The PhotoChemical Decomposition of Acetone at 3130A

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The photo-chemical decomposition of gaseous acetone in light of 3130A has been investigated at 26°C under conditions of high acetone pressure and low absorbed light intensities. The ratio C_2H_6/CO has been found to decrease substantially below unity at sufficiently low absorbed intensities, under which condition methane has been found as a major product, exceeding the amount of ethane at very low intensities. A kinetic analysis of these data has shown that only a free radical process for the formation of ethane and methane suffices to explain the experimental observations. The energy of activation for the reaction of a methyl radical with an acetone molecule to form methane has been determined as $E=6.5$ kcal./mole.

A LTHOUGH many investigations of the photo-chemical decomposition of acetone have been reported, completely unequivocal conclusions regarding several aspects of this reaction remain impossible. Particularly in the region of "banded absorption" about 3000A and above, the need for more data to permit an evaluation of the excited molecule mechanism proposed by Spence and Wild[1] was apparent.

Previous workers[2] have reported that the ratio of ethane to carbon monoxide in the products approaches a lower limiting value of unity with decreasing absorbed intensity and with increasing pressure of acetone. Differences in the experimental values of the C_2H_6/CO ratio reported by Spence and Wild[1] and by Herr and Noyes[2] led to a reinvestigation of the intensity dependence of the acetone decomposition. Davis[3] has re-

ported recently that the amount of methane formed at temperatures over 100°C may be quite large, and Spence and Wild[1] have shown that methane formation may be quite important at high pressures even at room temperature. A complete survey of the literature through 1946 has been made by Davis.[4]

This paper presents the results of experiments in which the absorbed intensity has been carried to a considerably lower range than has normally been employed in the photochemical decomposition of acetone.

EXPERIMENTAL

Two types of mercury arc lamp were used as the source of radiation: a Hanovia U A30 A2 medium pressure arc; a General Electric Company AH-6 high pressure arc. The filters used to provide monochromatic illumination with 3130A have been described.[5] The equations for the

[1] R. Spence and W. Wild, J. Chem. Soc., 352 (1937); 590 (1941).
[2] D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc. 62, 2052 (1940).
[3] W. Davis, Jr., J. Am. Chem. Soc., in press.
[4] W. Davis, Jr., Chem. Rev. 40, 201 (1947).
[5] R. E. Hunt and W. Davis, Jr., J. Am. Chem. Soc. 69, 1415 (1947).

557

TABLE I.

| Run no. | Temperature °C | Pressure mm | Absorbed intensity q/sec./cc $\times 10^{-12}$ | Fraction of gaseous products | | | $\dfrac{C_2H_6}{CO}$ | $\dfrac{\Phi_{CH_4}}{\Phi_{C_2H_6}^{\frac{1}{2}}}$ |
				CO	C_2H_6	CH_4		
8*	26.6	158.7	3.74	0.398	0.450	0.152	1.13	0.0834
7*	27.8	153.6	3.68	0.487	0.401	0.112	0.82	0.0665
2a, b	25.5	153.0	0.610	0.402	0.383	0.215	0.95	0.165
1	25.9	155.2	0.311	0.449	0.328	0.223	0.73	0.189
3	26.5	159.5	0.194	0.427	0.293	0.279	0.69	0.289
6	26.1	158.7	0.114	0.416	0.210	0.374	0.51	0.437

* AH-6 arc.

TABLE II.

| Run no. | Temperature °C | Pressure mm | Absorbed intensity q/sec./cc $\times 10^{-12}$ | Fraction of gaseous products | | | $\dfrac{\Phi_{CH_4}}{\Phi_{C_2H_6}^{\frac{1}{2}}}$ |
				CO	C_2H_6	CH_4	
9*	121.9	117.4	2.86	0.500	0.297	0.204	0.529
4b	121.2	107.2	0.203	0.434	0.114	0.458	2.07
4a	121.8	107.4	0.201	0.407	0.101	0.492	2.43
11	123.2	123.2	0.0875	0.439	0.077	0.485	2.66
12	122.9	115.1	0.0743	0.402	0.067	0.531	3.22

* AH-6 arc.

calculation of absorbed intensity have been presented in detail.[6,7]

The light intensity was reduced where necessary, by inserting in the light path additional filters of Corning No. 9863 glass, and, in the run with the lowest absorbed intensity, by interposing a thin-blown Pyrex window.

The photo-chemical decomposition of acetone itself was used as an actinometer, since it has been shown by various workers[2,8] that the
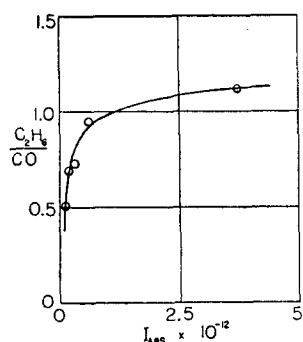

FIG. 1. The effect of absorbed intensity (quanta/cm³/sec. in the light beam) on the ratio of ethane to carbon monoxide during photo-chemical decomposition of acetone at 26°C and pressure of 156 mm. $\lambda = 3130A$.

