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ABSTRACT

The pyrolysis of anisole has been investigated at temperatures ranging from 447-522°C in a static system in the presence of excess of toluene as a radical scavenger. The rates of production of the primary products, methane, phenol, dibenzyl, carbon monoxide, xylenes and ethyl benzene were measured over a range of pressures and ratios of toluene/anisole. Hydrogen was a secondary product. The rates of formation of methane, phenol and dibenzyl were first order with respect to anisole at each of four temperatures.

A mechanism is proposed for the decomposition of anisole in the presence of toluene which accounts for the experimental results. The main points of the mechanism are:

a) Initiation takes place mainly by the unimolecular decomposition of anisole to give $CH_3\cdot$ and $C_6H_5O\cdot$ radicals,

$$C_6H_5OCH_3 \longrightarrow CH_3\cdot + C_6H_5O\cdot$$

b) Toluene scavenges the radicals by the following reactions,

$$\left.\begin{array}{l} CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot \\ C_6H_5O\cdot + C_6H_5CH_3 \longrightarrow C_6H_5OH + C_6H_5CH_2\cdot \end{array}\right] \text{chain breaking}$$

c) Termination takes place mainly by the combination of two benzyl radicals,

$$2C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2$$

From the rate of formation of methane, the rate constant for reaction (a) was measured over the range of temperature, 447-522°C. From the Arrhenius plot of the rate constant, the activation energy for reaction (a) was obtained. The rate constant can be expressed as

$$\log k = (13.4 \pm 0.6) - (57300 \pm 1900)/2.303RT$$

The measured rate constant was unchanged by replacing the unpacked vessel ($S/V=1\ cm^{-1}$) by a packed reaction vessel ($S/V=9\ cm^{-1}$). It was concluded that the reaction was homogeneous. Assuming the energy of activation for the recombination reaction between $CH_3\cdot$ and $C_6H_5O\cdot$ radicals to be zero, the measured activation energy was identified with the dissociation energy of the O-C bond in anisole.

CHAPTER 1.

INTRODUCTION

1. Bond dissociation energy

The dissociation energy [1], $D(R_1{-}R_2)$ of a bond $R_1{-}R_2$ is the change in the energy at absolute zero in the ideal gas state, ΔE_0^o, for the reaction

$$R_1{-}R_2 \rightarrow R_1 + R_2 \qquad (1)$$

the products being in their ground states. The bond dissociation energy of a chemical bond $R_1{-}R_2$ can also be defined as the enthalpy change of the reaction (1) in the ideal gas state. At a particular temperature, the relationship becomes

$$\Delta H^o_{(T)} = \Delta E^o_{(T)} + \Delta nRT \qquad (1')$$

Δn being +1, in the case of the reaction of the type (1). Bond dissociation energies in polyatomic molecules are referred to $298^oK(D_{298})$, since this is a standard temperature for thermodynamic data. Corrections to results obtained at other temperatures are usually small and are sometimes neglected when the accuracy of the determination is low. For determinations where precision is high, such as D(C-H) values in the lower alkanes, temperature corrections become important. The value of $\Delta H^o(1)$ at 25^oC, when used in place of

$\Delta E^o_o(1)$ for the dissociation energy, does not differ greatly from the true value of D. The reason is that the heat capacity change of reaction (1) is always positive, so that the value of $\Delta H(1)$ at normal temperature will always be greater than $D(R_1-R_2)$ as defined above by the equation (1). This is because reactions of this type involve the creation of new translational and rotational degrees of freedom at the expense of vibrational degrees of freedom. For a nonlinear polyatomic molecule dissociating into two nonlinear polyatomic fragments, three new translational and three new rotational degrees of freedom are created at the expense of six vibrational degrees of freedom. The increase in C_v, the molar heat capacity at constant volume, at ½R per mole per degree of freedom, is 3R. Therefore ΔC_p, the change at constant pressure will be 4R, since one mole is added in the dissociation reaction. We know that

$$\Delta H^o_{(T)} - \Delta H^o_{(T_o)} = \Delta C_p(T-T_o)$$

or

$$\Delta H^o_{298} - \Delta E^o_o = 4RT \simeq 2.4 \text{ Kcal mole}^{-1}$$

This is of course an upper limit, because in general, the vibration will contribute something to the heat capacity.

The bond dissociation energy, $D(R_1-R_2)$, can be written in terms of heat of formation of radicals as follows.

$$D(R_1-R_2) = \Delta H^o(1) = \Delta H^o_f(R_1) + \Delta H^o_f(R_2) - \Delta H^o_f(R_1-R_2) \qquad (2)$$

where ΔH^o_f is the heat of formation. The temperature at which the measurements are made should be specified.

The heats of formation of molecules are usually available from combustion data. If the heat of formation of one of the radicals, R_1, is known then the measurement of $D(R_1-R_2)$ gives a measurement of $\Delta H_f^o(R_2)$. Thus, the determination of one dissociation energy leads to a whole series of dissociation energies involving a common radical, simply by the systematic exploitation of Hess's law. For example, the reliable determination of any one bond dissociation energy $D(CH_3-X)$ leads to values for many other dissociation energies involving a methyl radical and an atom, because the heats of formation of most of the compounds concerned are known. The determination of bond dissociation energies is building up a body of knowledge of the heats of formation of radicals and atoms, which can be combined to give other dissociation energies in just the same ways as tables of heats of formation of more stable molecules can be used to give the thermochemistry of reactions involving molecules.

Bond dissociation energy, commonly referred to as 'bond strength', must not be confused with the thermochemical mean bond energy, E. The latter quantity applies to compounds of the general type AB_n and is defined from the equation $AB_n = A + nB$. Hence

$$E(A-B) = \frac{1}{n}\left[\Delta H_f^o(A) + n\Delta H_f^o(B) - \Delta H_f^o(AB_n)\right] \qquad (3)$$

or, in other words, the average energy per bond required to dissociate the molecule into its constituent atoms.

Bond dissociation energy is the most direct measure of the strength of a bond and therefore of the stability of the chemical combination between two atoms or radicals from which it is formed. The stabilities of chemical combinations are important facts for the study of chemical reactions. Reliable experimental values of dissociation energies are of fundamental importance for theories of chemical binding.

It is now established that many chemical reactions proceed via unstable intermediates, radicals or atoms. In order to discuss whether some postulated atom or radical reaction is likely to occur, it is necessary to know something of the thermochemistry of these active species. Since we can rarely have a sufficiently large concentration of free radicals to carry out thermochemical measurements on them in bulk, it is necessary to deduce their heats of formation from dissociation energies.

2. Methods of measurement

Bond dissociation energies can be determined by a variety of methods. The most common are:

a) Thermal equilibrium methods,
b) Spectroscopic methods,
c) Photochemical methods,
d) Electron impact methods and
e) Kinetic methods.

a) In thermal equilibrium methods, the heat of dissociation can be determined thermodynamically if the equilibrium concentrations of R_1, R_2 and R_1R_2 are known over a range of temperature or if the entropy is known from their values at one temperature. The difficulty here is to determine the concentrations which can often not be measured directly. An example of this method was the determination of D(I-I) from the equilibrium system $I_2 \rightleftharpoons 2I$ by vapour density measurements at high temperatures by Perlman and Rollefson [2]. They found D(I-I) to be 35.514 Kcal $mole^{-1}$ in excellent agreement with the spectroscopic result [3] of 35.556 Kcal $mole^{-1}$.

b) The ultraviolet spectrum of many diatomic molecules offers the most accurate method of measuring their dissociation energies, because of the great accuracy with which wave length measurements can be made. If the products of dissociation are known at a wavelength at which dissociation takes place, the accuracy of the dissociation energy is often limited only by the accuracy of the measurement of the wavelengths of the absorbing light. Unfortunately, however, the lack of knowledge of the dissociation products may lead to two equally plausible and equally precise values of the dissociation energy. Less accurate but unambiguous thermal methods may often be used to decide between the spectroscopic values. Often spectroscopy may only provide an upper limit to the true value.

The spectroscopic method has been succesfully applied in the determination of the bond dissociation energy of the I_2 molecule [3] in complete agreement with those obtained by other methods. On the other hand, dissociation energies of such important molecules as CO, N_2 and NO were for many years undecided. The spectra of polyatomic molecules are usually too complicated to be used to determine the dissociation energies.

c) In a photochemical reaction, a substance may be decomposed by the action of radiation. It is sometimes possible to identify the minimum energy of radiation required for dissociation with a bond dissociation energy. This can be reliably done only if the mechanism of the absorption of radiation and the subsequent decomposition can be established and if the usual kinetic assumption of zero activation energy for the reverse reaction is accepted. Definite evidence of the initial step in a photochemical reaction was obtained by Terenin and Neujmin [4]. They obtained $D(H-OH) = 115$ Kcal mole^{-1} in agreement with the result obtained by the other methods.

d) In the electron impact method, electrons of known energy are allowed to interact with molecules to produce ionization and dissociation. If certain conditions are fulfilled, the lowest electron energy required to produce a given ion by dissociation and ionization is equal to the sum of the dissociation energy and the ionization potential of the fragment.

If $A_o(A^+)$ is the appearance potential of the ion A^+ at rest, I(A) is the ionization energy of A to A^+ and Ee(A) is the electronic energy above the ground state of atom or radical A, we have the following relationship between appearance potentials and dissociation energies for the following type of dissociative ionization:

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

$$A_o(A^+) = D(A-B) + I(A) + Ee(A^+) + Ee(B) \qquad (4)$$

The determination of $A_o(A^+)$ from mass-spectrometric experiments, together with a knowledge of I(A) and of the electron excitation energy Ee of the products, is sufficient to give D(A-B) as shown in equation (4).

The electron impact method has been used for both diatomic [5] and polyatomic [6,7] molecules, but for the latter identification of the process taking place is often difficult and the required knowledge of ionization potentials of radicals is not easily obtained. However, apart from very few equilibrium results, it is the only method other than the kinetic method for obtaining the dissociation energies in polyatomic molecules.

e) This method can be applied to unimolecular reactions involving a single bond rupture as shown in equation (1). The enthalpy change for this reaction is related to the activation energies (E_1, E_{-1}) of the forward and reverse reactions by the equation

$$\Delta H_T^o = \Delta E + RT = E_1 - E_{-1} + RT \qquad (5)$$

The RT term allows for the change in the number of moles, but this is approximately offset by the correction which should be applied to E_1 to bring it to 298°K, for pyrolyses done at temperatures of about 500°C. Hence, $\Delta H_T^o \simeq E_1 - E_{-1}$. The reverse of equation (1) is a radical-radical combination reaction for which it is usually assumed that the activation energy is zero. The enthalpy change which defines $D_{298}(R_1-R_2)$ is thus directly given by E_1.

There is considerable experimental justification for the assumption of zero energy of activation for recombination reactions involving atoms or radicals [8-13]. The situation for polyatomic molecules is more complex, mainly because of the experimental difficulties involved in measuring the rates of recombination of radicals. A number of these rates have been measured and the activation energy of recombination has been found to be zero, or very nearly zero [8-13]. Furthermore, Benson [14] has illustrated the validity of the zero activation energy for radical-radical recombination from the standpoint of heat capacities.

The precise relationship of the experimental activation energy (derived from the Arrhenius equation, $k = Ae^{-E/RT}$ where k is the first order rate constant for the dissociation reaction) to the dissociation energy has been discussed by Szwarc [1]. He has shown that on certain assumptions about the shape of the potential energy curve, if $\bar{k}T \gg h\nu_o$ (where ν_o is the fundamental vibration frequency of the bond broken), the observed activation energy E_a is exactly equal to D, the dissociation energy and if $h\nu_o \gg \bar{k}T$, $E_a = D + RT$. The first condition corresponds to a very weak bond or very high temperature. The second assumption probably applies more often, but the final result is uncertain because of the assumptions made, which are certainly not exactly valid. It is sufficient that this treatment shows that the experimental activation energy of the dissociation reaction gives a good approximation to the bond dissociation energy.

Whereas thermal equilibrium methods are most suited to diatomic molecules, the kinetic methods may be used for polyatomic molecules. The dissociation products of diatomic molecules are stable enough for equilibrium measurements to be made. The products from polyatomic molecules , on the other hand, are usually very reactive, and the kinetic method is often the only way of obtaining the dissociation energy. Although it is often easy enough to measure a rate of decomposition, it may be difficult to relate this to the rate of the desired reaction. Here the correct interpretation of the kinetic results is very important and techniques which can give unambiguous bond dissociation processes are particularly valuable.

Kinetic methods can be classified in several ways:

i) Direct thermal decomposition

Under favourable circumstances the thermal decomposition of a compound may occur by means of an initial split into radicals, followed by fast, non-chain reactions to give the ultimate products. If the initial bond fission is rate determining, the overall kinetics of formation of the products will be first order, and the observed activation energy will be the dissociation energy of ~~the~~ bond concerned. Often the interpretation of the results of kinetic measurements on the thermal decomposition of a substance is very difficult, and the allocation of the activation energy to a particular reaction is correspondingly uncertain. In some cases, the initial step may not be bond scission, but a unimolecular rearrangement, and the activation energy will then be less than the bond dissociation energy. Sometimes both types of reaction may occur together. The presence of radicals may be detected by various methods, although this does not suffice to show that all or even the major part of the reaction is proceeding by a radical mechanism. The thermal decomposition of di-tert-butyl peroxide [15-17] has been fairly extensively studied in order to obtain the dissociation energy of the peroxide link, which is expected to be the weakest in the molecule.

ii) Metathetical reactions

The enthalpy change of a metathetical reaction is given by the difference in activation energies of the forward and reverse reactions. Hence for the generalised reaction

$$R + R_1X \rightleftharpoons RX + R_1 \qquad (6)$$

we have $\Delta H_{6,-6} = E_6 - E_{-6}$, there being no change in the number of moles in the reaction. From the definition of bond dissociation energy, it follows that

$$D(R_1-X) - D(R-X) = E_6 - E_{-6} \qquad (7)$$

In other words, the difference in dissociation energy between the bond broken and the bond formed is equal to the difference in activation energies of the forward and reverse reactions. If one of the bond dissociation energies is known, the other can be determined from the activation energy difference. Kistiakowski and Van Artsdalen [18] were first to use this general method which has subsequently been applied in many forms. Bond dissociation energies determined by this procedure are among the most reliable known for polyatomic molecules. This method is particularly suited to determining differences in bond dissociation energies in a series of related compounds.

There are many ways for measuring the activation energies of metathetical reactions of the type described above. It is important to realize that equilibrium is never established and that these are rate measurements and not the thermodynamic equilibrium studies. This method is illustrated by the determination of $D(CH_3-I)$ from kinetic measurements on the system [19]

$$CH_3I + HI \rightleftharpoons CH_4 + I_2 \qquad (8)$$

iii) Shock-tube reactions

Reactions in shock tubes have sometimes proved useful in deciding between different values obtained spectroscopically for dissociation energies in diatomic molecules. The major advantages of the method are the high temperatures obtainable and the completely homogeneous reaction conditions, but against this must be set the difficulty of measuring the exact reaction temperature and exact reaction time. The method consists of carrying out comparative or competitive reactions involving pairs of reactants in a single-pulse shock tube, where one of the reactions, with previously established kinetics, serves as an internal thermometer and timing device. Dehydro-halogenation reactions [20-21] were first studied with the decomposition of isopropyl bromide,

$$i\text{-}C_3H_7Br \longrightarrow C_3H_6 + HBr \qquad (9)$$

as the reference reaction.

