chloride–sodium hydroxide ratio for the amount of dissolved silver chloride. The extrapolation of these corrected values of pK_2' is shown in Fig. 3. With these corrections the chloride solutions yield a value for pK_2, 7.192 or a value for K_2, 6.427×10^{-8}. Because of the uncertainties which prevailed with the use of the silver–silver chloride electrodes, in sulfite solutions, the authors have taken K_2, 6.24×10^{-8}, as the best value for this constant.

These values are in qualitative agreement with the previously reported pK_2 values. Britton and Robinson[16] report in measurements with glass electrodes by a titration method a value of pK_2, 6.99. Rumpf[17] reported a value of pK_2, 6.96, also measured by electrometric titration with glass electrodes; Britton and Robinson[18] 7.74 by titrations with the antimony-antimonous oxide electrode and 8.78 by titration experiments with tungsten electrodes.[19]

The correction for the solubility of silver bromide was found insignificant and therefore the value of the constant as determined by the bromide electrode is taken as the more reliable. The fact that the solubility correction for the chloride solutions is in the direction of the bromide value supports this view.

Summary

Determinations of the first and second ionization constants of sulfurous acid at 25° have been described. The values obtained are 1.72×10^{-2} for the first constant and 6.24×10^{-8} for the second. The first of these values is in fair agreement with previous determinations made by conductivity measurements. The value for the second constant is only in qualitative agreement with other reported values made by much less accurate methods.

The general behavior of glass electrodes in sulfite solutions has been described.

An investigation of the solubility of silver chloride in sodium sulfite has been described in consequence of which the complex ion, $Ag(SO_3)_2^{=}$, was detected.

SEATTLE, WASHINGTON RECEIVED NOVEMBER 18, 1940

[16] Britton and Robinson, *Trans. Faraday Soc.*, **28**, 531 (1932).

[17] Rumpf, *Compt. rend.*, **197**, 686 (1933).

[18] Britton and Robinson, *J. Chem. Soc.*, 458 (1931).

[19] Britton and Dodd, *ibid.*, 829 (1931).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Some Reactions of the Acetyl Radical

BY H. W. ANDERSON AND G. K. ROLLEFSON

The presence of the acetyl radical as an intermediate in the photolysis of certain carbonyl compounds has been reported by several investigators,[1-6] and its instability at higher temperatures has been noted. If, in addition to its decomposition into a methyl radical and carbon monoxide, the acetyl radical disappears by some other reactions which do not liberate carbon monoxide, the yield of carbon monoxide should be a measure of the importance of the decomposition relative to other competing reactions. If the stability of the acetyl radical decreases with increasing temperature, the carbon monoxide yields in the photolyses of different compounds which can form an acetyl radical might be expected to show similarities in their variation with temperature. To test this point, the temperature dependence of the carbon monoxide yield in the photolysis of acetone, diacetyl, and acetyl bromide vapor has been investigated from 0 to 140°, and is reported in this paper.

Experimental Details

Apparatus.—The vapors were decomposed in a cylindrical quartz reaction cell 5.0 cm. in diameter, 5.5 cm. in length, with plane faces. The cell was connected to a click gage, a reservoir closed by a greaseless glass valve, and a high vacuum system. The volume of the reaction system was 113.5 cc., of which 3.3% was dead space. The connection between the reaction system and pumps was closed by a stopcock lubricated with Airco Hy-Vac grease, which proved very resistant to the vapors of acetone and acetyl bromide. Sufficient experiments were run with acetone and acetyl bromide in which the stopcock was replaced by a greaseless glass valve to show that the presence of stopcock grease had no appreciable effect. Pressures were measured by a sulfuric acid manometer connected through the click gage to the reaction system. The gaseous products of the photolyses were transferred

[1] Barak and Style, *Nature*, **135**, 307 (1935).

[2] Spence and Wilde, *J. Chem. Soc.*, 352 (1937).

[3] Glazebrook and Pearson, *ibid.*, 567 (1937).

[4] Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[5] Etzler and Rollefson, THIS JOURNAL, **61**, 800 (1939).

