

Reactions of phenyl radicals

by

Frederic J. Duncan, B.Sc.

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# ABSTRACT OF THESIS

Name of Candidate Frederic James Duncan

Address \_\_\_\_\_

Degree Ph.D. Date September, 1961.

Title of Thesis Reactions of phenyl radicals.

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Phenyl radicals were produced by photolysis of acetophenone between 280 and 420°C and two reactions of the radicals with the parent compound have been examined in detail. These are (a) hydrogen abstraction from acetophenone to produce benzene and (b) addition to acetophenone to produce diphenyl. The Arrhenius parameters and rate constants for these reactions have been determined by comparison with the same constants for formation of diphenyl by combination of phenyl radicals. This combination reaction has been assumed to have zero activation energy and a rate constant equal to  $10^{14} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ .

Methyl radicals were also produced during the photolysis and the Arrhenius parameters and rate constants for formation of methane by abstraction of hydrogen from acetophenone have been determined.

The hydrogen abstraction reactions of phenyl radicals with isobutane, cyclopropane and methane were investigated. The Arrhenius parameters and rate constants for these reactions have been compared with these for reaction of other radicals with the same hydrocarbons, and it was concluded that the reactivity of the phenyl radical was similar to that of the methyl, trifluoromethyl and methoxyl radicals.





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## I. INTRODUCTION

### 1.1 General

Free radicals were first detected in 1929 by Paneth and Hofeditz<sup>(1)</sup>, who heated tetramethyl lead in a stream of hydrogen or nitrogen and showed that mirrors of lead and similar metals placed close to the reaction zone were gradually removed. They concluded that this removal of metallic mirrors was due to reaction with free methyl radicals, very reactive compounds of short lifetime. Various other alkyl radicals were soon detected by the same method. In the following years, many workers examined the reactions of these free radicals qualitatively and quantitatively, both in solution and in the gas phase, and, as a result, a mass of information concerning these reactions is now available. However, the phenyl radical has not so far been subjected to detailed quantitative examination, though evidence of its existence and of its modes of reaction has been forthcoming. This introduction will therefore consist mainly of a review of such work concerning the phenyl radical.

### 1.2 Evidence for, and reactions of phenyl radicals in the gas phase.

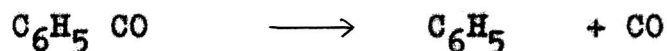
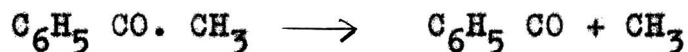
The first attempts to prepare the phenyl radical were made by Dull and Simons<sup>(2,3)</sup>, and Paneth and Lautsch<sup>(4)</sup>. Dull and Simons studied the thermal decomposition of tetraphenyl lead and found that at 252°C. the product of reaction was 100% diphenyl, while at 400°C. the diphenyl yield had dropped to 20%, benzene was formed, and charring occurred. In the presence of mercury, diphenyl was again formed, together with diphenyl mercury. It was suggested that these reactions were due to the initial formation of phenyl radicals. However, Paneth and Lautsch, on decomposing the same substance, tetraphenyl lead, in a stream of hydrogen showed that lead and tellurium mirrors placed close to the reaction zone were not attacked as in the decompositions of tetramethyl - and tetraethyl lead. They concluded that either the free phenyl radical was not formed, or else it had a far shorter lifetime than the methyl or ethyl radical.

Another reaction examined was that of bromobenzene with sodium vapour. Horn and Polanyi<sup>(5)</sup> found that a small quantity of diphenyl was formed during the reaction, and obtained iodobenzene on introducing iodine into the system. Paneth and Lautsch<sup>(4)</sup> repeated this

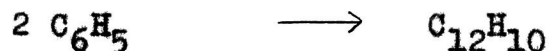
experiment using tellurium mirrors to detect the phenyl radicals, but found no positive evidence for their existence.

In view of the conflicting nature of these results, Glazebrook and Pearson<sup>(6)</sup> examined the photolysis of two aromatic ketones - acetophenone and benzophenone. Acetophenone yielded diphenyl plus small quantities of benzil and dibenzoyl ethane as products and, when a tellurium mirror was placed close to the reaction zone, dimethyl-, diphenyl-, and phenylmethyl tellurides were formed. The reaction with tellurium indicates the intermediate formation of phenyl and methyl radicals, while the production of benzil and dibenzoyl ethane indicates the presence of benzoyl and phenacyl radicals. The following reaction scheme was proposed to account for some of the products.

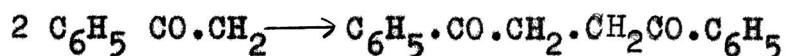
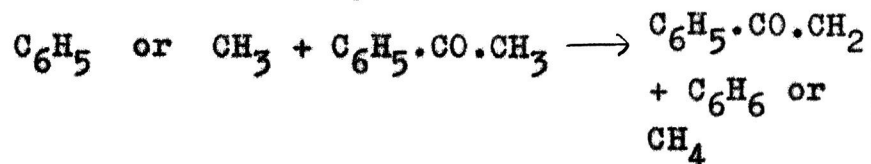
(a) Formation of free radicals



(b) Formation of diphenyl



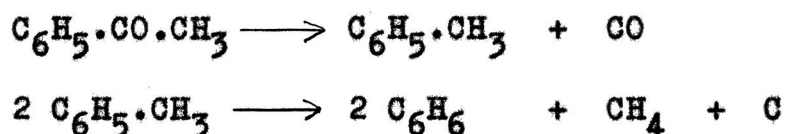
(c) Formation of dibenzoyl ethane





Benzophenone was also photolysed and free radicals were shown to be present by removal of tellurium mirrors.

Further examination of the decomposition of acetophenone was carried out by Smith and Hinshelwood<sup>(7)</sup> who showed that in the thermal decomposition the products obtained were benzene, methane, carbon and a trace of toluene. They also found that the addition of nitric oxide, an inhibitor for radical reactions, and of diethyl ether, which would decompose to give free radicals, did not affect the reaction, and concluded that the thermal decomposition was a first order molecular reaction. The reaction scheme proposed was



It is difficult to reconcile this scheme with the findings of Glazebrook and Pearson, or with later work by Clark and Pritchard<sup>(8)</sup> who, using the "toluene carrier" technique, showed that the decomposition gives rise to methyl and phenyl radicals, the activation energy and frequency factor being 77.6 kcal/mole and  $5.1 \times 10^{15} \text{ sec}^{-1}$  respectively.

Clark and Pritchard also examined the decomposition

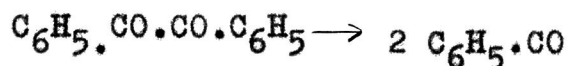
of trifluoroacetophenone and found an activation energy of 73.8 kcal/mole and a frequency factor of  $1.8 \times 10^{15}$  for the primary decomposition to phenyl and trifluoromethyl radicals and carbon monoxide. The photolysis of trifluoroacetophenone was examined at the same time by Smith and Calvert<sup>(9)</sup>. They dealt mainly with the formation and subsequent reactions of the trifluoromethyl radicals, showing that these could combine to form hexafluoroethane, or abstract hydrogen to form trifluoromethane. Other products obtained were benzene, carbon monoxide and some benzene. No diphenyl was detected. It was suggested that the initial step was formation of trifluoromethyl and benzoyl radicals, some of the latter decomposing to phenyl radicals plus carbon monoxide. As only small amounts of benzene and no diphenyl were detected, it was assumed that the steady state concentration of phenyl radicals was very low.

Smith and Hinshelwood<sup>(10)</sup> examined the thermal decomposition of benzaldehyde, showing that there were two modes of reaction, one of which involved formation of the phenyl radical.

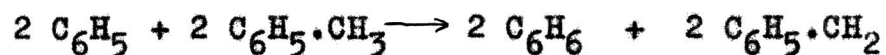
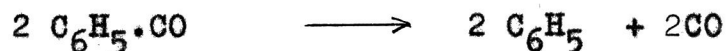
The "toluene carrier" technique mentioned previously is a good method for investigating radical reactions. Developed by Szwarc in 1949, this technique

involves the passage of the compound under investigation through a reaction vessel in a stream of toluene, which is in large excess. The advantage of this method is that any radicals formed are rapidly removed from the system by abstracting hydrogen from the toluene to produce relatively stable benzyl radicals, which then dimerize to dibenzyl. The radicals produced in the primary decomposition are thus removed before any secondary reactions can occur.

This technique was used by Ladacki, Leigh and Szwarc<sup>(11)</sup> to investigate the decomposition of benzoyl bromide, and by Jaquiss and Szwarc<sup>(12)</sup> for decomposition of iodobenzene, bromobenzene, benzyl benzoate and benzil. While some evidence for production of phenyl radicals was obtained with iodobenzene and bromobenzene, the results were unsatisfactory owing to formation of Iodine atoms and molecules from iodobenzene, and the rather high temperatures required for decomposition of bromobenzene. However, benzoyl bromide, benzyl benzoate and benzil were shown to be good sources of phenyl radicals. Using benzil as an example, the reaction scheme is as follows

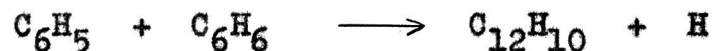


7.



Thus, for every molecule of benzil decomposed, one molecule of dibenzyl and two molecules of carbon monoxide and benzene should be formed. In the experiments it was found that the ratio of dibenzyl to half the carbon monoxide was just under one (0.95) showing that almost all the phenyl radicals formed had reacted with the toluene.

The decomposition of benzil has also been examined in a static system by Taylor<sup>(13)</sup>, who found that the main product was a tarry residue plus small amounts of benzene. No diphenyl was detected unless benzene was added, when large amounts were formed. This suggests that diphenyl was formed by reaction of phenyl radicals with benzene.

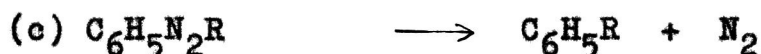
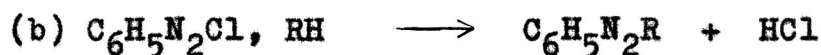
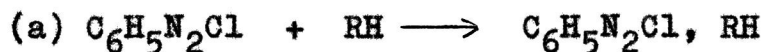


and not by dimerization of phenyl radicals. The same mechanism was proposed by Scott and Steacie<sup>(14)</sup> to explain diphenyl formation during the mercury sensitised photolysis of benzene, though Steacie<sup>(15)</sup> later suggested that the diphenyl formation was by combination of two phenyl radicals.

In 1953 the first non-chemical evidence for the existence of phenyl radicals was put forward by Lossing and Ingold<sup>(16)</sup>, who investigated the pyrolysis of various aromatic compounds with the aid of a mass spectrometer. They found that phenyl radicals were produced easily from anisole and diphenyl ether, and in trace quantities from benzene, toluene, benzaldehyde and diphenyl.

1.3 Evidence for, and reactions of phenyl radicals in solution.

Before the detection of free radicals by Paneth in 1929, Hantzsch and many other workers had examined the reactions of substances such as benzenediazonium chloride with various aromatic solvents and proposed that reaction occurred by formation of an addition complex which then decomposed to give nitrogen plus substituted diphenyl derivatives

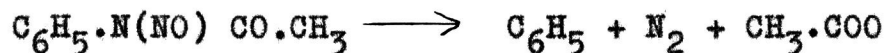


assuming (b) to be the rate-determining step, which would be dependent on the nature of the solvent, and (a) and (c) to be more rapid. However Pray<sup>(17)</sup>, finding that the rate of evolution of nitrogen was of the same order for the reactions of benzenediazonium salts with a series of aliphatic solvents, concluded that this mechanism was incorrect but was unable to propose any mechanism to fit his experimental results.

Another strange phenomenon which could not be explained was that in reactions of benzenediazonium salts and other azo and diazo compounds with aromatic solvents, the phenyl group was always seen to have

entered the aromatic nucleus in the ortho and/or para position to the so-called "directing" group, even when this group was normally meta directing.

In 1934, after Dull and Simons had demonstrated the existence of phenyl radicals in the gas phase, Grieve and Hey<sup>(18,19)</sup> suggested these reactions could be explained by the initial decomposition of the diazonium salts into nitrogen and free radicals. These free radicals, being neutral, would not be affected by the alkalinity of the solution and would always substitute in the ortho or para positions, where reaction was more rapid, as a result of the phenyl group being able to accept or donate electrons. Both these points were studied and confirmed in the reactions of sodium benzenediazotate and benzenediazonium chloride with benzene and various benzene derivatives. The same workers also investigated the reactions of nitrosoacetanilide with various aromatic solvents, and found that the rate of evolution of nitrogen was the same in all cases, as Pray had already found with diazonium salts in aliphatic solvents, thus strengthening their theory. The first, rate-determining, step was thus the decomposition of nitrosoacetanilide



followed by reaction of phenyl radicals with the solvent. Subsequently Waters<sup>(20)</sup> suggested that the acetate radical, formed together with the phenyl radical, could react in two ways, either by abstraction of hydrogen to form acetic acid, or by decomposition to carbon dioxide and a methyl radical. On determining the amounts of acetic acid and carbon dioxide produced, he was able to show that the total amount of these two substances was equivalent to the amount of nitrogen produced, thus giving further substance to the theory.

Meanwhile Razuvaev and Koton<sup>(21,22)</sup> had found that on heating diphenyl mercury in various aliphatic solvents benzene was always produced, and had also shown that on heating tetraphenyl lead, tetraphenyl tin or diphenyl mercury in paraffin oil containing sulphur, diphenyl disulphide ( $C_6H_5S SC_6H_5$ ) was produced. They concluded that in both cases phenyl radicals were produced.

General reviews of the evidence for the existence of phenyl radicals in solution were published by Hey and Waters<sup>(23)</sup> in 1937 and by Waters<sup>(24)</sup> in 1948. In both reviews the type of evidence put forward was similar to that of Grieve and Hey, showing that

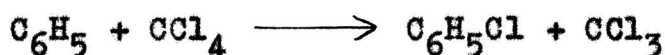


reactions of diazonium salts, diazohydroxides, nitrosoacylarylamines, arylazotriarylmethanes and diaroylperoxides in solution gave rise to similar products and that the initial step in each case was decomposition to produce phenyl radicals. The main characteristics of the phenyl radical in solution were summarised as follows:

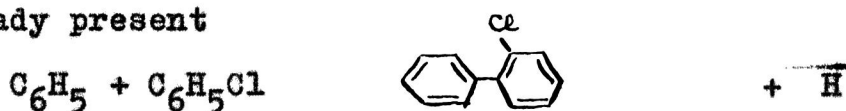
(a) The phenyl radical is an extremely reactive substance of short lifetime.

(b) No combination of phenyl radicals to produce diphenyl can be detected.

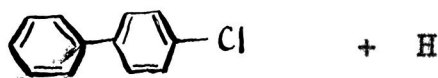
(c) Reaction with non-aromatic solvents containing hydrogen yields benzene and with those containing halogens yields halogen substituted benzenes, i.e. abstraction of an atom by the radical.



(d) Reaction with aromatic solvents yields substituted diphenyls (or diphenyl if benzene is the solvent) in which the radical invariably enters the nucleus at the ortho or para position to the group already present

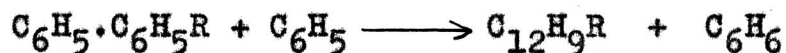
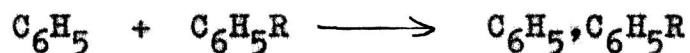


or



Further evidence was provided by Waters<sup>(25)</sup>, who decomposed benzenediazonium chloride in acetone containing suspensions of metals such as mercury, tin, tellurium and selenium and showed that the corresponding organometallic compounds were formed. As the solution had been kept neutral to ensure that no ionic mechanism could be involved, it was assumed that phenyl radicals had been formed from the decomposition of the benzenediazonium chloride and then reacted with the metal.

The mechanism of the reaction of phenyl radicals with aromatic solvents has been subjected to further investigation by Barson and Bevington<sup>(26)</sup>, and Blair, Bryce-Smith and Pengilly<sup>(27)</sup>. From a study of the decomposition of benzoyl peroxide, tetraphenyl lead and diphenyl mercury in various aromatic solvents it is suggested that the reaction is not a single step as previously assumed, but consists of two stages. A phenyl radical first adds to the aromatic nucleus and then another radical abstracts hydrogen from the complex



where R can be in either the 2 or 4 position.

In recent years it has been shown by Hey, Pengilly and Waters<sup>(28,29)</sup> that the phenyl radical can abstract an  $\alpha$  hydrogen atom from the side chain of alkylbenzenes, the resulting radicals dimerizing. Thus 2:3 diphenyl 2:3 dimethyl butane is formed from isopropylbenzene. With isopropyl benzene 60% of the phenyl radicals abstract the  $\alpha$  hydrogen and 40% form isopropyldiphenyl, and with ethylbenzene the two reactions occur equally. However, with toluene the main product is methyl diphenyl and only very small amounts of benzene and dibenzyl are obtained, while with t-butylbenzene, which contains no  $\alpha$  hydrogen atoms, no reaction of this type was observed. The reactivity of the  $\alpha$  hydrogen atom towards the phenyl radical thus appears to be in agreement with general hydrogen abstraction reactions, where the order of reactivity is tertiary  $>$  secondary  $>$  primary.

#### 1.4 Comparison of reactions of phenyl radicals in solution and in the gas phase.

It has been established that in solution the phenyl radical adds to an aromatic nucleus to form a diphenyl derivative. However, in the gas phase, except for the work of Taylor, no evidence has been found for this type of reaction. Jaquiss and Szwarc<sup>(12)</sup> have suggested that the initial step of such a reaction would be formation of a  $\pi-\pi$  bond between the radical and the aromatic nucleus, the complex thus formed containing a large excess of energy. In the gas phase, the high temperatures and low concentrations normally used would tend to favour decomposition of this complex, while in solution the excess energy could be removed by collision to give a stabilised complex, which would then lose a hydrogen atom. Recent work in solution has suggested that the reaction does involve several steps, the first being formation of a complex by addition of the radical to the nucleus, followed by abstraction of a hydrogen atom by another radical.

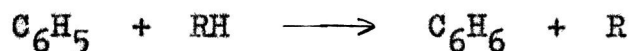
Abstraction of hydrogen atoms from the side chain of certain aromatic hydrocarbons appears to occur both in solution and in the gas phase. Toluene has been converted into benzyl radicals, which then combine to

form dibenzyl, in the gas phase and, though the same reaction does not occur readily with toluene in solution, ethylbenzene and isopropylbenzene have been converted into the dimers corresponding to abstraction of  $\alpha$  hydrogen atoms.

