AN ELECTRON DIFFRACTION INVESTIGATION OF SEVERAL UNSATURATED CONJUGATED MOLECULES

THESIS

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF DOCTOR OF PHILOSOPHY,

CALIFORNIA INSTITUTE OF TECHNOLOGY,

PASADENA, CALIFORNIA

1940

Acknowledgment

The author wishes to express his appreciation for the kind advice and many helpful discussions with Dr. Linus Pauling, Dr. D. P. Stevenson, and Dr. Verner Schomaker.

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THE NATURE OF CONJUGATED SYSTEMS

INTRODUCTION

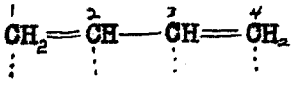
There are three types of systems containing two double bonds; the "cumulated" or "twinned" type in which the two double bonds are adjacent to each other, the "conjugated" type in which the double bonds are separated by one single bond, and the "isolated" type in which they are separated by two or more single bonds. A conjugated system may contain several double bonds conjugated with each other as in the carotenoids.

The conjugated system is the most stable of the three for although at ordinary temperatures these compounds do not change over into each other, at elevated temperatures, cumulated systems (of four or more carbon atoms) or isolated systems change over into the isomeric conjugated compounds.(1) Increasing the length of the conjugated chain by addition of successive -CH=CH- groups causes a progressive shift of the absorption maximum to the red end of the spectrum, and as the number of conjugated linkages increase, it becomes relatively more easy to produce electronic changes in the system, which means that the absorption will shift to the low energy end of the spectrum, the red. Chemical evidence has shown that with increasing length, the thermal reactivity of conjugated systems becomes progressively greater.(2) Nearly all substances containing a conjugated system which includes an oxygen atom show halochromism, the property of forming with strong acids colored salt-like products which are more or less readily decomposed by water.(3) Conjugated hydrocarbons show optical exaltation,

that is the molecular refraction is higher than the value calculated on the basis of isolated double bonds; this effect however is not shown by closed circuits of alternate single and double bonds as in benzene, toluene, or cyclooctatetrene.(4) Dipole moments of conjugated systems generally deviate from predicted values.(5) Conjugated systems such as acrolein and crotonaldehyde show much greater photochemical stability than the corresponding unconjugated isomers.(6) Conjugated systems show greater chemical stability than the isomeric unconjugated systems.

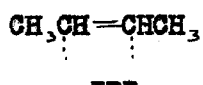
Old Theories

Diolefins add many reagents as for example the halogens. The addition may take place in steps. When the addition to a conjugated system is carried out in steps, the reaction often takes an unexpected course for at the first step, the addends are often attached to the first and fourth carbon atoms rather than the adjacent carbon atoms. This reaction is called conjugate addition or 1,4 addition. Thus butadiene and bromine yield 1,4 -dibromo-2-butene, and addition of a second molecule of bromine yields 1, 2, 3, 4 tetrabromobutane. That is, butadiene reacts as if the terminal carbon atoms were the most unsaturated. Thiele in 1899 explained conjugate addition with his theory of partial valence or residual affinity.(7) The initial assumption is made that not all the available affinity is used by a double bond between the two atoms; the residual affinity on each atom is a partial valence and is represented graphically by dotted lines as in I.



I

II



III

In a conjugated system, the partial valences on the intermediate atoms (2 and 3 in formula I) neutralize each other so that the effective unsaturation is localized at the ends of the system as in II. Addition to such a system will take place at the end atoms and since the addendam will require more affinity than is available from the partial valences, the double bonds will be broken and a new double bond will be formed; the final product will be III. Thiele's theory was eagerly adopted but it failed to explain 1,2 addition in conjugate systems. Hinrichsen modified the theory so as to take into consideration the nature of the substituents in the conjugated system and the nature of the addend.(8)

The hypothesis of initial 1,4 addition to the system C=C-C=O followed by subsequent isomeric change explains why the ethylenic linkage in unsaturated ketones and acids appears to possess the unusual property of forming addition compounds with substances such as ammonia, hydrogen cyanide and sodium bisulphite. The Diels - Alder reaction or the diene synthesis(9) is characteristic of conjugated systems. It consists of the 1,4 addition of α-β unsaturated carbonyl compounds to a conjugated diene such as the reaction of butadiene with acrolein, acetaldehyde (as vinyl alcohol) and maleic anhydride to form a cyclic compound. The reaction is quite often spontaneous. Conjugated systems also add alkali metals readily. Conjugated systems have lower heats of combustion and are definitely more stable.(10)

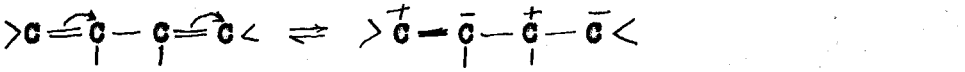
Thiele claimed that the tendency to form conjugated systems promotes enolization. In β-diketones and β-ketonic esters, a carbonyl group in the β-position has the effect of stabalizing the enolic form, although this does not happen when the carbonyl group is

is in the contiguous α-position. Thiele pointed out that the enolic form of the β compounds contain a conjugated system which is absent both in the ketonic form of these compounds and in the hypothetical enolic forms of the α and γ diketones.

Conjugate systems are characterized by a transmission of chemical reactivity from one atom to another (alternate atoms acquire similar polarities and reactivities). Thus in the α-β unsaturated ketones, the negative polarity of the oxygen which enables it to unite with a proton is transferred to the α-carbon atom and the positive polarity of the carbon in the carbonyl group is transmitted to the β carbon atom.(11) Lapworth in 1898 put forward this concept of alternation.(12) It was suggested that in intramolecular changes, the labile group moves from a α-atom to attach itself to a γ atom or more generally that "a labile group might move along a chain of alternately singly and doubly bound atoms, the ethylenic and single linkages changing place in the path of the labile group."

Modern Theories

Lowry in 1923 working upon the assumption that only activated molecules undergo chemical change postulated that the additive properties of the olefins under the influence of polar reagents depend upon the ionization of one link of the double bond.(13) "It then becomes obvious that the characteristic property of a conjugated chain of atoms is its ability to develop a series of alternate positive and negative charges on alternate atoms by activation of the double bonds".(14) Polar activation of conjugated systems may be symbolized:



Ingold introduced the term electromeric change for the process of consecutive electron displacement.(15) The essential characteristic of conjugated systems consists in their ability to undergo a rearrangement of bonds whereby a valency electron can be handed on from end to end of the conjugated system. Ingold has recently developed Theile's idea of conjugation stabilizing the molecule in wave mechanical language(16 He terms it the mesomeric effect.

Application Of The Resonance Concept To Conjugated Systems

Pauling and his coworkers use the term resonance rather than mesomerism.(17) Thus if a substance may be represented by two or more valence bond structures, the molecule is said to resonate between these structures. Thus the four structures

$H_2\overset{+}{C}-CH=CH-\overline{C}H_2$ (I)

$H_2C=CH-CH=CH_2$ (II)

$H_2\overline{C}-CH=CH-\overset{+}{C}H_2$ (III)

$H_2C-CH=CH-CH_2$ (IV)

may be written for butadiene. None of these structures give the actual structure of butadiene, thus quoting from Pauling(18) "A substance showing resonance between two or more valence bond structures does not contain molecules with the configurations and properties usually associated with these structures." Resonance between these various valence bond structures tends to stabilize the molecule and give it "extra resonance energy." Extra resonance energy is the extra energy that the molecule acquires due to resonance among several valence bond structures.

