Picrate

$$\Delta H = 16,855 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p^{1/2} = 2705 \text{ cal.}$$

Sulfate

$$\Delta H = 4360 \text{ cal./mole}$$
$$\Delta F^\circ_{298.1} = -RT \ln p = 2131 \text{ cal.}$$

Summary

1. A new hydrate of hydrazonium dibromide is reported.

2. Dissociation pressures over a range of temperature are given for four of the five known hydrated hydrazonium salts, and transition points determined for two of them.

3. Calculations of the change in heat content and standard free energy change of hydration are made.

The Chain Decomposition of Dimethyl Ether Photosensitized by Acetone

BY JOHN A. LEERMAKERS[1]

In a study of the photolysis of acetaldehyde at high temperatures[2] the author recently obtained experimental support of the chain theory of decomposition of organic compounds which was advanced by Rice and Herzfeld.[3] It was felt that this case might not be representative of the general type of decomposition which these authors consider, inasmuch as the course of the thermal decomposition of acetaldehyde[4] is best expressed by a kinetic equation which is not first order, while the other reactions discussed by them have been generally accepted as being unimolecular and are first order at high pressures.

The present investigation was undertaken in order to obtain some evidence as to the general validity of the chain mechanism by a study of several reactions whose thermal decompositions have been heretofore considered to be unimolecular. One such reaction discussed by Rice and Herzfeld is the decomposition of acetone.[5] Another reaction also considered by these authors is the decomposition of dimethyl ether. This latter reaction was studied by Hinshelwood and Askey.[6] Rice and Herzfeld postulate that the decompositions of acetone and dimethyl ether are chain reactions, and that methyl radicals are the chain carriers in each case.

It is possible to test this idea by introducing methyl radicals into these two compounds at temperatures below those at which the normal ther-mal decompositions proceed. In the present investigation methyl radicals were liberated in acetone by the photolysis of the vapor. In the case of dimethyl ether the radicals were produced in the reaction cell containing the ether by illuminating mixtures of ether and acetone with light of wave length 3130 Å. Dimethyl ether does not absorb light of this wave length, and the light absorbed by the acetone almost certainly results in the production of methyl radicals.[7] The studies of acetone alone under conditions which obtained when mixtures were investigated showed that the photochemical decomposition of acetone except for the primary act was not significant when ether was present. There was no appreciable dark reaction with either acetone or with mixtures.

Rates of decomposition of acetone alone and of dimethyl ether in mixtures of acetone and ether were studied over a range of pressures, temperatures and light intensities. The results show that the high temperature photolysis of acetone is not a chain reaction, that dimethyl ether can be caused to decompose by means of methyl radicals and that this decomposition results in the establishing of a chain. A few experiments were performed with mixtures of acetone and diethyl ether; these will be briefly discussed.

Experimental

Apparatus and Materials.—The apparatus has been described in the paper on the photolysis of acetaldehyde[2] and was unchanged except that the acetaldehyde was replaced by acetone, and a 2-liter flask containing dimethyl ether was sealed to the tubing leading to the reaction cell.

Dimethyl ether was prepared from methyl alcohol and

(1) National Research Fellow in Chemistry.
(2) Leermakers, THIS JOURNAL, 56, 1537 (1934).
(3) Rice and Herzfeld, ibid., 56, 284 (1934).
(4) Fletcher and Hinshelwood, Proc. Roy. Soc. (London), A141, 41 (1933); Kassel, J. Phys. Chem., 34, 1166 (1930).
(5) Hinshelwood and Hutchinson, Proc. Roy. Soc. (London), A111, 245 (1926).
(6) Hinshelwood and Askey, ibid., A115, 215 (1927).
(7) Norrish, Trans. Faraday Soc., 30, 103 (1934).

sulfuric acid. The gas passed through a saturated solution of potassium permanganate and was collected at $-78°$. It was distilled at $-25°$ through a tube containing fused potassium hydroxide and was further fractionated in vacuum, the middle fraction being retained. The ether was stored in the 2-liter flask after having been freed of air by freezing with liquid air and pumping out non-condensed gases.

The acetone was a Kahlbaum product, purified through the bisulfite derivative. It was distilled in vacuum. Two samples were employed, one of which was dried by distillation from magnesium perchlorate. The two samples gave identical results.

