It was pointed out earlier that the spectrum of the brown complex is qualitatively of the charge-transfer type. If charge-transfer forces contribute to the formation of the peroxo bridge, therefore, the present results suggest that these forces are much stronger with two $\mathrm{OH^-}$ ions in the coördination sphere of $\mathrm{Co^{++}}$ than if only one $\mathrm{OH^-}$ ion is present.

These conclusions do not imply that reactions *a* and *c* are unimportant in the formation of II, but, rather, that reactions *b* and *d* are at least equally important as reactions *a* and *c*, despite the fact that the equilibrium concentration of $\mathrm{Co(GG)_2(OH)_2^{=}}$ must be much smaller than that of $\mathrm{Co(GG)_2OH^-}$.

Changes in *p*H.—Some of the experiments in the unbuffered range of *p*H 10 to 11 were conducted with a view to measuring *p*H changes, rather than light absorption. The solutions were prepared in the complete absence of oxygen, and their *p*H values measured. Oxygen was then bubbled through the solutions, and the usual brown color rapidly was formed. During this process a sharp drop in *p*H was observed. As the brown color was transformed to the red product, however, an accompanying *p*H increase was found. Qualitatively, this result is in accord with the mechanism proposed in this paper, for the formation of II requires the absorption of $\mathrm{OH^-}$ ions from the solution, and these are released again in the transformation to I.

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The Photolysis of Biacetyl

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The vapor phase photochemical decomposition of biacetyl has been studied over a wide range of temperature, wave length, concentration and light intensity. Quantum yields are reported for the products, carbon monoxide, ethane, methane and acetone, all of which were determined mass spectrometrically. Ketene and possibly 2,3-pentanedione were found as products. Some photolyses were conducted in the presence of iodine vapor. In these cases the products were carbon monoxide, methyl iodide and a small quantity of acetone. The results may be explained by assuming two primary processes and secondary reactions involving free radicals. The importance of the various secondary reactions changes considerably with temperature and under the influence of iodine as a free radical trap. Revised values of 7.7 and 6.6 kcal./mole are reported for the activation energies of the acetone and methane forming reactions, respectively, both of which involve a methyl radical attack on the biacetyl molecule. At room temperature the primary quantum yield is related to the sum of the ethane and acetone quantum yields. At temperatures of 100° and above, the primary quantum yield for the uninhibited photolyses is shown to be equal to the ethane quantum yield, and that for the iodine inhibited photolyses is shown to be equal to one-half the quantum yield of carbon monoxide. All values of the primary quantum yield are much less than unity.

The photochemical decomposition of biacetyl has been studied in the second absorption region.[1] The preliminary results, obtained at 2654 Å., and a mechanism based on those results were presented in a previous report.[2] Additional data, including further evidence in support of the proposed mechanism, have been obtained by conducting the photolysis over a range of temperature, wave length, concentration and intensity and also by conducting the photolysis in the presence of iodine vapor. Iodine is an effective radical trap and inhibits normal secondary reactions. Experiments in which iodine was added for this purpose are designated herein as iodine inhibited photolyses.

Experimental

Apparatus and Procedure.—The apparatus and experimental procedure used in these experiments were essentially as described previously.[2] The reaction system consisted of a cylindrical quartz reaction cell, 30 mm. inside diameter and 20 cm. in length, and two precision stopcocks, all of which were mounted in an air thermostat of such construction that it could be heated to 200°. The reaction system was joined to a biacetyl supply and to a gas train which was utilized to fractionate the products at the end of a run.

Monochromatic light was supplied by a constant pressure mercury arc and a crystal quartz monochromator. Intensities were measured at all temperatures by means of a photocell–thermopile combination. The desired vapor pressure was obtained by observing the photocell response. In no case was more than 2% of the vapor photolyzed. At the end of an experiment, the excess biacetyl and products were fractionated in the gas train, and the residual biacetyl was condensed in a trap at Dry Ice temperature. The trap was removed from the system and the contents weighed; the true concentration of biacetyl was calculated from this weight and the volume of the reaction system. The weight of the products condensed at −80° and the weight of the biacetyl lost in the fractionation were negligible.

