Free Radical Determination in Biacetyl Photolysis

Ralph G. Ascah, Milton Burton, John E. Ricci, and Thomas W. Davis

Free Radical Determination in Biacetyl Photolysis

RALPH G. ASCAH,[1] MILTON BURTON,[2] JOHN E. RICCI, AND THOMAS W. DAVIS

Department of Chemistry, New York University, New York, New York

(Received March 29, 1946)

Biacetyl vapors have been decomposed by radiation of wave-length 2537A in a flow system. The total amount of decomposition was determined by collection and analysis of the gaseous products. The amount of methyl radical formed was determined by allowing the products to pass over and react with lead mirrors. The amount of lead transported establishes the maximum quantity of methyl formed assuming a ratio of CH_3 to Pb of 4:1. The data show that approximately one methyl group is released for every two or three molecules of carbon monoxide in the products and consequently that about half of the total reaction proceeds without the primary formation of free radicals. A Spence and Wild type of reaction scheme will explain both the analytical data and observations on fluorescence.

THE formation of biacetyl in the products of acetone photolysis has been taken as indicating the intermediate formation of acetyl radicals.[3] Some confirmation of this conclusion is to be found in observations using mirrors.[4] The non-appearance of biacetyl when the walls of the reaction system are kept at temperatures above 60° has been taken as evidence that acetyl radicals are unstable at higher temperatures.[5] The instability of acetyl radicals has been investigated by mirror methods;[6] it is found that the half-life of radicals from acetone decomposition is greater at 45° than at 100°. The reason assigned is that the acetyl radicals decompose according to the equation

$$CH_3CO \rightarrow CH_3 + CO, \qquad (1)$$
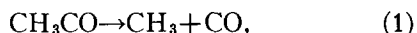
the reaction being slower at 45° than the disappearance of methyl radicals. The effect of (1) is constantly to renew the supply of methyl radicals as long as acetyl radicals remain. At 100°, on the other hand, reaction (1) is so fast that the gas stream carries only methyl radicals and without a supplementary source of additional radicals, the measured half-life is accordingly less than at 45°.

Since it would be desirable to have independent measurements of the rate of reaction (1), an attempt at such a measurement was made in connection with the study of the photo-chemical decomposition of biacetyl as a source of acetyl radicals, using the lead mirror technique. The plan was to remove all methyl radicals by contact with lead at one point, and then to pick up and count, by means of a second lead mirror further downstream, the new methyl radicals formed by acetyl radical decomposition in the intermediate region. It was further intended that through the use of different temperatures in this intervening zone, a variation in the rate of reaction (1) could be effected, whereupon an experimental energy of activation might be determined.

Actually this project proved impossible of accomplishment with lead as the agent for detecting the methyl radicals because the mirrors became insensitive when used at ordinary temperatures, and to maintain their sensitivity the mirrors had to be kept at 100°. At this temperature, the acetyl radicals decompose and the experiments give information only on the total radical content of the gas, that is, methyl plus all the acetyl radicals without distinguishing the kinds. Nonetheless the experiments were continued because they shed light not on the behavior of the radicals after they were released but rather on the nature of the original decomposition itself. If the initial reaction proceeds wholly to give free radicals (whether methyl or acetyl makes no difference when the mirrors are kept at 100°), the metal deposits should count one methyl radical for each molecule of carbon

[1] Present address: Canadian Industries, McMasterville, Quebec, Canada.
[2] Present address: Department of Chemistry, University of Notre Dame, Notre Dame, Indiana.
[3] M. Barak and D. W. G. Style, Nature 135, 307 (1935).
[4] H. H. Glazebrook and T. G. Pearson, J. Chem. Soc. 567 (1937).
[5] R. Spence and W. Wild, Nature 138, 206 (1936).
[6] M. H. Feldman, J. E. Ricci, and M. Burton, J. Chem. Phys. 10, 618 (1942).

Temperature °C	−13	0	10	15	21	26	30
Pressure mm		5.2	12	21	28	39	45	67

monoxide formed. It is on this investigation that we report in the present paper.

