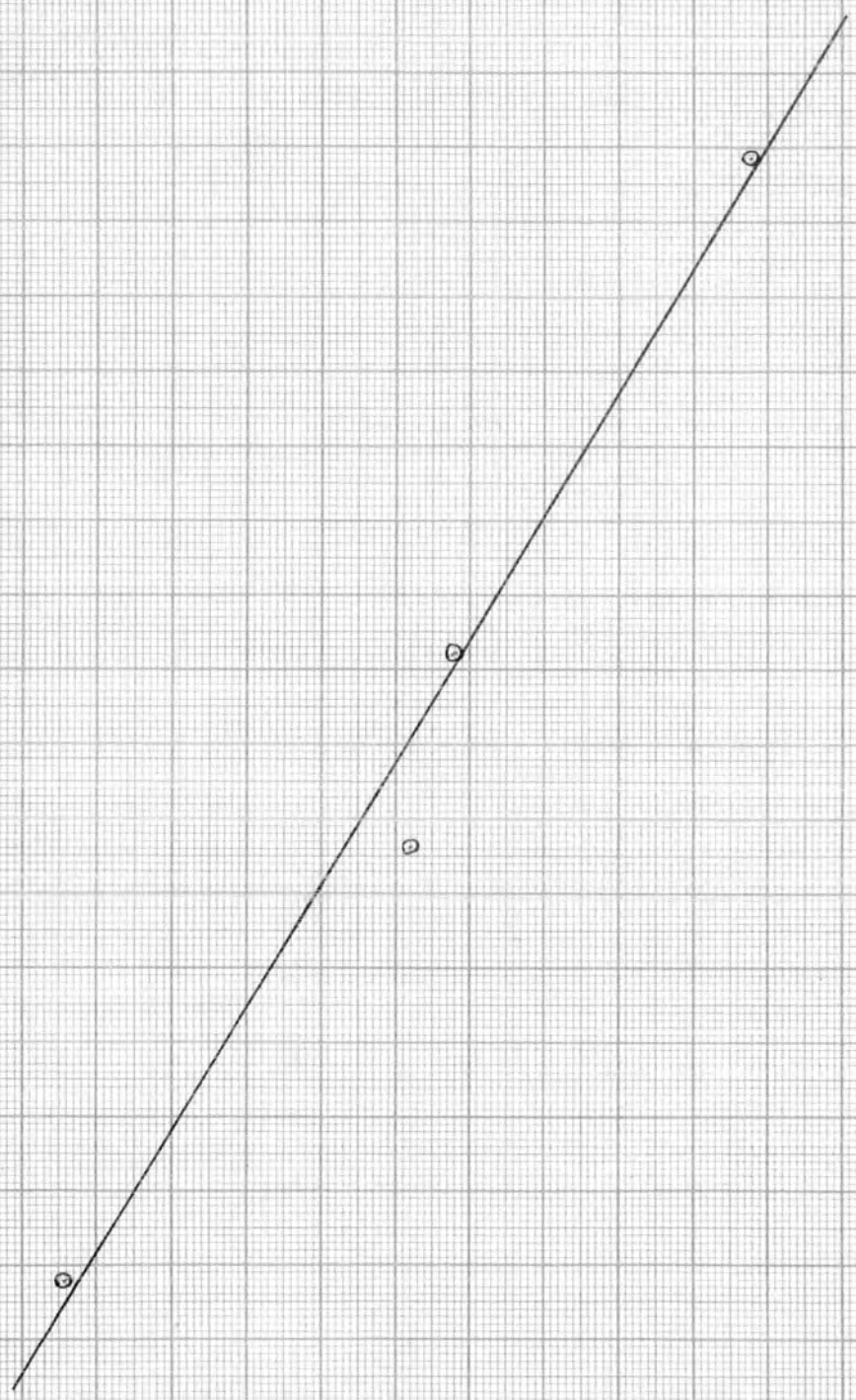
V

0.521

0.001

0.510

$\text{Log}_{10} A$



2.5

3.0

3.5

4.0 $\times 10^{-1}$ SEC.

in order to distil the excess onto the thin section at the rear. It was found by using a standard mirror of this type each time and using an end-window type Geiger tube mounted vertically, that a constant decrease in rate of counting for periods of over an hour could be obtained.

In order to increase the accuracy of counting, runs were tried using Sb^* immediately after it had been irradiated. It then contained an appreciable amount of the short lived Sb^{121} with a half-life of 2.5 days and therefore had a much higher specific activity. Graphs IV and V show results obtained using the standard mirror and Sb^* with a higher specific activity. The furnace temp. was again $500^{\circ}C$, the $Pb(C_2H_5)_4$ trap at $-25^{\circ}C$ and the pressure in the reaction tube about .5 mm. Hg. The value for the half life period obtained by the usual calculation is 1.0×10^{-3} sec.

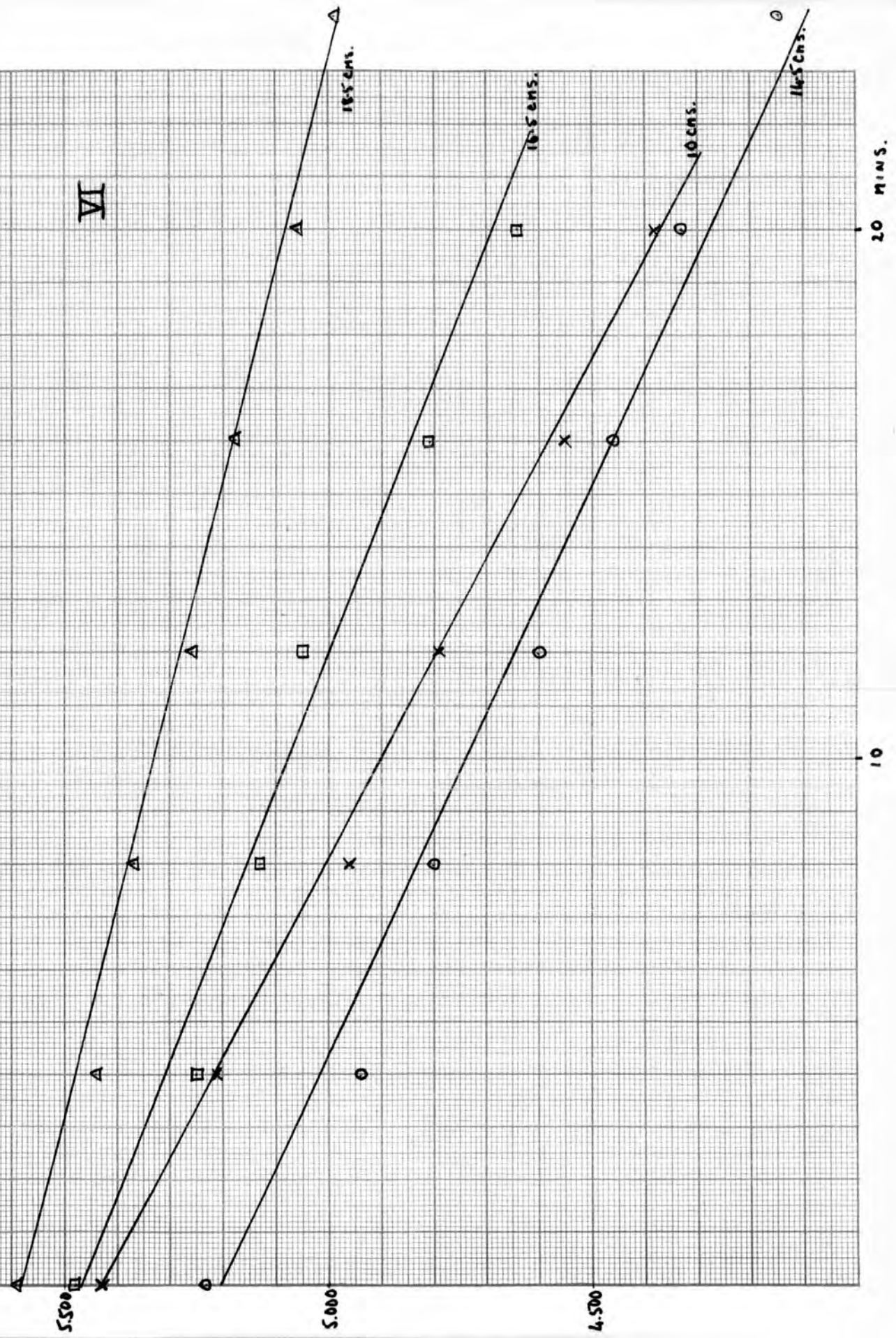
SECTION C

During a series of runs using $\text{Pb}(\text{C}_2\text{H}_5)_4$ as the agent for producing free ethyl, a heavy deposit of lead was produced downstream from the furnace and it was thought that this probably cut down the concentration of free radicals entering the reaction tube. It was decided therefore to use some other agent which was known to give free radicals but which had no solid thermal decomposition products. Acetaldehyde had been used by several workers and apparently given good yields of free methyl. In the present apparatus however only poor yields of free radicals were obtained when the furnace temp. was between 500° and 600°C . Complete decomposition appeared to take place and amounts of carbon were deposited behind the furnace.

