THE PYROLYSIS OF PHENYLMERCAPTOACETIC ACID

by

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INTRODUCTION

Chemical changes involve the breaking of bonds in the reacting molecules and the formation of bonds in the products; they are usually accompanied by energy changes. Although the stability of a molecule or a radical, as expressed in terms of bond strengths, and its reactivity do not necessarily go hand in hand, a knowledge of the former is essential for the full understanding of the other factors which influence the cource of chemical processes. In consequence, it is evident that the magnitudes of bond dissociation energies are of fundamental importance for both chemical kinetics and chemical equilibria.

Fajans (1) first introduced the idea of "bond energy". He postulated that a constant amount of energy was required to break a particular bond. This was characteristic for each type of bond and independent of the environment of the bond within the molecule. This quantity was called the bond energy or the bond energy term (2,3). The sum of all bond energies corresponding to the bonds existing in a molecule was equal to the heat of atomization of the molecule. For a polyatomic molecule of the type MA_n, the bond energy (M-A) was given by 1/n of the heat of atomization of the molecule MA_n. For a polyatomic molecule with more than one type of bond, the bond energy of a particular bond was equal to the difference between the sum of the bond energies of all the other bonds in that molecule and the heat of atomization of the molecule.

The concept of "bond energy" has been critically discussed by Szwarc and Evans (5). They concluded that the average bond energy could be defined as the amount of work required for the rupture of the bond in question in a process in which all the other bonds were stretched independently and simultaneously with the above bond, and thus the molecule indefinitely without losing its original shape. In the light of this definition the sum of average bond energies is equal to the heat of atomization of the molecule, and the average bond energies corresponding to identical bonds are equal. The concept of the average bond energy is based on the notion of the heat of atomization; there is no other experimental method which would make it possible to determine it.

The bond dissociation energy, $D(R_1R_2)$, of a bond R_1-R_2 is defined (5) as the endothermicity of the reaction

$$R_1R_2 \longrightarrow R_1\cdot + R_2\cdot$$

in the gaseous state. The molecule or radical, R_1R_2, and fragments (atoms, radicals or molecules) R_1 and R_2 are in their ground states or specified electronic states at zero pressure and at $0^{\circ}K$. This energy, a quantity which can be measured experimentally, is independent of the path of the reaction which leads to dissociation. Thus, for the above process, one may write the following thermochemical relation:

$$\Delta H_f(R_1R_2) + D(R_1-R_2) = \Delta H_f(R_1) + \Delta H_f(R_2)$$

where ΔH_f terms represent the heats of formation.

Within the last two decades, several experimental methods have been invented which made it possible to determine the dissociation energies of various bonds in polyatomic molecules. For example, with respect to the dissociation energies of the two OH bonds in the H_2O molecule, it can be readily shown on the basis of the known heats of formation of H_2O and of H and O atoms, that the sum of the two dissociation energies must amount to 219 kcal/mole. The energy required to dissociate the O-H bond in the OH radical, i.e., D(O-H), has been recently determined as 101.5 kcal/mole (4), and therefore it follows that the first OH dissociation energy in water, i.e., D(H-OH), is equal to 117.5 kcal/mole. Thus, it is obvious that the assumption of constancy of bond energy can not be retained.

Methods of Determining Bond Dissociation Energies:

Theoretically, bond dissociation energies can be calculated directly from the fundamental quantities of atomic mass and electronic charge. In fact, it was applied by Jaffe (6), Hylleraas (7) and others to calculate the dissociation energy of the hydrogen molecule ion H_2^+. Their results were in complete agreement with experimental work. However, this was an isolated case, and for other molecules the application of mathematical theory leads to equations much too complicated to be soluble (8). Therefore, it is desirable to develop methods to measure the bond dissociation energies.

In the last decade, reasonably accurate bond dissociation energies have been determined by various experimental techniques. These may be classified as the spectroscopic methods, the electron impact methods, the calorimetric methods, the equilibrium methods and the chemical kinetic methods.

The Spectroscopic Methods:

Atoms may be brought together either in the normal state or in any of their excited states to form a molecule. In general, from each of the combinations of the excited atoms several electronic states of the molecule arise. The different electronic states belonging to the same combination of atomic states have different potential energy curves. The dissociation limit is defined as the difference in energy between the lowest vibrational level in the electronic ground state and the asymptote of the potential energy curve. There are as many different dissociation limits as there are combinations of the different states of the two atoms. The distance of the lowest dissociation limit, corresponding to the dissociation into normal atoms from the ground state of the molecule, is the bond dissociation energy. Since in many cases the atoms formed are in their excited states, two steps are involved in the spectroscopic methods, namely, the determination of the dissociation limit of the molecule, that is, the apparent dissociation energy, and the determination of the products of dissociation at this limit. The true bond dissociation energy is then obtained by subtracting the excitation energies of the atoms from the apparent dissociation energy.

Because of the great accuracy with which wavelength measurements can be made, the spectroscopic methods are, at least in principle, the most accurate methods for the determination of bond dissociation energies of diatomic molecules. They have been applied successfully to the determination of the dissociation energies of I_2, Br_2 and Cl_2 (9). These methods are not applicable to polyatomic molecules, since the spectra of polyatomic molecules are generally too complicated.

The Calorimetric Methods:

Direct calorimetric measurement of the energy absorbed in the bond breaking process is impossible. Calorimetric methods are only applicable to the measurement of the heat liberated in the process of recombination of radicals or atoms. Bichowsky and Copeland (10) were able to estimate the heat of recombination of hydrogen atoms in the formation of hydrogen molecules. They obtained a value of 105 ± 3.5 kcal/mole as the dissociation energy of the hydrogen molecule. This agrees satisfactorily with the present accepted spectroscopically derived value of 103.2 kcal/mole. Copeland (11) and Rodebush and Troxel (12) applied similar methods to the oxygen molecule. They obtained a value of 131 ± 6 kcal/mole as the dissociation energy of the oxygen molecule. This is far from the present accepted value of 117.96 ± 0.04 kcal (13).

The Equilibrium Methods:

According to the Van't Hoff isochore, $\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}$.

If the equilibrium constant, K, of the gaseous reaction,

$$R_1R_2 \rightleftharpoons R_1 + R_2$$

(where R_1 and R_2 denote the radicals or atoms produced by the breaking of the bond in R_1R_2) can be measured accurately at different temperatures, the heat of dissociation can be computed, and the dissociation energy can be obtained by recalculation of the heat of dissociation at zero pressure and at $0^{o}K$. This is the basic principle of the equilibrium methods.

The equilibrium methods thus depend on measuring the concentrations of the reactant and its products. These can only be applied to simple molecules which produce radicals that do not react with the parent molecule and which are thermally stable. These methods are particularly suitable for the estimation of the bond dissociation energies of diatomic molecules of the X_2 type. The dissociation energies of I_2 (14), Br_2 (15), Cl_2 (16) were determined by the direct manometric method. Other equilibrium methods have been used, and have been described elsewhere in detail (17, 18).

The Electron Impact Methods:

A beam of electrons with sufficient kinetic energy is made to collide with gaseous molecules thus causing ionization and dissociation. This is the basis of the electron impact methods, for which three sets of data are required:

(1) the mass-charge ratio of the ion produced

(2) the accelerating potential of the electrons at which the appropriate ion just appears. This accelerating potential is called the "appearance potential".

(3) the kinetic energies possessed by the ions produced.

The dissociation energy is readily obtained by subtracting the sum of ionization potential and the kinetic energies possessed by ions produced after the electron impact, from the appearance potential. In most cases, the radicals and radical ions are produced in their ground states (19), therefore the dissociation energy is equal to the difference between the appearance potential and the ionization potential. Thus, for the process

$$R_1R_2 + e \longrightarrow R_1^+ + R_2 + 2e,$$

$$A(R_1^+) = I(R_1) + D(R_1R_2)$$

where $A(R_1^+)$ is the appearance potential of R_1 and $I(R_1)$ is the ionization potential of R_1.

Two electron impact methods have been used extensively in the determination of bond dissociation energies. In the direct method, the appearance potential and ionization potential of the same ion are measured. Bond dissociation energy is then obtained by the difference between them. For example, the dissociation energy of the first CH bond in methane, $D(CH_3\text{-}H)$, may be calculated from the following relations:

$$CH_4 + e \longrightarrow CH_3^+ + H + 2e \qquad A(CH_3^+) = 14.44 \pm 0.1 \text{ ev.}$$

$$CH_3 + e \longrightarrow CH_3^+ + 2e \qquad A(CH_3^+) = 10.0 \pm 0.1 \text{ ev.}$$

Subtracting the two equations we get

$$CH_4 \longrightarrow CH_3 + H \qquad D(CH_3\text{-}H) = 4.4 \pm 0.2 \text{ ev.}$$

In the indirect method, the dissociation energy is calculated by combining the appearance potentials of the ions produced from two different but related molecules, with relevant thermochemical data without a knowledge of ionization potentials. For example, by measuring the appearance potential of the $C_2H_5^+$ ion in the mass spectra of ethane and propane, and in conjunction with the heats of formation of methane, ethane and propane, and the dissociation energy of hydrogen, the dissociation energy of methane, $D(CH_3-H)$, can be readily computed (20).

$$C_2H_6 + e \longrightarrow C_2H_5^+ + H + 2e \qquad A = 15.2 \text{ ev.} \qquad (1)$$

$$C_3H_8 + e \longrightarrow C_2H_5^+ + CH_3 + 2e \qquad A = 14.5 \text{ ev.} \qquad (2)$$

$$C_2H_6 + CH_4 \longrightarrow C_3H_8 + 2H \qquad \Delta H_{298^\circ} = 5.08 \text{ ev.} \qquad (3)$$

adding (2) and (3) and subtracting (1) gives

$$CH_4 \longrightarrow CH_3 + H \qquad D(CH_3-H) = 4.38 \text{ ev.}$$

<u>The Chemical Kinetic Methods</u>:

For a chemical reaction involving the rupture and formation of bonds the heat of reaction is equal to the sum of the dissociation energies of the bonds broken minus the sum of the dissociation energies of the bonds formed:

$$\Delta H = D \text{ (bonds broken)} - D \text{ (bonds formed)}$$

In the chemical kinetic methods, the bond dissociation energies are derived from measurements of appropriate activation energies. Thus, for the general reaction

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

the following relation holds

$$\Delta H = E_f - E_r$$

The best known example of this application to the determination of bond dissociation energies, is the study of the photochemical and thermal bromination of hydrocarbons by Kistiakowsky and co-workers from which the values for $D(CH_3-H)$ and $D(C_2H_5-H)$ were derived as 102 ± 1 kcal/mole and 99 ± 1 kcal/mole, respectively (18).

For the unimolecular decomposition of the type

$$R_1R_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R_1 + R_2$$

involving the rupture of the molecule into two fragments, R_1 and R_2, the bond dissociation energy of the bond (R_1-R_2) is equal to the difference in activation energies for the forward and the reverse reactions. It has been demonstrated (17) that in most reactions leading to the formation of free radicals, the activation energy of the reverse step is either very small or equal to zero. Therefore, to a satisfactory approximation, it is possible to assume that the activation energy of the process leading to the rupture of the bond is equal to the bond dissociation energy.

In most unimolecular decompositions, the radicals produced are quite active and hence a chain reaction is set up. The whole process is complex, and it is difficult to sort out the mechanism sufficiently to enable an accurate estimate of the rate of the initial rupture of the bond to be made. Ideally a system should be chosen in which the radicals or atoms formed after the initial rupture of the weakest bond are inert, relatively stable, or are removed irreversibly before reacting with the undecomposed molecules.

The C-I bond dissociation energies of various organic iodides were estimated by Butler and Polanyi (21) by measuring the rate of the pyrolysis of a series of organic iodides in a flow system. A flow method has the advantage of limiting the time of reaction to a second or less, thus limiting the total decomposition to a very small percentage and minimizing the chances of secondary reactions. This method has the added advantage that the products can be accumulated over extended periods of time. The weakest bond in organic halides is the C-I bond, it is therefore obvious that the first step in the pyrolysis of the compounds involves the rupture of this bond in preference to that of any other, that is

$$RI \longrightarrow R + I$$

The iodine atoms may only dimerize, and since Butler and Polanyi assumed that the back reaction was negligible and that the R radicals did not initiate a chain reaction, the rate of formation of iodine was taken as a measure of the initial rate of the decomposition.

For many iodides these assumptions were plausible and the derived bond dissociation energies agreed well with those obtained by other methods (22, 23).

Various complications, however, could not be completely prevented. For example, Butler, Mandel and Polanyi (24) showed that appreciable recombination vitiated the results with isopropyl, tert-butyl, dichloromethyl, dibromomethyl, diiodomethyl and β-chloro-ethyl iodides. Furthermore, the organic iodide might decompose by a molecular mechanism, splitting out hydrogen iodide. Butler and Polanyi concluded that in some cases the activation energies calculated from the temperature coefficient of the rate constant were not reliable. Instead, they chose the rate constants obtained from experiments performed at the lowest temperatures and with the smallest percentage decompositions, assuming a value for the frequency factor of $10^{13}sec^{-1}$. Under these conditions the side reactions were reduced to a minimum. In many cases the results agree well with current accepted values.