EXPERIMENTAL

Apparatus and Procedure

The experimental set-up resembles closely that used in earlier investigations in this laboratory.[7, 8] The procedure consisted of passing biacetyl vapor, drawn from a reservoir of the liquid, through a quartz tube 13 cm of which was illuminated by the radiation from a low pressure spiral mercury resonance lamp surrounding the tube. The lamp was operated on a 5000-v transformer, the primary current of which was maintained at 6.4 amp. from a 110-v circuit. The lamp gives light principally of wave-length 2537A. The gases leaving the illuminated region were allowed to flow over lead mirrors and the products resulting from this procedure were trapped and subsequently examined for their content of volatile lead compounds and for other gaseous constituents. As a rule, the experiments were run in two successive parts, without lapse of time between. Provision was made for collecting the gaseous products during only one of the two periods but lead was determined for both. This procedure not only allowed duplicate determination of lead but permitted a verification of the undiminished reactivity of the mirror. Any poisoning of the mirror during the experiment would be revealed by disagreement in the amounts of lead recovered during the two periods. In all experiments, the temperature of the illuminated zone was kept at 100°–105° but the tubing between the reaction zone and the mirror, when the two were not adjoining, was at room temperature.

Mirrors

The method of preparation of the mirrors has been described earlier.[6, 8] The sharpening of the

mirrors, and the clean-up of lead downstream were done with acetone, however, rather than with biacetyl. The acetone was supplied, of course, from a storage bulb separate from the biacetyl. Such use of acetone avoided deposition of non-volatile decomposition or polymerization products with consequent deactivation of the metal deposits. Furthermore, the availability of the acetone made possible a convenient testing of the effect of biacetyl on the mirror. The sharpening of the leading edge of the mirrors was especially necessary when the metal deposit was close to the illuminated zone because the gradient of free radical concentration in this region is high. Slight variations in the position of the mirror, therefore, would have a large effect on the amount of lead picked up. All mirrors were 3.0 cm or more in length, a length found sufficient to give full lead recovery. After a mirror was laid down and sharpened, the system was thoroughly pumped out to remove residual acetone vapors before the mirror was put to use. A new mirror was prepared for each experiment.

It was observed rather early in the course of the present work that the photolysis products of biacetyl desensitize mirrors kept at room temperature. The loss of sensitivity was shown by a decrease in the amount of lead picked up during a standard experiment with acetone. Similar poisoning by acetaldehyde and propionaldehyde has been attributed to polymer formation.[9] The notion that the poisoning of mirrors is caused by precipitation thereon of some slightly volatile material is supported by certain preliminary experiments. It was observed that in two successive runs with the same mirror at room temperature, the lead pick-up was reproducible if the apparatus was thoroughly pumped out between runs. On the other hand, the lead pick-up was much less for a continuous ten-minute run than twice that for a five-minute run. With the mirrors at 100°, the desensitization largely disappears; consequently, in all the experiments reported here the mirrors were kept at 100° by heating with steam.

[7] L. May, H. A. Taylor, and M. Burton, J. Am. Chem. Soc. 63, 249 (1941).
[8] M. H. Feldman, M. Burton, J. E. Ricci, and T. W. Davis, J. Chem. Phys. 13, 440 (1945).

[9] T. G. Pearson and R. H. Purcell, J. Chem. Soc. 1151 (1935).

Lead Analysis

The determination of lead was accomplished essentially by the procedure already described in the modified end-point technique.[6, 8] With known samples of lead nitrate and lead tetramethyl, containing 20 to 50 μg of lead, the accuracy of the determination was about 0.5 μg.

Gas Analysis

The gaseous products of the reaction were separated into two fractions, one consisting of gases volatile at liquid nitrogen temperatures, and the other of gases volatile at $-131°$ but not volatile at $-196°C$. The analyses were carried out in a semi-micro apparatus.[10] The gas volatile at $-196°$ is largely carbon monoxide as shown by the behavior over heated copper oxide and alkali. The remainder was shown by combustion with oxygen to be ethane. The material volatile at $-131°$ was found on combustion to behave exactly like a known sample of ethane and is reported therefore as ethane.

Materials

The biacetyl was a commercial preparation carefully fractionated, the portion boiling from 88.7 to 89.1°C being retained. The refractive index at 18.5°, namely 1.3930, checks closely the literature value. The biacetyl was stored at dry-ice temperatures and was carefully shielded from light. The vapor pressure of the substance was determined in the temperature range, $-13°$ to $+30°$. The measurements were made by immersing the storage bulb of biacetyl in constant temperature baths and observing on a mercury manometer the pressure developed by the vapor. The data are recorded in Table I.