For the iodine-inhibited photolyses, a trap for introducing the iodine and a magnetic pump for circulating the biacetyl and iodine vapors were added to the reaction system inside the air thermostat. The procedure for the iodine work was similar to that described by others.[3] Extra precautions were take to ensure that the reaction system was anhydrous and free of mercury vapor. Iodine vapor concentrations were determined from the weight of iodine introduced into the system. During the fractionation at the end of a run, the excess iodine and biacetyl both condensed at −80°. The quantity of biacetyl was obtained by subtracting the weight of iodine from the weight of the condensable fraction.

Appreciable absorption by the iodine vapor, with a maximum at 2804 Å., was observed. Others also have observed an absorption spectrum for iodine in this region.[4-6] This absorption by the iodine was assumed not to affect the quantum yield calculations because the cell-empty intensities were measured behind the reaction cell after vaporiza-

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[1] The first absorption region of biacetyl extends from about 4600 to 3500 Å., and the second from 3200 to below 2200 Å.

[2] F. E. Blacet and W. E. Bell, *Faraday Soc. Disc.*, **14**, 70 (1953).

[3] F. E. Blacet and J. Heldman, THIS JOURNAL, **64**, 889 (1942).

[4] A. Coehn and K. Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

[5] W. C. Price, *Phys. Rev.*, **48**, 477 (1935).

[6] D. T. Warren, *ibid.*, **47**, 1 (1935).

tion of the iodine and prior to the introduction of the biacetyl vapor. The iodine inhibited photolyses were free of polymer formation.

Biacetyl and Iodine Purification.—Eastman Kodak Co. white label biacetyl was purified as described previously.[2] J. T. Baker reagent grade resublimed iodine was used. It was stored in a desiccator and that used in part of the experiments was sublimed again.

Product Analysis.—The products and excess biacetyl were fractionated in a series of six traps mounted between the reaction cell and a Toepler pump. The excess biacetyl was collected at −80°; all the 2,3-pentanedione produced was presumably included in this fraction. Ethane, acetone and ketene were collected in a trap at liquid nitrogen temperature. A precision stopcock and a standard taper joint were connected to the trap on a side arm and, on completion of the fractionation, this trap was removed and attached to the mass spectrometer for analysis. The non-condensed gaseous fraction, consisting of methane, carbon monoxide and a small fraction of the ethane, was collected with the Toepler pump. The analysis for all components was performed in the mass spectrometer. Acetone standards, which consisted of solutions of acetone in biacetyl, were carried through the same analytical procedure used to separate the photolysis products.

The analysis procedure for the iodine work was similar to that described above. The excess biacetyl and iodine was collected at −80°, methyl iodide and traces of acetone and ethane were collected at liquid nitrogen temperature. The non-condensable gaseous fraction consisted of carbon monoxide and traces of methane. Methyl iodide standards were run the same as the acetone standards.

Temperature Variation of the Molecular Extinction Coefficient.—Average values of the molecular extinction coefficient determined at 2654 Å. over the temperature range of 28 to 200° are shown in Table I. The coefficients were used to recalculate previously reported biacetyl concentrations[2] which had been based upon the assumption that the change in absorption with temperature is negligible. The corrected values of the concentrations are given in Table II. These values take into account the temperature variation of the light absorption, and in addition they are based on weighed quantities rather than on pressure measurements and application of the ideal gas law. The corrections do not affect the accuracy of the quantum yield determinations; they do, however, give a more accurate value for the concentrations at which the respective quantum yields were determined.

TABLE I

TEMPERATURE VARIATION OF THE MOLECULAR EXTINCTION COEFFICIENT OF BIACETYL AT 2654 Å.

Average values determined at a concentration of approximately 1.8 mmoles/l.

Temp., °C.	Mol. extinction coefficient, l./cm. moles	Temp., °C.	Mol. extinction coefficient, l./cm. moles
28	9.03	100	11.2
50	9.89	150	12.2
65	10.4	175	13.0
75	10.4	200	14.0

Results

Uninhibited Photolyses.—Table II summarizes the results of the uninhibited photolyses. Quantum yields are reported for carbon monoxide, ethane, methane and acetone. The results at 2654 Å. were reported previously[2] except for the revised values of the concentrations. Based on the qualitative observation of a peak at mass 100, 2,3-pentanedione appears to be a minor product at the higher tempertures.[2] A five-hour dark run conducted at 200° indicated thermal decomposition in the temperature range of these experiments to be negligible.

