only be used as an approximate guide until the magnitudes of the rate constants are more firmly established.

Diffusion Effect: Conclusions.—For the smaller cell used, diffusion of radicals out of the light beam may be neglected provided the temperature is above 100° and the acetone pressure is above 100 mm. There is, however, a small effect present even under these conditions, which becomes more marked the smaller the light beam relative to the cell. In addition surprisingly large errors can be made in determining the volume of a small light beam so that measurements with such beams show a wide experimental spread. At 26°, on the other hand, the radicals diffuse out of the beam to such an extent that it is necessary to use the cell volume in calculations instead of the light volume. For these two reasons it is recommended that measurements should be made with the whole reaction cell filled with light. This involves risking that an unknown surface reaction contributes to the effect being studied: the agreement between different workers makes this risk small in the case of the acetone photolysis.

For photochemical reactions in general the magnitude of the diffusion effect can be calculated by the method given by Hill.[6a] This method requires that all the rate constants involved are known to a fairly high accuracy. Even for acetone the constants are not known well enough for a definite answer to be given; hence it seems that for any less well known reaction only a direct experimental test can decide whether radical diffusion is important or not.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. XLIV. Pyridine and Mixtures of Acetone and Pyridine[1]

BY ROBERT H. LINNELL AND W. ALBERT NOYES, JR.

The rates of formation of methane and of ethane as functions of temperature, volume of light beam, cell length and pressure have been determined for acetone vapor. Pyridine vapor shows little or no decomposition at 2537 A. but does decompose at shorter wave lengths with formation of a brown deposit, hydrogen and C_2 hydrocarbons. Methyl radicals do not abstract hydrogen appreciably from pyridine to form methane under the conditions of these experiments at temperatures from 120 to 210°.

The reactions of methyl radicals to produce methane and ethane during photochemical decomposition of acetone both with and without the addition of foreign gases have been studied by several authors recently.[2] If these two reactions may be written in general terms as

$$CH_3 + CH_3 = C_2H_6; \qquad R_{C_2H_6} = k_1(CH_3)^2 \tag{1}$$

$$CH_3 + RH = CH_4 + R; \qquad R_{CH_4} = k_2(CH_3)(RH) \tag{2}$$

where $R_{C_2H_6}$ and R_{CH_4} are the rates of ethane and of methane formation, respectively, in molecules per cc. per second; it is possible from the slope of a plot of $R_{CH_4}/R_{C_2H_6}^{1/2}$ *vs.* (RH) (where (RH) is concentration in molecules per cc.) to obtain $k_2/k_1^{1/2}$ in (molecules sec.)$^{-1/2}$ cc.$^{1/2}$. This has been done for several different molecules RH by Trotman-Dickenson and Steacie[2b] by assuming that the line goes through the origin.

Gomer,[3] by a rotating sector technique, has obtained recently a value for k_1. If this value is accepted, absolute values of k_2 for several different RH molecules can be obtained from existing data.

Due to the fact that (1) is second order with respect to CH_3 radicals while (2) is first order, and the fact that RH may be any molecule present (including products of acetone photolysis, such as biacetyl), this method of calculation must be examined critically before the reliability of $k_2/k_1^{1/2}$ values can be assessed. Certain aspects of this problem have been discussed,[4] and systematic data bearing on this problem are presented and discussed in the preceding article.[5] The present article contributes certain data of interest, and in addition the reactions of methyl radicals with pyridine are discussed.

The photochemistry of pyridine vapor seems to have received little attention, although the spectrum has been analyzed.[6]

Experimental

The purification of the acetone and the general gas analysis procedure have been described in previous articles.[2a] One modification was introduced since one of the troublesome aspects of earlier procedures was the incomplete separation of ethane from methane and carbon monoxide at the temperature of liquid nitrogen. This was accomplished by using liquid nitrogen cooled to about −215°. Liquid nitrogen was placed between the walls of a cylindrical double-walled vessel which could be connected to an oil-pump. This jacket was placed inside of a standard dewar vessel, and the entire dewar and jacket were filled with liquid nitrogen. Pumping on the nitrogen lowered the temperature to the desired point. The temperature was measured by a thermocouple attached to the outside of the finger in which the gases were condensed. This finger was placed in the inner cylinder of the double-walled vessel. Analyses of known mixtures indicated that carbon monoxide and meth-

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[1] This work was supported in part by Contract N6onr.241, Task I, with the Office of Naval Research, United States Navy.