[6] Herr and Noyes, *ibid.*, **62**, 2052 (1940).

by means of a Töpler pump to a micro gas analysis apparatus of the type described by Blacet, Leighton, and others.[7] The quartz cell could be surrounded by a removable furnace with a plane quartz window. The furnace was controlled manually to within ±1° of the desired temperature. The arc was a low pressure, gas-filled mercury arc which draws 25 m. a. at 15,000 v. Spectrograms showed that the mercury line at $\lambda 2537$ Å. constituted at least 90% of the effective radiation. The arc could be clamped into a fixed position to ensure nearly constant incident light intensity over the series of runs. The constancy of light intensity was checked by means of a photronic cell connected to a sensitive galvanometer.

Materials.—The acetone, diacetyl, and acetyl bromide, commercial products, were repeatedly fractionated and stored in the dark. The nitric oxide was prepared by reducing nitrite ion with iodide ion in acid solution. The gas was bubbled through sodium thiosulfate solution to remove iodine and dried over phosphorus pentoxide. Nitric oxide purified by more elaborate means gave identical results.

Carbon Monoxide Yield.—The differences in the course of the photolysis of the three compounds makes necessary a slightly different definition of the carbon monoxide yield in each case. For acetone, the carbon monoxide yield is calculated as the ratio of carbon monoxide formed to acetone decomposed at ~20% completion, for acetyl bromide it is the ratio of carbon monoxide formed to acetyl bromide decomposed at completion, and for diacetyl it is the ratio of carbon monoxide produced in twenty minutes of illumination to diacetyl initially present. The reasons for the different definitions of carbon monoxide yield are apparent from a consideration of the specific features of each case which are presented in the following paragraphs.

Acetone.—The principal products in the photolysis of acetone are carbon monoxide, ethane, diacetyl, and small amounts of methane.[2] Carbon monoxide and methane were pumped off at liquid air temperatures and ethane at −117°, the melting point of ethanol. The −117° fraction consisted solely of ethane. To avoid extensive decomposition of diacetyl by light of $\lambda 2537$ the decompositions were carried only to about 20% completion. It was possible to account with good accuracy for all of the products. From the initial pressure, the final pressure, the amounts of carbon monoxide, methane, and ethane pumped off, and the assumption that the residue involatile at −117° consists solely of diacetyl and acetone, the amounts of diacetyl formed and acetone decomposed can be calculated. At temperatures above 115°, where the ethane–carbon monoxide ratio is unity, the amount of carbon monoxide formed was taken as a measure of the amount of acetone decomposed. The material balances calculated from these data agree for the most part to within 1 or 2%; in certain cases, especially at low pressures, the error is as much as 5%. This generally good agreement indicates that whatever product accompanies the formation of methane may be neglected. Early experiments with acetone showed wide variations in carbon monoxide yield and rate of decomposition. Before reproducible results could be obtained it was necessary to run several photolyses at high temperatures; this treatment apparently conditioned the surface. It was also necessary to exclude traces of air; the first few runs after air was admitted to the reaction system were always erratic, even after prolonged pumping on the reaction cell.

Diacetyl.—Diacetyl decomposes photochemically to give carbon monoxide, ethane, and a small amount of methane, but the fact that the ratio of carbon monoxide to ethane is always greater than 2, even in experiments carried to completion, indicates that other products involatile at −117° are formed. However, by observing the same precautions as with acetone, the rate of formation of carbon monoxide is reproducible.

Acetyl Bromide.—Unlike acetone, acetyl bromide does not form diacetyl upon photolysis, but Etzler and Rollefson[5] were able to decrease the carbon monoxide yield markedly by the addition of an excess of nitric oxide, presumably due to the removal of an oxygen-containing radical by combination with nitric oxide.[8] In our experiments the carbon monoxide yield in the photolysis of acetyl bromide in the presence of a 4-fold excess of nitric oxide was studied. Since it was difficult to determine the extent of the decomposition under these conditions, illumination was continued until the decomposition of acetyl bromide was complete, as indicated by the absence of further pressure change. The gases not condensed by liquid air, consisting of carbon monoxide, some of the nitric oxide, and an inert residue, were pumped off and analyzed. Blank experiments showed that the RNO complex, produced in the room temperature photolysis, does not yield carbon monoxide thermally or photochemically at 120°, that nitric oxide and acetyl bromide do not react in the dark at 150°, and that the carbon monoxide yield is not affected by exposure to the arc for at least two hours after pressure change has ceased.