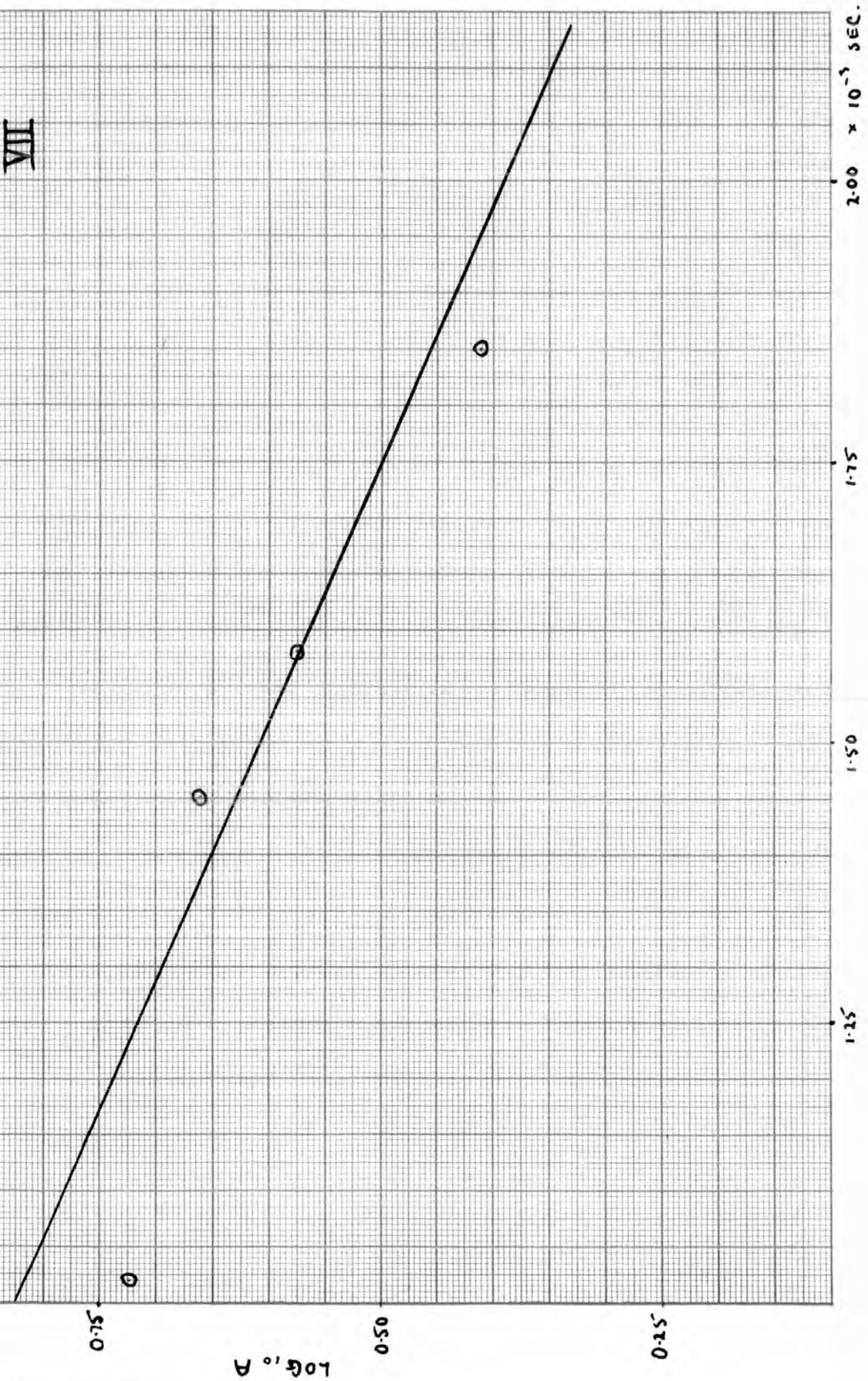
Azomethane was next tried after a difficult preparation by the method of Thiele(12). Here again carbon was deposited even when the temperature of the furnace was such that only low yields of radicals were obtained.

As the maximum furnace temp. obtainable with the apparatus was about 650°C a substance with a low activation energy was desirable in order to obtain reasonable yields of radicals. Rice (13) showed that trimethylamine produced free methyl on thermal decomposition and calculated

VI



VII



its activation energy to be 50.8 Kilocals. The activation energy of triethylamine should therefore not be very much greater than this and as a supply was to hand it was decided to investigate this with a view to producing free ethyl. Experiments showed that good yields of free radicals could be obtained from triethylamine and the similarity in half-life period to the radicals from $\text{Pb}(\text{C}_2\text{H}_5)_4$ suggests that they are in fact free ethyl radicals. In runs using triethylamine no carrier gas was used. Taps 1 and 4 in fig. I were closed during a run, the triethylamine vapourizing into the reaction tube through taps 3 and 2. Also trap A was changed for a graduated trap in which the liquid level could be read to .01 ml. Readings were taken of the $(\text{C}_2\text{H}_5)_3\text{N}$ level every 2 mins. during a run and the readings plotted against the time in order to obtain the rate of evaporation. In this way a more accurate estimate of the gaseous flow rate through the reaction tube could be obtained. From Graphs VI and VII a value of 0.9×10^{-3} secs. is obtained for the half life period.

CONCLUSION

The use of radioactive antimony mirrors does not seem to have increased the accuracy in measuring the half life of free radicals. The main difficulty arises in producing pure mirrors; these laid down by distilling metal from a pellet down the tube appear to become contaminated by impurities picked up from the walls. Thin mirrors formed by heating the tube whilst alkyl vapour is passing are the more reactive and enable reproducible results to be obtained even with non-radioactive mirrors. In order to synthesise radioactive antimony alkyls to give sufficiently active thin mirrors, antimony with a higher specific activity would be required. Present neutron sources however are not sufficient to do this.

The values for the half life period of the ethyl radical obtained in the previous experiments are of the same order as these quoted by other workers in the field. The fact that the main reaction which removes radicals in flow experiments is heterogeneous and therefore depends for its rate on the nature of the reaction vessel and its surface to volume ratio, makes it impossible to attach any significance to the absolute values enumerated. The reactivity to a given radical of the metal used in forming mirrors has been found

to differ widely from one persons experiments to another. This again emphasises the necessity of using extremely pure mirrors and inhibiting surface oxidation.

When estimating the concentrations of free radicals by using the mirror technique in a flow system the greatest drawback is that the whole of the radicals are removed from the reacting system. This means that their concentrations cannot be found whilst they are taking part in a reaction without disturbing the equilibrium. Radical concentrations must then be calculated from a prior knowledge of the rate of the radical producing reaction and the activation energy required for reaction between a radical and a gas molecule on collision. The importance of knowing the order of the life time of a free radical under given conditions of collision with gas molecules or reaction vessel walls arises from the large number of reactions in which their transient existance occurs. In polymerisation, thermal decomposition and oxidation reactions of hydrocarbons in the gas phase it is useful to be able to calculate whether a free radical produced by a primary process will act as a chain carrier or will be deactivated too rapidly by collision with inert molecules.

The next chapter describes experiments carried out with a view to measuring the stability of free radicals undergoing collisions in the gas phase.

PART II

"A kinetic study of the thermal decomposition of the n-propyl radical."

INTRODUCTION

After the firm establishment of the constitution of free methyl and ethyl by the work of Paneth, Rice and their collaborators, a search was made for gaseous free radicals having a longer chain of carbon atoms. The first attempt was by Paneth and Lautsch (2) who decomposed $\text{Pb}(\text{n-C}_3\text{H}_7)_4$ and $\text{Pb}(\text{iso-C}_4\text{H}_9)_4$ in their apparatus at 400°C and passed the resulting radicals over Sb mirrors. No propyl or butyl compounds of antimony however were found in the products of the reaction, only bis-dimethyl antimony. From this they gathered that if the propyl and butyl radicals did exist, they had an extremely short lifetime before they decomposed to give the free methyl radical and unsaturated hydrocarbons. They tried again later (6) using a different method of radical production in order to keep down the temperature of the reaction and hence the amount of decomposition of the radical. Electrical discharge and the reaction between sodium and alkyl halide were the low temperature methods employed but they failed also to give propyl, butyl or phenyl radicals. The benzyl radical however was detected in decomposing $\text{Sn}(\text{Bz})_4$; it was characterised by means of dibenzyl selenide and mercury dibenzyl. It is probable that appreciable amounts of propyl radicals were present at the mirrors in the

experiments of Paneth and Lautsch even at 400°C as results given later in this work will show. The small amount of alkyl antimony products resulting from the reaction of propyl and methyl radicals with antimony mirrors would be extremely difficult to analyse and would account for the author not identifying free propyl. Rice (14) suggested that free propyl decomposed to give free methyl and ethylene and endeavoured to increase the backward reaction by using ethylene as a carrier gas for the propyl radical. He only detected free methyl however and proposed that all gaseous free radicals having more than two carbon atoms decompose rapidly above 450°C . He estimated the activation energy of this decomposition reaction to be about 25 K.cals.

Following this was a report by Rice and Evering that was opposed to the theory of higher radicals being short-lived and unstable (15). They claimed to have detected long-lived fragments in the decomposition products of acetone-azoisopropane mixtures by the mirror technique and suggested they were propyl radicals. The products of these fragments with metallic mirrors were not investigated however and the conclusions arrived at from their observations were probably not justified.

The first reliable indications of the existence of free propyl came from the work of Bamford and Norrish (16) on the

photolysis of di-n-propyl ketone. They found that the products of the reaction were hexane and carbon monoxide and proposed that free propyl was the initial product of the reaction, two such radicals uniting to give hexane. Proof of this mechanism was given by Pearson and Purcell (7) who irradiated di-n-propyl ketone with ultra-violet light, using a streaming method and passing the products of the photolysis over distilling mercury. The organo-mercury compounds so formed were reacted with mercuric bromide and fractionally sublimed, when a product was obtained identical with n-propyl mercury bromide. This showed the n-propyl radical to be reasonably stable at room temperature; furthermore it was found to have a life-time comparable with that of free methyl.

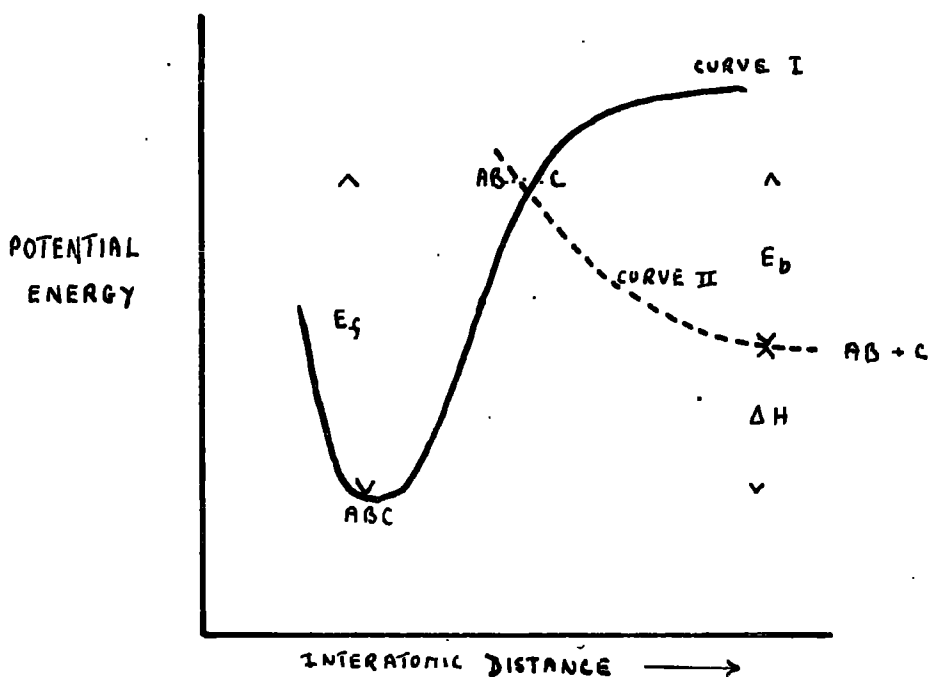
From the foregoing it would appear that the n-propyl radical decomposes at temperatures not far removed from normal and to be completely transformed at about 400°C. However Steacie and Dewar (17) found H₂ and hexane to be the main products of the mercury sensitized photolysis of propane at 310°C, so that only a small amount of decomposition of free n-propyl can have taken place even at so high a temperature as this. Likewise Allen (18) reacted free methyls with propane at the same temperature and obtained butanes as products which undoubtedly came from the interaction of free methyls

and n- and iso-propyl radicals, again demonstrating the thermal stability of the propyl radical at 310°C.

