

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

Photochemical Studies. XXXIII. The Photochemical Decomposition of Acetone in the Presence of an Inert Gas

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The literature concerning the photochemical decomposition of acetone is extensive and will not be reviewed here.¹ It may be pointed out that in order to explain the variation of quantum yield of carbon monoxide formation with wave length, it was necessary to assume² that part of the acetyl radicals formed during the primary process retained enough energy to decompose spontaneously, the amount of energy so retained being a function of wave length. However, additional formation of carbon monoxide must result from the thermal decomposition of the acetyl radicals which have more or less attained equilibrium with the gas in the reaction vessel. Other important reactions of acetyl radicals may be: (1) combination to form biacetyl; (2) recombination with methyl radicals to form acetone; (3) reaction with methyl radicals to give ethane and carbon monoxide.³

In the previous work² it was assumed, with a good deal of justification, that the combination reaction of acetyl radicals to form biacetyl occurs largely on the walls. It seemed that the other reactions of acetyl radicals proceeded largely, if not entirely, in the gas phase.

In a recent article, Anderson and Rollefson⁴ have presented data relative to the behavior of acetyl radicals and have concluded that the association to biacetyl and the decomposition to carbon monoxide and methyl radicals are either both homogeneous or both wall reactions. This conclusion is based on results obtained with biacetyl in which approximately four times as much nitrogen as biacetyl was present.

Some experiments have been performed with large amounts of added carbon dioxide in an endeavor to decide more definitely whether the decomposition of acetyl radicals is homogeneous or heterogeneous.

While a quantitative interpretation of the data in terms of expressions for the quantum yield is difficult, the following variations with a high for-

eign gas pressure might be expected in the light of the mechanism previously advanced:² (1) since diffusion to the walls will be hindered, the homogeneous decomposition of the acetyl radical would be increasingly preferred as the pressure of foreign gas is increased, providing all other reactions of the acetyl radical are wall reactions; (2) since the recombination of methyl and acetyl radicals to give acetone was supposed to be a homogeneous reaction of low activation energy and high rate, its rate will not be markedly affected by the presence of foreign gas but, if anything, it should have a rate which will decrease slightly as the foreign gas pressure is increased *at a given concentration of radicals*; (3) since a relatively large fraction of the carbon monoxide is produced as a direct result of the primary process, the effect of foreign gas pressure on quantum yield of carbon monoxide formation will not be large, at least at room temperature.

On the basis of the reasoning outlined in the preceding paragraph, one should expect the quantum yield of carbon monoxide formation to increase, the quantum yield of acetone disappearance to increase slightly, and the ratio of ethane to carbon monoxide to decrease as the pressure of foreign gas is increased. Unfortunately, the analysis for ethane in the presence of a large amount of carbon dioxide did not prove to be very reliable so that all of these conclusions are not tested in the present work.

Experimental

Merck reagent acetone was dried with anhydrous calcium sulfate, fractionally distilled four times, and stored at -78° .

The carbon dioxide for most runs was "dry-ice" distilled once at -78° and twice at -130° . For some runs it was prepared by heating J. T. Baker potassium bicarbonate. The carbon dioxide was condensed by liquid nitrogen and separated from most of the water by distillation at -78° . It was then repeatedly passed through anhydrous magnesium perchlorate and distilled at -130° .

The apparatus and technique have largely been described.² The acetone and carbon dioxide were condensed into a wide trap attached directly to a two-liter spherical flask, and the gas uncondensed by liquid nitrogen was pumped off. The acetone was vaporized by warming the trap to 55° for thirty minutes while dry-ice was placed on

(1) For a recent summary see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," The Reinhold Publishing Co., New York, N. Y., 1941, pp. 356, ff.

(2) Herr and Noyes, *THIS JOURNAL*, **62**, 2052 (1940).