The idea of Butler and Polanyi was further extended by Szwarc (25) to the estimation of the C-H bond dissociation energy in toluene, i.e. $D(C_6H_5CH_2\text{-}H)$. Toluene was made to flow through a hot furnace at 680°C - 850°C under a pressure of 2-15 mm Hg. To prevent side reactions, the contact time was kept to less than one second, and the decomposition to 0.01% to 1%. Under these conditions, the mechanism of the thermal decomposition of toluene was simple, and could be represented by the following mechanism:

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + H \quad (1)$$

$$C_6H_5CH_3 + H \longrightarrow C_6H_5CH_2 + H_2 \quad (2)$$

$$C_6H_5CH_3 + H \longrightarrow C_6H_6 + CH_3 \quad (3)$$

$$C_6H_5CH_3 + CH_3 \longrightarrow C_6H_5CH_2 + CH_4 \quad (4)$$

$$2\ C_6H_5CH_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 \quad (5)$$

It was found that the reaction was a first order homogeneous gas reaction, and that the molar ratio of hydrogen to methane was 1.5 to 1. The rate of formation of $(H_2 + CH_4)$ was used to measure the rate of the initial dissociation of the CH bond. Assuming that the activation energy of the recombination of $C_6H_5CH_2$. and H. was zero, $D(C_6H_5CH_2 - H)$ was found to be equal to 77.5 ± 1.3 kcal/mole, and the experimental frequency factor was estimated as $2 \times 10^{13}sec^{-1}$.

Since the publication of Szwarc's paper, the pyrolysis of toluene has been reinvestigated by Blades, Blades and Steacie (26), and recently by Takahasi (27). Blades, Blades and Steacie performed the experiments in the temperature range 860°-940°C. Using deuterated toluene they obtained evidence (28) confirming the mechanism for the decomposition of toluene proposed by Szwarc. However, in contrast to Szwarc, they observed that the first order rate constant increased, as the contact time was increased and that the rates of the decomposition were surface dependent. They calculated the apparent activation energy of the pyrolytic reaction to be 90 kcal, keeping the contact time constant at 0.068 sec. However, they concluded that it was premature to assign any definite value to the bond dissociation energy of the (C_6H_5-CH_2-H) bond. Takahasi carried out the pyrolysis of toluene by the flow technique under various conditions, and measured the rates of decomposition over the wide temperature range 737°-953°C at contact time 0.02 to 0.3 sec. The plot of log k versus 1/T appeared to be linear but more precise analysis showed it to be slightly concave, and the activation energy tended to increase, as the reaction temperature was raised. To test the involvement of ring-hydrogen in the pyrolysis, Takahasi (29) investigated the pyrolysis of toluene-3-d and toluene -4-d. The fact that ring-hydrogen takes part in the pyrolysis has been confirmed from the formation of HD and CH_3D. Takahasi concluded that reacting ring-hydrogen may compete with the fission of the C-H bond of the methyl group. This may modify the activation energy of the fission of the methyl bond of toluene, if the experiment is carried out over a wide temperature range.

The dissociation energy of the ($C_6H_5CH_2$- H) bond has been redetermined by various workers using a variety of techniques. Some have confirmed the value claimed by Szwarc, that is 77.5 ± 1.3 kcal, while others have obtained higher values. Schissler and Stevenson (30) derived a value of 77 ± 3 kcal by the electron impact method. Anderson, Scheraga and Van Artsdalen (31) studied the thermal bromination of toluene, and they derived 89.5 kcal for the upper limit of the bond dissociation energy of the ($C_6H_5CH_2$- H) bond. Benson and Buss (32) reviewed various attempts to determine D($C_6H_5CH_2$- H), and they attempted a measurement of the equilibrium constant for the reaction:

$$C_6H_5CH_3\ (g) + Br_2\ (g) \rightleftharpoons C_6H_5CH_2Br\ (g) + HBr\ (g)$$

at 150°C. Together with the known thermal data, this gave the bond dissociation energy of toluene to be 84 kcal. The whole problem has been reviewed by Sehon and Szwarc (33). They have proposed 83 kcal for D($C_6H_5CH_2$- H).

The fact that benzyl radicals are stabilized by resonance and eventually dimerize to form dibenzyl, led Szwarc to develop the "toluene carrier technique", which was used in this investigation.

The use of toluene as a carrier gas simplified the kinetics of the decomposition process. In principle, the radicals formed in the initial dissociation process

$$R_1R_2 \longrightarrow R_1 + R_2$$

abstract hydrogen atoms rapidly, giving stable molecules R_1 H and R_2 H. The benzyl radicals dimerize to give dibenzyl, and both the possible back-reaction and/or chain process are prevented. The rate of the initial decomposition may be measured by the rate of the formation of R_1 H, of R_2 H, or of dibenzyl.

The toluene carrier technique has the following limitations:

(1) The bond being broken in the molecule under investigation must be considerably weaker than the C-H bond in toluene, preferably with a bond dissociation energy 10 kcal lower than $D(C_6H_5CH_2-H)$.

(2) The radicals or atoms produced by the rupture of the parent molecule should be able to abstract a hydrogen atom from toluene very rapidly.

Although the universality of the toluene carrier technique has been questioned by some workers (32, 34), to date it is still considered as a suitable method for the determination of bond dissociation energies. The results obtained by the toluene carrier method are in good agreement with those obtained by other methods, which strongly supports the reliability of this method. The method has been applied successfully to the pyrolysis of a large number of compounds, for example, ethyl benzene (35), benzyl bromide (36), benzylamine (37), allyl bromide (38), substituted benzyl bromides (39), and other organic bromides and chlorides (33), 1-butene (40), to the study of organic halides (33), and of some sulphur compounds (41, 42).

Thermodynamics of Organic Sulphur Compounds:

In the past two decades, rapid progress has been made in the study of organic sulphur compounds. An avalanche of research papers by chemists, biochemists, pharmacologists, bacteriologists and innumerable industrial scientists clearly demonstrates the ever increasing importance of organic sulphur chemistry in many disciplines.

Relatively few thermodynamic studies of organic sulphur compounds were made before 1949 (43). This may be due to the fact that physical chemists, who do most thermodynamic research, found some of the properties of sulphur compounds too unpleasant to allow such compounds in calorimetric laboratories. Another reason was that the study of sulphur compounds posed difficult problems that had to be solved before much progress could be made.

One of the difficulties has been the formation of both sulphur dioxide and sulphur trioxide when a sulphur compound is burned in an atmosphere of pure oxygen. The composition of this mixture is variable and may change slowly during the after-period of the combustion experiment. Another difficulty has been that the sulphur trioxide produced by the combustion reaction dissolves in the bomb liquid to form sulfuric acid, and, if precautions are not taken, the concentration of the acid will not be identical in different parts of the bomb. The heat of dilution of sulfuric acid is large and is not a linear function of concentration. Variation in the concentration of the acid between different parts of the bomb may cause significant errors.

Following recent progress thermodynamicists have turned their attention to sulphur compounds and have solved many of the early problems.

With the development of the moving-bomb calorimetric method, the following advances have been achieved (44):

(a) the final bomb solution is sufficiently homogeneous;

(b) conditions may be adjusted so that the combustion process converts all sulphur to the +6 valence state, which can be determined by available analytical methods;

(c) by the dilution used in the moving-bomb methods, thermochemical uncertainties caused by the presence of nitrogen oxides and acids in concentrated sulfuric acids are eliminated; and

(d) the increased dilution also effectively eliminates nitrogen oxides from the gas phase.

Many important phenomena of rubber, petroleum and protein chemistry involve the formation and rupture of the sulphur bond. The dissociation energy of any bond involving sulphur may be expressed in the form

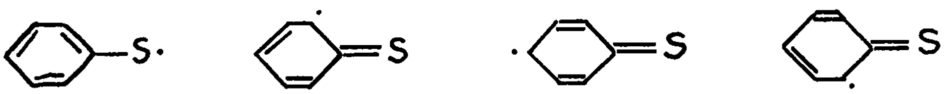
$$D(R_1 - SR) = \Delta H_f(R_1)g + \Delta H_f(SR)g - \Delta H_f(R_1\ SR)g$$

where ΔH_f terms are the heats of formation of R_1, SR, and R_1 SR. Therefore, a knowledge of the relevant bond dissociation energies can be used to predict the heats of combustion of sulphur compounds, and help to interpret thermodynamically the phenomena observed in rubber, petroleum and protein chemistry. Unfortunately, very few reliable dissociation energies involving the sulphur bond have been measured directly and precisely. Fundamental quantities such as the heat of formation of the sulphur atom and the dissociation energies of the bonds in H_2S are still uncertain (18).

The dissociation energies of the C-S bond in mercaptans and sulphides have been determined by Sehon and others (45, 46, 47) with the help of the toluene carrier technique. They obtained 51 kcal for $D(C_6H_5CH_2 — SCH_3)$, 53 kcal for $D(C_6H_5CH_2—SH)$ and 60 kcal for $D(C_6H_5S—CH_3)$. The reaction mechanisms of methyl and ethyl mercaptans are kinetically complex, and the suggested derived values for the dissociation energies, 67 and 63.5 kcal respectively, are open to considerable doubt. They are however in rough agreement with the electron impact results of 74.2 and 73.4 kcal, respectively (19).

The Present Investigation:

The phenylsulphide radical may resonate among canonical structures similar to those of the benzyl radical.



A preliminary investigation by Back and Sehon (47) showed that it is stabilized by resonance of about 15 kcal. If this is the case, the weakest bond in the phenylmercaptoacetic acid will be the ($C_6H_5S — CH_2COOH$) bond. The phenyl sulphide radical was found to be able to abstract hydrogen atoms rapidly from toluene (47). If the CH_2COOH radical does not react with the parent molecules, the rate of decomposition may be determined by the rate of formation of mercaptan. With the usual assumption that the recombination process involves no activation energy, the activation energy of the dissociation process may be identified as the D(C - S).

The present investigation, which describes the thermal decomposition of phenylmercaptoacetic acid, was undertaken with a view to measuring the C-S bond dissociation energy in this compound. Another purpose of this investigation was to gain some information about the fate of the CH_2COOH radical, which has so far not been discussed in the literature.

EXPERIMENTAL

Materials

Phenylmercaptoacetic acid, melting point 63°C, was obtained from Evans Chemetics, Inc., and was recrystallized three times using benzene and petroleum ether (boiling point range 60°C-70°C) as solvent-pair. The purity of the sample, as determined by titration against standard sodium hydroxide, was 99.9%. The toluene was generously supplied by the Gulf Petroleum Company, Pittsburgh, Pa. It was stirred for twenty hours with calcium chloride and distilled through a column. The fraction boiling at 110.5°C was collected and used in all experiments in this investigation.