No comparison can be made for the reactions of phenyl radicals with aliphatic compounds as no work of this nature has been carried out in the gas phase. However in solution there is ample evidence to show that abstraction of hydrogen or halogens can occur readily.

1.5 Aim of the present work.

This was to examine the metathetical reactions of phenyl radicals in the gas phase



where RH is an aliphatic hydrocarbon, and to obtain values of the rate constants at different temperatures.

The Arrhenius equation

$$k = Ae^{-E/RT}$$

where  $k$  is the rate constant,  $A$  is the A factor,  $E$  is the activation energy,  $R$  is the gas constant and  $T$  is the absolute temperature, can then be used in its logarithmic form

$$\log_{10}k = \log_{10}A - \frac{1}{2,303} \frac{E}{RT}$$

to obtain values of the A factors and activation energies of the above reactions by plotting graphs of  $\log_{10}k$  against  $1/T$ . The slope of this line will be  $-\frac{1}{2,303} \cdot \frac{E}{R}$  and the intercept at  $\frac{1}{T} = 0$  will be  $\log_{10}A$ .

These values of rate constants, A factors and activation energies could then be compared with the values obtained for the similar reactions of other radicals.

### 1.6 Radical Source.

The sources of phenyl radicals reviewed in sections 1.2 and 1.3 are many, but very few of these are suitable for the present work. In general, most are involatile substances suitable for solution work but unsuitable for gas phase work. Also, no detailed study has been carried out on the secondary reactions of the radicals produced from the parent molecule, so the suitability from this point is unknown, and the radical source must be examined carefully before a study of the reactions of radicals with other compounds can be investigated.

Metallic phenyl compounds and azo compounds have both been used extensively in solution, but their low volatility prevents their use in gas phase work. Similarly benzil and benzophenone are unsuitable.

The most suitable sources from the point of volatility would be benzoyl halides or benzene. However, the benzoyl halides would produce halogen atoms as well as phenyl radicals, in the initial decomposition, and these would complicate the mechanism. Benzene would be completely unsuitable as a radical source as it would be the product of any metathetical reactions of phenyl radicals, and thus these reactions could not be examined.

Two possible sources of radicals are the photolysis of benzaldehyde or acetophenone, which are both reasonably volatile, and have been examined to a certain extent. Much work has been done using aldehydes and ketones as sources of alkyl radicals in the gas phase, and it would be expected that they might also be used for production of phenyl radicals. Benzaldehyde was accordingly examined as a source, but it was soon found that the kinetics of formation of benzene were complex, and attention was switched to acetophenone.

The ketone, acetophenone, has been used as the source of phenyl radicals throughout the present work, and the kinetics of benzene formation have been established relative to the kinetics of diphenyl formation.



## 2. EXPERIMENTAL.

### 2.1 Apparatus.

Experiments were carried out in a high vacuum static system (fig. 2.1.1) constructed from pyrex glass. All stopcocks were lubricated with Silicone High Vacuum Grease. For convenience the system will be treated as consisting of four parts, these being the pumping system, the reaction and storage system, and two separate analysis systems.

#### (a) Pumping System.

This consisted of a large bore pyrex tube connected to a two stage mercury diffusion pump backed by a "Hyvac" rotary oil pump. The pressure in the apparatus could be reduced to  $10^{-5}$  mm, measured on a Macleod gauge, within 20 minutes. A low vacuum system for the Toepler pump/gas burette and the pump down traps was provided by another rotary oil pump.

#### (b) Reaction and Storage System.

Acetophenone was stored in the vessel A and injected into the reaction vessel by surrounding the storage vessel with an electrically heated jacket. The other reactants, nitric oxide or various hydrocarbons, were stored in a 2 litre bulb fitted with a mercury blow off and a trap for degassing purposes.

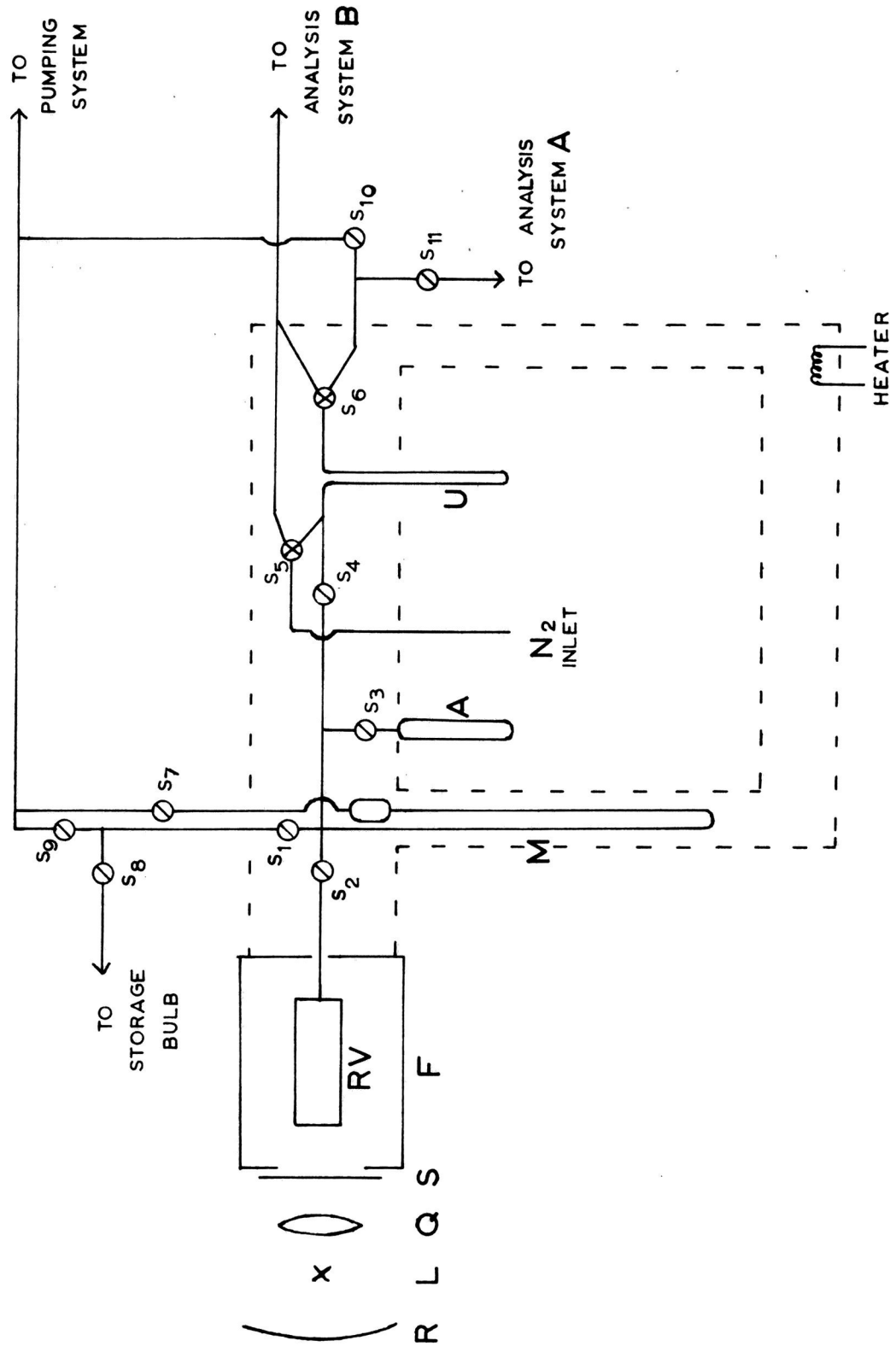


FIG. 2.1.1. GENERAL APPARATUS

The pressures of the reactants injected into the reaction vessel were measured by a mercury manometer M.

The cylindrical reaction vessel, of length 10 cm and diameter 5 cm, was constructed of quartz, and was connected to the pyrex system by means of a quartz to pyrex graded seal. The volume of this vessel was 160 cm<sup>3</sup>. It was contained in an electrically heated co-axial furnace (F), the temperature gradient along the reaction vessel being maintained level to  $\pm 1^{\circ}\text{C}$  by a 0-150 ohm variable resistance in parallel with part of the furnace heating element. Temperatures were measured by a thermocouple constructed of commercial T<sub>1</sub> and T<sub>2</sub> wires (British Driver Harris). This was laid along the top of the reaction vessel, the "hot" junction being placed half way along, and the "cold" junction in a flask of water at approximately 20°C. The potential was read on a Doran thermocouple potentiometer and the corresponding temperature was obtained from the calibration data provided by the manufacturers of the T<sub>1</sub> and T<sub>2</sub> wires. As this calibration data was for use when the "cold" junction was maintained at 20°C, the correct temperature was calculated from the equation

$$T = t_1 - (20 - t_2)$$

where  $T$  is the furnace temperature,  $t_1$  is the temperature read off the calibration graph, and  $t_2$  is the temperature of the "cold" junction.

A quartz window was fitted to one end of the furnace to permit illumination of the reaction mixtures by the unfiltered light of a 125 watt medium pressure mercury lamp (L). A reflector (R) of polished aluminium foil and a quartz lens (Q) of focal length 10 cm were used to increase the intensity of illumination. The time of illumination was controlled by a shutter (S) as, prior to each run, the lamp was warmed up for 15 minutes.

After illumination, the products were collected in the trap (U), which could be connected to either of the vacuum system, the reaction vessel, the Toepler pump/gas burette or the gas chromatography unit by suitable adjustment of stopcocks  $S_4$ ,  $S_5$  and  $S_6$ .

Stopcocks  $S_1$  to  $S_6$  and the mercury manometer were enclosed in a heating jacket maintained at  $150^\circ\text{C}$  to prevent condensation of products, and to allow acetophenone pressures up to 15 cms to be injected into the reaction vessel. This jacket was constructed of two horizontal wood asbestos boxes, one surrounding the stopcocks and two vertical wide bore pyrex tubes, one

surrounding the manometer, thus providing a circulatory system to maintain an even temperature throughout.

Heating was provided electrically by a 250 watt heater coiled on a former placed under one of the vertical tubes, and another 250 watt heater laid under the taps and down the tube surrounding the manometer. Glass extensions were fitted to the stopcocks to allow their manipulation from outside the heating jacket.

The heating system had two disadvantages, in that the stopcocks required to be lubricated every two weeks instead of every two months for the stopcocks at room temperature, and that two days pumping was necessary to degas the fresh grease.

(c) Analysis system A.

This consisted of a combined Toepler pump and gas burette (fig. 2.1.2) for analysis of methane, ethane and carbon monoxide.

The gas burette was calibrated before fitting to the apparatus by filling it with mercury, and weighing the amount held between the various calibration marks.

The volumes of the various sections were

|               |   |                       |
|---------------|---|-----------------------|
| a             | = | 0.321 cm <sup>3</sup> |
| a + b         | = | 0.819 "               |
| a + b + c     | = | 3.041 "               |
| a + b + c + d | = | 15.13 "               |

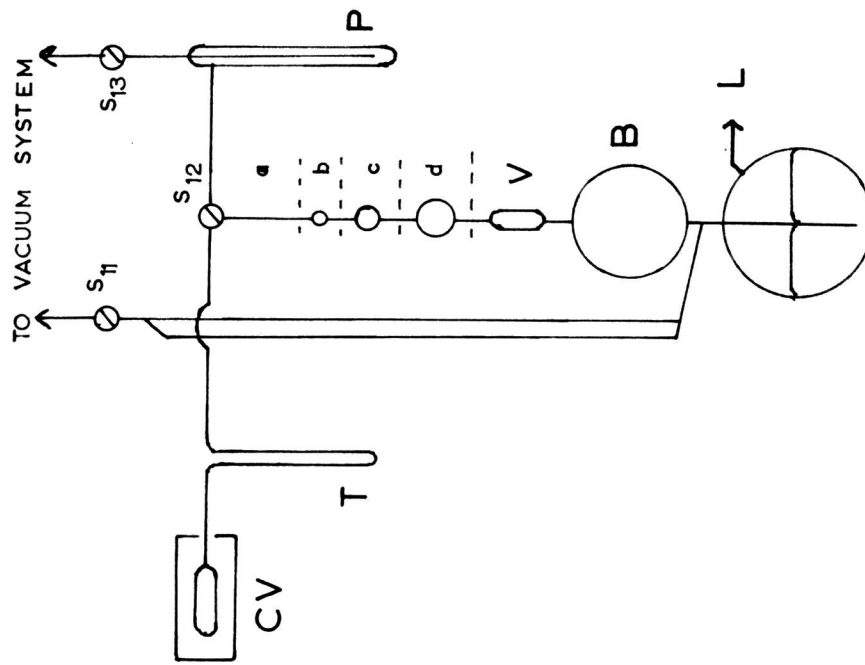


FIG. 21.2. ANALYSIS SYSTEM A  
TOEPLER PUMP / GAS BURETTE

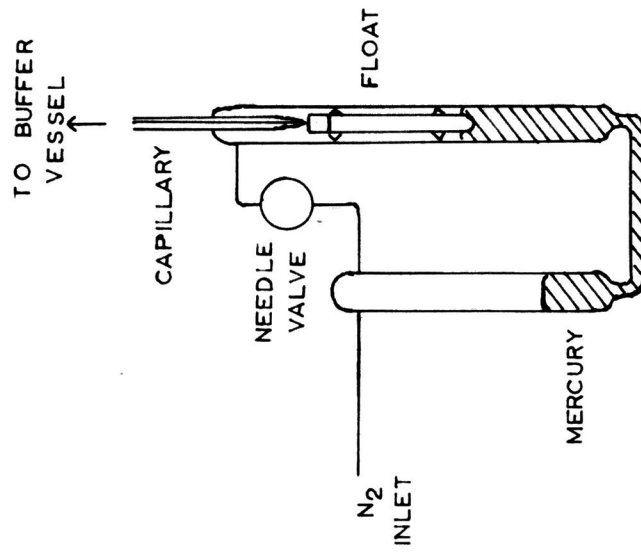


FIG. 21.4. FLOW REGULATOR

In any analysis for the gaseous products, trap U was maintained at  $91^{\circ}\text{C}$  to hold the condensable materials. This temperature was obtained by surrounding the trap with a boiling tube containing toluene at its freezing point.

The gases were removed from the reaction vessel and trap by the Toepler pump, being held in the gas burette by the non-return mercury float valve (F). Normally 12 strokes of the pump were sufficient to remove these gases. The gases were then forced through the stopcock  $S_{12}$  into the pump down trap (P), where ethane was condensed at approximately  $-208^{\circ}\text{C}$  within 10 minutes. By lowering the mercury level to the bottom of bulb (B) with the valve held open by a magnet, the methane and carbon dioxide were removed and, with stopcock  $S_{12}$  closed, the total amount of these gases was measured. To enable the amount of methane to be determined, the mixture was then forced through stopcock  $S_{12}$  into a small tube containing activated copper oxide maintained at  $300^{\circ}\text{C}$  by an electrically heated furnace (CF). After 1 hour, during which time the gases were mixed occasionally by raising and lowering the mercury level, the carbon dioxide formed from the carbon monoxide was frozen down in trap (T) at  $-183^{\circ}\text{C}$  and the methane was drawn

back into the gas burette and measured. The amount of carbon monoxide was found by subtracting the amount of methane from the total amount of methane plus carbon monoxide. Meanwhile, stopcock S<sub>13</sub> was opened to the vacuum system for 5 mins to remove the residual methane and carbon monoxide from the pump down trap. The gas burette was then evacuated and ethane in the pump down trap was warmed to room temperature, drawn into the gas burette and measured.

During the above procedure, small amounts of all products were lost owing to sharing between the gas burette and the copper oxide tube or pump down trap. Accordingly, correction factors were applied to the amounts of gases determined, these factors being 1.03 for ethane and the total of methane and carbon monoxide, and 1.05 for methane.

(d) Analysis system B.

This consisted of the gas chromatography unit shown in figure 2.1.3 and was designed to analyse for benzene toluene and diphenyl. The carrier gas, nitrogen, was split into three streams after passage through a calcium chloride drying tube, one stream leading to a mercury blow off, and the other two to the analysis and balancing columns.



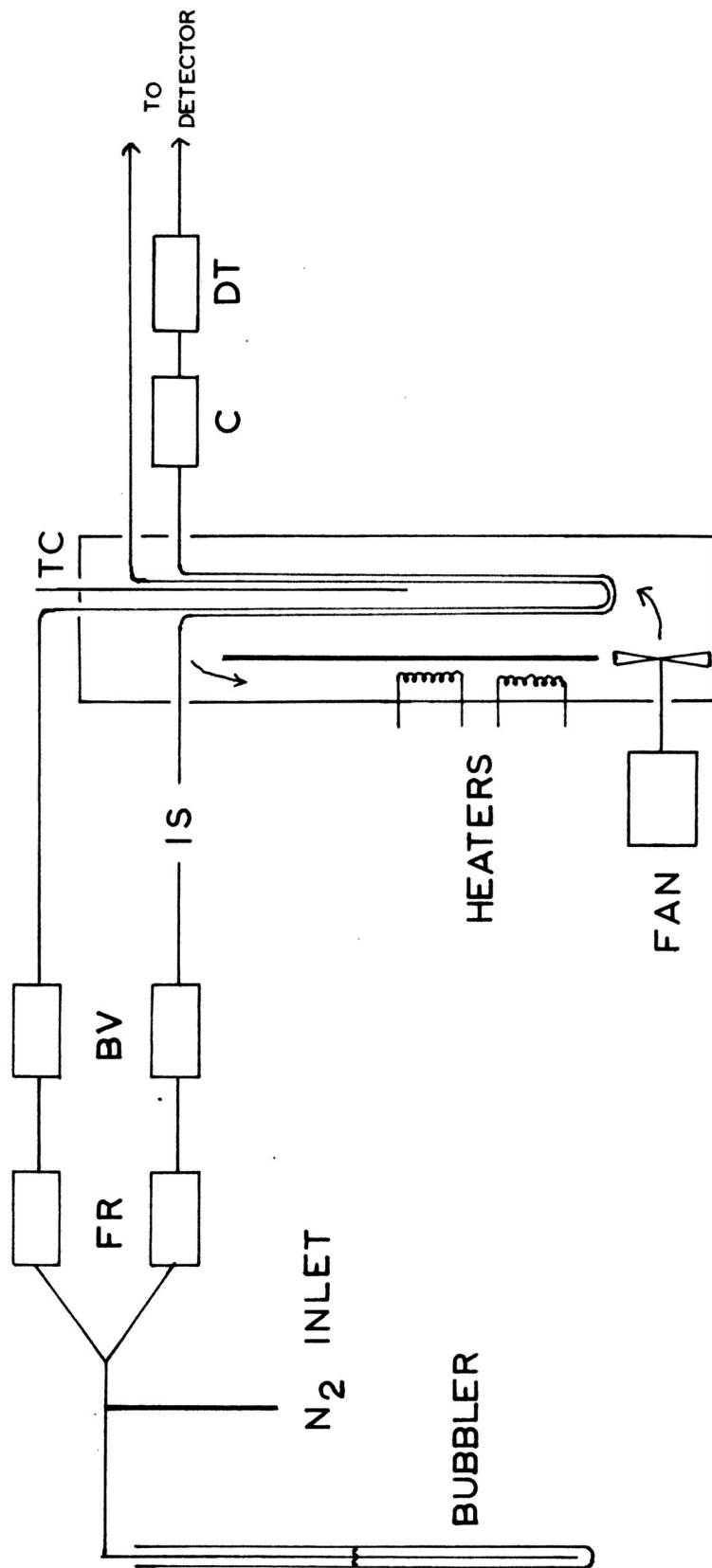


FIG. 2.1.3. ANALYSIS SYSTEM B  
GAS CHROMATOGRAPHY

The columns were contained in an oven to enable benzene to be eluted at 60°C and diphenyl at 160°C. This oven was constructed of wood asbestos insulated with fibre board. Two heaters were used, one, of 250 watts being controlled by a Sunvic T.S.8 bimetal strip regulator connected to a Sunvic relay, the other being a 500 watt booster for higher temperatures. An electric fan was used to circulate air in the direction shown on the diagram and thus maintain an even temperature throughout the oven. The heating system was capable of raising the temperature from 60 to 160°C within 15 minutes.