The results obtained by this method are in excellent agreement with previous values obtained by conventional kinetic methods. Benson and DeMore [22] have noted that problems may arise with the competitive shock tube method, owing to fall-off in the rate constants at higher temperature, if the two reactions do not have the same fall-off characteristics. With a proper choice of systems, however, the method shows considerable promise in determining bond dissociation energies.

iv) Toluene carrier technique

Most of the accepted bond dissociation energies from pyrolyses have been derived from flow experiments, which overcome the disadvantage of complicating side reactions that beset measurements in static systems. The most widely applied flow system is the toluene carrier technique developed by Szwarc [1b] and recently modified by replacing toluene with aniline [23-24]. Szwarc found that toluene acts as a radical scavenger according to the following reaction

$$C_6H_5CH_3 + R \longrightarrow C_6H_5CH_2 + RH \qquad (10)$$

The benzyl radicals are particularly stable and unreactive. They neither decompose nor initiate chain reactions but eventually dimerize to form dibenzyl outside the hot zone of the reaction vessel. If a dissociation reaction is carried out in a flow system using toluene as carrier gas, the radicals R_1 and R_2 formed react preferentially with the toluene which is present in very large excess. The stable molecules R_1H and R_2H are formed thus suppressing chain reactions. The rate of initial decomposition may be measured by the rate of formation of R_1H or R_2H or dibenzyl. Moreover, the molar ratio of $R_1H : R_2H$: dibenzyl ought to be 1 : 1 : 1. The appearance of dibenzyl among the products of decomposition makes it possible to distinguish between two modes of decomposition, namely the decomposition into radicals and the direct decomposition into molecules.

To eliminate possible secondary reactions, it is essential to prevent the formation and decomposition of dibenzyl in the hot zone. This can be achieved by using very short contact times. The prevention of dimerization is also aided by working at low pressures, high temperatures and low fractions of decompositions.

The method can be illustrated by the pyrolysis of cumene [1e] where the initial dissociation is the following

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_5CH\cdot(CH_3) + CH_3\cdot \qquad (11)$$

In the presence of a large excess of toluene, the highly reactive methyl radicals are removed from the system by the reaction

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot \qquad (12)$$

Chain reactions are prevented since the benzyl radicals, which are resonance stabilized and much less reactive than methyl, eventually dimerize outside the reaction zone.

$$2C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2 \qquad (13)$$

To determine the unimolecular rate constant k_{11} for the reaction (11), the rate of formation of methane is measured, since this is the exclusive product of the methyl radicals from the decomposition. The rate constant is then calculated from the first order equation,

$$k_{11} = \frac{1}{t}\ln\frac{a}{(a-x)} \qquad (14)$$

where t is the contact time, a is the amount of cumene passed through the furnace during the experiment and x is the yield of methane in time t. It is also possible to follow the decomposition by measuring the amount of dibenzyl formed in equation (13), the analysis of which has become possible with the use of gas chromatography. It is important that the rate constants be shown to be independent of contact time, partial pressure of reactant in the carrier gas and surface to volume ratio of the reaction vessel, in order to establish that the reaction is truly unimolecular and homogeneous. The activation energy is then obtained from an Arrhenius plot of the rate constants determined over the widest possible range of temperatures.

This technique is particularly suitable for studying decompositions which give rise to a resonance-stabilized radical (S) as well as a reactive radical (R). The bonds in such compounds (S-R) are considerably weakened by the effect of resonance, thereby avoiding the necessity of a high temperature study. At the same time the mechanism is simplified as there is only one reactive radical.

The advantage of toluene as a carrier is seen in its high thermal stability. Below 700°C, the decomposition of toluene is negligible, being less than 0.01% [25] at contact time of about one second and approaching 1% only at 800°C.

The thermal decomposition of toluene has been studied by several workers [25-30]. The mechanism proposed is very complex. The first order rate constant for the thermal decomposition of toluene was given by Price [25],

$$\log k(\sec^{-1}) = 14.8 - 85000/2.3RT \qquad (15)$$

Many of the experimental difficulties experienced by these workers have arisen out of the use of a flow system where mixture compositions can not be easily varied and the residence time is difficult to measure. Mulcahy and Pethard [31] have discussed the errors due to non-turbulent flow and thermal inertia of the entering gases, with particular reference to toluene pyrolysis.

Recent work on toluene pyrolysis using a static system, operating at lower temperatures and higher reaction times than previously used, has been reported by Brooks, Cummins and Peacock [32]. The results agreed substantially with previous studies in a flow system. The most important result was the autocatalytic nature of the reaction which explained the increase of the rate constant with increasing residence time observed by Blades [27] and Price [25]. The rate constant k of initiation was given by

$$k = 10^{15.96}\exp(-88900/RT)\ \mathrm{sec}^{-1} \qquad (16)$$

From these parameters, an important limitation of the toluene carrier technique can be seen. The method can not be used for the determination of bond dissociation energies greater than that for the carbon-hydrogen bond in toluene. The decomposition of toluene gives an additional source of methyl radicals and hence methane via equation (12) and can make studies of the pyrolysis of compounds containing labile $R\text{-}CH_3$ bonds ambiguous.

As a general rule, the most favourable case is that in which the dissociation energy of the bond to be broken is at least 10 Kcal $mole^{-1}$ lower than $D(C_6H_5CH_2-H)$.

Recent studies both by the toluene and aniline carrier techniques [33-34] have shown that the results on the decompositions of small molecules are sometimes misleading. In the range of pressure available for carrier experiments, the rates of decomposition of these molecules can be affected by the overall pressure in the system, as predicted by the theories of unimolecular reactions. Accordingly, the activation energy observed experimentally in the pressure fall-off region may be several Kcal/mole less than the limiting high pressure activation energy (E_∞) which is identified with the bond dissociation energy. Generally the study of pressure effects on first order rate constants is not readily achieved in flow systems.

Although the abstraction of a hydrogen atom [35] occurs predominantly from the methyl group, ring abstraction has also been observed to the extent of about 4% of the overall abstraction [25, 29, 30, 36].

It was initially thought that the stable benzyl radicals did not react in the hot zone under the experimental conditions used. More recent studies [37-39] have shown that recombination of benzyl and methyl radicals may occur to a significant extent. This implies that the formation of ethyl benzene must be included in the decomposition mechanism for it accounts in part for the removal of methyl radicals. It has been considered that equilibrium[40] may be established between the benzyl radicals and dibenzyl i.e., $2C_6H_5CH_2^{\cdot} \rightleftharpoons (C_6H_5CH_2)_2$. The extent of this equilibrium has been estimated at a toluene pressure of 10 torr and temperature of 1000°K where the ratio of benzyl to dibenzyl is very near to unity. This accounts for the presence of free benzyl radicals in the system.

In conclusion, it may be said that toluene carrier experiments can lead to reliable rate data and hence reliable bond dissociation energies provided i) the mechanism is well established, ii) the decomposition is not in the pressure sensitive region, iii) the initial bond scission process is shown to be homogeneous and iv) values of first order rate constants are determined over a wide range of temperature.

3. Introduction to the present research

The object of the present research has been the determination of the dissociation energy of the $C_6H_5O\text{-}CH_3$ bond of anisole and hence the measurement of the heat of formation of the phenoxy radical. As the phenoxy radical is iso-electronic with the benzyl radical it is of interest to compare the resonance stabilization of the phenoxy radical with that of the benzyl radical.

The uncatalyzed thermal decomposition of ethers has not received much attention in the past. Reviews of thermolytic mechanisms by Steacie [41] and by DePuy and King [42] reflect the general scarcity of information on this reaction up to 1960. Numerous contributions by Stavely and Hinshelwood [43], Magram and Taylor [44], Lossing and Ingold [45] and Elkobaisi and Hickenbottom [46] have established the free radical character of the thermal cleavages taking place in di-alkyl, di-aryl and alkyl aryl ethers. Even cyclic ethers [47] such as dioxane, dioxalane and tetrahydrofuran react in this fashion. Finally, preliminary reports on the thermolysis [48] of divinyl ether also suggest the operation of a free radical mechanism. Unsaturated ethers, on the other hand, with the exception of divinyl ether, undergo unimolecular rearrangement with simple stoichiometry. The Claisen rearrangement is one of the best known examples of this type of reaction taking place in aryl allyl ethers [49].

In the radical chain reaction, the C-O bond is the point of initial decomposition. Subsequent reactions follow the general Rice-Herzfeld pattern. The reported Arrhenius parameters of the two ether bond fission reactions - those of diethyl [50] and dimethyl [51] ethers - have been obtained from a detailed analysis of free radical, chain decomposition mechanisms. In those investigations, Arrhenius parameters were based on assignments of parameters for the pertinent elementary reactions in the proposed mechanism. The final error is probably large. Nevertheless, few reliable experimental data for the bond dissociation energies in ethers are available [52].

In the present study, in order to eliminate complicating chain reactions, a radical scavenging process has been adopted using toluene as radical scavenger. A simple radical scavenging mechanism may be proposed for the decomposition of anisole in the presence of toluene.

$$C_6H_5OCH_3 \xrightarrow{k_1} C_6H_5O\cdot + CH_3\cdot \qquad \text{(initiation)} \quad (17)$$

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2\cdot \qquad \text{(chain breaking)} \quad (18)$$

$$C_6H_5O\cdot + C_6H_5CH_3 \longrightarrow C_6H_5OH + C_6H_5CH_2\cdot \qquad \text{(chain breaking)} \quad (19)$$

$$2C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2 \qquad \text{(termination)} \quad (20)$$

Under conditions where this mechanism was operative, the rate of reaction (17) may be obtained from the rate of formation of methane or phenol and from measurements over a range of temperature, the activation energy for reaction (17) may be obtained. The results reported in this thesis describe the investigation of this system and the measurement of the rate of reaction (17) over the temperature range of 447-522°C.

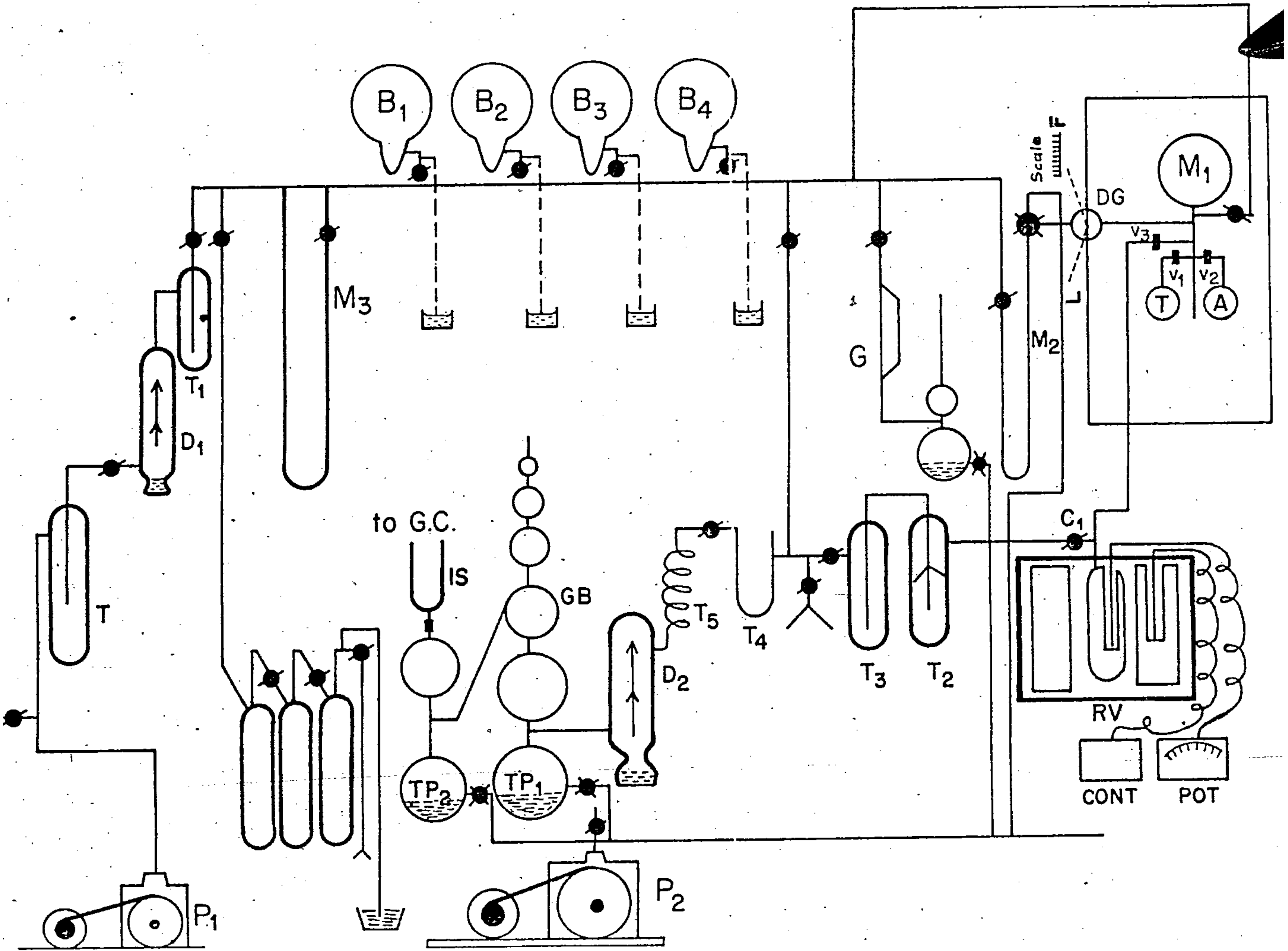
CHAPTER 2.

EXPERIMENTAL METHODS AND TECHNIQUES

1. Apparatus

The experiments were performed in a conventional static system, which is shown schematically in Figure 1. All glass stopcocks were lubricated with high vacuum silicone grease. The entire system could be evacuated to pressures less than 10^{-5}mm Hg by means of the mercury diffusion pump D_1 which was in series with a liquid nitrogen trap T_1 and a single stage Welch rotary pump P_1. The residual pressure was measured with a McLeod gauge G. A single manifold connected all parts of the apparatus.

