

complete exchange and possibly more; it is doubtful whether any appreciable exchange occurred.

The photochemical experiments were carried out as follows. A solution of radioactive bromine and trichlorobromomethane in carbon tetrachloride was frozen with liquid air; the space above the solution was evacuated in order that oxygen might be largely removed. The solution was melted and separated *in vacuo* into two approximately equal portions which were then sealed off. One portion was thermostated and illuminated for a measured time with filtered radiation from a 500-watt tungsten lamp; the filter transmitted chiefly in the range 5000 to 6100 Å. The other portion was kept in the dark at the same temperature for the same time. After the illumination was completed, both solutions were cooled in the dark; the bromine was extracted from the same volume of each and converted to silver bromide for electroscopic measurements. A small volume of each solution was also analyzed for bromine.

A thermal exchange experiment was performed using the same technique; the solution was separated *in vacuo* into two portions; bromine from one portion was converted immediately to silver bromide; the other portion was kept in the dark at a high temperature for some time before the bromine extraction.

The results obtained with solutions containing about 0.003 mole of bromine and 0.08 mole of trichlorobromomethane per liter were as follows: thermal, solution heated at 76° for seventy-five minutes, -3% exchange; photo-

chemical, solution illuminated at 76° for seventy minutes, 98% exchange. Two experiments in which solutions containing 0.003 mole of bromine and 0.02 mole of trichlorobromomethane per liter were illuminated at 76° for twenty minutes resulted in 86 and 97% exchange. Other experiments at higher temperatures or with longer illumination times also gave 85 to 100% exchange.

Summary

Investigation of the exchange of bromine between radioactive bromine and various bromine compounds has led to the following results: a rapid exchange occurs with arsenious bromide and with stannic bromide at room temperature in carbon tetrachloride solution (!); in the same solvent no exchange beyond the limits of experimental uncertainty was observed to occur with either ethylene bromide or trichlorobromomethane in the dark at 100°; a rapid exchange with trichlorobromomethane is induced by green light at 76°.

A convenient method has been described for the preparation of dilute and highly radioactive solutions of bromine in carbon tetrachloride.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 743]

The Molecular Structures of Glyoxal and Dimethylglyoxal by the Electron Diffraction Method

BY JAMES E. LUVALLE¹ AND VERNER SCHOMAKER

Introduction.—Extension to open chain heteroatomic aliphatic compounds of the structural investigations² of the constitutional effect of different bonds upon adjacent bonds should provide useful information concerning the electronic structures and the extent of resonance in these molecules. The recent electron diffraction studies of formaldehyde³ and acetaldehyde⁴ have given a reliable value for the carbon-oxygen double bond distance. We have now extended the investigation of compounds containing the carbonyl group to glyoxal and dimethylglyoxal, both of which

contain a pair of conjugated carbon-oxygen double bonds and present the possibility of free rotation around the carbon-carbon bond connecting the adjacent carbonyl groups. Furthermore, both substances are colored, glyoxal being the simplest colored compound whose molecules have a conjugated system. Of the compounds glyoxal, dimethylglyoxal, oxalyl chloride, oxamide, and oxalic acid, it is found that glyoxal and dimethylglyoxal are colored whereas the remaining compounds are colorless. All five of these compounds may be represented by the formula RCORCO and the difference in color between the first two compounds and the remaining three compounds suggests that there may be a structural difference between the two groups of compounds. Oxalyl chloride is now under investigation in these Laboratories by the electron diffraction method, and the X-ray study of crystals of oxamide is also under way.

(1) Julius Rosenwald Fellow.

(2) (a) L. Pauling, L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **57**, 2705 (1935); (b) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937); (c) L. Pauling, H. D. Springall and K. J. Palmer *ibid.*, **61**, 927 (1939); (d) V. Schomaker and L. Pauling *ibid.*, **61**, 1769 (1939).

(3) D. P. Stevenson, J. E. LuValle and V. Schomaker, *ibid.*, **61**, 2508 (1939).

(4) D. P. Stevenson, H. D. Burnham and V. Schomaker, *ibid.*, **61**, 2922 (1939).