The rise in temperature during analysis caused the base line obtained from the detector to fluctuate markedly owing to a drop in the carrier gas flow rate at the higher temperature, so two flow regulators (FR) were incorporated in the system. These are illustrated in figure 2.1.4. They were constructed of pyrex, the float being fitted with spacers to ensure that it remained central below the capillary outlet, and a rubber stopper on top. The stopper was fitted to make good contact with the capillary outlet, which was drawn down and then ground. To prevent the float sticking to the outlet, bentonite was occasionally dropped down the capillary onto the rubber stopper. The desired

flow rate was obtained by adjustment of the needle valve. It was found that for the flow rate normally used in the present work (30 mls. per minute), the optimum conditions were an inlet pressure of 60 cms and a pressure drop across the needle valve, as measured from the level of mercury in the two limbs, of 5 cms.

Buffering vessels (BV) were placed after each flow regulator to remove any rapid fluctuations in the gas flow, and one stream of gas was led directly from these to the balancing column and then to the detector. The other stream was led to the injection system (I.S.) consisting of the trap (U), and then to the analysis column. After separation on this column, the products were converted to carbon dioxide to increase the sensitivity of the detector for diphenyl. The conversion was carried out by means of copper oxide wire in a 21 cm length of 1 cm diameter aluminous porcelain tubing wound with heating wire and insulated with mineral wool. It was found that, if this convertor was maintained at over  $650^{\circ}\text{C}$ , the calibration curves for benzene, toluene and diphenyl coincided, when plotted as the amount of carbon dioxide produced by complete combustion, against peak area. Thus 1  $\mu$  mole of diphenyl, 1.7  $\mu$  moles of toluene and 2  $\mu$  moles

of benzene would each produce 12  $\mu$  moles of carbon dioxide, suggesting that complete combustion was occurring. During all work the temperature was maintained at 700°C. Water formed by the combustion was removed by a small tube containing anhydrous magnesium perchlorate before reaching the detector.

The detector used was a thermal conductivity gauge of conventional design, the two tungsten filaments, resistance 10 ohms, being the sections  $R_1$  and  $R_2$  of a Wheatstone bridge circuit (fig. 2.1.5). The other sections  $R_3$  and  $R_4$  were of approximately 100 ohms resistance. A 0 - 11,000 ohm variable resistance ( $V_1$ ) was connected in parallel with resistance  $R_3$  to control the balance of the bridge. Another 0 - 11,000 ohm variable resistance ( $V_2$ ) controlled the sensitivity of the mirror galvanometer (G) used to measure the off-balance current obtained when carbon dioxide passed through the detector. The whole circuit was run off two 2-volt accumulators with a small variable resistance in series so that a constant voltage of 4 volts was applied. The readings from the galvanometer were plotted and the peak areas of the graphs produced in this way were measured with a planimeter.

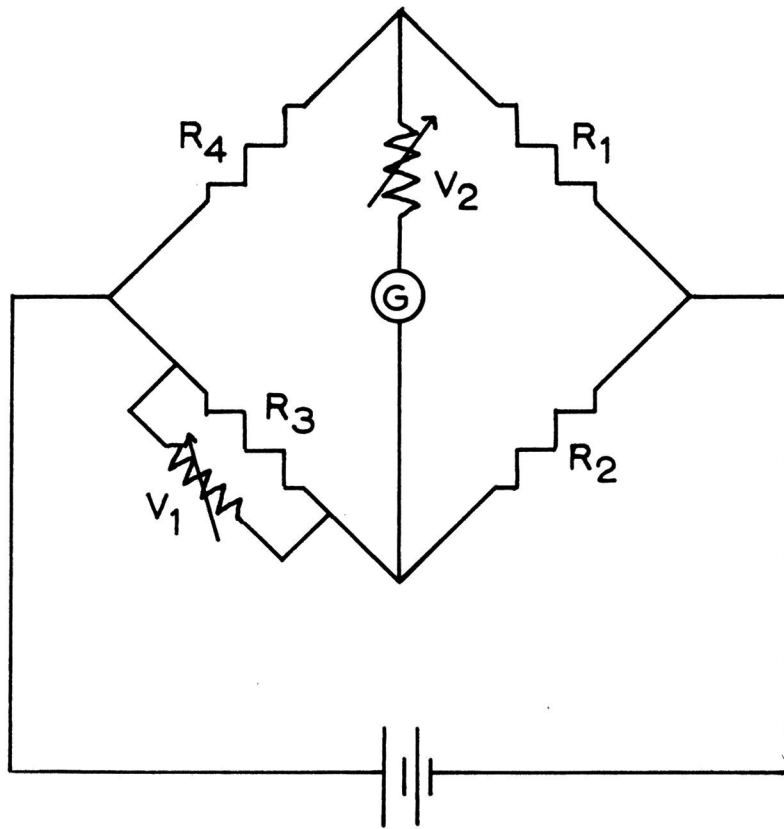


FIG. 2.1.5. WHEATSTONE BRIDGE CIRCUIT

2.2 Materials.

## (a) Radical Source.

Acetophenone was obtained as B.D.H. laboratory reagent, and contained 1% impurity, mainly benzene. The impurities were removed by fractional distillation under vacuum, only a few middle fractions, whose refractive index ( $n_{20}^D$ ) was determined as 1.5342 by means of an Abbe refractometer, being retained. The pure acetophenone was degassed by trap to trap distillation, and was then distilled into the storage vessel.

## (b) Hydrocarbons.

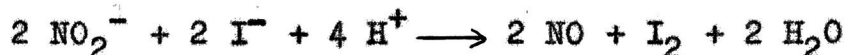
Three hydrocarbons, methane, cyclopropane and isobutane were used

|              | Source                    | Purity   |
|--------------|---------------------------|--|
| Isobutane    | B.P. Cylinder             | Pure   |
| Cyclopropane | B.O.G. medicinal cylinder | Pure   |
| Methane      | B.O.G. cylinder           | 2% C <sub>2</sub> → C <sub>4</sub><br>hydrocarbons |

Isobutane and cyclopropane were degassed several times. Methane was distilled several times from -183°C to -208°C to remove impurities.

(c) Inhibitor - Nitric Oxide<sup>(30)</sup>

This was prepared in accordance with the equation.



17 gm sodium nitrite and 40 gm potassium iodide

were dissolved in 100 mls water in a three necked flask fitted with a stirrer, dropping funnel and delivery tube. After flushing the system with nitrogen, 100 mls of 50% hydrochloric acid was added slowly with stirring. The nitric oxide evolved was trapped at  $-183^{\circ}\text{C}$  and was purified by low temperature distillation.

(d) Gas Chromatography.

Nitrogen was obtained from a B.O.G. cylinder, and was dried by passage over calcium chloride.

Celite (John Mansville) was treated and coated with liquid phase according to Phillips.<sup>(31)</sup> Throughout the present work 60-80 mesh Celite was used. The liquid phase was 20% by weight of Silicone High Vacuum grease, manufactured by Midland Silicones Ltd. The material was contained in a 4 foot length of 5 mm diameter pyrex tubing.

Copper oxide was obtained in the form of  $\frac{1}{8}$  to  $\frac{1}{4}$  inch lengths of wire, and was activated by repeated reduction and oxidation.

Magnesium Perchlorate (dried) was B.D.H. laboratory reagent, sold under the trade-name "Anhydrone".

(e) Freezing Mixtures.

Temperature

|                        |  |
|------------------------|--|
| $-91^{\circ}\text{C}$  | Toluene cooled to its freezing point by liquid oxygen. |
| $-183^{\circ}\text{C}$ | Liquid oxygen  |
| $-208^{\circ}\text{C}$ | Liquid oxygen boiling under reduced pressure.          |

### 2.3 Procedure

The apparatus was first evacuated to a pressure of  $10^{-5}$  and acetophenone and other reactants were degassed. With the shutter in place, the lamp was switched on to warm up for 15 minutes. During this warming up period acetophenone was injected into the reaction vessel to the required pressure. If another reactant was being used, this was allowed into the section of the apparatus bounded by stopcocks  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$  and  $S_9$  and  $S_8$  was closed again.  $S_2$  was then opened slowly till the pressure shown on the manometer was steady, when  $S_2$  was closed again. The pressure of this second reactant was noted. In the experiments with methane, when pressures over 15 cms were required, the procedure was repeated with more methane in the system  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$  and  $S_9$ . This double injection allowed pressures up to 25 cms to be obtained in the reaction vessel.

The run was started by removing the shutter and simultaneously starting a stopwatch. After the desired time of illumination, the run was stopped by switching off the lamp. The temperature was noted at the beginning of the run.

When acetophenone was photolysed alone, the



condensable products were frozen down in trap U at  $-91^{\circ}\text{C}$  while the non-condensable gases were pumped out of the reaction vessel and trap by the Toepler pump. The gaseous products were then analysed by the gas burette and the non-condensable products by the gas chromatography unit as described in section 2.1.

If reactants were added to the acetophenone, no analysis was carried out on the gaseous products. When methane or nitric oxide were used, they would pass through the trap even at  $-183^{\circ}\text{C}$  and thus swamp the gas burette. In the cases of cyclopropane and isobutane a temperature of  $-183^{\circ}\text{C}$  would hold these reactants in the trap, but might also retain some of the ethane.

Specimen Run.

Acetophenone Pressure Effect - Run No. 51.

Furnace Temperature =  $549^{\circ}\text{A}$

$\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$  pressure = 4.87 cm

$[\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3]$  =  $1.42 \times 10^{-6}$  mole  
 $\text{cm}^{-3}$

Length of run = 120 seconds

Analysis of non-condensable gases - gas burette.

| Product                       | Pressure<br>(cm) | Volume<br>(cm <sup>3</sup> ) | $\mu$ moles | $10^{11} \times R_{pr}$<br>(mole cm <sup>-3</sup><br>sec <sup>-1</sup> ) | $10^{11} R_{pr}^*$<br>(mole cm <sup>-3</sup><br>sec <sup>-1</sup> ) |
|-------------------------------|------------------|------------------------------|-------------|--|---|
| CO + CH <sub>4</sub>          | 11.44            | A+B+C                        | 20.4        | 106.3  | 109.5   |
| CH <sub>4</sub>               | 5.11             | A+B                          | 2.45        | 12.7   | 13.4  |
| C <sub>2</sub> H <sub>6</sub> | 8.65             | A+B                          | 4.15        | 21.6   | 22.3  |
| CO                            | -                | -                            | -           | -  | 96.1  |

Analysis of condensable products - gas chromatography.

| Product  | Peak Area<br>(sq.ins.) | Sensitivity of<br>galvanometer | $\mu$ moles | $10^{11} \times R_{pr}$<br>(mole cm <sup>-3</sup><br>sec <sup>-1</sup> ) |
|----------|------------------------|--------------------------------|-------------|--|
| Benzene  | 0.93                   | 5.00%                          | 7.40        | 38.52  |
| Toluene  | 0.33                   | 100.0%                         | 0.112       | 0.585  |
| Diphenyl | 0.67                   | 100.0%                         | 0.133       | 0.693  |

$R_{pr}$  = rate of formation of the product.

$R_{pr}^*$  = rate corrected for loss in the traps.

### 3. RESULTS

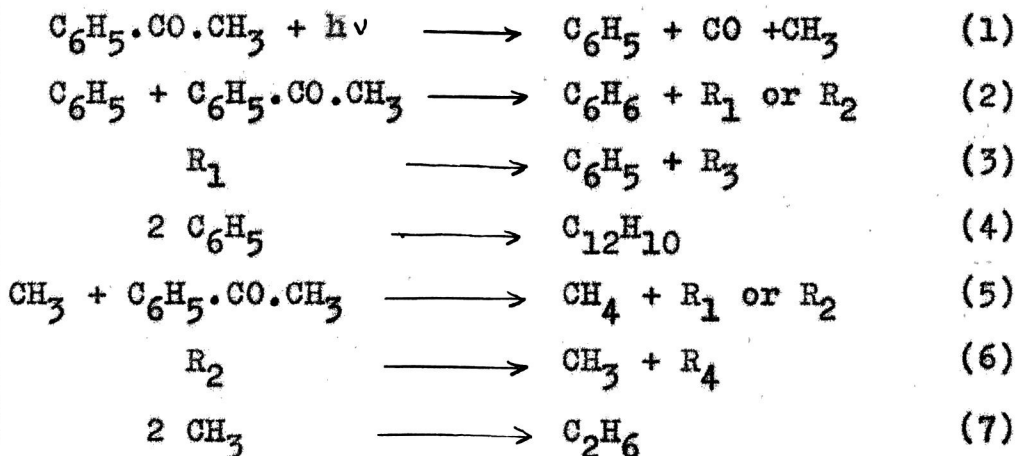
#### 3.1 Decomposition of Acetophenone.

This decomposition was studied, not to obtain the full mechanism of reaction, but with a view to using acetophenone as a source of phenyl radicals for investigation of metathetical reactions with hydrocarbons. Accordingly, as benzene would be the product of any such metathetical reactions, the kinetics of formation of benzene during the primary decomposition must be determined.

To investigate these kinetics, some method of determining the concentration of phenyl radicals must be found and in the present work this comes from the formation of diphenyl, assuming that the activation energy of combination of radicals is zero and the rate constant is  $10^{14} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ . No investigation of this reaction has been carried out, but the assumption is made on the basis of the known values for combination of other radicals. In most cases where absolute values of the rate constant have been determined they have been in the range  $k = 10^{13} \rightarrow 10^{14} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$  and the activation energies have been fairly close to, or equal to, zero<sup>(32)</sup>. It seems unlikely that the phenyl radical should differ markedly

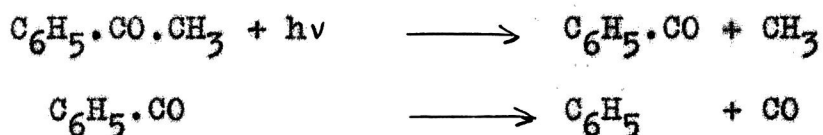
from other radicals in this respect.

The mechanism initially proposed for the photolytic decomposition was



of which the various steps shall be considered below.

The primary photolytic decomposition has been represented by reaction (1), though whether this occurs in one stage, as shown above, or in two stages



involving the intermediate formation of benzoyl radicals, is not definitely known. Clark and Pritchard (8) favour the one stage mechanism to account for the high value of the A factor ( $5 \times 10^{15} \text{ sec}^{-1}$ ) for the pyrolysis while Glazebrook and Pearson (6), having identified benzil as a reaction product, suggest the two stage mechanism. Possibly decomposition occurs by both modes. However, for the purpose of the present work

it is sufficient to know that phenyl radicals are formed, and no differentiation between the two modes of decomposition are required.

In reactions 2 and 5, phenyl and methyl radicals abstract hydrogen to form benzene and methane together with the radicals  $R_1$  or  $R_2$ . The composition of these radicals is uncertain, as it is not known whether the hydrogen atom is abstracted from the methyl group to produce a phenacyl radical ( $C_6H_5.CO.CH_2$ ) or from the phenyl group to give a substituted phenyl radical ( $CH_3.CO.C_6H_4$ ). The subsequent reaction of these two radicals is also uncertain, as they could dimerise, combine with other radicals, or decompose, in which case phenyl radicals would be formed from the phenacyl radicals, and methyl radicals from the substituted phenyl radicals, as shown in reactions 3 and 6, together with  $R_3$  and  $R_4$ , whose composition is unknown. No detailed examination of quantum yields was made, so it is not definitely known whether chain reactions of this type occur.

Reactions 4 and 7 represent the combination of radicals to produce diphenyl and methane. The rate constant for methane formation in this way has been determined by the rotating sector (33, 34, 35) and other methods (36, 37) and the value used in the present

work is  $k = 10^{13.34} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ . The rate constant for phenyl radical combination has been assumed as  $10^{14} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ .

Applying the steady state treatment to the mechanism suggested, the rate of formation of benzene would be

$$R_{C_6H_6} = k_2 [C_6H_5] [C_6H_5 \cdot CO \cdot CH_3]$$

and the rate of formation of diphenyl

$$R_{C_{12}H_{10}} = k_4 [C_6H_5]^2$$

Combining these equations,

$$\frac{R_{C_6H_6}}{(R_{C_{12}H_{10}})^{\frac{1}{2}}} = \frac{k_2}{k_4^{\frac{1}{2}}} [C_6H_5 \cdot CO \cdot CH_3]$$

or,

$$k_2 = \frac{k_4^{\frac{1}{2}} R_{C_6H_6}}{(R_{C_{12}H_{10}})^{\frac{1}{2}} [C_6H_5 \cdot CO \cdot CH_3]}$$

A similar treatment on the formation of methane and ethane would give

$$k_5 = \frac{k_7^{\frac{1}{2}} R_{CH_4}}{(R_{C_2H_6})^{\frac{1}{2}} [C_6H_5 \cdot CO \cdot CH_3]}$$

Values of the rates of formation of benzene, diphenyl, methane and ethane were determined by analysis, and the concentration of acetophenone was assumed to be the initial concentration. This assumption is only valid if the extent of decomposition is small. In the

present work, the extent of decomposition was measured by analysis of carbon monoxide, of which one molecule is formed for every molecule of acetophenone decomposed and the maximum percentage decomposition was approximately 12%, though in most experiments it was less than 8%.

During preliminary runs (table 3.1.1) at 277°C it was found that the values of  $k_2$  dropped on increasing the acetophenone concentration, while the values of  $k_5$  appeared to be constant within the limits of accuracy obtained.

TABLE 3.1.1.

$k_2$  and  $k_5$  at 277°C.

| $10^6 \times [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]$<br>(mole.cm <sup>-3</sup> ) | $10^{-8} k_2$<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) | $10^{-8} k_5$<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) |
|--|--|--|
| 0.733  | 22.18  | 0.502  |
| 0.925  | 15.73  | 0.724  |
| 1.171  | 11.77  | 0.517  |
| 1.392  | 10.48  | 0.499  |
| 1.450  | 8.92   | 0.689  |

It would therefore appear that some other reactions occur to produce either benzene or diphenyl.

Benzene could be produced by some form of molecular

rearrangement such as



If this reaction occurred, addition of nitric oxide as an inhibitor of radical reaction would show a reasonably large residual formation of benzene. The results obtained on addition of varying amounts of nitric oxide are shown in table 3.1.2 and the rates of formation of benzene and diphenyl, and variation of  $k_2$  are plotted against the nitric oxide concentration in Figures 3.1.2a and 3.1.2b. It can be seen that the rates of formation of both products drop rapidly almost to zero, and  $k_2$  drops to a constant residual value one tenth of the original value. This means that any residual reaction can be neglected in comparison with the radical mechanism.

Diphenyl could be formed in two other ways. One, involving addition of phenyl radicals to the benzene produced in the reaction, is unlikely as the concentration of benzene present in the system is very low, even at the end of reaction. The other possible source of diphenyl would be addition of phenyl radicals to acetophenone, followed by loss of an acetyl radical.

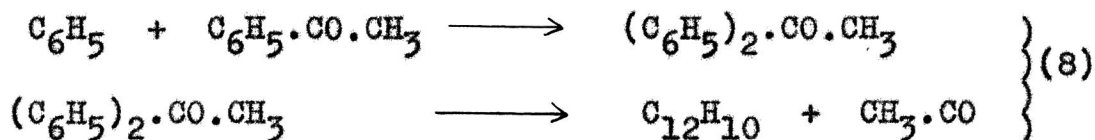




TABLE 3.1.2

## Effect of nitric oxide

| Run No. | Temp (°A) | $10^6 [A]$ (mole $\text{cm}^{-3}$ ) | $10^6 [\text{NO}]$ | Time (sec) | $\text{C}_6\text{H}_6$ | $\text{C}_{12}\text{H}_{10}$ | $\text{C}_6\text{H}_5\cdot\text{CH}_3$ | $\log k_p$ | $10^3 \cdot \frac{\text{C}_{12}\text{H}_{10}}{\text{C}_6\text{H}_6}$ | $\frac{\text{C}_6\text{H}_6}{A^2}$ | $10^{-8} k_2$ (mole $^{-1}$ cm $^3$ sec $^{-1}$ ) |
|---------|-----------|-------------------------------------|--------------------|------------|------------------------|------------------------------|--|------------|--|------------------------------------|---|
| 8       | 604       | 1.07                                | 0.138              | 300        | 21.2                   | 0.145                        | -                                      | 9.218      | 6.84   | 186                                | 16.5  |
| 7       | 604       | 1.07                                | 0.234              | 600        | 13.1                   | 0.093                        | 0.176                                  | 9.106      | 7.07   | 115                                | 12.8  |
| 4       | 605       | 1.07                                | 0.262              | 600        | 12.1                   | 0.121                        | -                                      | 9.016      | 9.97   | 107                                | 10.4  |
| 13      | 600       | 1.06                                | 0.294              | 600        | 8.28                   | 0.075                        | 0.096                                  | 8.958      | 9.00   | 74.3                               | 9.08  |
| 3       | 603       | 1.08                                | 0.432              | 915        | 6.18                   | 0.027                        | -                                      | 9.040      | 4.42   | 53.2                               | 11.0  |
| 6       | 600       | 1.08                                | 0.454              | 900        | 4.33                   | 0.021                        | 0.069                                  | 8.944      | 4.81   | 37.3                               | 8.79  |
| 14      | 602       | 1.07                                | 0.578              | 900        | 2.53                   | 0.035                        | 0.045                                  | 8.604      | 13.7   | 22.1                               | 4.02  |
| 15      | 600       | 1.08                                | 0.623              | 900        | 2.21                   | 0.028                        | 0.037                                  | 8.588      | 12.6   | 18.8                               | 3.87  |
| 1       | 602       | 1.07                                | 1.32               | 1800       | 0.515                  | 0.0042                       | -                                      | 8.374      | 8.10   | 4.53                               | 2.37  |
| 10      | 601       | 1.09                                | 1.48               | 1500       | 0.731                  | 0.0083                       | -                                      | 8.364      | 11.4   | 6.10                               | 2.31  |

$\text{C}_6\text{H}_6$ ,  $\text{C}_{12}\text{H}_{10}$ ,  $\text{C}_6\text{H}_5\cdot\text{CH}_3$  - Rates of formation -  $10^{-11}$  mole  $\text{cm}^{-3}$  sec $^{-1}$

[A] - concentration of acetophenone

[NO] - concentration of nitric oxide

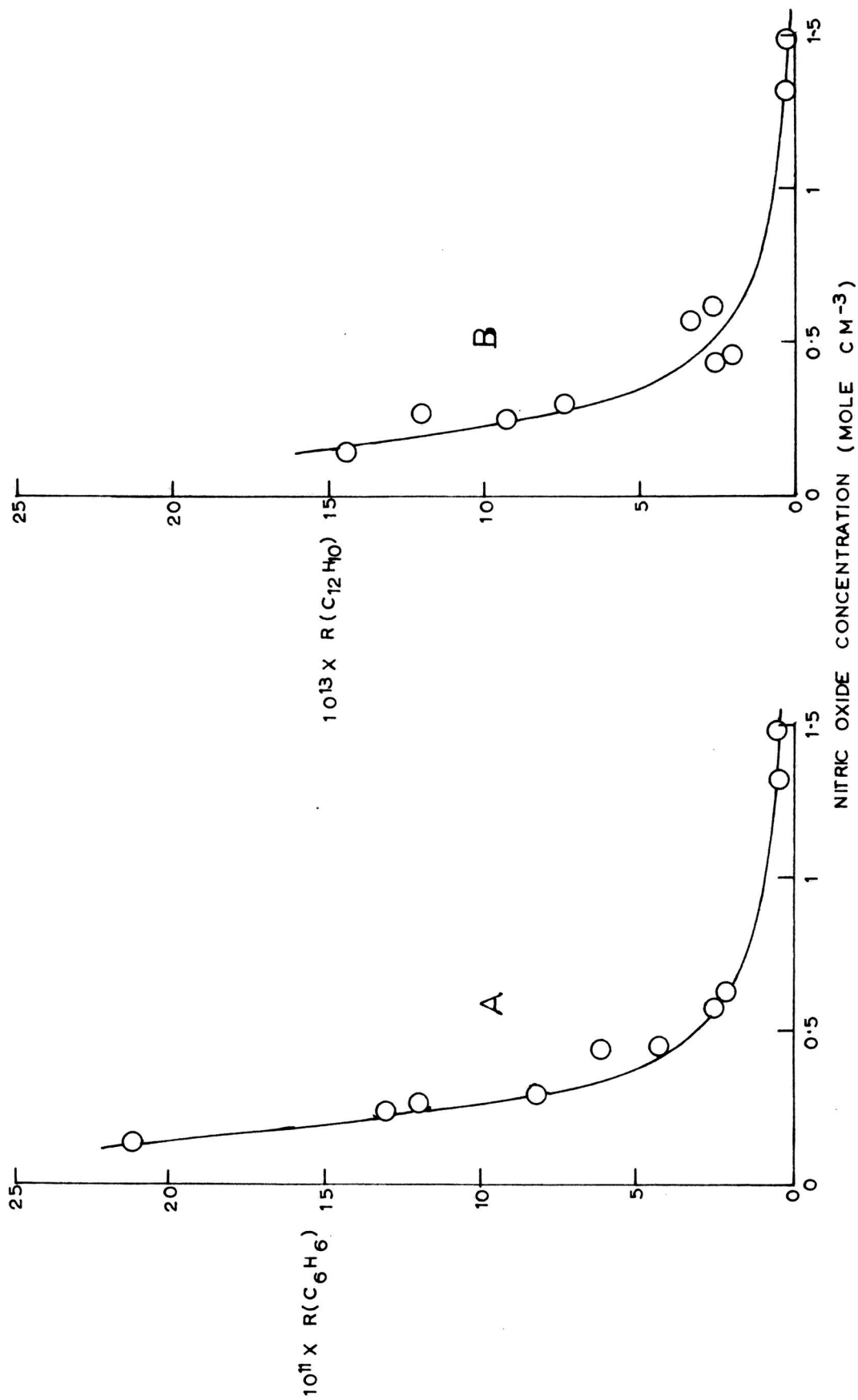


FIG. 3.12 a EFFECT OF NITRIC OXIDE ON

A. RATE OF FORMATION OF BENZENE

B. " " " " DIPHENYL

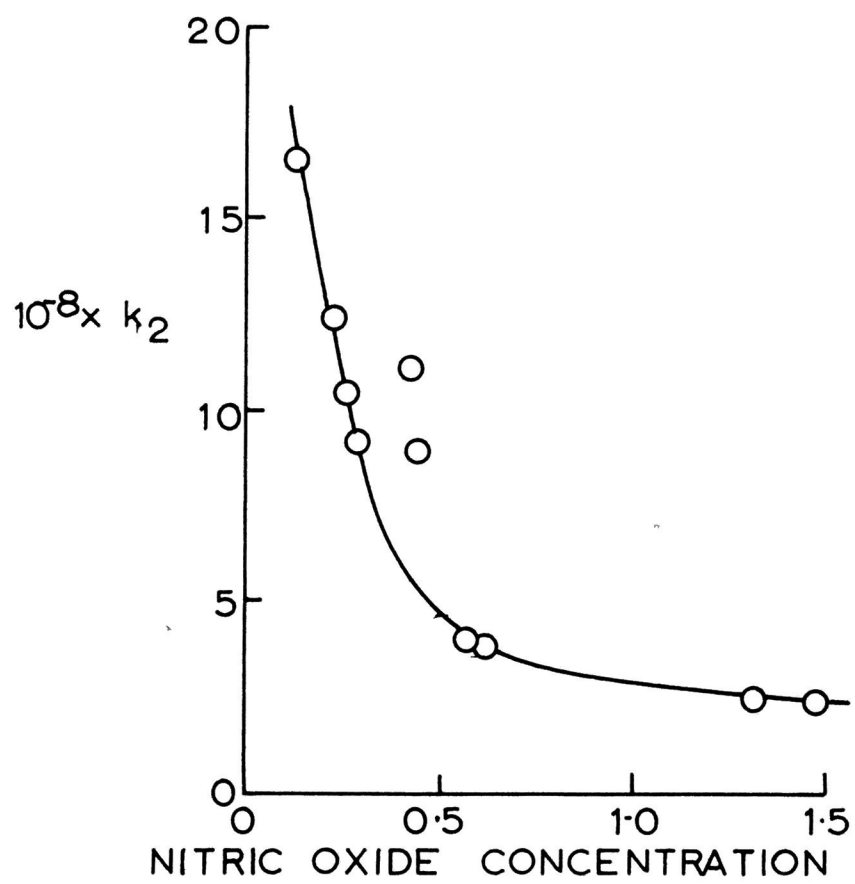
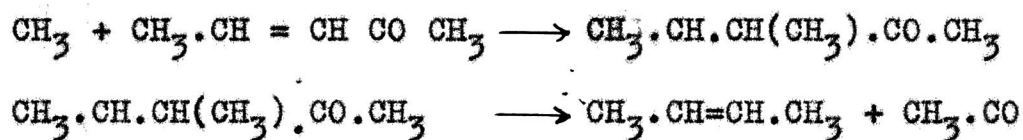


FIG. 3.1.2.b. EFFECT OF NITRIC OXIDE ON  $k_2$

This type of reaction has been suggested by Pitts<sup>(38, 39)</sup> to account for formation of 2 - butene during photolysis of methyl propenyl ketone



Also these reactions are similar to many reactions of phenyl radicals in solution, where the phenyl radical adds to the solvent to produce substituted diphenyl derivatives.

From reactions 2, 4 and 8, applying the steady state treatment once more the rate of formation of benzene would be

$$R_{\text{C}_6\text{H}_6} = k_2 [\text{C}_6\text{H}_5] [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]$$

as before, but the rate of formation of diphenyl would now be

$$R_{\text{C}_{12}\text{H}_{10}} = k_4 [\text{C}_6\text{H}_5]^2 + k_8 [\text{C}_6\text{H}_5] [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]$$

where  $k_3$  is the overall rate constant for the two reactions shown as reaction 8.

Combining these equations for  $R_{\text{C}_6\text{H}_6}$  and  $R_{\text{C}_{12}\text{H}_{10}}$ ,

$$R_{\text{C}_{12}\text{H}_{10}} = k_4 \left( \frac{R_{\text{C}_6\text{H}_6}}{k_2 [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]} \right)^2 + \frac{k_8}{k_2} R_{\text{C}_6\text{H}_6}$$

or

$$\frac{R_{\text{C}_{12}\text{H}_{10}}}{R_{\text{C}_6\text{H}_6}} = \frac{k_4}{k_2^2} \frac{R_{\text{C}_6\text{H}_6}}{[\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]^2} + \frac{k_8}{k_2}$$

which is an equation of the general type  $y = mx + c$ .

Thus plots of  $\frac{R_{C_{12}H_{10}}}{R_{C_6H_6}}$  against  $\frac{R_{C_6H_6}}{[C_6H_5 \cdot CO \cdot CH_3]^2}$  should have a slope equal to  $\frac{k_4}{k_2}$  and an intercept of  $\frac{k_8}{k_2}$ .

Plots of this type were obtained in two ways, either

(a) by addition of various amounts of nitric oxide, or (b) by variation of the acetophenone concentration.

(a) Addition of nitric oxide.

The results of this work at  $327^\circ C$  are shown in Table 3.1.2 and figure 3.1.2c. The graph shows that, although no line can be drawn accurately owing to the large scatter, a rough line can be drawn, having a slope of approximately  $8 \times 10^{-6}$  and an intercept of approximately  $6 \times 10^{-3}$ . Thus, assuming  $K_4$  equal to  $10^{14} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$ ,

$$k_2 = 35 \times 10^8 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

$$k_8 = 0.21 \times 10^8 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}.$$

Because of the large scatter, and thus lack of accuracy, in these results no further work at other temperatures was carried out.

(b) Variation of acetophenone concentration.

The acetophenone concentration was varied from 0.8 to  $3.2 \text{ moles cm}^{-3}$ , the results being shown in Table 3.1.3 and figures 3.1.3a→d. In general, good straight