[2] (a) L. M. Dorfman and W. A. Noyes, Jr., *J. Chem. Phys.*, **16**, 557 (1948); (b) A. F. Trotman-Dickenson and E. W. R. Steacie, THIS JOURNAL, **72**, 2310 (1950); *J. Chem. Phys.*, **18**, 1097 (1950); *J. Phys. Colloid Chem.*, **55**, in press (1951). These articles contain references to pertinent earlier work.

[3] R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

[4] W. A. Noyes, Jr., *J. Phys. Colloid Chem.*, **55**, in press (1951). This paper was presented at the symposium on reaction kinetics organized by the Division of Physical and Inorganic Chemistry, American Chemical Society, Minneapolis, June 20, 1950.

[5] A. J. C. Nicholson, THIS JOURNAL, **73**, 3981 (1951).

[6] H. Sponer and H. Stücklen, *J. Chem. Phys.*, **14**, 101 (1946).

ane could be removed quantitatively from ethane by a Toepler pump under these conditions.[7]

Pyridine was Eastman Kodak Co. practical grade. It was precipitated as the zinc chloride double salt and recrystallized from absolute ethyl alcohol. The pyridine was liberated by concentrated sodium hydroxide and then stored over sodium hydroxide sticks. It was purified finally by bulb to bulb distillation, the middle third being retained.

A Hanovia S-100 medium pressure mercury arc was used usually as a light source. Radiation at 3130 Å. was obtained by interposition of a Pyrex plate 1 mm. in thickness. Longer wave lengths are not absorbed by the system under investigation, but some radiation at 3020 Å. would be transmitted by the Pyrex and absorbed by the acetone. For 2537 Å. radiation a quartz cell 5 cm. long filled with chlorine gas at 1 atm. pressure was interposed. A Hanovia SC2537 end-on lamp was used as a source of mercury resonance radiation. A Hanovia water cooled hydrogen lamp was used in a few experiments when wave lengths below 2000 Å. were needed. An aluminum spark similar to that described by Wiig and Kistiakowsky[8] was also used.

Results

(a) Effect of Pressure on $k_2/k_1^{1/2}$.—Methane and ethane were determined during photolysis of pure acetone in two different cells, one approximately 10 cm. in length and the other approximately 20 cm. in length. The calculations were performed by two methods: (1) by assumption that the true rates are given by the number of molecules formed per second divided by the volume of the light beam itself; (2) by the assumption that the true rates are given by the number of molecules formed per second divided by the volume of the vessel. In some instances the light beam was allowed to fill the entire vessel so that the two methods of calculation give the same ratio of constants.

Table I shows data obtained at different temperatures at various acetone pressures.

(b) Photochemistry of Pyridine.—The exposure of pyridine to 2537 Å. radiation at temperatures up to 240° produces little or no decomposition. The quantum yield of gaseous products is estimated to be below 10^{-5}. No decomposition was observed for the mercury photosensitized reaction at 2537 Å.

The mercury arc without any filter, a hydrogen discharge tube, and an aluminum spark all caused some decomposition of the pyridine, but the results are not quantitative. It is concluded that radiation of wave length less than 2000 Å. is essential for this decomposition. A polymer is deposited on the walls when these short wave lengths are used, and in this respect pyridine resembles benzene.[9] The polymer was extremely inert and resembled cuprene. Since it absorbs the radiation, the reaction does not proceed far before the rate becomes immeasurably slow. At low pressures of pyridine the polymer was more uniformly distributed throughout the vessel, and more gaseous products could be obtained.

TABLE I

EFFECT OF PRESSURE ON $k_2/k_1^{1/2}$

When only one value of $k_2/k_1^{1/2}$ is given, the light beam filled the entire cell. The products were measured in a volume of 820 cc. at 25°.