On this basis the Polanyi method of producing free radicals (19) by reacting sodium atoms with the corresponding alkyl halide is feasible for producing propyl radicals. A vapour pressure of 10^{-3} mms. Hg of sodium can be obtained at 250°C. and negligible decomposition of propyl radicals should result. It was therefore decided to investigate the thermal stability of the n-propyl radical using the sodium "flame" technique of Polanyi in order to produce the radicals. A method involving the use of radioactive iodine was developed for the detection and estimation of the methyl and propyl radicals present after the radicals stream had been subjected to the cracking process.

REACTION KINETICS

The rate and activation energy of a reaction can usually be calculated with a fair degree of accuracy from published thermochemical data and the following is an outline of the theoretical considerations necessary. We shall consider a unimolecular reaction in which a molecule ABC breaks down to give AB and C.



In the above diagram Curve I represents the variation of potential energy of ABC as the distance between B and C is increased; exchange forces are involved here which are attractive in character. As C moves farther away, the bond between A and B will increase in strength and hence the interatomic distance between them will decrease. These three variables can only be plotted on a three dimensional graph. However if the two variations in bond length have co-ordinates at right angles to each other in the same plane, contour lines joining points of equal energy, an energy surface will be obtained. The above diagram will then

correspond to a section at right angles to this surface along the line of reaction. The minimum in the curve represents the zero point energy of ABC and is equal to the heat of formation. The asymptote at the fullest extension of bond B-C corresponds to the dissociation energy required if no other process interfered.

Curve II illustrates the effect of the repulsive forces between the products of reaction AB and C as they approach each other. The point of crossing of the two curves depends on the strength of the bond that is formed between B and C; if it is strong then Curve II will be comparatively flat and the interaction energy will be low. The crossing point corresponds to the formation of an activated complex $AB..C$ which holds an equilibrium position, it has the possibility of either reverting to the original molecule or splitting and following Curve II. The rate at which the activated complex takes the second course is the measured rate ^{of} the forward reaction. The activation energy E_a is the difference in potential energy between the energy level of the activated complex and the zero-point energy of the reactant; it is obtained from the sum of the heat of reaction and the activation energy E_b of the reverse reaction. This latter

value is sometimes known experimentally or if not, as it is usually small, an estimate can be made without too much loss of accuracy.

During reaction the energy required to produce the activated complex is transferred to a small number of molecules by collision. These molecules then becoming "activated" i.e. having an energy content greater than the activation energy. These activated molecules must be deactivated by collision at a rate similar to the activation rate in order that a state of equilibrium may be reached. When this equilibrium concentration of activated molecules is produced, the frequency of molecular collisions does not decide the rate of reaction but rather the rate at which the activated complex is produced. The "activated complex" describes activated molecules in which the energy of activation is concentrated in the direction of the reaction coordinate. In complicated molecules this rearrangement of energy will take a correspondingly longer time and for a given concentration of activated molecules reaction will be slower. The rate of reaction will then depend on the velocity with which the activated complex spontaneously decomposes. This is illustrated by the following equations.

Let the concentration of activated molecules be 'a' and that of normal molecules 'c' ; the rate of reaction is

$$-\frac{da}{dt} = K_1 a$$

This will be the difference between activating and deactivating rates, i.e.

$$\begin{aligned} K_1 a &= K_2 c^2 - K_3 ca \\ &= \frac{K_2 c^2}{1 + \frac{K_3}{K_1} c} \end{aligned}$$

and as long as the concentration of normal molecules is high enough, will approximate to

$$-\frac{da}{dt} = \frac{K_1 K_2}{K_3} C$$

and will have first order characteristics.

If however the concentration drops to a low value such that $\frac{K_3 c}{K_1}$ is small compared with 1, then

$$-\frac{da}{dt} = K_2 C^2$$

and the reaction will follow a second order law. One method of maintaining the frequency of activating and deactivating collisions is to add an inert gas, such as nitrogen, in vapour phase reactions thus keeping first order characteristics at low pressure of reactant.

The rate constant is dependent on temperature and a semi-empirical relationship was evolved by Arrhenius to relate the two properties. He proposed that the rate constant

$$k = A e^{-\frac{E}{RT}}$$

where 'E' is the activation energy and 'A' is a frequency factor of the order of 10^{13} sec⁻¹ and being independent of temperature. A more refined equation has been proposed by Eyring after it was found that the frequency factor in the equation of Arrhenius was not strictly independent of temperature. This equation was reached from a statistical mechanical treatment of rate processes and is as follows.

$$k_{uni} = K e^{\frac{kT}{h}} e^{-\frac{E}{RT}} e^{\frac{\Delta S^\ddagger}{R}}$$

ΔS^\ddagger is the change of entropy of the system on forming the activated complex and 'K' is the transmission coefficient. K is a measure of the probability that once formed the activated complex will decompose; it is usually taken as unity for a unimolecular reaction.

A calculation of the activation energy from a knowledge of the absolute rate at a certain temperature would be feasible if the value of the entropy factor were known. Estimation of this would be difficult however as the exact configuration of the activated complex cannot be decided as resonance effects tend to lower its potential energy. By obtaining values for the rate constant at various temperatures a more accurate value for the energy of activation may be obtained. On inspection of the above equations it is

seen that logarithmic differentiation yields the same result in both cases, assuming the entropy change remains constant viz

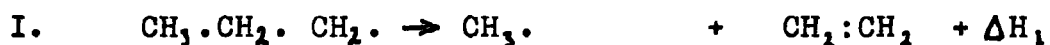
$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

Thus a graph of Log K against $\frac{1}{T}$ should give a straight line the slope of which will be $2.3R \frac{E}{T^2}$

APPLICATION TO THE n-PROPYL RADICAL

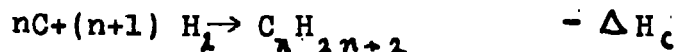
There are three possible ways in which the propyl radical can disrupt, each one however having a different activation energy. If these energies differ by substantial amounts that reaction having the lowest will be the one that occurs at a given temperature to the virtual exclusion of the others.

The three reactions are:-



In order to calculate the necessary heats of reaction one needs to know the heats of formation of the free radicals occurring in these reactions. They are obtained from the heat of formation of the corresponding hydrocarbon, the energy of removal of a hydrogen atom from it, and the dissociation energy of a hydrogen atom. The only value that is uncertain

here is the removal energy of the hydrogen atom; this will introduce an inaccuracy of one or two K.Cals., in the heats of formation of these free radicals and this error will also appear in the values calculated for heats of the radical decomposition reactions. The heats of formation of the relevant radical can be calculated by substituting the appropriate heats of reaction in the following equations:-



Summing these three equations then gives the heat of formation H_f of the radical. The following have been calculated in the above manner.

<u>Radical</u>	<u>H_f</u>
$C_3H_7 \cdot$	+ 18.7 K.Cals.
$C_2H_5 \cdot$	+ 25.3 K.Cals.
$C H_3 \cdot$	+ 32.1 K.Cals.
$C H_2$	+ 78 K.Cals.

Methylene is taken to be a di-radical: if however it is considered a reactive molecule containing divalent carbon instead the heat of formation will be decreased. The actual diminution will be related to the energy liberated in the electronic transition $^5S \rightarrow ^3P$ of the carbon atom. This is estimated

by Long and Norrish (20) to be about 65 K.Cals.

It is now possible to work out the heats of reaction for the propyl decompositions using the above data.

$$\begin{aligned}\Delta H_1 &= (H_f \text{ CH}_3\cdot + H_f \text{ CH}_2 : \text{CH}_2 - H_f \text{ C}_3\text{H}_7\cdot) \\ &= (+32.1 + 12.5 - 18.7) \\ &= \underline{25.9 \text{ K.cals.}}\end{aligned}$$

$$\begin{aligned}\Delta H_2 &= H_f \text{ C}_3\text{H}_6 + H_f \text{ H} - H_f \text{ C}_3\text{H}_7\cdot \\ &= 4.9 + 52 - 18.7 \text{ K.Cals.} \\ &= \underline{38.2 \text{ K.Cals.}}\end{aligned}$$

$$\begin{aligned}\Delta H_3 &= H_f \text{ C}_2\text{H}_5\cdot + H_f \text{ CH}_2 - H_f \text{ C}_3\text{H}_7\cdot \\ &= 25.3 + 78 - 18.7 \text{ K.Cals.} \\ &= \underline{84.6 \text{ K.Cals.}}\end{aligned}$$

In reaction I the back reaction has been investigated by Raal and Danby (21). They were observing the effect of ethylene on the decomposition of acetaldehyde after a study of the rate of decomposition of acetaldehyde alone. It was found that the ethylene competed with unchanged acetaldehyde for the methyl radical produced in the primary split. The difference in activation energy of the two reactions being obtained from the temperature coefficient of the overall reaction rate. This value added to the known activation energy of the reaction of $\text{CH}_3\cdot + \text{CH}_3\text{CHO}$ gives the value of 7 K.Cals. for the energy of the reaction $\text{CH}_3\cdot + \text{CH}_2 : \text{CH}_2 \rightarrow \text{C}_3\text{H}_7\cdot$.

Adding this to the heat of reaction I gives for the activation energy

$$\begin{aligned} E_1 &= \Delta H_1 + 7 \text{ K.Cals.} \\ &= \underline{33 \text{ K.Cals}} \end{aligned}$$

Similarly the reverse of reactions II and III will involve only small energy changes; the activation energy of II being 7 K.Cals. as was I. This value was obtained from the work of Rabinowitch, Winkler and Davies (26) who investigated the reaction of hydrogen atoms with propylene. The energy of the reverse of reaction III will be very small, involving as it does the recombination of two radicals and for the purpose of this calculation can be taken as zero. From this it is apparent that $E_2 = \underline{45 \text{ K.Cals.}}$ and $E_3 = \underline{85 \text{ K. Cals.}}$

If methylene did not have an appreciable life time as a diradical but was formed in the divalent state of carbon as suggested by Pearson, Purcell and Saigh (22) ΔH_3 would be reduced by the difference of energy between C (5S) and C (3P). If we accept Long and Norrish's value of 65 K.Cals. for this transition, then ΔH_3 is brought down to 20 K.Cals. A reasonable value for the activation energy of the reverse reaction would be slightly less than 10 K.Cals. and this would mean that reaction III is the most probable one at temperatures around 300° C. In this event Paneth would

have found evidence of ethyl and not methyl radicals on passing the radicals from decomposing $\text{Pb}(\text{C}_3\text{H}_7)_4$ over antimony mirrors.