43.  
TABLE 3.1.3

| Run No. | Temp (°A) | $10^6 [A]$<br>(mole $\text{cm}^{-3}$ ) | Time (sec) | CO   | $\text{C}_6\text{H}_6$ | $\text{C}_{12}\text{H}_{10}$ | $\text{C}_6\text{H}_5\cdot\text{CH}_3$ | $\text{CH}_4$ | $\text{C}_2\text{H}_6$ | $\log k_5$<br>(mole $^{-1}$ $\text{cm}^3$ sec $^{-1}$ ) | $10^3 \frac{\text{C}_{12}\text{H}_{10}}{\text{C}_6\text{H}_6}$ | $\frac{\text{C}_6\text{H}_6}{A^2}$ |
|---------|-----------|--|------------|------|------------------------|------------------------------|--|---------------|------------------------|---|--|------------------------------------|
| 52      | 557       | 1.14                                   | 120        | 114  | 38.2                   | 0.838                        | 0.729                                  | 7.89          | 24.0                   | 7.433   | 22.0   | 295                                |
| 4       | 552       | 1.17                                   | 120        | 120  | 40.7                   | 0.875                        | 0.745                                  | 7.75          | 25.0                   | 7.293   | 21.5   | 298                                |
| 5       | 549       | 1.17                                   | 120        | 107  | 35.6                   | 0.667                        | 0.604                                  | 7.29          | 19.4                   | 7.319   | 18.7   | 259                                |
| 47      | 549       | 1.18                                   | 120        | 90.9 | 37.4                   | 0.755                        | -                                      | 15.0          | 35.8                   | 7.497   | 20.2   | 267                                |
| 8       | 553       | 1.39                                   | 120        | 116  | 42.7                   | 0.859                        | 0.818                                  | 9.37          | 21.6                   | 7.331   | 20.1   | 221                                |
| 51      | 549       | 1.42                                   | 120        | 96.1 | 38.5                   | 0.693                        | 0.585                                  | 13.4          | 22.3                   | 7.469   | 18.0   | 190                                |
| 50      | 548       | 1.76                                   | 120        | 82.5 | 37.8                   | 0.516                        | 0.641                                  | 12.5          | 20.8                   | 7.362   | 13.6   | 122                                |
| 49      | 550       | 1.78                                   | 120        | -    | 42.5                   | 0.663                        | 0.886                                  | -             | -                      | -   | 15.6   | 134                                |
| 53      | 558       | 2.17                                   | 120        | -    | 45.3                   | 0.588                        | 0.990                                  | -             | -                      | -   | 13.0   | 96.2                               |
| 54      | 550       | 2.57                                   | 120        | -    | 37.6                   | 0.466                        | 0.865                                  | -             | -                      | -   | 11.9   | 56.8                               |
| 17      | 595       | 0.774                                  | 30         | -    | 69.7                   | 1.53                         | 1.21                                   | -             | -                      | -   | 22.0   | 1160                               |
| 14      | 597       | 0.792                                  | 60         | 145  | 64.4                   | 1.47                         | 1.56                                   | 15.2          | 33.9                   | 7.689   | 22.8   | 1030                               |
| 15      | 592       | 0.965                                  | 60         | -    | 64.7                   | 1.29                         | 0.82                                   | -             | -                      | -   | 20.0   | 695                                |
| 10      | 599       | 1.09                                   | 60         | 192  | 68.8                   | 1.04                         | 1.63                                   | 23.9          | 34.6                   | 7.741   | 15.1   | 576                                |
| 11      | 597       | 1.32                                   | 60         | 173  | 77.3                   | 1.22                         | 1.43                                   | 23.4          | 50.5                   | 7.567   | 15.8   | 442                                |
| 12      | 599       | 1.41                                   | 60         | 184  | 72.0                   | 1.07                         | 1.68                                   | 24.8          | 35.3                   | 7.641   | 14.9   | 362                                |
| 13      | 597       | 1.72                                   | 60         | -    | 72.0                   | 1.07                         | 1.71                                   | -             | -                      | -   | 14.9   | 243                                |
| 16      | 602       | 2.01                                   | 60         | 189  | 93.0                   | 1.07                         | 1.24                                   | 30.8          | 26.7                   | 7.642   | 11.5   | 230                                |
| 37      | 614       | 1.06                                   | 60         | -    | 82.9                   | 1.93                         | 1.49                                   | -             | -                      | -   | 23.2   | 736                                |
| 44      | 614       | 1.26                                   | 60         | 199  | 95.4                   | 1.93                         | 1.77                                   | 35.2          | 60.2                   | 7.724   | 20.2   | 596                                |
| 46      | 614       | 1.49                                   | 60         | 198  | 105                    | 1.89                         | 2.18                                   | 36.0          | 35.0                   | 7.783   | 18.0   | 474                                |
| 40      | 616       | 1.57                                   | 60         | 195  | 97.9                   | 1.49                         | 2.49                                   | 43.1          | 79.6                   | 7.658   | 15.2   | 397                                |
| 43      | 619       | 2.31                                   | 60         | -    | 111                    | 1.33                         | -                                      | -             | -                      | -   | 12.0   | 209                                |
| 38      | 618       | 2.31                                   | 60         | -    | 99.0                   | 1.28                         | 2.39                                   | -             | -                      | -   | 12.9   | 185                                |
| 45      | 618       | 3.07                                   | 70         | 257  | 119                    | 1.45                         | 2.68                                   | 31.1          | 44.8                   | 7.665   | 12.2   | 127                                |
| 35      | 683       | 0.951                                  | 30         | -    | 129                    | 1.70                         | 3.13                                   | -             | -                      | -   | 13.2   | 1430                               |
| 20      | 678       | 0.984                                  | 30         | -    | 134                    | 2.52                         | 3.13                                   | -             | -                      | -   | 18.8   | 1390                               |
| 31      | 675       | 1.03                                   | 30         | 253  | 131                    | 2.17                         | 3.35                                   | 40.6          | 42.7                   | 7.949   | 16.5   | 1230                               |
| 30      | 681       | 1.04                                   | 30         | 189  | 103                    | 2.04                         | 3.35                                   | 38.3          | 35.5                   | 7.963   | 19.8   | 957                                |
| 29      | 676       | 1.04                                   | 30         | 247  | 128                    | 2.10                         | 3.07                                   | 28.9          | 39.8                   | 7.664   | 16.5   | 1180                               |
| 33      | 666       | 1.05                                   | 30         | 245  | 129                    | 2.10                         | 3.50                                   | 57.3          | 46.7                   | 8.071   | 16.3   | 1170                               |
| 25      | 664       | 1.13                                   | 30         | -    | 130                    | 2.08                         | 2.71                                   | -             | -                      | -   | 16.1   | 1020                               |
| 24      | 666       | 1.14                                   | 30         | 249  | 116                    | 1.33                         | 2.56                                   | 51.2          | 40.2                   | 8.022   | 11.4   | 900                                |
| 28      | 669       | 1.35                                   | 30         | -    | 135                    | 2.00                         | 3.50                                   | -             | -                      | -   | 14.8   | 739                                |
| 21      | 679       | 1.39                                   | 30         | 317  | 138                    | 1.91                         | 3.81                                   | 67.7          | 35.6                   | 8.090   | 13.9   | 712                                |
| 22      | 685       | 1.83                                   | 30         | 303  | 149                    | 1.83                         | 4.60                                   | 67.4          | 43.6                   | 7.917   | 12.3   | 446                                |
| 34      | 671       | 1.92                                   | 30         | 235  | 118                    | 0.99                         | 2.77                                   | 54.6          | 26.8                   | 7.909   | 12.0   | 319                                |
| 23      | 684       | 3.16                                   | 60         | 298  | 163                    | 1.02                         | 3.83                                   | 76.8          | 25.0                   | 7.865   | 6.24   | 163                                |

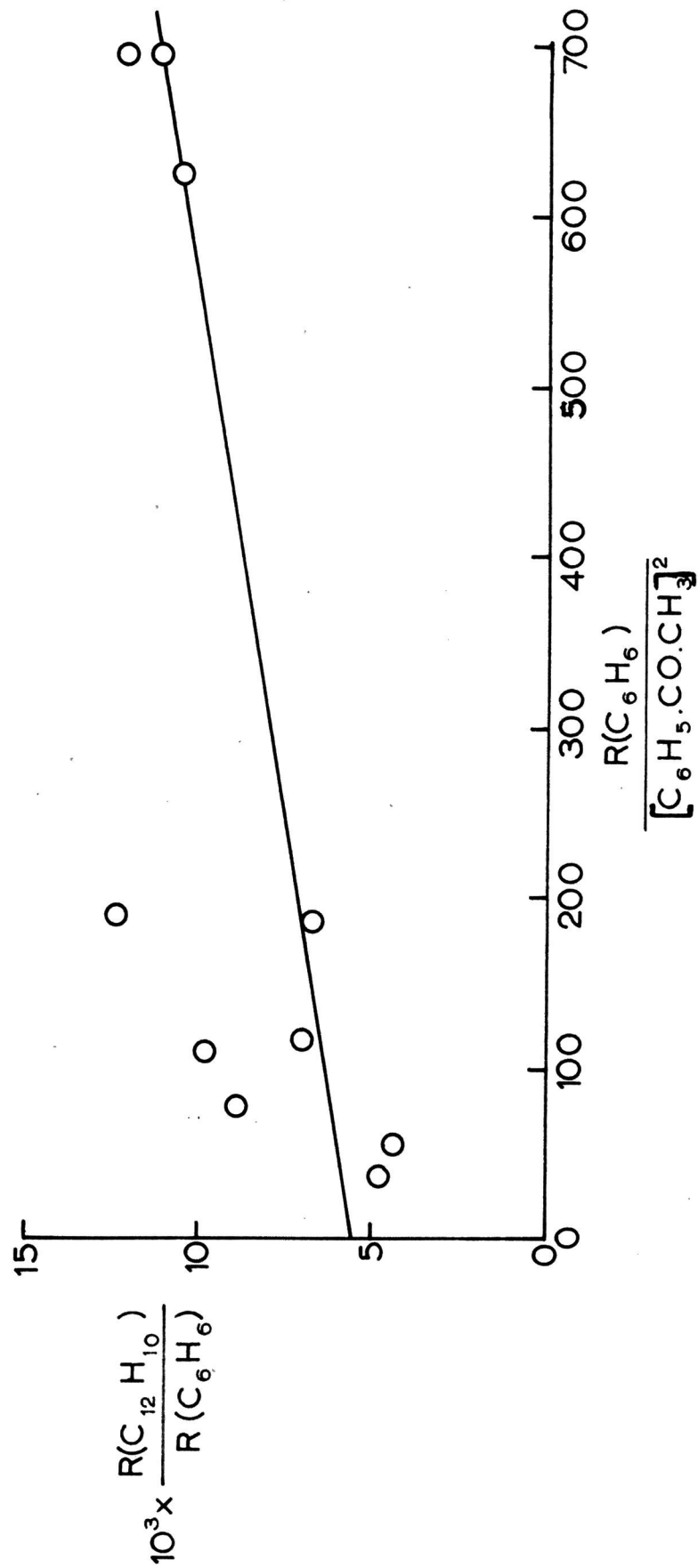


FIG. 312.c. ADDITION OF NITRIC OXIDE

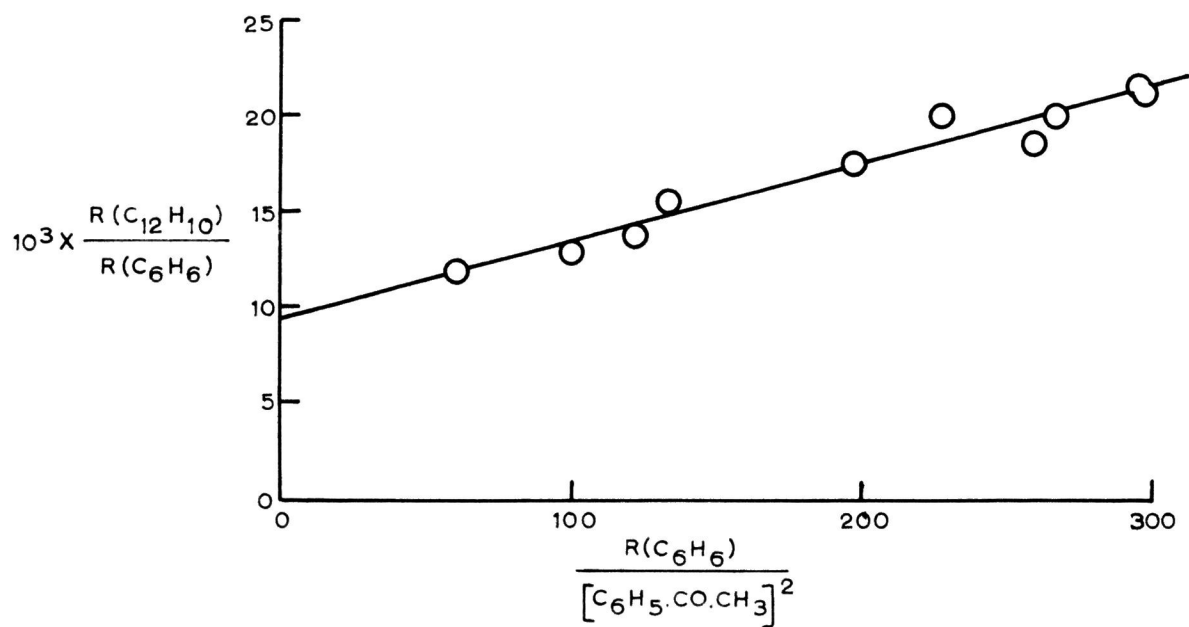


FIG. 3.13a. VARIATION OF ACETOPHENONE CONCENTRATION AT 550°C

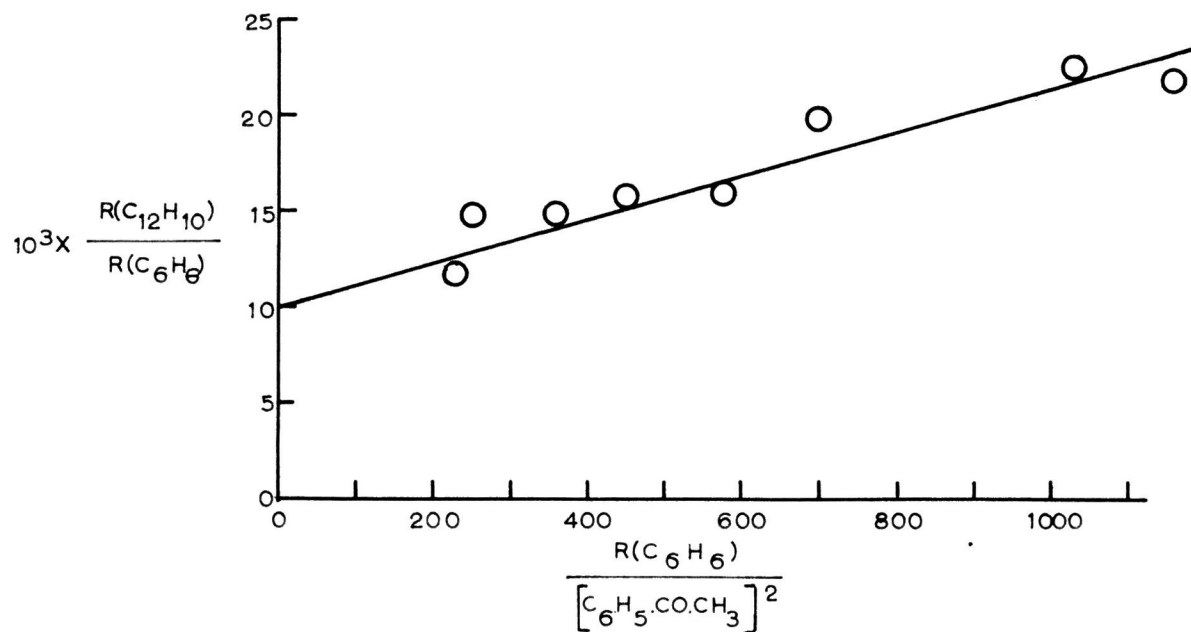


FIG. 3.13b. VARIATION OF ACETOPHENONE CONCENTRATION AT 599°C



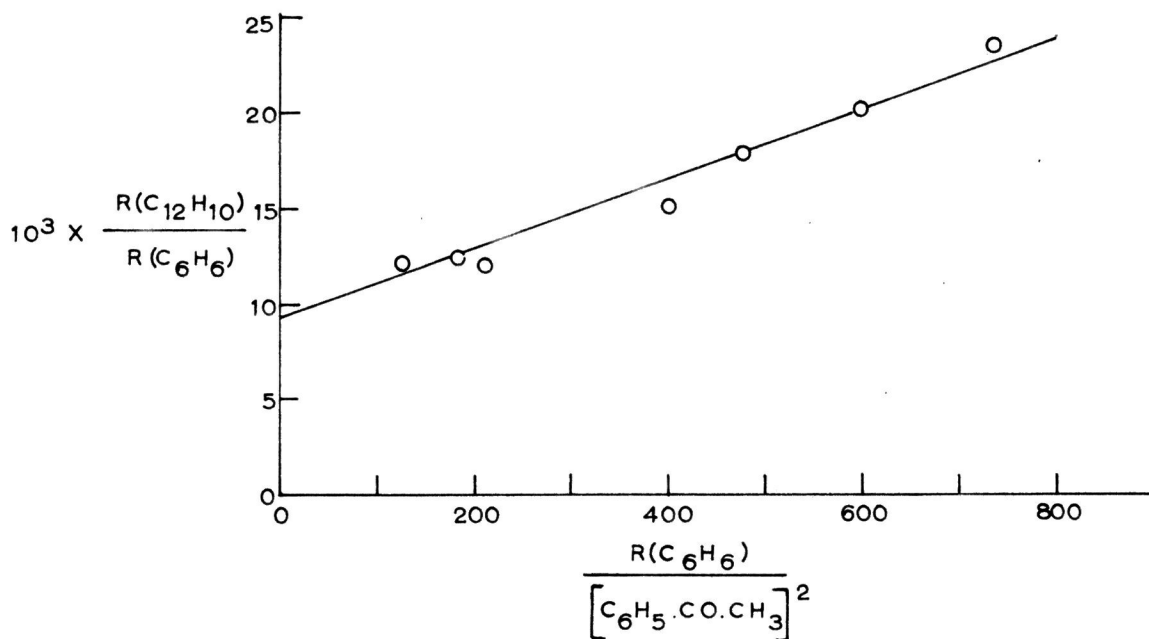


FIG. 3.1.3.c. VARIATION OF ACETOPHENONE CONCENTRATION AT 615°C

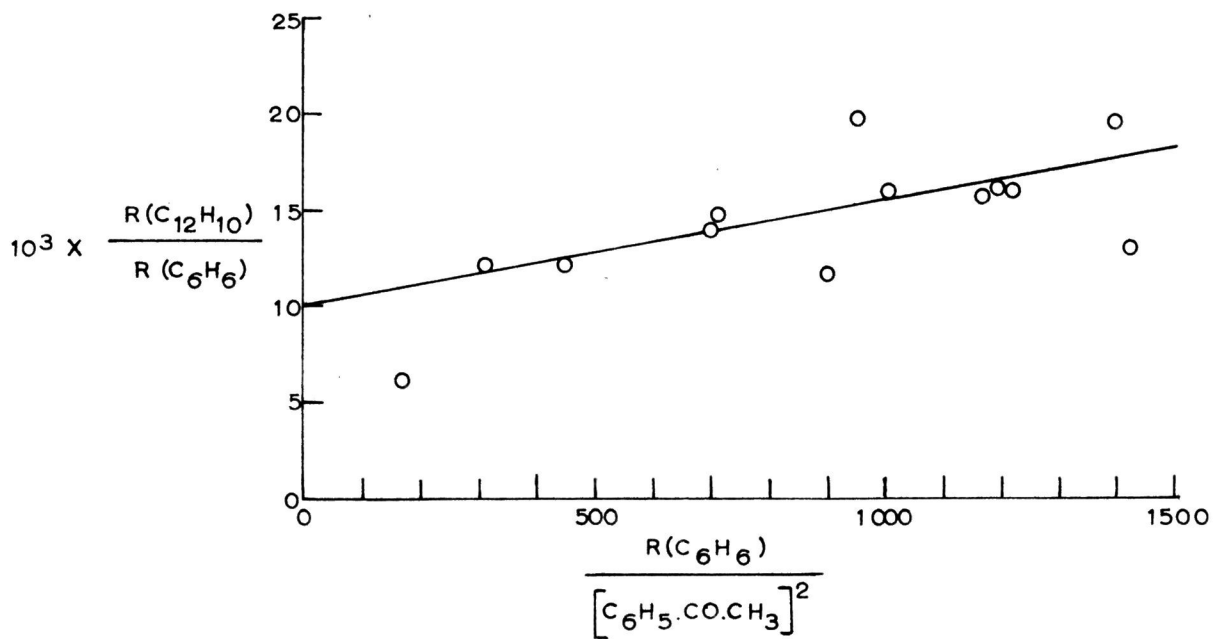


FIG. 3.1.3.d. VARIATION OF ACETOPHENONE CONCENTRATION AT 680°C

line plots were obtained. The results are summarised in Table 3.1.4.

