distribution function for the 29% solution, so the model is believed to represent a good picture of the solution. Table I lists the results for the other concentrations and indicates that this close-packed arrangement becomes less and less ordered as the concentration decreases.

The number of molecules in the average potassium laurate micelle, at various concentrations, can now be computed[20] from the number of molecules per unit volume and the number of micelles per unit volume. The number of molecules is calculated from the concentration and the density (1.018 g./cm.^{3} for the 29% solution). The results for the 29.6, 24.1, 19.7 and 15.1% solutions, respectively, are 63, 55, 64 and 70 molecules per micelle. At the lowest concentration the micelles may deviate enough from the close-packed arrangement to cause appreciable error in the corresponding figure. The error of ± 2 Å. in the determination of the separation of micelle centers introduces an uncertainty of ± 8 molecules in these results.

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[20] R. W. Mattoon, R. S. Stearns and W. D. Harkins, *J. Chem. Phys.*, **16**, 644 (1948).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Photolysis of Glyoxal Vapor at Wave Length 3130 Å.[1]

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A quantitative study of the rates of formation of carbon monoxide and hydrogen products from the vapor phase photolyses of pure glyoxal vapor was made in experiments at several temperatures, intensities of 3130 Å. radiation, and concentrations of pure glyoxal and in mixtures of glyoxal with carbon dioxide. The data indicate that the quantum yields of carbon monoxide and hydrogen, about 1.2 and 0.13, respectively, are relatively insensitive to changes in all of the experimental variables. The results are consistent with the reaction mechanism (1), (2) and (9) given in the text. It seems probable that no glyoxal molecules absorbing 3130 Å. radiation are deactivated and that all of the activated glyoxal molecules decompose by either reaction (2) or (9) with the probabilities for each mode of decomposition being 0.15 and 0.85, respectively.

Norrish and Griffiths[2] found the following reaction mechanism was consistent with the products identified and the rate studies made in glyoxal photolyses in unfiltered mercury arc light (chiefly wave lengths 4360, 4050 and 3660 Å.)

$$(HCO)_2 + h\nu \longrightarrow (HCO)_2{}^* \qquad (1)$$

$$(HCO)_2{}^* \longrightarrow H_2 + 2CO \qquad (2)$$

$$(HCO)_2^* + (HCO)_2 \longrightarrow CO + C_3H_4O_3 \qquad (3)$$

$$nC_3H_4O_3 \longrightarrow \text{polymer} \qquad (4)$$

$(HCO)_2^*$ indicates a light activated glyoxal molecule; $C_3H_4O_3$ represents a molecule of glycerosone. The effect of added acetaldehyde and carbon dioxide on the ratio of the products of glyoxal photolysis at 3660 Å. was investigated by Blacet and Moulton.[3] Methane could not be detected in the products of the photolysis of glyoxal with added acetaldehyde. It was concluded that formyl radical formation by reaction (5)

$$(HCO)_2^* \longrightarrow 2HCO \qquad (5)$$

does not occur in glyoxal photolysis at 3660 Å. since reaction (5) would be followed presumably by a sequence of reactions producing methane

$$HCO + CH_3CHO \longrightarrow H_2 + CO + CH_3CO \qquad (6)$$

$$CH_3CO \longrightarrow CH_3 + CO \qquad (7)$$

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \qquad (8)$$

Blacet and Moulton explained their results qualitatively in terms of the Norrish mechanism and the additional reaction (9)

$$(HCO)_2^* \longrightarrow CH_2O + CO \qquad (9)$$

For several reasons the evidence given for the proposed glyoxal photolysis scheme is not compelling. A very limited range of the experimental variables was used in these studies; *e.g.*, all of the photolyses were carried out at the one temperature of 25°. In addition the experiments were complicated by the occurrence of the rapid thermal reaction of glyoxal polymerization. The exclusion of reaction (5) on the basis of the previous work is also open to question. Provided that sufficient energy per quantum of adsorbed light is available to cause (5) and that this reaction occurs in glyoxal photolysis, then it is probable that reactions such as (10) and (11)

$$2HCO \longrightarrow H_2CO + CO \qquad (10)$$

$$2HCO \longrightarrow (HCO)_2 \qquad (11)$$

would be the dominant modes of formyl radical reaction at 25°,[4,5] and reaction (6) and the subsequent reactions (7) and (8) would be unimportant at this low temperature. If this is the case the presence of the radicals and the occurrence of (5) could not have been detected in the previous work. The present study was made to provide a more rigorous test of the proposed mechanism of glyoxal photolysis and to investigate the possible use of this photodecomposition as a source of formyl radicals at wave lengths energetically favorable to reaction (5).