Results and Discussion

The results which we have obtained are shown in Tables I–IV and Figs. 1–3. They are tabulated in terms of moles and may be converted to concentration in moles per liter by multiplying by 8.8. Table I contains data from typical experiments which show the effect on the composition of the products of adding nitric oxide. $\Delta P/P_i$ is the change in the number of gaseous molecules present divided by the number of photoactive molecules initially present. Tables II and III and Fig. 1 show the effect of temperature on the composition of the products. Table IV and Figs. 2 and 3 show the change of carbon monoxide yield with pressure. In the acetyl bromide–nitric oxide experiments the ratio of nitric oxide to acetyl bromide initially present was approxi-

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[7] (a) Blacet and Leighton, *Ind. Eng. Chem., Anal. Ed.*, **3**, 766 (1931). (b) Blacet, MacDonald and Leighton, *ibid.*, **5**, 272 (1933). (c) Blacet and MacDonald, *ibid.*, **6**, 334 (1934). (d) Blacet and Volman, *ibid.*, **9**, 44 (1937).

[8] *Cf.* Rollefson and Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 118.

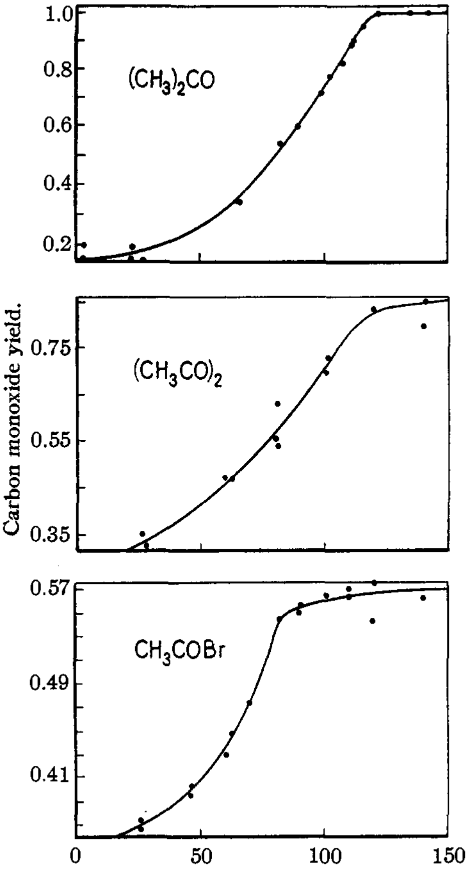

Fig. 1.—Effect of temperature on carbon monoxide yield.

mately 4; the points in Fig. 1 were obtained with an initial acetyl bromide concentration of $\sim 6 \times 10^{-4}$ mole per liter. Data on the effect

TABLE I

EFFECT OF NO

$(CH_3)_2CO$

Temp. 25°. Time of run 15 min.

Initial $(CH_3)_2CO$ (moles × 10^5)	8.05	8.39
Initial NO (moles × 10^5)	0	45.51
$\Delta P/P_i$ (%)	4.85	−24.8
Products (moles × 10^5):		
CO	0.39	0.15
CH_4	.05	< .02
C_2H_6	1.03	< .01
$(CH_3CO)_2$	0.69	...
NO	0	36.49[a]
$(CH_3)_2CO$ decomposed	1.77	...

[a] 2.6 × 10^{-5} moles of N_2 or N_2O are also formed.

$(CH_3CO)_2$

Temp. 25°. Time of run 20 min.