Quantum mechanical calculations(17) indicate that the single bonds in a conjugated system have about 20% double bond character and that the

extra resonance energy resulting from the conjugation of the two double bonds is about five to eight kcals/mole. It is also shown by the calculations that a double bond and a benzene nucleus are about equivalent in conjugating power. The thermochemical data(20) for biphenyl, phenylethylene, and stilbene correspond to a value of about seven kcals/mole for the conjugation energy of a double bond and a benzene ring or of two benzene rings. The conjugation energy in dienes from data on the heats of hydrogenation(21) ranges from two to six kcals/mole. From data on the heats of hydrogenation of ethyl vinyl ether and vinyl ether, the conjugation energy of a double bond and a free electron pair on an oxygen atom is found to be about three kcals/mole(22). The data on the ethers shows that the conjugation energy of a free electron pair with one double bond is the same as the conjugation energy with two double bonds. If vinyl ether is coplanar, only one free electron pair is free for resonance, and then this result might be expected.

Conjugation and Interatomic Distances

The resultant bond shortening which appears in the carbon-carbon single bonds in conjugated systems is a measure of the extra resonance energy and also determines the amount of double bond character in the bond due to conjugation. The relation between interatomic distance and the amount of double bond character is shown in Fig. 1. which was copied from Pauling's "Nature of the Chemical Bond" page 164. The points on the curve are empirical. The carbon-carbon single bond distance is taken as 1.54Å, the double bond distance as 1.33Å. These two values provide the end points of the curve. A third point at fifty percent

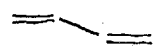
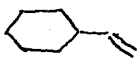
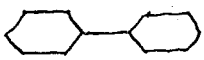
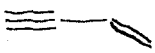
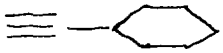
double bond character is provided by benzene with carbon-carbon distance of 1.39Å. A fourth point at thirty-three and one third percent double character is provided by graphite with a distance of 1.42Å. A smooth curve is drawn through these four points. The double bond covalent radius of a given atom may be determined from its single bond covalent radius by subtracting 0.21Å.

There are other conjugated systems than these composed of conjugated double bonds and a table is here reproduced from Pauling, Springall, and Palmer's data on acetylenic compounds(23), Table I.

Table I shows that the conjugating power of a triple bond is much greater than the conjugating power of a double bond or a benzene ring. A correction of 0.04A is applied to the triple bond shortening due to the change in the acetylenic carbon radii.

Table I

Interatomic Distances for Single Bonds in conjugated Systems

Type of conjugated system	Substance	Observed C-C distance Å	Amount of double bond character %
	Butadiene	1.46 ± 0.03	18 ± 10
	Cyclopentadiene	1.46 ± 0.03	18 ± 10
	Stilbene	1.44 ± 0.02	25 ± 7
	P-Diphenylbenzene	1.46 ± 0.04	18 ± 12
	Biphenyl	1.48 ± 0.04	13 ± 12
	Vinylacetylene		
	Tolane	1.40 ± 0.02	33 ± 8
	Diacetylene	1.36 ± 0.03	44 ± 13
	Cyanogen	1.37 ± 0.02	38 ± 10
	Dimethyldiacetylene	1.38 ± 0.03	34 ± 13

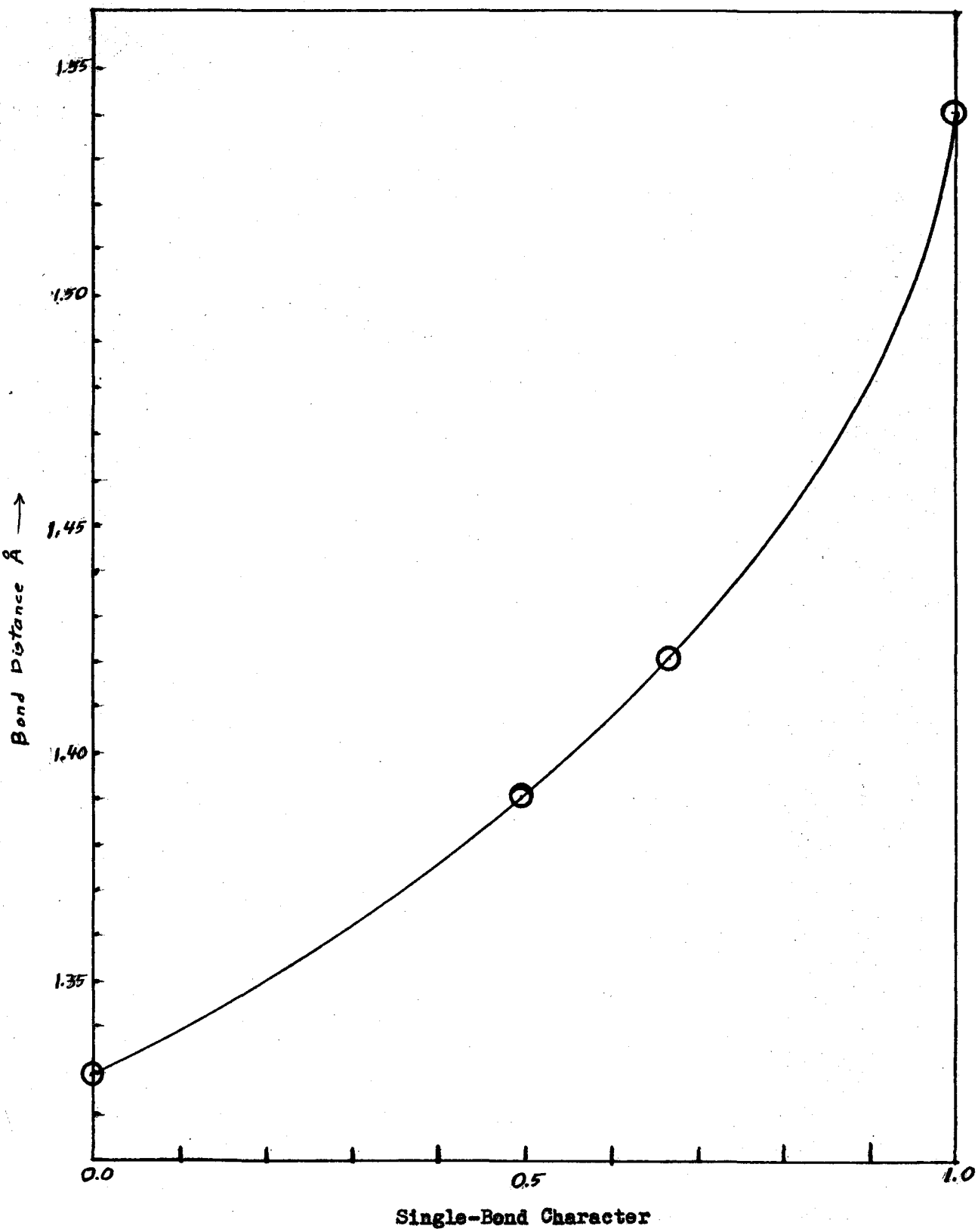


Fig. 1--The relation between interatomic distance and amount of double-bond character for single-bond--double-bond resonance of carbon-carbon bonds.

The resonance concept can account in a qualitative way for the chemical properties of conjugated systems especially their power of transmitting the effects of groups. It also accounts for the 1,2 addition to conjugate systems as well as the 1,4 addition. Many of the properties of the carotenoids may be directly attributed to the conjugated system of double bonds which characterize them.(24) Pauling(25) has based a theory of the color of dyes upon the transmission of resonance effects along conjugated systems.

The resonance concept has proven very useful in explaining chemical effects, and it should prove even more useful in the future as there are many fields in which the concept of resonance may well serve to explain heretofore more or less ambiguous data.

Reasons for The Investigation

Most of the information heretofore obtained concerning conjugated systems has dealt with systems containing carbon-carbon double bonds. Systems containing carbon-oxygen double bonds are very important in chemistry and hence this investigation has been devoted to such systems. Data upon vinyl ether and oxalyl chloride are reported for the first time in this dissertation. Data upon formaldehyde, glyoxal and dimethylglyoxal have already been published and the reprints of these publications are included in the thesis. A summary of the final results obtained from this investigation appears in the concluding section of the dissertation.