The plot of log p vs. $1/T$ is quite linear and the heat of evaporation calculated therefrom is 109 cal. g^{-1}.

RESULTS

Data on the photolysis of biacetyl in the absence of a lead mirror appear in Table I .

The ratio of CO to C_2H_6 should be 2.0 If the sole products of decomposition are COi and

[10] K. W. Saunders and H. A. Taylor, J. Chem. Phys. 9, 616 (1941).

TABLE II. Products of biacetyl photolysis.
$\lambda = 2537A$; $t = 105-110°C$.

Expt. No.	Inlet flow pressure, mm	Time, min.	Gaseous products			−131°C fraction, vol.	Rate of production of CO[b]	Ratio CO/C₂H₆
			Liq. nitrogen fraction					
			Total vol.[a]	CO vol.	Vol. of residue			
23	3.6	5	13.50	12.70	0.82	4.83	2.54	2.2
24	3.6	5	12.90	12.70	0.21	5.31	2.54	2.3
25	3.6	10	25.4	24.9	0.47	11.05	2.49	2.2
26	3.6	10	25.7	24.9	0.75	—	2.49	—
76	3.6	5	8.51	—	—	—	(1.70)	—
77	3.6	5	8.21	—	—	—	(1.64)	—
89	3.6	5	6.85	—	—	3.13	(1.37)	<2.2
90	2.1	5	5.26	—	—	2.42	(1.05)	<2.2
93	2.1	5	5.35	5.11	0.24	2.36	(1.02)	2.0
94	1.6	10	6.97	6.65	0.32	2.78	(0.67)	2.1

Av.: <2.2

[a] All volumes are in units of 10^{-2} ml at S.T.P.
[b] Units of 10^{-2} ml/min.

C_2H_6. The average value of 2.2 suggests the formation of products more highly methylated than the starting substance. Several possibilities will be considered in the discussion below. A trend in the absolute amounts of carbon monoxide produced is without theoretical significance. It was noted that the figures for the amount of carbon monoxide produced per unit of time decreased with continued use of the apparatus. This trend is probably a consequence of decreased light input which in turn was caused by the repeated heating of the tube during the preparation of the mirrors. The quartz tube, it was noted, became visibly darker during the course of the experiments and no doubt this affected the transparency to ultraviolet.

Data from runs with mirrors at "zero" distance, that is to say, immediately adjacent to the region of illumination, appear in Table III. In preparing this table, it is assumed that the only reaction proceeding at the lead surface is $Pb + 4CH_3 \rightarrow Pb(CH_3)_4$. Each microgram of lead, therefore, is equivalent to 4.335×10^{-4} ml of gaseous CH_3 at S.T.P. or to one-half of this amount of ethane. The symbol ΣC_2H_6 is defined as a sum, viz.,

$$\Sigma C_2H_6 = C_2H_6 + \tfrac{1}{2}CH_3.$$

It is the total volume of ethane to be expected if all the methyl radicals were to combine to give ethane. The ratio $CO/\Sigma C_2H_6$ in experiments with mirrors replaces the ratio CO/C_2H_6 in experiments without mirrors as a kind of material-balance for the reaction. The expected

TABLE III. Products from biacetyl photolysis with mirrors at zero distance.

Expt. No.	Inlet pressure, mm	Time, min.	Pb found, μg	CH₃ (vol.)[a] equivalent to Pb	Gases (vol.)[a] CO	C₂H₆	CO production rate[b]	CO/CH₃	Ratios CO/C₂H₆	CO/ΣC₂H₆
69	3.6	5.0	41							
		2.5	21							
74	3.6	2.5	23							
		5.0	42	1.82	8.45		1.69	4.6		
75	3.6	2.5	17							
		5.0	40	1.73	8.45		1.69	4.9		
83	3.6	2.5	22							
		5.0	47	2.04	7.92	3.43	1.58	3.9	2.3	1.8
86	3.6	5.0	33							
		5.0	43	1.86	7.69	2.84	1.54	4.1	2.7	2.0
87	3.6	5.0	40							
		5.0	44		7.27	2.72	1.45	3.8	2.7	2.0
										Av. 1.9
71	2.1	5.0	43							
		2.5	21							
79	2.1	2.5	15							
		5.0	30	1.30	6.45		1.29	5.0		
80	2.1	2.5	14							
		5.0	33	1.43	6.33	2.42	1.27	4.4	2.6	2.0
81	2.1	2.5	14							
		5.0	32	1.39	6.33		1.27	4.6		
82	2.1	2.5	22							
		5.0	34	1.47	6.26	2.42	1.25	4.3	2.6	2.0
										Av. 2.0
78	1.6	2.5	8							
		5.0	19	0.82	4.61		0.92	5.6		
84	1.6	5.0	10	0.43	4.08	1.42	0.82	9.4	2.9	2.5
85	1.6	10.0	26							
		10.0	30	1.30	7.69	2.72	0.77	5.9	2.8	2.3
88	1.6	10.0	41							
		10.0	42	1.82	7.04	2.42	0.70	3.9	2.9	2.1
										Av. 2.3