Initial $(CH_3CO)_2$ (moles × 10^5)	6.88	6.95	6.90
Initial N_2 (moles × 10^5)	0	26.42	
Initial NO (moles × 10^5)	0	0	27.31
$\Delta P/P_i$ (%)	32.9	29.8	−15.2
Products: (moles × 10^5)			
CO	2.41	2.37	0.33
CH_4	0.07	...	...
C_2H_6	.69	0.61	< 0.03
NO	...	...	23.00
CO yield	.351	.341	0.048

CH_3COBr

Temp. 25°. Time of run 120 min.

Initial CH_3COBr (moles × 10^5)	8.52	7.02
Initial NO (moles × 10^5)	0	27.36
$\Delta P/P_i$ (%)	94.6	−60.5
Products (moles × 10^5)		
CO	8.17	2.57
CH_4	0.74	0
CO yield	.959	0.366

TABLE II

$(CH_3)_2CO$

CHANGE IN PRODUCTS WITH TEMPERATURE

Temp., °C.	Initial $(CH_3)_2CO$ moles × 10^5	Products (moles × 10^5) CO	CH_4	C_2H_6	$(CH_3CO)_2$
3	24.39	0.80	0.09	2.85	2.20
3.5	24.75	1.10	.17	2.93	2.18
22	25.82	0.74	.08	2.69	2.01
22.5	25.33	.87	.12	2.58	1.76
26.5	25.23	.72	.09	2.70	2.04
64.5	24.95	1.68	.10	3.16	1.56
65.5	24.26	1.49	.13	2.74	1.40
82	24.18	2.99	.17	4.09	1.21
88	24.55	3.66	.19	4.57	1.19
98	24.71	4.51	.15	5.30	0.86
102	24.63	4.34	.16	4.70	.59
107.5	24.47	2.53	.23	2.67	.26
109.5	25.32	3.72	.22	3.91	.24
110	24.63	4.46	.15	4.62	.27
114.5	25.33	4.46	.18	4.48	.11
120.5	24.59	5.80	.20	5.70	0
133	24.02	3.63	.21	3.57	0
140	25.20	5.45	.40	5.29	0

TABLE III

$(CH_3CO)_2$

CHANGE IN PRODUCTS WITH TEMPERATURE

Time of illumination 20 min.

Temp., °C.	Initial $(CH_3CO)_2$ moles × 10^5	$\Delta P/P_1$, %	Products (moles × 10^5) CO	CH_4	C_2H_6
26	6.88	32.9	2.41	0.07	0.69
27.5	6.95	28.5	2.26	.10	.57
60	6.75	43.0	3.17	.02	.91
62.5	7.14	43.6	3.35	.08	.95
80	6.90	53.4	3.83	.09	1.23
80.5	7.04	57.5	4.41	.09	1.38
81	6.94	51.0	3.75	.14	1.15
100	6.85	66.5	4.76	.18	1.74
101	7.01	70.5	5.05	.25	1.87
119.5	7.10	82.5	5.91	.18	2.64
140	6.85	79.5	5.81	.29	2.26
140.5	7.10	78.5	5.69	.27	2.51

of pressure in the case of acetone are in agreement with the work of Herr and Noyes[6] and are not presented.

TABLE IV

$(CH_3CO)_2$

RELATIONSHIP OF CO YIELD TO PRESSURE

Temperature 25°. Time of illumination, 20 min.

Initial $(CH_3CO)_2$ moles $\times 10^5$	$\Delta P/P_1$, %	Products (moles $\times 10^5$)			CO yield
		CO	CH_4	C_2H_6	
0.61	123.0	0.71	0.03	0.35	1.16
3.16	64.5	2.11	.08	.73	0.668
19.61	12.3	3.08	.07	.78	.157
27.93	9.1	2.42	.07	.68	.087