Experimental.—Glyoxal was prepared by the oxidation of ethylene with selenium dioxide after the method of Riley and Friend.⁵ The ethylene was oxidized in a 3 × 30 cm. Pyrex tube containing equal amounts by weight of phosphorus pentoxide and finely-ground selenium dioxide placed in alternating layers. At the ends of the tube there were longer (7 cm.) columns of phosphorus pentoxide and plugs of "Pyrex wool" (No. 9930). Gentle heating was necessary for starting the reaction. The glyoxal was collected in a trap at -60°. The ethylene was obtained from the Ohio Chemical Company and the selenium dioxide from the Eimer and Amend Company, New York.

Eastman "white label" dimethylglyoxal (b. p. 87-88.5°) was used without further purification.

The electron diffraction photographs were prepared with the apparatus described by Brockway.⁶ The values of $s_0 = (4\pi/\lambda)\sin \theta/2$ given in the tables are averages of the values found by visual measurement of the ring diameters for ten or more films. The wave length of the electrons determined from transmission pictures of gold foil ($a = 4.070 \text{ \AA.}$) was 0.0611 \AA. and the camera distance was 10.84 cm. The radial distribution functions⁷ were calculated using the s_0 values of both the maxima and minima, and the coefficients, C_K , were determined from these s_0 values and the visually estimated intensities, I_K , according to the method recommended by Schomaker.⁸

Glyoxal.—The photographs of glyoxal are very good, extending to $s_0 = 27$ and showing thirteen maxima and shelves. The radial distribution curve (Fig. 1) calculated with the C_K and s_0 values of Table I shows four principal peaks at 1.18, 1.48, 2.34 and 3.45 Å., the last two peaks being more reliable than the first two. The peak at 1.18 Å. corresponds to the carbon-oxygen double bond distance, that at 1.48 Å. to the carbon-carbon distance, and that at 2.34 Å. to the long carbon-oxygen distance. These distances indicate a value of about 121° for the C—C=O angle. Resonance probably causes the molecule to be coplanar. Of the two coplanar configurations, the *trans* form is suggested by the strong radial distribution peak at 3.45 Å., this value being very close to that calculated for a *trans* model

having the above parameters (3.41 Å.). The remaining small radial distribution peaks are probably without significance.

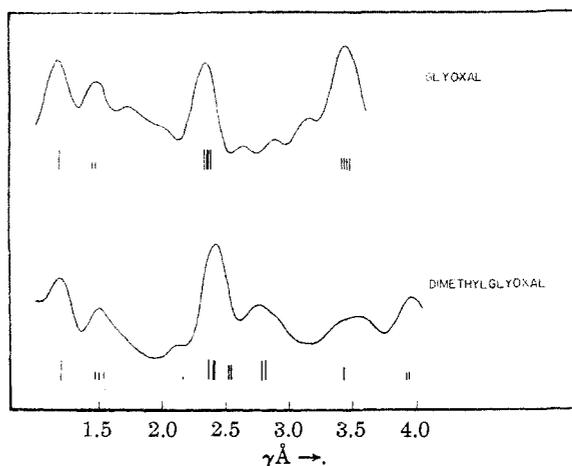


Fig. 1.—Radial distribution curves for glyoxal and dimethylglyoxal. The vertical lines beneath the curves show the various interatomic distances of the models used in the final determination of distances by the correlation method.

Twenty-four intensity curves were calculated with the ratio C—C/C=O varying from 1.38/1.20 to 1.52/1.20 and the angle C—C=O varying from 116° to 128°. The eight intensity curves of Fig. 2 were calculated for coplanar *trans* models with the distance C—H = 1.09 Å. and the angle H—C—C = 114°. A temperature factor was introduced into all the hydrogen terms in the intensity function.⁶ If the C—H parameter here assumed were in error by 0.03 Å. the change would not be detected since the contribution of the hydrogen terms is small. The H—C—C angle parameter is likewise unimportant. The longer carbon-oxygen distance and the oxygen-oxygen distance in these models are compatible with the strong radial distribution peaks at 2.34 Å. and 3.45 Å. The faint seventh and tenth shelves which were measured and used in the radial distribution function cannot be distinguished definitely on any of the theoretical curves; however, this is shown by the work of Schomaker and Stevenson⁹ on the interpretation of electron diffraction photographs not to be especially surprising.

Curves D and F of Fig. 2 reproduce the photographs satisfactorily, and curves C and E are nearly as good; in the final evaluation of parameters all four models have been used with models

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

(6) L. O. Brockway, *Rev. Mod. Physics*, **8**, 231 (1936).