It seems more probable however that some of the energy of the carbon atom: $^5\text{S} \rightarrow ^3\text{P}$ transition is taken up in extending the two (C - H) bonds in methylene. Walsh (23) has calculated that 70 K.Cals. would be absorbed by the (C - H) bonds in methylene on passing from the triplet to the singlet state which is higher than the estimate of Norrish and Long for the C (^5S) \rightarrow C (^3P) transition energy. However a value of 96.4 K.Cals. for this latter value has been put forward by Shenstone (32) based on spectrographic evidence; using this value in conjunction with that of Walsh for the (C - H) bond weakening, the energy difference between the diradical and molecular form of methylene available as heat of reaction, would be 27 K.Cals. This value is in agreement with that of Bawn and Dunning (33) obtained from an investigation of the luminescence appearing when sodium atoms react with methylene dihalides. They estimate a minimum value of 27 K.Cals. for the energy liberated when methylene produced as the diradical reverts to the form having divalent carbon.

ΔH_3 would be reduced to 54 K.Cals. if only 27 K.Cals. are liberated in the triplet to singlet transition of methylene; the activation energy of reaction III would then still be too high even if the methylene was split off in the singlet state for it to be any importance in the thermal decomposition of n-propyl at temperatures around 600°K.

By comparing the rate constants of reactions I and II calculated from the Arrhenius equation, the relative importance of each reaction at an arbitrary temperature can be found. The ratio of the two rate constants is

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} e^{-\frac{[E_1 - E_2]}{RT}}$$

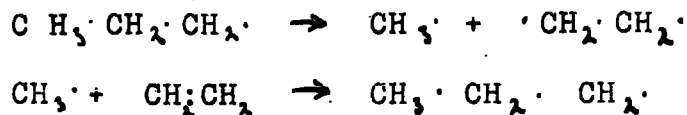
It is justifiable to take the ratio of the two frequency factors A_1 and A_2 as unity because both reactions have similar mechanisms i.e. they involve the breaking of a single covalent bond. Therefore at 600°K

$$\frac{k_1}{k_2} = e^{\frac{12,000}{1.200}}$$

$$k_1 = 10^4 k_2$$

From the above calculations we find that reaction I will predominate at 600°K which means that the n-propyl radical will decompose to give free methyl and ethylene with an estimated activation energy of 33 K.Cals.

The activation energy of this reaction has been calculated in a more thorough manner by Bawn (24). He evaluated energy surfaces for the reactions.



and by combining these two surfaces was able to estimate the height of the energy barrier for the first reaction.

There are a number of inaccuracies inherent in this method however. One is the difficulty in estimating the relative proportions of Coulombic and exchange energy in the potential energy terms for each pair of atom groups in the system. These ratios must be known in order to apply the equation of Heitler and London used to obtain the total energy of the system for a given separation of the atom groups. Bawn takes 15% of the total binding energy as the Coulombic contribution which is presumably estimated from the 14% known to hold for the hydrogen molecule.

Another is in the value taken for the radius of the methyl radical, the structure of which is still undecided. The greatest error appears from the uncertainty in the value for the (C-C) bond energy which is necessary for this calculation. Bawn uses two values for this, the first being 73.5 K.Cals. and the second 97.6 K.Cals.; the discrepancy

being due to the two groups of values put forward for the heat of sublimation of carbon. One group centres about 125 K.Cals. and the other at 170 K.Cals. /gm.Mol. Long and Norrish have suggested that the higher value is the more correct, the difference being explained by assuming the lower value to be that for the sublimation to the ³P energy level of carbon and the higher, that to the 4 valent ⁵S level. Bawn actually carries out two calculations using the two (C-C) bond energies and obtains values of 24 and 39 K.Cals. which he states to be minimum and maximum values for the decomposition of free n-propyl.

The thermochemical calculation outlined earlier gives a value midway between Bawn's results. In the 1948 Tilden lecture to the Chemical Society, Bawn himself quotes a value of 33 K.Cals. for the energy required to dissociate free n-propyl into a methyl radical and ethylene but does not state in what manner he arrives at this value.

Obviously, in order to find the correct value for the activation energy, direct experiment using usual techniques would be practically impossible owing to the difficulty of estimating free radical mixtures at the low concentration obtained in the gas phase production of free radicals. It is possible to overcome this last obstacle by using a

radioactive tracer technique. In order to "fix" free radicals, Gorin (34) used iodine in the vapour phase because of the very low activation energy of interaction between radical and iodine. In this way the radicals were removed from the system before they reacted with themselves or other molecules. Iodine is also a suitable element for use as a radioactive tracer as it has an isotope I^{131} with a conveniently long half-life, 8 days. I^{131} emits β particles with an energy of 0.6 M.E.V. which can be counted with no great difficulty and the isotopes may be extracted from the fission products of U^{235} . A method involving the use of I^{131} has been developed therefore in order to find the experimental activation energy of the decomposition of the n-propyl radical and compare this with the calculated value.

ANALYSIS OF FREE RADICAL MIXTURES

The presence of free alkyl radicals in the gas phase reaction between sodium and alkyl halides was proved by Polyani, Horn and Style (25). They reacted sodium with methyl and ethyl bromides, then reacted the radicals so formed with iodine in a flow system, finally freezing out the alkyl iodides in a trap cooled in liquid air. The alkyl iodide was estimated by hydrolysis and oxidation followed by titration of the liberated iodine. The very small yield of alkyl halide obtained by this method made identification of the free radical practically impossible, using normal analytical procedures; the amount of alkyl iodide produced in the reaction amounts to several micro-moles and hence does not allow of boiling point or refractive index measurements.

The present work, involving radioactive tracer techniques describes a method of identifying free alkyl radicals and analysing a mixture of gaseous free radicals produced in micro-gram amounts. This is obviously useful for investigating any reaction in which low instantaneous concentrations of free radicals are produced.

The radicals are allowed to react with iodine containing a proportion of the radioactive isotope I^{131} having a β -particle activity high enough to enable reasonable counting accuracy of the final diluted sample to be attained. The activity obtained in the following experiments was of the order of

one micro-curie per milli-gram I_2 . The alkyl iodides are then frozen out on a cold finger, excess iodine extracted and finally mixed with micro-amounts (one to two mls. accurately measured) of the appropriate non-radioactive alkyl iodides. The mixture is then fractionally distilled and pure fractions of the iodides collected. It may be emphasised here that the whole of each fraction need not be collected as long as the initial weights of carrier are known accurately, also the specific activity of the iodine need not be estimated if only radical ratios are required. In order to make the alkyl halides more amenable to counting they are precipitated as silver iodide using alcoholic silver nitrate and then well washed with water followed by acetone. About 0.2 gram of this silver iodide is then transferred to a tared tray with acetone, dried off under a radiant heater, reweighed and the activity measured using an end-window type Geiger tube.

The total activity due to the alkyl iodide formed in the reaction can then be calculated from the amount of inactive carrier added initially and the activity of the silver iodide aliquot. The ratio of the activities of the alkyl iodides so produced is obviously that of the gaseous free radicals at the point of reaction with the iodine, as the activation energy of this reaction is extremely small and almost every collision leads to combination of the radical with iodine.

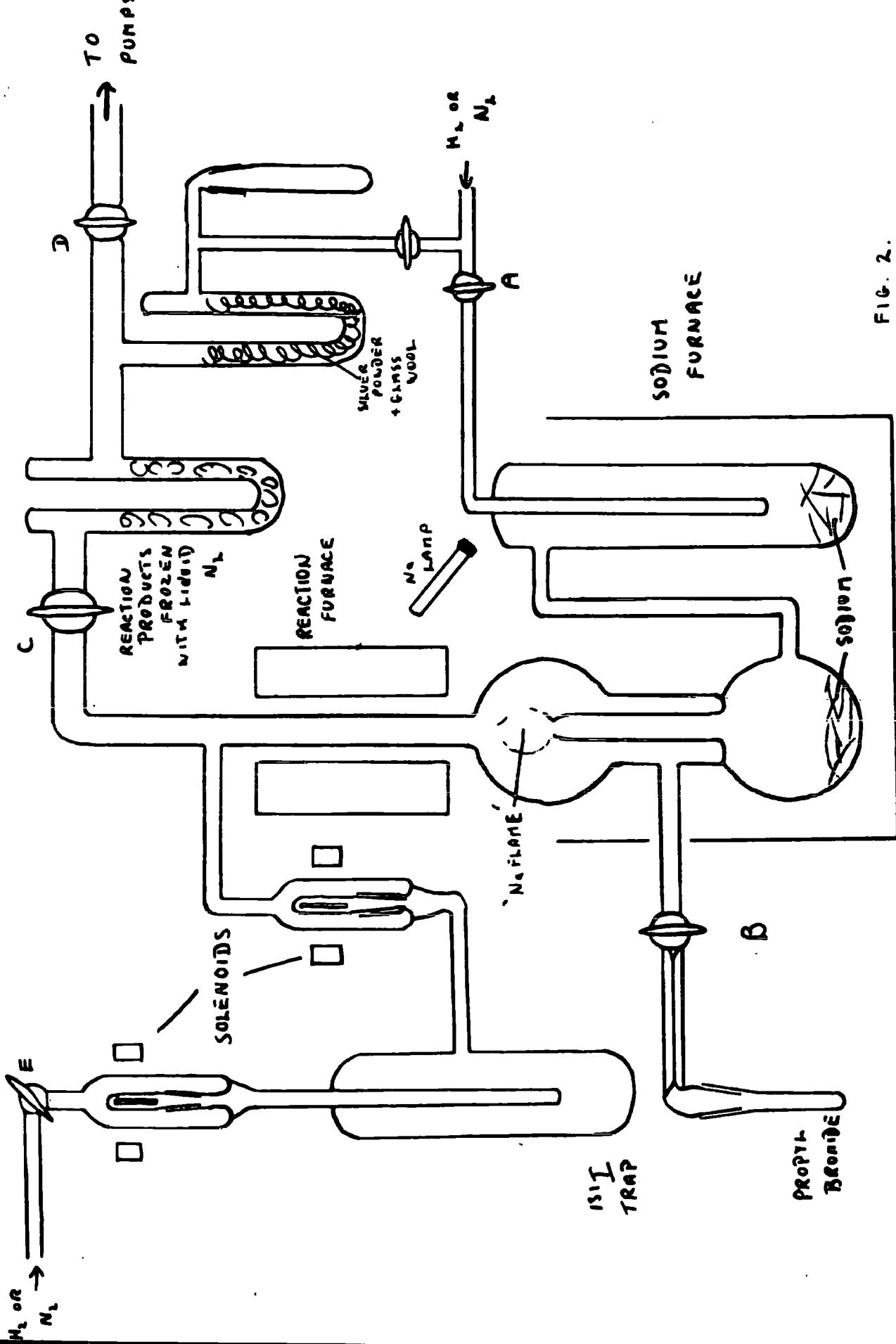


FIG. 2.