Experimental Procedure

Photolysis Equipment and Procedure.—The photolysis, gas handling and optical systems, and the 3130 Å. light source and light measuring equipment used in this study were similar to those described previously.[6] The metal

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[1] Presented in part before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September, 1952.

[2] R. G. W. Norrish and J. G. A. Griffiths, *J. Chem. Soc.*, 2829 (1928).

[3] F. E. Blacet and R. W Moulton, THIS JOURNAL, **63**, 868 (1941).

[4] F. E. Blacet and W. J. Blaedel, *ibid.*, **62**, 3374 (1940).

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

[6] J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

valves used in the previous system were replaced with high vacuum stopcocks lubricated with high temperature silicone stopcock grease. A unique feature of the photolysis system was the elimination of contact between glyoxal vapor and cold surfaces of glass, mercury and stopcock grease, all of which catalyze glyoxal polymerization. With this equipment no measureable polymerization of glyoxal vapor occurred even during the seven-hour period of the longest runs. During the usual photochemical experiment not more than 0.5% of the original glyoxal was decomposed. The photolysis procedure and method of collection and analysis of the products were the same as that used in the previous study.

Glyoxal Preparation.—The procedure of Riley and Friend[7] was modified to prepare glyoxal vapor by reaction between ethylene and selenium dioxide in the presence of phosphorus pentoxide in a flow system. Dry ethylene gas was introduced to a tube which was about 1 m. in length and 20 mm. in diameter. The tube was wrapped with resistance wire and asbestos insulation and heated to about 80°; it was prepared under anhydrous conditions and contained an intimate mixture of equal portions of selenium dioxide and phosphorus pentoxide suspended on triple-turn helices (identical to those used for distillation column-packing). This mixture had a large surface area and was sufficiently porous to allow rapid gas flow. Unreacted ethylene and glyoxal vapor passed through the column and into a series of three traps at −5° and finally into a trap at −78°. The first traps served to remove traces of selenium dioxide. The −78° trap contained the majority of the glyoxal formed; it was sealed from the generating apparatus and evacuated, and the sample was purified further by vacuum distillation to a final storage bulb connected to the photolysis system. The glyoxal prepared by this procedure was stored in the form of the yellow solid at −78° for a period of six weeks without serious polymerization. The sample was warmed slightly when glyoxal vapor was desired. The molecular weight of the vapor as determined by the Dumas method was 58.7 ± 0.9 g./mole. Approximate vapor pressures of the product in mm. were: 52 at −1°, 60 at 0°, 90 at 6°, 143 at 13°, 169 at 16°, and 284 at 26°; m.p. about 15°.

Experimental Results

The Thermal Decomposition.—The thermal decomposition of glyoxal became significant in runs at 300° during the times of exposure necessary in the present work. The rates of carbon monoxide formation in dark runs at 303 and 253° indicate an activation energy for the reaction of decomposition of about 45 kcal./mole, in qualitative agreement with the value, 54 ± 10 kcal./mole, estimated by Steacie, Hatcher and Horwood.[8] An 18% correction for thermal reaction was made to the rates of the 303.6° run in the series B experiments of Table I. The only other data affected measurably by thermal decomposition are those of the 253.3° run which required 0.6% correction.

Glyoxal Absorption Coefficients.—At a fixed temperature the absorption of 3130 Å. radiation by glyoxal vapor follows Beer's law within the experimental error of the determinations over the range of pressure used, 25–250 mm. The molecular extinction coefficients, ϵ, for glyoxal vapor at wave length 3130 Å. are 22.5 and 24.6 at 157 and 251°, respectively, where $\log_{10}(I_0/I) = \epsilon cl$; c is the concentration in moles/l., and l is the path length in cm.