(3) Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

(4) Anderson and Rollefson, *THIS JOURNAL*, **63**, 816 (1941).

top of the flask. The mixture was allowed to stand four to ten hours, and then expanded through an all-glass magnetic valve into a cylindrical quartz reaction vessel (2.5×20 cm.). The light absorptions of pure acetone and of acetone mixed with carbon dioxide proved to be identical within 1%.

The carbon monoxide resulting from the reaction was removed by a Toepler pump while the acetone and carbon dioxide were condensed by liquid nitrogen. The analysis was performed by the method of Manning.⁵ The validity of the analysis in the presence of carbon dioxide was shown by adding carbon dioxide after exposure of the acetone to radiation but before the analysis.

As pointed out above, since only about 0.02% of the acetone was decomposed, the analyses for ethane proved to be unreliable. Rough measurements using liquid oxygen in place of liquid nitrogen as the condensing agent, and prolonged operation of the Toepler pump indicated that the ratio of ethane to carbon monoxide was still greater than unity in the runs made with carbon dioxide present.

It is assumed, as in the previous work,² that ethane, carbon monoxide and biacetyl are the only products. This is probably a very valid assumption.^{6,7}

Monochromatic light of wave length 3130 Å. was used,² although at high intensities the light was not so monochromatic as at low, and the quantum yields are slightly high under those conditions due to the presence of some radiation of short wave length. The results are shown in Table I.

TABLE I

EFFECT OF PRESSURE OF ADDED CARBON DIOXIDE ON THE QUANTUM YIELD OF CARBON MONOXIDE FORMATION FROM ACETONE

Temp., $25 \pm 1^\circ$; wave length, 3130 Å.; volume of vessel, 98 cc.

Acetone pressure, mm.	Carbon dioxide pressure, mm.	Absorbed intensity (quanta $\times 10^{-11}$ /cc./sec.)	Quantum yields		
			Acetone decomp.	Biacetyl formation	Carbon monoxide formation
67	0	1.18	0.264	0.052	0.160
64	0 ^a	1.12			.169
63	0 ^a	1.00			.158
65	320	1.11			.187
64	385	1.08			.212
63	413	1.06			.212
64	0 ^{a,b}	0.83			.169
64	511 ^b	.84			.233
69	0	23.0	.401	.133	.135
68	0 ^a	22.8			.139
70	258	22.4			.148
66	424 ^b	20.9			.163

^a 400 mm. of carbon dioxide was added after irradiation.

^b This carbon dioxide was prepared from potassium bicarbonate.

Discussion of Results

The results in Table I indicate quite clearly that the addition of several hundred millimeters of

(5) Manning, *THIS JOURNAL*, **56**, 2589 (1934).

(6) Barak and Style, *Nature*, **135**, 307 (1935).

(7) Spence and Wild, *ibid.*, **133**, 206 (1936); *J. Chem. Soc.*, 352 (1937).

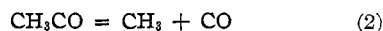
carbon dioxide produces a marked increase in the yield of carbon monoxide at relatively low intensities, but that the effect at high intensities is smaller in spite of the greater biacetyl formation under these conditions.

As pointed out previously,² the variation of the ratio of ethane to carbon monoxide with intensity necessitates the assumption that the reaction



proceeds to some extent homogeneously, as well as on the walls. At high intensities, therefore, where eq. (1) may proceed to a large extent in the gas phase the effect of added foreign gas in causing an increase in quantum yield of carbon monoxide formation would be expected to be small. This is in agreement with the findings of Anderson and Rollefson⁴ on the effect of added nitrogen on the decomposition of biacetyl since these authors used intensities several hundred fold larger than in either the previous² or the present work.

At low intensities the increase in quantum yield of carbon monoxide formation with added carbon dioxide is in good agreement with the assumption that eq. (1) takes place largely on the walls and the decomposition



is largely homogeneous.

While it is not possible to predict the effect of foreign gases on the quantum yield with high precision from the equations already published it can be shown that the addition of 400 mm. of carbon dioxide to 65 mm. of acetone should increase the yield of carbon monoxide from about 0.16 to about 0.20. This may be compared with the value of about 0.21 found in Table I.