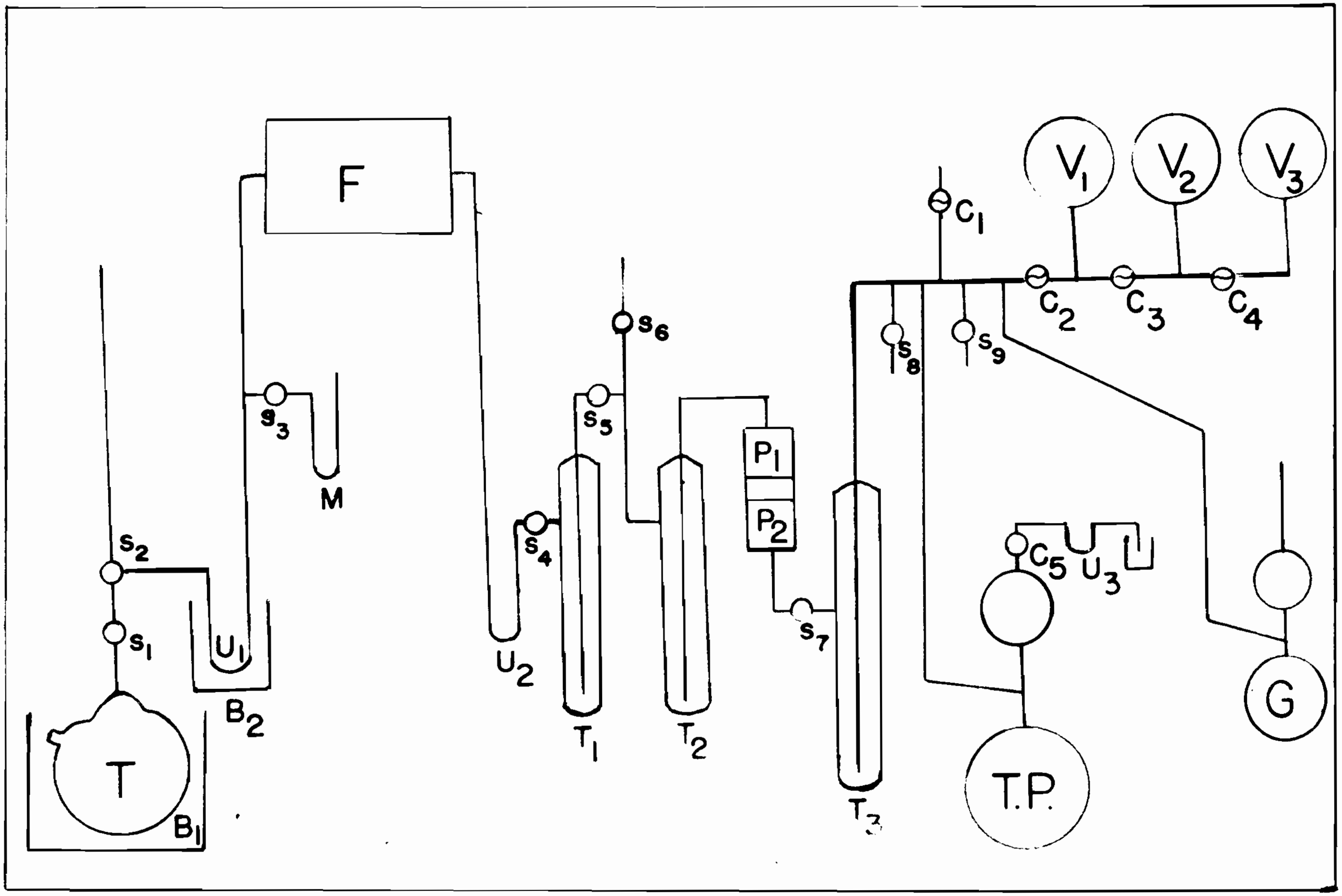
Apparatus

The thermal decomposition of phenyl mercaptoacetic acid was performed in a high vacuum flow system represented diagrammatically in Fig. 1. The toluene was introduced from a toluene bottle, T, from where it passed through the sample to the reaction vessel. The toluene bottle consisted of a 150 ml round bottom flask, fitted with a side arm provided with a ground joint cap. In the neck of the flask was a capillary type stopcock, S_1. The toluene bottle was connected to a second stopcock, S_2, by a ground joint to the rest of the system. During each experiment, the flask was surrounded by a water bath, B_1. The bath could be maintained at any desired temperature by the use of a heater, and controlled by a Fisher Energy Regulator.

A known weight of sample was introduced, in the form

Figure 1

Apparatus


F
V_1
V_2
V_3
C_1
C_2
C_3
C_4
C_5
s_1
s_2
s_3
s_4
s_5
s_6
s_7
s_8
s_9
M
U_1
U_2
U_3
B_1
B_2
T
T_1
T_2
T_3
P_1
P_2
T.P.
G

of pellets, into a U-tube, U_1. This method of introducing the sample proved to be more convenient and accurate, and avoided errors due to handling losses of the solid powder. One arm of the U-tube was provided with a side arm, which was connected to the toluene reservoir with stopcock S_2, and the other arm led to the furnace, F. Details of this section of the apparatus are shown in Fig. 2. During an experiment, the U-tube was heated by a removable oil bath, B_2. The temperature of which was maintained constant using a Fisher thermostatically controlled Autemp heater.

The tube leading to the furnace was heated electrically with Nichrome wire (one ohm per foot). It was kept at a high enough temperature to ensure that no condensation of the sample occurred. A small manometer, M, made of pyrex glass tubing (12 mm i.d.), was connected to this section of the apparatus in order to measure the pressure during an experiment. A cathetometer, giving an accurate reading up to ± 0.01 mm, was used to read the pressure. The manometer was connected to the apparatus by a stopcock, S_3. This stopcock allowed the manometer to be kept under vacuum when no experiments were being done and, as a consequence, the surface of the mercury remained clear for a long period.

The silica reaction vessel, shown in Fig. 3, was connected to the rest of the apparatus with silica-pyrex graded seals. The temperature along the length of the reaction vessel was measured by a chromel-alumel thermocouple placed in the central thermocouple well of the reaction vessel. The voltage was

Figure 2

Section of apparatus for introducing pellets of acid (U_1)

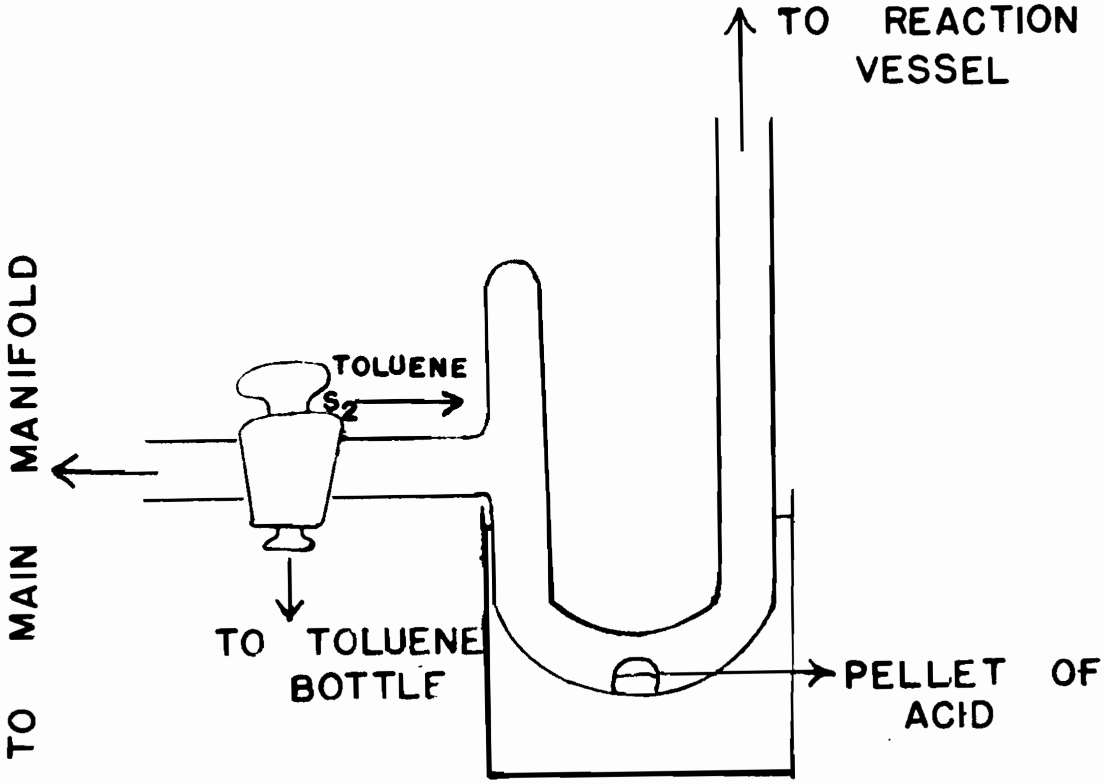
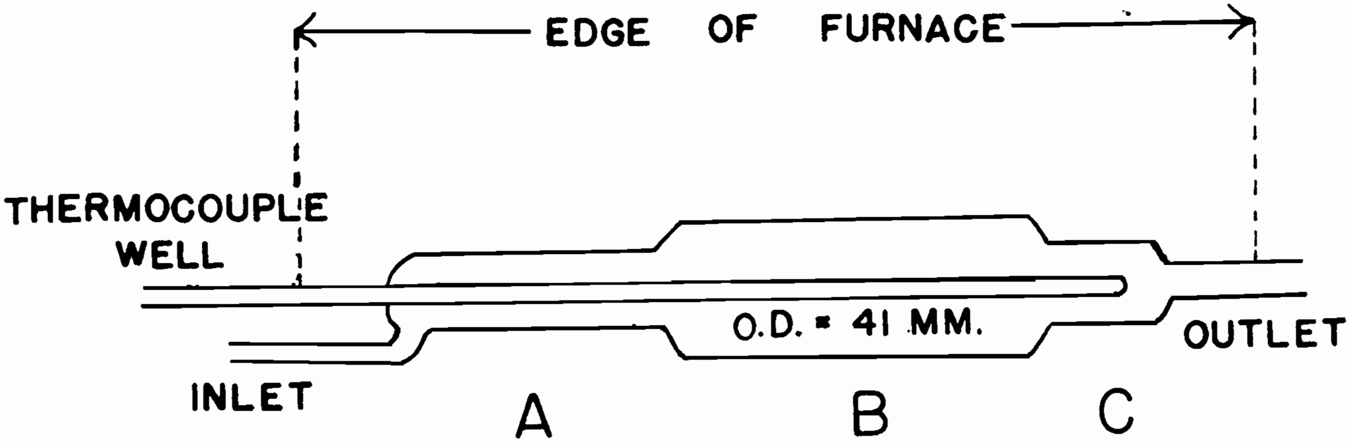

TO REACTION VESSEL
TO MAIN MANIFOLD
TOLUENE
S_2
TO TOLUENE BOTTLE
PELLET OF ACID

Figure 3

Reaction vessel



	A	B	C
VOLUME CC.	69·6	211·1	23·6
LENGTH CM.	24·7	21·7	7·0

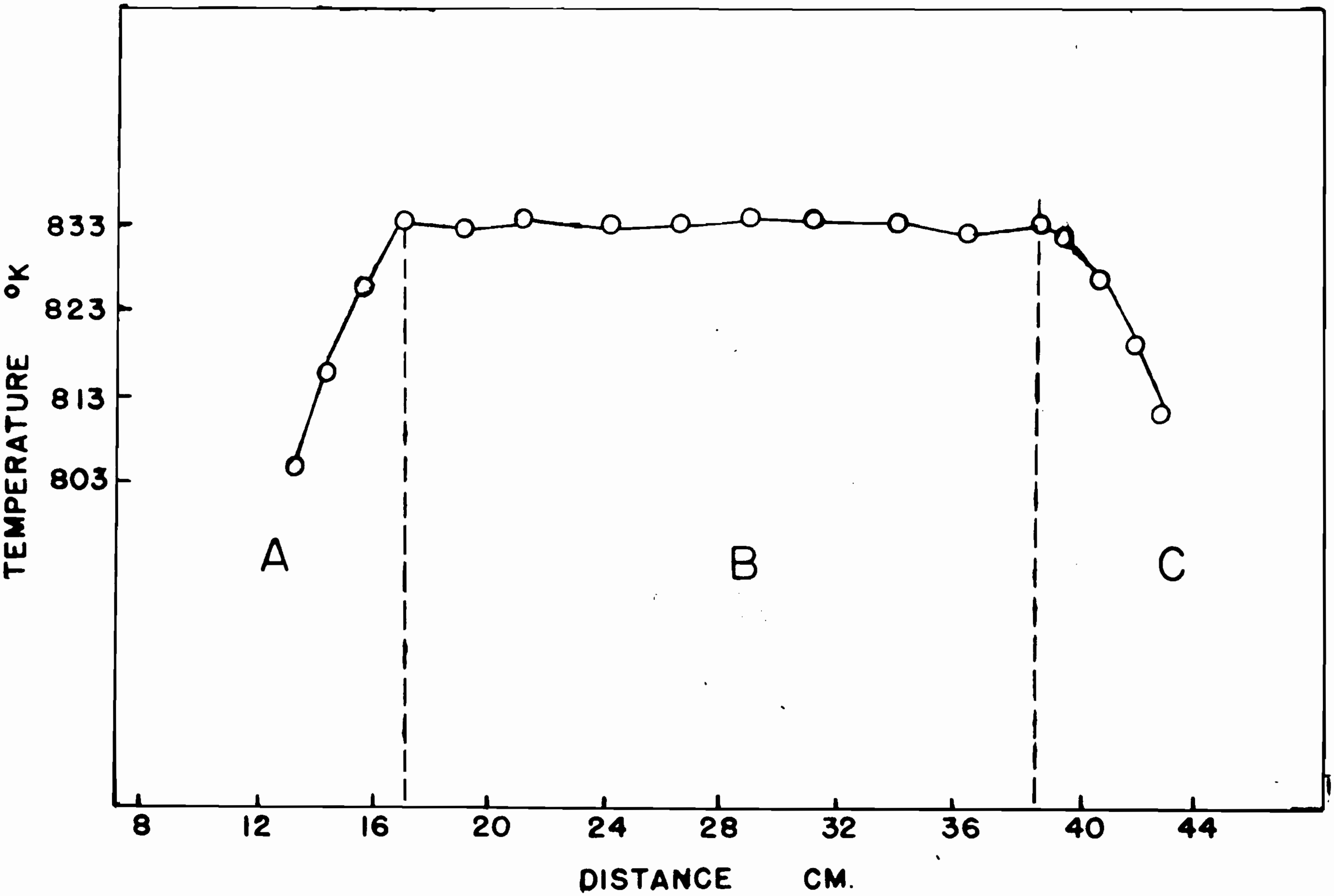
measured by a Rubicon potentiometer with a light spot galvanometer. The cold junction of this thermocouple was immersed in a Dewar flask containing an ice-water mixture.

Section B of the reaction vessel was considered to be the effective reaction volume. The temperature gradient over this section was less than 2°C but fell sharply across sections A and C, (see Fig. 4). The quartz reaction vessel was wrapped with asbestos. This assembly was placed within an inconel tube, concentric with the alundum core of the furnace, which tended to reduce the temperature gradient within the reaction vessel. The ends of the furnace were packed with asbestos fibre. The furnace was heated electrically by Nichrome Wire, which was wound around the alundum core. The wire was divided into five sections to allow for adjustment of the temperature gradient along the reaction vessel. The temperature of the furnace was regulated by a Thermo Electric regulator which maintained the temperature within ± 2°C. A chromel-alumel thermocouple was used as the temperature sensing element for this thermoregulator and was placed in the asbestos insulation layer.