(7) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

(8) Verner Schomaker, American Chemical Society Meeting, Baltimore, April, 1939.

(9) V. Schomaker and D. P. Stevenson, to be published.

TABLE I
GLYOXAL

Max.	Min.	I	C_K	s_0	Model C ^a		Model D		Model E		Model F	
					s	s/s_0	s	s/s_0	s	s/s_0	s	s/s_0
	1	-10	-6	3.16	3.20	(1.013) ^b	3.30	(1.044)	3.20	(1.013)	3.30	(1.044)
1		4	2	4.02	3.50	(0.871)	3.60	(0.896)	3.40	(0.846)	3.50	(0.871)
	2	-6	-6	4.87	4.48	(0.920)	4.32	(0.930)	4.55	(0.934)	4.50	(0.928)
2		10	6	6.06	6.07	1.002	6.10	1.007	6.06	1.000	6.08	1.003
	3	-5	-6	7.26	7.40	(1.019)	7.60	(1.047)	7.40	1.019	7.60	1.047
3		5	5	8.12	7.90	(0.973)	8.00	(0.985)	7.90	(0.974)	8.00	(0.985)
	4	-2	-3	8.81	8.80	0.999	8.80	0.999	8.77	0.995	8.80	0.999
4		3	4	9.51	9.10	0.957	9.50	0.999	9.22	0.970	9.20	0.967
	5	-7	-8	10.34	9.95	(0.962)	10.07	(0.974)	9.90	(0.957)	10.00	(0.962)
5		8	12	11.54	11.40	0.988	11.52	0.998	11.32	0.981	11.49	0.996
	6	-4	-6	12.53	12.66	1.010	12.87	1.027	12.47	0.987	12.64	1.009
6		3	5	13.40	13.32	0.994	13.50	1.007	13.28	0.991	13.38	0.999
	7	-1	-1	14.36 ^d
7		2	3	15.06 ^d
	8	-8	-13	15.28	15.30	(1.001)	15.40	(1.008)	15.22	(0.996)	15.22	(0.996)
8		7	12	16.90	16.83	0.996	17.05	1.009	16.77	0.992	16.90	1.000
	9	-2	-3	17.76	18.05	(1.016)	18.33	(1.032)	17.90	(1.008)	18.22	(1.026)
9		1	2	18.67	18.58	0.995	18.80	1.007	18.40	0.986	18.73	1.003
	10	-1/2	-1	19.47 ^d
10		1/2	1	20.18 ^d
	11	-8	-10	20.37	20.05	(0.984)	20.05	(0.984)	20.70	(1.016)	20.05	(0.984)
11		5	8	22.25	22.18	0.997	22.40	1.007	22.08	0.992	22.25	1.000
	12	-8	-8	23.50	23.60	1.004	23.90	1.017	23.54	1.002	23.70	1.009
12		2	3	24.38	24.10	0.989	24.60	1.009	23.90	0.980	24.40	1.001
	13	-3	-2	25.53	25.20	(0.976)	25.35	(0.991)	25.10	(0.984)	25.24	(0.987)
13		3	4	27.08	27.43	(1.013)	27.63	(1.020)	27.28	(1.007)	27.60	(1.019)
Average					0.994		1.008		0.989		0.999	
Average deviation					0.008		0.006		0.008		0.006	
(C=O) = 1.20 × ($\overline{s/s_0}$)					1.193		1.208		1.187		1.199	
(C—C) = 1.46 × ($\overline{s/s_0}$)					1.451		1.472					
= 1.48 × ($\overline{s/s_0}$)									1.464		1.479	
(C=O) = 1.20 ± 0.01 Å.												
(C—C) = 1.47 ± 0.02 Å.												

^a The models are described in the legend to Fig. 2. ^b Less reliable values, not included in taking the averages, are shown in parentheses. ^c The theoretical curve indicates no precisely measurable feature at this point. ^d The values of s_0 used in the radial distribution function were somewhat different than the ones given here; the weights show these terms were relatively unimportant.

D and F assigned weights three times as great as models C and E. Curves A, B, G and H are not at all satisfactory and the corresponding models were discarded.