A cylindrical quartz reaction vessel RV, which had a volume of 342.3 cc and a surface/volume ratio of 1.0 cm^{-1}, was enclosed in an electrically heated iron cylinder, the walls of which were about 2.5 cm thick. The iron cylinder was well insulated with asbestos. Temperatures were measured with a chromel-alumel thermocouple connected with a potentiometer POT, which can be read to ± 0.025 millivolt, corresponding to $\pm 0.5^{\circ}C$ in the range of temperature studied. The temperature was



B1
B2
B3
B4
Scale
F
M1
DG
v3
v1
v2
T
A
L
M3
M2
G
T1
D1
T
to G.C.
IS
GB
T5
T4
T3
T2
C1
D2
RV
CONT
POT
TP2
TP1
P1
P2

FIGURE 1

Schematic diagram of the apparatus

controlled with a Thermoelectric thermo-regulator CONT connected with control relay. The controller was activated by means of a chromel-alumel thermocouple placed half-way along the reaction vessel in the wall of the furnace. The temperature variation during a run was not more than ±0.5°C. A temperature gradient along the thermocouple wall of the reaction vessel was not detected.

The reactants were mixed in a 3 litre vessel M_1. Anisole and toluene were stored in flasks A and T respectively, connected to the mixing vessel M_1 by two Hoke diaphragm-seal stainless steel valves.

The pressure in the mixing vessel was measured with a glass-diaphragm gauge DG. The gauge was operated by adding a balancing pressure to the outside of the gauge such that zero deflection of the light beam was observed. The balancing pressure was measured on manometer M_2.

The mixing vessel and the storage flasks were enclosed in an oven which was maintained at a constant temperature of about 110°C, to ensure sufficient pressure of toluene and anisole. Small holes were provided in the oven door, so that the three metal valves inside the oven could be operated from outside with a torque meter.

In order to minimize dead space, capillary tubing was used to connect the reaction vessel with stopcock C_1 and with the mixing vessel M_1. The dead space of the reaction vessel was less than 1% of the volume of the reaction vessel. The connecting tubes from outside the heated mixing vessel to the reaction vessel and to the first removable trap T_2 were heated with heating tape to prevent condensation of anisole and toluene as well as high molecular weight products.

Low molecular weight products were analysed with a gas chromatographic system assembled from components used for the manufacture of the Perkin-Elmer vapour fractometer model 154. As a detection unit, the Gow-Mac Co. thermal conductivity cell was used, supplied by power from Trygon Electronics Inc. power supply. The current through the filament in the detector was 150 m.A. The signal from the bridge was recorded with a 1 m.V. Leeds and Northrup Co. Speedomax recorder, Model S. Edwards pressure controllers were inserted in both the reference flow and the sample flow of the chromatograph. Samples were admitted through U-trap IS.

High molecular weight products were analysed on an F.M. Model 720 gas-chromatographic apparatus. Samples were injected with a syringe. The injection port and detector block temperature were maintained at 170°C. Helium was the carrier gas for all chromatographic analyses. To remove water vapour and CO_2, He was passed through an ascarite trap.

2. Materials

The toluene used was research grade (99.9% pure) obtained from Phillips Petroleum Co.. Anisole was reagent grade from Fisher Scientific Co.. Analysis by gas chromatography showed that the most probable impurities, benzene, toluene, methyl anisole and phenetole were absent. The limits of these impurities, if present, were less than 0.1%. Anisole and toluene were introduced into the storage flask by vacuum distillation. A middle fraction was retained. Hydrogen, methane, carbon monoxide and ethane, used for calibrations of the chromatograph were obtained from phillips Petroleum Co.. Their purity was stated as research grade and they were not subjected to further purification.

Table 1 contains other materials used for calibration.

3. Procedure for experiments

A mixture of anisole and toluene was made by first admitting anisole to the mixing vessel to the required

TABLE 1

Additional materials used for calibration with source and purity

Name of the compound	Source	Purity
1. Benzene	J.T. Baker Chemical	Spectrophotometric reagent
2. Xylenes (o, m & p)	Eastman Organic Chemicals	Reagent grede
3. Ethyl benzene	Fisher Scientific	Reagent grade
4. Cresols (o & m)	Fisher Scientific	Reagent grade
5. Cresol (p)	British Drug House	Reagent grade
6. Phenyl ether	Fisher Scientific	Reagent grade
7. Dibenzyl ether	British Drug House	Reagent grade
8. Dibenzyl	Eastman Organic Chemicals	Reagent grade
9. Phenol	British Drug House	Chromatographic special
10. Benzaldehyde	J.T. Baker Chemical	Reagent grade
11. p-Methyl anisole	East Organic Chemicals	Reagent grade
12. Phenetole	Eastman Organic Chemicals	Reagent grade
13. α-Phenyl p-cresol & α-Phenyl o-cresol	Eastman Organic Chemicals	Reagent grade

pressure. Toluene was then admitted as a gas since its pressure always exceeded that of anisole. The final pressure less the initial pressure of anisole was the pressure of toluene. The reagents were allowed to mix for at least 18 hours.

Before each experiment, the system was evacuated to a pressure lower than 10^{-5}mm. The mixture was introduced into RV by opening momentarily the metal valve V_3. The final pressure in the mixing vessel was equal to that in the reaction vessel.

At the end of an experiment, the products and the reactants were fractionated through a series of traps. The first fraction was collected at -78°C in a removable trap T_2. The second fraction was collected at -196°C in the traps T_4 and T_5. The non-condensible gases were collected in the gas burette GB with a Toepler pump TP_1 aided by a mercury diffusion pump D_2. After collection was completed, the products were transferred by means of the Toepler pump TP_2 and the Edward vacuum pump P_2 into the U-traps IS.

4. Analyses of products

Non-condensible products were analysed on a 3 metre silica gel column (60/80 mesh) of ¼ inch diameter maintained at -35°C (dry ice and dichloroethane). The temperature of the column could be maintained to within ±2°C. To obtain a good resolution of all products, the silica gel was initially heated [53] for several hours at 600°C. The order of elution was H_2, air, CO and CH_4. The determination of hydrogen in helium poses a problem because the thermal conductivity of hydrogen is higher than that of helium and a negative peak should result. In actual fact, at low concentrations, the thermal conductivity of H_2 shows anomalous behaviour and a positive response peak is observed. These peaks are reliable for quantitative determination of H_2 in He [54-55]. Large amounts of H_2 give rise to peaks corresponding to both directions - so called W-peaks - and these double peaks are not reliable for quantitative measurements. Fortunately, in the present experiments, the amounts of H_2 formed were small and the response was linear and reproducible. In some experiments, the amount of H_2 was calculated as the difference between the total volume of all non-condensible gases and the sum of volumes of CH_4 and CO obtained chromatographically.

After the analysis of the non-condensible gases, the silica gel column was brought to room temperature. The fraction condensed in liquid N_2 trap was collected and measured in the gas burette and then analysed on the silica gel column at room temperature.

The fraction collected at -78°C was weighed accurately. The volume was calculated by assuming that since more than 90% of the liquid was toluene, the density may be taken equal to that of toluene. The column was 3 metres of 4% silicone grease SE 30 on chromosorb G. The temperature of the column initially was 100°C. Forty minutes after injection, it was raised quickly to 170°C. In the first 40 minutes, the major products, phenol, xylenes together with reactants toluene and anisole were eluted. After the change in temperature, the output was stabilized after about 5 minutes and the product dibenzyl was eluted.

5. Calibrations

Non-condensible gases were calibrated using the gas burette GB. The capillary and the three smallest bulbs of the burette were calibrated by weighing with mercury. The error in the volume from this method was about 0.1%. The number of moles of gas was calculated assuming the ideal gas law. In the calibration procedure, the peak height was plotted against the number of moles. This relation was always linear. The reproducibility of the calibrations, except that of H_2, was within ±2%.

For the calibrations of the condensible products, solutions of known concentration were made in toluene. A measured volume of solution was injected with a syringe. Peak heights were plotted against the number of moles and a linear relation was obtained. The reproducibility of these calibrations was about ±5%.

CHAPTER 3.

RESULTS AND INTERPRETATIONS

1. Decomposition of pure toluene

- In order to check the experimental procedure and to obtain information about the formation of methane in the absence of anisole, under the experimental conditions of this work, a series of experiments was made with pure toluene at different temperatures. First order rate constants for the decomposition of toluene were calculated from the integrated rate expression

$$k = \frac{1}{t} \ln \frac{a}{(a-x)} \quad \sec^{-1} \qquad (21)$$

where t is the reaction time in second, a is the initial concentration of toluene and x is the amount of $(CH_4 + H_2)$ which was produced in a period of time t. The total amount x of non-condensible products of decomposition of toluene were measured by the calibrated gas burette GB shown in Figure 1. The amount of H_2 present in the sample could not be estimated by the gas chromatographic analysis, because the amount obtained was at the limit of measurement. It was shown, however, that oxygen or nitrogen was not present. Table 2 shows the results obtained. The rate constants for toluene decomposition and for anisole decomposition are given in the last two columns.

TABLE 2

Kinetic data for the decomposition of pure toluene

Temp. (^oC)	Pressure of toluene (cm)	Time (sec)	CH_4+H_2 (moles)	$k_{toluene}$ (sec^{-1})	$k_{anisole}$ (sec^{-1})
464	16.6	1800	$5.60x10^{-8}$	$1.68x10^{-8}$	
467					$0.295x10^{-3}$
522					$4.57x10^{-3}$
528	20.0	3600	$2.05x10^{-7}$	$4.16x10^{-8}$	
557	18.6	3600	$2.32x10^{-6}$	$5.24x10^{-7}$	
560	16.8	3600	$2.61x10^{-6}$	$6.55x10^{-7}$	
560	20.5	3600	$3.16x10^{-6}$	$6.49x10^{-7}$	
567	19.3	3600	$2.98x10^{-6}$	$6.56x10^{-7}$	

It is difficult to compare the above $k_{toluene}$-values with the similar results available in the literature [25-30, 32] as the corresponding pyrolyses were carried out at temperature ranges higher than that of the present study. However, extrapolating Price's [25] values, which agreed well with those of Brooks et al [32], it was found that $k_{toluene}$-value for the homogeneous and heterogeneous processes, both at 528^oC, are $3.80x10^{-9}$ sec^{-1} and $5.01x10^{-6}$ sec^{-1} respectively. From the comparison with the present value at the same temperature ($4.16x10^{-8}$ sec^{-1}), it may be inferred that a certain amount of heterogeneous decomposition is taking place at this low range of temperature.

In both sets of experiments, with and without anisole, the pressure of toluene ranged from 12cm to 30cm. Comparing the rate constants, it may be concluded that decomposition of toluene is insignificant in the temperature range of 447-522°C where the decomposition of anisole was studied.

2. Products of decomposition

The major products were methane, phenol, hydrogen and dibenzyl. Carbon monoxide, ethyl benzene, xylenes together with benzyl phenyl ether, $C_6H_5CH_2OC_6H_5$, were minor products. Xylenes, phenol and dibenzyl were identified by the coincidence of retention time on two columns : (a) 3 metre column of 4% apiezon grease M on celite and (b) 3 metre column of 4% silicone SE 30 on chromosorb G. A small amount of the cross combination product, $C_6H_5CH_2OC_6H_5$, was not positively identified but was assumed to have a retention time intermediate between that of $C_6H_5OC_6H_5$ and $C_6H_5CH_2OCH_2C_6H_5$. The amount of xylenes and ethyl benzene was always less than 5% of methane or phenol formed in any particular experiment. Benzaldehyde and cresols were shown to be absent.

3. Effect of toluene pressure on the rate of formation of products

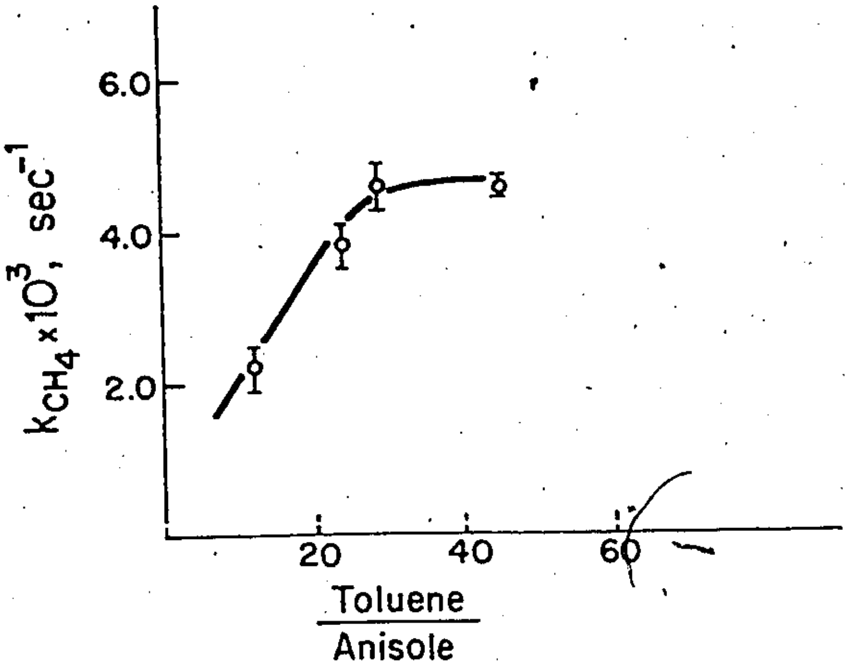
To determine the pressure of toluene necessary to scavenge all the methyl radicals formed by the decomposition of anisole by equation (17), a range of ratios of toluene to anisole was studied. The variation of the rate constant for the formation of methane as a function of the ratio of toluene/anisole at 522°C, is shown in Figure 2. For this calculation, the rate of formation of methane has been assumed to be first order with respect to anisole. Evidence to support this assumption will be presented later. It can be seen that complete scavenging of the methyl radicals starts at a ratio of toluene/anisole around 30. In the subsequent series of experiments, the ratio of toluene/anisole was kept in this region.