Procedure.—The procedure was the same as described previously except that two initial pressures were read, the first after the introduction of the acetone into the cell, and the second after the introduction of the ether. The difference between the two readings gave the pressure of the ether. The molal absorption coefficient of the acetone was measured at room temperature and at 180°. It was assumed to be independent of temperature, and absorptions at higher temperatures were calculated. After exposure, the gases not condensed in liquid air were pumped off and measured as previously described and the amount of carbon monoxide determined.

Experimental Results

A number of experiments were performed in which acetone was illuminated in the absence of ether. The results of these experiments are given in Table I.

TABLE I

Acetone, mm.	T, °C.	I_0	A	t, sec.	CO, cc.	ϕ	CO, %
156.2	405	20.2	0.316	1140	0.0660	1.3	31.8
89.0	403	20.2	.191	2220	.0801	1.3	32.8
32.3	403	20.2	.0746	3600	.0532	1.2	33.6
12.6	403	20.2	.0344	4440	.0254	1.2	35.3
122.0	403	10.9	.256	2340	.0597	1.3	33.6
140.3	405	4.55	.284	6720	.0801	1.3	33.8
116.5	303	18.0	.236	2940	.1080	1.2	39.2
89.0	305	17.3	.180	3600	.0957	1.2	40.9
148.5	212	16.7	.300	3780	.1260	0.9	49.6
126.8*	163	26.7	.265	1413	.0695	1.0	50.0
109.9*	182	24.9	.233	1640	.0686	1.1	50
133.2*	402	25.2	.272	545	.0286	1.3	30.7

The first column gives the partial pressure of acetone; the second, the temperature; the third, the incident light intensity in cm. galvanometer deflection; the fourth, the fraction of light absorbed; the fifth, the exposure time; the sixth, the cc. of carbon monoxide measured at room temperature and atmospheric pressure; the seventh, the number of moles of carbon monoxide produced per einstein of light absorbed; the eighth, the percentage of carbon monoxide in the total, non-condensed products. Since only a small fraction of the acetone was decomposed in

an experiment, it was assumed that the light absorption remained constant during its course. The number of moles of carbon monoxide produced per second in the reaction cell was calculated by dividing the cc. of gas by the total time and multiplying this by the proper factor. The number of einsteins absorbed per second was equal to the product of the quantities given in columns three and four multiplied by another factor. These two factors have been given previously.[2] The experiments in Table I marked with an asterisk were performed with a different sample of acetone.

Several samples of acetone were photolyzed at room temperature. The results agreed within the accuracy of the method with those of Damon and Daniels.[8]

Table II gives the results of the experiments made with various mixtures of ether and acetone.

TABLE II

Acetone, mm.	Ether, mm.	T, °C.	I_0	A	t, sec.	CH₄	k' × 10³	k × 10²
14.0	85.1	403	23.8	0.0344	375	0.148	1.88	4.6
10.5	159.0	400	22.2	.0247	360	.245	1.88	4.6
13.3	156.4	400	22.2	.0306	360	.250	1.97	4.9
9.4	157.4	399	20.4	.0222	360	.216	1.78	4.4
11.8	75.0	400	20.4	.0277	720	.236	1.99	4.9
11.7	35.0	400	20.4	.0275	1560	.253	2.07	5.1
10.7	12.3	400	21.9	.0252	1920	.0900	1.68	4.2
57.3	58.9	399	21.9	.128	615	.173	2.16	5.3
51.0	14.6	400	21.9	.114	1200	.0695	1.90	4.7
37.0	154.9	400	21.9	.0844	440	.316	2.08	5.1
77.5	79.4	400	22.9	.173	480	.199	2.30	5.7
89.2	36.9	400	22.9	.191	1350	.201	1.82	4.5
14.5	90.4	399	10.4	.0339	840	.220	1.89	4.7
11.9	81.4	400	4.28	.0279	1200	.176	1.82	4.5
14.5	79.7	400	1.35	.0346	2340	.179	1.70	4.2
9.7	81.7	377	21.6	.0236	960	.214	1.19	2.9
16.5	73.0	377	22.0	.0402	960	.207	1.27	3.1
13.2	72.8	352	22.0	.0336	1860	.250	0.779	1.8
13.7	72.5	352	22.0	.0349	2220	.306	.805	1.9
16.6	111.6	329	21.0	.0434	1800	.249	.529	1.2
16.1	110.0	330	21.0	.0421	1800	.250	.538	1.3
12.6	117.0	302	21.0	.0344	1800	.129	.256	0.59
13.6	115.8	301	21.0	.0371	1800	.127	.256	.59
12.5	147.0	280	21.0	.0356	1800	.101	.155	.35
10.3	148.3	270	19.7	.0294	3180	.137	.119	.27