TABLE 3.1.4

| Temp<br>(°A) | $10^{-8} k_2$<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) | $10^{-8} k_8$<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) |
|--------------|--|--|
| 552          | 15.7   | 0.15   |
| 598          | 29.3   | 0.29   |
| 615          | 23.7   | 0.23   |
| 680          | 43.4   | 0.44   |

Graphs of log k against  $1/T$  were then drawn for both  $k_2$  and  $k_8$ , and are shown in figure 3.1.4. From these graphs the activation energies and A factors were determined as

|            | E<br>(kcal mole <sup>-1</sup> ) | log A<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) | $10^{-8} k$ (333°C)<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) |
|------------|---------------------------------|--|--|
| Reaction 2 | 6.2                             | 11.7   | 25   |
| Reaction 8 | 6.4                             | 9.8  | 0.25   |

During the work on variation of the acetophenone concentration, methane and ethane were analysed, and the rate constants for reaction 5, hydrogen abstraction from acetophenone by methyl radicals, were calculated

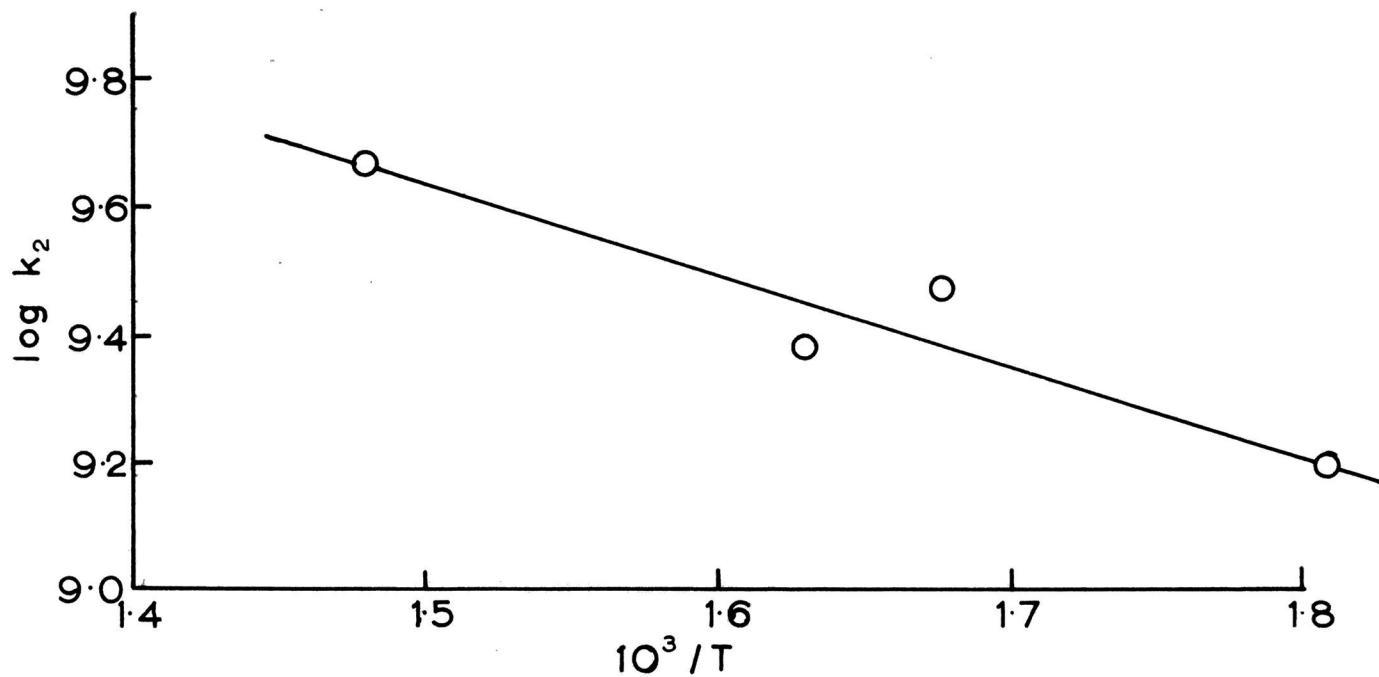


FIG.3.1.4.a. HYDROGEN ABSTRACTION FROM ACETOPHENONE

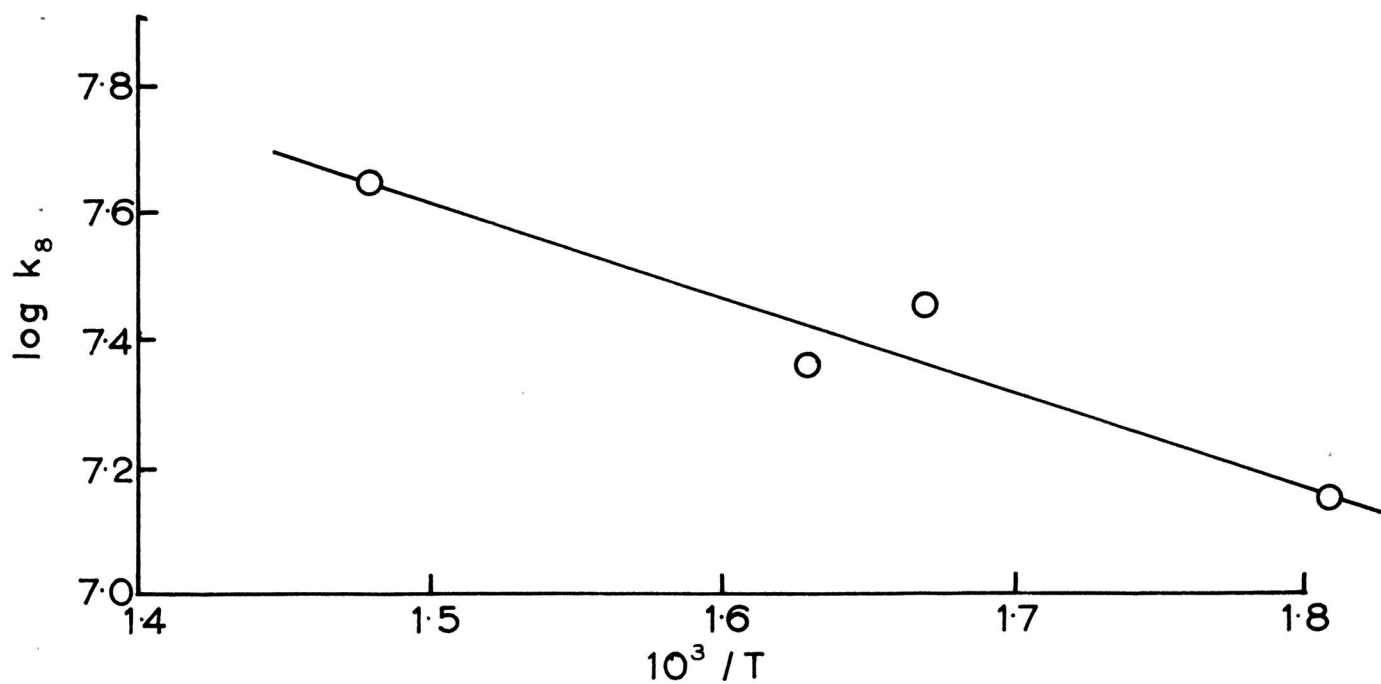


FIG.3.1.4.b. DIPHENYL FORMATION FROM ACETOPHENONE

from the equation

$$k_5 = \frac{k_7^{\frac{1}{2}} R_{\text{CH}_4}}{(R_{\text{C}_2\text{H}_6})^{\frac{1}{2}} [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]}$$

The values of  $k_5$  are presented in Table 3.1.3 and the plot of  $\log k_5$  against  $1/T$  is shown in figure 3.1.5. From this plot, the following results were obtained.

$$\begin{aligned} \text{Activation energy} &= 7.4 \quad \text{kcal mole}^{-1} \\ \text{A factor} &= 10^{10.7} \\ k_5 (333^\circ\text{C}) &= 0.8 \times 10^8 \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \end{aligned}$$

Another product obtained during the decomposition was toluene. This could be formed in several ways, either by combination of methyl and phenyl radicals, attack of methyl or phenyl radicals on acetophenone, or by elimination of carbon monoxide from acetophenone. The quantities of toluene analysed have been quoted in the tables, but no detailed treatment of the various possible modes of formation gave satisfactory results, and the actual reaction to produce toluene has thus not been determined.

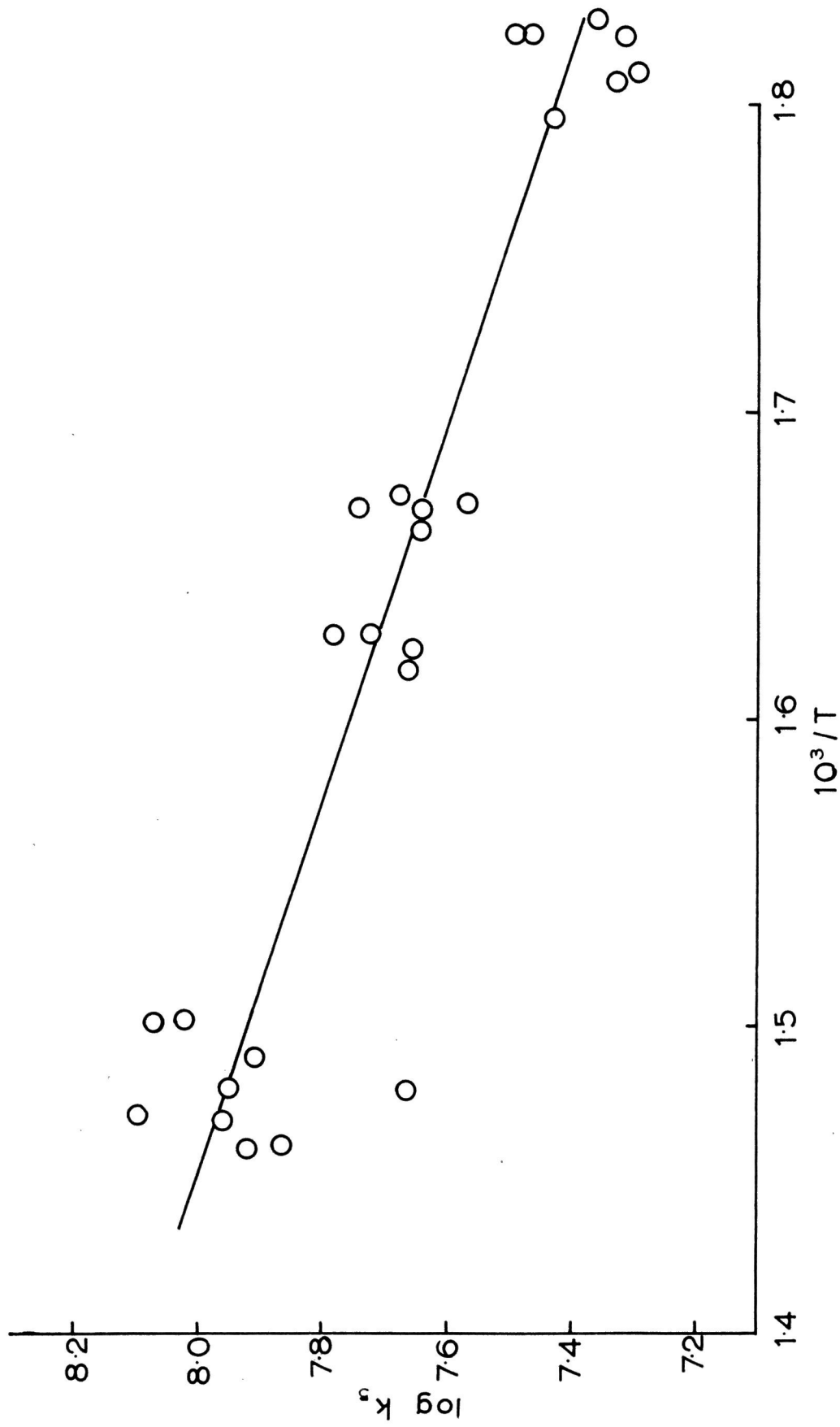
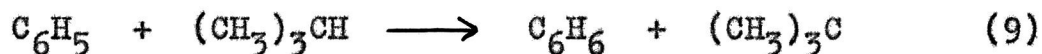


FIG.3.1.5. HYDROGEN ABSTRACTION FROM ACETOPHENONE BY METHYL RADICALS

3.2 Reactions with Isobutane.

Phenyl radicals react with isobutane by abstraction of hydrogen atoms



It would be expected that abstraction of the tertiary hydrogen atom would account for the bulk of the benzene formed, and only small amounts of benzene will come from abstraction of primary hydrogen atoms. However, the rate constants and activation energies obtained are overall values, and no differentiation has been made between the two reactions.

Various isobutane concentrations were mixed with a standard concentration of acetophenone ( $\approx 1 \times 10^{-6}$  mole  $\text{cm}^{-3}$ ) in the reaction vessel, the general procedure for reaction and analysis being the same as for acetophenone alone.

There are now two sources of benzene, from reaction 9 as well as reaction 2, so the rate of formation of benzene is now

$$\begin{aligned} R_{\text{C}_6\text{H}_6} &= k_2 [\text{C}_6\text{H}_5] [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3] + k_9 [\text{C}_6\text{H}_5] [(\text{CH}_3)_3\text{CH}] \\ \therefore [\text{C}_6\text{H}_5] &= \frac{R_{\text{C}_6\text{H}_6}}{k_2 [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3] + k_9 [(\text{CH}_3)_3\text{CH}]} \end{aligned}$$

Diphenyl is formed as before, therefore

$$R_{\text{C}_{12}\text{H}_{10}} = k_4 [\text{C}_6\text{H}_5]^2 + k_8 [\text{C}_6\text{H}_5] [\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_3]$$

Combining these last two equations,

$$\begin{aligned}
 & k_9^2 \cdot R_{C_{12}H_{10}} \cdot [(CH_3)_3 \cdot CH]^2 \\
 & + k_9 \cdot 2k_2 \cdot R_{C_{12}H_{10}} \cdot [C_6H_5 \cdot CO \cdot CH_3] \cdot [(CH_3)_3 \cdot CH] \\
 & - k_9 \cdot k_8 [C_6H_5 \cdot CO \cdot CH_3] \cdot [(CH_3)_3 \cdot CH] \cdot R_{C_6H_6} \\
 & + k_2^2 \cdot R_{C_{12}H_{10}} \cdot [C_6H_5 \cdot CO \cdot CH_3]^2 - k_4 (R_{C_6H_6})^2 \\
 & - k_2 k_8 [C_6H_5 \cdot CO \cdot CH_3]^2 \cdot R_{C_6H_6} = 0
 \end{aligned}$$

The concentrations of acetophenone and isobutane are those measured at the beginning of the run,  $R_{C_6H_6}$  and  $R_{C_{12}H_{10}}$  were determined by analysis, and  $k_2$  and  $k_8$  were read off the appropriate  $\log_{10} k$  against  $1/T$  graphs.  $k_4$  was assumed to be  $10^{14}$  mole<sup>-1</sup> cm<sup>3</sup> sec<sup>-1</sup> as before. The quadratic equation was then solved.

The results are shown in table 3.2.1 and a plot of  $\log_{10} k_9$  against  $1/T$  in figure 3.2.1. From this plot the following results were obtained.

|                   |   |   |
|-------------------|---|---|
| Activation Energy | = | 6.7 kcal mole <sup>-1</sup>   |
| A factor          | = | $10^{11.8}$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup>        |
| $k_9$ (333°C)     | = | $25.2 \times 10^8$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> |

Notes on tables 3.2.1, 3.3.1, 3.4.1.

- [A] - concentration of acetophenone
- [I.B] - concentration of isobutane
- [C] - concentration of cyclopropane
- [CH<sub>4</sub>] - concentration of methane

CO, C<sub>6</sub>H<sub>6</sub>, C<sub>12</sub>H<sub>10</sub>, C<sub>6</sub>H<sub>5</sub>·CH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>

These are the rates of formation of each product  
in the units 10<sup>-11</sup> mole cm<sup>-3</sup> sec<sup>-1</sup>.