It is concluded that the glyoxal molecule has the configuration and distances described by the following parameters: C—H = 1.09 Å. (assumed), C=O = 1.20 ± 0.01 Å., C—C = 1.47 ± 0.02 Å., angle C—C=O = 123° ± 2°. The molecule is probably coplanar and *trans*; the evidence for this view provided by the radial distribution function is supported by a strong dependence of the intensity curves upon the relative orientation of the carbonyl groups of the glyoxal molecule. Theoretical considerations¹⁰ indicate that resonating

systems tend to be coplanar. The electron diffraction data are not incompatible with a mixture containing a small fraction of molecules with the *cis* configuration. The data indicate that the amplitude of libration around the carbon-carbon bond is small.

Dimethylglyoxal.—The photographs of dimethylglyoxal are excellent, extending out to s_0 = 27 and showing eleven maxima and shelves. The s_0 , I_K , and C_K values are given in Table II. The radial distribution curve (Fig. 1), calculated with the s_0 and C_K values of this table, has peaks at 1.19, (1.50), (2.12), 2.41, 2.75, (3.56), and 3.95 Å. (The less reliable peaks are enclosed in parentheses.) We can assume coplanarity of the molecule as it possesses a resonating system. The peak at 1.19 Å. corresponds to the carbon-oxygen

(10) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 679 (1933); W. G. Penney, *Proc. Roy. Soc. (London)*, **A168**, 306 (1937).

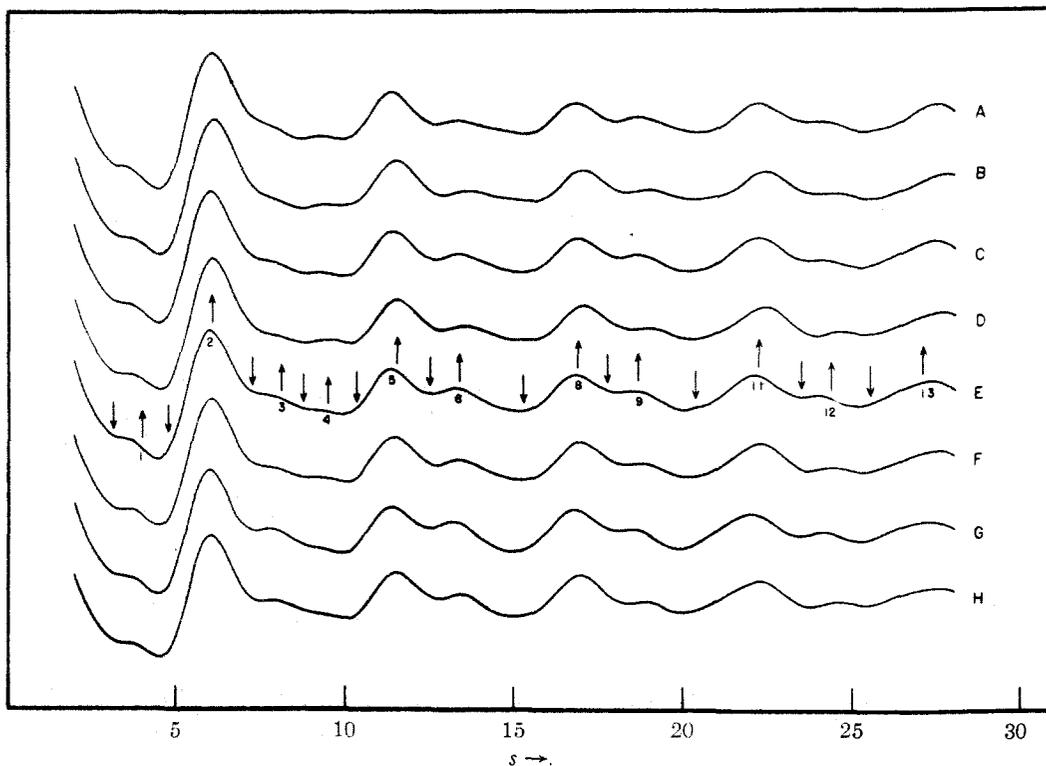


Fig. 2.—Theoretical intensity curves for glyoxal. Denoting the C—C=O by α and the ratio of the C—C distance to the C=O distance by ρ :

Curve A, $\alpha = 128^\circ$, $\rho = 1.42/1.20$;
 Curve C, $\alpha = 125^\circ$, $\rho = 1.46/1.20$;
 Curve E, $\alpha = 125^\circ$, $\rho = 1.48/1.20$;
 Curve G, $\alpha = 122^\circ$, $\rho = 1.52/1.20$;

Curve B, $\alpha = 125^\circ$, $\rho = 1.42/1.20$;
 Curve D, $\alpha = 122^\circ$, $\rho = 1.46/1.20$;
 Curve F, $\alpha = 122^\circ$, $\rho = 1.48/1.20$;
 Curve H, $\alpha = 119^\circ$, $\rho = 1.52/1.20$.