4. Effect of time of reaction on yields of products

The yields of methane and phenol were studied as a function of time and the results are shown in Figures 3 and 4 for methane and in Figure 5 for phenol. The individual points in these Figures 3 and 5 have been interpolated for a particular pressure of anisole from several series of experiments each done for a particular time but with decreasing pressure of anisole. These plots

FIGURE 2

Variation of rate constants for the formation of methane as a function of the ratio of toluene/anisole at 522°C



$k_{CH_4} \times 10^3$, sec^{-1}
6.0
4.0
2.0
20
40
60
Toluene / Anisole

FIGURE 3

Yield of CH_4 as a function of time at different temperatures

○ ..... 522°C

● ..... 489°C

▲ ..... 467°C

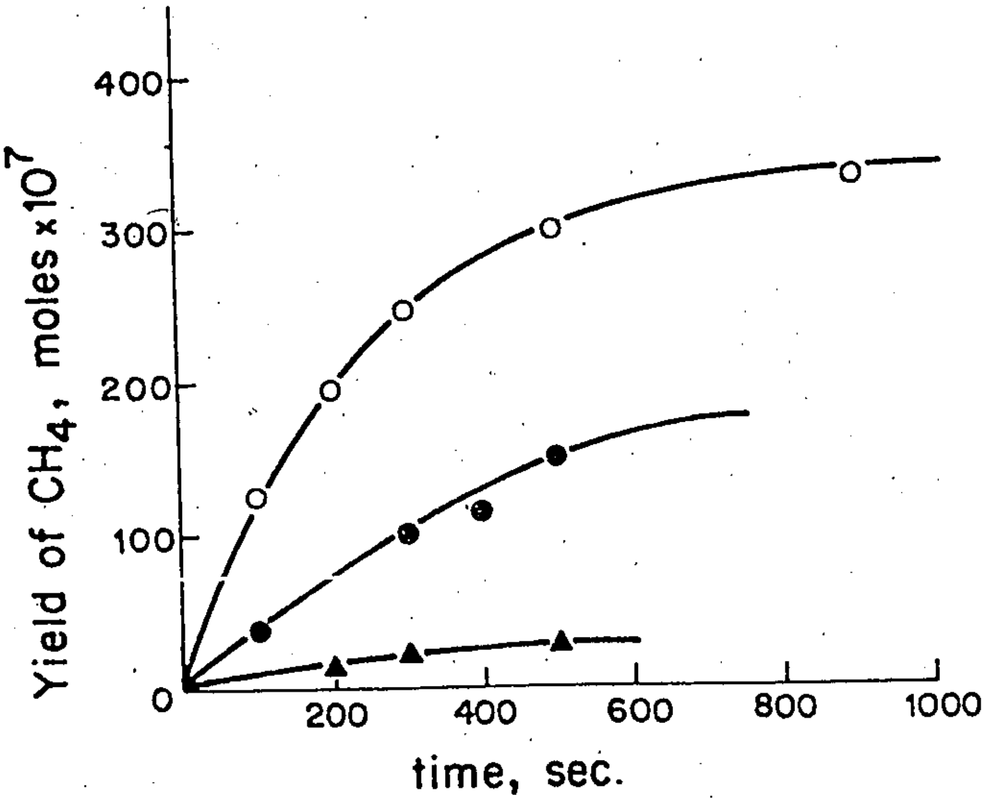

Yield of CH_4, moles x 10^7
400
300
200
100
0
200
400
600
800
1000
time, sec.

FIGURE 4

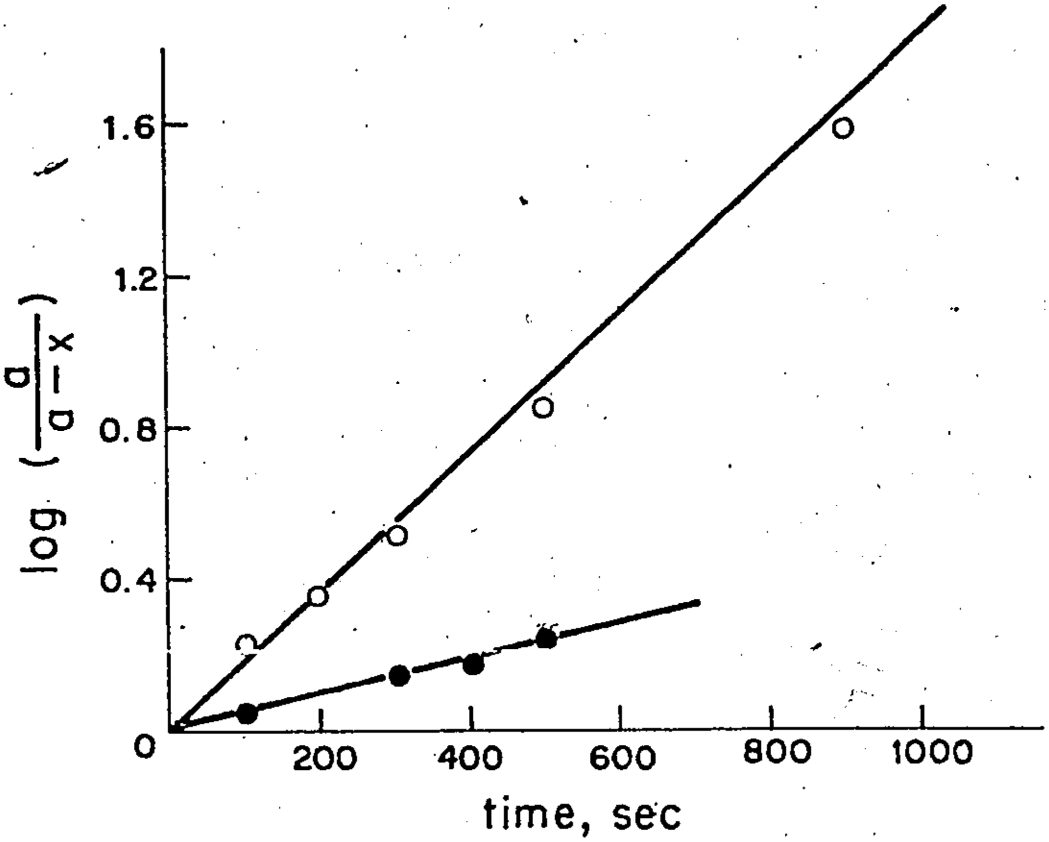
$\log \frac{a}{(a-x)}$ against time at different temperatures

a = initial concentration of anisole

x = yield of methane in time t

○ ..... 522°C

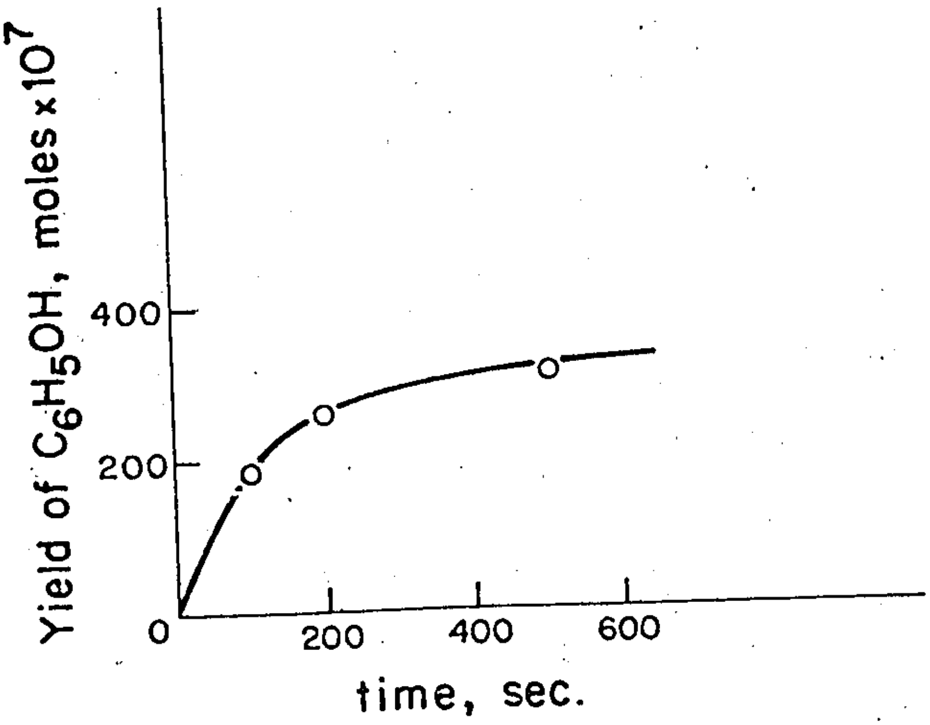
● ..... 489°C



1.6
1.2
0.8
0.4
0
log $\left(\frac{a}{a-x}\right)$
200
400
600
800
1000
time, sec

FIGURE 5

Yield of C_6H_5OH as a function of time at 522°C


Yield of C_6H_5OH, moles x 10^7
400
200
0
200
400
600
time, sec.

of yield against pressure are presented in Section 6. The yield-time plots show clearly that both methane and phenol are primary products of the decomposition. From the yield-time plot of Figure 3, the integrated first order rate equation has been used to test the order of the reaction and obtain a rate constant. Figure 4 shows the plot of $\log\frac{a}{(a-x)}$ against t for methane at 522°C and 489°C. These plots show that the rate of formation of methane is a first order reaction. The rate constants obtained are 4.22×10^{-3} sec^{-1} and 1.08×10^{-3} sec^{-1} at 522°C and 489°C respectively.

5. Stoichiometry

According to the simple mechanism outlined in page 23, the yields of phenol and methane should be equal and the ratio of (phenol + methane)/dibenzyl should be equal to two. Table 3 shows the ratios of phenol/methane, dibenzyl/methane and hydrogen/methane under various conditions. The ratio of phenol/methane is close to one under most conditions and is independent of time, which also indicates that they are both primary products. On the other hand, hydrogen was a secondary product. The ratio of hydrogen/methane is shown as a function of time at three different temperatures in Figure 6. The ratio

TABLE 3

Ratios of phenol/methane, dibenzyl/methane and hydrogen/methane under different conditions

Temp. (^oC)	Pressure of anisole (cm)	Time (sec)	Methane (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	Hydrogen (molesx10^7)	Phenol/Methane	Dibenzyl/Methane	Hydrogen/Methane
522	1.00	500	578	622	217	174	1.08	0.38	0.30
	0.92		545	556	232	156	1.02	0.43	0.29
	0.85		513	498	169		0.97	0.33	
	0.79		456	478	198	146	1.05	0.44	0.32
	0.72		437	475	202	113	1.09	0.46	0.26
	0.67		384	449	200	126	1.17	0.52	0.33
489	0.94	300	192	171	144	25	0.89	0.75	0.13
	0.88		185	161	128	12	0.87	0.69	0.06
	0.82		173	155	131	20	0.90	0.76	0.12
	0.76	100	59	46	47		0.78	0.80	
	1.26		91	82	80	1	0.90	0.87	0.01
	1.17		89	75	79		0.84	0.89	
	1.08		80	69	67	2	0.86	0.83	0.02
	1.01		78	66	65	1	0.84	0.83	0.02
	0.94	400	224	250	151	36	1.16	0.68	0.16
	0.87		205	205	138	35	1.00	0.67	0.17
	0.81		194	211	136	31	1.09	0.70	0.16
	0.76		177	181	115	31	1.02	0.65	0.18

TABLE 3 (cont'd)

Temp. (°C)	Pressure of anisole (cm)	Time (sec)	Methane (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	Hydrogen (molesx10^7)	$\frac{\text{Phenol}}{\text{Methane}}$	$\frac{\text{Dibenzyl}}{\text{Methane}}$	$\frac{\text{Hydrogen}}{\text{Methane}}$
467	1.02	300	59	43	44		0.72	0.74	
	0.95		55	43	35	6	0.79	0.64	0.11
	0.88		51	48	42	5	0.94	0.82	0.10
	0.83		50	42	46		0.83	0.92	
	0.77	500	77	80	62		1.03	0.80	
	0.72		76	69	56		0.90	0.74	
	0.67		69	62	57		0.89	0.83	
	0.63		69	62	49		0.89	0.71	
447	1.00	600	50	48	42	3	0.97	0.84	0.07
	0.93		49	44	39	3	0.91	0.80	0.06
	0.87		45	41	39		0.90	0.86	
	0.81		44	35	38	3	0.81	0.86	0.06
	0.75		41	41	37		1.00	0.90	
	1.24		44	39	51		0.90	1.17	
	1.16		42	41	42		0.96	1.00	
	1.07		39	34	39		0.87	1.00	
	1.00		35	34	35		0.97	1.00	