TABLE 3.2.1

Hydrogen abstraction from isobutane

| Run No. | Temp (°A) | $10^6 [A]$<br>(mole $cm^{-3}$ ) | $10^6 [IB]$ | Time (sec) | $C_6H_6$ | $C_{12}H_{10}$ | $C_6H_5 \cdot CH_3$ | $Log_{-9}$ |
|---------|-----------|---------------------------------|-------------|------------|----------|----------------|---------------------|------------|
| 6       | 551       | 1.18                            | 0.518       | 120        | 53.9     | 0.724          | 0.713               | 9.270      |
| 5       | 553       | 1.19                            | 0.711       | 120        | 60.2     | 0.766          | 0.708               | 9.208      |
| 7       | 553       | 1.20                            | 1.30        | 120        | 67.9     | 0.682          | -                   | 9.140      |
| 3       | 552       | 1.20                            | 1.40        | 120        | 72.6     | 0.468          | 0.568               | 9.356      |
| 4       | 552       | 1.19                            | 1.56        | 120        | 72.7     | 0.745          | 0.693               | 9.072      |
| 2       | 554       | 1.17                            | 2.26        | 120        | 87.2     | 0.578          | 0.599               | 9.174      |
| 1       | 553       | 1.18                            | 2.43        | 120        | 89.4     | 0.562          | 0.693               | 9.171      |
| 24      | 606       | 1.07                            | 1.19        | 120        | 122      | 1.14           | -                   | 9.340      |
| 21      | 599       | 1.10                            | 2.12        | 120        | 124      | 0.630          | -                   | 9.406      |
| 23      | 602       | 1.09                            | 2.32        | 120        | 126      | 0.531          | -                   | 9.462      |
| 22      | 599       | 1.09                            | 3.32        | 120        | 145      | 0.500          | -                   | 9.414      |
| 8       | 668       | 0.954                           | 0.805       | 30         | 164      | 1.78           | 1.89                | 9.542      |
| 9       | 664       | 0.952                           | 2.26        | 30         | 199      | 1.08           | 1.85                | 9.581      |
| 10      | 660       | 0.965                           | 2.28        | 30         | 166      | 0.581          | 1.21                | 9.623      |
| 11      | 663       | 0.954                           | 3.75        | 60         | 216      | 0.662          | 1.836               | 9.534      |
| 17      | 684       | 0.934                           | 1.53        | 70         | 213      | 1.357          | 2.795               | 9.580      |
| 15      | 682       | 0.951                           | 2.48        | 60         | 218      | 0.684          | -                   | 9.735      |
| 18      | 684       | 0.952                           | 2.58        | 60         | 195      | 0.643          | -                   | 9.690      |
| 19      | 682       | 0.952                           | 2.89        | 60         | 218      | 0.580          | 1.844               | 9.744      |
| 16      | 682       | 0.953                           | 3.27        | 60         | 214      | 0.478          | -                   | 9.769      |

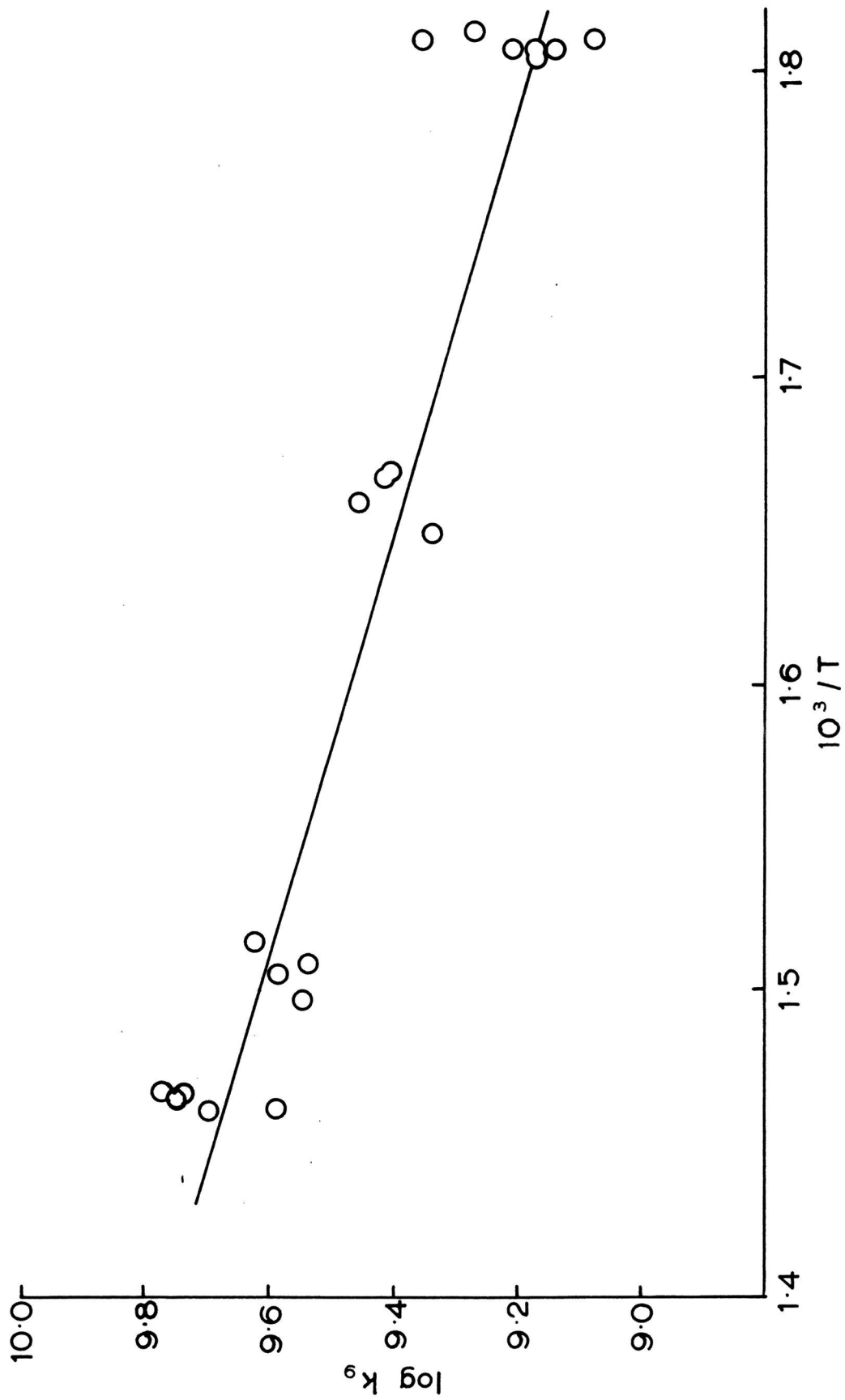
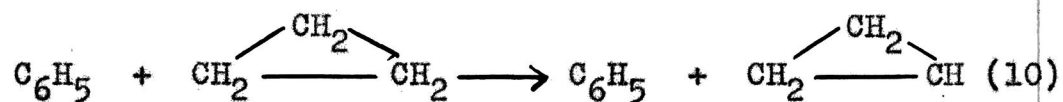


FIG. 3.2.1. HYDROGEN ABSTRACTION FROM ISOBUTANE

3.3 Reaction with Cyclopropane

The hydrogen abstraction reaction in this case is



The procedure was the same as in the isobutane experiments, and results were calculated in the same way, substituting  $k_{10}$  for  $k_9$ , and cyclopropane concentration in place of isobutane concentration in the quadratic equation.

The results are shown in table 3.3.1 and a plot of  $\log_{10} k_{10}$  against  $1/T$  in figure 3.2.1. It was found that

|                   |   |  |
|-------------------|---|--|
| Activation Energy | = | 8.5 k.cals mole <sup>-1</sup>  |
| A factor          | = | $10^{11.4}$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup>       |
| k (333°C)         | = | $2.2 \times 10^8$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> |

TABLE 3.3.1

Hydrogen abstraction from cyclopropane

| Run No. | Temp (°A) | $10^6$ [A] (mole cm <sup>-3</sup> ) | $10^6$ [C] (sec) | C <sub>6</sub> H <sub>6</sub> | C <sub>12</sub> H <sub>10</sub> | C <sub>6</sub> H <sub>5</sub> ·CH <sub>3</sub> | log k <sub>10</sub> |
|---------|-----------|-------------------------------------|------------------|-------------------------------|---------------------------------|--|---------------------|
| 21      | 577       | 1.15                                | 1.60             | 61.3                          | 1.10                            | 1.21   | 8.276               |
| 22      | 585       | 1.14                                | 2.06             | 70.5                          | 1.24                            | 1.25   | 8.253               |
| 20      | 587       | 1.10                                | 2.88             | 76.8                          | 1.35                            | 1.51   | 8.225               |
| 19      | 582       | 1.12                                | 4.23             | 75.6                          | 1.28                            | 1.33   | 8.139               |
| 16      | 620       | 1.05                                | 1.35             | 101                           | 1.74                            | 1.87   | 8.494               |
| 18      | 621       | 1.08                                | 1.54             | 101                           | 1.75                            | 1.78   | 8.368               |
| 15      | 620       | 1.05                                | 1.78             | 97.8                          | 1.67                            | 1.91   | 8.364               |
| 17      | 613       | 1.05                                | 3.08             | 106                           | 1.45                            | 1.60   | 8.562               |
| 12      | 683       | 0.949                               | 0.898            | 116                           | 1.63                            | 2.68   | 8.755               |
| 11      | 686       | 0.951                               | 1.24             | 129                           | 1.81                            | 2.23   | 8.678               |
| 6       | 676       | 0.970                               | 1.32             | 115                           | 1.72                            | 2.50   | 8.387               |
| 9       | 683       | 0.940                               | 2.53             | 136                           | 1.77                            | 2.68   | 8.607               |
| 8       | 676       | 0.961                               | 2.62             | 137                           | 1.78                            | -  | 8.602               |
| 7       | 675       | 0.952                               | 3.54             | 129                           | 1.37                            | 2.32   | 8.705               |

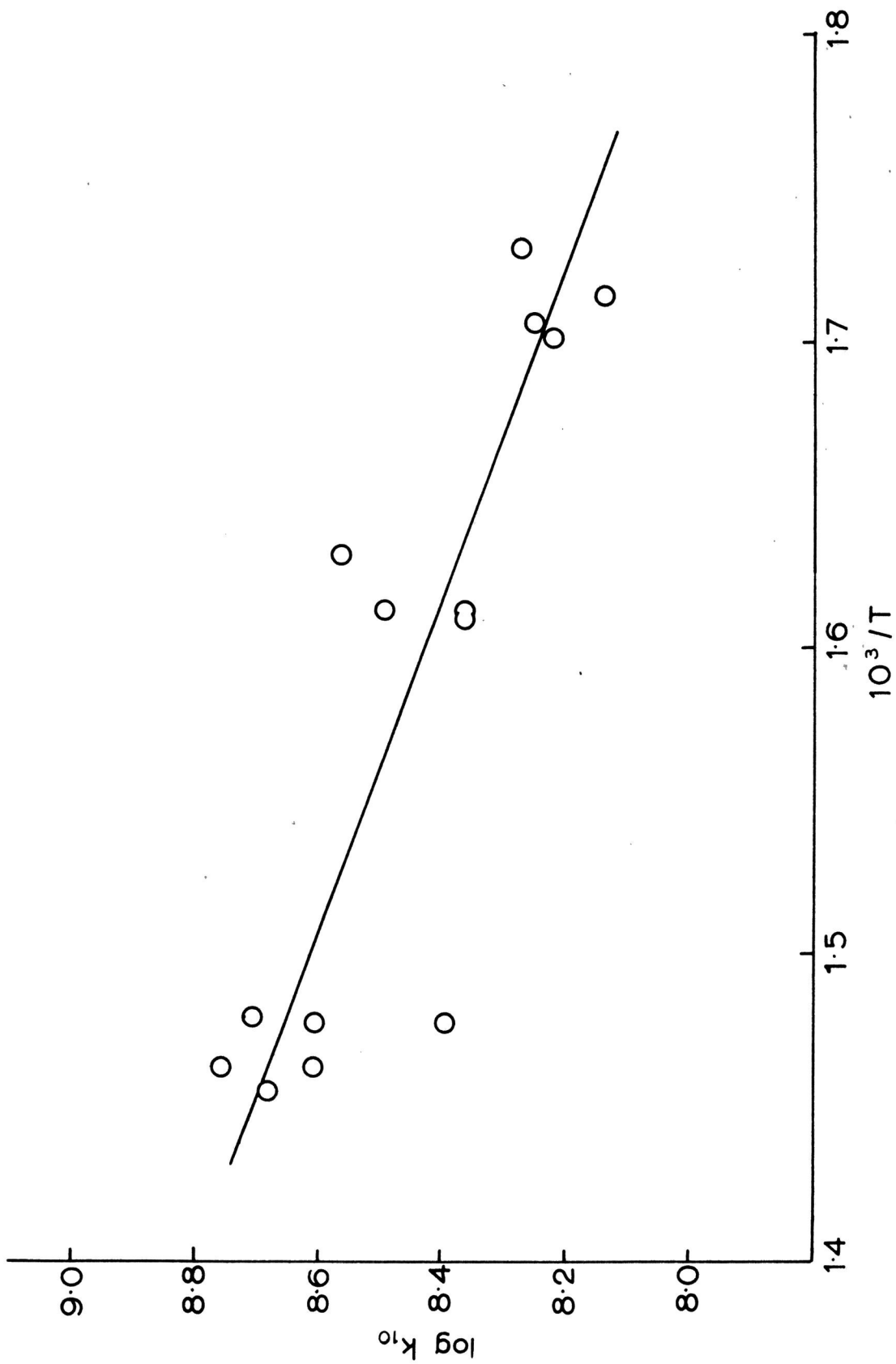
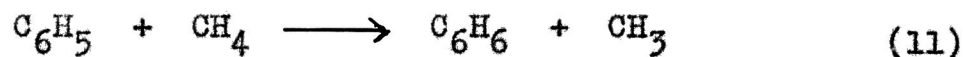


FIG. 3.3.1. HYDROGEN ABSTRACTION FROM CYCLOPROPANE

3.4 Reaction with Methane.

Again, the reaction is hydrogen abstraction



the procedure being similar to that with the other hydrocarbons, except that higher concentrations of methane were used. Calculation of the results was carried out using the same equation, this time substituting  $k_{11}$  for  $k_9$  and the methane instead of isobutane concentration.

The results are shown in table 3.4.1 and a graph of  $\log_{10} k_{11}$  against  $1/T$  in figure 3.4.1. It was found that

|                   |   |  |
|-------------------|---|--|
| Activation Energy | = | 11.1 k.cals mole <sup>-1</sup>   |
| A factor          | = | $10^{11.9}$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup>       |
| k (333°C)         | = | $0.8 \times 10^8$ mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> |



TABLE 3.4.1

Hydrogen abstraction from methane

| Run No. | Temp (°A) | $10^6 [A]$<br>(mole $cm^{-3}$ ) | $10^6 [CH_4]$<br>(mole $cm^{-3}$ ) | Time (sec) | $C_6H_6$ | $C_{12}H_{10}$ | $C_6H_5 \cdot CH_3$ | $\log k_{11}$ |
|---------|-----------|---------------------------------|------------------------------------|------------|----------|----------------|---------------------|---------------|
| 4       | 561       | 1.16                            | 2.39                               | 120        | 42.7     | 0.828          | -                   | 7.622         |
| 3       | 561       | 1.17                            | 3.60                               | 120        | 40.3     | 0.724          | 0.865               | 7.623         |
| 1       | 557       | 1.15                            | 4.19                               | 120        | 38.6     | 0.724          | 0.740               | 7.511         |
| 5       | 557       | 1.17                            | 6.51                               | 120        | 39.3     | 0.686          | 0.966               | 7.545         |
| 18      | 600       | 1.08                            | 2.76                               | 60         | 73.8     | 1.36           | -                   | 7.865         |
| 17      | 599       | 1.09                            | 3.84                               | 60         | 75.5     | 1.34           | -                   | 7.907         |
| 15      | 596       | 1.09                            | 5.78                               | 60         | 72.1     | 1.20           | 1.48                | 7.866         |
| 16      | 596       | 1.10                            | 6.46                               | 60         | 78.0     | 1.28           | 1.62                | 7.903         |
| 8       | 691       | 0.929                           | 1.41                               | 30         | 146      | 2.06           | 3.10                | 8.506         |
| 10      | 692       | 0.946                           | 1.91                               | 30         | 140      | 2.06           | 4.19                | 8.408         |
| 12      | 694       | 0.939                           | 3.09                               | 35         | 146      | 2.02           | 3.77                | 8.381         |
| 6       | 688       | 0.956                           | 3.31                               | 30         | 146      | 2.10           | 4.19                | 8.271         |
| 13      | 692       | 0.925                           | 5.04                               | 30         | 151      | 1.79           | -                   | 8.467         |
| 14      | 697       | 0.930                           | 5.71                               | 30         | 156      | 1.83           | 3.04                | 8.425         |

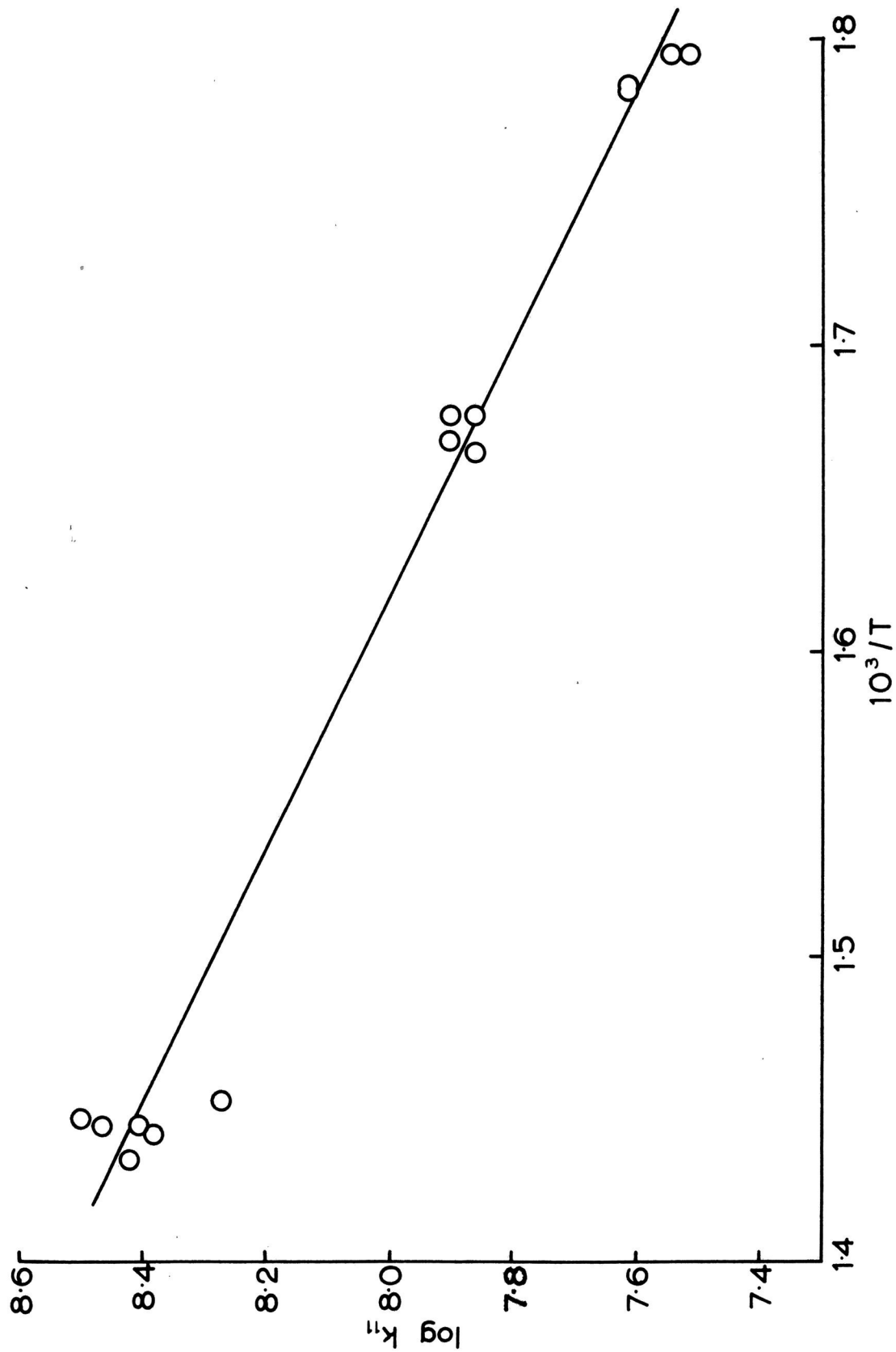


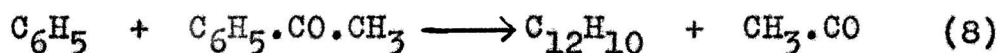
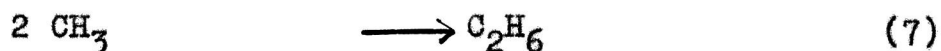
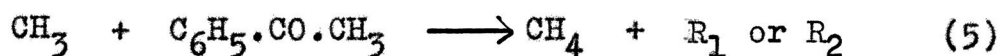
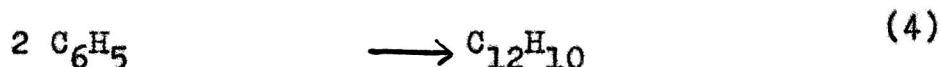
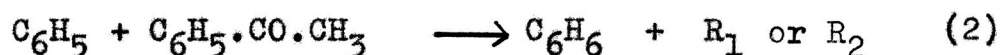
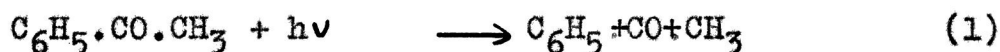
FIG. 3.4.1. HYDROGEN ABSTRACTION FROM METHANE



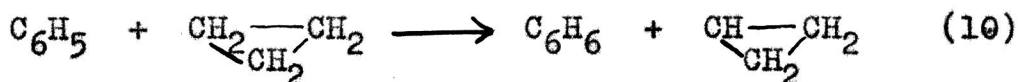
#### 4. DISCUSSION

##### 4.1 Summary of results.

In section 3 it has been shown that acetophenone decomposes to give benzene, diphenyl, methane, ethane, carbon monoxide and toluene as products. While the exact mechanism of toluene formation is unknown, the following reaction scheme is proposed to account for formation of the other products.