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24. M. T. Bogert Organic Chemistry Page 1140-1219 H. Gilman, Editor Wiley(1938)

25. L. Pauling Proc. Nat. Acad. Sci. 25, 577 (1939)

THE MOLECULAR STRUCTURES OF VINYL ETHER AND OXALYL CHLORIDE BY THE ELECTRON DIFFRACTION METHOD

INTRODUCTION

The determination of the structures of vinyl ether and oxalyl chloride by the electron diffraction method is an extension of the work upon simple resonating molecules containing oxygen.(1) The structure of vinyl ether is of special interest for the information it may provide regarding the forces restricting internal rotation and the extent of conjugation(2) of the unshared electron pairs of the oxygen atom with the carbon-carbon double bonds of the molecule. Oxalyl chloride is of interest from several points of view. Wierl (1f) investigated the possibility of free rotation around the carbon-carbon bond in oxalyl chloride and reported that the electron diffraction data was incompatible with unrestricted rotation around the carbon-carbon bond,but he did not give any parameter values nor an estimate of the amount of restricted rotation in the molecule. Resonance between a free electron pair on an atom, X, and a conjugated double bond with the resultant shortening of the bond, C-X, of the type found in the chloroethylenes(3) and the chlorobenzenes(4) is possible in oxalyl chloride. There is a strong possibility that the resonance of the carbon-oxygen double bond with a free electron pair on the chlorine atom may have an effect upon the resonance between the conjugated carbon-oxygen double bonds.

Experimental

Merck's vinyl ether was washed with several portions of water, dried over calcium chloride, and then dried over sodium wire. The dry ether was then fractionated in an atmosphere of nitrogen, the fraction distalling at 28.1° -- 28.2° C was used to obtain the diffraction photographs.

Eastman "white label" oxalyl chloride was twice vacuum distilled, only the middle third of the distillate being retained in each distillation. The stopcock lubricant recommended by Krauskoff and Rollefson(5) served satisfactorily.

The electron diffraction photographs were prepared with the apparatus described by Brockway.(6) The electron wavelength determined from transmission pictures of gold foil a = 4.070Å was 0.0615Å for the vinyl ether pictures and 0.0611Å for the oxalyl chloride pictures, and the camera distance was 10.84 cm in each case. The radial distribution function(7) were calculated using the S_0 values of both the maxima and the 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).

Vinyl Ether

The photographs of vinyl ether are good, having the rings extending to $S_0 = 28$. The radial distribution curve (Fig. 2, Curve E) calculated with the C_k and S_k values of Table II has peaks at 1.36, (2.08), 2.37, (2.77), and ((3.7))Å, the values in parenthesis being less reliable than the other values. The peak at 1.36Å is contributed to by both the

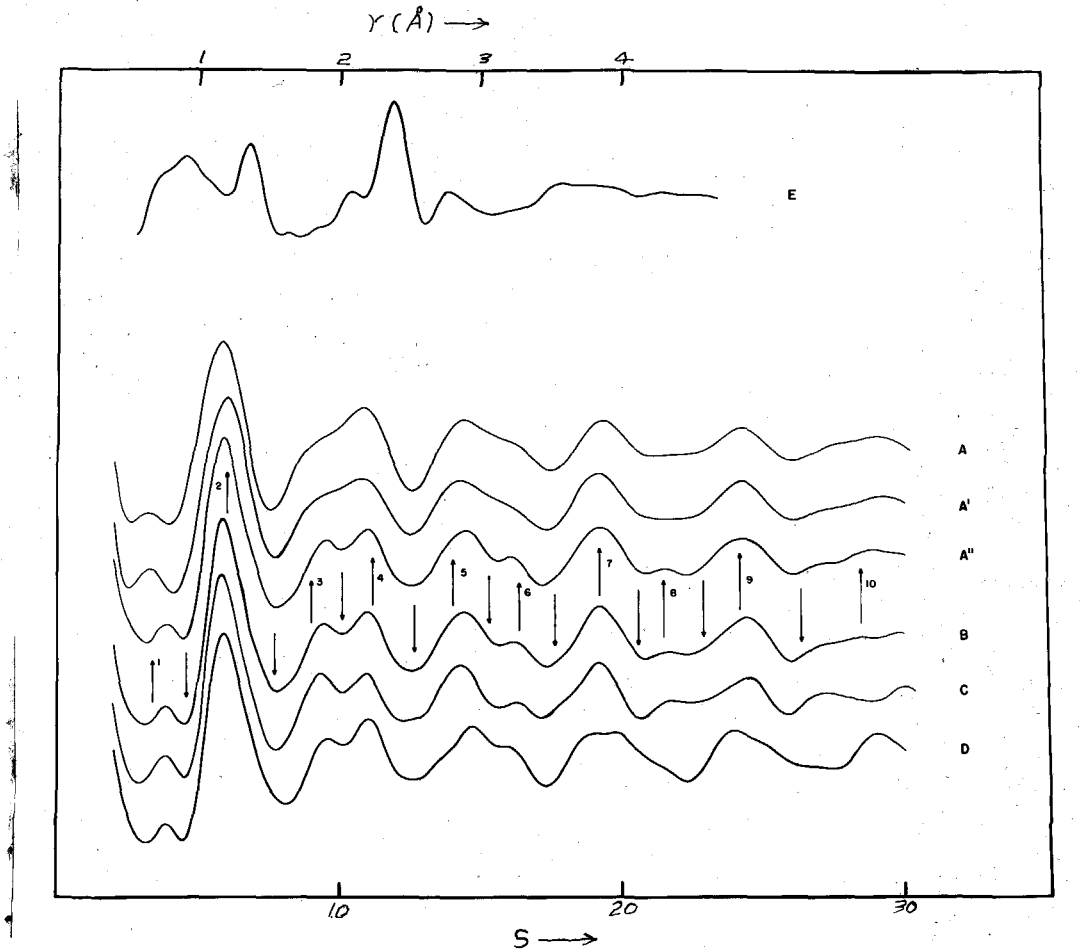

Fig. 2 Curves for Vinyl Ether. Denoting the C = C — O angle by α, the C — O — C angle by β, and the ratio C — O/C = C by ρ:

	α	β	ρ
Curve A*	122°	111°	1.40/1.34
Curve A^1	122°	111°	1.40/1.34
Curve A^{11}	122°	111°	1.40/1.34
Curve B	121°	113°	1.40/1.34
Curve C	120½°	111°	1.43/1.34
Curve D	126°	111°	1.32/1.34
Curve E	Radial Distribution function		

*Difference in A, A^1, and A^{11} are explained in the text.

Table II

Vinyl Ether

Max	Min	I_k	C_k	S_o	Model B[a] S	Model B[a] S/S_o	Model A[a] S	Model A[a] S/S_o
1		7	5	3.35	3.86	(1.153)[b]	3.80	(1.135)
	2	-10	-14	4.54	4.53	(0.998)	4.44	(0.978)
2		10	12	5.99	5.83	0.974	5.86	0.978
	3	-3	-7	7.69	7.78	1.011	7.73	1.005
3		6	11	8.95	9.42	(1.053)	9.53	(1.064)
	4	-1	-3	10.05	10.04	0.999	10.06	1.001
4		7	14	11.16	10.98	(0.984)	10.96	(0.982)
	5	-8	-21	12.62	12.56	0.995	12.55	0.994
5		$5\frac{1}{2}$	13	14.01	14.32	(1.022)	14.50	(1.035)
	6	-4	-10	15.26	15.69	(1.028)	15.54	(1.018)
6		5	13	16.32	16.18	(0.991)	16.06	(0.984)
	7	-9	-21	17.59	17.33	0.985	17.18	0.977
7		$6\frac{1}{2}$	16	19.15	19.17	1.001	19.23	1.004
	8	-4	-8	20.55	20.80	1.012	20.83	1.014
8		$\frac{1}{2}$	3	21.46	21.61	1.006	21.49	1.001
	9	-5	-8	22.85	22.29	0.975	22.25	0.974
9		3	6	24.15	24.41	1.011	24.26	1.004
	10	-8	-9	26.29	25.96	(0.987)	25.98	(0.988)
10		5	7	28.42	28.44	(1.001)	28.80	(1.013)
				Av.		0.995± 0.012		0.997± 0.012

[a] Models are described in legend to Fig. 2

[b] Less reliable values, not included intaking the average, are shown in parenthesis.

carbon-carbon bond distance and the carbon-oxygen bond distance; the peak at 2.37Å is contributed to by the long carbon oxygen distance and the α- carbon-carbon distance. Of the three possible coplanar configurations, the completely cis (cis -- cis) configuration is ruled out by steric factors; and the completely trans (trans -- trans) form is suggested by the broad flat peak at 3.7Å and the small peak at 2.77Å. If the molecule was in the trans - cis configuration the peak at 3.7Å would be sharper and the peak at 2.77Å would be at 2.7Å with about half the intensity of the peak at 2.37Å.