TABLE II
 DIMETHYLGLYOXAL

Max. Min.	I	C_K	s_0	Model C ^a		Model D	
				s	s/s_0	s	s/s_0
1	50	4	3.05	2.94	(0.964)	2.90	(0.951)
2	-100	-10	4.36	4.27	(0.979)	4.25	(0.975)
2	100	12	5.59	5.75	(1.028)	5.82	(1.041)
3	-30	-2	7.35	7.23	0.984	7.30	0.993
3	60	11	8.20	8.27	1.008	8.30	1.012
4	-10	-2	8.86
4	5	1	9.37	9.30	0.993	9.30	0.993
5	-50	-12	10.23	10.20	0.997	10.26	1.003
5	50	12	11.44	11.52	1.007	11.50	1.005
6	-40	-11	12.37	12.43	1.005	12.42	1.004
6	55	14	13.44	13.46	1.001	13.42	0.999
7	-60	-24	15.29	15.13	0.990	15.10	0.988
7	60	17	16.21	16.77	(1.035)	16.64	(1.027)
8	-30	-10	17.64	17.73	1.005	17.57	0.996
8	20	5	18.84	18.47	(0.980)	18.34	(0.973)
9	-60	-15	20.19	19.90	0.986	19.88	0.985
9	45	13	21.48	21.50	1.001	22.30	1.038
10	-20	-7	23.26	23.80	1.023	23.63	1.017
10	10	3	24.34	24.70	(1.015)	24.40	(1.002)
11	-25	-7	25.23	25.05	(0.993)	25.60	(1.015)
11	30	8	26.87	27.53	(1.025)	27.35	(1.018)
Average					0.998		1.001
Average deviation					0.007		0.010

^a The models are described in the legend to Fig. 3. The theoretical curves do not show a precisely measurable feature at this point.

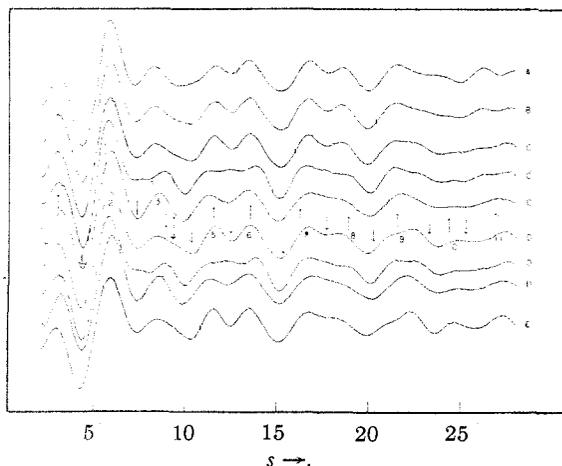


Fig. 3.—Theoretical intensity curves for dimethylglyoxal. All the curves have the following parameters in common: C—H = 1.09 Å. (assumed), C=O = 1.20 Å., C₂—C₃ = 1.47 Å., C₁—C₂ = 1.54 Å., and angle CO—C=O (α) = $123^\circ \pm 2^\circ$. Denoting angle CH₃—C=O by β we have: Curve A, $\beta = 125^\circ$; Curve B, $\beta = 124^\circ$; Curves C, C', and C'', $\beta = 123^\circ$; Curves D, D', and D'', $\beta = 122^\circ$; Curve E, $\beta = 121^\circ$.

double bond distance, that at 1.50 Å. to the 2-3 carbon-carbon distance and the two 1-2 carbon-carbon distances, and that at 2.41 Å. to the 1-3 carbon-carbon distance and the two carbon-oxygen distances. The peak at 2.75 Å. may be attributed to the long carbon-oxygen distance of the molecule with the *trans* configuration or possibly to the long carbon-carbon distance for the *cis* configuration, and the broad peak at 3.56 Å. may represent the oxygen-oxygen distance for the *trans* configuration or the long carbon-oxygen distance for the *cis* configuration. However, the peak at 3.95 Å. can be attributed only to the long carbon-carbon (1-4) distance of the *trans* form, which indicates strongly that the molecule has the *trans* configuration.

