Summary and Discussion

Measurements have been described above of the electromotive forces at 25 and 0° of cells of the type

$$Pt + H_2\,(1\ \text{atm.}), HClO_4\,(c'), \left\{ HNO_3\,(c) + \frac{Tl^{III}\,(c_2)}{Tl^{I}\,(c_1)} \right\}, Pt$$

From these measurements presented in Table I the formal oxidation potential E^0 of the reaction $Tl^{III} + 2E^{-I} = Tl^{I}$ has been computed to have the value **1.2303** ± 0.0007 volt at 25° and the value **1.193** ± 0.001 volt at 0° in nitric acid solution. This value is shown to remain substantially constant when the ratio Tl^{I}/Tl^{III} is varied one hundred-fold and when the concentration of nitric acid is varied from 0.5 to 2 *f*. This constancy of the potential shows that neither hydrolysis of the thallic nitrate (by a reaction like $Tl^{+++} + H_2O = TlOH^{++} + H^{+}$), nor formation of nitrate complexes occurs to a considerable extent with thallic salts in nitric acid solutions between 0.5 and 2.0 formal.

This value, 1.230 volts, of the formal potential is slightly lower than those found by Sherrill and Haas[4] for the thallous–thallic potential in perchloric acid solution, who obtained at 25° 1.260 volts for the formal potential in 1.0 *f* perchloric acid and 1.247 volts for the extrapolated molal potential for thallous–thallic ions.

Noteworthy is the fact that the thallous–thallic potential in sulfuric acid solution, determined by Partington and Stonehill[3] to be 1.20 to 1.22 volts, is of about the same magnitude as the potentials in nitric and perchloric acids indicating that the formation of sulfate complexes by thallic sulfate is not very extensive.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE EXPERIMENT STATION][1]

The Electron Diffraction Study of Paraldehyde

BY D. C. CARPENTER AND L. O. BROCKWAY

Paraldehyde has been shown[2] to exist as the trimer $(CH_3CHO)_3$ in the gaseous state and in solution in phenol, and metaldehyde as the tetramer $(CH_3CHO)_4$ in phenol solution. In the present work the configuration of paraldehyde has been established by electron diffraction methods as a staggered six-membered ring of alternate carbon and oxygen atoms with a hydrogen atom and a methyl group attached to each of the ring carbon atoms, the methyl carbon atoms being approximately coplanar with the ring oxygen. The technique of the electron diffraction method of determining the structure of molecules has been described,[3] and the method now represents one of the most direct and feasible means of determining bond angles and distances.

Experimental

The sample of paraldehyde used in this study was purified by repeated fractional distillation and boiled at 124.0 ± 0.2°. Smits and deLeeuw[4] record the boiling point as 123.7°.

The low vapor pressure of paraldehyde at room temperature prevented the use of the ordinary unheated gas nozzle. In this investigation the sample was placed in a small glass bulb which was sealed to a copper tube leading through an all-metal high vacuum valve and up into the apparatus where it terminated in a nozzle just below the electron beam. The sample bulb, connecting tubes, valve and nozzle were all heated by spirals of resistance wire enclosing the entire path of the vapor. The valve was constructed so that a stiff spring pressing on the valve stem compensated for relative expansion of the valve parts and the valve was vacuum tight both at ordinary and elevated temperatures. Four thermocouples were used to follow the temperatures of the various parts of the assembly. This arrangement for handling vapors at high temperatures differs from those used by other investigators in which the gas stream flows continuously and is regulated by changes of the temperature of the sample holder. Here the gas flow is controlled by a quick-acting valve.

Fifteen photographs of paraldehyde were obtained in three sets with the temperature of the sample ranging from 103 to 115°. The exposure

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[1] Published as paper No. 542 from the Gates Chemical Laboratory and approved by the Director of the New York State Experiment Station for publication as Journal Article No. 141.

[2] W. Burstyn, *Sitzber. Wiener Akad.*, 511 (1902).

[3] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[4] A. Smits and H. L. deLeeuw, *Z. physik. Chem.*, **77**, 269 (1911).

times were adjusted so that the inner rings could be measured on some photographs and the outer rings on others. The de Broglie wave length of the electrons was 0.0606 Å. as determined by calibration with gold foil. The distance from gas orifice to photographic film was 10.43 cm.

The photographs show seven rings of which the second and fifth are very strong. The fourth is close to the third and weaker than the third and fifth rings. The sixth ring is weaker than the fifth and seventh. Measurements of the diameters were made by two observers and the corresponding values of s (equal to $(4\pi \sin \theta/2)/\lambda$) are given in Table I.