The Effects of Experimental Variables on the Rate of Product Formation. (a) **Light Intensity.**—The results are summarized in Table I. Carbon monoxide and hydrogen are the only products of glyoxal photolysis which are not condensed at liquid nitrogen temperature and these are the only products for which analyses were made. In a given series of runs summarized in Table I the incident light intensity was essentially constant. The light intensity was decreased regularly in series A experiments by placing calibrated uniform density filters in the light beam. Because of the very long exposures necessary in the experiments at low light intensities, aging of the arc was most serious during this series of experiments. A measure of the decrease in the incident light intensity because of the aging of the arc is had by comparison of the duplicate runs made at the start and finish of the series. The order in which the runs are tabulated indicates the chronological order of the series A experiments. The decrease in volume of products as a result of the aging of the arc was assumed to be a linear function of arc operating time, and the volumes of carbon monoxide formed were corrected to eliminate this aging effect; these corrected values appear in parentheses in column (4) of Table I. The ratios given in column (8) of Table I are calculated for each series of experiments by taking the volume of carbon monoxide product (S.T.P.) in μl./90 min., given in column (4), divided by the product of the fraction of light absorbed by the glyoxal in column (3), and the light intensity incident at the front of the cell given in column (7), taking full intensity, F, as unity. The use of this ratio provides a convenient means of demonstrating the kinetics of the reaction.

(b) **Temperature.**—Given in the series B experiments of Table I are the photolysis rate data at various temperatures in the range 106–304°. Actinometry with malachite green leucocyanide[9] indicated that a total of about 5% lowering of the incident intensity of 3130 Å. radiation occurred during the entire series B runs. No correction for this lowering was made in series B, C or D experiments; the chronological order of the runs was not the same as the order in which the runs are tabulated but was arranged so that a scatter of the results rather than a uniform drift would be the resultant effect of arc aging, and the effect of the variable studied would not be masked.

(c) **Concentration of Glyoxal and Carbon Dioxide.**—Concentration of glyoxal was varied from 0.00190 to 0.00930 M in series C experiments in Table I. In series D experiments the second run duplicated the conditions of the first except that a concentration of carbon dioxide about ten times that of the glyoxal was added.

Quantum Yield Determination.—Quantitative estimates of the total 3130 Å. radiation incident just inside the front window of the photolysis cell were made following the second run of series D experiments using malachite green leucocyanide[9] and uranyl oxalate[10] actinometry; the values found by the two systems were 5.42×10^{14} and 5.34×10^{14} quanta/sec., respectively. The first estimate was made using a 13-minute exposure to the 3130 Å. radiation which was reduced to 2.00% of its full value by a calibrated uniform density filter. The determination using uranyl oxalate required 12-hours exposure time to the full intensity of the beam and is probably low because of aging of the arc during this time. In the photolysis run which preceded these determinations 3.17×10^{14} and 0.34×10^{14} molecules of carbon monoxide and hydrogen, respectively, were formed/sec., and 47.9% of the incident intensity was absorbed by the glyoxal. From these data the quantum yields of carbon monoxide and hydrogen are estimated to be 1.22 and 0.13, respectively. The rate data show that the quantum yields are relatively insensitive to changes in light intensity, concentration, temperature and added inert gas.

Discussion of Results

The Reaction Mechanism.—The data of this study confirm the conclusion of the previous investigators[2,3] that formyl radical formation is unimportant in the photodecomposition of glyoxal. All of the present results are consistent with the following reaction mechanism for glyoxal photolysis at wave length 3130 Å.

$$(\mathrm{HCO})_2 + h\nu \longrightarrow (\mathrm{HCO})_2^* \qquad (1)$$

Reaction (1) is rapidly followed by

$$\begin{array}{lll} (\mathrm{HCO})_2^* \longrightarrow & \mathrm{H_2} + 2\mathrm{CO} & (2) \\ \phantom{(\mathrm{HCO})_2^*} \longrightarrow & \mathrm{CH_2O} + \mathrm{CO} & (9) \end{array}$$

The rate equation for carbon monoxide formation derived from this mechanism is

$$\mathrm{d}[\mathrm{CO}]/\mathrm{d}t = I_0(1 - e^{-\epsilon cl})(\phi_9 + 2\phi_2) \qquad (12)$$

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(7) H. L. Riley and W. A. C. Friend, *J. Chem. Soc.*, 2342 (1932).

(8) E. W. R. Steacie, W. H. Hatcher and J. F. Horwood, *J. Chem. Phys.*, **3**, 291 (1935).

(9) L. Harris, J. Kaminsky and R. G. Simard, THIS JOURNAL, **57**, 1151, 1154 (1935); J. G. Calvert and H. J. L. Rechen, *ibid.*, **74**, 2101 (1952).

(10) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

TABLE I

THE EFFECT OF SEVERAL VARIABLES ON THE RATE OF PRODUCT FORMATION IN THE PHOTOLYSIS OF GLYOXAL VAPOR AT 3130 Å.