[6] R. E. Hunt and T. L. Hill, J. Chem. Phys. 15, 111 (1947).
[7] W. Davis, Jr. and W. A. Noyes, Jr., J. Am. Chem. Soc. 69, 2153 (1947).
[8] J. A. Leermakers, J. Am. Chem. Soc. 56, 1899 (1934); C. A. Winkler, Trans. Faraday Soc. 31, 761 (1935).

quantum yield of carbon monoxide in this photolysis is unity at temperatures slightly in excess of 100°C.

The reaction vessel consisted of a cylindrical quartz cell, 200 mm in length and 22 mm in inside diameter. The light beam obtained from the U A30 A2 arc was parallel with a diameter of 15 mm, and consequently provided an illuminated volume of 35.4 cc. The AH-6 arc provided a slightly divergent beam with an incident cross section of 1.97 cm² and an emergent cross section of 2.39 cm² and, hence, an illuminated volume of 43.6 cc. The absorbed light intensity is expressed in quanta per second per cm³ of illuminated volume. It has been assumed that the absorbed intensity is uniform over the entire path length. The inaccuracy in this assumption is serious only at high percentage absorption.

Reagent acetone was purified by distillation in a 35-plate column, the middle third being retained, then dried over anhydrous copper sulfate. The gaseous products, CO, CH_4, and C_2H_6 were completely removed at −135°C using a Ward apparatus and Toepler pump. The products were analyzed by combustion on a hot platinum wire and in some experiments by combustion on hot copper oxide as well. These methods have been described by various authors.[2,7,9]

[9] W. M. Manning, J. Am. Chem. Soc. 56, 2589 (1934).

RESULTS AND DISCUSSION

The results which are recorded in the following tables are for runs which have been carried out at sufficiently high acetone pressures to ensure that wall reactions play only a negligible role. The homogeneity of the elementary reactions which occur is accepted as the basis for the theoretical considerations which follow. The validity of this assumption is established by the curves for C_2H_6/CO as a function of pressure obtained by Herr and Noyes[2] and by the work of Howland and Noyes.[10] The value of this ratio falls off sharply below 60 mm, but undergoes no profound change as the acetone pressure is increased above 100 mm.

Table I consists of the runs at room temperature, in which the absorbed intensity has been varied over a 32-fold range. Table II contains the runs carried out at 122°C, in which the absorbed light intensity has been varied 38-fold.

As may be seen in Table I, the value of the ratio C_2H_6/CO falls well below unity with decreasing absorbed intensity, and does not have a lower limiting value of unity as has previously been supposed. The curve of this quantity as a function of absorbed intensity is shown in Fig. 1. Similarly, a plot of C_2H_6/CO against acetone pressure would seem to result in a family of curves, each member of which approaches a lower limit as the pressure is increased. This lower limit for each individual member depends upon the intensity parameter, and falls well below unity at low intensities. This is shown in Fig. 2.

Methane becomes an important product at low intensities, and, in fact, at sufficiently low values of absorbed intensity, exceeds the amount of ethane in the products. It is clear then that the conclusion reached by Spence and Wild,[1] that at high pressures the single step decomposition of an activated molecule to form ethane and carbon monoxide is the most important process, cannot be correct.

Ethane may be formed by the recombination of methyl radicals:

$$CH_3 + CH_3 = C_2H_6; \quad k_1(CH_3)^2. \quad (1)$$
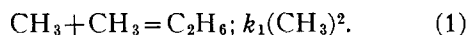
At the high experimental pressures used, this

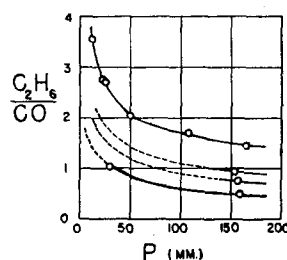[10] J. J. Howland, Jr. and W. A. Noyes, Jr., J. Am. Chem. Soc. 66, 974 (1944).

FIG. 2. The effect of pressure on the ratio of ethane to carbon monoxide during the photo-chemical decomposition of acetone at 26°C. The upper curve is from Herr and Noyes.[2]

reaction is homogeneous. Methane may be formed by the removal of a hydrogen atom from acetone by a methyl radical:

$$CH_3 + CH_3COCH_3 = CH_4 \\ + CH_2COCH_3; \quad k_2(CH_3)(CH_3COCH_3). \quad (2)$$
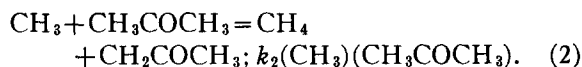
If reactions (1) and (2) represent the sole modes of formation of ethane and methane, respectively, the quantum yields of these products will be related by the following equation:

$$\Phi_{CH_4}/\Phi_{C_2H_6}^{\frac{1}{2}} = (k_2/k_1^{\frac{1}{2}})(Acetone/I_a^{\frac{1}{2}}). \quad (3)$$

Figure 3 shows a plot of $\Phi_{CH_4}/\Phi_{C_2H_6}^{\frac{1}{2}}$ as a function of $(Ac)/I_a^{\frac{1}{2}}$. The curve which results, a straight line through the origin, establishes the validity of reactions (1) and (2).