Existence of the Acetyl Radical.—The presence of diacetyl among the products of the photolysis of acetone is in itself strong evidence that the acetyl radical is one of the primary products of the photodissociation. The formation of acetyl iodide when acetone is decomposed in the presence of iodine[4] substantiates this view. The data in Table I furnish additional evidence that the acetyl radical is one of the primary products in the photolysis of diacetyl and acetyl bromide as well as acetone. In each case nitric oxide decreases the carbon monoxide yield by a large factor. Nitric oxide is known to react with aliphatic radicals to form stable addition compounds, and the low carbon monoxide yields in the presence of nitric oxide suggest the formation of a stable compound between an acetyl radical and nitric oxide. The fact that a 4-fold excess of nitric oxide entirely eliminates the formation of methane and ethane but does not completely eliminate carbon monoxide formation from these substances indicates that acetyl reacts less readily with nitric oxide than does methyl. Thus, in Fig. 2, it is seen that even at very high concentrations of nitric oxide an appreciable amount of carbon monoxide is formed from acetyl bromide.[9] Furthermore, the absence of hydrocarbon formation from acetone and diacetyl under these conditions shows that the decomposition is probably entirely a free radical process when λ2537 Å. is used for excitation.

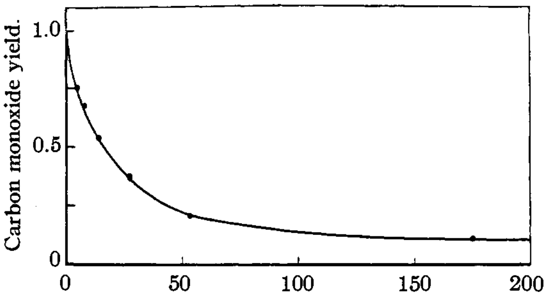

Fig. 2.—Effect of nitric oxide on carbon monoxide yield from acetyl bromide.

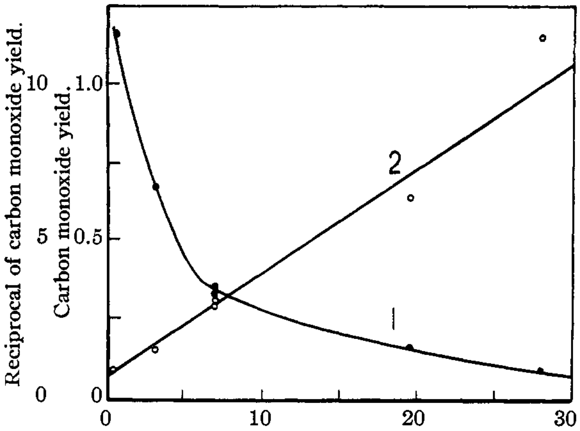

Fig. 3.—Effect of diacetyl pressure on carbon monoxide yield: Curve 1, carbon monoxide yield; curve 2, reciprocal of carbon monoxide yield.

Diacetyl offers the possibility of splitting into radicals in several ways, the two most probable being the rupture into two acetyl radicals and into a methyl and CH_3COCO radical. The data in Table I show that, under closely similar conditions, the carbon monoxide yield is decreased from 0.35 to 0.05 by the presence of nitric oxide. This, together with the entire similarity of diacetyl to acetone in the variation of its carbon monoxide yield with temperature, is good evidence that diacetyl splits into two acetyl radicals in the primary process.

Instability of the Acetyl Radical.—The temperature variation of the carbon monoxide yield for acetone, diacetyl, and acetyl bromide (Tables II and III) is plotted in Fig. 1. In this figure a different ordinate scale is used for each compound in order to emphasize the similarity of the 3 curves. In every case the carbon monoxide yield

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[9] In the experiments of Etzler and Rollefson[5] on mixtures of acetyl bromide and nitric oxide, it was found that the pressure change in the reaction approached a limit which was interpreted as corresponding to the reaction of every acetyl radical formed with nitric oxide. In our experiments we have found that this limit to the pressure change cannot be interpreted quantitatively as was done in that paper because some of the nitric oxide enters into a side reaction to form nitrogen and probably nitrous oxide. The direct determination of the carbon monoxide eliminates this difficulty. The nitrous oxide has not been identified by any positive test. What has been found in this work and some other done in this laboratory is that a gas is present at the end of the reaction which does not pump off completely at liquid air temperatures and which appears as nitrogen at the end of the analysis. Nitrous oxide seems to be the only substance which would fit these conditions.