The outlet of the tube from the furnace was also heated with Nichrome wire. It contained a length of capillary tubing which controlled the flow rate and a series of three traps was connected to the outlet of the tube. The first trap, U_2, was a U-tube made of 14 mm O.D. tubing, while the others, T_1 and T_2, were of the conventional removable type ground joint. During experiments, the U-trap was surrounded by brine (-5°C); the second and third traps were surrounded with dry ice-acetone (-78°C)

Figure 4

Temperature profile along the reaction vessel


TEMPERATURE °K
833
823
813
803
A
B
C
8
12
16
20
24
28
32
36
40
44
DISTANCE CM.

and liquid air (-188°C), respectively.

Two mercury diffusion pumps, P_1 and P_2, were connected in series to the third trap through a stopcock, S_7. The non-condensable gases were pumped by these two pumps through a liquid air trap, T_3, into three big bulbs, V_1, V_2 and V_3, of calibrated volume. The bulbs were connected to each other by a mercury cutoff, C. A McLeod gauge, G, and a Toepler pump, T.P., were also connected to this section. The Toepler pump led to a small gas burette, which was in its turn connected through a mercury cutoff, C_5, to a small U-tube, U_3, and to a tube containing copper oxide. This copper oxide tube was heated electrically to about 350°C during the combustion period by a glass tube wrapped with asbestos paper and wound with Nichrome wire.

Gas Chromatography Apparatus:

The apparatus for gas-liquid chromatography was essentially similar to that described by Callear and Cvetanovic (48). The power input was regulated with a Sorenson a.c. voltage regulator, model 500S. The d.c. low power regulator was kindly supplied by the Applied Chemistry Division of the National Research Council of Canada and was a homemade model providing a current at 6 volts with a noise less than one millivolt. A Gow-Mac thermal conductivity cell model TR 11 B with tungsten filaments was used as a detector. The resistance of this cell was adjusted with a 1.075 ohm Muirhead variable resistor type A-2-A. The off-balance signal was fed through an amplifier to a pen Speedomax Recorder Type G with full scale sensitivity of 50 millivolts. The amplifier used in this work was the C.C.

Keithley micro-volt-ammeter model 150A with full scale sensitivities of ± 1 microvolt and ± 1 millimicroampere (with a power sensitivity greater than 4×10^{-19} watt).

Helium was used as the carrier gas. For the analysis of the contents in the liquid air trap, a column made of pyrex glass tubing (1/4" i.d.) filled with 10 g of dinonyl phthalate on 24 g of celite 505 was used.

Procedure and Analysis:

The phenylmercaptoacetic acid sample (between 0.04 g to 0.2 g) was weighed and introduced into the inlet of the U-tube, U_1 (see Fig. 1) which was subsequently sealed. The reaction system was evacuated to 10^{-5} mm pressure* with the help of a (Edward Speedivac I M 2) mercury diffusion pump. The two mercury diffusion pumps, P_1 and P_2, were also operated at their full capacities. The toluene flask was weighed and attached, through a B29 taper joint, to stopcock S_2. It was degassed by successively freezing and melting until the final measured pressure was about 10^{-5} mm. After degassing, the water bath was adjusted to the temperature that would give the desired vapour pressure of toluene. The water bath was then placed around the flask.

Three Dewar flasks which contained brine (-5°C), dry ice-acetone (-78°C), and liquid air (-188°C) were placed around traps U_2, T_1 and T_2, respectively. The temperature of the

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* The phenylmercaptoacetic acid sample does not sublime at room temperature when the reaction system is evacuated to 10^{-5} mm.

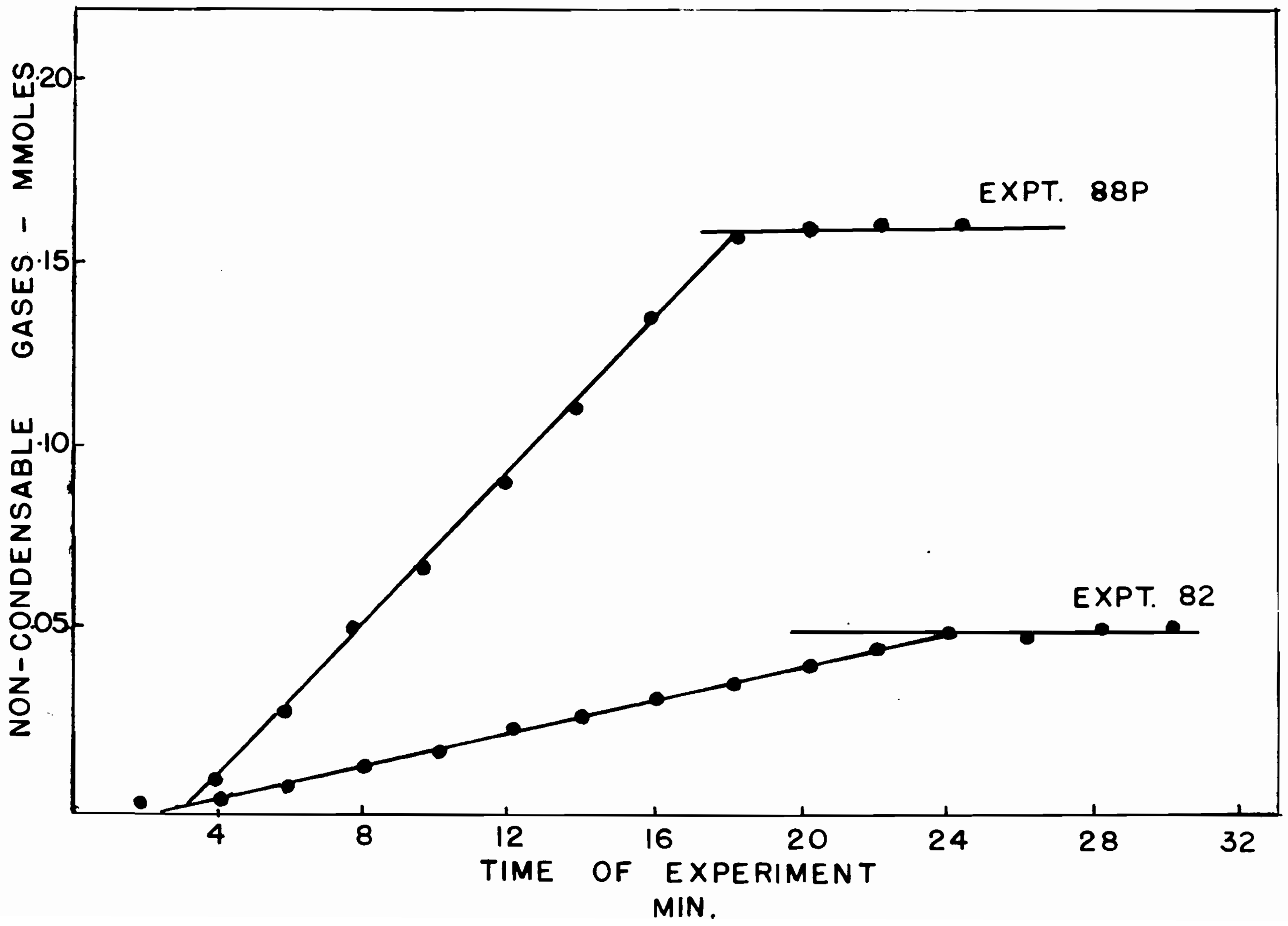
reaction vessel was recorded. The stopcock, S_1, was opened. A stop-watch was started simultaneously. The pressure of the collection system was read by the McLeod gauge, at two-minute intervals.

After three minutes, the oil bath was placed around the U-tube containing the pellet of acid. The pressure of the collection system was again recorded at two-minute intervals. The total pressure of the toluene and the sample was measured with the manometer, M, (with a cathetometer) and the temperature of the reaction vessel was recorded at five-minute intervals throughout an experiment. When all the acid had passed through the furnace, no further significant increase in the pressure of the non-condensable gases in the collection system could be detected. The toluene was allowed to flow for five minutes longer in order to estimate the amount of non-condensable gases produced from the decomposition of toluene. In most experiments the total time for the toluene to flow was about 20 minutes. The amount of non-condensable gases from the decomposition of toluene was found to be very small, less than 5% of the total non-condensable gases. Some typical curves showing the rate of accumulation of non-condensable gases in the collection system are shown in Figure 5.

The stopcock of the toluene bottle, S_1, was closed. The stopwatch was stopped simultaneously. The two mercury diffusion pumps, P_1 and P_2, were continued in operation for five minutes longer to assure complete removal of all materials from the reaction vessel. Stopcock S_7 was then closed, and the

Figure 5

Accumulation of non-condensable gases during two typical experiments



NON-CONDENSABLE GASES - MMOLES
·20
·15
·10
·05
EXPT. 88P
EXPT. 82
4
8
12
16
20
24
28
32
TIME OF EXPERIMENT
MIN.

pressure of the collection system was recorded. The toluene bottle was weighed after the experiment.

The toluene pressure was varied from 7 to 18 mm by changing the temperature of the water bath from 10°C to 35°C. The partial pressure of acid was varied from 0.08 mm to 0.44 mm by varying the oil bath surrounding the acid pellet between 138°C and 165°C. The contact time of the gas in the reaction vessel varied from about 0.2 seconds to 1.4 seconds.

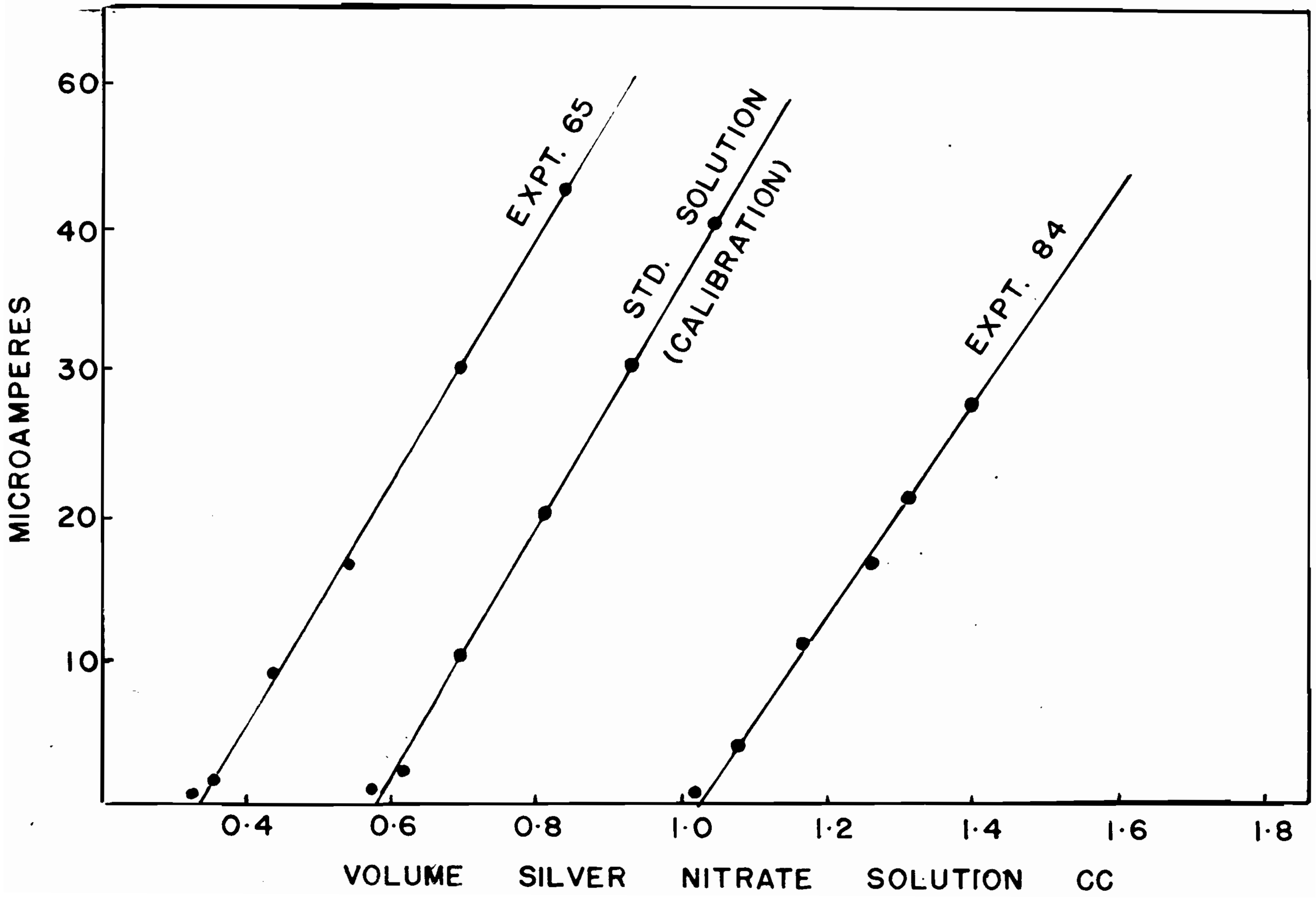
The compounds condensed in the U-trap consisted primarily of dibenzyl and the undecomposed phenylmercaptoacetic acid. The U-trap was weighed before and after an experiment. The substances in the U-trap were dissolved in ethyl alcohol, then diluted with water and titrated with 0.050 N NaOH, using phenolphthalein as indicator. The number of equivalents of NaOH used was considered to be equal to the amount of unreacted acid and the amount of dibenzyl was calculated by deducting from the weight of the contents of the U-trap the weight corresponding to the unreacted acid. The validity of this procedure was established by "controlled" experiments, performed with the furnace temperature at 200°C, where no decomposition could be detected. It was thus shown that the acid could be completely trapped at -5°C in the U-trap. To identify dibenzyl, after titration with NaOH, the contents of the U-trap formed over several experiments, were collected. This product was extracted with ether and recrystallized several times. The melting point of a mixture of the product with a pure sample of dibenzyl was 52°C.