Intensity curves for eighteen models were calculated with the ratio C—O/C=C varying from 1.37/1.34 to 1.43/1.34, the angle α (C=C—O) varying from 119° to 126°, and the angle β (C—O—C) varying from 109° to 115°. The six intensity curves of Fig. 2 were calculated for the coplanar trans — trans model with C—H distance assumed to be 1.09Å. Three curves were calculated for each model; one curve which contained no hydrogen terms, and only these terms which are independent of rotation around the carbon-oxygen bond such as Curve A; one curve which contained all terms independent of rotation around the carbon-oxygen bond such as Curve A'; and one curve which contained all terms such as Curve A". Curves A" and B represent the photographs best. The model which would represent the photographs best would lie between the models A" and A' or between the corresponding B models. Unfortunately practically all the maxima in vinyl ether exhibit the St. John's effect which makes quantitative comparison difficult. A small temperature factor is needed in vinyl ether but estimation of the magnitude of the temperature factor is rather difficult for such molecules as vinyl ether.

It is concluded that the vinyl ether molecule is essentially coplanar trans--trans with librations of small magnitude around the

carbon-oxygen bonds. The parameter values are: C−H = 1.09Å (assumed), C=C = 1.34 ± 0.03Å, C−O = 1.40 ± 0.03Å, angle α (C= C − O) = 121½° ± 2°, and angle β (C−O−C) = 112° ± 2°. The electron diffraction data are not incompatible with a mixture containing a small fraction of cis-trans molecules.

Oxalyl Chloride

The photographs of oxalyl chloride are good showing twenty-six measurable features extending to $s_0 = 25$. The radial distribution function, (fig. 3, Curve A) was calculated with the C_k and s_k values of Table III. The radial distribution maxima are at 1.49(shelf), 1.72, 2.35 (shelf), 2.61, 2.96, 3.38, and 4.25Å. The maxima at 2.61, 2.96, and 4.25Å give the most reliable values of interatomic distances in the molecule. The shelf at 1.49Å corresponds to the carbon-carbon bond distance, the maxima at 1.72Å to the carbon-chlorine bond distance, and the shelf at 2.35Å to the α-carbon-oxygen distance. The maximum at 2.61Å is contributed to by the α-carbon-chlorine distance and the chlorine-oxygen distance (chlorine and oxygen attached to the same carbon atom), and the maximum at 2.96Å corresponds to the cis chlorine-oxygen distance for the trans molecule. If the molecule were cis this maximum would be contributed to by the oxygen-oxygen distance and the chlorine-chlorine distance. Resonance tends to make the molecule coplanar, of the two coplanar configurations, the trans form is suggested by the weak maximum at 3.38Å (the trans oxygen-oxygen distance) and the strong maximum at 4.25Å (the trans chlorine-chlorine distance). If the molecule were cis, a maximum should occur at about 3.9Å (trans oxygen-chlorine distance in the cis molecule).

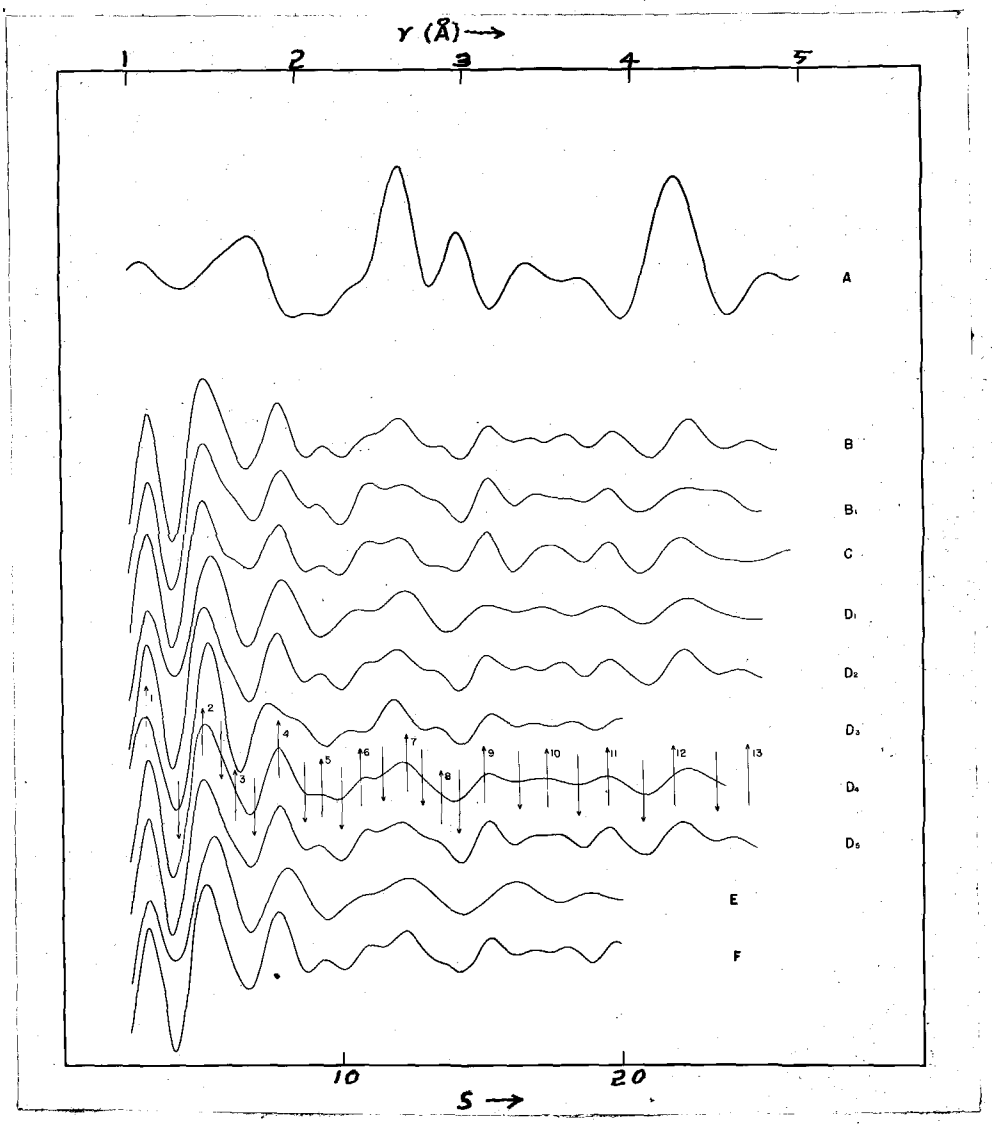

Fig. 2. Curves for Oxalyl Chloride. Denoting the angle C-C=O by α, the angle Cl-C=O by β, the asimuthal angle by φ, the ratio of the C-C distance to the C=O distance by ρ, and the ratio of the C-Cl distance to the C=O distance by η:

Curve A -- Radial Distribution function

	α	β	φ	ρ	η
Curve B	123°	123°	0°	1.47/1.20	1.72/1.20
Curve B_1	123°	121°	22½°	1.47/1.20	1.72/1.20
Curve C	123°	123°	0°	1.50/1.20	1.68/1.20
Curve D_1^*	123°	123°	0°	1.50/1.20	1.72/1.20
Curve D_2	123°	123°	0°	1.50/1.20	1.72/1.20
Curve D_3	123°	123°	180°	1.50/1.20	1.72/1.20
Curve $D_4^\dagger$	123°	123°	0°	1.50/1.20	1.72/1.20
Curve D5	123°	123°	17°	1.50/1.20	1.72/1.20
Curve E	123°	121°	0°	1.53/1.20	1.68/1.20
Curve F	125°	125°	0°	1.53/1.20	1.72/1.20

* terms dependent upon φ omitted
† temperative factor used.