The first column gives the partial pressure of acetone; the second, the partial pressure of dimethyl ether; the third, the temperature; the fourth, the incident light intensity in cm. galvanometer deflection; the fifth, the fraction of light absorbed by the acetone; the sixth, the exposure time in seconds. The seventh column gives the number of cc. of methane produced. This quantity was obtained by subtracting from the initial volume of gas twice the volume of carbon monoxide found. This choice of a measure of the amount of reaction is probably justified. In the

(8) Damon and Daniels, THIS JOURNAL, 55, 2363 (1933).

thermal decomposition of dimethyl ether, the products are carbon monoxide, hydrogen and methane;[5] formaldehyde is known to be an intermediate. In the present experiments, any formaldehyde which did not decompose would be frozen out at liquid air temperature, and any which had decomposed would yield equal quantities of hydrogen and carbon monoxide. Consequently, for each volume of carbon monoxide in the gaseous products there is present an equal amount of hydrogen. The rest is methane. The carbon monoxide from the acetone photolysis is negligible where the chain length is long; where the chain length is short not much error is introduced since from the study of acetone it was found that the carbon monoxide was from 30 to 50% of the gas and the subtraction of twice the carbon monoxide approximately corrects for the acetone photolysis. Further evidence that the decomposition of the formaldehyde gives equal amounts of carbon monoxide and hydrogen was found in the fact that the absorption of gas by the silver oxide used as reagent for carbon monoxide was rapid for about fifteen minutes and that after this time there followed a period of much slower absorption. Silver oxide is known to absorb hydrogen slowly. In one case, after allowing the gaseous products to remain in contact with the oxide overnight, it was found that as much gas was further absorbed as was taken up in the first fifteen minutes. Before consistent results were obtained in the present experiments it was found necessary to determine how much time was required for complete absorption of carbon monoxide, and in all later experiments to allow the gases to remain in contact with the silver oxide for only this period of time. The uncertainty involved in this procedure probably accounts for the greater part of the variations found in the calculated rate constants.

An examination of the data given in Table II indicated that the results could be expressed by the equation

$$\frac{d(CH_4)}{dt} = k' \sqrt{\frac{I_{abs.}}{(CH_3)_2CO}} (CH_3OCH_3)$$

where $I_{abs.}$ is the product of the incident light intensity and the fraction of light absorbed by the acetone. Column 8 gives the values of k' so calculated, where the units are those of the first 7 columns. Column 9 gives the values of the rate constant k, calculated from k', where the units are einsteins per cc. per second and moles per cc.,

and k has the dimensions of $moles^{1/2}$, $einsteins^{-1/2}$, $sec.^{-1/2}$. A plot of log k against $1/T$ for the experiments of Table II is shown in Fig. 1. The straight line gives an activation energy of 16,000 calories per mole, and $k = 7.3 \times 10^3 e^{-16,000/RT}$, $moles^{1/2}$, $einst.^{-1/2}$, $sec.^{-1/2}$.
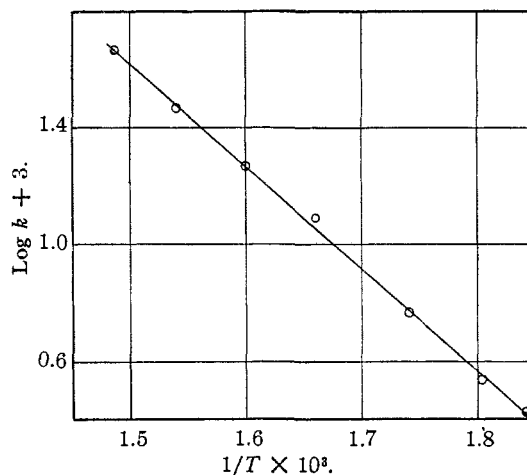

Fig. 1.—Plot of log k against $1/T$.