begins to rise above 50° and levels off to a constant value at temperatures of $\sim$120° and above. In view of the similarity of the 3 curves, this increase in carbon monoxide yield with temperature may be attributed to the increasing rate of decomposition of acetyl relative to other reactions it may undergo which do not liberate carbon monoxide. The assumption of the instability of the acetyl radical has been used by other investigators to account for the variation in products with temperature in the acetone photolysis,[2,3,4,10] and to account for the decrease in intensity of fluorescence of various carbonyl compounds at elevated temperatures.[11] At a sufficiently high temperature all of the acetyl radicals should decompose. The levelling off of the curves above 120° suggests that such a condition has been attained, but the analyses show that this is not true in all cases. In acetone the carbon monoxide yield approaches unity as it should. In the mixtures of nitric oxide and acetyl bromide, however, the yield is far short of one, although in the absence of nitric oxide it reaches that value. Indications that the theoretical yield of carbon monoxide is not liberated in nitric oxide–acetone mixtures even at 140° have been obtained in this research. Gorin[4] has reported the formation of appreciable amounts of acetyl iodide in acetone–iodine mixtures under similar conditions. All of these facts point to the same conclusion: namely, that although the acetyl radical becomes increasingly unstable as the temperature is raised above 60°, it still has a lifetime long enough for it to enter into other reactions.

The reactions of the acetyl radical which must be considered in our experiments are: (1) decomposition into methyl and carbon monoxide, (2) formation of diacetyl, (3) reaction with nitric oxide when that gas is present, (4) reformation of the original substance. Any or all of these may occur partially or even entirely on the walls of the reaction vessel. Herr and Noyes[6] in the discussion of their work on acetone considered the formation of diacetyl and ethane from radicals to be heterogeneous, the combination of methyl and acetyl and the decomposition of acetyl as homogeneous. They considered that some of the acetyl radicals decompose on account of the high internal energy they contain at the moment of formation and the others lose this energy and decompose only after acquiring the necessary activation energy from other molecules. In our experiments the light intensities were approximately 300 times as great as in the experiments of Herr and Noyes. Although this fact should increase the importance of homogeneous reactions of the radicals over heterogeneous, the necessity for conditioning the walls of the reaction vessel by running several experiments before results became reproducible indicates that surface reactions must be considered even under these conditions. The conclusions which we believe can be drawn from our experiments on the three substances acetyl bromide, acetone and diacetyl are for the most part in agreement with those of Herr and Noyes based on acetone alone.

The hypothesis that some acetyl radicals decompose on account of the surplus energy they possess immediately after formation receives definite support from our data. If such an effect did not exist we should expect the carbon monoxide yield, especially for acetone and acetyl bromide, to approach zero instead of the finite value indicated by our experiments at low temperature (Fig. 1). The idea that those radicals which lose this initial energy decompose in a homogeneous first order reaction encounters difficulties with our data. If the reaction is homogeneous the carbon monoxide yield must approach unity as the temperature is raised since the decomposition of the acetyl radical is increasing in rate relative to the other reactions and in the limit must become the only reaction of significance. The observed behavior, especially for acetyl bromide, is definitely different so some limiting factor must be found. In our opinion the most reasonable assumption to make is that the decomposition of the radical is heterogeneous and the limit of the carbon monoxide yield is reached when every radical which reaches the wall decomposes. Thus, in the case of acetyl bromide the limit is determined by a competition between the reaction with nitric oxide and the diffusion to the wall.[12]

Further information concerning reactions of the acetyl radical can be obtained from the effect of nitrogen on the photolysis of diacetyl, as shown in Table I, and from the variation of carbon monoxide yield with diacetyl pressure shown in Table

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(10) Taylor and Rosenbloom, *J. Chem. Phys.*, **6**, 119 (1938).

(11) Matheson and Zabor, *ibid.*, **7**, 536 (1939).

(12) An alternative mechanism can be given if it is assumed that nitric oxide reacts with a photoactivated acetyl bromide molecule. Some evidence for such a reaction of nitric oxide has been obtained in some experiments in which diacetyl was illuminated with λ4358 Å.