The dry ice-acetone trap was found to contain toluene, phenylmercaptan, acetic acid and phenyl methyl sulphide. A portion of the products in the dry ice-acetone trap was extracted with 0.050 N NaOH. It was then back titrated with 0.050 N HCl. Another portion was titrated for mercaptan amperometrically with 0.100 N silver nitrate solution using a rotating platinum electrode and a microammeter (49). This procedure was calibrated with standard phenyl mercaptan solutions. Some of the titration curves are shown in Figure 6. This method enabled determination of amounts of the order of 5 mg of mercaptan with an error of only 0.2%. Phenyl methyl sulphide has been found to give deep red color with chloranil, and an orange yellow with quinone (50). In a few experiments, the contents of the dry ice-acetone trap were tested for the presence of phenyl methyl sulphide with chloranil and quinone. Positive results were obtained. Due to the presence of a large excess of toluene, a quantitative determination of phenyl methyl sulphide was not successful.

To determine the amount of products trapped in the liquid air trap, the calibrated section was evacuated to 10^{-5} mm, and the liquid air trap was replaced by a dry ice-acetone trap. The gas released was expanded to the calibrated volume, and the pressure was determined with a McLeod gauge. The gas was analyzed by gas chromatography. A home made column containing 10 g of dinonyl phthalate (The British Drug Houses Ltd) on 24 g of celite 505 (Johns-Manville) was used for the gas chromatographic analysis. Only one major peak was observed; its retention

Figure 6

Titration curves for mercaptans


MICROAMPERES
60
40
30
20
10
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
VOLUME SILVER NITRATE SOLUTION CC
EXPT. 65
STD. SOLUTION
(CALIBRATION)
EXPT. 84

was three minutes, which was identical to that of pure CO_2. Three very small peaks, which were negligible compared to the CO_2 peak, came after the CO_2 peak.

The contents of the liquid air trap were tested painstakingly for the presence of ketene. Two methods were employed: (i) The products in the liquid air trap were expanded into a tube containing degassed water which was kept at -188°C (51). After 12 hours at room temperature with occasional shaking, the solution of acetic acid thus formed was boiled gently to remove carbon dioxide, and thereafter titrated with sodium hydroxide solution. (ii) The contents of the liquid air trap were subjected to infrared analysis using a Perkin-Elmer (model 21) double beam infrared spectrophotometer. A peak was observed at 2150 cm^{-1}, which was believed to be due to $-C = C = O$ asymetric stretching vibration (52).

For the purpose of standardizing the method of analysis for ketene, ketene was prepared by the pyrolysis of Fisher's reagent grade acetone in a standard ketene apparatus (53). The ketene produced was passed through three traps at -40°C, -78°C and -188°C, respectively. The condensate at -188°C was mostly ketene. It was degassed several times and stored as a solid under liquid air to prevent polymerization. The spectrum of the ketene so prepared corresponded to the spectrum defined in relevant publications (54, 55). However, a peak at 1750 cm^{-1} and a peak at 950 cm^{-1} were also observed. These two peaks were believed to be due to the presence of small amounts of acetone and ethylene (52). The spectrum of ketene is shown in Figures 7 and 8.

Figure 7

Infra-red spectrum of ketene in the region $3600\ cm^{-1}$ - $1550\ cm^{-1}$

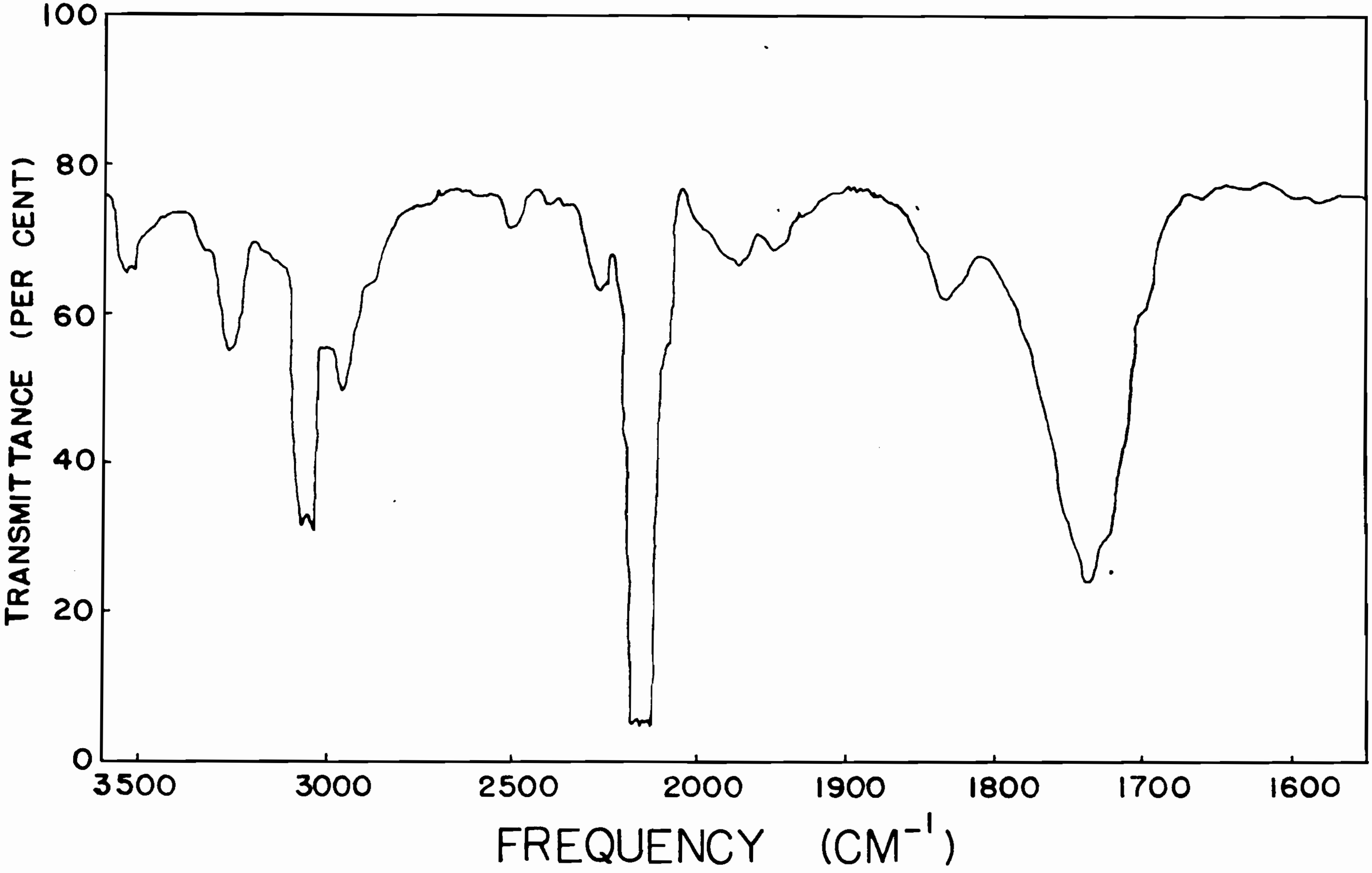
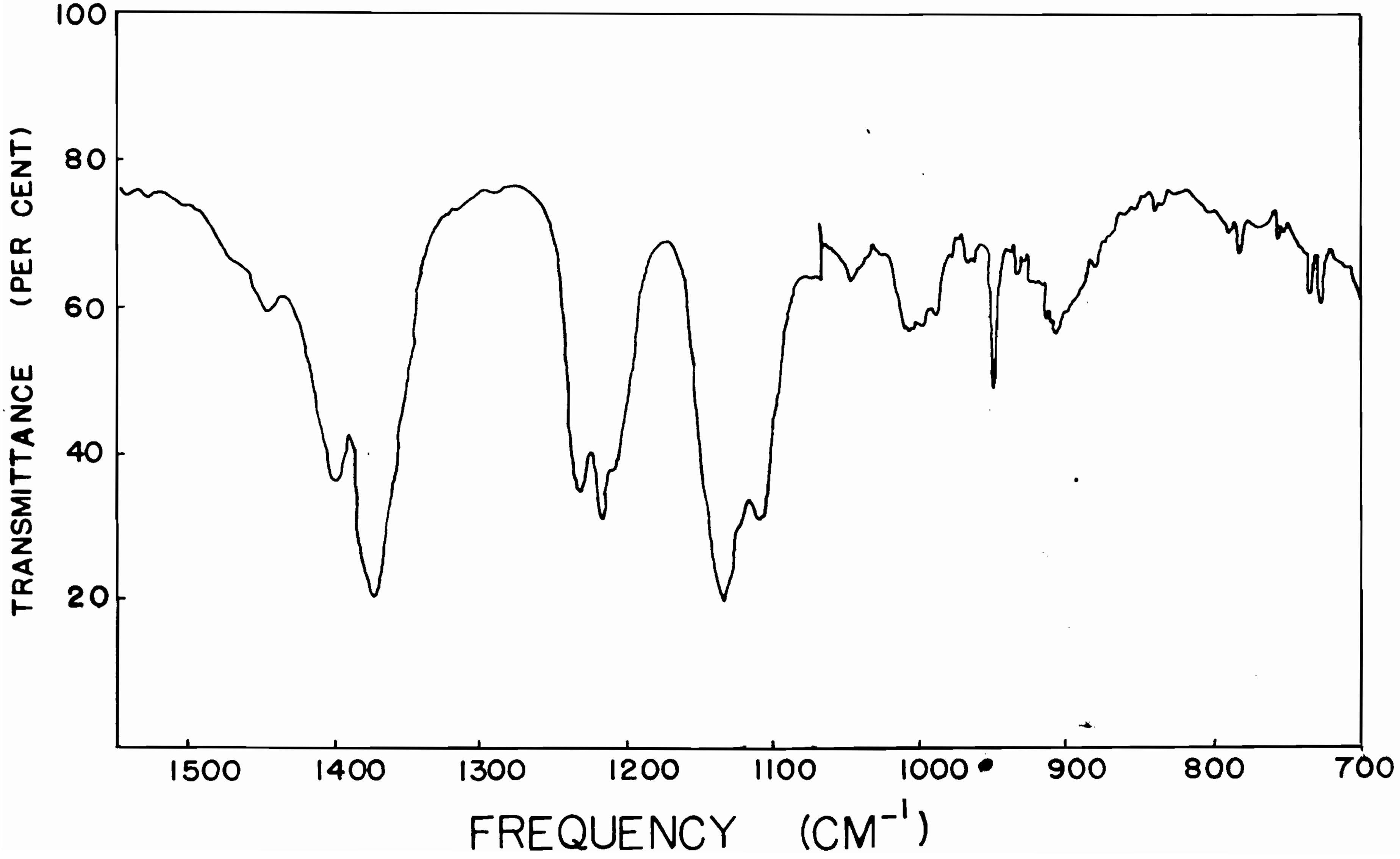

100
80
60
40
20
0
TRANSMITTANCE (PER CENT)
3500
3000
2500
2000
1900
1800
1700
1600
FREQUENCY (CM^{-1})

Figure 8

Infra-red spectrum of ketene in the region

1550 cm^{-1} - 700 cm^{-1}


100
80
60
40
20
TRANSMITTANCE (PER CENT)
1500
1400
1300
1200
1100
1000
900
800
700
FREQUENCY (CM^{-1})

The pressure of non-condensable gases in the calibrated section was measured with a McLeod gauge. A sample of the non-condensable gases was removed by the Toepler pump into the small gas burette. The initial pressure of the sample, P_1, was measured and it was admitted to the combustion furnace through the mercury cut-off. The U-trap connected to the combustion furnace was surrounded with liquid air. The furnace was maintained at about 350°C. About three hours were allowed for complete combustion. The combustion process involved the oxidation of hydrogen to water and carbon monoxide to carbon dioxide. The unburnt gas, methane, was returned to the gas burette and the pressure, P_2, was measured. The liquid air surrounding the U-trap was then replaced by a dry ice-acetone bath. The carbon dioxide released was also returned to the gas burette. The increase in pressure over the previous, $P_3 - P_2$, represented the amount of carbon monoxide in the sample, while the difference between this pressure and the initial pressure, $P_1 - P_3$, was taken as a measure of the hydrogen. The composition of the non-condensable gases was then calculated from these measurements. The analysis was checked with known mixtures of methane, hydrogen and carbon monoxide.