[a] In 10^{-2} ml at S.T.P.
[b] In 10^{-2} ml/min.

value is 2.0. The average value observed is about 2.1 with a few scattered results as high as 2.5 or as low as 1.8. There is no trend in the ratios deviating considerably from the average.

Correction for Radical Disappearance

Not all the radicals formed in the photolysis reach the mirrors even when the mirrors are immediately adjacent to the irradiated zone because some of the radicals disappear while traveling past the lamp on their way to the mirror. To determine the proportion of radicals thus escaping detection as lead tetramethyl, it is necessary to know the half-life of the radicals and the time taken to reach the mirrors. The time of transport was determined by weighing the amount of biacetyl flowing in a fixed time with various inlet pressures. The measurements indicated an initial velocity of 1380 cm sec.$^{-1}$ when the inlet pressure was 2.1 mm. The formula of Paneth and Lautsch may be used to convert distance of flow into time.[11] This formula corrects for the change in velocity due to change in pressure as the gas flows through the tube.

The half-life of the methyl radicals was established by measuring lead recovery with mirrors at different distances from the region where the radicals are formed. The half-life was found to be 2.5×10^{-3} sec., a figure which may be compared with 8×10^{-3} sec. and 4.8×10^{-3} sec. for the half-lives of methyls from acetone photolysis at streaming velocities of 3000 cm sec.$^{-1}$ and 1800 cm sec.$^{-1}$, respectively.[6, 7] These values point to a possible dependence of half-life on rate of gas flow. Since the same type of apparatus of nearly identical dimensions was used in all three investigations, the differences in half-lives cannot be attributed to differences in geometry or differences in general procedure. The data on which the half-life is based in the present study appear in Table IV and are plotted in Fig. 1.

If no allowance is made for a concentration gradient over a given cross section of the reaction tube, a first-order disappearance of methyl radicals should lead to a straight-line plot of $\log \gamma$ vs. z where z is the time of transport and γ is the quantity of alkylated lead recovered per unit amount of carbon monoxide. The experimental data when plotted in this way do fall on a nearly straight line. But a plot of $(\gamma)^{\frac{2}{3}}$ vs. z is also nearly linear as required for a three-halves order reaction. The data, therefore, do not cover a sufficient range to allow a decision as to

[11] F. Paneth and W. Lautsch, Ber. **64**, 2708 (1931).
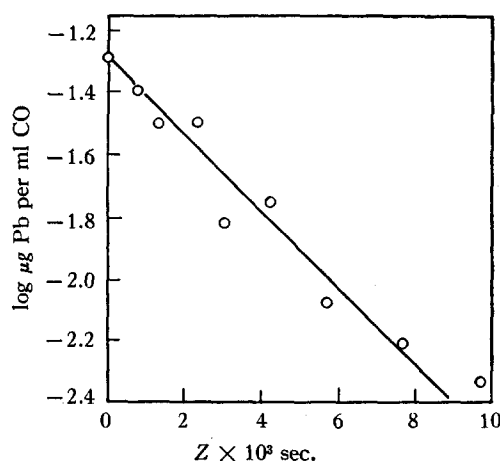

FIG. 1. Plot of first-order disappearance of methyl radicals outside the illuminated zone.

whether the disappearance is first or three halves order. Both possibilities are considered in further calculations.

The calculation of the quantity of free radicals disappearing within the illuminated zone is made by the method already described for the photolytic decomposition of acetone.[8] The rate of change of methyl in the illuminated region is given by the expression

$$\frac{d[CH_3]}{dz} = k_1 - k_2[CH_3]^n.$$

k_1, the rate of production of CH_3, is assumed constant for fixed conditions of T, P, and illumination (valid if the percentage of decomposition of biacetyl is very small). k_2 is the disappearance rate constant; its value, depending on the order assumed, i.e., n, is estimated from the half-life experiments.