Ketene has been reported[7] to be a product of biacetyl photolysis. Mass spectral analyses of the liquid nitrogen fractions furnished additional evidence for the production of this compound. In all runs conducted at 100° and above, the mass 14 and 42 peaks were larger than could be accounted for by the other products. Variation of key peak intensities with time also indicated the presence of a compound such as ketene. At 200°, methane and ketene appear to be produced in almost equivalent amounts; however, as the temperature is lowered, the quantity of methane exceeds that of ketene.

Inhibited Photolyses.—Results obtained with iodine vapor added to the photolysis system are given in Table III. The products consisted of carbon monoxide, methyl iodide, small amounts of acetone and traces of methane and ethane. Neither the non-condensable gaseous fraction nor the liquid nitrogen fraction furnished evidence for other iodine compounds, such as hydrogen iodide or acetyl iodide. The mass range of 12 to 200 was covered for each of the liquid nitrogen fractions and the spectrum was entirely free of extraneous peaks except for small peaks at mass 50 and 52. These two peaks were attributed to methyl chloride, which probably resulted from small amounts of ICl in the iodine. Acetyl iodide, if produced, was probably collected with the excess biacetyl and iodine at Dry Ice temperature. Unsuccessful attempts were made to analyze this fraction. A dark run at 150° of five-hour duration indicated the contribution of thermal decomposition or of a thermal reaction between biacetyl and iodine to be negligible. The methane and ethane quantum yields are of the order of 1% or less of the corresponding values in the uninhibited runs conducted under approximately the same conditions. They are considered sufficiently small to be neglected. The acetone quantum yields, however, are of the order of 5 to 10% of the corresponding values in the uninhibited runs and must be considered further.

Discussion

Primary Processes.—The experimental results may be explained with the aid of the following primary decomposition processes.

$$CH_3COCOCH_3 + h\nu \longrightarrow 2CH_3CO \qquad (I)$$

$$CH_3COCOCH_3 + h\nu \longrightarrow CH_3COCH_3 + CO \qquad (II)$$

The small amount of acetone produced in the iodine inhibited photolyses indicates that process II may occur to a small extent. As noted in Table III, the acetone quantum yield increases with shorter wave lengths, being five times greater at 2380 than at 3130 Å. This indicates that the intramolecular process may become more probable as the energy of the quanta increases. This is consistent with the behavior of other such processes; for example, the aldehydes all show more intramolecular rearrangement at the shorter wave lengths.[8] At the shortest wave length used, acetone formation in the presence of iodine was still small, and therefore process I will be considered as the means of primary decomposition in the remaining discussion. The absence of methane and ethane as products in the inhibited photolyses proves that these compounds are produced as a result of secondary reactions.

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(7) F. E. Blacet and W. E. Bell, Communication, *Faraday Soc. Disc.*, **14**, 131 (1953).

(8) F. E. Blacet and J. N. Pitts, Jr., THIS JOURNAL, **74**, 3382 (1952).

