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

Photochemical Studies. XXXVII. Some Tests of Mechanism for the Photochemical Decomposition of Acetone

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A study of the photochemical decomposition of acetone vapor was published several years ago.[2] Two important questions remain to be answered: (1) the importance of the decomposition of acetyl radical into methyl radical and carbon monoxide; (2) the homogeneity of this decomposition. Anderson and Rollefson[3] and Feldman, Ricci and Burton[4] as well as work in this Laboratory[5] have thrown much light on these important questions.

Spence and Wild[6] have published a discussion of earlier work[7] and have presented some new data. Comparisons were made between results obtained under different conditions, and some deductions made which may not have been justified.

It was claimed that the Herr and Noyes mechanism[2] explained the results only over a very narrow range of low intensities. The work herein presented was performed in an endeavor to answer some of the questions raised in the article of Spence and Wild.[6]

Herr and Noyes assumed a primary dissociation at all wave lengths whereas Spence and Wild assumed a primary dissociation only in the "continuum" below 2900 Å. The following steps have been proposed for the mechanism

(1) $CH_3COCH_3 + h\nu = CH_3CO + CH_3$ ϕI_a
(2) $CH_3CO = CH_3 + CO$ $b\phi I_a$
(3) $CH_3CO = CH_3 + CO$ $k_2\ (CH_3CO)$
(4) $2CH_3 + M = C_2H_6 + M$ $k_a\ (CH_3)^2\ (M)^{.5}$
(5) $CH_3CO \overset{\text{walls}}{=} 1/2(CH_3CO)_2$ $k_3\ (CH_3CO)/P$
(6) $2CH_3CO + M = (CH_3CO)_2 + M$ $k_b\ (CH_3CO)^2\ (M)^y$
(7) $2CH_3CO = (CH_3CO)_2$ $k_4\ (CH_3CO)^2$
(8) $CH_3 + CH_3CO + M = CH_3COCH_3 + M$ $k_c\ (CH_3)(CH_3CO)\ (M)^z$
(9) $CH_3CO + CH_3 = CH_3COCH_3$ $k_5\ (CH_3CO)(CH_3)$
(10) $CH_3 + CH_3CO = C_2H_6 + CO$ $k_d\ (CH_3)(CH_3CO)$
(11) $CH_3CO + M = CH_3 + CO + M$ $k_e\ (CH_3CO)\ (M)$
(12) $CH_3 \overset{\text{walls}}{=} 1/2\ C_2H_6$ $k_6\ (CH_3)/P$

The Spence and Wild mechanism is based on equations 1, 4, 6, 8, 10 and 11 whereas the mechanism proposed by Herr and Noyes is based on 1, 2, 3, 5, 7, 9, and 12, although reaction 7 was not considered in deriving the rate equations.

Spence and Wild emphasize the following points: (1) At low intensities the ratio ethane/carbon monoxide in the reaction products approaches unity with increasing acetone pressure whereas in their experiments at very high intensities they found the ratio to rise with pressure. These effects are predicted if the exponents y and z are less than 0.5. (2) The Herr and Noyes mechanism does not account for the rise in the above ratio with increasing intensity. This can be explained by the introduction of reaction 6 or reaction 7, a suggestion made by Herr and Noyes.[2]

There is no evidence that reaction 10 is important under any conditions. In any case it is unnecessary since 3 has been clearly demonstrated.[3,4] Acetone was photolyzed in a flow system in which methyl radicals were removed by a lead mirror, and the remaining acetyl radicals passed through a section warmed to 45°.[4] New methyl radicals were produced as shown by the formation of $Pb(CH_3)_4$ at a second lead deposit.[4]

For wave lengths above 3000 Å. (the so-called "banded" region) Spence and Wild have proposed an elaborate scheme involving two kinds of excited acetone molecules

(13) $CH_3COCH_3 + h\nu = CH_3COCH_3^*$
(14) $CH_3COCH_3^* = CH_3CO + CH_3$ $\tau = 10^{-8}$ sec.
(15) $CH_3COCH_3^* + M = CH_3COCH_3^{**} + M$
(16) $CH_3COCH_3^{**} = CH_3COCH_3$
(17) $CH_3COCH_3^{**} = C_2H_6 + CO$ $\tau = 10^{-2}$ sec.
(18) $CH_3COCH_3^{**} \overset{\text{walls}}{=} C_2H_6 + CO$

This mechanism was based on the fact that apparent reduction in the mean distance from the positions of the absorbed quanta to the walls of the vessel causes a decrease in the ethane/carbon monoxide ratio. The authors also felt that results of the full mercury arc lamp could not be explained by adding the effects of the separate spectral regions. Thus the observed ratio rose to a maximum of 2 and then fell to 1.5 with increasing intensity whereas in the "continuum" alone it rose steadily toward a value of 2.5.