EXPERIMENTAL PROCEDURE

(I) Manipulation of Apparatus

The apparatus used to investigate the reaction is shown diagrammatically in Figure 2. Hydrogen carrier gas was prepared from zinc and hydrochloric acid, then purified by first bubbling through caustic soda solution followed by conc. sulphuric acid to remove moisture. Possible traces of oxygen were eliminated by adsorption onto active charcoal cooled with liquid nitrogen. Cylinder nitrogen and argon were purified by passing through a tube containing heated copper powder in order to remove oxygen. An extra trap containing heated sodium removed vestigial traces of reactive impurities. Propyl bromide was purified by first saturating with molecular iodine to remove unsaturated compounds, then removing excess iodine with mercury and finally fractionally distilling. The fraction distilling at 70.9°C under 760 mms. pressure was used in all experiments. Methyl and propyl iodides were also purified by fractional distillation; the boiling point of methyl being 42.5°C and propyl 102.4°C . at 760 mms.

Pure sodium was obtained by first washing the crude metal in petroleum ether before placing in a glass bulb attached to

a further series of such bulbs sealed onto the main sodium trap of the apparatus. This trap and train of bulbs were evacuated and the sodium distilled from bulb to bulb whilst still evacuating. Each bulb was sealed off after the bulk of the sodium had been distilled into the following one. The final distillation gave an amount of sodium sufficient to carry out three or four runs, by which time the surface of the sodium was encrusted and stopped diffusion of the sodium vapour into the gas stream. This usually coincided with the time when the radioactive iodine had decayed to such an extent that it did not allow of reasonable counting rates for the silver iodide precipitates. The sodium flame section of the apparatus would then be taken out, unused sodium removed with alcohol, the section replaced and the above procedure repeated.

At the commencement of a run propyl bromide was pipetted into the calibrated reservoir and frozen by placing a Dewar vessel containing liquid nitrogen around it. Tap B was then opened and the reservoir evacuated through the capillary until all traces of permanent gas were removed. In order to be certain that all the oxygen had been pumped out, tap B was closed and the sodium trap heated until the

first signs of the characteristic yellow fluorescence of sodium atoms appeared with the sodium resonance lamp switched on. This corresponds to a partial pressure of sodium atoms in the reaction vessel of about 10^{-5} mms. If on opening tap B with the propyl bromide still frozen any diminution of the fluorescence occurred it meant that traces of a reactive gas were still present. In such a case the reservoir would be evacuated further until the fluorescence attained its original intensity. There was then nothing remaining to interfere with the sodium - propyl bromide reaction and tap B would then be closed and the reservoir allowed to warm up to room temperature.

The sodium furnace was next warmed up to 290°C . producing a vapour pressure of 10^{-2} mms. of sodium in the carrier gas which was now admitted to the system. The rate of flow of this gas was controlled by tap A; this was set to give an input of 0.2 ccs. per second at atmospheric pressure. Tap B was then opened allowing propyl bromide to vapourise, its partial pressure being controlled by means of the capillary and slight adjustments of tap B. The "dilute flame" of sodium fluorescence now issuing from the nozzle of the reaction vessel was then adjusted by varying the partial pressure of

propyl bromide. The optimum size for this flame is such that it does not touch the walls of the vessel where a heterogenous reaction would set in and a dark space between the top of the flame and the reaction furnace assures the exclusion of sodium atoms from the main section.

The iodine trap was then cooled with liquid nitrogen in order to reduce the vapour pressure of the iodine to a negligible value whilst the magnetic valves were opened. Carrier gas was then admitted, passing over the iodine and entering the main gas stream immediately after the radical decomposition furnace. The velocity of this stream was adjusted by tap E and the rate of flow of gas maintained at a slightly lower value than that of the gas passing over the sodium. This avoided back diffusion of iodine into the reaction zone when a run was in progress. The total pressure obtaining at the furnace during a run was about 0.7 mms. when nitrogen was being used and 0.5 mms. using hydrogen.

The reaction furnace was switched on next; this was operated from a bank of six volt accumulators in order to maintain a steady potential across the furnace, once a given temperature had been reached with the aid of a sliding resistance in series with the furnace. The core was six centimetres in length and consisted of a large mass of copper

with a recess to take either a thermometer or a thermocouple. Its high heat capacity cut down small fluctuations in furnace^{temp.} due to draughts. It was found possible to keep the temperature within one degree of the set temperature by using this method.

When the furnace had reached the required temperature, the liquid nitrogen was removed from around the iodine trap and replaced by a solid CO_2 - acetone mixture at -40°C . This corresponds to a partial pressure of about 10^{-4} mms. of iodine which was sufficient to react with all the radicals issuing from the furnace.

After this, liquid nitrogen was added to the cold finger which condensed out the reaction products: the actual timing of the run commenced at this point. Runs were of an hours duration each time over which period conditions remained sensibly constant. It was only necessary to keep the liquid nitrogen trap filled, watch for any slight variations in temperature of the furnaces and counter-act them. The iodine trap was maintained at -40°C by adding small pieces of solid CO_2 to the CO_2 -acetone mixture. About 0.1 cc. propyl bromide evaporated through the system during a run.

At the end of the hours run, tap C was closed and the carrier gas cut off. The furnaces were switched off, evaporation of propyl bromide stopped by closing tap B, and the magnetic valves closed in order to isolate the iodine. The vacuum distillation unit between taps C and D was then evacuated and tap D closed whilst the cold finger still contained liquid nitrogen.

The liquid nitrogen was then allowed to evaporate from the cold finger causing the products to distil through a trap containing glass wool sprinkled with silver powder into a removable side-arm which was cooled in liquid nitrogen. Any excess iodine was removed by this treatment and a colourless condensate was obtained. Dry carrier gas was then bubbled into the section until atmospheric pressure was reached when the side arm was taken off and the non-radio active alkyl iodide carriers added immediately.

(II) Distillation of products

A small distillation column 20 cms. high and 8 mms. in diameter was used to separate the alkyl iodides. It was packed with stainless steel wire gauze rings $\frac{1}{16}$ " in diameter and height. Owing to its small size and the considerable difference in boiling points of the alkyl iodides, no external heating of the column was necessary. It was however

lagged with an asbestos - sodium silicate sludge to prevent heat losses. A small boiler holding about 10ccs. of liquid was fitted to the column by means of a ground glass joint and held in place with wire passing over glass lugs. No refluxing of the vapour was aimed at, some did take place through condensation on the thermometer bulb, and complete take-off at the rate of about 3 ccs. an hour was maintained.

The amounts of non-radioactive alkyl iodides used as carriers in this series of experiments were two ccs. methyl iodide, three ccs. propyl iodide and 0.5 ccs. methylene iodide. This latter carrier was added to hold back in the distillation any radioactive disubstituted alkyl iodide that could conceivably have been formed during an experiment and would otherwise distil with the propyl iodide fraction; it was expected that ethylene produced in the reaction would react with the iodine in such a way. About four ccs. Xylene were also added, boiling at 138°C , to enable all the propyl iodide to be distilled. Methylene iodide decomposes at its boiling point of 180°C so that this fraction could not be distilled over.

In preliminary runs it was found that the methylene iodide

remaining in the boiler had an activity comparable with that of the combined methyl and propyl iodide fractions. When runs were carried through with propyl bromide purified as mentioned previously however the activity of the methylene iodide fraction was reduced to less than one percent of the total. This shows that the ethylene does not react with the iodine to produce diiodoethane, but the earlier activity in the methylene iodide must have been due to reaction of the iodine with some high boiling unsaturated compound present in the propyl bromide, probably during the period in which the cold finger was warming up.

(III) Preparation of sources

Series of 0.2 ccs. samples of the methyl and propyl iodide fractions were collected, the activity of samples taken at the correct boiling points were found to be reasonably constant. 10 ccs. of a 20% solution of silver nitrate in alcohol (with sufficient water to give complete solution) were added to each alkyl iodide sample. These were then placed in a water bath at about 50°C for about half an hour when precipitation of the iodide as the complex $\text{AgI} - \text{AgNO}_3$ went to completion. Washing with water decomposed the complex and the excess AgNO_3 was washed out. The precipitates were centrifuged and washed with acetone using a pipette

with a rubber bulb endeavouring to obtain a precipitate of small grain size. Each precipitate was then transferred with acetone to a weighed silver tray and the excess acetone evaporated using a radiant heater in order to obtain a level layer of silver iodide. Reweighing the trays then gave the aliquots of silver iodide taken, The volume of alkyl iodide added as carrier was converted to its equivalent weight of silver iodide in order to estimate the total activity associated with each of the alkyl iodides.

The silver trays were of a standard size 3.2 sq. cms. in area stamped from a sheet of silver 0.025 mms. thick. Silver was used in place of aluminium because silver iodide attacks aluminium trays.

(IV) Counting techniques

Standard commercial counting equipment was used to measure the activity of the silver iodide samples. An end window type Geiger-Muller tube was mounted in a lead castle and the sources were placed on an aluminium pillar which was extensible, allowing the source to be brought near to or away from the window of the counter. The solid aluminium head of the pillar ensured that back scattering of β -particles reached its maximum value. Provision was also made for placing absorbers between source and tube so that an

absorption curve for the radiation being measured could be made and in this way it was ensured that the activity was due to I^{131} . A high voltage unit with a stabilised output feeding into a potentiometer network produced any voltage from 500 to 2000 at the collecting electrode of the Geiger tube. The output pulses were fed into a scaling unit with a decimal scale.