The effect of the surface of the reaction vessel on the rate of the reaction was examined by using a packed reaction vessel. The dimensions of the packed reaction vessel were identical to those of the unpacked one; the central section of the former vessel (section B in Fig. 3) was packed with silica wool supplied by Micro Chemical Specialties, Berkeley, California. The silica fibres had an average diameter of 3×10^{-3} cm and their average length was 15 cm. The surface area per fibre was calculated as about 0.15 cm^2, the weight per fibre was about 3×10^{-4} gm, and about 12 grams of silica wool were used for packing the reaction vessel. The total surface area of the silica wool was thus about 6000 cm^2, as compared to an area of about 230 cm^2 for the surface of the reaction vessel. The surface/volume ratio of the unpacked vessel was thus about 1.1 cm^{-1}, while that of the packed vessel was about 29.5 cm^{-1}. The surface/volume ratio was therefore increased by a factor of about 27 in the packed reaction vessel.

<u>Sample Calculations</u> (Calculations for Experiment 84)

1. Moles of phenylmercaptoacetic acid = 0.591×10^{-3}

   Time of experiment = 26.5 min.

   Moles of toluene flowing in 26.5 min. = 74.4×10^{-3}

   Time for phenylmercaptoacetic acid to pass through furnace

   = 18.6 min.

   Moles of toluene flowing during time of reaction =

$$\frac{18.6}{26.5} \times 74.4 \times 10^{-3} = 52.3 \times 10^{-3}$$

$$\frac{\text{Moles of toluene}}{\text{Moles of acid}} = \frac{52.3 \times 10^{-3}}{0.591 \times 10^{-3}} = 88.6$$

   Total pressure = 15.69 mm Hg

$$\text{Partial pressure of toluene} = 15.69 \times \frac{52.3 \times 10^{-3}}{(52.3 + 0.591) \times 10^{-3}}$$

$$= 15.51 \text{ mm Hg}$$

   Partial pressure of acid = 15.69 - 15.51 = 0.18 mm Hg

2. Volume of gas flowing through per second = $\frac{n\ R\ T}{P}$

where n = Total number of mmoles of gas flowing through per second

T = Temperature of the reaction vessel, ^{o}K

P = Total pressure, atmosphere

$$n = \frac{52.3 + 0.59}{18.6 \times 60} = \frac{52.9}{1116} = 0.0474 \text{ mmoles/sec.}$$

Volume of gas flowing through per second

$$= \frac{(0.0474) \times (0.08205) \times (833) \times (760)}{15.69}$$

= 157 ml/sec.

The time of contact in seconds

$$= \frac{\text{Volume of reaction vessel}}{\text{Volume of gases flowing through/sec.}}$$

$$= \frac{211.1 \text{ ml}}{157 \text{ ml/sec.}} = 1.34 \text{ sec.}$$

3. Acid recovered = 0.095 mmoles

= 0.01598 gms.

4. Weight of contents of -5^{o}C trap = 0.05325 gms.

Weight acid = 0.01598 gms.

Weight dibenzyl = 0.03727 gms.

mmoles dibenzyl = 0.205

5. Total yield of non-condensable gases = 0.0759 mmoles

Combustion: P_1 = 10.7 cm.

P_2 = 2.27 cm.

P_3 = 9.44 cm.

$$\% \ CH_4 = \frac{P_2}{P_1} = \frac{2.27}{10.7} = 21.2\%$$

$$\% CO = \frac{P_3 - P_2}{P_1} = \frac{7.17}{10.7} = 67.1\%$$

$$\% \, H_2 = \frac{P_1 - P_3}{P_1} = \frac{1.26}{10.7} = 11.7\%$$

6. Total CO_2 = 0.278 mmoles

Total acidity in the dry ice-acetone trap = 0.487 mmoles

C_6H_5SH = 0.287 mmoles

Acetic acid = 0.200 mmoles

7. $$k_o = \frac{1}{t} \ln \frac{a}{a - x}$$

$$= \frac{1}{1.34} (2.303) \log \frac{0.591}{0.095}$$

$$= 1.36 \text{ sec}^{-1}$$

8. $$k_1 = \frac{(\phi SH)_t}{(A)} k_o \left[1 - \exp(-k_o t)\right]^{-1}$$

$(\phi SH)_t$ = 0.287

(A) = 0.591

k_o = 1.36

$\exp(-k_o t)$ = 0.1613

$1 - \exp(-k_o t)$ = 0.8387

$$k_1 = \frac{0.287}{0.591} (1.36)(0.8387)^{-1}$$

$$= 0.789 \text{ sec}^{-1}$$

RESULTS AND DISCUSSION

Results:

The pyrolysis of phenylmercaptoacetic acid was studied in the temperature range 760°K to 833°K. The main products of the decomposition were (as shown in Table I) carbon dioxide, phenylmercaptan, acetic acid, dibenzyl, phenyl methyl sulphide and carbon monoxide. As mentioned previously, phenyl methyl sulphide was detected only qualitatively. Small quantities of CH_4, ketene, and traces of hydrogen were also found.

The contents of the U-trap (-5°C) when warmed to room temperature, in the presence of air, turned slightly yellow. An infra-red analysis of the contents of this trap revealed the presence of undecomposed acid and dibenzyl only. It is, therefore, concluded that the substance responsible for the yellow color was produced in negligible amounts.

The presence of ketene was demonstrated by the two methods described in the previous section for its analysis and corresponded to about 2% of the contents of the liquid air trap.

The amount of the total non-condensable gases varied between 23% to 54% of the phenylmercaptan formed, and it increased up to 90% in the experiments performed in the packed reaction vessel. Carbon monoxide constituted about 60% to 70% of the total non-condensable gases and the remainder consisted of methane. At the highest temperatures used, a small amount of hydrogen was also formed. The amount of hydrogen was equal to, within experimental accuracy, the hydrogen from the decomposition

TABLE 1

Products of the Decomposition of Phenylmercaptoacetic Acid

Expt. No.	Temp. (^oK)	Total Press. (mm)	PT/PA	Contact time (sec.)	Acid (mmole) initial	Acid (mmole) recovered	Acid (mmole) de-composed	C_6H_5SH (mmole)	Acetic Acid (mmole)	Dibenzyl (mmole)	CO_2 (mmole)	Non-Condensable Gases Total (mmole)	Non-Condensable Gases $\%H_2$	Non-Condensable Gases $\%CH_4$	Non-Condensable Gases %CO
75	760	12.01	37.7	0.44	1.065	.894	.171	.018	.015	–	.067	0.005	–	–	–
77	764	12.68	74.9	0.43	.813	.768	.045	.020	.010	–	.026	0.007	–	–	–
74	767	13.36	49.8	0.46	.888	.772	.116	.013	.007	–	.150	0.006	–	–	–
66	779	10.92	56.3	0.44	.926	.823	.103	.027	.005	.011	.065	0.025	–	–	–
60	783	18.08	157.0	0.55	.540	.483	.057	.012	.010	–	–	0.002	–	–	–
63	783	15.50	94.3	0.61	.859	.751	.108	.032	.020	–	.075	0.009	–	–	–
64	783	15.07	90.0	0.65	1.040	.899	.141	.038	.016	.014	.071	0.014	–	–	–
65	783	11.42	47.5	0.61	.852	.744	.108	.034	.013	.012	.068	0.015	–	27.8	72.2
67	793	10.04	54.0	0.46	.944	.784	.160	.052	.030	.035	.103	0.018	–	28.6	71.4
68	793	15.57	58.3	0.37	.982	.839	.143	.045	.030	.029	.088	0.017	–	28.6	71.4
87	795	11.94	53.6	1.11	.605	.369	.236	.082	.035	.075	.150	0.045	3.7	22.5	73.8
73	804	10.97	88.1	0.45	.296	.229	.067	.029	.010	.032	.040	0.013	4.7	13.3	82.0
69	813	9.80	59.8	0.47	.666	.475	.191	.081	.050	.069	.124	0.027	4.2	20.5	75.3
70	813	17.50	108.5	0.33	.601	.440	.161	.058	.042	.058	.091	0.018	3.9	24.1	72.0
86	813	5.28	20.6	0.21	1.065	.916	.149	.067	.040	.026	.100	0.024	5.7	11.2	83.1
89P	813	11.07	53.8	1.17	.572	.193	.379	.154	.012	.137	.224	0.140	3.7	6.8	89.5
88P	815	12.04	58.8	1.04	.692	.218	.474	.184	.022	.133	.300	0.153	1.1	10.7	88.2
72	823	8.00	44.6	0.46	.285	.175	.110	.051	.025	.039	.068	0.021	10.1	23.5	66.4
80	828	7.86	17.0	0.48	.577	.304	.273	.104	.052	.095	.184	0.033	9.8	19.5	70.7

TABLE 1 (Continued)

Expt. No.	Temp. (°K)	Total Press. (mm)	PT/PA	Contact time (sec.)	Acid (mmole)			C_6H_5SH (mmole)	Acetic Acid (mmole)	Dibenzyl (mmole)	CO_2 (mmole)	Non-Condensable Gases			
					initial	recovered	decomposed					Total (mmole)	$\%H_2$	$\%CH_4$	%CO
79	829	9.20	134.0	0.41	.255	.141	.114	.055	.030	.047	.071	0.017	9.4	23.4	67.2
84	833	15.69	88.6	1.34	.591	.095	.496	.287	.200	.205	.278	0.076	11.7	21.2	67.1
85	833	5.90	56.0	0.21	.849	.615	.234	.086	.040	.057	.152	0.034	10.0	18.4	71.6
81	833	8.00	66.3	0.49	.353	.161	.192	.097	.060	.077	.133	0.024	10.2	20.0	69.8
91P	833	12.02	69.0	1.08	.309	.051	.258	.110	.005	.076	.156	0.095	1.0	10.8	88.2
82	835	15.06	235.0	0.38	.867	.452	.415	.216	.220	.160	.209	0.049	12.3	19.2	71.5

\- Indicates that products were not large enough to be measured.

The experiments marked P refer to those done in the packed reaction vessel.

of toluene. Carbon monoxide constituted about 60% to 70% of non-condensable gases in the unpacked reaction vessel. This percentage rose to about 90% in the experiments performed in the packed reaction vessel.

Discussion:

The results given in the previous section suggest that the thermal decomposition of phenylmercaptoacetic acid might occur primarily by two simultaneous processes: (1) the dissociation of the C - S bond resulting in the formation of the phenyl-sulphide and CH_2COOH radicals and (2) the molecular reaction yielding phenyl methyl sulphide and CO_2,

$$C_6H_5SCH_2COOH \xrightarrow{k_1} C_6H_5S + CH_2COOH \qquad (1)$$

$$C_6H_5SCH_2COOH \xrightarrow{k_2} C_6H_5SCH_3 + CO_2 \qquad (2)$$

and that reaction (2) is predominant. If each phenylsulphide radical abstracted a hydrogen atom from toluene, the sum of phenyl mercaptan and CO_2 would be expected to be equal to the total amount of phenylmercaptoacetic acid decomposed. Furthermore, if each of the CH_2COOH radicals reacted with toluene by abstracting a hydrogen atom, the ratio of phenylmercaptan to acetic acid would be unity.

$$C_6H_5S + C_6H_5CH_3 \longrightarrow C_6H_5SH + C_6H_5CH_2 \qquad (3)$$

$$CH_2COOH + C_6H_5CH_3 \longrightarrow CH_3COOH + C_6H_5CH_2 \qquad (4)$$

As shown in Table 1, the amount of acetic acid was always less than that of phenyl mercaptan and, therefore, it must be concluded that reaction (4) was not sufficiently rapid to remove all the CH_2COOH radicals.

From Table 2, it is evident that the ratio of ($C_6H_5SH + CO_2$) produced to the amount of acid decomposed varied from 95% to 120%. Some CO_2 may have been produced also by the decomposition of the CH_2COOH radicals formed in reaction (1) according to step (5).

$$CH_2COOH \longrightarrow CH_3 + CO_2 \qquad (5)$$

The methyl radical thus formed would be expected to abstract a H atom from toluene to yield methane,

$$CH_3 + C_6H_5CH_3 \longrightarrow CH_4 + C_6H_5CH_2 \qquad (6)$$

Hence the amount of CH_4 formed in the reaction (after correction for the small amount of methane formed from the decomposition of toluene) was assumed to be equal to the amount of CO_2 formed in reaction (5).

From a comparison of the data given in the last two columns of Table 3 it is obvious that the amount of CH_4 formed was rather small, and one can, therefore, conclude that reaction (5) occurred only to a negligible extent. Furthermore, one should expect the ratio of C_6H_5SH + (total CO_2 - CH_4^{*}) to the total phenylmercaptoacetic acid decomposed to be equal to unity. In effect, this is almost the case.