Spence and Wild also point out that the data of Herr and Noyes for 3130 Å. show no decrease in quantum yield of acetone disappearance with increasing intensity as was found to be true at 2537 Å. They conclude that a mechanism not involving free radicals was indicated for the "banded" region.

Spence and Wild believe that reaction 14 and the free radical reactions which follow are important only at low pressures whereas at higher pressures 15 predominates and ethane and carbon

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[1] Fellow under the Sherman Clarke Fund for 1942–1943.

[2] D. S. Herr and W. Albert Noyes, Jr., THIS JOURNAL, **62**, 2052 (1940).

[3] H. W. Anderson and G. K. Rollefson, *ibid.*, **63**, 816 (1941).

[4] M. H. Feldman, J. E. Ricci and M. Burton, *J. Chem. Phys.*, **10**, 618 (1942).

[5] J. J. Howland, Jr., and W. Albert Noyes, Jr., THIS JOURNAL, **63**, 3404 (1941).

[6] R. Spence and W. Wild, *J. Chem. Soc.*, 590 (1941).

[7] R. Spence and W. Wild, *ibid.*, 352 (1937).

monoxide would be formed by 17 or 18. These last two reactions are theoretically improbable.[8]

There is no sound basis for believing that there is a difference in primary process as the wave length is changed. The so-called "continuum" below 3000 Å. and the diffuseness of the bands above 3000 Å. may be explained in the first case as a great deal of overlapping of structure[9] and in the second case possibly by predissociation.[10]

A major objection to the mechanism embodied in reactions 13 to 18 is its inability to explain the rise of the quantum yields to unity as the temperature is raised to 100°.[2] Only a small rise of absorption coefficient is observed experimentally up to this temperature and hence pronounced absorption from higher levels in the ground state can scarcely be the correct explanation.

The present paper presents results designed to test the various mechanisms more thoroughly since the quantum yields as well as the ratio of the gaseous products have been determined. At short wave lengths and high intensities the mechanism of Spence and Wild predicts a rise in biacetyl yield and a fall of carbon monoxide yield. For long wave lengths their mechanism predicts a decrease in biacetyl with decrease in cell size at constant intensity. Also a smaller cell should cause the yield of acetone decomposed to rise. The mechanism of Herr and Noyes leads to the opposite conclusion in the first two instances and to a rise in acetone yield for a smaller cell at all wave lengths. Also the mechanism of Herr and Noyes leads to little change with wave length except that b in equation 2 should increase with decrease in wave length, leading to higher yields of everything except biacetyl.

Experimental Procedure

The apparatus used was nearly identical with that of previous work in this Laboratory[2,5] using the Manning[10] gas analysis technique. Merck reagent acetone was redistilled three times, dried with anhydrous calcium sulfate and then distilled at room temperature into a blackened trap which was kept at −78°. A Hanovia Uviarc mercury lamp was the source of radiation. Filters of cobalt and nickel sulfates and of potassium biphthalate gave very pure 3130 Å. light. With this light the absorption by acetone obeyed Beer's law within the experimental error of 1–2%. For the shorter wave lengths, the biphthalate filter was replaced by one of chlorine gas. The latter combination transmitted all the lines from 2320 to 2804 Å. in significant intensities.

A series of photographs of the spectrum of the mercury arc were made with and without the filters to determine their transmission for the various lines. Lines on the plates were matched at densities where the reciprocity law is approximately valid. Then from the known distribution of the intensity throughout the lines of the arc[11] and the absorption coefficients of acetone,[12] the percentage absorption was calculated at both 57 and 160 mm. pressure. The calculated percentages agreed with those measured by the photoelectric cell within 1%. The calculations also showed that the 2537 and 2654 Å. lines account for 68% of the incident light, and 83% of it is between 2480 and 2700 Å. It will be referred to as 25–2700 Å.