Table III

Oxalyl Chloride

Max.	Min.	I	C_k	S_o	S	S/S_o
1		6	3	3.02	3.04	(1.007)
	2	-8	-5	4.11	3.93	(0.956)
2		10	9	4.98	5.05	(1.014)
	3	-3	-3	5.69	...	... [a]
3		4.5	5	6.18	...	...
	4	-10	-13	6.83	6.70	0.981
4		7.5	13	7.74	7.75	1.001
	5	-4	-7	8.67	8.70	1.003
5		3.5	7	9.26	9.16	0.989
	6	-6	-11	9.97	9.93	0.996
6		5	9	10.66	10.88	(1.020)
	7	-4.5	-9	11.44	11.27	(0.985)
7		4.5	10	12.35	12.10	(0.980)
	8	-5	-5	12.88	12.95	(1.005)
8		3	7	12.53	13.40	(0.990)
	9	-7	-15	14.20	14.20	1.000
9		5.5	13	15.09	15.23	1.009
	10	-5.5	-12	16.35	16.18	0.990
10		4.3	9	17.34	17.40	1.003
	11	-3.5	-7	18.46	18.62	1.009
11		4	8	19.51	19.53	1.001

(a) These features did not appear on the theoretical intensity curves.

Table III (Con't)

Oxalyl Chloride

Max.	Min.	I	C_k	S_o	S	S/S_o
	12	-4.5	-8	20.75	20.80	1.002
12		3	5	21.87	22.12	1.011
	13	-3	-4	23.38	23.37	(1.000)
13		2	2	24.50	24.03	(0.981)
Average[b]						1.000±0.006

(b) Average taken by excluding figures in parenthesis. If only the first three features are excluded in taking the average value of S/S_o, the average obtained is 0.999±0.009

Interatomic distances were calculated for thirty-five models, in all of which the carbon-oxygen double bond was assumed to be 1.20Å (the value found in glyoxal and dimethylglyoxal). (2G) The term, model, includes all models derived from the model without rotational terms by inclusion of these terms with varying values of the azimuthal angle. The ratio of C−Cl/C=O was varied from 1.68/1.20 to 1.76/1.20 and the ratio of C—C/C=O from 1.43/1.20 to 1.53/1.20. The angles α (∠ C−C=O), β (∠ Cl−C=O), and φ (the azimuthal angle) were varied from 120° to 125°, 119° to 125°, and 0° to 180° respectively. The azimuthal angle is 0° for the trans model and 180° for the cis model.

Theoretical intensity curves were calculated for eleven of these models so chosen that the behavior of the theoretical intensity curves for the remaining models can be predicted from the calculated curves. In the calculation of these curves, the Z_i in the simplified theoretical intensity function were replaced by $(Z_i - f_i) / \sqrt{(Z-f)_O\,(Z-f)_{Cl}}$. The f_i were obtained from Pauling and Sherman's Tables(9). Curves B...F, Fig. 3 are some of the theoretical intensity curves for oxalyl chloride. Curve D_5 gives the best representation of the diffraction photographs. Maximum 3 of Table 3 did not appear on any of the theoretical curves. The intensity curves for the cis models confirmed the conclusions derived from the radial distribution function, i.e., the cis molecule alone could not give the observed diffraction pattern.

It is difficult to make an exact structure investigation of oxalyl chloride as the determination of the structure is a five-parameter problem even when the length of the carbon-oxygen bond is assumed. In the determination of the structure every possible model was not eliminated, instead models were chosen which approximately satisfied the

radial distribution function and a choice of structure made from among these models. A series of trans models were calculated and a temperature factor applied to the best one, D_2, in an attempt to gain some information concerning the librations around the carbon-carbon bond. However the factor a =0.0054 in the function e^{-as^2} corresponds to a very large amplitude of libration. The curve D_4 corresponding to D_2 with the large temperature factor is however a good representation of the photographs. The best trans models were then rotated through the azimuthal angle until the chlorine-chlorine distance became 4.25Å and the corresponding curves calculated. Curve D_5 derived from D_2 gives the best representation of the photographs. The average deviation of the corresponding interatomic distances in D_5 from the three most reliable maxima in the radial distribution function is 0.01Å. Comparison of curves D_2, D_4, D_5, and the photographs indicate that a small temperature factor (a =0.002) would improve D_5; however, as the effect of this temperature factor is obvious, the curve was not calculated. The radial distribution function does not give a reliable value for the length of carbon-carbon bond; there is only a slight shelf at 1.49Å; however the curves for models with C—C =1.47Å and C—C =1.53Å were not as satisfactory as the curves for models with C—C =1.50Å. (Curves (E, F, B, C)).

It is concluded that a model with the following parameters is a good representation of the oxalyl chloride molecule: C—O =1.20Å (assumed), C—C =1.50 ± 0.03Å, C—Cl =1.72 ± 0.03Å, angle α (C—C=O) 123° ± 2°, angle β (Cl—C=O) 123° ± 2°, and angle γ =17°. A temperature factor is necessary.

Discussion

Vinyl Ether:-- The heats of hydrogenation(10) of vinyl ether and ethyl vinyl ether give values for the resonance energy of a free electron pair with a double bond of 2.4 kcal/mole and 3.1 kcal/mole respectively. These values are equal within the experimental error of the work. Then the resonance in each carbon oxygen bond of vinyl ether is approximately half that in the single carbon-oxygen bond involved in resonance in ethyl vinyl ether. It follows then that the observed bond shortening in vinyl ether is approximately half the shortening that would be expected in a compound in which the free electron pair is conjugated against only one double bond.

Stuart(11) showed that the Kerr constant for ethyl ether demands the extended structure. Ethyl ether has a dipole moment(12) of 1.18 Debye, vinyl ether 1.09 Debye and furan 0.71 Debye. If vinyl ether has the extended trans-trans structure assigned to it, it is expected that the dipole moment of vinyl ether would be less than ethyl ether, as the dipole induced by resonance is opposite in sign to the dipole due to the carbon-oxygen bonds. The resultant induced dipole is small in magnitude as the two induced dipoles have an angle of about 173 degrees between them. In furan on the other hand, the two induced dipoles have a much smaller angle between them and the resultant dipole is rather large; hence, it is expected that furan will have a moment somewhat less than vinyl ether. The dipole moment data thus support the assignation of the extended trans-trans configuration to vinyl ether.

Oxalyl Chloride:-- The observed shortening of 0.04Å in the carbon-carbon bond in oxalyl chloride is 0.03Å less than that reported for glyoxal and dimethylglyoxal.(2G) Resonance across the carbon-carbon bond

between the conjugated double bonds causes this shortening. The observed shortening of 0.04Å in the carbon-chlorine bond in oxalyl chloride is 0.03Å less than that reported for the substituted chloroethylenes(3) containing one or two chlorine atoms. Resonance between a free electron pair on the chlorine atom and the carbon-oxygen double bond causes this shortening. The sum of the shortening in the two bonds is just equal to the shortening found in a single bond in a molecule in which only one of these resonance effects is found. If it is postulated that the resonance of the carbon-oxygen double bond with a free electron pair on an adjacent chlorine atom cuts down the resonance of the carbon-oxygen double bonds across the carbon-carbon bond and vice-versa, then the experimental results may be explained in terms of the competitive resonance. The total resonance energy in oxalyl chloride is then of the same order of magnitude as that in glyoxal or in the chloroethylenes.