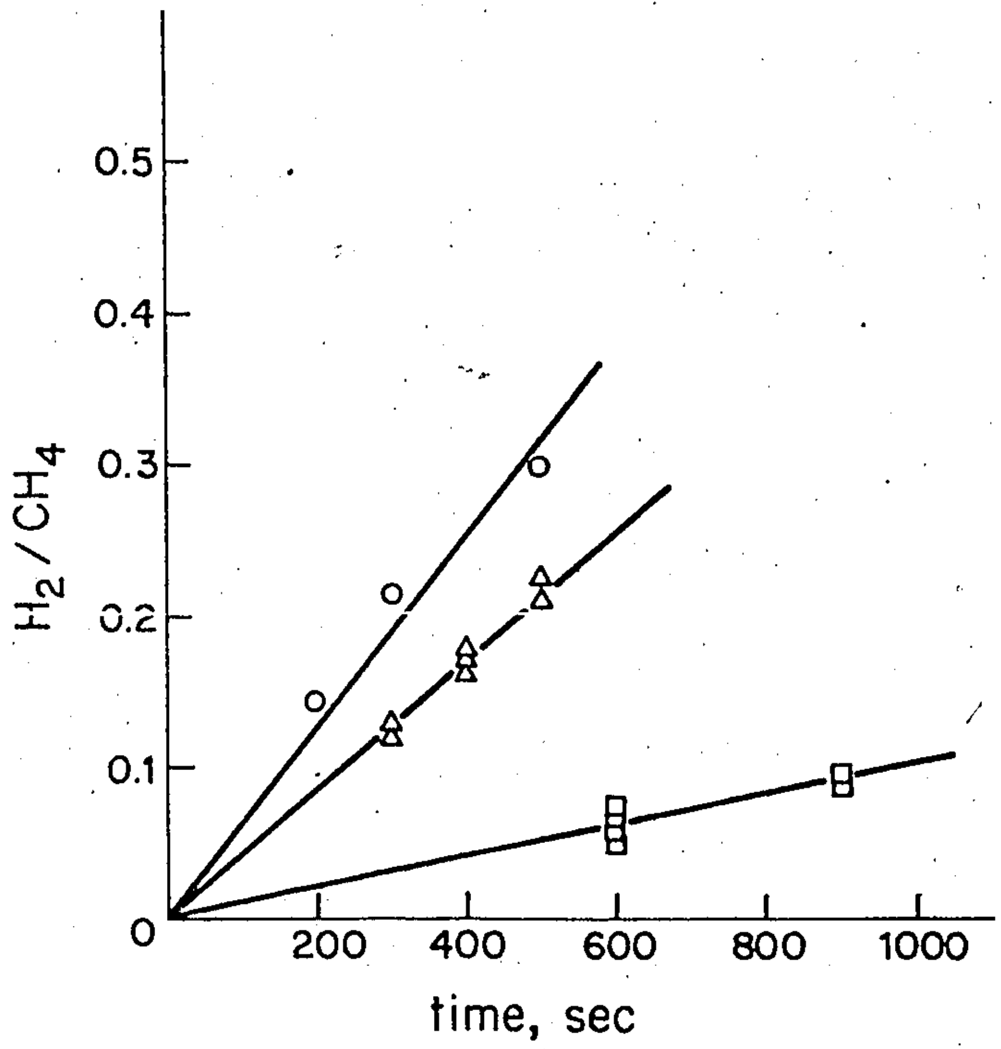
FIGURE 6

H_2/CH_4 as a function of time at different temperatures

○ ..... 522°C

△ ..... 489°C

□ ..... 447°C



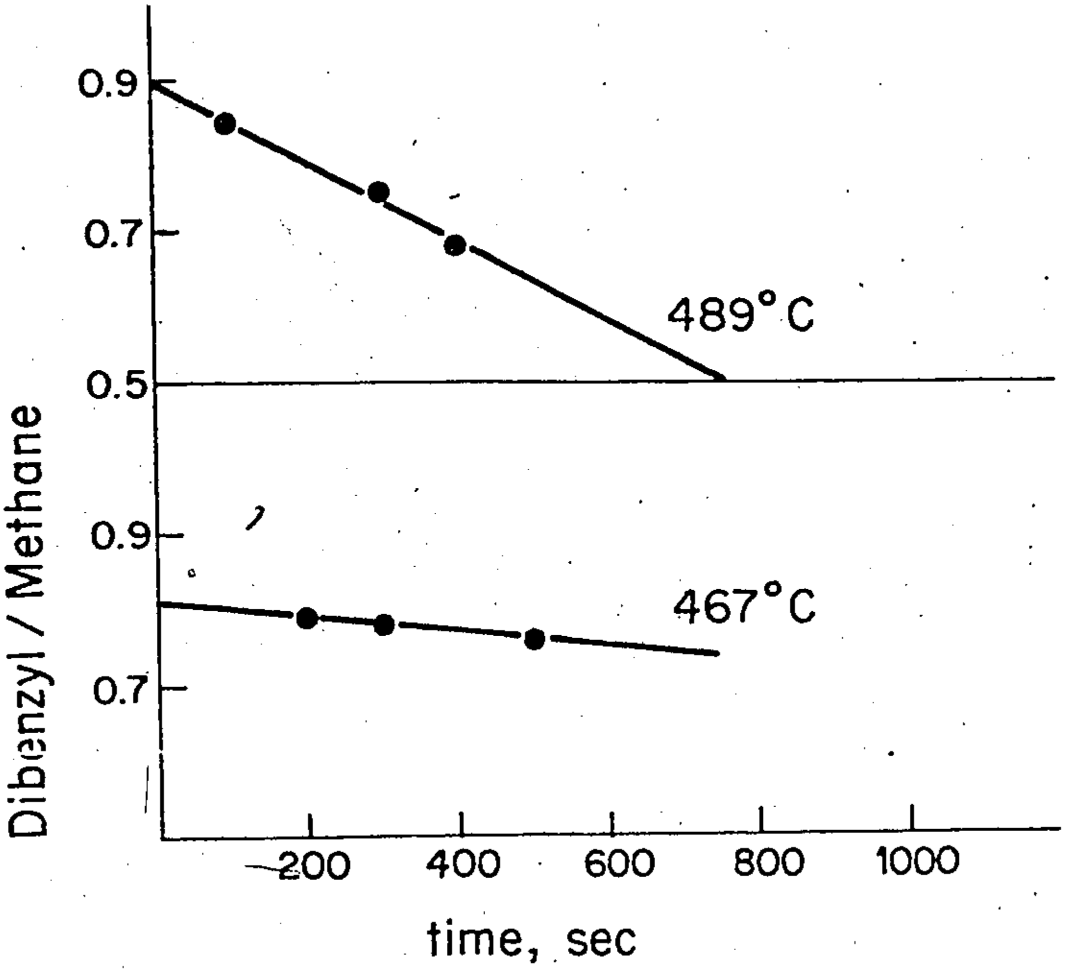
0.5
0.4
0.3
0.2
0.1
0
H_2/CH_4
200
400
600
800
1000
time, sec

of hydrogen/methane clearly becomes zero at the start of the reaction which shows that hydrogen is a secondary product of the decomposition.

The ratio of dibenzyl/methane has been plotted as a function of time in Figure 7. This ratio decreases with time and the decrease is more prominent at higher temperatures. The value of the ratios extrapolated to t=0 appears to be less than one. According to the simple mechanism shown in page 23, the ratio of dibenzyl/methane should be equal to one. The linear extrapolation may, however, not necessarily be correct. The shape of the curves of Figure 7 could not be ascertained from the present results. Nevertheless, some difficulty was experienced with the analysis for dibenzyl which may account for the low ratio of dibenzyl/methane. The complete collection of dibenzyl was difficult because of its low volatility. Small amounts might have been lost in the tube connecting the reaction vessel with the first removable trap in spite of care being taken to heat the connecting tube. Also, the error in the calibration of dibenzyl was sometimes more than ±5% whereas the reproducibility of the methane calibration was always within ±2%. The reason for this difference was the temperature programming required for the analysis of dibenzyl. For the analyses of the high molecular weight

FIGURE 7

Dibenzyl/CH_4 as a function of time at 489°C and 467°C


0.9
0.7
0.5
0.9
0.7
489°C
467°C
Dibenzyl / Methane
200
400
600
800
1000
time, sec

products, the column was maintained at 100°C for 40 minutes and then the temperature was quickly raised to 170°C. The dibenzyl peak sometimes appeared before the column became stabilized at 170°C. Another factor contributing to a low yield of dibenzyl is a loss due to decomposition. That such loss is important in our system is illustrated by Figure 7. The decomposition may occur by two possible ways:

a) molecular decomposition of dibenzyl giving hydrogen and stilbene,

$$C_6H_5CH_2CH_2C_6H_5 \longrightarrow H_2 + C_6H_5CH = CHC_6H_5 \qquad (22)$$

b) primary decomposition of the type

$$C_6H_5CH_2CH_2C_6H_5 \longrightarrow C_6H_5CH_2CH{\cdot}C_6H_5 + H{\cdot} \qquad (23)$$

Since the main secondary product observed in our experiments was H_2, it seems reasonable to conclude that H_2 is a decomposition product of dibenzyl.

Horrex and Miles [56] studied the pyrolysis of dibenzyl in a flow system in the presence of N_2 at low pressures of 0.01-0.4 torr in the temperature range of 630-774°C. A primary dissociation into benzyl radicals was suggested. In the absence of a scavenger, H_2 was a minor product. But more relevant to this work are the results of Blades et al [27] where in a few experiments dibenzyl was pyrolysed in the presence of toluene in the temperature range of 860-940°C. They found H_2 as an important product. In the present system therefore, it is reasonable to suggest that H_2, which was the main secondary product observed in our experiments, was produced by the decomposition of dibenzyl.

6. Effect of pressure on yields of products

The yields of methane, phenol and dibenzyl are shown as a function of anisole pressure in Figures 8-13. These plots show that the rates of formation of methane, phenol and dibenzyl are first order with respect to anisole concentration. The first order rate constants for methane have been calculated from the integrated first order rate equation (21) where in this case a is the initial concentration of anisole and x is the amount of CH_4 formed in the time period t. These first order rate constants are shown in Table 4. Thus both the time and concentration dependence of the rate of formation of these products show that they are formed in a first order reaction.

7. Test for surface reaction

In order to test for a heterogeneous reaction, the unpacked reaction vessel was replaced by one packed

FIGURE 8

Yield of CH_4 against anisole pressure at 522°C

● ..... 100 sec

▲ ..... 300 sec

o ..... 500 sec

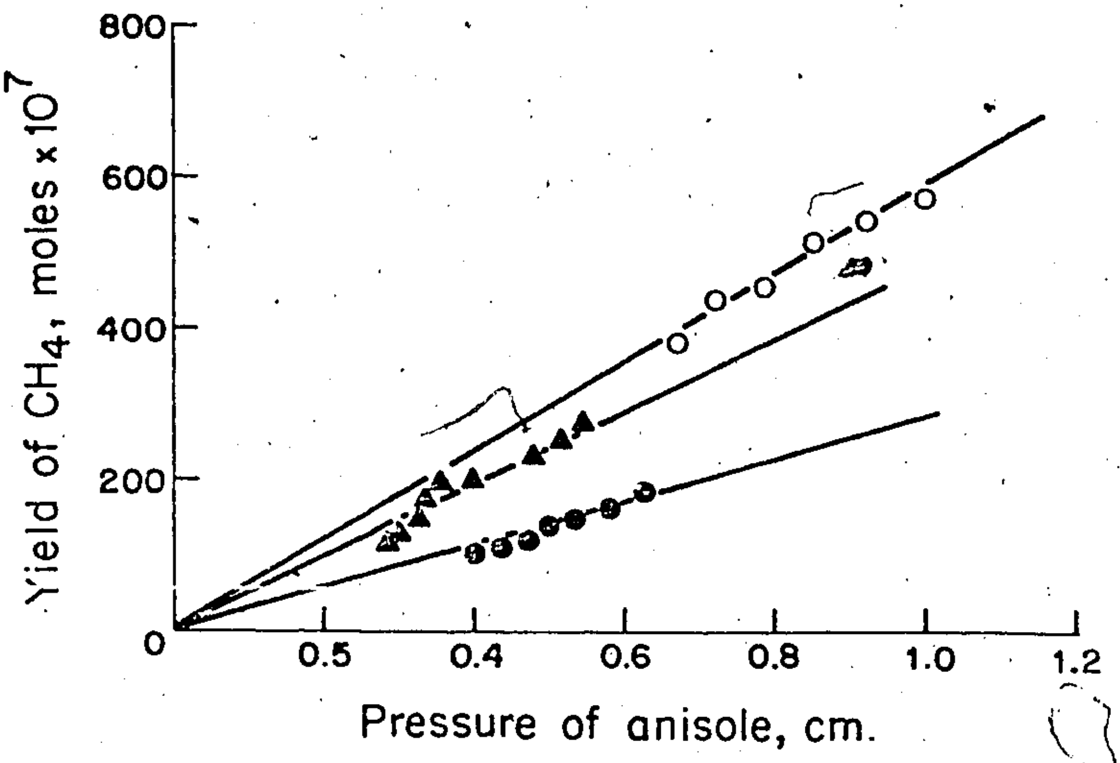

Yield of CH$_4$, moles x 10^7
800
600
400
200
0
0.5
0.4
0.6
0.8
1.0
1.2
Pressure of anisole, cm.

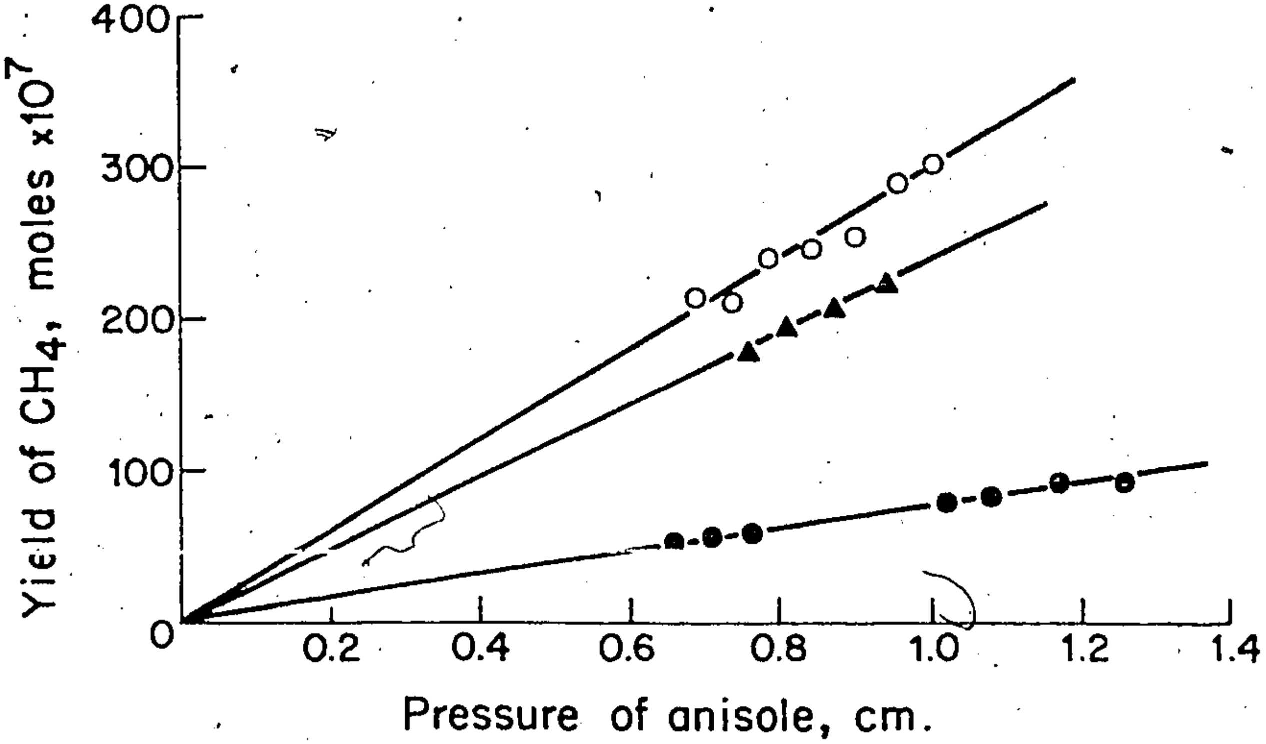
FIGURE. 9

Yield of CH_4 against anisole pressure at 489°C

● ..... 100 sec

▲ ..... 400 sec

○ ..... 500 sec



Yield of CH_4, moles $\times 10^7$
400
300
200
100
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Pressure of anisole, cm.

FIGURE 10

Yield of CH_4 against anisole pressure at 467°C

● ..... 200 sec

▲ ..... 300 sec

○ ..... 500 sec

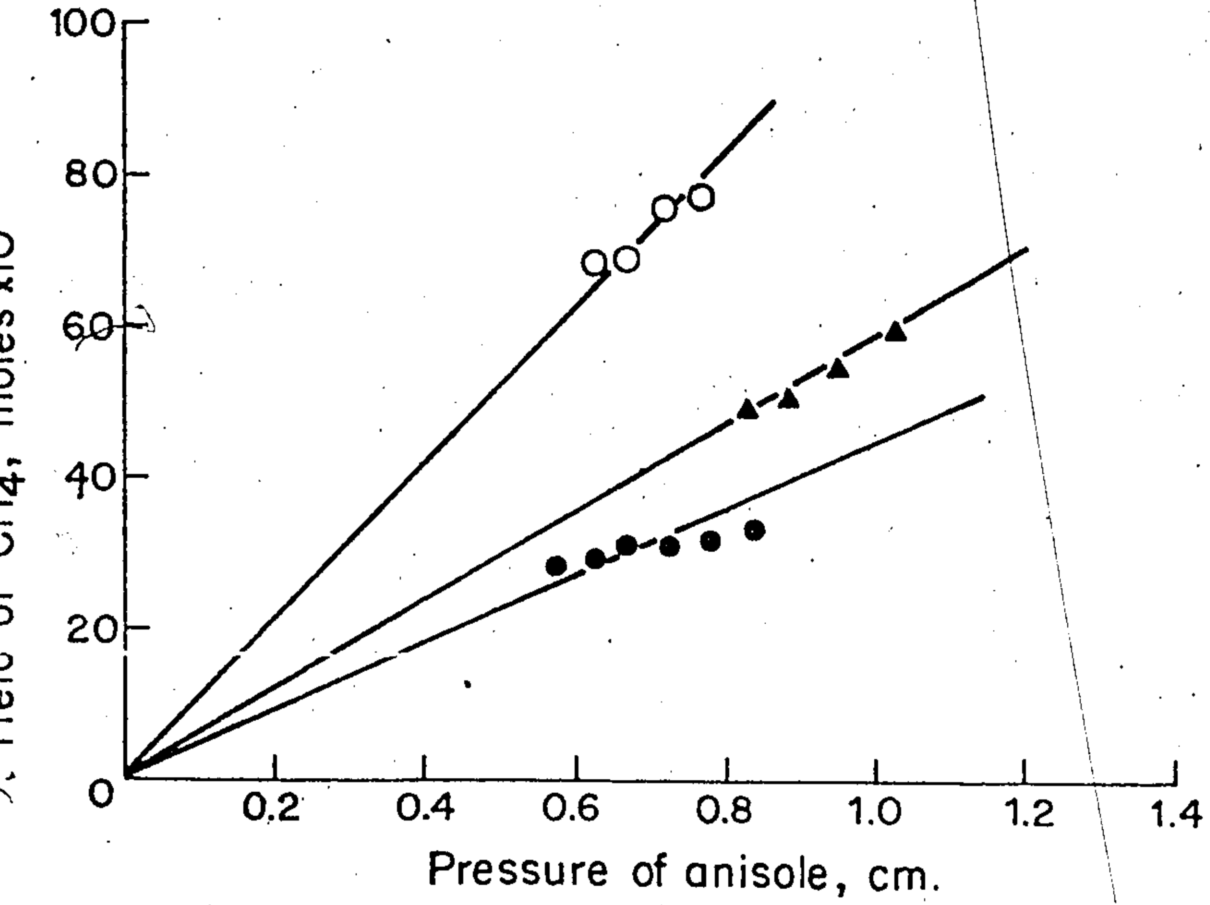

100
80
60
40
20
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Yield of CH_4, moles x10^7
Pressure of anisole, cm.