Integration gives k_1 in terms of k_2, n, $[CH_3]$ and z, or $k_1 = f(k_2, n, [CH_3], z)$; the total amount of CH_3 produced is then $z_0 k_1$ or $z_0 f(k_2, n, [CH_3], z)$, where z_0 is the time of travel through the illuminated zone. The introduction therefore of the specific values of $[CH_3]_0$ and z_0, ($[CH_3]_0$ being the amount of CH_3 equivalent to the lead picked up per unit time at z_0, that is, as the gases leave the illuminated zone), gives $z_0 k_1$, or the total production of CH_3 per unit time, for any given value of n and hence of k_2; and $z_0 k_1$ may then be compared with the amount of CO produced per minute, as the final significant ratio. On the

TABLE IV. Rate of disappearance of methyl radicals from a gas stream at room temperature.

Expt. No.	Inlet pressure, mm	Duration of expt., min.	Mirror distance, cm	Time to reach mirror, ms.	Pb found, μg	CH₃ (vol.)[a] equivalent to Pb	Gas (vol.)[a] CO	C₂H₆	CO/ΣC₂H₆
100	2.1	5	1.8	0.81	20				
		5			22	0.95	5.44	2.07	2.1
99	2.1	5	3.0	1.35	16				
		5			17	0.74	5.50	2.30	2.1
104	2.1	5	5.4	2.38	14				
		10			34	1.47	10.51	4.14	2.2
98	2.1	5	7.0	3.05	9				
		5			9	0.39	5.86	2.54	2.1
103	2.1	5	10.0	4.26	8				
		10			20	0.87	11.40	4.55	2.3
97	2.1	5	13.8	5.70	5				
		5			5	0.22	5.97	2.60	2.2
101	2.1	15	19.5	7.70	12.5				
		15			10.5	0.45	17.5	6.74	2.5
102	2.1	15	26.0	9.70	8.2				
		15			7.6	0.33	16.1	7.15	2.2
									Av. 2.2

[a] In 10^{-2} ml at S.T.P.

assumption that $n=1$, we find 0.42 ml of CH₃ produced per ml of CO. With $n=\frac{3}{2}$, we calculate 0.55 ml of CH₃ per ml of CO. These results refer to decomposition at 2.1 mm pressure of biacetyl. The corresponding figures, with $n=1$, and assuming k_2 independent of pressure (because data on half-lives were secured at the one pressure only), are 0.37 and 0.39 ml of CH₃ per ml of CO at 1.6 mm and 3.6-mm pressure, respectively. The "corrected" figures for total CH₃ production therefore are about double the uncorrected values.

The free radical disappearance in the illuminated zone is calculated as if this zone were at room temperature. This procedure leads to a maximum calculation of free radical production because the rate of decay of free radicals is less at higher temperatures than at low. That some of the radicals disappear in the gas phase as well as at the wall is possible but the experimental k_2 values do not distinguish between the processes. Use of the experimental k_2's includes allowance for both reactions.

While the over-all precision of the results is low, refinements in the calculations resulting from consideration of temperature gradients along the reaction tube and possible formation of Pb₂(CH₃)₆, etc., would lead to smaller calculated free radical production. The ratio of reaction proceeding by rearrangement to total reaction may be regarded, therefore, as a minimum value.
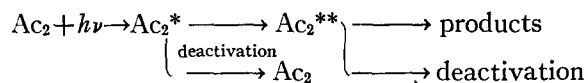
DISCUSSION

To be useful in interpreting the course of the reaction, the lead transported in these experiments must represent all or a known fraction of the methyl radicals produced. The experiments of Paneth and his co-workers show that probably all the methyl radicals reaching a film of lead are converted to lead tetramethyl.[12] A fuller discussion of the possibilities appears in an earlier paper,[8] and the arguments there presented apply equally well here. The weight of

[12] F. Paneth, W. Hofeditz, and A. Wunsch, J. Chem. Soc. 372 (1935).

evidence indicates that all the radicals coming to the mirrors are converted to volatile lead alkyls and probably to lead tetramethyl. On the basis of this statement, the data of this paper establish the fact that a very appreciable fraction of the biacetyl photolysis proceeds by a direct rearrangement into stable products. If the photolysis were wholly a process giving free radicals, 2.31 mg of Pb, equivalent to 1 ml of CH_3, should be recovered for every ml of CO produced. Actually the amount of lead found was much smaller than this and, as shown earlier, the value is between 0.86 and 1.25 mg, corresponding to .37–.55 ml of CH_3. Half of the reaction, therefore, seems to involve no free radicals at all.