TABLE II

EXPERIMENTAL RESULTS OF BIACETYL PHOTOLYSIS

Wave length, Å.	Temp., °C.	Time, sec. × 10^{-3}	$I_a \times 10^{-14}$ [a] quanta/sec.	Q_m [b]	Biacetyl(B), mmoles/l.	Quantum yields, Φ CO	Ethane	Methane	Acetone
2380	150	9.90	1.24	0.365	1.54	2.60	0.25	1.20	0.64
2380	150	9.97	1.32	.375	1.63	2.84	.25	1.31	.72
2537	150	5.84	5.00	.515	1.57	2.16	.33	0.80	.40
2654	28	11.11	6.39	.608	2.23	0.55	.15	.017	.22
2654	50	8.64	5.19	.643	2.30	0.68	.21	.042	.26
2654	50	4.41	7.06	.605	2.07	0.64	.19	.031	.20
2654	75	6.93	5.00	.595	1.90	1.16	.36	.10	.23
2654	75	6.59	6.65	.597	1.89	0.97	.32	.088	.22
2654	100	7.01	7.14	.605	1.82	1.08	.34	.17	.15
2654	125	4.97	6.58	.584	1.61	1.45	.36	.34	.25
2654	150	3.80	6.52	.583	1.52	2.14	.39	.71	.42
2654	175	2.91	6.29	.566	1.38	2.34	.36	.82	.50
2654	200	1.33	6.24	.599	1.43	3.38	.34	1.55	.78
2804	150	9.12	4.77	.480	1.30	1.48	.27	0.53	.28
3130	30	18.66	4.04	.200	1.92	0.095	.014	.0057	.045
3130	65	14.64	4.96	.222	1.79	.26	.053	.034	.049
3130	100	11.31	5.04	.212	1.79	.49	.084	.12	.077
3130	150	8.99	4.42	.194	1.54	.88	.074	.38	.21
3130	150	12.59	2.41	.194	1.60	1.06	.057	.53	.25
3130	150	5.71	10.3	.348	3.24	0.72	.040	.35	.17
3130	150	4.86	17.9	.546	6.60	0.60	.020	.33	.16
3130	200	5.34	7.95	.235	1.46	2.02	.14	1.04	.50

[a] I_a is the rate of light absorption for the entire cell. [b] Q_m is the average fraction of light absorbed during an experiment.

TABLE III

EXPERIMENTAL RESULTS OF IODINE INHIBITED PHOTOLYSES OF BIACETYL

Wave length, Å.	Temp., °C.	Time, sec. 10^{-3}	$I_a \times 10^{-14}$ [a], quanta/sec.	Q_m [b]	Biacetyl (B), mmoles/l.	Iodine (I_2), mmoles/l.	Quantum yields, Φ CO	CH_3I	C_2H_6	CH_4	Acetone
2380	150	14.22	1.71	0.454	2.23	0.193	1.00	0.98	None	0.008	0.04
2537	150	5.39	5.81	.520	1.50	.178	0.87	.81	None	.005	.02
2654	65	7.35	6.13	.573	1.77	.174	.57	.61	0.002	.001	.02
2654	100	7.32	6.29	.596	1.77	.188	.71	.63	.001	.004	.02
2654	150	7.26	5.87	.580	1.49	.127	.72	.78	.003	.005	.02
2804	150	17.61	4.50	.502	1.65	.157	.44	.41	None	.004	.009
3130	65	16.79	5.10	.204	1.79	.168	.10	.10	None	.0002	.004
3130	100	8.94	3.69	.174	1.61	.150	.19	.19	None	.0006	.009
3130	150	14.69	4.70	.193	1.36	.146	.20	.19	None	.001	.008

[a] I_a is the rate of light absorption for the entire cell. [b] Q_m is the average fraction of light absorbed during an experiment.

Secondary Reactions.—The results are in accord with the following series of secondary reactions.

$$CH_3CO \longrightarrow CH_3 + CO \tag{1}$$

$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \tag{2}$$

$$2CH_3 \longrightarrow CH_3CH_3 \tag{3}$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_4 + CH_2COCOCH_3 \tag{4}$$

$$CH_2COCOCH_3 \longrightarrow CH_3CO + CH_2CO \tag{5}$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CH_3CO \tag{6}$$

$$CH_3 + CH_2COCOCH_3 \longrightarrow CH_3CH_2COCOCH_3 \tag{7}$$

$$2CH_3CO \longrightarrow CH_3COCOCH_3 \tag{8}$$

The evidence for reactions 1 through 8 has been discussed[2] and will be considered only briefly here. The formation of ethane and methane furnishes evidence for reactions 3 and 4. The variation of the acetone quantum yields with temperature indicates two acetone producing reactions, 2 and 6. The acetyl radicals decompose by reaction 1 to produce methyl radicals, and above 100° virtually all of them decompose before they have the opportunity to react with other species. This is evident from the constancy of the ethane quantum yields above 100°.

The high quantum yields of methane and acetone at the higher temperatures and the constancy of the ethane quantum yield above 100° indicate that the methyl radicals used in reactions 4 and 6 must be regenerated. This could occur by decomposition of the acetyl radicals produced by reactions 5 and 6. Evidence for reaction 7 is provided by the qualitative indications for 2,3-pentanedione; however, the contribution of this reaction is presumed to be small because of the constancy of the ethane quantum yield with temperature. The constancy of the primary quantum yield, to be shown later, over the entire temperature range indicates the contribution of reaction 8 to be small even at room temperature.