FIGURE 11

Yield of C_6H_5OH against anisole pressure at 522°C

● ..... 100 sec

o ..... 500 sec

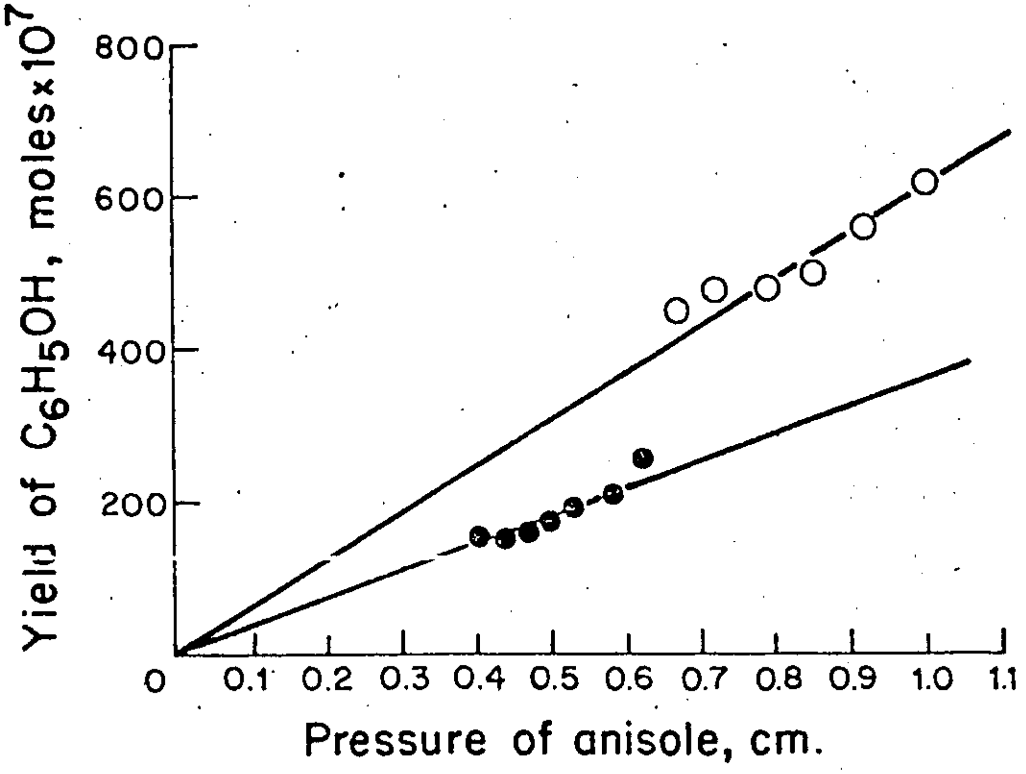

Yield of C_6H_5OH, moles × 10^7
800
600
400
200
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
Pressure of anisole, cm.

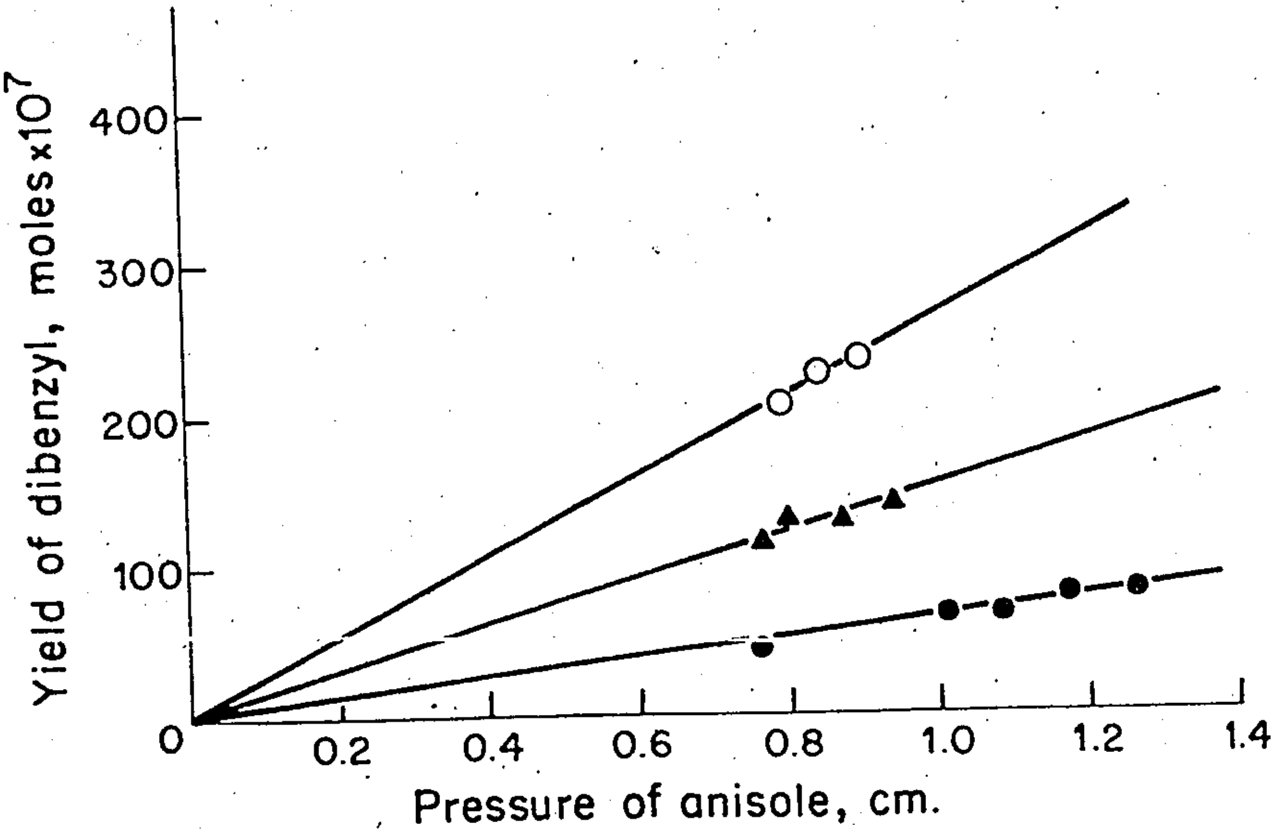
FIGURE 12

Yield of dibenzyl against anisole pressure at 489°C

● ..... 100 sec

▲ ..... 300 sec

o ..... 500 sec



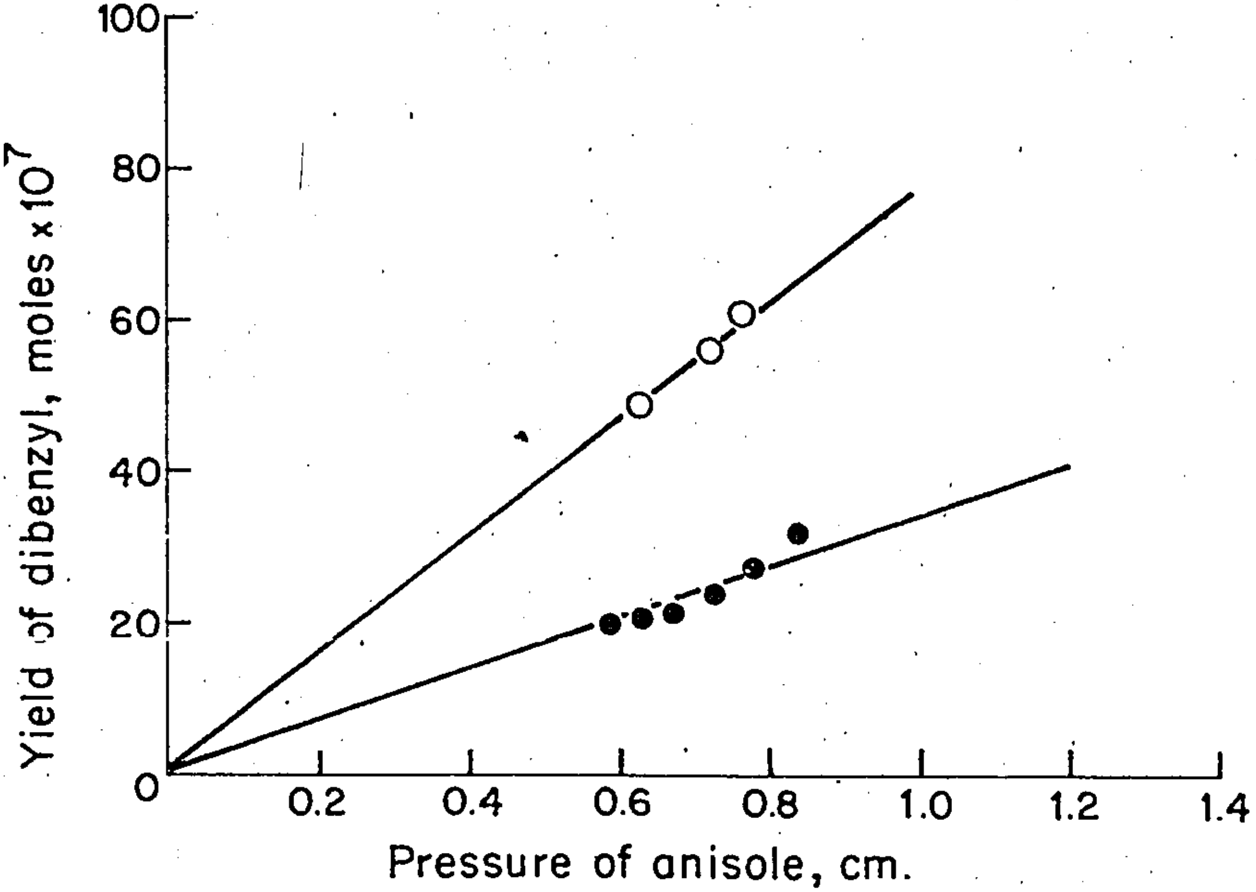
Yield of dibenzyl, moles x10^7
400
300
200
100
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Pressure of anisole, cm.

FIGURE 13

Yield of dibenzyl against anisole pressure at 467°C

● ..... 200 sec

o ..... 500 sec



Yield of dibenzyl, moles x 10^7
100
80
60
40
20
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Pressure of anisole, cm.

TABLE 4

First order rate constants for the formation of methane in unpacked and packed reaction vessels

Temp. (°C)	Pressure of anisole (cm)	Time (sec)	Yield of CH_4 (moles$\times10^7$)	k_{CH_4} (sec$^{-1}\times10^3$)	Mean k_{CH_4} (sec$^{-1}\times10^3$)
Unpacked reaction vessel of volume 342.3 cc					
522	0.54	300	287	4.91	4.574
	0.51		256	4.29	
	0.47		230	4.13	
	0.39		207	4.89	
	0.33		175	4.73	
	0.47	100	122	4.72	
	0.44		109	4.50	
	0.41		103	4.56	
	0.38	200	156	4.44	
489	1.03	500	302	1.04	1.078
	0.96		289	1.08	
	0.90		256	1.00	
	0.84		248	1.05	
	0.79		239	1.09	
	0.74		212	1.01	
	0.69		215	1.13	
	0.94	300	192	1.12	
	0.88		185	1.16	
	0.82		173	1.16	

TABLE 4 (cont'd)

Temp. (^{o}C)	Pressure of anisole (cm)	Time (sec)	Yield of CH_4 (molesx10^7)	k_{CH_4} (sec^{-1}x10^3)	Mean k_{CH_4} (sec^{-1}x10^3)
489	0.76	100	59	1.13	1.078
	0.71		57	1.17	
	0.66		52	1.14	
	1.26		91	1.06	
	1.17		89	1.12	
	1.08		80	1.09	
	1.01		78	1.14	
	0.94	400	224	1.00	
	0.87		205	0.99	
	0.81		194	1.00	
	0.76		177	0.98	
467	0.84	200	33	0.27	0.295
	0.78		32	0.28	
	0.72		31	0.30	
	0.67		31	0.32	
	0.63		29	0.32	
	0.59		28	0.33	
	1.02	300	59	0.27	
	0.95		55	0.27	
	0.88		51	0.27	
	0.83		50	0.28	
	0.77	500	77	0.29	
	0.72		76	0.31	
	0.67		69	0.30	
	0.63		69	0.32	

TABLE 4 (cont'd)

Temp. (^{o}C)	Pressure of anisole (cm)	Time (sec)	Yield of CH_4 (molesx10^7)	k_{CH_4} (sec^{-1}x10^3)	Mean k_{CH_4} (sec^{-1}x10^3)
447	1.00	600	50	0.11	0.118
	0.93		49	0.12	
	0.87		45	0.12	
	0.81		44	0.12	
	0.75		41	0.12	
	0.56	900	38	0.10	
	0.53		41	0.12	
	0.49		41	0.13	
Packed reaction vessel of volume 150.4 cc					
448	1.35	1800	75	0.10	0.108
	1.30		74	0.10	
	1.26		78	0.11	
	1.22		77	0.12	
468	1.25	900	95	0.29	0.282
	1.20	700	70	0.28	
	1.44	600	70	0.27	
479	1.06	500	81	0.54	0.540
	1.03		77	0.53	
	1.09		84	0.55	

with glass tubing in order to increase the surface to volume ratio. The packed vessel had a S/V ratio equal to 9 cm^{-1}. The rate will be observed to increase in proportion to the S/V ratio if a significant proportion of the reaction is heterogeneous. Rate constants, calculated from the formation of methane, are included in Table 4 and are in good agreement with those reported in the same table for the formation of methane in the unpacked reaction vessel (S/V = 1 cm^{-1}), thus confirming the absence of a surface reaction.