Thus it is seen that the mechanism already advanced accounts satisfactorily, although qualitatively, for the data as long as the intensity is not too high.

Several other points should be mentioned. The role of collisions in deactivating the excited acetyl radicals produced from the primary process is not known. If the radicals do not decompose at once so that part of the primary process may really be written

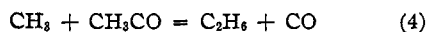


collisions may exert a deactivating effect. There seems to be no reason to believe this to be true on the basis of present data.

It might be possible also for perturbations due to collisions to cause dissociation of the excited

acetyl radicals. No evidence on these points is available, although the data of Anderson and Rollefson⁴ rather tend to disprove such an assumption. The decrease in carbon monoxide yield at low pressures is probably not sufficient to lend support to this hypothesis, although perhaps data at still lower pressures would be necessary to prove the point.

The reaction



suggested by Gorin³ is not very plausible from a theoretical standpoint, although kinetic studies do not offer very definite evidence one way or the other in this connection.

In conclusion it may be stated that the work herein presented supports the conclusion, previously drawn,² that the reaction leading to biacetyl and the reaction leading to carbon monoxide are both largely homogeneous at high intensities. Thus we agree with Anderson and Rollefson that the reactions are either both homogeneous or both heterogeneous under these conditions. At low intensities, however, we find support for the conclusion that the reaction leading to bi-

acetyl is largely a wall reaction and the reaction leading to carbon monoxide (apart from the primary process) is largely a homogeneous gas phase reaction. The picture of acetone decomposition is quite consistent and satisfactory, although it is unfortunate that quantitative expressions embodying all of the steps become so complicated that they cannot be applied to the data.

Summary

1. At low intensities the addition of large amounts of carbon dioxide to acetone causes an increase in the quantum yield of carbon monoxide formation from the latter.

2. It is pointed out that the data agree with the mechanism previously presented in which the reaction leading to carbon monoxide formation is a homogeneous gas phase decomposition of the acetyl radical. Part of the carbon monoxide is also formed during the primary process. The reaction leading to biacetyl seems to be largely a wall reaction at low intensities and to become increasingly a homogeneous gas phase reaction at high intensities and also at high pressures,

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The Base Catalyzed Decomposition of Nitramide in Aqueous Solution

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The first systematic study of the decomposition of nitramide $\text{H}_2\text{N}_2\text{O}_2$, into nitrous oxide and water was reported by Brønsted and Pedersen,¹ who showed that the decomposition was catalyzed by the ions of weak acids, the weaker the acid the greater the effect. As a result of this study they enunciated their theory of generalized acid and base catalysis. Thus the base catalyzed reaction was expressed by the equation

$$k_c K^\nu = G \quad (1)$$

where k_c is the rate of the reaction, K is the dissociation constant of the acid, G is a constant, and ν is a continuous function of K which varies from 0 for very weak acids, to 1 for very strong acids. This expression they derived by making the following assumptions: (1) if HA is a stronger acid than HB, then the specific rate of dissociation of HA is greater than that for HB and in

(1) Brønsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); see also Brønsted, *Chem. Rev.*, **5**, 231 (1928).

addition, the specific rate of association of H^+ and A^- is less than the corresponding rate for H^+ and B^- . (2) The catalysis by a base is of the same character as its association reaction with hydrogen ion, and so the specific catalytic rate is proportional to the rate of association. (3) In the region of very weak acids the association reaction approaches the limit where every collision is effective and so the base catalyzed reaction also must approach a limit. The variation in K in this region is due almost entirely to a variation in the rate of dissociation. The first assumption requires that ν be less than unity, the third, that it approach zero in the strong base region. The variation in ν introduces a curvature in the plot of $\log k$ vs. $\log K$. In the nitramide decomposition, ν was found to be a constant. This Brønsted and Pedersen attributed to the fact that the catalysts which they employed did not differ sufficiently in base strength.