In the experiments at 400° given in Table II the ratio of acetone to ether has been varied 50-fold, the partial pressure of ether has been varied 10-fold, that of acetone 10-fold, and the incident light intensity 17.5-fold. The average deviation of the individual constants from the average constant is 7%. As previously mentioned, the greater part of this variation probably arises from the method of determining the amount of methane produced.
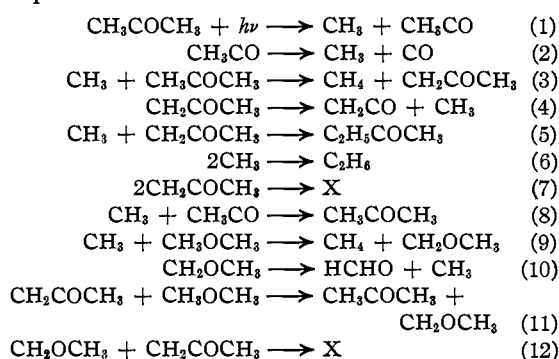
The quantum yields of methane production, or, what is assumed to be equivalent, of ether decomposition, can be calculated as outlined for the case of acetone. At 400°, for the experiment of lowest light intensity, the yield was 230. At the same temperature, for the experiment where the ratio of acetone to ether was greatest, the yield was 5. The other yields lie between these, depending on the various pressures and upon the light intensity. For the experiment at 270° the quantum yield was 11.

A number of experiments were performed in which mixtures of diethyl ether and acetone were illuminated. The results of these experiments led to no satisfactory rate expression. Roughly, it was found that acetone inhibited the decomposition of the ether, although to a lesser extent than in the case of dimethyl ether, that the rate was proportional to a power of the light intensity

between first and one-half order and that the decomposition was approximately proportional to the ether concentration. The quantum yields of carbon monoxide production were only about one-tenth as great as those of dimethyl ether decomposition under similar conditions. Probably the principal uncertainty in the results lies in the lack of knowledge of the reaction products, and the use of the amount of carbon monoxide as a measure of the ether decomposition cannot be justified without further examination of the reaction products. Unfortunately, there was not sufficient time to do further work on this compound. From the results of these experiments it can be said that methyl radicals do react with diethyl ether and that chains of short length result.

Discussion

Rice and Herzfeld have given detailed mechanisms for the decompositions of acetone and dimethyl ether. We shall write a number of the reactions given by them and add certain others which may take place under the conditions of our experiments.

$$CH_3COCH_3 + h\nu \longrightarrow CH_3 + CH_3CO \quad (1)$$
$$CH_3CO \longrightarrow CH_3 + CO \quad (2)$$
$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3 \quad (3)$$
$$CH_2COCH_3 \longrightarrow CH_2CO + CH_3 \quad (4)$$
$$CH_3 + CH_2COCH_3 \longrightarrow C_2H_5COCH_3 \quad (5)$$
$$2CH_3 \longrightarrow C_2H_6 \quad (6)$$
$$2CH_2COCH_3 \longrightarrow X \quad (7)$$
$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \quad (8)$$
$$CH_3 + CH_3OCH_3 \longrightarrow CH_4 + CH_2OCH_3 \quad (9)$$
$$CH_2OCH_3 \longrightarrow HCHO + CH_3 \quad (10)$$
$$CH_2COCH_3 + CH_3OCH_3 \longrightarrow CH_3COCH_3 + CH_2OCH_3 \quad (11)$$
$$CH_2OCH_3 + CH_2COCH_3 \longrightarrow X \quad (12)$$

The mechanisms here discussed are admittedly *ad hoc* and undoubtedly many other plausible reactions could be written. With the present state of knowledge of such reactions involving radicals it seems unwise to speculate too far; we shall therefore confine ourselves to those listed above.

The first five reactions were given by Rice and Herzfeld to account for the thermal decomposition of acetone. The work of Norrish[7] indicates that reaction 1 almost certainly occurs. The fact that dimethyl ether can be made to decompose by the products of the photolysis of acetone and that the decomposition leads to a chain also offers strong evidence in favor of this primary act. Reaction 2 is plausible and would probably occur

quite rapidly at high temperatures. Reaction 3 also seems probable. Reaction 4, however, must have an activation energy so large that it does not occur at all rapidly at temperatures around 400°. This reaction is the chain propagator for the acetone decomposition according to Rice and Herzfeld. The experiments in Table I show the following facts. The quantum yields of carbon monoxide production are, within the experimental accuracy, unity from 200 to 400°. Over the same temperature range, the carbon monoxide in the measured reaction products decreased from 50 to approximately 33%. This means that at 400° two molecules of gas not condensed in liquid air are formed for each molecule of carbon monoxide. At 200° one molecule of non-condensed gas is formed for each carbon monoxide. The non-condensed gas is either ethane or methane.

