

[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. LUVALLE² 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. Bru³ 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 table⁵ 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 rule⁸ applied to the carbon-oxygen frequency gives 1.21 Å.⁹ for the distance.

The moments of inertia have been determined very accurately¹⁰ 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 Kistiakowsky¹⁰ found it possible to maintain a pressure of 100 mm. of H₂CO 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 ($s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) 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 $Z_i Z_j$, $\frac{(Z_i - f_i)(Z_j - f_j)}{e^{-A_{ij}}}$ was used in the expression

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

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.

(3) L. Bru, *Ann. soc. españ. fis. quim.*, **30**, 483 (1932).

(4) Cf. V. Schomaker and D. P. Stevenson, *THIS JOURNAL*, to be published.

(5) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934); L. Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

(6) D. P. Stevenson and H. Burnham, *ibid.*, to be published.

(7) G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).

(8) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934), and **3**, 710 (1935).

(9) H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, 1391 (1937).

(10) G. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.*, **45**, 4 (1934).

(11) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

(12) V. Schomaker, to be published.

(13) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

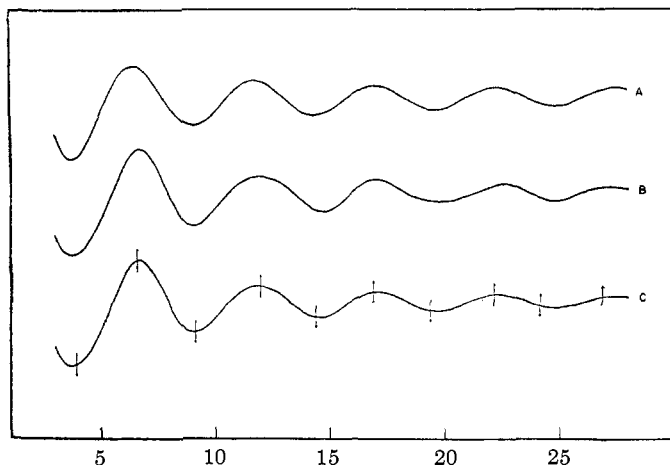


Fig. 1.—Theoretical intensity curves for formaldehyde: A, sin $1.20s/1.20s$; B, ordinary intensity curve for C-O = 1.20 Å., C-H = 1.09 Å., $\angle\text{H-C-H} = 120^\circ$; C, like B with coefficients including the atomic scattering factors and a "temperature factor."

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

TABLE I

Max.	Min.	s	s_{scaled}^a	s_o/s_o
	1	3.95	3.73	(0.944) ^b
1	2	6.62	6.71	1.014
	2	9.15	9.12	0.997
2	3	11.95	11.89	0.995
	3	14.40	14.59	1.013
3	4	16.90	17.10	1.012
	4	19.40	19.61	1.011
4	5	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 = $1.20 \times 1.011 = 1.213 \pm 0.008$ Å.

^a From curve calculated with C-O = 1.20, C-H = 1.09, $\angle\text{H-C-H} = 120^\circ$, with temperature factor. ^b Omitted from average.

Discussion

Dieke and Kistiakowsky¹⁰ 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 Nielsen¹⁴ from an incompletely resolved infrared band at 4.5μ have determined rough values for the moments of inertia of deuterioformaldehyde. Although their value for the small moment of inertia is in good agreement with that of Dieke and Kistiakowsky¹⁰ for light formaldehyde, their value for the large moment is not sufficiently accurate to be used in determining the structure of formaldehyde.

Thompson and Linnett⁹ using the frequencies of Nielsen¹⁵ and a five constant potential function have found $k_{\text{C-O}} = 12.3 \times 10^5$ dynes/cm. and $k_{\text{C-H}} = 4.3 \times 10^5$ dynes/cm. With these values Badger's rule⁸ 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 Linnett⁹ find the