Assuming that the distances and the C—C=O angle found for glyoxal hold for dimethylglyoxal, five models were set up and fifteen intensity curves calculated, five for the *cis* form, five for the *trans* form, and five in which the terms dependent upon the relative orientation of the acetyl groups were omitted from the intensity function. The angle β was varied from 119 to 125°.

Of the curves shown in Fig. 3, A, B, C, D and E are for the *trans* models, C' and D' are for the *cis* models, and C'' and D'' are the incomplete intensity curves corresponding to C and D, respectively. Curves C and D both give satisfactory agreement with the photographs except for the ninth and tenth maxima. On curve C, the ninth maximum is observed to have shifted to a smaller s value than that measured and the tenth maximum is too weak, whereas on curve D, the ninth maximum is observed to have shifted to a larger s value than that measured and the tenth maximum is too strong. The best model accordingly lies between model C and D. Examination of Fig. 3 shows that the remaining *trans* models, A, B, and E, are unsatisfactory and the *cis* models C' and D' are out of the question. Curves C'' and D'' show that the libration around the 2-3 carbon-carbon bond is not of great amplitude.

It is concluded that the dimethylglyoxal molecule is essentially coplanar and *trans* with the following parameter values: C—H = 1.09 Å., C₂—C₃ = 1.47 ± 0.02 Å., C₁—C₂ = 1.54 ± 0.02 Å., C=O = 1.20 ± 0.02 Å., angle CO—C=O (α) = 123° ± 2°, and angle CH₃—C=O (β) = 122.5° ± 1°. The electron diffraction data are not incompatible with a mixture containing a small fraction of *cis* molecules. The data indi-

cate that the amplitude of libration around the (C₂—C₃) carbon-carbon bond is small. It must be emphasized that the determination of the configuration and distances in dimethylglyoxal is not as precise as that for glyoxal. The radial distribution curve strongly indicates this model but a model in which the 2-3 carbon-carbon bond is somewhat lengthened and the 1-2 and 3-4 carbon-carbon bonds are slightly shortened cannot be eliminated by the qualitative comparison, but such a model does not agree with the radial distribution function as well as our final model.

Discussion.—The observed shortening in both molecules of 0.07 Å. for the carbon-carbon bond connecting the adjacent carbonyl groups corresponds to 15 or 20% double bond character,^{2b} and is nearly the same as that (1.46 Å.) reported for butadiene.^{2d} The electron diffraction data for both glyoxal and dimethylglyoxal indicate restricted rotation around the carbonyl-carbonyl bond.

Calculation of the potential restricting rotation around the 2-3 carbon-carbon bond in dimethylglyoxal by the method of Beach and Stevenson¹¹ using Zahn's values¹² of the dipole moment and Smyth's values¹³ of the group moments indicates that the potential barrier restricting rotation is steeper than a parabolic barrier and greater than 12 kcal. in height. Zahn¹² finds an amplitude of approximately 30° for the libration in dimethylglyoxal. Dipole moment data are not available for glyoxal, so that the corresponding calculation could not be made; however, the potential barrier should be of the same order of magnitude for both substances.

Calculation of the coulombic interactions for the *cis* and *trans* models of glyoxal and dimethylglyoxal using Smyth's values¹³ of the bond moments shows that the *trans* glyoxal molecule is about 6.9 kcal./mole more stable than the *cis* configuration and that the *trans* dimethylglyoxal molecule is about 1.7 kcal./mole more stable than the *cis* configuration. Calculations of the ratio of the partition functions of *cis* to *trans* glyoxal and dimethylglyoxal are simplified by the assumption that the vibrational partition functions are the same for both the *cis* and *trans* configurations, the translational partition functions are the same; therefore, the calculation becomes the cal-

(11) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 635 (1938).

(12) C. T. Zahn, *Phys. Rev.*, **40**, 291 (1932).