The polychromatic nature of this light discredits any conclusion drawn from the apparent variations in the quantum yields with pressure or cell size. Beer's law failed even for small percentages of absorption. This filter system was also used by Spence and Wild and was the only combination which made possible the high intensities at which they found the pressure effect reversal. Light intensity was measured by a plane quartz window photoelectric cell which was calibrated both by means of a uranyl oxalate actinometer[13] and by runs on acetone at 100° where the quantum yields are believed to be unity.[2] The observed light absorption was corrected for reflections back into the reaction vessel from its rear window and from the window of the photoelectric cell. Since for light of 3130 Å. each window reflects 7.3% of the light incident upon it, and the transmission of the 1.5-mm. rear window is about 0.88,[14] the true absorption is

$$I_a = I_a' + 0.129 I_t I_a'/I_0$$

where I_0 is the intensity at the rear of the front window, I_t is the intensity at the front of the rear window, and $I_a' = I_0 - I_t$. At 25–2700 Å.

$$I_a = I_a' + 0.138 I_t I_a'/I_0$$

The correction for loss at the rear window was incorporated into the photoelectric cell calibration.

One of the cylindrical quartz vessels was 2.35 cm. inside diameter × 20 cm. long; the second was 2.2 cm. × 1.00 cm. Their respective volumes were 87 cc. and 3.80 cc.

Assuming that carbon monoxide, ethane, and biacetyl are the only products, the yields of acetone decomposed were calculated by the relation

$$N_{\mathrm{CH_3COCH_3}} = 2N_{\mathrm{C_2H_6}} - N_{\mathrm{CO}}$$

and those of biacetyl formed by

$$N_{\mathrm{(CH_3CO)_2}} = N_{\mathrm{C_2H_6}} - N_{\mathrm{CO}}$$

TABLE I

EFFECT OF PRESSURE ON QUANTUM YIELDS

T = 27°; wave length, 3130 Å.; I_a, 3 × 10^{12} quanta/cc./sec.

		Quantum yields			
P	$N_{\mathrm{C_2H_6}}/N_{\mathrm{CO}}$	CO formation	C_2H_6 formation	Biacetyl formation	Acetone decomposition
54	2.02	0.089	0.180	0.091	0.271
82	1.61	.099	.159	.060	.219
121	1.34	.106	.142	.036	.178
203	1.12	.125	.140	.015	.155
T = 27°; wave length, 25–2700 Å.; I_a = 1.2 × 10^{12} quanta/cc./sec.					
52	1.46	.268	.391	.123	.514
82	1.44	.261	.376	.115	.491
118	1.40	.250	.350	.100	.450
158	1.40	.244	.342	.098	.440
T = 27°; wave length, 25–2700 Å.; I_a = 1.2 × 10^{12} quanta/cc./sec.					
57	1.76	.240	.423	.183	.606
82	1.52	.240	.363	.125	.490
116	1.42	.228	.324	.096	.420
160	1.39	.211	.293	.082	.375

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(8) J. P. Howe and W. Albert Noyes, Jr., THIS JOURNAL, **58**, 1404 (1936).

(9) E. J. Bowen and H. W. Thompson, *Nature*, **133**, 571 (1934).

(10) W. M. Manning, THIS JOURNAL, **56**, 2589 (1934).

(11) Bulletin No. 112, General Electric Vapor Lamp Company, Hoboken, N. J., p. 2.

(12) C. W. Porter and C. Iddings, THIS JOURNAL, **48**, 40 (1926).

(13) P. A. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(14) W. Albert Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corporation, New York, N. Y., 1941, pp. 80, 84.

Table II

Experiments in Small Reaction Vessel, T = 27°; Wave Length, 3130 Å.

I_a	P	$N_{C_2H_6}/N_{CO}$	Quantum yields: CO formation	Quantum yields: C_2H_6 formation	Quantum yields: Biacetyl formation	Quantum yields: Acetone decomposition
2.76	53	1.95	0.100	0.195	0.095	0.290
3.19	215	1.38	.098	.136	.038	.174
T = 27°; wave length, 25–2700 Å.						
4.03	53	1.60	.236	.378	.142	.520
4.42	214	1.39	.220	.306	.086	.392
24.7	53	1.99	.222	.442	.220	.662
23.9	214	1.58	.206	.326	.120	.446

Results and Discussion

In order to make comparisons of the two reaction cells, some data are given in the form of tables. Other results are shown graphically only. Since the variation of quantum yields and of C_2H_6/CO ratio with pressure at 3130 Å. are nearly identical with those of the earlier work at about a five-fold lower intensity, they are not plotted here.