Total products $\times 10^3$ mm.	Time, minutes	Fraction of total gas products			Pressure, mm.	$k_2/k_1^{1/2}$ $\times 10^{13}$ light vol.	$k_2/k_1^{1/2}$ $\times 10^{16}$ cell vol.
		CO	CH_4	C_2H_6			
Cell: 9.8 cm. × 2.3 cm., inside dimensions. Light beam diameter: 1.23 cm. (entrance), 1.33 cm. (exit).							
$T = 120°$							
25.92	700	0.494	0.285	0.221	56	5.0	2.8
19.85	360	.468	.348	.184	92	5.0	2.8
18.91	268.5	.451	.388	.161	122	5.0	2.8
20.72	249	.440	.406	.154	154	4.6	2.6
20.74	190	.439	.417	.144	207	4.2	2.4
19.55	180.5	.429	.419	.152	209	4.1	2.3
19.91	170	.425	.437	.138	237	4.1	2.3
13.77	131.5	.448	.439	.203	131.5	3.3	
14.37	206.7	.461	.237	.302	48	3.2	
27.65	107.1	.435	.411	.154	238	3.0	
17.34	65.0	.440	.408	.152	232	3.1	
13.69	215.8	.446	.393	.161	116.5	5.1	2.8
26.61	110	.433	.385	.182	185	3.2	
21.12	240	.423	.402	.175	171	4.0	2.2
$T = 150°$							
19.59	207	.439	.490	.0813	156	8.7	4.9
20.94	194	.417	.505	.0778	188	8.1	4.6
17.14	305	.432	.475	.0928	82.5	11.5	6.5
17.47	535	.465	.411	.124	45.0	12.1	6.8
Cell: 19.8 cm. × 2.4 cm., inside dimensions. Light beam diameter: 1.1 cm. (entrance), 1.4 cm. (exit).							
$T = 120°$							
11.52	448	0.466	0.142	0.392	6.3	5.2	
25.42	410	.473	.304	.323	17.2	4.7	
26.05	231	.474	.241	.285	32.2	4.1	
34.4	200	.474	.289	.237	55.9	4.0	
21.38	65	.450	.377	.173	131	3.6	
25.78	180	.485	.246	.269	42.0	4.0	
24.06	160	.476	.276	.248	45.1	4.3	
23.04	226	.479	.233	.288	29.6	4.2	
23.12	225.5	.475	.231	.294	29.7	4.2	
28.22	180	.441	.399	.160	118.2	5.8	3.0
17.72	108	.445	.395	.160	124.5	5.6	3.0
$T = 180°$							
15.92	336	0.439	0.413	0.148	10.5	23.3	
22.86	162	.420	.487	.093	32.6	19.1	
24.78	123	.413	.505	.0824	49.1	16.8	
40.12	130	.399	.558	.043	88.7	17.5	
$T = 210°$							
27.12	549	0.416	0.502	0.082	9.4	46.1	
31.83	251	.396	.524	.080	26.0	28.2	
49.89	180	.382	.593	.025	66.4	32.4	

The analysis of the products obtained at these short wave lengths was difficult because of the small quantity. Empirically the hydrocarbons had the formula about C_2H_3, and considerable hydrogen was formed. Thus tentatively the products may be assumed to be a mixture of H_2, C_2H_2 and C_2H_4. No product containing nitrogen could be identified, but the work in this respect should not be considered to be conclusive.

(c) Reaction of Methyl Radicals with Pyridine.—Mixtures of acetone and pyridine vapor were irradiated by 3130 Å. radiation which is ab-

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(7) Detailed data showing the usefulness of the method and other details concerning the work herein described may be found in the Ph.D. Thesis of R. H. Linnell, Department of Chemistry, University of Rochester, 1950. This thesis has been circulated as a report to the Office of Naval Research, United States Navy.

(8) E. O. Wiig and G. B. Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

(9) *Cf.* J. E. Wilson and W. A. Noyes, Jr., *ibid.*, **63**, 3025 (1941).

sorbed only by the acetone. The rates of ethane and of methane formation were determined. The results of these experiments are shown in Table II.

TABLE II

PHOTOCHEMISTRY OF ACETONE–PYRIDINE MIXTURES AT 3130 Å.

The light beam filled the cell in all of these experiments, and $k_2/k_1^{1/2}$ is calculated as though the pyridine were not present. The products were measured in a volume of 820 cc.