The phenylsulphide radicals may dimerize to give diphenyldisulphide, but this seems to be unlikely, because of the low concentration of the phenylsulphide radicals. The phenylsulphide radicals may recombine with benzyl radicals to

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CH_4^{*} = [Total CH_4] - [CH_4 from the decomposition of toluene]. (Assuming all the H_2 formed came from toluene, and each 1.5 moles of H_2 formed was accompanied by 1 mole of CH_4).

TABLE 2

C_6H_5SH + ($CO_{2(T)}$-CH_4^{*})/Acid Decomposed

Expt. No.	Temp. (°K)	C_6H_5SH (mmole)	Total CO_2 (mmole)	Acid decomposed (mmole)	$C_6H_5SH+CO_{2(T)}$ / Acid decomposed	C_6H_5SH+ ($CO_{2(T)}$-CH_4^{*}) / Acid decomposed
77	764	.020	.026	.045	1.02	.980
74	767	.015	.130	.116	1.25	1.250
66	779	.027	.065	.103	.92	.850
63	783	.032	.075	.108	.99	.973
64	783	.038	.071	.140	.78	.779
65	783	.034	.068	.100	.95	.905
67	793	.052	.103	.160	.97	.950
68	793	.045	.088	.140	.95	.93
87	795	.082	.150	.236	.983	.96
73	804	.029	.040	.067	1.03	.97
69	813	.081	.124	.190	1.08	1.03
70	813	.058	.091	.160	.93	.905
86	813	.067	.100	.149	1.12	1.08
89P	813	.154	.224	.379	.997	.955
88P	815	.184	.300	.474	1.02	.98
72	823	.051	.068	.110	1.08	1.025
80	828	.104	.184	.273	1.055	1.03
79	829	.055	.071	.114	1.10	1.08
84	833	.287	.278	.496	1.14	1.10
85	833	.086	.152	.234	1.20	1.17
81	833	.097	.133	.192	1.02	.996
91P	833	.110	.156	.258	1.03	.962
82	835	.216	.209	.415	1.025	.997

The experiments marked P refer to those done in the packed reaction vessel.

CH_4^{*} = [Total CH_4-CH_4 from the decomposition of toluene]. (Assuming all the H_2 formed came from toluene, and each 1.5 moles of H_2 formed were accompanied by 1 mole of CH_4).

give phenyl benzyl sulphide. If recombination reactions of the phenylsulphide radicals occurred, a deviation in the linearity of the Arrhenius plot of log k_1 (where k_1 represents the rate constant of reaction (1)) versus 1/T at high temperature should have been observed. As will be discussed later in the section dealing with the calculation of $D(C_6H_5S - CH_2COOH)$, no deviation from linearity of the Arrhenius plot was observed. It was, therefore, concluded that all of the phenylsulphide radicals were scavenged by the toluene. Thus, the rate of production of phenylmercaptan may be taken as a measure of the rate of decomposition of phenylmercaptoacetic acid to yield phenyl sulphide and CH_2COOH radicals.

Fate of the CH_2COOH radical:

The CH_2COOH radical may abstract a hydrogen atom from toluene to give acetic acid, or decompose to give either ketene and a hydroxyl radical, or carbon dioxide and a methyl radical;

$$CH_2COOH + C_6H_5CH_3 \longrightarrow CH_3COOH + C_6H_5CH_2 \qquad (4)$$

$$CH_2COOH \longrightarrow CH_2CO + OH \qquad (4')$$

$$CH_2COOH \longrightarrow CH_3 + CO_2 \qquad (5)$$

If all the CH_3 radicals abstracted a hydrogen atom from toluene, and assuming that all the benzyl radicals dimerized to give dibenzyl:

$$2\ C_6H_5CH_2 \longrightarrow (C_6H_5CH_2)_2 \qquad (7)$$

the following stoichiometry should have been observed:

$$(CH_3COOH) + (CH_2CO) + (CH_4) = (C_6H_5SH) = (\text{dibenzyl})$$

However, the data listed in Table 1 indicate that

$$(C_6H_5SH) > (\text{dibenzyl}) > (CH_3COOH) + (CH_4)$$

Since the amount of ketene was negligible it is reasonable to assume that some ketene was either decomposed or dimerized. This suggestion was supported by the existence of large amounts of CO in the reaction products. The ratio of dibenzyl to C_6H_5SH varied between 0.7:1 and 0.9:1 instead of being unity. Previous studies have shown that dibenzyl may not be trapped quantitatively in a U-trap at about -5°C from a stream of toluene, and recovery may be only 80% - 90% of the expected amount (41). It was, therefore, concluded that the amount of dibenzyl actually formed in this investigation may be considered to be equal to the amount of C_6H_5SH.

The existence of ketene as one of the products indicated the occurrence of reaction (4'). The possible reaction of ketene with water to form acetic acid leads to the question of the source of water. It has been suggested (56) that water may be produced by the reaction of OH radical with toluene,

$$OH + C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + H_2O \qquad (8)$$

Due to technical difficulties in the establishment of a water-free system, no attempt was made to detect the presence of water in this investigation, but it was believed that some water was produced. The acetic acid formed could thus be due to either reaction (4) or the reaction of ketene with water. If reaction (4) occurred, an increase in toluene pressure should increase the formation of acetic acid. This trend was indeed observed (Table 3).

The dimerization of the CH_2COOH radicals may also occur.

TABLE 3

Effect of Toluene Pressure on CH_3COOH/C_6H_5SH

Expt. No.	Temp. (^oK)	Toluene Press. (mm Hg)	CH_3COOH/C_6H_5SH
65	783	11.18	.500
60	783	17.97	.834
67	793	9.85	.577
68	793	15.33	.667
69	813	9.63	.617
70	813	17.34	.724
81	833	7.87	.620
82	835	15.00	1.020

$$2\ CH_2COOH \longrightarrow (CH_2COOH)_2 \qquad (9)$$

It has not been attempted to analyze for the presence of $(CH_2COOH)_2$, and since $(CH_2COOH)_2$ will also be titrated as an acid, it is rather difficult to draw any conclusion. However, due to the low concentration of the CH_2COOH radicals, reaction (4) is considered more likely than reaction (9).

Carbon monoxide constituted about 70% of the total non-condensable gases (Table 1). The amount of CO increased considerably in the packed reaction vessel. For example, at 833°K, in experiment #85, the CO formed was only about 25% of the ØSH formed; while in experiment 91_p , the ratio increased to 77%. In experiment 86 at 813°K, the ratio was about 28%, but in 89_p , the ratio increased to 82%. Thus it would appear that the formation of CO was due to some reaction of ketene on the wall of the reaction vessel.

Calculation of $D(C_6H_5S\text{-}CH_2COOH)$

If the rate of the overall decomposition were first-order with respect to phenylmercaptoacetic acid, the overall rate constant k_o could be calculated with the help of the following rate expression:

$$k_o = 1/t \ln (A/A-X) \qquad (a)$$

where t = time of contact in seconds, A = amount of phenylmercaptoacetic acid introduced and (A-X) = amount of phenylmercaptoacetic acid recovered in the trap U_2. Furthermore, if the two modes of decomposition

$$C_6H_5SCH_2COOH \xrightarrow{k_1} C_6H_5S + CH_2COOH \qquad (1)$$

$$C_6H_5SCH_2COOH \xrightarrow{k_2} C_6H_5SCH_3 + CO_2 \qquad (2)$$

postulated in the previous section were first-order reactions, and if reaction (3) were very fast by comparison with reaction (1) one could write the following rate expressions,

$$\frac{d(C_6H_5SH)}{dt} = k_1(A - X) \qquad (b)$$

$$\frac{d(C_6H_5SCH_3)}{dt} = \frac{d(CO_2)}{dt} = k_2(A - X) \qquad (c)$$

It is also obvious that

$$\frac{d(C_6H_5SH + CO_2)}{dt} = \frac{-d(A - X)}{dt} = (k_1 + k_2)(A - X)$$

$$= k_o(A - X) \qquad (d)$$

and that in consequence $k_o = k_1 + k_2$.

From equation (a) it follows that

$$(A - X) = A \exp(-k_o t)$$

Combining this expression with equation (b) leads to the relation

$$\frac{d(C_6H_5SH)}{dt} = k_1 \cdot A \exp(-k_o t)$$

from which k_1 is obtained by integration,

i.e. $$k_1 = \frac{(\text{ØSH})t}{(A)} k_o \left[1 - \exp(-k_o t)\right]^{-1} \qquad (e)$$

where $(\text{ØSH})_t$ is the amount of phenylmercaptan formed during time t. Similarly, k_2 may be obtained by the following expression

$$k_2 = \frac{(CO_2)t}{(A)} k_o \left[1 - \exp(-k_o t)\right]^{-1} \qquad (f)$$

where $(CO_2)_t$ represents the amount of carbon dioxide formed by reaction (2) in time t.

By varying the partial pressure of the acid by a factor of 2 to 5.5, the toluene pressure by a factor of 2, and the time of contact by a factor of 2 to 6.5, the overall rate constant k_0 and the rate constant k_1 for reaction (1) did not change significantly within the experimental accuracy. The results are shown in Tables 4, 5 and 6. Furthermore, the plot of log k_0 versus 1/T (see Figure 9) and log k_1 versus 1/T (see Figure 10) were linear. The applications of equations (a), (e) and (f) are, therefore, considered as justifiable. The values of k_0 and k_1 are shown in Table 7.

The effect of the surface on the overall rate of decomposition k_0 and on the rate of decomposition of reaction (1) is shown in Table 8. By increasing the surface to volume ratio by a factor of 27, the rate constants k_0 and k_1 were practically unaltered. It is, therefore, concluded that reaction (1) and the overall decomposition of phenylmercaptoacetic acid are homogeneous, first-order reactions.

The plots of log k_0 versus 1/T and log k_1 versus 1/T are shown in Figures 9 and 10, respectively. The overall activation energy, E_0, and the activation energy of reaction(1), E_1, were calculated as 46 kcal/mole and 59 kcal/mole, respectively, from the slope of the Arrhenius plots, and the corresponding frequency factors in the Arrhenius equation were 2×10^{12} sec^{-1} and 3×10^{15} sec^{-1}, respectively.

The source of error in the experimental measurements of the rate constants was considered to be the uncertainty in the determination of the exact temperature of the reaction

TABLE 4

Effect of Partial Pressure of Phenylmercaptoacetic Acid on Rate Constants

Expt. No.	Temp.(^{o}K)	Acid Press. (mm Hg)	k_o (sec^{-1})	k_1 (sec^{-1})
60	783	.11	.21	.07
65	783	.24	.23	.07
80	828	.44	1.33	.55
79	829	.08	1.44	.70
84	833	.18	1.36	.79
82	835	.06	1.73	.90

TABLE 5

Effect of Toluene Pressure on Rate Constants

Expt. No.	Temp.(^{o}K)	Toluene Press. (mm Hg)	k_o (sec^{-1})	k_1 (sec^{-1})
65	783	11.18	.234	.0692
60	783	17.97	.206	.0692
67	793	9.85	.404	.131
68	793	15.33	.429	.135
69	813	9.63	.726	.308
70	813	17.34	.946	.341
81	833	7.87	1.60	.807
82	835	15.00	1.73	.900

TABLE 6

Effect of Time of Contact on Rate Constants

Expt. No.	Temp.(^{o}K)	Time of Contact (sec)	k_o (sec^{-1})	k_1 (sec^{-1})
68	793	.368	.43	.14
87	795	1.110	.45	.15
69	813	.465	.73	.31
70	813	.331	.95	.34
86	813	.207	.95	.33
84	833	1.342	1.36	.79
81	833	.491	1.60	.81
85	833	.213	1.52	.76