The production of ketene provides further evidence for the validity of reaction 5. Since the contribution of reaction 7 is small, the quantity of ketene should almost equal that of methane. At 200°

these two products were found in almost equivalent amounts; however, at lower temperatures the quantity of methane exceeded that of ketene. The reason for this trend is not evident.

If reaction 7 is neglected, the mechanism requires that

$$\Phi_{CO} = 2\Phi_{C_2H_6} + \Phi_{CH_4} + \Phi_A \tag{9}$$

where Φ_{CO}, $\Phi_{C_2H_6}$, Φ_{CH_4} and Φ_A represent the quantum yields of carbon monoxide, ethane, methane and acetone, respectively. The experimental results are consistent with the equation under all conditions with approximately a 10% variation.

Kinetics.—The following equation may be derived from the over-all mechanism[2]

$$\log \frac{\Phi_{CH_4} I_a^{1/2}}{\Phi_{C_2H_6}^{1/2}(B)} = -\frac{(E_4 - {}^1/_2E_3)}{2.30RT} + \log \frac{A_4}{A_3^{1/2}} \tag{10}$$

Values of $\log \Phi_{CH_4} I_a^{1/2}/\Phi_{C_2H_6}^{1/2}(B)$ from all the uninhibited photolyses representing a wide variation in wave length, temperature, concentration and rate of absorption, are plotted against $1/T$ in Fig. 1. The slope of the best straight line through the points gives a value for $E_4 - {}^1/_2E_3$ of 7.7 kcal./mole. The activation energy of the methyl recombination reaction is small and generally assumed to be zero; therefore the value of 7.7 kcal./mole may be taken as the activation energy of reaction 4.

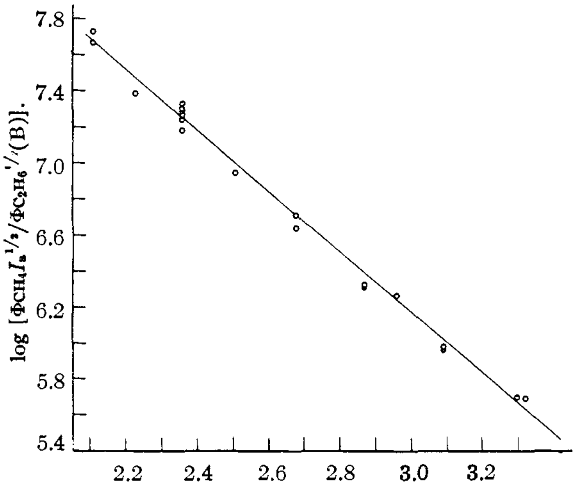

Fig. 1.—Plot of the logarithmic term *vs.* $1/T$ for the results of biacetyl photolysis. The best straight line through the points corresponds to an activation energy of 7.7 kcal./mole.

A change in wave length, which entails a change in the energy of the quanta absorbed, appears to have no effect on the location of the points with respect to the curve. As far as the rates of reactions 3 and 4 are concerned, variation in wave length simply changes the rate of primary decomposition, $\phi_I I_a$, in which ϕ_I is the quantum yield of primary decomposition and I_a is the rate of absorption.

The activation energy for reaction 6 may be estimated from an equation similar to the above. Figure 2 shows a plot of $\log \Phi_A I_a^{1/2}/\Phi_{C_2H_6}^{1/2}(B)$ against $1/T$. All values over the entire temperature range of 28 to 200° are included in order to show how the experimental results agree with the equation at 100° and above and disagree completely below that temperature. The slope of the best straight line through the points, evaluated for the experiments at 100° and above, gives a value for $E_6 - {}^1/_2E_3$ of 6.6 kcal./mole. If E_3 is assumed to be zero, the activation energy for reaction 6 is 6.6 kcal./mole. The points of Fig. 2, as did those of Fig. 1, represent a wide variation in experimental conditions; nevertheless they fall on the line within experimental error at 100° and above. Below 100° the points all fall above the extended line which indicates that the logarithmic term is too large. This is due to an excess of acetone and is explained by reaction 2.