Total products $\times 10^3$ mm.	Time, minutes	Fraction of total gas products			Acetone pressure, mm.	Pyridine pressure, mm.	$k_2/k_1^{1/2} \times 10^1$
		CO	CH_4	C_2H_6			
Cell: 19.8 cm. × 2.4 cm., inside dimensions.							
$T = 120°$							
22.74	90	0.479	0.379	0.142	109.8	16.6	4.2
23.97	311	.469	.233	.298	25.7	20.5	4.2
29.45	186	.473	.288	.240	56.0	20.1	3.8
$T = 180°$							
39.52	187	0.427	0.507	0.066	55.1	22.3	16.5
30.39	176	.421	.509	.070	45.7	20.7	18.2
$T = 210°$							
32.22	152	0.391	0.574	0.035	49.3	22.5	32
26.48	248	.394	.547	.058	24.3	23.8	34

Discussion

An examination of the data given in Table I will show in every case that the value of $k_2/k_1^{1/2}$ tends to increase at low pressures. This is true at all of the temperatures given, and it makes no difference whether the volume of the light beam or the volume of the cell is used in the calculations. The difficulty of choosing the proper volume to give the correct answer has been discussed elsewhere.[4,5] Usually, the agreement among various authors is better if the cell is filled with light and the volume of the cell is used.

The trend in $k_2/k_1^{1/2}$ with pressure may be due either to a possible effect of the walls or to the necessity for a third body for reaction (1). If the walls have an appreciable effect, the nature of the reaction occurring on them must be such as to lead to either too much methane or too little ethane relative to the reaction in the gas phase. No conclusive evidence exists for peculiarities of this type, but the necessity for a third body for reaction (1) needs to be explored.

A third body for reaction (1) may be introduced in several ways: (1) a truly triple collision may be necessary, *i.e.*, $R_{C_2H_6} = k_1(CH_3)^2(A)$; (2) two methyls may form a complex which can either be stabilized by collision or redissociate. This leads to an expression of the type

$$R_{C_2H_6} = k(CH_3)^2(A)/(1 + k'(A)) \qquad (3)$$

(3) one methyl may form a complex with another molecule, such as A which may either dissociate or react with the second methyl to form ethane. This leads to an expression of the type

$$R_{C_2H_6} = k(CH_3)^2(A)/(1 + k'(CH_3)) \qquad (4)$$

((A) denotes the concentration of acetone in the present experiments since this gas is presumed to be the one which acts as the third body).

The choice between the four possibilities, *i.e.*, a simple reaction (1) with no necessity for a third body and the three methods of introducing the third body is not absolutely definite. However, it will be noted in the data in Table I that in all cases the values of $k_2/k_1^{1/2}$ approach constancy at high pressures. This definitely disagrees with the first alternative in the preceding paragraph but is adequately accounted for by equation (3). The difficulty lies in choosing between equations (3) and (4),[5] but on the whole the evidence favors (3) rather than (4). In any case it is apparently not permissible to omit the third body completely from the rate expression unless the pressure is quite high. If it is so omitted, it must be remembered that the constant k_1 is in reality a complex constant.

No positive conclusions are possible from the data on the direct decomposition of pyridine except that absorption in the first banded region in the ultraviolet[6] does not lead to decomposition. Whether the pyridine molecule dissociates into acetylene and HCN at short wave lengths as might be expected by analogy with benzene[9] cannot be determined.

It is evident from the data in Table II that methyl radicals abstract hydrogen far more easily from acetone than they do from pyridine. There is sufficient scatter in the data to make it impossible to calculate any constant for the reaction

$$CH_3 + C_5H_5N = CH_4 + C_5H_4N \qquad (5)$$

since $k_2/k_1^{1/2}$ calculated as though the pyridine were not present agrees within experimental error with the values at corresponding temperatures interpolated from the data in Table I. It may be concluded either that the steric factor for reaction (5) is not over one per cent. of the steric factor for reaction (2) (if RH is acetone) or that the activation energy for reaction (5) is at least 2 kcal. greater than for reaction (2).

It should be remarked in conclusion that the data in Table I lead to the activation energy difference $E_2 - 1/2\ E_1$ for reactions (1) and (2) which agrees with that obtained by other authors.[2b,5] This is true whether the rates at high acetone pressures are used, or whether rates at low acetone pressures are used, but it is not possible to use the values at high pressures for one temperature and at low pressures for another and obtain the correct result. Thus ethane formation would seem to have the *same* activation energy either at low pressure or at high, and in both cases the evidence indicates it to be small.

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