From consideration of the work of Beach and Turkevich(13), Beach and Palmer(14), and LuValle and Schomaker(15) on the potential barrier restricting rotating rotation in the ethylene halides and dimethylglyoxal, the potential barrier restricting rotation in oxalyl chloride is estimated to be greater than five kcals/mole. It is ~~predicted~~ indicated from the results of this paper that the potential curve either has a very broad minimum or a double minimum. There are no dipole moment data available for oxalyl chloride, ~~hence a calculation of the approximate height of the potential barrier restricting rotation was impossible~~.

Summary

Vinyl ether is concluded to have the following parameter values C - H = 1.09Å (assumed), C = C = 1.34 ± 0.03Å, C — O = 1.40 ± 0.03Å, angle

α (C=C-O) = $121\frac{1}{2}^{\circ} \pm 2^{\circ}$, and angle β (C-O-C) = $112^{\circ} \pm 2^{\circ}$. There is a libration of small amplitude around the carbon-oxygen bonds.

Oxalyl chloride is found to have the structure given by the following parameters C=O = 1.20Å (assumed), C-C = 1.50 ±0.03Å, C-Cl = 1.78 ±0.03Å, angle α (C-C=O) = $123^{\circ} \pm 2^{\circ}$, angle β (Cl-C=O) = $123^{\circ} \pm 2^{\circ}$, and angle $\varphi = 17^{\circ}$. A temperature factor with a = 0.002 is needed.

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3. L. O. Brockway, J. Y. Beach, and L. Pauling J.A.C.S. 57, 2693 (1937)

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 718]

The Structure of Formaldehyde from Electron Diffraction

BY D. P. STEVENSON,[1] JAMES E. LUVALLE[2] AND VERNER SCHOMAKER

Introduction

The structure of monomeric formaldehyde is of particular interest since it is the simplest molecule containing a carbon–oxygen double bond. Bru[3] found the carbon–oxygen distance to be 1.15 ± 0.05 Å. by electron diffraction. The accuracy, ±0.05 Å., of this determination is very much less than is now obtainable in determining the size of simple molecules.[4] Furthermore, this value for the carbon–oxygen distance is about 0.1 Å. smaller than that predicted by the covalent radius table[5] for the carbon–oxygen double bond, 1.24 Å., and that found for the carbon–oxygen distance of acetaldehyde,[6] 1.22 Å., and glycine,[7] 1.24 Å. Badger's rule[8] applied to the carbon–oxygen frequency gives 1.21 Å.[9] for the distance.

The moments of inertia have been determined very accurately[10] but are insufficient by themselves to determine the structure uniquely. This will be discussed below. Since the carbon–oxygen distance appeared definitely to be shorter than predicted, we were led to redetermining it by the electron diffraction technique.

Experimental

Dieke and Kistiakowsky[10] found it possible to maintain a pressure of 100 mm. of H_2CO by heating paraformaldehyde. For this reason we first attempted to obtain photographs by heating Eastman Kodak Company White Label paraformaldehyde from 150 to 200° in the "high temperature nozzle." Some of the photographs obtained in this fashion had the expected pattern, namely, that of a diatomic molecule, while others showed a much more complicated pattern. The latter were probably due to small polymers (*e. g.*, trimer). In order to eliminate the possibility of polymer in the vapor we prepared 10 cc. of the monomeric liquid according to the method of Spence and Wilde.[11] The liquid was held at −25° in the side-arm of a 200-cc. flask attached to the apparatus. This gave an effective pressure of nearly one atmosphere. Since air was excluded carefully from the preparation, polymerization was delayed long enough to obtain photographs of the monomer. The photographs so obtained were excellent, having a pattern similar to that of a diatomic molecule.

The camera distance was 10.84 cm. and the wave length of the electrons was 0.0611 Å. based on transmission pictures of gold, the structure of which is known (a = 4.070 Å.).

Interpretation.—Only the photographs obtained by the second technique will be considered since polymers may have been present in the gas in the high temperature photographs. The photographs showed five minima and five maxima of gradually decreasing intensity. The measured values of $s\left(s_0 = \frac{4\pi}{\lambda}\sin\frac{\vartheta}{2}\right)$ are given in the third column of Table I. Comparison with a simple $\sin x/x$ curve indicated the carbon–oxygen distance to be about 1.20 Å. This distance and the moments of inertia (see below) give a carbon–hydrogen distance of 1.09 Å. and a hydrogen–carbon–hydrogen angle of 120°. A theoretical intensity curve was then calculated for the corresponding model. In place of the commonly used coefficients Z_iZ_j, $\overline{(Z_i - f_i)(Z_j - f_j)}e^{-A_{ij}}$ was used in the expression

$$I(s) = \sum_i \sum_j \overline{(Z_i - f_i)(Z_j - f_j)}e^{-A_{ij}}\frac{\sin l_{ij}s}{l_{ij}s}$$

The use of the "temperature factor," "$e^{-A_{ij}}$," will be discussed by one of us.[12] The atomic scattering factors "f" were obtained from Pauling and Sherman.[13] The curve so obtained is shown in Fig. 1, curve C, along with a common visual curve calculated for the same molecular dimension and the curve $\sin 1.20x/1.20x$. The vertical lines indicate the position of the measured maxima and minima. Quantitative comparison with the curve calculated with temperature fac-

(1) National Research Fellow.
(2) Julius Rosenwald Foundation Fellow.
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(4) *Cf.* V. Schomaker and D. P. Stevenson, THIS JOURNAL, to be published.
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(10) G. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.*, **45**, 4 (1934).
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(12) V. Schomaker, to be published.
(13) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

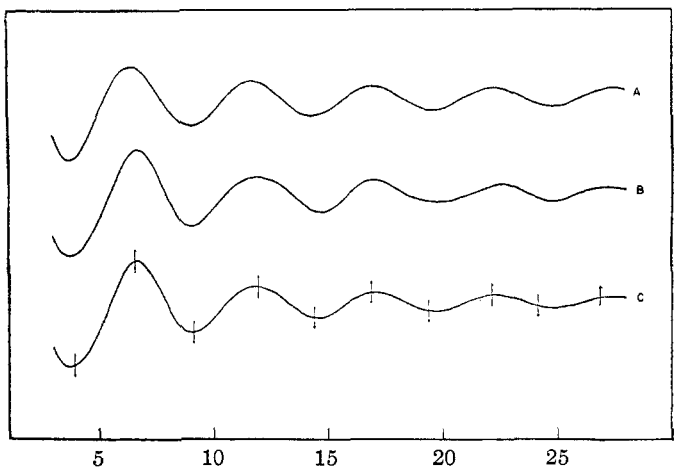

Fig. 1.—Theoretical intensity curves for formaldehyde: A, sin $1.20s/1.20s$; B, ordinary intensity curve for C–O = 1.20 Å., C–H = 1.09 Å., ∠H–C–H = 120°; C, like B with coefficients including the atomic scattering factors and a "temperature factor."

tor is given in Table I. It leads to a carbon–oxygen distance of 1.213 ± 0.008 Å.

TABLE I

Max.	Min.	s_1	$s_{calcd.}$[a]	s_c/s_0
	1	3.95	3.73	(0.944)[b]
1		6.62	6.71	1.014
	2	9.15	9.12	0.997
2		11.95	11.89	0.995
	3	14.40	14.59	1.013
3		16.90	17.10	1.012
	4	19.40	19.61	1.011
4		22.15	22.21	1.003
	5	24.16	24.81	1.027
5		26.86	27.50	1.024
Average of 9 features				1.011 ± 0.008
Carbon–oxygen distance = 1.20 × 1.011 = 1.213 ± 0.008 Å.				

[a] From curve calculated with C–O = 1.20, C–H = 1.09, ∠H–C–H = 120°, with temperature factor. [b] Omitted from average.