8. Arrhenius plot

The Arrhenius equation for k_{CH_4} as function of $T^{o}K$ has been computed from a least squares fit of the data shown in Figure 14. The rate constants k_{CH_4} for the packed reaction vessel have also been included in this computation from which E and log A have been found to be (57.3 ± 1.9) Kcal/mole and (13.4 ± 0.6) respectively, the corresponding unit for A being sec^{-1}.

The errors involved in the activation energy and frequency factor are discussed in Section 10.

9. Minor primary products

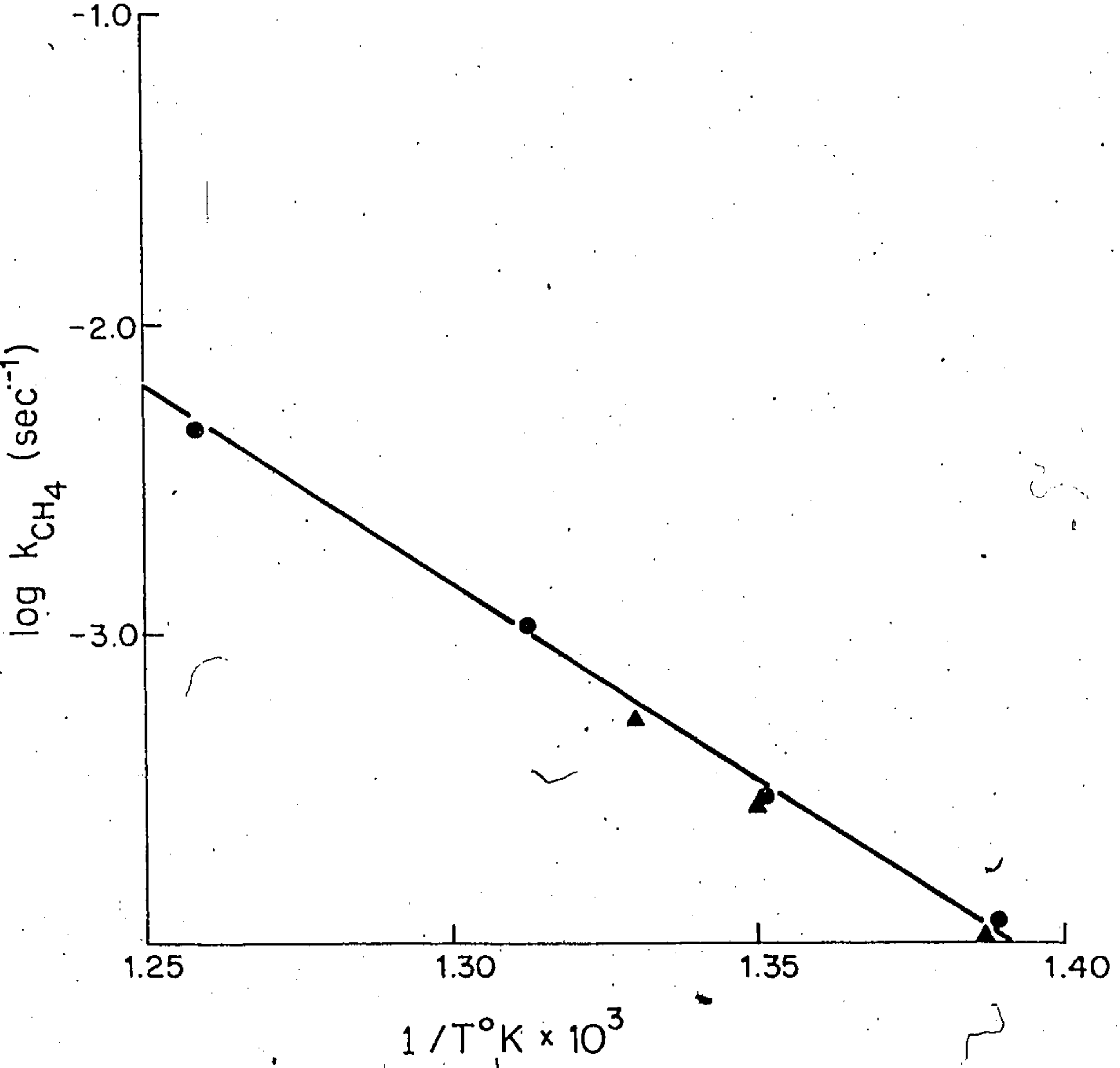
Although the abstraction of a hydrogen atom occurred predominantly from the methyl group, the formation

FIGURE 14

Arrhenius plot of log k_{CH_4} against 1/T °K

● ..... unpacked reaction vessel

▲ ..... packed reaction vessel


-1.0
-2.0
-3.0
log k_{CH_4} (sec^{-1})
1.25
1.30
1.35
1.40
1/T°K × 10^3

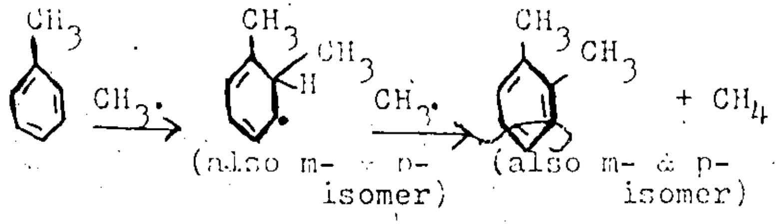
of xylenes suggested that ring abstraction [29, 30, 36] also occurred. From the relative yield of xylenes, it was estimated that ring abstraction was about 5% of the overall abstraction from the side chain. The formation of the xylenes may occur by the following reactions:

a) abstraction of ring hydrogen by methyl radical [29, 30]

$$CH_3\cdot + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_4\cdot CH_3 \text{(tolyl radical)}$$

$$C_6H_4\cdot CH_3 + CH_3\cdot \longrightarrow C_6H_4(CH_3)_2 \qquad (24)$$

b) addition [36a],



(25)

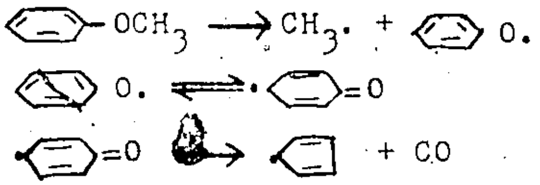
Trotman-Dickenson and Steacie [36b] gave data for the relative rates of abstraction from benzene and toluene by methyl radical at 177°C. On extrapolation to 522°C, these data suggest that about 8% of the radicals will abstract from the ring in the temperature range of our experiments. It therefore appears that mechanism (a) is a probable source of xylenes. Nevertheless, mechanism (b) has also been suggested by Wilen and Eliel [36a] at lower temperature range and in solution:

Ethylbenzene was also found to a very minor amount (~2%) of the yield of methane. The most probable source of ethylbenzene is combination of benzyl and methyl radicals,

$$C_6H_5CH_2\cdot + CH_3\cdot \longrightarrow C_6H_5CH_2CH_3 \qquad (26)$$

The yields of both xylenes and ethylbenzene obtained from each experiment have been shown along with the other products of reaction in Table 7 in the Appendix.

A very small yield of carbon monoxide, about 3% of the total amount of phenol, was detected at the highest temperature of 522°C. The variation of the yield of carbon monoxide with anisole pressure shown in Figure 15 indicates clearly that the formation of carbon monoxide is first order with respect to anisole concentration. In the pyrolysis of anisole at 950°C by Harrison, Dauben and Lossing [57], significant yields of carbon monoxide were observed. It was suggested that carbon monoxide was formed by secondary decomposition of the phenoxy radical as follows;



(27)

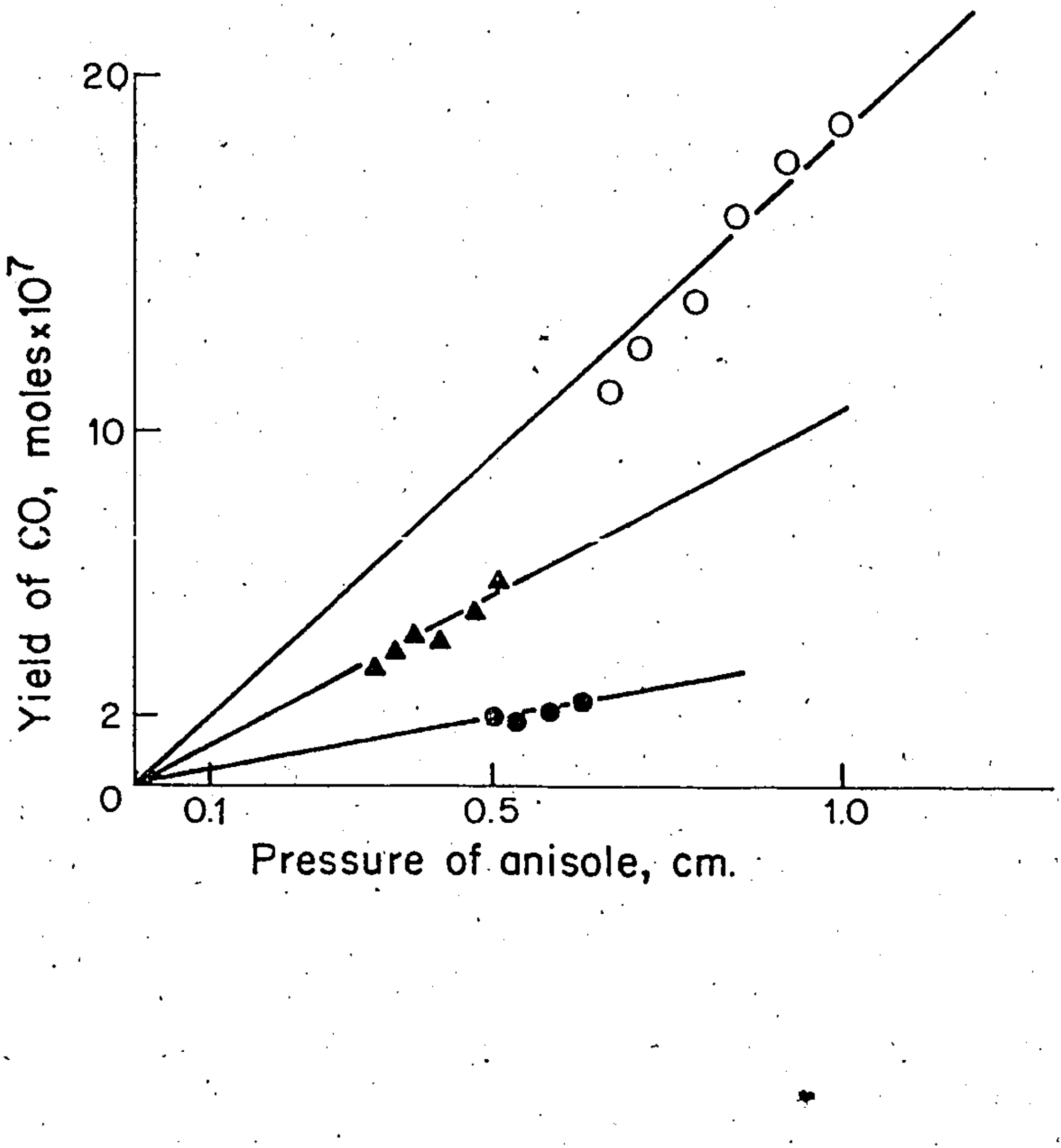
FIGURE 15

Yield of CO against anisole pressure at 522°C

● ..... 100 sec

▲ ..... 300 sec

○ ..... 500 sec


20
10
2
0
0.1
0.5
1.0
Yield of CO, moles x 10^7
Pressure of anisole, cm.

It is suggested that this reaction occurs to a small extent at the highest temperatures of the present study.

10. Errors

It is well-known that the most serious errors in kinetic studies are systematic ones. Furthermore, it is recognized that the most frequent systematic errors arise from secondary reactions, heterogeneous effects or other complications to the mechanism. By careful experimental techniques and precautions, random errors in analysis and temperature control can be kept to a minimum, but it can not be concluded that the real experimental errors are therefore small. Systematic errors may be present and their magnitude is difficult to estimate.

In the present case, a systematic error in the measurement of the amount of methane formed can lead to an error in k_{CH_4} and consequently in the activation energy of the dissociation process. Recent redeterminations [58] of free radical heats of formation by other methods [1e] (competitive bromination and iodination kinetic studies) have shown that the toluene carrier technique has, in the past, yielded erroneously low Arrhenius parameters. Several reasons for this have been suggested: chain in Figures 8-13. Therefore a reasonable estimate to the random error may be $\pm 2\%$. Taking into account the error of $\sim 5\%$ due to the formation of xylenes and ethyl benzene, the maximum error in the rate constants may be $\pm 7\%$.

The error in the measurement of temperature is generally the major source of error involved in the determination of rate constants and activation energies. In the present case, temperature fluctuations of the order of $\pm 0.5^{\circ}$C were observed. The percentage error[59] in k for temperature fluctuation of $\pm 0.5^{\circ}$C may be estimated as follows:

$$(\Delta k/k)\mathrm{x}100 = (E\Delta T/RT^{2}_{mean})\mathrm{x}100 = (57{,}255\mathrm{x}0.5/1.987\mathrm{x}757.5^{2})\mathrm{x}100$$
$$= 2.5\%$$

If it is assumed that both rate constants, at the lowest and the highest temperature of the experiments, were uncertain by about 10% each, then the maximum experimental error of the computed activation energy is

$$\Delta E = R\ \ln(1.1/0.9)/(1/720-1/795)\mathrm{x}1000 \simeq 3\ \mathrm{Kcal/mole}$$

and the corresponding error in log A given by the formula $\Delta(\log A) = \Delta E/2.3RT$ is 0.88. The standard errors from the least squares fitting (1.9 Kcal/mole and 0.6 in E and log A respectively) are less than the corresponding estimated maximum errors shown above. This is quite expected as the random errors to some extent cancel one another. A reasonable estimate of the error in the activation energy obtained from the present results is therefore ±2.5 Kcal/mole, and the corresponding error in log A is ±0.7.

CHAPTER 4.

DISCUSSION

1. Identification of activation energy obtained with the dissociation energy of O-C bond in anisole

The decomposition of anisole has been carried out in the presence of excess of toluene as radical scavenger. The methyl radical formed by the decomposition of anisole according to equation (17) reacted with toluene to yield methane. The kinetics of the decomposition measured by the rate of formation of methane obeyed the first order law, the activation energy for the formation of methane being (57.3±2.5) Kcal/mole. The reaction was found to be homogeneous. Now if it is assumed that the recombination of the fragments, formed in the dissociation process does not require any activation energy, then the activation energy of the dissociation process is equal to the bond dissociation energy. Therefore it can be concluded that the rate of formation of methane measures the rate of initial decomposition of anisole into methyl and phenoxy radicals and the observed activation energy represents the O-C bond dissociation energy in $C_6H_5OCH_3$.