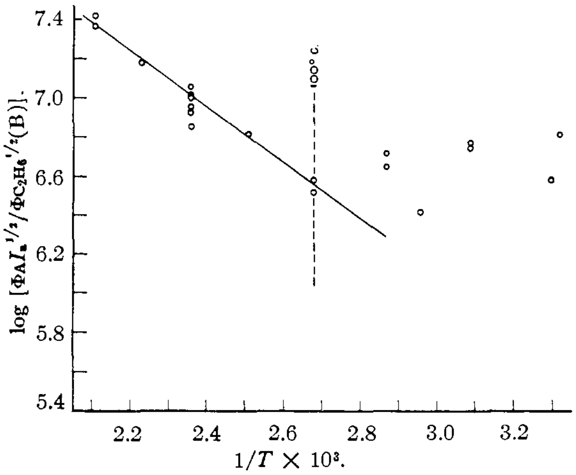

Fig. 2.—Plot of the logarithmic term *vs.* $1/T$ for the results of biacetyl photolysis. The best straight line through the points, evaluated for the experiments at 100° and above, corresponds to an activation energy of 6.6 kcal./mole.

Activation energies for reactions 4 and 6 were estimated as 7.1 and 5.6 kcal./mole, respectively, in the preliminary report based on the experimental results at wave length 2654 Å.[2] The values were low because the biacetyl concentrations as reported for the higher temperature experiments were low due to lack of information on the change of absorption coefficient with temperature. As explained above, the biacetyl concentrations were redetermined from data obtained in a study of the temperature variation of the molecular extinction coefficient.

The proposed mechanism may be subjected to another test by use of the following relationship.[2]

$$\frac{\Phi_{CH_4}}{\Phi_A} = \frac{P_4}{P_6} e^{-(E_4 - E_6)/RT} \tag{11}$$

The equation is valid at temperatures of 100° and above, and values of P_4/P_6 calculated from the equation should remain constant regardless of other experimental conditions. Fourteen determinations obtained over the temperature range of 100 to 200° and five wave lengths gave an average value of 6.6 ± 0.6 for P_4/P_6. This is a revision of the value 9.3 previously given.[2]

The Mechanism at Temperatures above 100°.—As explained above, the experimental evidence indicates that the acetyl radicals are relatively unstable at 100° and above and decompose before entering into reactions with other species. The process of primary decomposition essentially gives two methyl radicals and two carbon monoxide molecules and the following mechanism results.

$$CH_3COCOCH_3 + h\nu \longrightarrow 2CH_3CO \qquad \text{I}$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (1)$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_4 + CH_2CO + CO + CH_3 \qquad (12)$$

$$CH_3 + CH_3COCOCH_3 \longrightarrow CH_3COCH_3 + CO + CH_3 \qquad (13)$$

$$2CH_3 \longrightarrow CH_3CH_3 \qquad (3)$$

These reactions are derived by eliminating all reactions involving radicals other than the methyl radical. Reaction 7 is assumed to be unimportant for reasons given above and therefore equation 14 should hold.

$$\phi_{\text{I}} = \Phi_{C_2H_6} \quad (100° \text{ and above}) \qquad (14)$$

In this, ϕ_{I} represents the quantum yield of primary decomposition and $\Phi_{C_2H_6}$ the quantum yield of ethane. The relationship is restricted to the uninhibited photolyses, and for reasons given is valid only at temperatures of 100° and above. It may be noted from Table II that the ethane quantum yields at 2654 and 3130 Å. remain substantially constant over the range of 100 to 200°. This may be interpreted to mean that the primary quantum yields are temperature independent.

The Mechanism at Room Temperature.—By reference to the experimental results at 2654 Å., it can be seen that the methane quantum yield at room temperature is negligible in comparison to other quantum yields. This indicates that reaction 4 is not important at this temperature. Reactions 5 and 7 also are not important because they cannot occur at higher rates than reaction 4. The importance at room temperature of reaction 6 can be estimated from Fig. 2 by extrapolation. This gives a value for the logarithmic term from which the acetone quantum yield (resulting from reaction 6) at 2654 Å. is calculated to be 0.016. This value is negligible compared to the other quantum yield values. The same reasoning at 3130 Å. indicates that reactions 4 and 6 relatively are of some importance at this wave length even at room temperature. If reaction 8 is neglected, reactions I, 1, 2 and 3 account for the products which are significant at room temperature, at least at 2654 Å. These reactions require that

$$\phi = \Phi_{C_2H_6} + \Phi_{\text{A}} \quad (\text{room temperature}) \qquad (15)$$