(13) C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

ulation of the square root of the ratio of the product of the three principal moments of inertia for the two configurations. The ratios $[(I_1 I_2 I_3)_{cis} / (I_1 I_2 I_3)_{trans}]^{1/2}$ for the glyoxal and dimethylglyoxal molecules are 1.15 and 1.00, respectively. For the equilibrium $cis \rightleftharpoons trans$ these values combined with the ΔE values given above correspond to equilibrium constants of 87,000 and 20 for glyoxal and dimethylglyoxal, respectively; that is, the fraction of *cis* glyoxal is negligible and that of *cis* dimethylglyoxal may be about 5%. These results agree with our electron diffraction investigations.

We express our thanks to Dr. Linus Pauling for his helpful criticism and discussion and to Dr. D. P. Stevenson for assistance with the calculations and helpful discussion.

Summary

The configurations of glyoxal and dimethylglyoxal as determined by the electron diffraction method are given by the following parameters:

Glyoxal: C—H = 1.09 Å. (assumed), C=O = 1.20 ± 0.01 Å., C—C = 1.47 ± 0.02 Å., angle C—C=O = $123^\circ \pm 2^\circ$

Dimethylglyoxal: C—H = 1.09 Å. (assumed), C=O = 1.20 ± 0.02 Å., C₂—C₃ = 1.47 ± 0.02 Å., C₁—C₂ = 1.54 ± 0.02 Å., angle CO—C=O = $123^\circ \pm 2^\circ$, angle CH₃—C=O = $122.5^\circ \pm 1^\circ$

The electron diffraction data and the dipole moment data as well as chemical information indicate uniformly that both molecules are coplanar with the *trans* configuration and that rotation around the carbon-carbon bond connecting the adjacent carbonyl groups is restricted.

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[CONTRIBUTION FROM THE DEPARTMENT OF BOTANY AND DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Quantum Efficiency of Photosynthesis in *Chlorella*. II

BY H. G. PETERING,¹ B. M. DUGGAR AND FARRINGTON DANIELS

Photosynthesis in algae has been the object of an extended investigation in these laboratories. The quantum efficiency was found to be of the order of 0.05 molecule per quantum,² much lower than the older value of 0.25 reported by Warburg and Negelein.³ In order to study further the reasons for this large discrepancy, a new method was developed⁴ for the rapid determination of dissolved oxygen making use of the dropping mercury electrode. The respiration correction seemed to be the most important source of error, and the manometric method used by Warburg and Negelein involves a considerable time lag in determining the rate of respiration and of photosynthesis. If respiration is faster under the conditions imposed by photosynthesis, then a prompt determination of respiration after the light is turned off is necessary if arbitrary assumptions are to be minimized. Results obtained with the dropping mercury electrode are given here. They agree essentially with those reported earlier² and are in definite disagreement with those of

Warburg and Negelein.³ Recently Rieke⁵ has reported a value of 0.24 obtained with the manometric method in agreement with Warburg and Negelein.

Experimental Procedure

The material was *Chlorella pyrenoidosa*, of the same strain as used before.² It was grown in pure culture on agar slants and periodically transferred to fresh slants or to liquid media. The liquid culture was essentially the salt nutrient recommended by Warburg and Negelein.³ The composition was:

Agar medium, g.		Liquid nutrient, M	
NaNO ₃	0.25	MgSO ₄	0.020
CaCl ₂	.25	KNO ₃	.005
KH ₂ PO ₄	.25	KH ₂ PO ₄	.018
MgSO ₄	.25	FeSO ₄	.00001
Cane sugar	2.00		
Water	1 liter		

Distilled water from a block tin condenser was used in most of the experiments but no differences were noted when in some of the experiments tap water from Lake Mendota was used. The algae were grown in 300-cc. flasks on a water-cooled rack illuminated from the bottom, while air, to which had been added 5% carbon dioxide, was bubbled through. Warburg's recommendations were followed in a general way, exposing algal cultures to bright light (four 200-watt filament lamps at 30 cm.) for a week and then to weaker light (six 25-watt lamps at 45 cm.).

(1) Present address: Chemical Section, Michigan Experiment Station, East Lansing, Michigan.

(2) W. M. Manning, J. F. Stauffer, B. M. Duggar and F. Daniels, *THIS JOURNAL*, **60**, 266 (1938).

(3) O. Warburg and E. Negelein, *Z. physik. Chem.*, **106**, 191 (1923).

(4) H. G. Petering and F. Daniels, *THIS JOURNAL*, **60**, 2796 (1938).

(5) F. F. Rieke, *J. Chem. Phys.*, **7**, 238 (1939).