Discussion

Dieke and Kistiakowsky[10] have determined values for the moments of inertia of formaldehyde from the analysis of the rotational structure of six ultraviolet bands. Since the molecule is planar, there are only two independent moments of inertia while there are three parameters which determine the structure of the molecule, namely, the carbon–oxygen and carbon–hydrogen distances and the hydrogen–carbon–hydrogen angle. An independent determination of any one of these structural parameters along with the moments of inertia suffice to determine the other two structural parameters. In Fig. 2 we have plotted the values of the carbon–oxygen and carbon–hydrogen distances which are consistent with the moments of inertia as a function of the hydrogen–carbon–hydrogen angle. Our value of 1.213 Å. for the carbon–oxygen distance (marked by a circle on the graph) corresponds to an angle of 120° and a hydrogen–carbon distance of 1.086 Å. Ebers and Nielsen[14] from an incompletely resolved infrared band at 4.5 μ have determined rough values for the moments of inertia of deuteroformaldehyde. Although their value for the small moment of inertia is in good agreement with that of Dieke and Kistiakowsky[10] for light formaldehyde, their value for the large moment is not sufficiently accurate to be used in determining the structure of formaldehyde.

Thompson and Linnett[9] using the frequencies of Nielsen[15] and a five constant potential function have found $k_{C-O} = 12.3 \times 10^5$ dynes/cm. and $k_{C-H} = 4.3 \times 10^5$ dynes/cm. With these values Badger's rule[8] leads to a carbon–oxygen distance of 1.21 Å. and a carbon–hydrogen distance of 1.09 Å. in good agreement with our determination. Very little significance can be assigned to the agreement in the case of the carbon–oxygen bond distance since Thompson and Linnett[9] find the

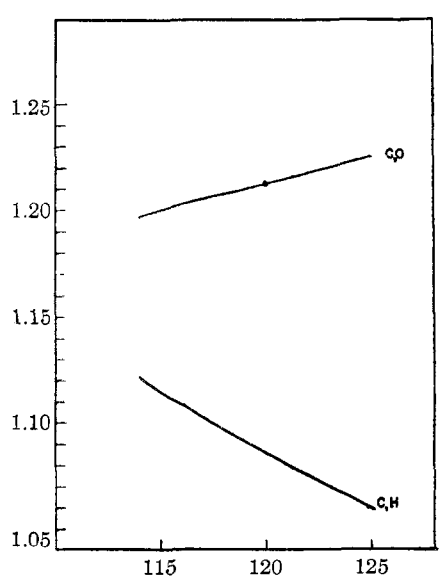

Fig. 2.—Graph of distances and angles consistent with the moments of inertia of formaldehyde: $I_1 = 2.941 \times 10^{-40}$ g. cm.²; $I_2 = 21.39 \times 10^{-40}$ g. cm.²

(14) E. S. Ebers and H. H. Nielsen, *J. Chem. Phys.*, **6**, 311 (1938).
(15) H. H. Nielsen, *Phys. Rev.*, **46**, 117 (1934).

same distance for ketene, which has been found by electron diffraction to have a carbon–oxygen distance equal to 1.17 Å.[16]

The large value of the hydrogen–carbon–hydrogen angle, 120°, may be interpreted as indicating that the bonding in formaldehyde is primarily of the sp^2, π type which gives three coplanar bonds at 120°. It has been found that in acetaldehyde[6] a similar situation obtains, the carbon–carbon–oxygen angle being 122 ± 2°. The carbon–oxygen distance in formaldehyde is definitely shorter than that predicted by the covalent radius table for a carbon–oxygen double bond.

(16) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

Summary

Electron diffraction photographs of monomeric formaldehyde have been obtained using fast electrons. Their interpretation leads directly to a carbon–oxygen distance equal to 1.21 ± 0.01 Å. Using this distance and the accurately known moments of inertia one finds the carbon–hydrogen distance to be 1.09 ± 0.01 Å. and the hydrogen–carbon–hydrogen angle to be 120 ± 1°.

PASADENA, CALIFORNIA RECEIVED JULY 10, 1939

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

By James E. LuValle[1] and Verner Schomaker

Introduction.—Extension to open chain heteroatomic aliphatic compounds of the structural investigations[2] 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 formaldehyde[3] and acetaldehyde[4] 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 Å.) was 0.0611 Å. and the camera distance was 10.84 cm. The radial distribution functions[7] 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.

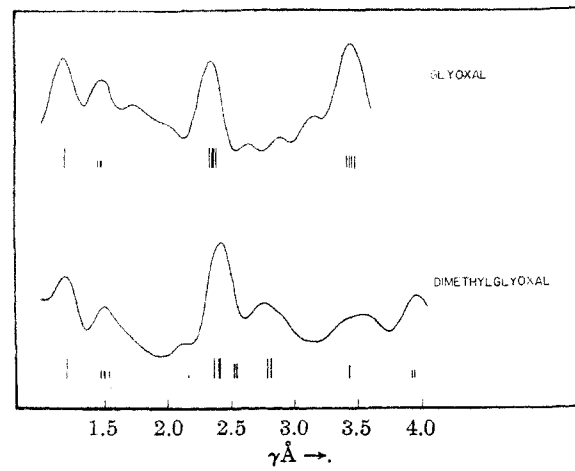

Fig. 1.—Radial distribution curves for glyoxal and dimethylglyoxal. The vertical lines beneath the curves show the various interatomic distances of the models used in the final determination of distances by the correlation method.

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 Stevenson[9] 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).

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TABLE I

GLYOXAL

Max.	Min.	I	C_K	s_0	Model C[a] s	Model C[a] s/s_0	Model D s	Model D s/s_0	Model E s	Model E s/s_0	Model F s	Model F 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]	...[c]	...	...	...	...	...	...	...
7		2	3	15.06[d]	...[c]	...	...	...	...	...	...	..
	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	− ½	− 1	19.47[d]	...[c]	...	...	...	...	...	...	...
10		½	1	20.18[d]	...[c]	...	...	...	...	...	...	...
	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 considerations[10] 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), **A158**, 306 (1937).

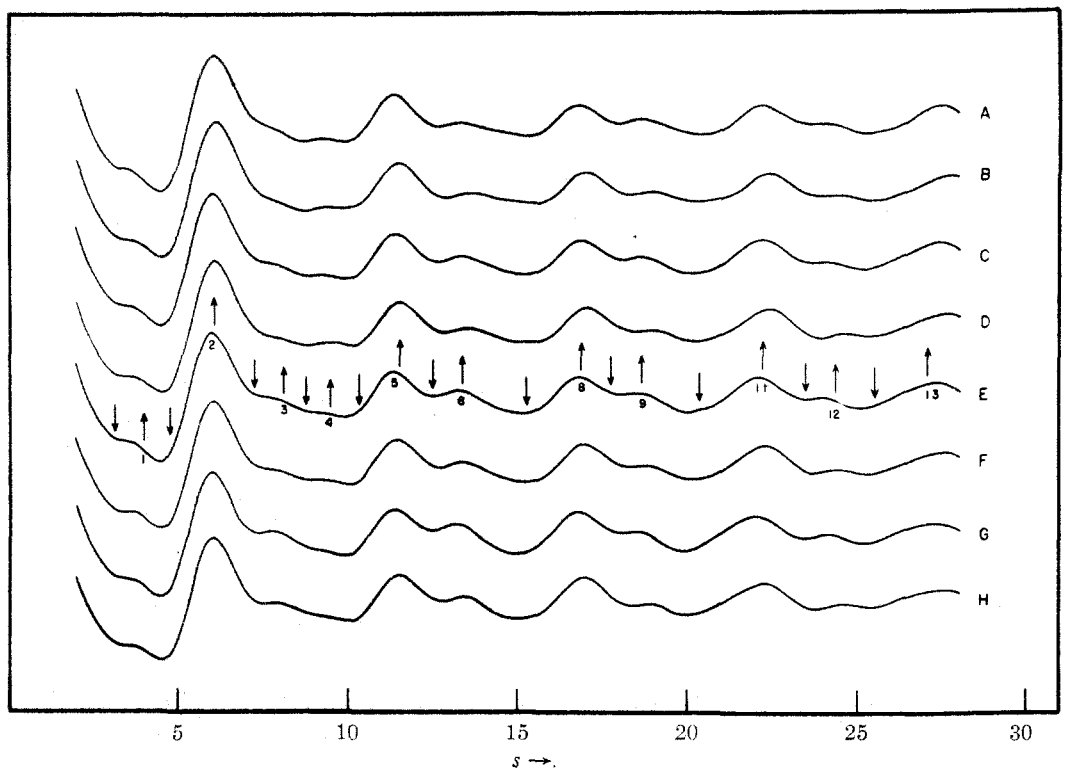

Fig. 2.—Theoretical intensity curves for glyoxal. Denoting the C—C=O by α and the ratio of the C—C distance to the C=O distance by ρ:

Curve A, $\alpha = 128°$, $\rho = 1.42/1.20$; Curve B, $\alpha = 125°$, $\rho = 1.42/1.20$;
Curve C, $\alpha = 125°$, $\rho = 1.46/1.20$; Curve D, $\alpha = 122°$, $\rho = 1.46/1.20$;
Curve E, $\alpha = 125°$, $\rho = 1.48/1.20$; Curve F, $\alpha = 122°$, $\rho = 1.48/1.20$;
Curve G, $\alpha = 122°$, $\rho = 1.52/1.20$; Curve H, $\alpha = 119°$, $\rho = 1.52/1.20$.

TABLE II

DIMETHYLGLYOXAL

Max.	Min.	I	C_K	s_0	Model C[a] s	Model C[a] s/s_0	Model D s	Model D 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	...[b]	...	...	...
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. [b] The theoretical curves do not show a precisely measurable feature at this point.

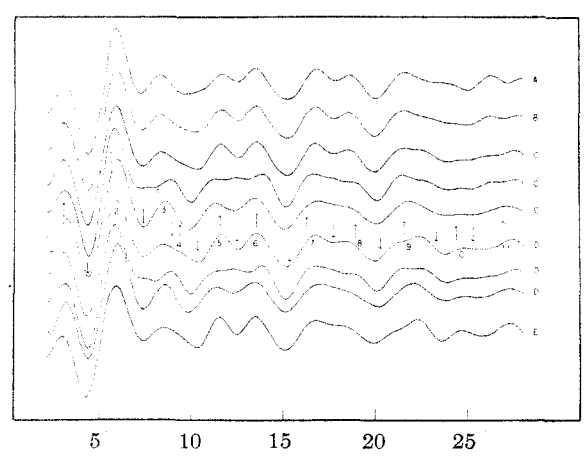

Fig. 3.—Theoretical intensity curves for dimethylglyoxal. All the curves have the following parameters in common: C—H = 1.09 Å. (assumed), C=O = 1.20 Å., C_2—C_3 = 1.47 Å., C_1—C_2 = 1.54 Å., and angle CO—C=O (α) = 123° ± 2°. Denoting angle CH_3—C=O by β we have: Curve A, $\beta = 125°$; Curve B, $\beta = 124°$; Curves C, C′, and C″, $\beta = 123°$; Curves D, D′, and D″, $\beta = 122°$; Curve E, $\beta = 121°$.

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., C_2—C_3 = 1.47 ± 0.02 Å., C_1—C_2 = 1.54 ± 0.02 Å., C=O = 1.20 ± 0.02 Å., angle CO—C=O (α) = 123° ± 2°, and angle CH_3—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 indicate that the amplitude of libration around the (C_2–C_3) 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 Stevenson[11] using Zahn's values[12] of the dipole moment and Smyth's values[13] of the group moments indicates that the potential barrier restricting rotation is steeper than a parabolic barrier and greater than 12 kcal. in height. Zahn[12] 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 values[13] 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).

culation of the square root of the ratio of the product of the three principal moments of inertia for the two configurations. The ratios $[(I_1I_2I_3)_{cis}(I_1I_2I_3)_{trans}]^{1/2}$ for the glyoxal and dimethylglyoxal molecules are 1.15 and 1.00, respectively. For the equilibrium *cis* $\rightleftarrows$ *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° ± 2°

Dimethylglyoxal: C—H = 1.09 Å. (assumed), C=O = 1.20 ± 0.02 Å., C_2—C_3 = 1.47 ± 0.02 Å., C_1—C_2 = 1.54 ± 0.02 Å., angle CO—C=O = 123° ± 2°, angle CH_3—C=O = 122.5° ± 1°

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.

PASADENA, CALIFORNIA RECEIVED OCTOBER 23, 1939

Summary

The electron-diffraction investigation of formaldehyde, glyoxal, dimethylglioxal, oxalyl chloride, and vinyl ether has shown that the conjugating power of two carbon-oxygen double bonds is of the same magnitude as the conjugating power of two carbon-carbon double bonds. The criterion for the magnitude of the conjugating power is the decrease in the carbon-carbon single bond distance. The carbon-carbon single bond distance in glyoxal and dimethylglioxal is 1.47Å (1g), and the carbon-carbon single bond distance in butadiene and cyclopentadiene is 1.46Å (1h). These distances are the same within the experimental error of the determination.

The investigation of formaldehyde (1i) gave a reliable value of the carbon-oxygen double bond distance of 1.21Å.

In oxalyl chloride the carbon-carbon bond distance is only 1.50Å instead of 1.47Å as in glyoxal and dimethylglyoxal(1g). The carbon-chlorine bond distance in the same molecule is 1.72Å, a shortening of 0.04Å. The value of 1.50Å may be explained by the competition of a free electron pair on the chlorine atom with the carbon-carbon single bond for the carbon-oxygen double bond.

In vinyl ether a bond shortening of only 0.02Å in each bond or 0.04Å total shortening is reported. The shortening may be summed in this molecule as the heat of hydrogenation data(10) show that the amount of resonance in vinyl ether is the same as in ethyl vinyl ether. The shortening is due to the resonance between a free electron pair on the oxygen atom and the two carbon-carbon double bonds. This shortening is less than that shown by the chloroethylenes(3) but the

difference in electronegativity of chlorine and oxygen may well explain this fact.

The molecules glyoxal, dimethylglyoxal, oxalyl chloride and vinyl ether are all found to be coplanar and trans with the exception of oxalyl chloride in which the (COCl) groups are rotated 17° from the trans position. The potential barrier restricting rotation in the first three molecules was found to be greater than five kcals. and it is indicated that the potential curve for oxalyl chloride will show a double minimum. No estimate was made of the potential barrier in vinyl ether.

PROPOSITIONS

1. The use of micro gas analytical apparatus similar to that developed by Blacet, MacDonald, and Leighton will enable investigations of thermolysis to be carried to much lower temperatures than those usually given as the threshold for thermal decomposition.
2. The investigation of propinal and 2-butinal by the electron diffraction method should give information concerning the amount of double bond character assumed by the carbon-carbon single bond between the triple bond and the double bond.
3. The resonance between a free electron pair and a double bond is of the same order in respect to bond energy and bond shortening as the resonance between two double bonds.
4. Color in organic molecules of the formula RCO.RCO is intimately related to the length of the carbon-carbon bond between the conjugated double bonds.
5. Electron diffraction photographs obtained by use of the Debye Camera will never completely supplant electron diffraction photographs obtained by the usual method.
6. Empirical temperature factors in polyatomic molecules may be obtained from theoretical intensity curves calculated for the rigid molecule.*
7. The electrophoresis cell as developed by Tiselius when used in conjunction with the modified schlieren method of Longsworth is an excellent device for the analysis of protein solutions.

*Original idea suggested by Dr. Schomaker.

8. Neither the ultra-centrifuge nor the electrophoretic method will establish the homogeneity of a protein unambiguously.

9. The term "denaturation" as applied in protein chemistry should be restriced to those processes which are reversible.

10. A method is needed which will absolutely prove the presence of free radicals such as a Stern-Gerlach experiment upon a molecular beam containing free radicals.

11. An adequate gymnasium is an important need of the California Institute. Facilities at the Institute at present are highly inadequate.