These observations are in agreement with the following interpretation of the course of the acetone photolysis. At 400° the two radicals resulting from 1 and 2 react bimolecularly with acetone molecules to form methane and the comparatively stable (CH_2COCH_3) radicals. These radicals do not further decompose, at least to yield a non-condensable gas, but disappear by recombination in the gas phase or on the wall. Should the radicals decompose according to 4, the carbon monoxide in the products would be less than one-third of the total. At 200° the radicals liberated in the primary act do not react with acetone molecules but disappear according to reactions 2 and 6; a molecule of ethane is formed for each carbon monoxide. At room temperature the quantum yield of acetone decomposition is about 0.04.[8] Since Damon and Daniels found that fluorescence accounted for no more than 5% of the light which did not result in decomposition of acetone, it seems reasonable that at this temperature there is considerable recombination of CH_3 and CH_3CO. At higher temperatures this simple recombination may not result because the CH_3CO radical has decomposed before collision with a CH_3. At temperatures between 200 and 400° both reactions 3 and 2 followed by 6 are important, and the carbon monoxide is between 33 and 50% of the gaseous products.

The experimental evidence in general seems to indicate that reaction 4 has a high activation energy. It is unfortunate that the apparatus employed in this work could not be used at tempera-

tures above 400° since it is possible that reaction 4 becomes important at temperatures in the neighborhood of those at which the thermal decomposition proceeds. It might be pointed out that the activation energy of 68,500 calories which Hinshelwood and Hutchinson[5] found for the first order decomposition of acetone is the same as that given by Rice and Herzfeld for the primary step. There is in this case no need of a chain mechanism unless further work shows that the value found by Hinshelwood and Hutchinson is too high.

The rate expression found for the acetone-sensitized decomposition of dimethyl ether can be formally derived by using reactions 1, 2, 3, 4, 5, 9 and 10. These reactions were all given by Rice and Herzfeld. As pointed out, however, reaction 4 is not important at 400° and without it the proper rate expression is not derivable. By using reactions 1, 2, 3, 9, 10, 11 and 12 the observed kinetic equation can be obtained. The following activation energies have been assumed: reaction 3, $Q = 20$ Cal.; reaction 9, $Q = 15$ Cal.; reaction 10, $Q = 35$ Cal.; reaction 11, $Q = 20$ Cal.; reaction 12, $Q = 10$ Cal. These values were chosen to justify the following approximations

$I_{abs.}$ is small compared to $k_3(CH_3)(CH_3OCH_3)$
$k_{11}(CH_2COCH_3)(CH_3OCH_3)$ and
$$\frac{k_{10}k_{11}}{k_3k_{12}} \frac{I_{abs.}}{(CH_3)} \frac{(CH_3OCH_3)}{(CH_3COCH_3)}$$
$k_9(CH_3OCH_3)$ is large compared to $k_3(CH_3COCH_3)$

With the activation energies assigned, the concentrations of the intermediates CH_3, CH_2COCH_3 and CH_2OCH_3 are the same. A possible justification for the choice of reaction 12 in preference to reactions involving methyl radicals may be that reactions of the latter type have a smaller collision efficiency than reactions in which the larger radicals combine. This is not certain. The choice of reaction 12 was made in this case because it led to the right rate expression.

Reaction 11 is essential to the mechanism. There is no obvious reason why it should be excluded. The strength of the carbon–hydrogen bond in acetone is probably nearly the same as that in dimethyl ether; the direction which an exchange reaction such as 11 will take probably depends upon a steric factor. The two methyl groups in acetone almost certainly occupy different positions with respect to each other than those in dimethyl ether. This difference, in conjunction with the fact that the moments of inertia of the two molecules are not the same, and

hence the rotational frequencies are dissimilar, may lead to a preferential reaction of CH_2COCH_3 with CH_3OCH_3.

The final expression for the rate of decomposition of dimethyl ether is

$$-\frac{d(CH_3OCH_3)}{dt} = \sqrt{\frac{k_9k_{10}k_{11}}{k_3k_{12}} \frac{I_{abs.}}{(CH_3COCH_3)}} (CH_3OCH_3) + \sqrt{\frac{k_{10}k_3k_{11}}{k_9k_{12}} I_{abs.}} (CH_3COCH_3)$$

The second term on the right-hand side of the equation is negligible. Considering only the first term, and assuming with Rice and Herzfeld that the coefficient of the exponential in first order reactions is 10^{14} and in second order reactions is 10^9, we find

$$k = \sqrt{\frac{k_9k_{10}k_{11}}{k_3k_{12}}} = 10^7 e^{-20,000/RT}$$

whereas the experimental value is

$$k = 10^4 e^{-16,000/RT}$$

In view of the assumptions made the discrepancy between these values is not surprising.