Counting conditions were standardised by using a standard source consisting of a sample of U_3O_8 in a tray with a coating of collodion to make it adhere. This source was then counted immediately before any sample of silver iodide, the voltage applied to the tube being altered until the standard counting rate was reached. This counting rate being that which occurred for that source about one third of the way along the plateau of the curve connecting counting rate and voltage applied to the tube. It was actually found that this voltage remained constant throughout any one series of activity measurements.

It was realised that self-absorption of the β - particles in the silver iodide samples was an important factor affecting the accuracy of the counting experiments. The half- thickness for this effect i.e. the density

required to reduce the actual activity by one half was found to be 75 mgm. per sq. cm. The density of silver iodide samples counted varied between about 50 and 75 mgm. per sq. cm. and this would therefore lead to a considerable variation in the amount of self-absorption by the samples. This inaccuracy was overcome by drawing up a graph in which the percentage reduction in counting rate was plotted against the corresponding thickness of sample. These results were obtained by observing the reduction in counting rate on mixing weighed amounts of inactive silver iodide with a comparatively weightless source of active AgI. From this graph a correction was applied to each aliquot of silver iodide counted depending on the density of the sample.

The half life of I^{131} is eight days so that no decay corrections were necessary provided that all specimens were counted within a few hours. Activity measurements varied from about 100 to several thousand counts per minute. It was endeavoured to obtain a result with a standard deviation no greater than 1% and in order to do this a total count of 10,000 counts was required. For the higher activities this entailed only several minutes counting but some of the less active samples had to be counted for about two hours.

(V) Extraction of I¹³¹

I¹³¹ is readily available from the products of the fission of U²³⁵ by slow neutrons. In order to obtain it in a form that could be easily worked up 25 grams of uranium trioxide were irradiated in the Harwell "Pile" for two weeks, when the 8-day iodine would have almost reached equilibrium with respect to rate of production and decay. This was then allowed to "cool" for a further week in order that short lived and hence highly active nuclides could decay. Another isotope of iodine, I¹³³ is also produced in fission having a half-life of 22 hours and if this was used along with the I¹³¹ a complex decay curve would result; the weeks decaying however reduces the amount of activity from this isotope to negligible proportions. The I¹³¹ would have also decayed to about half its original amount but the advantage gained in obtaining an activity with a simple decay curve outweighed this loss: it was still possible to extract several millicuries of I¹³¹. An appreciable amount of Br⁸² with a half life of 36 hours would still remain however and would be expected to follow the iodine if isotopic carrier was not added.

About 50mgms. KI and 10 mgms. KBr in water were therefore mixed with the irradiated UO₃ to act as carriers for the iodine

and bromine activities. They were followed by 10 cc. concentrated sulphuric acid with sufficient distilled water to bring all the UO_3 into solution. Due to radiation hazard all these operations were carried out under a hood with the apparatus containing the radioactive material shielded by a lead screen. It was found that no further oxidising agent was needed to liberate the iodine from iodide solution because on boiling the UO_3 and sulphuric acid both iodine and bromine distilled over. It was noted here that when the sulphuric was replaced by hydrochloric acid the iodine was oxidised right through to the iodate stage and hence could not be distilled out. If the uranium solution was now reduced to the U^{4+} stage with zinc or iron however the iodine vapour appeared and could be distilled.

The iodine and bromine were collected in a dilute sodium hydroxide solution and as the penetrating radiation from this was far less than that from the irradiated UO_3 , it was worked up, under a hood still because of the possibility of organic solvents evaporating and transporting active iodine, but with no shielding.

The iodine was separated from the bromine by addition of sodium nitrite followed by acidification with dilute

sulphuric acid and extraction of the iodine into ether. This ethereal solution of iodine was then well washed with water and the iodine taken out with sodium sulphite solution as iodide. In order to ensure complete removal of bromine activity from the iodine a further quantity of KBr carrier was added to the above solution and the iodine again extracted, using sodium nitrite and sulphuric acid to liberate the iodine and extracting into ether. The whole process of oxidation, extraction into ether and reduction with sodium sulphite of the active iodine was then repeated, without using KBr this time, in order to obtain the iodine as pure as possible. It was finally collected as iodide in sulphite solution.

(VI) Transference of the I^{131} to the apparatus

The radioactive iodine must necessarily be introduced into the apparatus in a pure and dry state and in order to do this use was made of the fact that palladous iodide breaks down on heating into elementary iodine and palladium. In order to obtain the extracted iodide as palladous iodide, the sulphite solution was boiled with a drop of concentrated hydrochloric acid to destroy sodium sulphite and expel SO_2 . It was found that sulphite interfered with the precipitation of palladous iodide but a low concentration of HCl did not.

A solution of palladous chloride was added to the boiling iodide solution drop by drop until precipitation of the palladous iodide was complete. This precipitate was then centrifuged and well washed with distilled water.

In early experiments this palladous iodide was transferred with acetone to a combustion tube having a U-tube leading from it, after which the acetone was evaporated off using a water pump. The combustion tube was then heated to about 400°C , at which temperature the palladous iodide decomposed, and the active iodine collected in the cooled U-tube. This was dissolved in the minimum quantity of ether necessary and placed in the iodine trap of the apparatus, frozen, and sealed off. The ether was then pumped away by cooling the trap to a temperature at which the iodine had a negligible vapour pressure yet at which the ether was still volatile.

After several inconclusive runs it was found that activity appeared in the final products even in blank runs in which the sodium was not heated and hence no radicals could possibly be produced. It was finally decided that this contamination must have been due to some volatile impurity in the iodine produced by occlusion of a small amount of solvent into the palladous iodide. Assuming this to be

acetone, it would react with the active iodine on decomposing the palladous iodide, the palladium acting as a catalyst. This active iodine substituted acetone would then be transported with the iodine in the apparatus and be frozen out with the reaction products. On fractional distillation of the products this active compound would then be randomly distributed between the various fractions, as only a minute yet highly active quantity would be present.

In order to overcome this difficulty the following procedure was adopted. After the palladium iodide had been well washed with water it was transferred to a combustion tube having a connection to a small glass trap. This trap was in turn sealed onto a sidearm leading from the main iodine trap. The whole system was evacuated for several hours with the palladous iodide maintained at about 100° C. to remove last traces of moisture. The section was next shut off from the main vacuum and dry nitrogen admitted until the system reached atmospheric pressure; this was necessary as heating under vacuum caused ^{the} combustion tube to suck in. After decomposing the palladous iodide, the first trap was cooled with liquid nitrogen and the section again evacuated causing the iodine to

condense in it. The tube which had contained the palladous iodide was then sealed off, the main iodine trap cooled with liquid nitrogen and the trap containing the iodine allowed to warm up. When the bulk of the iodine had diffused into the main trap the first one was sealed off to keep back any volatile impurity that might be present.

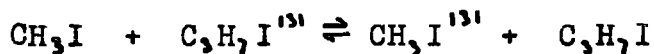
The active iodine was stored with several centimetres pressure of nitrogen and closed off with two magnetically operated valves in order to cut down diffusion of iodine to the sodium section of the apparatus. This type of valve was necessary to isolate the iodine because it was found that grease on normal taps absorbed iodine rapidly. They were made from ground glass joints, the male half of which contained an ironrod sealed into it. Solenoids wound round the outside of the iodine trap outlet tubes actuated the valves. Initially the iodine was isolated by break seals, this entailed using all the iodine in one run and was wasteful.

(VII) Investigation of exchange reactions.

In order that the different activities of the various alkyl iodides may be separated it is important that no exchange reaction should take place between iodine atoms

of different alkyl iodides. If this did occur at an appreciable rate it would mean that approximately equal specific activities would be found in each of the distilled fractions and would nullify results obtained by using I¹³¹ as a detector for the radicals.

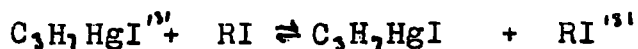
The obvious way to investigate this effect is to prepare propyl iodide or methyl iodide with the iodine atom labelled with I¹³¹, mix with inactive methyl or propyl iodide respectively and then fractionally distil the mixture. If no exchange of the type



takes place then the originally inactive component should show no activity when precipitated as silver iodide after being distilled and the specific activity of the labelled iodide remain the same. This experiment was carried out using labelled propyl iodide prepared by adding iodine containing a proportion of I¹³¹ to refluxing propyl alcohol with red phosphorus present. After washing with sodium sulphite to remove excess iodine and drying over calcium chloride, it was purified by distillation. Inactive methyl iodide was then added and the mixture fractionated using Xylene as ballast to bring over all the propyl iodide. Less

than one per cent of the total activity was found in the methyl iodide fraction showing that exchange of this kind is negligible during fractional distillation even when boiler temperature rises above 140°C.

In earlier experiments it was found that activity appeared in the condensate on the products trap even in blank runs and was first thought to be caused by reaction of the iodine with propyl bromide, catalysed by mercury vapour from a McLeod gauge. Several workers have shown that molecular iodine does not exchange with ethyl iodide at 90°C (27), or under the action of ultra-violet light (28), but mercuric iodide is soluble to a slight extent in organic solvents and might promote exchange even with the more strongly bound bromine atom through formation of a propyl mercury iodide. This was checked by dissolving active iodine in propyl bromide, removing it again with mercury and filtering off the precipitated mercuric iodide. To the propyl bromide was added alkyl iodide carrier and the usual fractionation made. Activity was then found in the iodide fractions although none appeared ^{if} in place of mercury, iodine was removed with silver powder. The mechanism for this exchange must then be



During the course of a run the walls of the apparatus in the vicinity of the cold finger were rapidly covered with mercuric iodide due to the McLeod used to measure the pressure at that point so it was taken out and precautions taken to avoid mercury vapour entering the vacuum distillation section.

Finally, blank runs on the apparatus under conditions of a normal experiment, even with the reaction furnace heated, gave negligible activity in the silver iodide precipitates.

(VIII) Estimation of flow rate

As it was desired to keep mercury vapour out of the apparatus, the rate of flow of gas through the section in which the decomposition reaction took place had to be evaluated before iodine and sodium were added. A McLeod gauge with a two-way tap was therefore sealed temporarily into the apparatus. One lead from the tap was attached to the reaction tube at its point of entry into the furnace to measure the pressure obtaining at the furnace whilst the other was sealed on near the

diffusion pump, where the pressure included that due to the entry of the gas stream carrying the iodine thus enabling the total flow rate to be estimated.