The same situation is encountered in acetone photolysis.[8] When acetone molecules absorb light of proper frequency, they either split rather quickly into free radicals or, as a result of collision with other molecules, are put into a metastable state from which they are removed by collisional deactivation or by fission into stable molecules. Such a scheme was originally suggested by Spence and Wild.[13] Bowen and Horton[14] have suggested a somewhat similar course is biacetyl photolysis, namely,

$$Ac_2 + h\nu \rightarrow Ac_2^* \longrightarrow Ac_2^{**} \longrightarrow products$$
$$\begin{cases} \xrightarrow{\text{deactivation}} Ac_2 \end{cases} \longrightarrow deactivation$$

where Ac_2^{**} may be a tautomeric form of biacetyl. Almy and Anderson[15] have proposed independently a corresponding mechanism to explain fluorescence phenomena in biacetyl, namely,

$$Ac_2 + h\nu \underset{\text{fluorescence}}{\rightleftarrows} Ac_2^* \rightleftarrows Ac_2^{**} \text{ (long lived).}$$
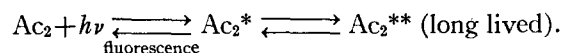
A combination of these schemes will account for the data presented in this paper if we assume also that the formation of free radicals occurs from the initially excited state and that the decomposition of the metastable molecules gives stable products.

The lead mirror experiments, while showing that the photo-decomposition proceeds partly by

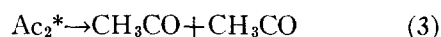[13] R. Spence and W. Wild, J. Chem. Soc. 352 (1937); 590 (1941).
[14] E. J. Bowen and A. T. Horton, J. Chem. Soc. 1505 (1934).
[15] G. M. Almy and S. Anderson, J. Chem. Phys. 8, 805 (1940).

way of free radicals and partly by ultimate molecule rearrangement, do not themselves establish the nature of the free radical intermediates. Bergmann and Samuel[16] have considered the photolysis of biacetyl theoretically and have concluded that at long wave-lengths, the important reaction is
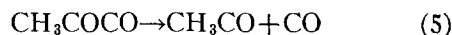
$$Ac_2 \rightarrow CO(^1\Sigma) + CH_3 + CH_3CO. \tag{2}$$
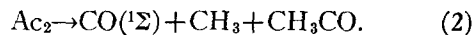
Other possibilities in our experiments leading to free radicals are

$$Ac_2^* \rightarrow CH_3CO + CH_3CO \tag{3}$$

and

$$Ac_2^* \rightarrow CH_3 + CH_3COCO, \tag{4}$$

followed at 100° by

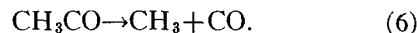$$CH_3COCO \rightarrow CH_3CO + CO \tag{5}$$

and

$$CH_3CO \rightarrow CH_3 + CO. \tag{6}$$
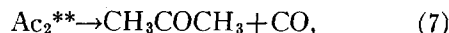
The molecular rearrangement would presumably be a slower reaction, depending, as it must, on the matching of several phase relations. The rearrangement may give three stable products, namely, ethane, acetone, and carbon monoxide, thus,

$$Ac_2^{**} \rightarrow CH_3COCH_3 + CO, \tag{7}$$

$$Ac_2^{**} \rightarrow C_2H_6 + 2CO. \tag{8}$$

These two reactions proceed simultaneously with the free radical splits.

The free radicals released in reactions (5) and (6) disappear ultimately by reaction with each other to give ethane and carbon monoxide. That they do not react with biacetyl molecules to cause cracking of the biacetyl is shown by the fact that the presence of a mirror has no effect on the total carbon monoxide production. The following reactions, therefore, have no large importance in our own experiments:

$$Ac_2 + CH_3 \rightarrow C_2H_6 + CH_3COCO, \tag{9}$$

$$Ac_2 + CH_3 \rightarrow CH_3COCH_3 + CH_3CO; \tag{10}$$

also,

$$Ac_2 + CH_3 \rightarrow CH_4 + CH_2COCOCH_3. \tag{11}$$

Reaction (11) is eliminated because no methane appeared in the products; had as much as 1 or 2 percent been formed, it would have responded to our repeated test for it.