The phenyl radical has also been shown to abstract hydrogen from three hydrocarbons, isobutane, cyclopropane and methane, as in reactions 9, 10, 11.



The values of the A factors, activation energies and rate constants of these reactions have been determined

and are listed in table 4.1.1.

TABLE 4.1.1.

| Reactant   | log A<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) | E<br>(kcal mole <sup>-1</sup> ) | 10 <sup>-8</sup> k (333°C)<br>(mole <sup>-1</sup> cm <sup>3</sup> sec <sup>-1</sup> ) |
|--|--|---------------------------------|---|
| H. abstraction by C <sub>6</sub> H <sub>5</sub>                            |  |                                 |   |
| C <sub>6</sub> H <sub>5</sub> .CO.CH <sub>3</sub>                          | 11.6   | 6.2                             | 25  |
| CH <sub>4</sub>  | 11.9   | 11.1                            | 0.8   |
| cyclo.C <sub>3</sub> H <sub>6</sub>  | 11.4   | 8.5                             | 2.2   |
| iso C <sub>4</sub> H <sub>10</sub>   | 11.8   | 6.7                             | 25  |
| H. abstraction by CH <sub>3</sub>  |  |                                 |   |
| C <sub>6</sub> H <sub>5</sub> .CO.CH <sub>3</sub>                          | 10.7   | 7.4                             | 1   |
| C <sub>6</sub> H <sub>5</sub> abstraction by C <sub>6</sub> H <sub>5</sub> |  |                                 |   |
| C <sub>6</sub> H <sub>5</sub> .CO.CH <sub>3</sub>                          | 9.8  | 6.4                             | 0.2   |

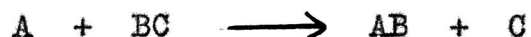
In this table all rate constants are quoted as absolute values. While this is valid in the case of the methyl radical reaction, where the rate constant for combination of radicals has been determined experimentally, it is not necessarily so for phenyl radicals as no data on

the combination of these radicals is available. It has therefore been assumed, as stated earlier, that the rate constant for phenyl radical combination is  $10^{14}$  mole<sup>-1</sup> cm<sup>3</sup> sec<sup>-1</sup>. When data on this combination becomes available it will be a simple matter to make any corrections required.

No errors in the activation energies have been quoted in table 4.1.1. The least mean squares treatment was not used to calculate these results as the accuracy of the work was not sufficiently high to warrant it. However, an estimate from the various graphs gives approximately  $\pm 1$  kcal mole<sup>-1</sup> for both types of phenyl radical attack on acetophenone,  $\pm 2$  kcal mole<sup>-1</sup> for methyl radical attack on acetophenone, and  $\pm 3$  kcal mole<sup>-1</sup> for phenyl radical attack on methane, cyclopropane, and isobutane as the possible errors.

4.2 Hydrogen abstraction by phenyl radicals.

Reactions of this type are specific cases of transfer reactions, represented by



in which B is transferred from C to A. Thus, bond BC is broken and AB is formed during reaction. If A and B remain the same while C is varied, it is found that the activation energies of the reactions vary. Polanyi<sup>(40)</sup> and co-workers suggested that this variation of activation energy was due to variation in the strengths of the bond BC broken during reaction. They examined the reaction of sodium atoms with alkyl chlorides



and showed that the activation energies and heats of reaction were related by the equation

$$E = \alpha \Delta H + C$$

where E is the activation energy,  $\Delta H$  is the heat of reaction, and  $\alpha$  is a constant. They found  $\alpha = 0.27$ .

Similarly, Trotman-Dickenson<sup>(41)</sup> proposed a value of

$\alpha = 0.5$  for reactions of methyl radicals with various alkanes. Unfortunately the values of activation energies and those of the bond strengths used in calculation of the heats of reaction are not known very accurately, so the values of  $\alpha$  are suspect.

Further evidence for the dependence of activation energy on the strength of the bond broken during reaction comes from the bromination of alkanes by Fettes, Knox and Trotman-Dickenson<sup>(42)</sup>, where the C-H bond strengths of the alkanes were calculated, assuming  $\alpha = 0.86$ . The results agree reasonably well with those obtained by electron impact.

In general, rate constants have been determined with greater accuracy than activation energies, and Trotman-Dickenson<sup>(43)</sup> has shown that the values of  $\log k$  at 254°C for hydrogen abstraction reactions of methyl and trifluoromethyl radicals fall on parallel straight lines of unit slope. This suggests that the rate constants of the reactions of these two radicals are determined by the same factors. It would seem probable that the strength of the C-H bond broken during reaction is the major cause of variations in the rate constants and activation energies. Thus, the weaker the C-H bond broken, the higher the rate constant, and the lower the activation energy.

It is of interest to compare the activation energies for the reactions of various radicals and atoms with a series of hydrocarbons (table 4.2.1).

TABLE 4.2.1Activation energies

| Radical                       | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | cycloC <sub>3</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | isoC <sub>4</sub> H <sub>10</sub> | Reference |
|-------------------------------|-----------------|-------------------------------|------------------------------------|-------------------------------|-----------------------------------|-----------|
| F                             | 1.2             | 0.3                           | 0                                  | 0                             | 0                                 | 44        |
| Cl                            | 3.9             | 1.0                           | 4.1                                | 0.3                           | 0                                 | 45        |
| CF <sub>3</sub>               | 10.3            | 7.5                           | -                                  | 6.5                           | 4.7                               | 47-50     |
| CH <sub>3</sub> O             | -               | 7.1                           | 9.7                                | 5.2                           | 4.1                               | 51,52     |
| C <sub>3</sub> F <sub>7</sub> | 9.5             | 9.2                           | -                                  | -                             | -                                 | 53        |
| C <sub>6</sub> H <sub>5</sub> | 11.1            | -                             | 8.5                                | -                             | 6.7                               | this work |
| CH <sub>3</sub>               | 12.8            | 10.4                          | 10.3                               | 8.3                           | 7.5                               | 54        |
| Br.                           | 18.3            | 13.4                          | -                                  | 10.2                          | 7.5                               | 55-58     |

In general, the activation energy drops for attack of any radical on the series of alkanes in the order CH<sub>4</sub> > C<sub>2</sub>H<sub>6</sub> > C<sub>3</sub>H<sub>8</sub> > iso C<sub>4</sub>H<sub>10</sub>, and this can be related to the type of C-H bonds present. Thus, methane > primary > secondary > tertiary. Cyclopropane, though containing secondary C-H bonds appears to be different from propane, in that the activation energy is either similar to, or higher than that for attack on the primary bonds in ethane.

Table 4.2.2 shows the variation in the rate constants relative to those of ethane for attack of the radicals and atoms on alkanes.

TABLE 4.2.2Relative rate constants

| Radical                                      | Temp. | CH <sub>4</sub> | C <sub>2</sub> H <sub>6</sub> | cyclo.C <sub>3</sub> H <sub>6</sub> | C <sub>3</sub> H <sub>8</sub> | isoC <sub>4</sub> H <sub>10</sub> | References |
|--|-------|-----------------|-------------------------------|-------------------------------------|-------------------------------|-----------------------------------|------------|
| F  | 25°C  | 0.1             | 1                             | 0.9                                 | 1.4                           | 1.7                               | 44         |
| Cl   | 250°C | 0.02            | 1                             | 0.03                                | 2.0                           | 2.2                               | 45         |
| OH   | 18°C  | -               | 1                             | 0.18                                | 2.8                           | 3.1                               | 46         |
| CF <sub>3</sub>                              | 182°C | 0.05            | 1                             | -                                   | 3.0                           | 7.5                               | 47-50      |
| CH <sub>3</sub> O                            | 230°C | -               | 1                             | 0.35                                | 3.6                           | 5.9                               | 51,52      |
| C <sub>3</sub> F <sub>7</sub>                | 127°C | 0.04            | 1                             | -                                   | -                             | -                                 | 53         |
| C <sub>6</sub> H <sub>5</sub> <sup>(a)</sup> | 333°C | 0.2             | (1)                           | 0.5                                 | -                             | 6                                 | this work  |
| CH <sub>3</sub>                              | 127°C | 0.04            | 1                             | 0.55                                | 3.3                           | 10                                | 54         |
| Br   | 98°C  | 0.002           | 1                             | -                                   | 43                            | 1050                              | 55-58      |

(a) Although the rate constant for phenyl radical attack on ethane was not determined, it was calculated assuming an activation energy of 9 kcal mole<sup>-1</sup> from inspection of table 4.2.1 and an A factor of 10<sup>11.7</sup>, which was an average value from the hydrogen abstraction reactions of the phenyl radical.

The increase in the relative rate constant is thus parallel to the decrease in activation energy throughout the series of alkanes, i.e., CH<sub>4</sub> < C<sub>2</sub>H<sub>6</sub> < C<sub>3</sub>H<sub>8</sub> < iso C<sub>4</sub>H<sub>10</sub>. The relative rate constant for attack on cyclopropane is, as with the activation energy, not similar to that of compounds containing secondary C-H bonds, but is less than that for attack on the

primary bond in ethane.

Tables 4.2.1 and 4.2.2, as well as showing the general pattern for ease of removal of hydrogen atoms from alkanes, can be used to compare the reactions of the different radicals. Thus, fluorine is very reactive, as is shown by the low or near zero activation energies, and is also unselective, there not being much difference in either the activation energy or rate constants for reaction with any alkanes. Bromine, on the other hand, is far less reactive and very selective.

The phenyl radical appears to have a similar reactivity to the trifluoromethyl, methoxyl and methyl radicals, all of which are intermediate between fluorine and bromine atoms.



4.3 Hydrogen abstraction from Acetophenone.

Values for the A factors, activation energies and rate constants for hydrogen abstraction from acetophenone by both methyl and phenyl radicals are shown in table 4.1.1, and are compared with those for the reactions of methyl radicals with toluene and benzene, and trifluoromethyl radicals with trifluoroacetophenone in table 4.3.1.

TABLE 4.3.1

| Reaction   | Temp. | log A | E   | $10^{-8}$ k | Reference |
|--|-------|-------|-----|-------------|-----------|
| $\text{CH}_3 + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$               | 333°C | 10.7  | 7.4 | 1           | this work |
| $\text{C}_6\text{H}_5\cdot + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$ | 333°C | 9.8   | 6.4 | 0.2         | this work |
| $\text{CH}_3 + \text{C}_6\text{H}_5\cdot\text{CH}_3$                             | 182°C | 11.1  | 7.8 | 0.16        | 59-60     |
| $\text{CH}_3 + \text{C}_6\text{H}_6$   | 182°C | 10.4  | 9.2 | 0.01        | 59        |
| $\text{CF}_3 + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CF}_3$               | 289°C | -     | 7.2 | 0.006       | 61        |

In table 4.2.1 it can be seen that the activation energy for hydrogen abstraction reactions of trifluoromethyl radicals is generally 2 kcal mole<sup>-1</sup> less than that for the corresponding reactions of methyl radicals. Thus attack of methyl radicals on trifluoroacetophenone would probably have an activation energy of approximately 9 kcal mole<sup>-1</sup> for abstraction of hydrogen from the phenyl group by comparison with the value of

7.2 kcal mole<sup>-1</sup> for the reaction of trifluoromethyl radicals. This activation energy would agree closely with that for hydrogen abstraction from benzene by methyl radicals.

However, the activation energy of 7.4 kcals mole<sup>-1</sup> for hydrogen abstraction from acetophenone by methyl radicals is near to that for abstraction from toluene, where it is known that hydrogen is removed from the methyl group rather than from the phenyl group. Thus, though no products were identified in the present work to show whether hydrogen was removed from the methyl or phenyl group of acetophenone, it would seem more probable that hydrogen is abstracted from the methyl group.

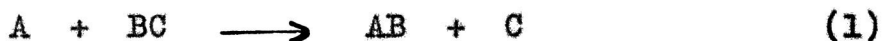
#### 4.4 Formation of diphenyl from acetophenone.

In aromatic solution phenyl radicals add to the solvent to give substituted diphenyl derivatives with loss of a hydrogen atom. Up to the present time, only two instances of this type of reaction have been proposed in the gas phase, these being the formation of diphenyl by phenyl radical addition to benzene suggested by Taylor<sup>(13)</sup>, and Scott and Steacie<sup>(14)</sup>.

In the present work, this reaction is proposed to account for the dependence of  $k_2$ , calculated assuming all diphenyl was formed by combination of phenyl radicals, on the concentration of acetophenone. The only difference between this reaction and those observed in solution is that in the gas phase an acetyl radical is lost from the addition complex while in solution a hydrogen atom is lost.

4.5 C-H Bond dissociation energy in benzene.

For any reaction

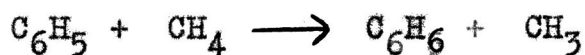


the difference in activation energy between the forward and back reactions is equal to the difference in the bond dissociation energies of BC and AB.

$$E = E_1 - E_{-1} = D(B-C) - D(A-B)$$

Thus if the two activation energies can be determined experimentally, and one of the bond dissociation energies is known, the other can be calculated.

In the present work the activation energy for hydrogen abstraction from methane has been determined, and the back reaction of methyl radicals with benzene was examined by Trotman-Dickenson and Steacie<sup>(59)</sup> and found to have an activation energy of 9.2 kcal mole<sup>-1</sup>. By combining these two activation energies with the value of  $D(\text{CH}_3\text{-H}) \approx 103$  kcal mole<sup>-1</sup> (62,64), a value of  $D(\text{C}_6\text{H}_5\text{-H})$  has been obtained.



$$E = E_{11} - E_{-11} = D(\text{CH}_3\text{-H}) - D(\text{C}_6\text{H}_5\text{-H})$$

$$11.1 - 9.2 = 103 - D(\text{C}_6\text{H}_5\text{-H})$$

$$D(\text{C}_6\text{H}_5\text{-H}) \approx 101 \text{ kcal mole}^{-1}$$

While this value of  $D(\text{C}_6\text{H}_5\text{-H})$  has a fairly large error ( $\pm 3$  kcal mole<sup>-1</sup>), it agrees within these limits

with the value of 102 kcal mole<sup>-1</sup> proposed by Szwarc and Williams<sup>(63)</sup>. These workers examined the decomposition of bromobenzene, and assumed that the activation energy (70.9 kcal mole<sup>-1</sup>) was equal to the bond dissociation energy.

$$\text{Thus, } D(\text{C}_6\text{H}_5 - \text{Br}) = 70.9 \text{ kcal mole}^{-1}.$$

From this value, they calculated the heat of formation of the phenyl radical by the equation

$$D(\text{C}_6\text{H}_5 - \text{Br}) = \Delta H_f(\text{C}_6\text{H}_5) + \Delta H_f(\text{Br}) - \Delta H_f(\text{C}_6\text{H}_5\text{Br})$$

$$\text{assuming } \Delta H_f(\text{Br}) = 26.7 \text{ kcal mole}^{-1}$$

$$\text{and } \Delta H_f(\text{C}_6\text{H}_5\text{Br}) = 25.4 \text{ kcal mole}^{-1}$$

$$\text{and found that } \Delta H_f(\text{C}_6\text{H}_5) = 69.6 \text{ kcal mole}^{-1}.$$

This value of the heat of formation of the phenyl radical was then used to calculate the C-H bond dissociation energy in benzene.

It is of interest to compare the reactivity of various radicals with the strength of the C-H bond formed by abstraction of hydrogen from alkanes, shown in table 4.5.1.

TABLE 4.5.1

| Radical                       | D(X-H) | Reference     |
|-------------------------------|--------|---------------|
| F                             | 134    | 64            |
| Cl                            | 102    | 64            |
| OH                            | 117.5  | 64            |
| CF <sub>3</sub>               | 103    | 64            |
| CH <sub>3</sub> O             | 102    | 51,52         |
| C <sub>6</sub> H <sub>5</sub> | 102    | this work, 63 |
| CH <sub>3</sub>               | 103    | 62,64         |
| B                             | 86     | 64            |

D (X-H) is in kcal mole<sup>-1</sup>.

By comparison with table 4.2.2 it can be seen that in general the reactivity of a radical is high when the bond dissociation energy of the C-H bond formed is high. Thus fluorine which is the most reactive radical listed has the highest bond dissociation energy, while bromine, the least reactive, has the lowest bond dissociation energy. The radicals containing carbon all have bond dissociation energies close to 102 kcal mole<sup>-1</sup>, and it is found that these radicals also have similar reactivity.

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