The qualitative results found with diethyl ether allow of very few conclusions. It is not possible to make any statements about the thermal decomposition of this compound since it is not known that methyl radicals are formed in the first step. It is apparent that methyl radicals are capable of initiating short chains and that the chain lengths are about one-tenth as great as those observed with dimethyl ether. The difference may lie in the fact that for dimethyl ether a carbon–oxygen bond must break in order to perpetuate the chain, while with diethyl ether it may be a carbon–carbon bond which must rupture. There are not sufficient data from which to draw definite conclusions.

The results of the present experiments suggest that acetone might be a chain breaker in other chain reactions involving methyl radicals. Its use may therefore afford a means of testing the chain nature of organic decompositions which are thought to be propagated by such radicals.

In conclusion, the experiments with dimethyl ether substantiate the views of Rice and Herzfeld that methyl radicals are capable of initiating chains in the decomposition of this compound. The experiments with acetone afford an indication that the interpretation of the acetone decomposition given by Rice and Herzfeld is not valid at temperatures below 400°. The very fundamental question has not been answered unambiguously as to whether the primary act in the

thermal decomposition of these organic compounds leads to radical production. The experiments of Rice and collaborators suggest that they are formed. If this is so, the present experiments support the chain mechanism of the thermal decomposition of dimethyl ether.

One thing further might be deduced from the present study and from the work on acetaldehyde.[2] Norrish[7] has expressed the opinion that the primary act in the photolysis of aldehydes is of a different type than that which occurs with ketones. The work on acetaldehyde definitely disproves this. Norrish also considers that the fractional quantum yields found for ketones are due to a new type of predissociation. This explanation is not necessary, although it may be correct. The facts can be satisfactorily accounted for by assuming a simple recombination of the radicals liberated on the absorption of light.

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Summary

1. Studies of the high-temperature photolysis of acetone have shown that methyl radicals do not initiate a chain decomposition of the acetone at temperatures below 400°.

2. The acetone-sensitized photo-decomposition of dimethyl ether has been investigated over a range of pressures, temperatures and light intensities. The rate of decomposition of the ether was proportional to the square root of the absorbed light and to the first power of the ether concentration; it was inversely proportional to the square root of the acetone concentration. The rate constant was found to be $10^4 \, e^{-16,000/RT}$, $\mathrm{moles}^{1/2}$, $\mathrm{einsteins}^{-1/2}$, $\mathrm{sec.}^{-1/2}$. Chain lengths of the ether decomposition were as great as 230 molecules decomposed per quantum of light absorbed.

3. Possible mechanisms of the acetone and of the ether decomposition have been discussed.

4. Diethyl ether was found to decompose in the presence of methyl radicals, with chains about one-tenth as great as those observed for dimethyl ether resulting.

The Velocity of Hydrolysis of Stereoisomeric Hydrazones and Oximes

BY RAYMOND WRIGHT JOHNSON[1] AND JULIUS STIEGLITZ

Although some data have been obtained on the rates of formation of hydrazones and oximes by the reaction of ketones with hydrazine and hydroxylamine, respectively, no information has been available concerning the rates with which the hydrolysis of these compounds proceeds.

The present investigation is the first of a series in which a study is being made to determine whether any essential differences in the rates of hydrolysis of the respective members of pairs of stereoisomeric hydrazones and oximes can be detected. It includes the search for possible differences in rates of hydrolysis due to other types of stereochemical influences. It is hoped that by such studies a deeper insight into the mechanism

of hydrolytic decompositions may be obtained than has thus far been developed.

The purpose of this first of the series of studies was to obtain a method for the determination of such rates and to apply it to the determination of the relative rates of hydrolysis of benzophenone hydrazone and oxime and the individual pairs of stereoisomeric hydrazones and oximes of *p*-methoxybenzophenone. The method described, although empirical, yielded this information.

Preparation of Materials

Benzophenone Hydrazone.—This compound was prepared from benzophenone and hydrazine hydrate by the method of Curtius and Rauterberg;[2] m. p. 98–99°.

p-**Methoxybenzophenone.**—This compound was prepared by the Friedel–Craft reaction according to the method of Gattermann, Ehrhardt and Maisch;[3] m. p. 62°.

(1) From the dissertation of R. W. Johnson, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, August, 1932.

(2) Curtius and Rauterberg, *J. prakt. Chem.*, **44**, 194 (1891).

(3) Gattermann, Ehrhardt and Maisch, *Ber.*, **23**, 1204 (1890).