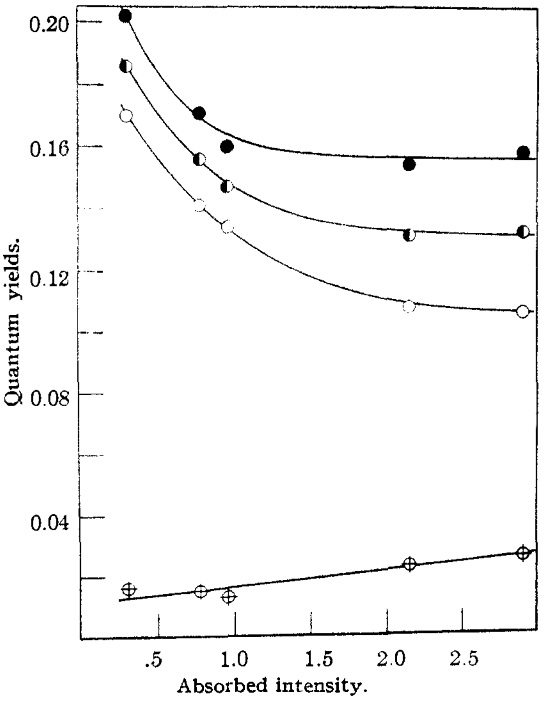

Fig. 1.—Effect of intensity on quantum yields: pressure, 120 mm.; wave length, 3130 Å.; ○, carbon monoxide; ◐, ethane; -⊕-, biacetyl; ●, acetone.

It is apparent that the quantum yield of acetone decomposition does fall off with increasing intensity even at 3130 Å. A higher pressure was selected than in the earlier[2] runs in order that the reactions of excited acetone molecules should have predominated if the Spence and Wild mechanism were correct.

The experiments using the smaller reaction cell and 3130 Å. show the reverse of the effect previously reported.[6] In that comparison, however, use was made of three different sets of data, two by the authors, four years apart, and with different analytical methods, and the third by Herr and Noyes.[2] Unfortunately, the mean distance from points of absorption of quanta to the walls in the work of Herr and Noyes was taken as 1 cm., the estimate given by the authors.[2] To be consistent with the mean distances used for the other two vessels, the mean shortest distance of 0.4 cm. ($^1/_3$ of the radius) should lie between the 0.6 and the 0.25 cm. used for the other cells. In the data of Spence and Wild the rise in ethane/carbon monoxide ratio with this mean distance at constant intensity is only from 1.05 to 1.2. The results in the larger cells scatter badly, one value being 0.89.

Although the light intensity in the "continuum" was well into the range where the rise in C_2H_6/CO ratio was reported, the opposite effect was found. The older results for about the same light intensity are given in Table III. Their units of I_a are cc. × 10^5 of acetone decomposed/hr./cc. 100 of these units equals 12 × 10^{12} quanta/cc./sec. Their effect is not great except for the run at 32 mm.

Table III

Results of Spence and Wild[5,6]

P, mm.	I_a	$N_{C_2H_6}/N_{CO}$
70	83.9	1.94
70	100.8	1.92
160	95.4	2.18
32	51.5	1.62
160	43.5	2.23

The drop in the yield of carbon monoxide with increasing pressure in the "continuum" favors the use of reaction (5). However, the apparent variation in quantum yields when using such polychromatic light should be viewed with suspicion. The combination of weaker absorption of acetone and greater sensitivity of the photoelectric cell at shorter wave lengths would be expected to cause an apparent drop in quantum yields with increased pressure (greater percentage absorption), since the increased absorption is actually less than measured and less than calculated by Beer's law.

The use of the smaller cell at 3130 Å. showed a slight increase in the yield of acetone decomposed as predicted by both mechanisms.