(1) $[(HCO)_2] \times 10^3$ M	(2) Temp., °C.	(3) Fraction light absorbed	(4) Vol. product formed, μl. (S.T.P.)/90 min. CO	(5) H_2	(6) Φ_{H_2}/Φ_{CO}	(7) I_0, (F = full)	(8) (4)/(3)(7), (F = 1)
A. Intensity							
3.79	157.7	0.722	120.7	15.8	0.13	F	167
3.71	157.3	.714	17.3(18.3)	2.3	.13	0.152F	169
3.75	156.0	.718	41.3(46.0)	5.0	.12	.380F	169
3.71	156.5	.714	59.0(68.1)	6.8	.11	.570F	168
3.73	156.5	.716	103.6(120.7)	12.0	.12	F	(167)
B. Temperature							
5.08	105.6	0.804	136.6	18.4	0.13	F	170
4.94	155.3	.811	144.3	15.3	.11	F	178
5.00	204.3	.829	156.1	20.6	.13	F	188
4.90	253.3	.836	156.5[a]	22.7[a]	.15[a]	F	187[a]
4.97	303.6	.853	180.4[a]	29.0[a]	.16[a]	F	211[a]
C. Concentration of glyoxal							
1.90	158.1	0.473	71.5	9.2	0.13	F	151
5.53	159.0	.845	124.6	17.6	.14	F	147
7.40	159.0	.918	134.6	17.5	.13	F	147
9.30	157.9	.957	141.3	22.0	.16	F	148
D. Added carbon dioxide							
1.89	156.8	0.472	65.1	8.7	0.13	F	138
1.93 18.1 (CO_2)	156.6	0.479	63.7	6.9	0.11	F	133

[a] These data are only approximate since rates have been corrected for thermal reaction.

where I_0 is the 3130 Å. light intensity incident just inside the photolysis cell front window, $(1 - e^{-\epsilon cl})$ is the fraction of the incident light absorbed as calculated from Beer's law, ϵ is the molar extinction coefficient for glyoxal, c is the concentration of glyoxal, l is the path length of the photolysis cell, and ϕ_9 and ϕ_2 are the quantum efficiencies of reactions (9) and (2), respectively.

Interpretation of the Data in Terms of the Proposed Mechanism. (a) Effect of Light Intensity.—At constant concentration of glyoxal (therefore $(1 - e^{-\epsilon cl})$ = a constant) and constant temperature, the first-order dependency of the rate on the incident light intensity suggested by the theoretical rate law (12) is shown by the constancy of the ratio, $(d[CO]/dt)/I_0(1 - e^{-\epsilon cl})$, given in the data in column (8) of the series A experiments of Table I.

(b) **Effect of Glyoxal and Added Gas Concentrations.**—At constant incident light intensity and temperature the ratio given in column (8) of series C experiments of Table I is independent of the glyoxal concentration as predicted by the rate law (12). These data prove the unimportance of reaction (3) at wave length 3130 Å. and point to product formation by unimolecular decomposition of the activated molecules. The data of series D experiments of Table I indicate that the rate is independent of large concentrations of added inert gas; this suggests that collisional deactivation of activated molecules is unimportant under the conditions of these experiments.

(c) **Effect of Temperature.**—The data of column (8) in the series B experiments of Table I show that the rate of carbon monoxide formation is virtually insensitive to temperature change when the absorbed light intensity is constant. The slight increase in rate observed corresponds to an apparent activation energy of carbon monoxide formation of about 0.4 kcal./mole. These data provide evidence for the absence of formyl radical formation, reaction (5), in these experiments; presumably chain decomposition of glyoxal by reactions such as (13), (14) and (15)

$$HCO \longrightarrow H + CO \qquad (13)$$

$$H + (HCO)_2 \longrightarrow H_2 + HCOCO \qquad (14)$$

$$HCOCO \longrightarrow HCO + CO \qquad (15)$$

would follow (5) at the temperatures used in this study and a marked temperature dependence of the rate of product formation would be observed if (5) occurred. The molecular extinction coefficients indicate increased absorption with increase in temperature, but the change is not sufficient to account for the entire temperature dependence observed. The increase in rate with increase in temperature may reflect the increasing importance of reaction (2). It appears that the ratio Φ_{H_2}/Φ_{CO} increases slightly with increasing temperature (see column (6) of series B experiments of Table I); the suggestion of the increasing efficiency of reaction (2) with temperature increase is also in line with this result.