2. Determination of heat of formation of the phenoxy radical and prediction of bond dissociation energies of some related compounds

Considering the initial split of anisole to be

$$C_6H_5OCH_3 \longrightarrow C_6H_5O. + CH_3. \qquad (17)$$

we have,

$$\Delta H_f^o(C_6H_5OCH_3)+D_{298}(C_6H_5O\text{-}CH_3)=\Delta H_f^o(C_6H_5O.)+\Delta H_f^o(CH_3.) \quad (28)$$

where ΔH_f^o refers to the heat of formation at 25°C. Correction to the bond dissociation energy of anisole obtained at the temperature range of our experiments has been neglected because it will be less than 1 Kcal/mole. $D_{298}(C_6H_5O\text{-}CH_3)$ has therefore been taken as 57 Kcal/mole.

Using the values of the heats of formation of methyl radical and anisole from Table 5, $\Delta H_f^o(C_6H_5O.)$ is calculated to be 5 Kcal/mole. Taking this value of $\Delta H_f^o(C_6H_5O.)$ together with other values for heats of formation given in Table 5 and applying the equation similar to (28), bond dissociation energies of related compounds were calculated and are shown in Table 6.

3. Resonance energy of the phenoxy radical

The benzyl radical has long been known to be fairly stable thermally and relatively unreactive [26, 62]. These properties have been attributed to its conjugated structure

TABLE 5

Data of heats of formation used in calculation

Radical or compound	ΔH_f^o Kcal/mole	Reference
CH_3	34.0	60
H	52.1	60
C_2H_5	26.0	60
C_6H_5	80.0	60
C_6H_5O	5.0	This work
$C_6H_5CH_2$	45.0	69
$C_6H_5OCH_3$	-18.0	60
C_6H_5OH	-23.1	61
$C_6H_5OC_2H_5$	-26.3	61
$C_6H_5OC_6H_5$	11.9	61
$C_6H_5CH_3$	12.0	40
$(C_6H_5CH_2)_2$	34.4	14 (p 404)
C_2H_6	-20.2	60
$C_6H_5CH_2CH_3$	7.2	14 (p 397)

TABLE 6

Values of bond dissociation energies

Compound	Bond	B.D.E Kcal/mole	Reference
C_6H_5OH	$C_6H_5O{-}H$	80.3	Calculated from this work
$C_6H_5OC_2H_5$	$C_6H_5O{-}C_2H_5$	57.3	"
$C_6H_5OC_6H_5$	$C_6H_5O{-}C_6H_5$	73.1	"
$C_6H_5OCH_3$	$C_6H_5O{-}CH_3$	57.0	This work
CH_3OCH_3	$CH_3O{-}CH_3$	81.0	51
CH_3OCH_3	$CH_3O{-}CH_3$	80.0	65
C_2H_6	$C_2H_5{-}H$	97.5	66
$C_6H_5CH_3$	$C_6H_5CH_2{-}H$	85.0	69
$(C_6H_5CH_2)_2$	$C_6H_5CH_2{-}CH_2C_6H_5$	55.6	14 (p. 404)
$C_6H_5CH_2CH_3$	$C_6H_5CH_2{-}CH_3$	70.0	23

which allows the free electron to be largely delocalized [63, 64]. Radicals with structures similar to that of the benzyl radical, such as the phenoxy radical, might also be expected to be stabilized by resonance and hence to form relatively weak bonds with other radicals. The usual definition of resonance energy is the difference in dissociation energy between similar bonds, one of them producing a resonance stabilized radical. An estimation of the resonance energy of the phenoxy radical can, therefore, be obtained from the difference between D(CH_3-OCH_3) and D(C_6H_5O-CH_3). Using the values given in Table 6, the resonance stabilization energy of the phenoxy radical is about 23-24 Kcal/mole. This value still includes the uncertainty in the value of D(CH_3O-CH_3) [51, 65], for which no direct measurement has been made.

4. Comparison with the resonance energy of other radicals

a) Benzyl radical

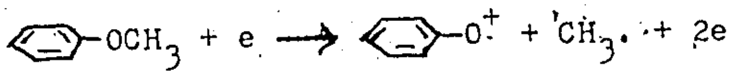
The resonance energy of the benzyl radical can be obtained from the energy difference between the C-H bond conjugated with the aromatic ring system and a simple bond in a saturated paraffin. For the latter, a value of 97.5 Kcal/mole may be regarded as representative for C-H bonds in ethane [66] or propane [67]. Methane should not be used for comparison since its bond strength is not typical [68]. Benson et al [69] determined accurate thermochemical parameters for benzyl iodide. They found that $D_{298}(C_6H_5CH_2-H) = (84.3 \pm 3.1)$ Kcal/mole, which adequately fixed the value at (85 ± 1) Kcal/mole in agreement with other measurements [23]. This gives the stabilization energy in the benzyl radical as (12.5 ± 1.0) Kcal/mole. On the other hand, if we compare $D(CH_3-CH_3)$ [70] with $D(C_6H_5CH_2-CH_2C_6H_5)$ [14] or $D(C_6H_5CH_2-CH_3)$ [23], the resonance energy of the benzyl radical becomes 16-18 Kcal/mole. This is in agreement with the value calculated by Pauling and Wheland [71] by the electron-pair bond method but higher than that calculated by Huckel [72] who found 11 Kcal/mole, using the molecular orbital method. The resonance energy of the benzyl radical is probably about 15 Kcal/mole.

b) Phenyl sulphide radical

Phenyl methyl sulphide, $C_6H_5SCH_3$, which is very similar to $C_6H_5OCH_3$ has been thermally decomposed by Back and Sehon [73]. Their value of 60 Kcal/mole may be tentatively identified with the dissociation energy of $C_6H_5S-CH_3$ bond. A value of 73 Kcal/mole was suggested by Palmer and Lossing [74] for $D(CH_3S-CH_3)$, on the basis of their results obtained by the mass spectrometric method. The difference between D(CH_3S-CH_3) and D(C_6H_5S-CH_3), which is 13 Kcal/mole, represents then the difference in resonance energies of the methyl sulphide and the phenyl sulphide radicals. Hence, the actual value of the resonance energy of the phenyl sulphide radical would be at least 13 Kcal/mole.

Thus, the phenoxy radical has more resonance stabilization than that of the benzyl or phenyl sulphide radical and consequently D(C_6H_5O-CH_3) is lower than D($C_6H_5CH_2$-CH_3) [23]. It must be concluded that the free electron of the phenoxy radical has more delocalization than that of the benzyl radical. This was also concluded by Mulcahy [75-78] when investigating the kinetics of reactions of the methyl radical with toluene [75] and phenol [76]. The greater complexity of the kinetics and products [77] of the reaction with phenol appeared to arise from the fact [76-77], that the free electron of the phenoxy radical is more associated with the ring than that of the benzyl radical.

The heat of formation of the phenoxy radical has not been determined before by kinetic experiments. An estimation of D(C_6H_5O-CH_3) can be obtained from the measurement of the vertical ionization potential of the phenoxy radical together with the appearance potential of $C_6H_5O^+$ from anisole. The ionization potential of C_6H_5O produced from the thermal decomposition of allyl phenyl ether[79] was 8.84 ev. The appearance potential of the $C_6H_5O^+$ fragment ion from anisole was found to be (11.92 ± 0.1) ev. The formation of this fragment ion is represented by the equation


(29)

If this process is a simple bond rupture in which the structural identity of the C_6H_5O fragment is preserved,

$$D(C_6H_5O\text{-}CH_3) \leq A(C_6H_5O^+) - I(C_6H_5O) \qquad (30)$$

Therefore, $D(C_6H_5O\text{-}CH_3) \leq 11.92$ ev-8.84 ev ≤ 71 Kcal/mole. The authors concluded that this dissociation energy was too high, because they expected the resonance energy of the phenoxy radical to be comparable to that of the benzyl radical. They therefore concluded that $A(C_6H_5O^+)$ was too large probably because it contained excess energy.

5. Frequency factor

The value of A for the bond fission reaction in equation (17) has been found to be 2.5×10^{13} sec^{-1}. A wide range of frequency factors from 10^{13} to 10^{18} sec^{-1} has been observed for bond fission reactions. High A-factors are taken to indicate a 'loose' transition state with a large degree of free rotation between resulting fragments. Steel and Laidler [80] have put forward theoretical arguments to account for high A-factors in unimolecular reactions. On the other hand, low A-factors are characteristic of a 'tight' transition state. Data on bond fission reactions collected by Richardson and O'Neal [81] suggested that A-factors in bond fissions (of large groups) not developing resonance in the transition states are consistently in the range, $A = 10^{16 \pm 1}$ sec^{-1}. This means that activation entropies, ΔS^{*}, are in the range (11 ± 4) $\text{cal.deg.}^{-1}\text{mole}^{-1}$. The relation of A to ΔS^{*} for a unimolecular reaction is given as follows:

$$A = \frac{\bar{k}T}{h} e^{\Delta S^{*}/R} \tag{31}$$

But resonance stiffening in the transition state seems to lower the activation entropies by about 3 e.u. per resonance interaction. Therefore, the following ranges of A-factors are 'reasonable' in simple bond fission reactions:

a) Single bond rupture, no resonance stiffening,

$$A = 10^{16 \pm 1}\ \text{sec}^{-1};\ \Delta S^{*} = 11 \pm 4\ \text{cal.deg.}^{-1}\text{mole}^{-1}.$$

b) Single bond rupture, one resonance stiffening i.e. giving rise to one resonance-stabilized radical,

$$A = 10^{15.3\pm1}\ \text{sec}^{-1};\ \Delta S^{*} = 8\pm4\ \text{cal.deg.}^{-1}\text{mole}^{-1}.$$

c) Single bond rupture, two resonance stiffenings,

$$A = 10^{14.7\pm1}\ \text{sec}^{-1};\ \Delta S^{*} = 5\pm4\ \text{cal.deg.}^{-1}\text{mole}^{-1}.$$

If the dissociation of anisole is classified under (c) because of the very high resonance stiffening of the phenoxy radical, then the value of A obtained is reasonable.

APPENDIX

TABLE 7

Kinetic data for the decomposition of anisole in presence of toluene

Temperature (^oC)	$\frac{\text{Toluene}}{\text{Anisole}}$	Anisole (cm)	Time (sec)	Methane (molesx10^7)	Hydrogen (molesx10^7)	Carbon monoxide (molesx10^7)	Xylenes (molesx10^7)	Ethyl benzene (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	k_{CH_4} ($sec^{-1}x10^3$)
522	12	1.59	900	890	582	67					1.86
		1.29		771	375	56					2.20
		1.19		706	393	48					2.17
		1.13		672	357	45					2.17
		1.03		644	292	44					2.65
		0.95		584	268	39					2.42
	30	0.54	300	287	69	7					4.91
		0.51		255	66	6					4.29
		0.47		230	75	5					4.13
		0.39		207	47	4					4.89
		0.33		175	35	3					4.73
	24	1.00	500	578	174	19			622	217	3.58
		0.92		545	156	18			556	232	3.89
		0.85		513	109	16			498	169	4,10
		0.79		456	146	14			478	198	3.63
		0.72		437	113	12			475	202	4.19
		0.67		384	126	11			449	200	3.53

TABLE 7 (cont'd)

Temperature (^oC)	Toluene/Anisole	Anisole (cm)	Time (sec)	Methane (molesx10^7)	Hydrogen (molesx10^7)	Carbon monoxide (molesx10^7)	Xylenes (molesx10^7)	Ethyl benzene (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	k_{CH_4} ($sec^{-1}x10^3$)
522	45	0.47	100	122	28		7		163	111	4.72
		0.44		109	26		5		153	112	4.50
		0.41		102	24		5		149	124	4.56
		0.38	200	156	21	1	7		208	176	4.44
489	30	1.03	500	302	68	5					1.04
		0.96		289	49	4					1.08
		0.90		256	57	3			355	236	1.00
		0.85		248	40	1	8	5	255		1.05
		0.79		239	39				371	206	1.09
		0.74		212	45	1	7	4	312	242	1.01
		0.69		215	29		7		275	299	1.13
		0.94	300	192	25	1	4		171	144	1.12
		0.88		185	12	1	3		161	128	1.16
		0.82		173	20	1	3		155	131	1.16
		0.76	100	59	6		1		46	47	1.13
		0.71		57	4						1.17
		0.66		52	6						1.14
		1.26		91	1				82	80	1.06
		1.17		89					75	79	1.12
		1.08		80	2				69	67	1.09
		1.01		78	1				66	65	1.14

TABLE 7 (cont'd)

Temperature (°C)	Toluene/Anisole	Anisole (cm)	Time (sec)	Methane (molesx10^7)	Hydrogen (molesx10^7)	Carbon monoxide (molesx10^7)	Xylenes (molesx10^7)	Ethyl benzene (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	k_{CH_4} ($sec^{-1}x10^3$)
489	30	0.94	400	224	36	3	4		250	151	1.00
		0.87		205	35	2			205	138	0.99
		0.81		194	31	2	2	1	211	136	1.00
		0.76		177	31	1	3	1	181	115	0.98
467	30	0.84	200	33	2		2		21	32	0.27
		0.78		32	2				21	27	0.28
		0.72		31	2				18	24	0.30
		0.67		31	1		1		17	22	0.31
		0.63		29	2				16	21	0.32
		0.59		28	2				13	20	0.33
		1.02	300	59					43	44	0.27
		0.95		55	6				43	35	0.27
		0.88		51	5				48	42	0.27
		0.83		50	3				42	46	0.28
		0.77	500	77	5				80	62	0.29
		0.72		76					69	56	0.31
		0.67		69					62	57	0.30
		0.63		69	5				62	49	0.32
447	20	1.24	600	44	7		1		39	51	0.08
		1.16		42	4		1		41	42	0.08
		1.07		39	5		1		34	39	0.08
		1.00		35	5		1		34	35	0.08

TABLE 7 (cont'd)

Temperature (°C)	Toluene/Anisole	Anisole (cm)	Time (sec)	Methane (molesx10^7)	Hydrogen (molesx10^7)	Carbon monoxide (molesx10^7)	Xylenes (molesx10^7)	Ethyl benzene (molesx10^7)	Phenol (molesx10^7)	Dibenzyl (molesx10^7)	k_{CH_4} ($sec^{-1}x10^3$)
447	30	1.00	600	50	3		1		48	42	0.11
		0.93		49	3		2		44	39	0.12
		0.87		45	4		1		41	39	0.12
		0.81		44	3		1		35	38	0.12
		0.75		41					41	37	0.12
		0.56*	900	38	4		1		48	51	0.10
		0.53		41	4		1		48	53	0,12
		0.49		41	4		1		52	55	0,13

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