Secondary Reactions of Iodine Inhibited Photolyses.—The quantities of ethane, methane and acetone produced in the inhibited photolyses are small enough to be neglected; therefore the following secondary reactions may be postulated.

$$CH_3CO \longrightarrow CH_3 + CO \qquad (1)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (16)$$

$$CH_3CO + I_2 \longrightarrow CH_3COI + I \qquad (17)$$

The iodine atoms presumably disappear by recombination or by reactions similar to 16 and 17. These reactions require that

$$\Phi_{CO} = \Phi_{CH_3I} \qquad (18)$$

The quantum yields of carbon monoxide and methyl iodide in Table III show that within experimental error this relationship does pertain. Primary quantum yields may be obtained from the following equation which should be valid over the entire temperature range.

$$\phi_{\text{I}} = {}^1/_2\Phi_{CO} + {}^1/_2\Phi_{CH_3COI} \qquad (19)$$

Acetyl iodide was not determined in these experiments; however, there is evidence to indicate that the quantity produced would be small, at least for temperatures of 100° and above. In Table III, it can be seen that at wave lengths 2654 and 3130 Å. the quantum yield of carbon monoxide remains constant over the range of 100 to 150°. If there were appreciable quantities of acetyl iodide produced at 100°, the reactions given above indicate that an increase in temperature would be accompanied by an increase in carbon monoxide yield since the acetyl radical becomes increasingly unstable at higher temperatures. It is assumed, of course, that the quantum yield of primary decomposition remains constant. It may be said, therefore, that the constancy of the carbon monoxide quantum yield at 100° and above indicates that virtually all the acetyl radicals have decomposed to give carbon monoxide and methyl radicals; the latter react with the iodine vapor and produce methyl iodide.

The same is not true at temperatures less than 100°. The quantum yields of carbon monoxide at both 2654 and 3130 Å. increase substantially over the range of 65 to 100°. This indicates that at lower temperatures the acetyl radicals are being removed from the system. This could occur by a recombination to form acetone, or a reaction with an iodine molecule or atom to form acetyl iodide. For reasons given above, the contribution of the recombination reaction is presumed to be small even at room temperature, and the reaction to form acetone is eliminated because acetone was not found in greater yield at 65° than at 100°. The evidence therefore indicates that at 65° acetyl iodide may be formed at wave lengths 2654 and 3130 Å. with quantum yields of not more than 0.14 and 0.09, respectively. These values are simply the difference between the carbon monoxide yields at 65 and at 100°. This reasoning indicates that the quantum yield of acetyl iodide in equation 19 can be neglected at 100° and above and the quantum yield of primary decomposition for inhibited photolyses is given by the equation

$$\phi_{\text{I}} = {}^1/_2\Phi_{CO} \quad (\text{inhibited}) \qquad (20)$$

Quantum Yields of Primary Decomposition.—Primary quantum yields at various temperatures are compared in Table IV. These values were cal-

TABLE IV

EFFECT OF TEMPERATURES ON PRIMARY QUANTUM YIELDS CALCULATED FROM EQUATIONS 14 AND 15

Biacetyl concn., about 1.8 mmoles/l.

Temp., °C.	Wave length, Å. 2654	3130
28, 30	0.37	0.059
100	.34	.084
125	.36	
150	.39	.074
175	.36	
200	.34	.14

culated from equations 14 and 15 and indicate that at 2654 Å., and probably at 3130 Å., the primary quantum yield is independent of temperature. It should be noted that it is necessary to specify the approximate biacetyl concentrations, for it appears that increasing the concentration decreases the ethane quantum yield (see 3130 Å., Table II).

In Table V, primary quantum yields, calculated from equations 14 and 20 at various wave lengths, are compared. All the values are less than unity. This indicates that part of the activated biacetyl molecules lose their energy without dissociating.