IV and Fig. 3. The most probable reactions of acetyl in the presence of diacetyl are the decomposition and the association of two radicals to reform diacetyl. If these reactions of acetyl are both heterogeneous or both homogeneous, addition of nitrogen may be expected to have no effect on the carbon monoxide yield.[13] If one of the two reactions is homogeneous and the other heterogeneous, however, the rate of diffusion of acetyl to the wall and consequently the carbon monoxide yield should be affected by addition of nitrogen. The experiment listed in Table I shows no effect when approximately four times as much nitrogen as diacetyl is present, a result which has been confirmed by other experiments with various pressures of nitrogen. We therefore conclude that the reactions are either both homogeneous or both heterogeneous.

The variation of the carbon monoxide yield with diacetyl pressure illustrates the competition between the decomposition and association reactions of the acetyl radical. For the mechanism

$$\begin{aligned} A_2 + h\nu &= 2A \\ A &= CH_3 + CO \\ 2A &= A_2 \qquad (A = CH_3CO) \end{aligned}$$

it can be shown that for small fraction of light absorbed, constant incident light intensity, and small fraction of diacetyl decomposed, the carbon monoxide yield as we have defined it[14] is proportional to the quantity $[-C + \sqrt{C^2 + (A_2)}]/(A_2)$, where C is a constant. Although the fraction of the diacetyl decomposed at very low pressures was not small, the experimental curve in Fig. 3 is very similar in form to those obtained by plotting the above quantity as a function of diacetyl concentration. The deviations from the theoretical expression are best shown by a plot of the reciprocal of the carbon monoxide yield against diacetyl concentration; whereas the experimental points show almost linear variation with diacetyl concentration, those derived from the theoretical expression decrease in slope and deviate from linearity at high diacetyl pressures. This type of deviation might be expected if some diacetyl is reformed homogeneously by a 3-body process.

We are indebted to Mr. J. E. Tuttle for assistance with some of the experiments.

Summary

A study has been made of the carbon monoxide yield in the photolyses of acetone, diacetyl, and acetyl bromide between 0 and 140°. The results have been interpreted in terms of various reactions of the acetyl radical. It is concluded that the acetyl radicals are formed with such high energies that some of them decompose spontaneously into methyl and carbon monoxide. If this initial surplus of energy is lost by collisions, the radicals may either decompose or add to form diacetyl, the decomposition becoming increasingly important above 50°. The conditions under which these reactions occur and also the effect of adding nitric oxide have been discussed.

BERKELEY, CALIF. RECEIVED DECEMBER 9, 1940

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[13] It is possible that nitrogen may act as a third body in the association of two acetyl radicals, but it is known that nitrogen is not generally an efficient third body.

[14] Carbon monoxide yield = $(d(CO)/dt)/(A_2)$.

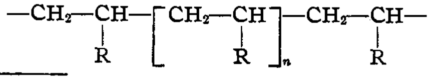
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Removal of Substituents from Vinyl Polymers. II[1]

BY FREDERICK T. WALL

When polyvinyl chloride or a copolymer of vinyl chloride and vinyl acetate is treated with zinc, part of the chlorine is removed as zinc chloride.[2] All of the chlorine is not removed because random removal of some of the atoms leaves others isolated in such a way that they can no longer be taken out. The amount of chlorine which remains after treatment with zinc depends upon the composition of the polymer and upon its structure.

The problem of calculating the fraction of chlorine remaining after treatment with zinc is a statistical one which has been considered for certain cases by P. J. Flory[3] and by F. T. Wall.[1] If the substituents are all in 1–3 relationship, such as



$$-CH_2-\underset{R}{\underset{|}{CH}}-\left[CH_2-\underset{R}{\underset{|}{CH}}\right]_n-CH_2-\underset{R}{\underset{|}{CH}}- \qquad (A)$$

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[1] For an earlier paper on this subject see THIS JOURNAL, **62**, 803 (1940).

[2] C. S. Marvel, J. H. Sample and Max F. Roy, *ibid.*, **61**, 3241 (1939).

[3] P. J. Flory, *ibid.*, **61**, 1518 (1939).