TABLE I

No. of readings	Max.	Min.	Visual intensity	S(obsd.)	S(calcd.)	l_{C-O}
12	1		20	3.73	3.50	(1,342)
9		2		4.68	4.40	(1.333)
15	2		30	6.13	5.65	(1.315)
15		3		7.70	7.40	(1.375)
15	3		10	9.05	9.12	1.440
15		4		10.14	10.10	1.425
15	4		5	11.27	10.75	(1.364)
15		5		12.71	12.60	1.418
15	5		10	14.07	14.00	1.423
3		6		15.45	15.35	1.416
3	6		1	16.62	17.00	(1.463)
6	7		1	18.82	18.90	1.436
				Weighted mean		1.427

C–O = 1.43 ± 0.02 Å.

Discussion

The estimated intensities of the visual maxima and the corresponding s values were used in the calculation of a radial distribution curve.[5] The data of Table I lead to the curve shown in Fig. 1. This curve shows two pronounced peaks corresponding to the most important interatomic distances in the molecule. The first peak occurs at 1.47 Å., exactly the value which would be predicted for models of the ring type shown in Fig. 2, in which there are six C–O and three C–C single bonds. The covalent radii lead to the values 1.43 and 1.54 Å., respectively. If these values are weighted according to the number and scattering power of the atoms involved, the single peak corresponding to the two unresolved distances should occur at 1.47 Å. the observed value. Accordingly, the single bonded ring structure is very probable.

A determination of the bond angle can be made by use of the second peak which occurs at 2.36 Å. This peak corresponds to the interaction of atoms bonded to the same atom. The ratio 2.36 to 1.47 is 1.61, which leads to the bond angle of 108° in close approximation to the tetrahedral angle of 109°28′. Similar values of the bond angle between carbon and oxygen have been found in other compounds, such as dimethyl ether and dioxane, and we accept the tetrahedral angle as being correct in the calculation of theoretical intensity curves.

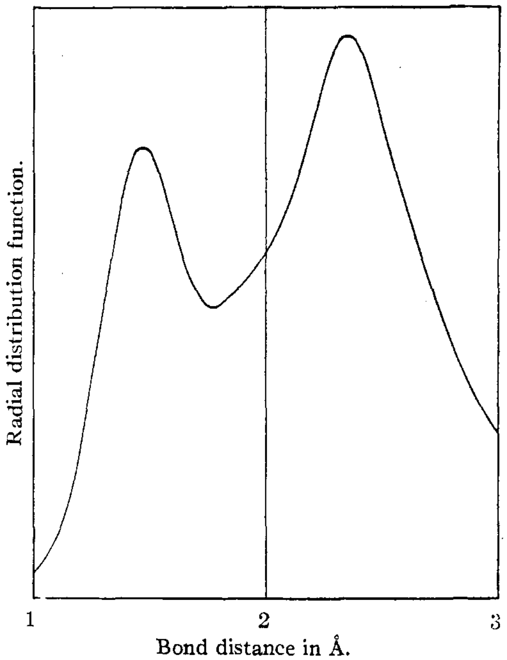

Fig. 1.—Radial distribution curves for paraldehyde.

Four ring models of the paraldehyde molecule are possible, corresponding to elevating the methyl groups successively above the plane of the –C–O–C–ring as shown in Fig. 2. Calculations of the theoretical intensity of scattering, $I = \Sigma_i\Sigma_j Z_i Z_j (\sin s l_{ij}/s l_{ij})$ where $s = (4\pi \sin \theta/2)/\lambda$ were made for each of the four models for s values up to 20. The distances between bonded atoms were taken as follows: C–O, 1.43 Å.; C–C, 1.54 Å.; C–H, 1.06 Å.; and the bond angles were taken as 109° 28′. The calculated curves are shown in Fig. 3. The observed positions of the maxima and minima are indicated at the bottom of the figure. The s values for the maxima and minima of the first theoretical curve (all methyl groups in the plane of the ring) are listed in the sixth column of Table I. The four curves all show the qualitative intensity features observed in the photographs. Particularly characteristic is the strong fifth maxi-

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[5] L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935).

mum. Differences in the four models are evident in the fourth and sixth rings. The fourth ring is displaced outward in going from model 1 to model 4, and models 3 and 4 are in definite disagreement with the photographs on this account. Similarly these last two models show an inward displacement of the sixth ring which is not observed.