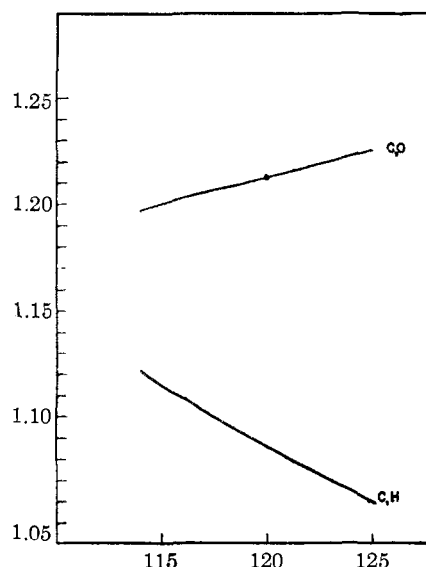


Fig. 2.—Graph of distances and angles consistent with the moments of inertia of formaldehyde: $I_1 = 2.941 \times 10^{-40}$ g. cm.²; $I_2 = 21.39 \times 10^{-40}$ g. cm.²

(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 acetaldehyde⁶ a similar situation obtains, the carbon-carbon-oxygen angle being $122 \pm 2^\circ$. The carbon-oxygen distance in formaldehyde is definitely shorter than that predicted by the

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

covalent radius table for a carbon-oxygen double bond.

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 $120 \pm 1^\circ$.

PASADENA, CALIFORNIA

RECEIVED JULY 10, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Hydrolysis of Ethylal¹

BY PAUL M. LEININGER² AND MARTIN KILPATRICK

In a study of the inversion of sucrose³ it was shown that the parameters of the Arrhenius equation

$$\ln k = B - (E_A/RT) \quad (1)$$

depended upon electrolyte concentration and temperature. The present paper extends the study to the hydrolysis of ethylal. This reaction was chosen because the velocity constant can be determined conveniently over similar ranges of hydrochloric acid concentration and temperature.

Skrabal and Schiffrer⁴ measured the rate of hydrolysis of ethylal in aqueous hydrochloric acid solutions by indirectly determining the amount of formaldehyde present at suitable intervals. The formaldehyde was oxidized to formic acid and titrated. In 1926 Skrabal and Eger⁵ continued the work at 25°, using a modification of the sulfite method of Lemme⁶ to determine the quantity of formaldehyde.

Subsequently the hydrolysis of ethylal was studied at 25 and 35° by Salmi⁷ and by Palomaa and Aalto⁸ using analytical methods. In 1934

Palomaa and Salonen⁹ measured the reaction rate dilatometrically. Löbering and Fleischmann¹⁰ investigated the hydrolysis at 10, 20 and 30° in sulfuric acid solutions.

If the claim of an accuracy of $\pm 4\%$ in the measurement of the rate constant, made by one of the authors,⁸ can be regarded as typical, it is apparent that for this reaction the data in the literature are insufficiently accurate for a study of the parameters of the Arrhenius equation. In addition, both the temperature and concentration ranges investigated are too limited to enable one to observe possible variations in the parameters, E_A and B .

The present investigation extends over a range of hydrochloric acid concentration from 0.5 to 3.0 molar, at 0, 10, 15, 20, 25, 30, 35 and 40° (concentrations resulting in too rapid reaction being omitted at the higher temperatures).

Experimental

Ethylal.—Ethylal from the Eastman Kodak Company was purified by fractional distillation, the fraction boiling between 87.0 and 88.0° (760 mm.) being used. That the preparation was free of acidic impurities was established by titration of an aqueous solution in an atmosphere of nitrogen using brom thymol blue as indicator. A further check upon the purity of the product was made by determining the refractive index by means of a Zeiss dipping refractometer. At 17.5° different preparations gave values of n_D varying from 1.3736 to 1.3745 as compared with

(9) Palomaa and Salonen, *ibid.*, **67**, 424 (1934).

(10) Löbering and Fleischmann, *ibid.*, **70B**, 1713 (1937).

(1) Abstracted from the dissertation of Paul M. Leininger presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirement for the degree of Doctor of Philosophy, April, 1939. Paper presented before the Baltimore Meeting of the American Chemical Society, April, 1939.

(2) E. I. du Pont de Nemours and Company Fellow, 1938-1939.

(3) Leininger and Kilpatrick, *THIS JOURNAL*, **60**, 2891 (1938).

(4) Skrabal and Schiffrer, *Z. physik. Chem.*, **99**, 290 (1921).

(5) Skrabal and Eger, *ibid.*, **122**, 349 (1926).

(6) Lemme, *Chem. Ztg.*, **27**, 896 (1903).

(7) Salmi, *Annal. Univ. Aboensis*, **A3**, no. 3 (1932).

(8) Palomaa and Aalto, *Ber.*, **66**, 468 (1933).