The sulphuric acid bubblers through which the carrier gas passed, were used as flow meters for the input of gas at atmospheric pressure and were calibrated by aspirating different volumes of gas through them in a given time and measuring the rate of bubbling. In order to measure the flow rate at the furnace the apparatus was opened to the vacuum pumps and carrier gas admitted as in a normal run, the pressure obtaining at the furnace being measured until a constant reading on the McLeod was obtained. This was done for several different input rates of carrier gas. The volume of gas entering the apparatus at atmospheric pressure was then converted to that pertaining to the pressure of the reaction tube in order to obtain the volume flow rate through the reaction zone.

This flow rate was found to be still within the limits of an experimental error of about 6% even when the input of gas to both sodium and iodine traps was varied greatly. The values obtained for the flow rate of carrier gas

through the apparatus were as follows

$$\underline{H_2} = \underline{228 \text{ ccs. per sec.}}$$

$$\underline{A \text{ and } N_2} = \underline{154 \text{ ccs. per sec.}}$$

EXPERIMENTAL RESULTS

Calculation of results

The rate of a unimolecular reaction is proportional to the first power of the concentration of reactant and the following differential equation applies

$$-\frac{dc}{dt} = KC$$

To find an expression giving the reaction constant "K" this equation must be integrated producing

$$K = \frac{1}{t} \ln \left(\frac{c_1}{c_2} \right)$$

where "t" is the time taken for the concentration of reactant to fall from c_1 to c_2 .

Applying this to the case of the decomposition of propyl radicals, the concentration of propyl radicals entering the reaction furnace is equal to the concentration of those leaving plus the concentration of methyl radicals produced. We now obtain the following equation giving "K" at a particular temperature

$$K = \frac{1}{t} \ln \left[1 + \left(\frac{[\text{METHYL}]}{[\text{PROPYL}]} \right) \right]$$

"t" is now the time a propyl radical takes to traverse the furnace. It is seen that a knowledge of the total number of radicals of each kind produced is not needed but only the ratio of methyl to propyl radicals leaving the

HYDROGEN AS CARRIER GAS

$t = 2.1 \times 10^{-2}$ secs.

RUN	TEMP. °C	<u>Methyl</u> <u>Propyl</u>	$\text{Ln} \left[1 + \frac{\text{Me}}{\text{Pr}} \right]$	K	Log K	$\frac{1}{T^0_K} \times 10^3$
0	280	0.002				
1	314	0.036	0.0353	1.68	0.225	1.704
2	326	0.053	0.0517	2.46	0.391	1.669
3	335	0.054	0.0526	2.51	0.400	1.645
4	342	0.068	0.0660	3.14	0.497	1.626
5	349	0.073	0.0706	3.36	0.526	1.608
6	356	0.133	0.1250	5.94	0.774	1.590
7	366	0.124	0.116	5.51	0.741	1.565

HYDROGEN
CARRIER

0.90

0.60

$\text{LOG}_{10} K$

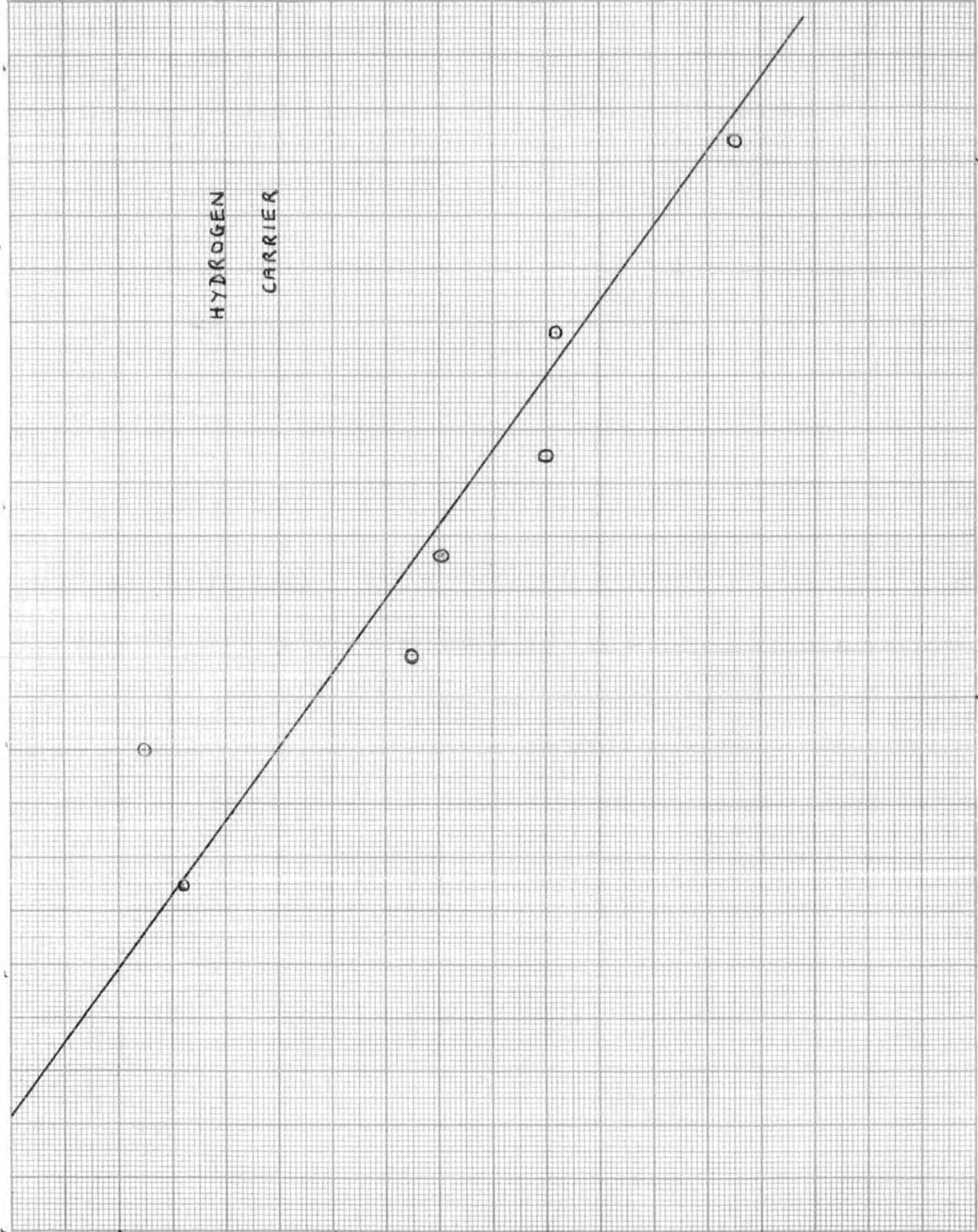
0.40

0.10

1.600

$\frac{1}{T} \times 10^3$

1.700

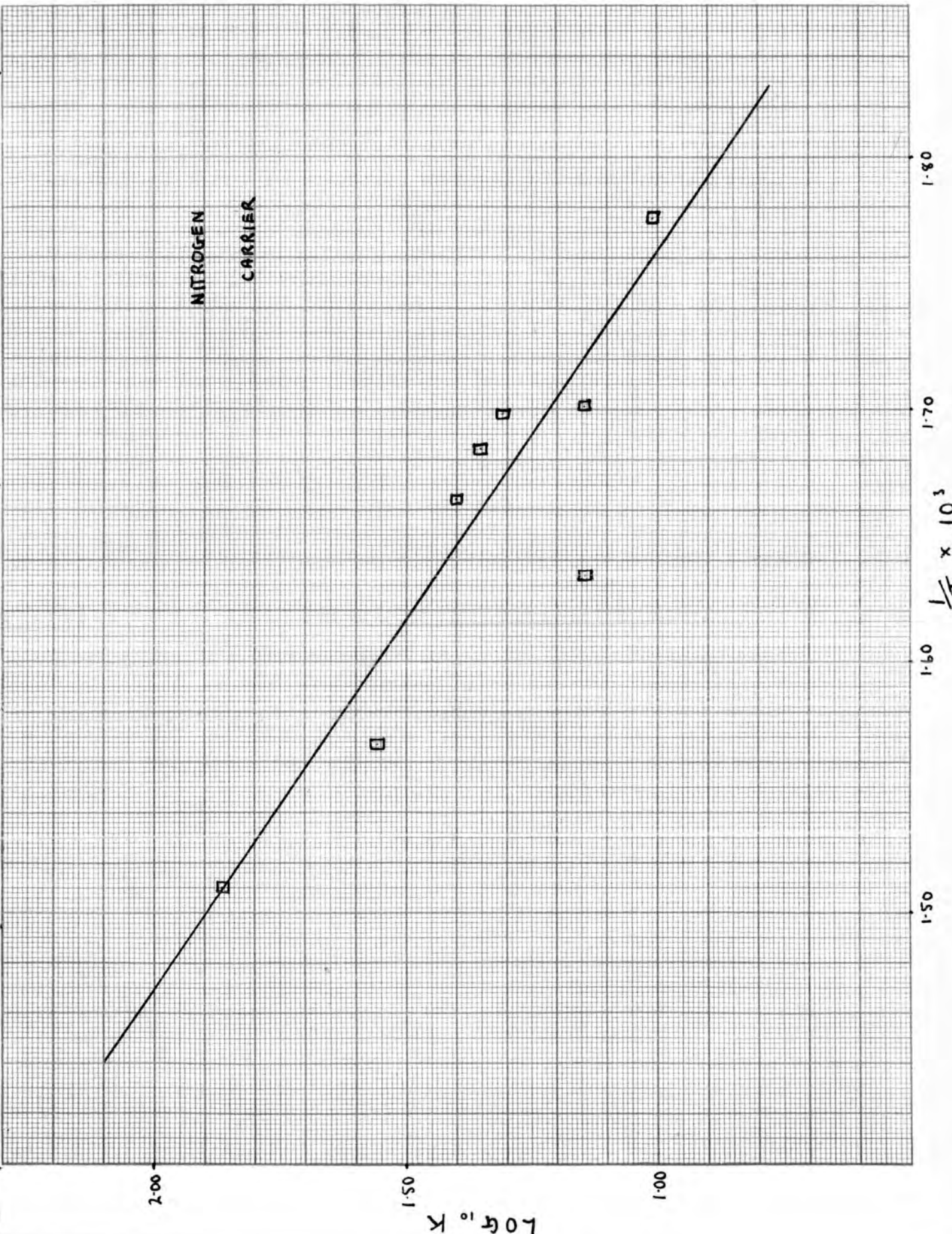


NITROGEN AS CARRIER GAS.

$t = 3.1 \times 10^{-2}$ secs.