Figure 9

Plot of log k_o vs. 1/T

Filled circles denote reactions
done in packed vessel

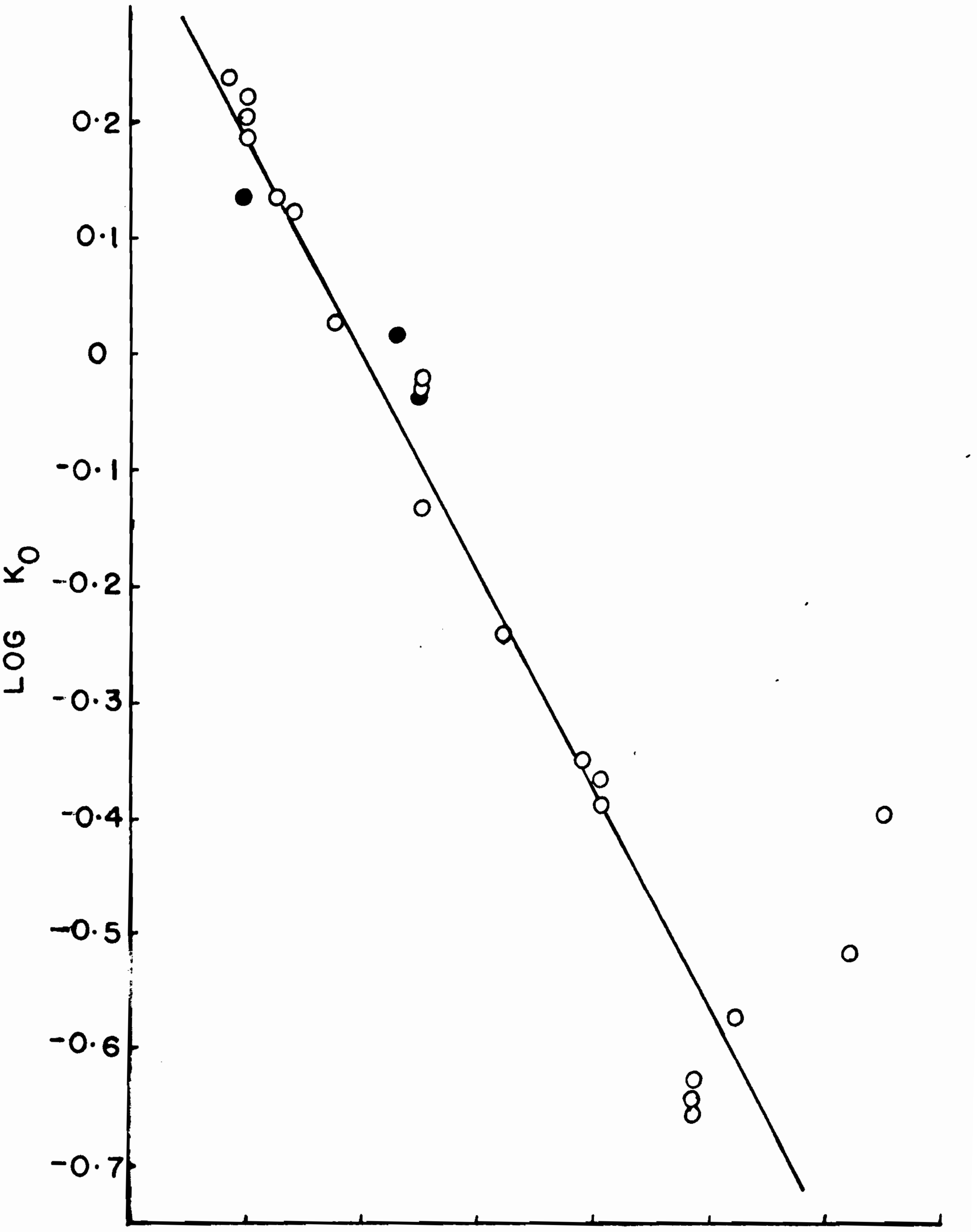
LOG K_O
0·2
0·1
0
-0·1
-0·2
-0·3
-0·4
-0·5
-0·6
-0·7
1·18
1·20
1·22
1·24
1·26
1·28
1·30
1·32
$\frac{1}{T} \times 10^3$

Figure 10

Plot of log k_1 vs. 1/T

Filled circles denote reactions
done in packed vessel

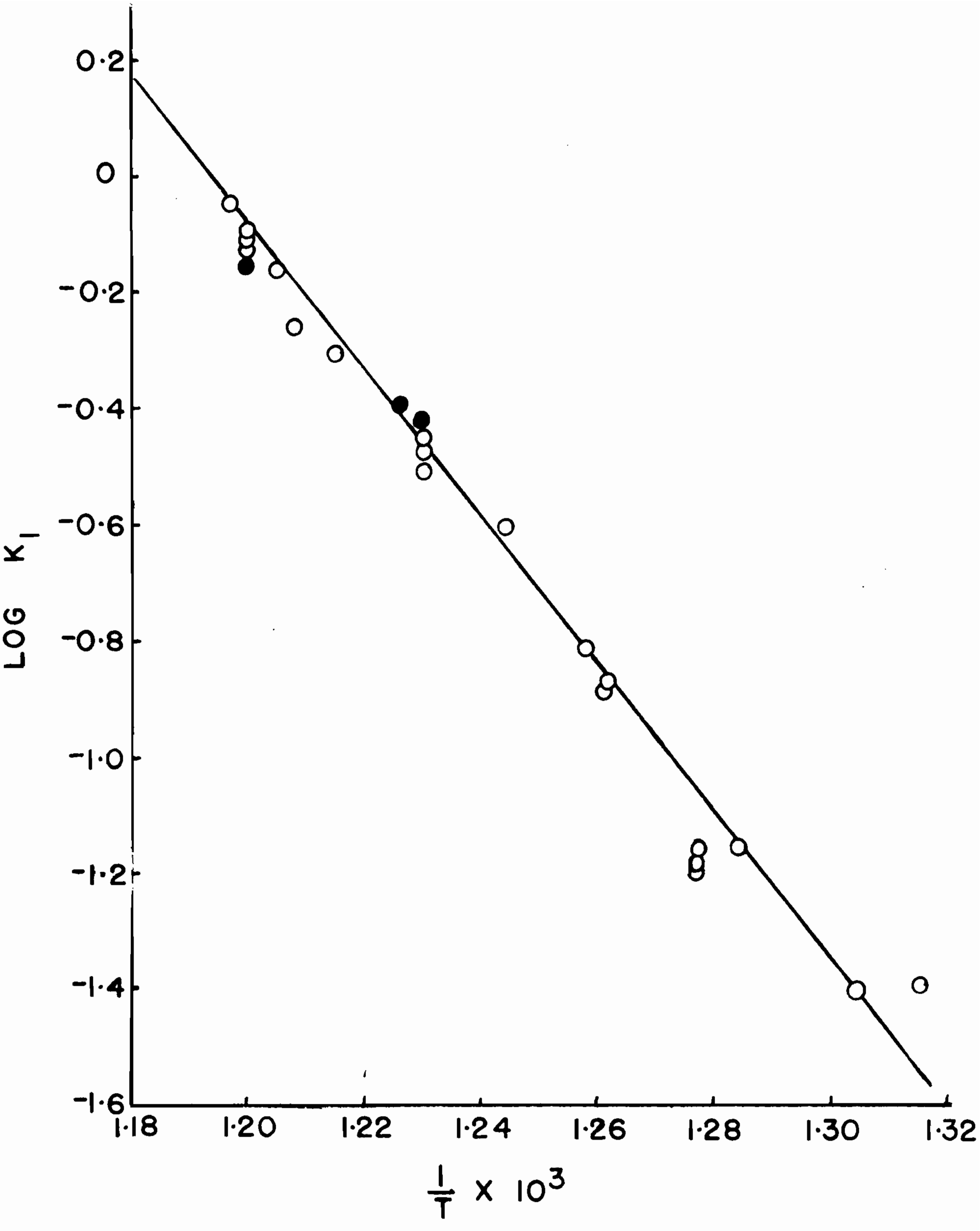
0·2
0
-0·2
-0·4
-0·6
-0·8
-1·0
-1·2
-1·4
-1·6
LOG K₁
1·18
1·20
1·22
1·24
1·26
1·28
1·30
1·32
1/T X 10³

TABLE 7

Rate Constants for the Pyrolysis of Phenylmercaptoacetic Acid

Expt. No.	Temp. (^{o}K)	Toluene Press. (mm Hg)	Acid Press. (mm Hg)	PT/PA	Contact time (sec)	Overall % Decomposition	k_o (sec^{-1})	k_1 (sec^{-1})
75	760	11.70	.29	37.7	.44	16.1	.40	.04
77	764	12.51	.17	74.9	.43	5.47	.12	.058
74	767	13.09	.27	49.8	.46	13.1	.30	.04
66	779	10.74	.18	56.3	.44	11.1	.27	.069
60	783	17.97	.11	157.0	.55	10.6	.21	.069
63	783	15.33	.17	94.3	.61	12.6	.22	.064
64	783	14.90	.17	90.0	.65	13.5	.23	.065
65	783	11.18	.24	47.5	.61	12.7	.23	.069
67	793	9.85	.19	54.0	.46	16.9	.40	.13
68	793	15.33	.24	58.3	.37	14.6	.43	.14
87	795	11.94	.22	53.6	1.11	39.0	.45	.15
73	804	10.85	.12	88.1	.45	22.5	.57	.25
69	813	9.63	.17	59.8	.47	28.7	.73	.31
70	813	17.34	.16	108.5	.33	26.9	.95	.34
86	813	5.04	.24	20.6	.21	14.0	.95	.33
89P	813	10.85	.22	53.8	1.17	66.3	.92	.38
88P	815	12.04	.23	58.8	1.04	68.5	1.04	.40
72	823	7.83	.17	44.6	.46	36.7	1.06	.49
80	828	7.42	.44	17.0	.48	47.3	1.33	.55

TABLE 7 (Continued)

Expt. No.	Temp. (^{o}K)	Toluene Press. (mm Hg)	Acid Press. (mm Hg)	PT/PA	Contact time (sec)	Overall % Decomposition	k_o (sec^{-1})	k_1 (sec^{-1})
79	829	9.12	.08	134.0	.41	44.7	1.44	.70
84	833	15.51	.18	88.6	1.34	84.0	1.36	.79
85	833	5.80	.10	56.0	.21	27.6	1.52	.76
81	833	7.87	.13	66.3	.49	54.4	1.60	.81
91P	833	11.85	.17	69.0	1.08	83.7	1.66	.71
82	835	15.00	.06	235.0	.38	47.9	1.73	.90

The experiments marked P refer to those done in the packed reaction vessel.

TABLE 8

Effect of Packed Reaction Vessel on Rate Constants

Expt. No.	Temp. (°K)	k_o (sec^{-1})	k_1 (sec^{-1})
89 P	813	.92	.38
86	813	.95	.33
70	813	.95	.34
69	813	.73	.31
88 P	815	1.04	.40
91 P	833	1.66	.71
85	833	1.52	.76
84	833	1.36	.79

The experiments marked P refer to those done in the packed reaction vessel.

vessel during an experiment. This uncertainty was due to the fluctuation of temperature in the reaction vessel in spite of the large heat capacity of the furnace and to the variation of the temperature along the length of the reaction vessel. Although this fluctuation was not more than ± 2°K, which represents only a small percentage error in the temperature range used, the resulting percentage error in the rate constant is high. For example, from the plot of log k_1 versus 1/T given in Figure 10, the corresponding rate constants at the temperatures 811°K and 813°K are .308 and .334 sec^{-1}, respectively. The error in the rate constant resulting from an uncertainty of 2°K is thus about 8%. An examination of the observed scatter in the rate constant k_1, shows that, in most experiments, it could be explained by the fluctuation in temperature. For example, the difference between the values of k_1 found in the pairs of experiments #63 and #65 is 7%, #68 and #67 is 3%, and #86 and #70 is 2%. However, the maximum spread among the four experiments #91, 81, 85, 84, is 14%, and among the three experiments #89p, 86, 70 is 13%. Therefore, one must conclude that additional sources of error, such as due to analysis, might have been involved.

Some uncertainties inherent in the assumption of a reaction mechanism might prevent the unequivocal identification of the measured rates with the postulated processes. Side reactions may affect the products by which the rate of the primary step is measured. The magnitude of such errors are difficult to assess, particularly when some of the possible side reactions may not have been accounted for. Taking into account all the uncertainties in the present investigation, the activation energy of 59 kcal/mole for reaction (1) was considered to be accurate within ± 2 kcal/mole. With the usual assumption that the reverse step does not require any activation energy, the value of the 59 ± 2 kcal/mole may then be identified with the C-S bond dissociation energy, $D(C_6H_5S-CH_2COOH)$.

In the pyrolysis of phenyl methyl sulphide, Back and Sehon (47) reported that the activation energy of the rate of decomposition was 60 kcal/mole. This is one kcal/mole greater than the activation energy of the decomposition of phenylmercaptoacetic acid, and may be due to a slight resonance stability of the CH_2COOH radical compared to that of the CH_3 radical.

SUMMARY

The pyrolysis of phenylmercaptoacetic acid was studied over the temperature range 760°-833°K in a stream of toluene. The main products of the decomposition were phenylmercaptan, carbon dioxide, acetic acid, dibenzyl, phenyl methyl sulphide, and ketene. The overall reaction was found to be homogeneous and first-order with respect to phenylmercaptoacetic acid.

From an analysis of the data it is suggested that the overall decomposition may be represented in terms of two parallel modes of decomposition of phenylmercaptoacetic acid;

$$C_6H_5SCH_2COOH \xrightarrow{k_1} C_6H_5S + CH_2COOH \tag{1}$$

$$C_6H_5SCH_2COOH \xrightarrow{k_2} C_6H_5SCH_3 + CO_2 \tag{2}$$

and these primary reactions were followed by rapid secondary steps:

$$C_6H_5S + C_6H_5CH_3 \longrightarrow C_6H_5SH + C_6H_5CH_2$$

$$CH_2COOH + C_6H_5CH_3 \longrightarrow CH_3COOH + C_6H_5CH_2$$

$$CH_2COOH \longrightarrow CH_2CO + OH$$

$$CH_2COOH \longrightarrow CH_3 + CO_2$$

$$OH + C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + H_2O$$

$$CH_3 + C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + CH_4$$

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

The activation energy of reaction (1) was calculated as 59 ± 2 kcal/mole and was identified with $D(C_6H_5S - CH_2COOH)$.

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