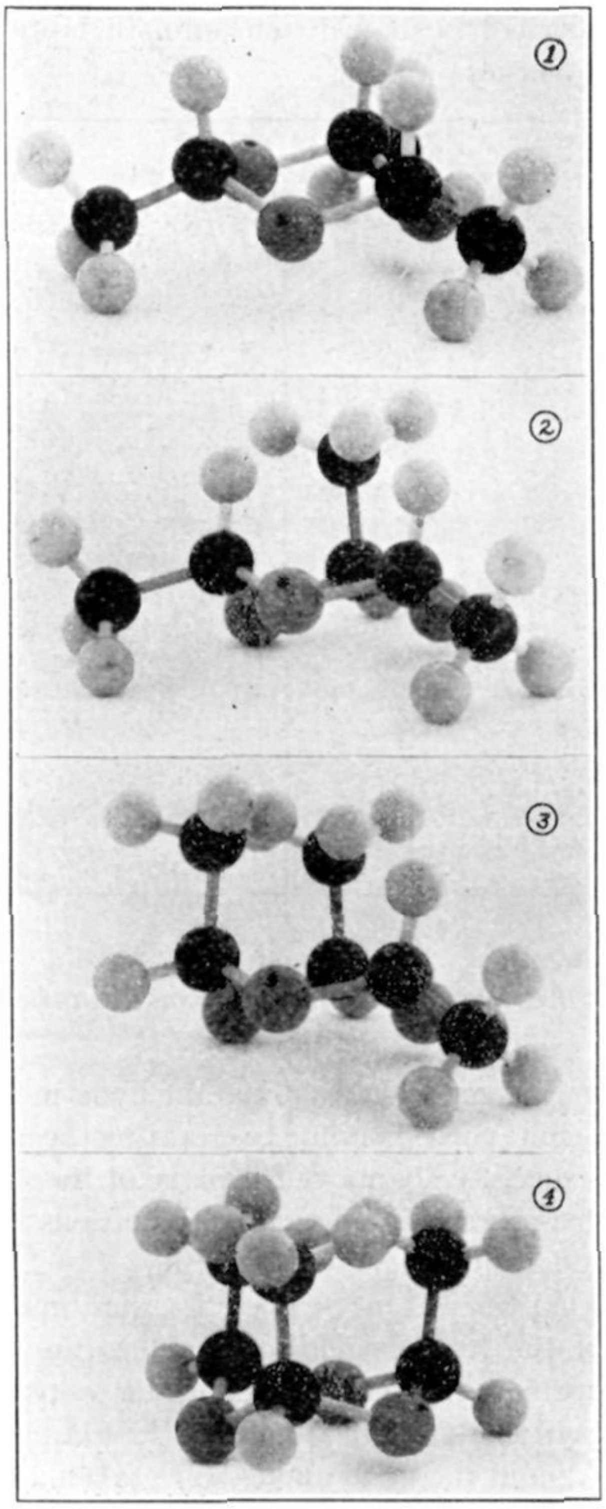

Fig. 2.—Models of paraldehyde molecule.

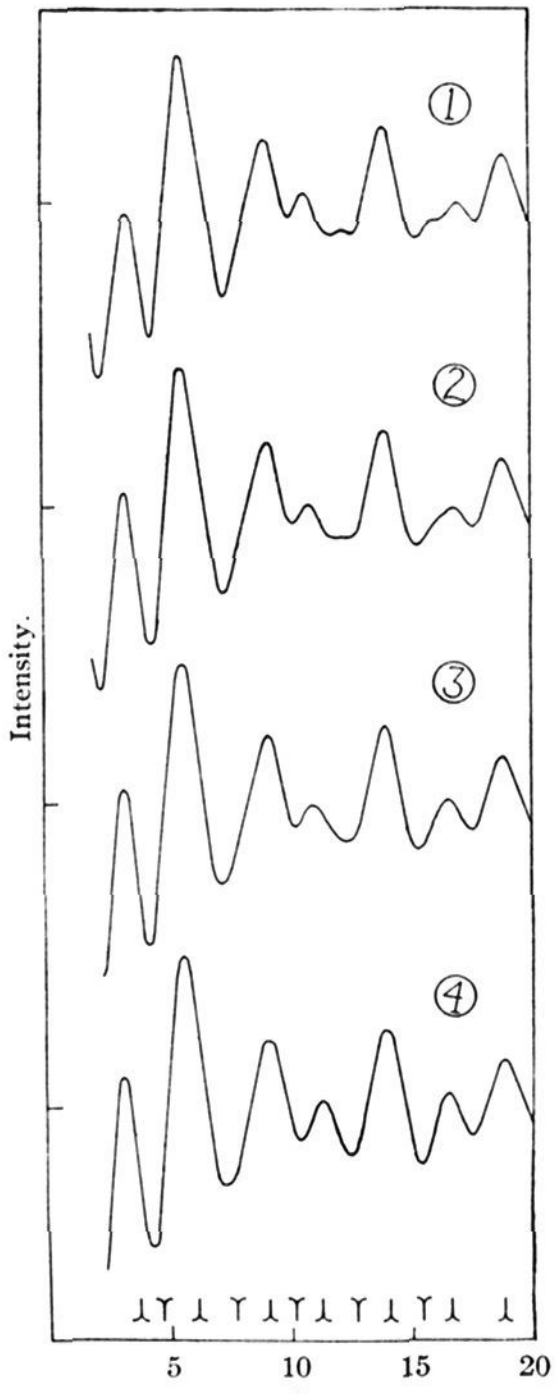

Fig. 3.—Theoretical intensity curves for paraldehyde models.