The acetonyl radicals may be disposed of by the formation of methyl ethyl ketone:[11]

$$CH_3 + CH_2COCH_3 \\ = CH_3CH_2COCH_3; \quad k_3(CH_3)(CH_2COCH_3), \quad (4)$$
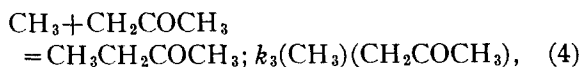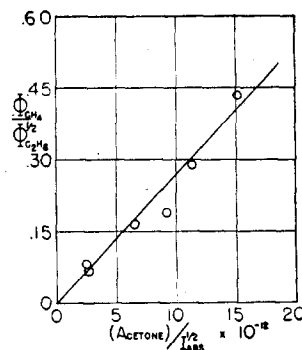
and by their combination to form acetonyl

FIG. 3. A plot of Eq. (3) at 26°C.

[11] A. O. Allen, J. Am. Chem. Soc. 63, 708 (1941).

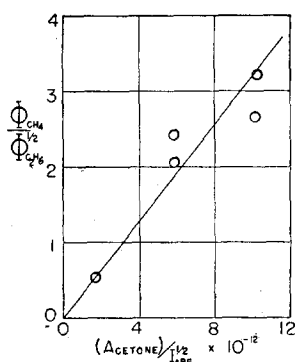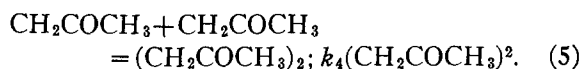FIG. 4. A plot of Eq. (3) at 122°C.

acetone:

$$CH_2COCH_3 + CH_2COCH_3$$
$$= (CH_2COCH_3)_2; \ k_4(CH_2COCH_3)^2. \quad (5)$$

This compound has been identified by Rice,

Rodowskas, and Lewis[12] as a product in the reaction of methyl radicals with acetone at 350°C.

The slope of the straight line in Fig. 3 gives $k_2/k_1^{\frac{1}{2}} = 2.70 \times 10^{-14}$ at 26°C. Figure 4 gives $k_2/k_1^{\frac{1}{2}} = 3.19 \times 10^{-13}$ at 122°C. Writing $k_2 = a_2 e^{-E_2/RT}$ and $k_1 = a_1 e^{-E_1/RT}$, these values may be used to calculate $E_2 - \frac{1}{2}E_1 = 5700$ cal. per mole. The $T^{\frac{1}{2}}$ factor in the pre-exponential term has been taken into account in this calculation. Taking the value of Cunningham and Taylor[13] for reaction (1), $E_1 < 1.5$ kcal./mole, gives

$$E_2 = 6500 \text{ calories per mole.}$$

This value is only slightly lower than the value of 7.1 kcal. mole obtained by Allen.[11]

[12] F. O. Rice, E. L. Rodowskas, and W. R. Lewis, J. Am. Chem. Soc. 56, 2497 (1934).
[13] J. P. Cunningham, and H. S. Taylor, J. Chem. Phys. 6, 359 (1938).

Thermodynamic Properties of the Internal Rotator. Double Minimum with Attractive Forces

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A previously outlined general method of calculating thermodynamic properties for an unsymmetrical internal rotation is applied to a double minimum with attractive forces, for which the potential energy has two maxima at the same height and two minima at different heights. The entropy is lower than that of the system of two equal potential valleys or that for a single valley, and can be lower than the former by as much as $R \ln 2$ when the potential barriers are high. This decrease tends to disappear in the region of close approach to free rotation, when the barriers are lower than RT. For very high potential barriers, if one of two equal minima is raised, the system acquires the properties of a simple harmonic oscillator.

IN a recent paper[1] it was shown that graphical old quantum-theory action integrals could be used to obtain mean positions of the energy levels of the symmetrical internal rotator from which the contributions of the internal rotation to the thermodynamic properties could be closely approximated. More recently[2] a scheme has been proposed for applying the old quantum theory when the rotation is not symmetrical. By assuming for the potential energy function a

succession of linked sections of simple cosine curve, it is possible to use the graphical integrations carried out for the symmetrical rotator to evaluate the properties of the unsymmetrical system. The results of these integrations are contained in a table (Table II, reference 2) showing ρ, a quantum-number index, as a function of E/V, the ratio of the energy to the barrier height when the zero of energies is placed at the bottom of the potential valley. For a rotation or vibration through the region above one or more potential minima, a new quantum-

[1] J. O. Halford, J. Chem. Phys. 15, 645 (1947).
[2] J. O. Halford, J. Chem. Phys. 16, 410 (1948).