To attempt to explain satisfactorily results for an unfiltered arc is a nearly impossible and perhaps useless undertaking. Spence and Wild suggest that the fall in the C_2H_6/CO ratio with intensity increase at very high intensities is due to a reaction between excited acetone molecules resulting from absorption in the "banded" region and acetyl radicals produced by light of the shorter wave lengths.

$$(19)\quad CH_3COCH_3^* + CH_3CO = CH_3COCH_3 + CH_3 + CO$$

They felt this to be necessary also because the ratio C_2H_6/CO was too much lower than for the case of "continuum" light only.

It should be pointed out that most of the drop in C_2H_6/CO ratio with increasing intensity occurs at intensities not attainable with filtered light. It is possible that the same effect would take place with "continuum" light of sufficiently high intensity.

The general conclusion from the present study is that there is no evidence which definitely indicates that the decomposition by light of 3130 Å. is anything but a free radical reaction, just as for shorter wave lengths. In the "continuum" region, either of the two mechanisms is satisfactory as far as its ability to explain the known facts is concerned. The scheme of Spence and Wild is more cumbersome in that it requires an additional step which can also be objected to on theoretical grounds. One test which might have decided between the two free radical mechanisms, the variation of the yield of CO with pressure at high intensity, was inconclusive because of the polychromatic nature of the light. The generally higher C_2H_6/CO ratios as a result of decreasing the reaction cell size, while not very pronounced, favor the use of a wall process for biacetyl formation as opposed to the supposition of pressure dependence for the decomposition of acetyl radical. One of those alternatives is sufficient to explain the general pressure effects.

Summary

1. The quantum yield of acetone decomposition falls off with increasing intensity at 3130 Å. just as it does around 2500 Å.

2. With all other conditions and techniques held constant, a decrease in the reaction cell size causes a rise in the C_2H_6/CO ratio regardless of the choice of intensity, pressure, and wave length.

3. The reported increase in the C_2H_6/CO ratio with increasing pressure at high intensity was not confirmed. The reverse effect resulted for all intensities.

4. Our previously modified mechanism is found to be adequate for correlation of the definitely established facts. Particularly, the use of reactions of excited acetone molecules at 3130 Å. seems unnecessary.

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The Ionization Constants of Very Weak Acids. Acetoxime, Methyl Ethyl and Diethyl Ketoximes

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Difficulty has always been encountered in determining the ionization constants of very weak acids or bases. The conductance method fails when ionization is so small that conductance of water and its normal impurities become comparatively large, and the interpretation of conductivity in buffered solutions is uncertain. Hydrogen or other electrode measurements are useful in special cases, but usually only with very careful planning and interpretation. Rate measurements in which hydrogen or hydroxyl ion concentrations are determined from their catalytic effect on a suitable reaction have been often used. This method is capable of considerable refinement, and while not as accurate in general as other methods for the ordinary weak electrolytes, may be the best available for exceedingly weak ones. In the past salt effects have generally been ignored or inadequately treated. The purpose of the present work was to develop a method for determining acid dissociation constants of the order of 10^{-12} to 10^{-13} as a function of ionic strength with a reasonable degree of precision.

The Method.—A solution of acetoxime, unless in exceptionally pure water, would have an indefinite hydrogen ion concentration because the ionization is so small. A reaction sufficiently sensitive to hydrogen ion to be used in buffered solutions would probably be sensitive to general acid catalysis. The best procedure in such a case is to add the weak acid to a solution of strong base, and measure the extent of neutralization by means of a reaction only moderately sensitive to hydroxyl ion. From the rates the "hydrolysis constant" of the salt may be calculated.

For this purpose the catalyzed decomposition of nitrosotriacetonamine was chosen. The reaction has been studied in some detail by Francis and his co-workers,[1] by Brönsted and King[2] and by Kilpatrick.[3] The hydroxyl ion determination was first standardized by using solutions of sodium hydroxide, with sodium chloride to make up the ionic strengths desired. The previous work indicates that anions of even exceedingly weak acids do not catalyze the reaction, and the present work confirms this. The assumption is also made that in the specific salt effect, differences due to chloride, hydroxyl and weak acid anions are negligible.

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[1] Francis, *et al.*, *J. Chem. Soc.*, **101**, 2358 (1912); **103**, 1722 (1913); **107**, 1651 (1915).

[2] Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

[3] Kilpatrick, *ibid.*, **48**, 2091 (1926).