The values for the C–O distances in the last column of Table I are derived by multiplying the ratio of S(calcd.) to S(obsd.) by the assumed value for the distance. In arriving at the weighted mean value we reject the values from the two innermost rings and from the fourth and sixth maxima. In the former case the contrast effect of the dense central image leads to interatomic distance values which are too small and in the latter case the notable asymmetry of maxima results in the expected shift explained by the St. John effect.[3] While these rings are not suitable for exact determination of the interatomic distances, they are valuable in confirming the ring structure of the molecule since the corresponding theoretical curve and the photographs show the same asymmetric features. The dimensions of the molecule are determined as 1.43 ± 0.02 Å. for the C–O bond distance and 1.54 ± 0.02 Å. for the C–C bond distance with the staggered ring arrangement of six alternating carbon and oxygen atoms well established.

The close similarity in the theoretical intensity curves corresponding to models 1 and 2 makes it impossible to distinguish on the basis of our data between the model with all of the methyl groups nearly in the plane of the ring and the model having one methyl group above the ring. A comparison can be made with the structure of metaldehyde determined by x-ray crystal studies.[6] Metaldehyde, which is the tetramer of acetaldehyde, has an eight-membered ring of alternating carbon and oxygen atoms with four methyl groups attached to the four carbon atoms and all four of the methyl groups lie in the plane of the carbon atoms in the ring. The molecules are packed together in such a way that the closest approach of methyl carbon atoms on adjacent molecules is 3.90 Å. with an average separation for the intermolecular methyl groups of 4.02 Å. Hydrogen atoms on these methyl groups are separated by 2.14 Å. In models 3 and 4 of paraldehyde which have two and three methyl groups above the ring the calculated separation of methyl carbons is 2.33 Å. and of the methyl hydrogens is 1.85 Å.; comparison of these distances with those observed in the metaldehyde crystals again eliminates these two models of paraldehyde. The observed configuration of the metaldehyde molecules makes model 1 of paraldehyde (all methyl groups nearly in the plane of the ring) seem most probable.

Electron diffraction pictures were taken of the vapor of metaldehyde and the photographs show that the gaseous molecule cannot be represented by any single configuration. This is to be explained by the ease with which the eight-membered ring can be distorted from the configuration found in the crystalline form of metaldehyde without stretching or bending the bonds between adjacent atoms. This labile nature of the ring is not found in the crystal because the interactions between molecules in the condensed state are strong enough to hold the molecules in a single equilibrium configuration. The six-membered ring of paraldehyde does not exhibit any such labile character because of the strains set up in any distortion of the smaller ring.[7]

We are indebted to Professor Linus Pauling for proposing the investigation and for many valuable suggestions and criticisms.

Summary

Paraldehyde has been studied by the electron diffraction method and found to consist of a staggered six-membered ring of alternate carbon and oxygen atoms having a C–O distance of 1.43 ± 0.02 Å. The bond angles are all tetrahedral and the three methyl groups are placed symmetrically about the molecule in nearly the same plane as the ring (*i. e.*, as fixed by the tetrahedral angles) with the possibility that only one of the methyl groups may be elevated above the plane of the ring. The methyl carbon atoms are attached to the carbon atoms of the ring by bonds having a length of 1.54 ± 0.02 Å.

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[6] L. Pauling and D. C. Carpenter, THIS JOURNAL, **58**, 1274 (1936).

[7] An electron diffraction study of paraldehyde vapor has been reported by Ackermann and Mayer (*J. Chem. Phys.*, **4**, 377 (1936)). These authors used electrons of only 6400 volts energy corresponding to a wave length of 0.15 Å. and obtained three maxima. While their observed *s* values for the first and second maxima and minima are from 3 to 10% lower than those reported in this paper the discrepancy may well be due to the differences in technique. As reported above, when the shorter wave-length (0.06 Å.) is used the apparent positions of the innermost rings is affected by the very dense central spot and they lead to unreliable interatomic distance values. This effect is evidently less serious when the inner rings occur at greater angles. The conclusions of Ackermann and Mayer are in fair agreement with the present results based on photographs showing seven maxima.