(d) **Quantum Yield Results.**—From the data of column (6) of Table I it appears that the ratio Φ_{H_2}/Φ_{CO} is independent of the various variables with the possible exception of the temperature. Using the average value of this ratio, 0.13, and assuming that all activated glyoxal molecules decompose completely by the proposed reaction scheme (no deactivation occurs), one estimates that the maximum possible quantum yields of products are: Φ_{CO} = 1.15 and Φ_H = 0.15. The agreement of these theoretical values with the experimental estimates of $\Phi_{CO} = 1.22$ and $\Phi_{H_2} = 0.13$ adds credence to the proposed mechanism which suggests the complete decomposition of light activated molecules. Glyoxal photolysis at 3130 Å. is unique in this respect. The previous investigations at 3660 Å.[2,3] point to the formation of a longer-lived activated molecule, and it seems probable that collisional deactivation and reaction (3) as well as (2) and (9) are important in photolyses at 3660 Å.

Nature of Reactions (2) and (9).—Analytical difficulties prevented the determination of the expected product formaldehyde in the large excess of glyoxal. However the occurrence of reaction (9) is well established; it is the only unimolecular process which one can propose to explain the large excess of carbon monoxide in the products. Reaction (9) is very similar to the intramolecular rearrangement of the aliphatic aldehydes which decompose in part according to the reaction, $RCHO + h\nu \rightarrow RH + CO$.

The energy changes involved in the reactions (2) and (9) are very similar, but the data show that decomposition of glyoxal molecules activated by 3130 Å. radiation occurs about 85% of the time by reaction (9) and only 15% of the time by reaction (2). The high efficiency of decomposition by reaction (9) may be a result of the more favorable steric conditions for the occurrence of this reaction. LuValle and Schomaker[11] have shown by electron diffraction studies that glyoxal is a planar molecule which exists in *cis* and *trans* forms as a consequence of the partial double bond character to the C–C bond of the molecule. The more stable *trans* form is probably the dominant form in the temperature range of the present experiments. Absorption of 3130 Å. radiation by the *cis* and *trans* forms may lead to different activated states in which rotation about the C–C bond is unimportant during the very short lifetimes of these states. Assuming these conditions one would predict from the geometry of the *cis*- and *trans*-glyoxal molecules that decomposition by reaction (2) would be more favorable sterically from the *cis* form of glyoxal, while rearrangement by reaction (9) would be about equally favorable from either the *cis* or *trans* form. This simple picture can explain qualitatively the observed predominance of reaction (9) and suggests that the slight increase in efficiency of reaction (2) with temperature increase may reflect the shift of the *cis–trans* equilibrium toward the *cis* form at higher temperatures. The previous studies of glyoxal photolysis[2,3] indicate that 3660 Å. light-activated glyoxal molecules react in part by (3) and by deactivation. The absence of analogous reactions for glyoxal molecules activated by 3130 Å. radiation is consistent with the proposal that a much shorter lived activated state of glyoxal is formed at 3130 Å. than at 3660 Å. However, unless the activated states formed at 3130 Å. are only transitory in their existence it is highly improbable that molecule configuration at the instant of light absorption is important in determining the mode of decomposition.

Energy Consideration of Reaction (5).—It can be argued that photocomposition of glyoxal at 3660 and 3130 Å. by reaction (5) does not occur because there is insufficient energy of the absorbed quantum of radiation at these wave lengths.[3] From available energy data[12] it can be estimated (very approximately) that the absorption of light of wave lengths less than about 2940 Å. is necessary to provide the energy required to promote reaction (5). To test this point a few qualitative rate studies of glyoxal photolysis were made at wave length 2537 Å. (isolated with a monochromator system) and in the temperature range 108 to 230°. The results showed a small temperature dependence of the product rates corresponding to an apparent activation energy of carbon monoxide formation of about 1.5 kcal./mole. The ratio $\Phi_{H_2}/\Phi_{CO} = 0.13$ was about the same as that found in the photolyses at 3130 Å. These results suggest that the occurrence of (5) is unimportant in glyoxal photolysis even at wave lengths where the energy per quantum is probably in large excess of that necessary to cause this reaction.

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[11] J. E. LuValle and V. Schomaker, THIS JOURNAL, **61**, 3520 (1939).

[12] "Selected Values of Chemical Thermodynamic Properties," Natl. Bur. Standards (U. S.), Circ. No. 500, pp. 120, 599 (1952). The enthalpy change of the reaction $CO(g) + H(g) = H\dot{C}O(g)$ is estimated (very approximately) to be −14 kcal./mole from the activation energy of the reverse reaction, about 14 kcal./mole,[5] and that of the forward reaction which is taken as zero; see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 352.