TABLE V

EFFECT OF WAVE LENGTH ON PRIMARY QUANTUM YIELDS CALCULATED FROM EQUATIONS 14 AND 15

Biacetyl concn., about 1.8 mmoles/l.

Wave length, Å.	ϕ, uninhibited	ϕ, iodine inhibited
2380	0.25	0.50
2537	.33	.44
2654	.39	.36
2804	.27	.22
3130	.074	.10

Evidence for collisional deactivation is furnished by the fact that primary decomposition at 3130 Å. decreases with increasing biacetyl concentration. No visible fluorescence was noted in any of these experiments.

At wave lengths 3130, 2804 and 2654 Å., the quantum yields of primary decomposition for both uninhibited and inhibited photolyses are almost equivalent. This was expected to be the case at all wave lengths. However, at 2537 and 2380 Å. more dissociation appears to occur in the presence of iodine than without it. Possibly at these wave lengths iodine begins to react directly with the highly excited molecules.

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The Photolysis of the Aliphatic Aldehydes. XVII. Propionaldehyde, *n*-Butyraldehyde and Isobutyraldehyde at 2380 and 1870 Å.

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Photochemical studies of the decomposition of propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were made at 2380 Å. in their first ultraviolet absorption region and at 1870 Å. in their second ultraviolet absorption region. Room temperature quantum yields for the non-condensable products were obtained at both wave lengths. Marked changes at the shorter wave lengths were observed in the quantum yields for the products and some new products were identified. Although a different electronic excitation state doubtless is involved at 1870 Å., the experimental results indicate that in determining the mode of decomposition, the increased energy of the quanta at the shorter wave lengths is more important than the electronic state, since results for the most part are a logical extrapolation of trends found down to 2380 Å. in the first ultraviolet absorption region. The quantum yield for carbon monoxide becomes greater than unity at 1870 Å. for all of these aldehydes. The quantum yields for methane, hydrogen and unsaturated compounds were large at 1870 Å. compared to those obtained at 2380 Å. Propane from the photolysis of propionaldehyde and butane from the photolysis of the butyraldehydes were identified for the first time in these studies. More polymerization was observed at the shorter wave length. Even though no work was done with free radical traps, it was possible, by making reasonable assumptions, to estimate the relative importance of the several primary processes that occur.

The photochemical decomposition of the aliphatic aldehydes has been studied in considerable detail in the easily accessible quartz region of the ultraviolet spectrum, and several primary processes have been established.[2,3] It has been possible to extend these photochemical decomposition studies into their second absorption region to 1870 Å. by developing new experimental equipment. Acetaldehyde was not investigated since it is highly transparent at this wave length.

Experimental Procedure

Monochromator.—A prism monochromator was designed and constructed using synthetic fluoride optics suitable for providing monochromatic light for photochemical studies in the short wave length ultraviolet to 1300 Å. The 60 degree fluorite prism was 30 mm. high and 40 mm. on its face. Two fluorite lenses 30 mm. in diameter were used. The radii of curvature for the two surfaces of the lens were chosen to minimize spherical aberration. Relatively short focal lengths (100 mm. at 2537 Å.) and wide apertures (1 mm.) were used to ensure maximum light intensities. The prism was moved mechanically in such a manner that minimum deviation of the light beam was maintained through the prism at all wave lengths. The resolution of the monochromator was such that the 2537 and 1849 Å. mercury resonance lines were separated by 7 mm. at its exit slit. A sealed case was provided so that an inert oxygen-free atmosphere could be maintained, if desired, for studies between 1800 and 1300 Å. Gas-tight seals on the control shafts allowed lens focusing and wave length and thermopile adjustments to be made without allowing air to enter the case.

Photolysis System.—This system consisted of a photolysis cell separated by two mercury valves from the aldehyde supply and the Toepler pump which was used to collect the non-condensable products. The photolysis cell was made by cementing two polished fluorite plates to the ends of a Pyrex tube 30 mm. in diameter and 40 mm. long. Glyptal lacquer was used for the cement. Windows clouded with

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[1] Dow Chemical Company, Pittsburg, California.

[2] F. E. Blacet and J. N. Pitts, Jr., THIS JOURNAL, **74**, 3382 (1952).

[3] F. E. Blacet and J. Calvert, *ibid.*, **73**, 661, 667 (1951).