RUN	TEMP °C	Methyl Propyl	$\text{Ln} \left[1 + \frac{\text{Me}}{\text{Pr}} \right]$	K	Log K	$\frac{1}{T} \times 10^3$
8	280	0.110	0.104	3.36	0.526	1.810
9	290	0.395	0.323	10.4	1.017	1.776
10	315	0.628	0.436	14.1	1.149	1.701
11	316	0.874	0.628	20.3	1.308	1.698
12	321	1.01	0.698	22.5	1.352	1.684
13	328	1.18	0.779	25.2	1.401	1.664
14	339	0.590	0.464	13.9	1.143	1.634
15	365	2.03	1.11	35.8	1.554	1.567
16	390	8.66	2.27	73.3	1.865	1.510

Runs 10 and 13 Argon used in place of Nitrogen.



furnace. The above equation was used to obtain the following results from experimental values of the methyl to propyl ratios using the first case hydrogen and in the second nitrogen as carrier gas. The best fit of the slopes to the points of the graphs was obtained by using the method of least squares. The experimental activation energies were then calculated by dividing the values of the slopes by $2.303 R$ where "R" is the gas constant expressed as calories per degree. These activation energies are as follows:-

$$\text{Hydrogen as carrier gas} \quad E_{\text{exp}} = \underline{18 \text{ K.Cals.}}$$

$$\text{Nitrogen as carrier gas} \quad E_{\text{exp}} = \underline{17 \text{ K.Cals.}}$$

Homogeneity of the reaction

In order to test whether the reaction was really a homogeneous one or whether it was a heterogeneous one taking place on the walls of the apparatus, Run 12 was carried through with a plug of glass wool in the reaction chamber. This gave a surface to volume ratio very much greater than in a normal run and if the reaction proceeded by a mechanism which entailed adsorption onto a surface for decomposition to occur, the reaction rate would be increased. A value for "K" would therefore be obtained

larger than that calculated from the Arrhenius equation at that temperature. The fact that the reaction constant does not show any marked deviation from the expected value obtained from the slope of the graph at that temperature, indicates that homogeneous gas reaction was being observed.

A run was also carried through in which the vapour pressure of sodium was reduced to 10^{-3} mms. This would give only one tenth of the concentration of radicals in a normal run yet the rate of reaction was still within the experimental error thus showing that the decomposition of n-propyl occurs by a monomolecular process.

DISCUSSION OF RESULTS

Activation energy of the reaction

The experimental activation energy of 18 K.Cals. for the reaction using hydrogen for the carrier gas is one K.Cal. higher than that using nitrogen. This however is not significant, the discrepancy being within the experimental error, and as the spread of the points of the Hydrogen graph is less, a value of 18 K.Cals. will be used throughout this discussion. The value for the rate constant at temperature around 600°K is then given by the expression

$$K = 10^{-4} e^{-\frac{18,000}{RT}}$$

which was calculated using the absolute rate of reaction found in the preceding experiments.

The 18 K.Cals. calculated from the temperature coefficient of the rate constant is even 8 K.Cals. lower than the heat of reaction calculated earlier and hence cannot be the true value for the activation energy. The only errors arising in the heat of reaction calculation are in the values for the dissociation energies of the carbon-hydrogen bonds in the hydrocarbons studied. These however are not so great as to produce an error of 8 K.Cals. in the heat of reaction.

Also the frequency factor is lower by a factor of 10^6 than that necessary to fulfil the Arrhenius or Eyring equations, both of which require a value of the order of 10^{13} sec^{-1} . A low frequency factor is often the cause of a reaction having a slower rate than expected and has been related to the entropy change in forming the activated complex by Eyring. The entropy change in unimolecular reactions can never be very great however, as the activated complex is generally formed by slight extensions of chemical bonds in the normal molecule entailing a small number of entropy units. In the present case something like - 28 E.U. would be required to produce a normal frequency factor which is highly improbable for the actual change of entropy.

It has been found by Evans and Swarc (29) that in the majority of unimolecular reactions involving bond rupture the experimental frequency factor is of the order of 10^{13} sec^{-1} . If we accept this value for the frequency factor and substitute it for the 10^7 in the equation giving the rate constant at a particular temperature, we find that in order to keep the same absolute rate, the activation energy term must be increased to 32 K.Cals. This is in good agreement with the value of 33 K.Cals. obtained by thermo-

at 1000
only be true
at one
temp.

chemical considerations as outlined earlier and appears to be the true value for the activation energy of the reaction.

The discrepancy between this result and that obtained from the temperature coefficient of the reaction constant is probably linked up with the complexity of the structure of free propyl. A complex having several vibrating atoms can absorb energy very efficiently on collision with an energy-rich molecule and hence fewer collisions are necessary to produce the activated state. Energy stored in the molecule in the form of vibrations between atoms in this way would also be available as activation energy when reaction proceeds by the breaking of such bonds. Each degree of freedom of the molecule will accommodate two "square terms" of energy; the phrase "square term" denotes the quadratic form of energy equations.

The expression for the variation of the rate constant with temperature now becomes (36)

$$K = \lambda \left(\frac{1}{\frac{1}{2}n-1} \right)! \left(\frac{E}{RT} \right)^{\frac{1}{2}n-1} e^{-\frac{E}{RT}}$$

where λ is the fraction of activated molecules decomposing per second and "n" is the number of "square terms" in which energy is stored in the molecule. When this expression is differentiated logarithmically the following

result is obtained

$$\frac{d \ln K}{dT} = \frac{E - (\frac{1}{2}n-1) RT}{RT^2} \quad \checkmark$$

The experimental activation energy obtained from a graph of $\frac{1}{T}$ against $\log K$ must therefore be corrected in order to arrive at the true activation energy which appears in the above equation.

$$\underline{E_{\text{True}}} = \underline{E_{\text{Exp}}} + (\frac{1}{2}n-1)RT$$

If the true activation energy is 32 K.Cals. as was calculated from the absolute rate, it would mean that "n" was 26 and 13 degrees of freedom would be required to contain these square-terms. This is obviously permissible as the number of vibrational degrees of freedom in $\text{CH}_3\text{CH}_2\text{CH}_3$ will be 24. The fact that all the degrees of freedom of the molecule are not used to accomodate energy may be due to difficulty in transferring kinetic energy to some of the vibrating bonds. The final form of the reaction equation will then be

$$K = 10^4 \frac{1}{12!} \left[\frac{32.000}{RT} \right]^{12} e^{-\frac{32.000}{RT} \text{ sec}^{-1}}$$

From the above equation the probability " λ " of an active molecule decomposing in unit time is seen to be of the order of 10^4 sec^{-1} . It has been shown on page 27 that

as the concentration or pressure of reacting molecules is lowered the order of reaction changes over from first to second at a critical concentration where the rate of spontaneous decomposition of active molecules and rate of deactivation become comparable. As most collisions will be deactivating in character the frequency with which any one molecule undergoes collision with the remainder in unit time will be a measure of the probability of an active molecule being deactivated. This probability can be estimated from a knowledge of the pressure obtaining during an experiment and in the case of the propyl radical the frequency of collisions with nitrogen (or hydrogen) only will be important, because the concentration of propyl radicals will be low compared with that of nitrogen. By estimating the probability of deactivation "P" for the conditions obtaining in the previous experiments and comparing it with the value of 10^4 for " λ ", one can find out whether they were carried out in the pressure region where the first order characteristics obtain or in the second order region.

The frequency of collision of an active molecule with nitrogen molecules is given by $2nD^2(4\pi RT/M)^{1/2}$ where "n" is

the number of nitrogen molecules per c.c. "D" is the collision diameter and "M" the mass of the nitrogen molecule. Thus for a pressure of 1mm. of nitrogen "P" is of the order of 10^8 sec^{-1} giving a ratio of deactivation to reaction of activated molecules of 10^4 to 1. Under these conditions then the decomposition of free propyl occurs by a first order mechanism with an activation of 32 K.Cals.

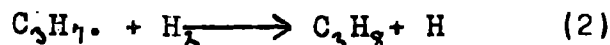
Effect of carrier gas on absolute rate

By comparing the absolute rate constants for hydrogen as carrier gas with those obtained using nitrogen or argon, it is found that the rate of decomposition of the n-propyl radical in nitrogen or argon is six times that in hydrogen; the temperature coefficient of the reaction constant however is the same in each case, within the limits of experimental error.

One explanation for this difference could be that the energy of activation transferred to the propyl radical in collision with carrier gas molecule is more readily concentrated in the (C - C) bond which breaks during reaction, when the carrier gas is nitrogen or argon, than when it is hydrogen. This would lead to a more rapid rate of reaction

as outlined on page 26. Rabinowitch and Wood (35) found that nitrogen was more efficient than hydrogen in promoting the recombination of bromine atoms. It is to be expected that there is some parallelism in efficiency of energy transfer between dissociation and recombination reactions, as the one energy surface represents both reactions; thus an efficient transfer of excess energy from combining atoms would mean a favourable transfer of energy to a dissociating molecule. The position of argon is anomalous in their work however as it appears to be less efficient than hydrogen; in order to account for the above discrepancy in reaction constants it would need to have the same efficiency as nitrogen in transferring translational or rotational energy into vibrational on collision.

Another line of inquiry into the reason for the slower rate of decomposition in hydrogen is the possibility of a bimolecular reaction between radical and hydrogen. As both methyl and propyl radicals are present the following two reactions have some probability of occurring.



In order to account for the slowness of the decomposition reaction in hydrogen one must assume that the methyl to propyl ratios obtained from these experiments were too low; this would mean that the methyl radicals were being removed at a greater rate than the propyl radicals.

This however does not seem feasible because the activation energies for the reactions (1) and (2) differ by only a very small amount according to Evans and Swarc (29).

The fact that the activation energy of the decomposition reaction does not alter on replacing nitrogen for hydrogen means that the activation energy of the reaction (1) must be equal to that of the decomposition reaction which again is improbable. It would appear therefore that the reaction of the radicals with hydrogen does not materially affect the rate of decomposition reaction.

CONCLUSION

A method involving the use of radioactive iodine for analysing mixtures of gaseous free radicals in a dynamic system has been developed. This technique has been used to investigate the thermal decomposition of the n-propyl

radical after having deduced from a consideration of thermochemical data a value of 33 K.Cals. for the activation energy of the radical break down: the temperature coefficient of the first order reaction constant gave a value of 18 K.Cals. for the experimental activation energy. By fitting the absolute rate constant to the Arrhenius or Eyring equations for first order reaction and using a normal frequency of 10^{13} sec⁻¹ a "true" activation energy of 32 K.Cals. was obtained. The difference between true and experimental activation energies has been related to the complexity of the propyl radical with the corresponding ability to store energy in its vibrational degrees of freedom.

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