[16] E. Bergmann and R. Samuel, J. Org. Chem. 6, 1 (1941).

Operating at somewhat higher pressures and higher temperatures, Roof and Blacet[17] observed a very important amount of methane in biacetyl photolysis and indeed, except at 25°, found more methane than ethane. The proportion of methane reported by Roof and Blacet nearly matches that in the pyrolysis as observed by Rice and Walters.[18] Reaction (9) is regarded by Rice and Walters as unlikely on theoretical grounds for it means capture of an exposed negative group by a free radical.[19] The reaction

$$CH_3 + CH_3CO \rightarrow C_2H_6 + CO, \qquad (12)$$

while not objectionable theoretically, is not important in acetone photolysis under conditions similar to those in our experiments, and probably plays no important part in the photodecomposition of biacetyl.

While hydrogen, methyl, or acetyl groups seem not to be captured from biacetyl molecules by free methyl radicals, there is the possibility that methyl radicals condense with biacetyl to give some kind of complex, presumably, first a radical and then a polymer. Perhaps the deposition of such a product is the cause of the decay in mirror activity when biacetyl is decomposed.[20] At 100°, either the complex is unstable (like the acetyl radical itself) or it is sufficiently volatile not to deposit on the metal surface. While the data are not very precise some support for this view is to be found in the behavior of the CO/C_2H_6 ratios in presence and absence of mirrors.

Quantum yields in biacetyl decomposition have been measured by Roof and Blacet, who observed that the CO quantum yield rises to rather high values above 100°. A rough extrapolation of their curves would indicate a yield in the neighborhood of 2 under the conditions of our experiments. The question arises at once, of course, as to whether our present experiments are compatible with this figure. There is no way for the direct ultimate-molecule reaction to give yields in excess of unity. While "cracking" re-actions, (9)–(11), may give rise to chains which would increase the quantum yields, they seem actually to be of minor importance under the conditions of our present experiments. A decomposition of biacetyl induced by "hot" radicals[21] or by photo-activated molecules in the meta-stable upper state will explain the observed quantum yields. The reaction sequence, therefore, may include reactions like

$$CH_3COCOCH_3 \xrightarrow{\text{induced by } M} C_2H_6 + 2CO, \qquad (13)$$
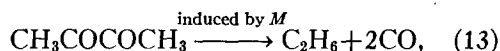
where M is a hot radical or an energy-rich photo-activated molecule. Reaction (13) is nearly thermoneutral so that one "M" may induce the decomposition of many biacetyl molecules. It may be noted that rough estimates of the free energy show biacetyl to be rather unstable with respect to ethane and carbon monoxide under ordinary conditions, so that reaction (13) could proceed "spontaneously."

A study of the effects of foreign gases in the photolysis of biacetyl may at first glance appear to contradict the present findings. Nitric oxide in large concentration, for example, completely inhibits the formation of ethane.[22] This means either that all the initial reaction gives methyls, all of which are removed by a very efficient combination with nitric oxide, or that the intermediate activated molecules, which would normally rearrange to give ethane, are converted by nitric oxide into other products. Actually no information is given by the nature of the products, in the presence of nitric oxide, concerning the relative importance of the two reaction paths.

Although the rate of flow of reactive vapors in the experiments reported in this paper was so slow that a considerable proportion of the methyl radicals was consumed before the vapors emerged from the lighted zone, there can be little doubt that some of the photoactivated biacetyl under ordinary conditions decomposes by direct rearrangement into stable products, a conclusion in keeping with observations on the fluorescence of biacetyl.

[17] J. G. Roof and F. E. Blacet, J. Am. Chem. Soc. 63, 1126 (1941).
[18] F. O. Rice and W. D. Walters, J. Chem. Phys. 7, 1015 (1939).
[19] Cf. F. O. Rice and E. Teller, J. Chem. Phys. 6, 489 (1938).
[20] Cf. P. A. Leighton and F. E. Blacet J. Am. Chem. Soc. 54, 3165 (1932).
[21] Cf. W. M. Garrison and M. Burton, J. Chem. Phys. 10, 730 (1942).
[22] H. W. Anderson and G. K. Rollefson, J. Am. Chem. Soc. 63, 816 (1941).