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Summary

1. It has been shown that when the reduction of molybdate is performed according to the method of Birnbaum and Walden in 2 normal hydrochloric acid, using a silver reductor, their conclusions are substantiated. Although traces of trivalent molybdenum may be formed in the process, exposure to the air oxidizes it to the quinquevalent state before the sample is titrated with ceric sulfate. Therefore their procedure produces quantitative reduction of the molybdate to the quinquevalent state.

2. When reduction of molybdate in 2 normal hydrochloric acid is performed in the silver reductor, using special precautions to avoid air oxidation, the reduction corresponds to slightly more than 1 equivalent in valence change of the molybdenum. If the acid concentration is greater than 4 normal, molybdenum in the molybdate is reduced mainly to the trivalent state. In high acid concentrations such as 10 normal, the reduction shows an apparent valence change as high as 3.1.

3. When reduction of molybdate is performed in a Jones reductor using precautions to prevent air oxidation, the apparent change of valence for molybdenum is not greater than three even though the acid concentration is as high as 6 normal.

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Internal Rotation in 1,1,2-Trichloroethane¹

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The problem of the freedom of rotation around the carbon-carbon single bond in halogen substituted ethanes recently has been attacked by the electron diffraction method. Studies have been made of ethylene chloride,² ethylene chlorobromide,³ and ethylene bromide.³ In all three cases it was found that the *trans* configuration was the stable configuration and that the potential barrier to internal rotation was 5 kcal./mole or greater. In this paper we shall report an electron diffraction investigation of the freedom of internal rotation in 1,1,2-trichloroethane.

The compound used was an Eastman Kodak Co. product, purified by fractional distillation in a 30-inch (76-cm.) column on which the reflux ratio could be controlled. The electron diffraction apparatus was similar to the one described by Brockway.⁴ The electron wave length was 0.0590 Å. and the distance from the photographic plate to the nozzle was 12.19 cm. The photographs, taken with the compound warmed to about 65°, show seven irregularly spaced maxima. The fourth maximum is weaker than the third or

fifth. The observed values of $s(=4\pi \sin \Theta/2)/\lambda$ and the visually estimated intensities, I , of the maxima and minima are tabulated in Table I.

TABLE I

VALUES IN PARENTHESES NOT INCLUDED IN THE AVERAGE									
Max.	Min.	I	C	s_0	s^a	s^a/s_0	s^b	s^b/s_0	
1		15	20	2.937	2.85	(0.907)	3.12	(1.062)	
	2	-13	-35	3.993	3.76	(.942)	3.86	(0.967)	
2		20	44	4.835	4.82	.997	4.89	1.011	
	3	-12	-51	6.851	6.08	.887	6.15	0.898	
3		16	51	7.654	7.61	.994	7.64	.998	
	4	-2	-9	8.645	8.59	.994	8.63	.998	
4		8	29	9.387	9.18	.978	9.24	.984	
	5	-7	-35	10.92	10.17	.931	10.21	.935	
5		12	48	11.85	11.86	1.001	11.87	1.002	
	6	-5	-24	12.88	13.06	1.014	13.07	1.015	
6		3	14	13.65	13.95	1.022	14.03	1.028	
	7	-3	-14	14.59	14.45	0.990	14.45	0.990	
7		2	14	15.29	15.08	.986	15.10	.988	
						Average	0.981		0.986
						C-Cl	1.73 Å.	C-Cl	1.74 Å.

^a Calculated for a model in which the interactions are assumed to be electrostatic plus exchange. ^b Calculated for a model in which the interactions are assumed to be electrostatic plus "corrected" exchange.

The photographs were interpreted by the radial distribution method⁵ and the usual visual method.⁶ Two radial distribution functions are shown in Fig. 1. Curve A was calculated by a method somewhat improved over the original one⁵

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

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

(1) These results were presented to the American Chemical Society at the Boston, Mass., meeting, September, 1939.

(2) J. Y. Beach and K. J. Palmer, *J. Chem. Phys.*, **6**, 639 (1938).

(3) J. Y. Beach and Anthony Turkevich, *THIS JOURNAL*, **61**, 303 (1939).

(4) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

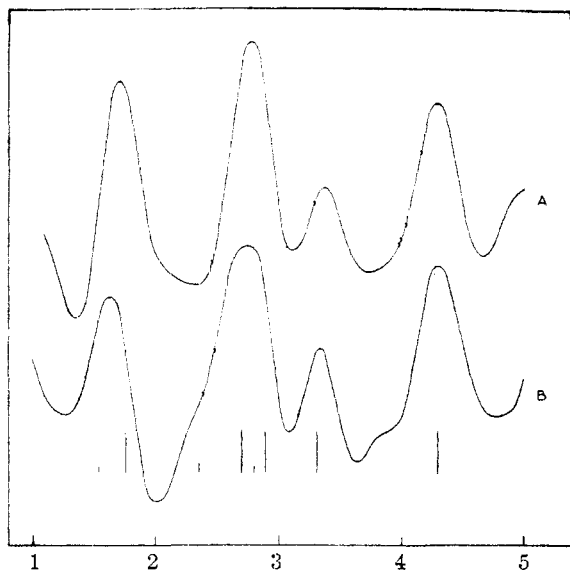


Fig. 1.—Radial distribution functions for 1,1,2-trichloroethane. In curve A the coefficients of the $(\sin ls)/ls$ terms are $s^2e^{-as^2}$ times the visually estimated intensities of the maxima. The minima are not used. a is determined by setting e^{-as^2} equal to 0.1 for the largest ring. Curve B is calculated according to the method of Schomaker. Both maxima and minima are used. The C 's in Table I are the coefficients of the $(\sin ls)/ls$ terms.

and has been called the modified radial distribution method in several previous publications.⁷ Curve B was calculated by a procedure suggested by Schomaker⁸ in which both maxima and minima are used in a slightly different way. The first peak at about 1.70 Å. represents the carbon-chlorine bond distance together with the carbon-carbon distance. The broad peak at 2.77 Å. represents the short chlorine-chlorine distance and the long carbon-chlorine distance. The two peaks at 3.36 and 4.30 Å. must represent distances between chlorine atoms bonded to different carbon atoms, and the interpretation of these two peaks leads to the most important result of the investigation—the most stable configuration of the molecule. In designating the internal configuration we shall use the relative azimuthal angle of the two ends of the molecule, ϕ . ϕ is 0° when the molecule is *cis* and 180° when it is *trans*. The *cis* and *trans* configurations are the only ones which possess a plane of symmetry. If, as might have been expected at first, the *trans* configuration were the most stable, the radial distribution function should possess a single maximum at 3.95 Å. in

(7) L. O. Brockway and J. Y. Beach, *THIS JOURNAL*, **60**, 1836 (1938); J. Y. Beach and Anthony Turkevich, *ibid.*, **61**, 299 (1939).

(8) V. F. H. Schomaker, paper presented to the American Chemical Society at Baltimore, Md., April, 1939.

place of the two at 3.36, 4.30 Å. In the *trans* configuration the atoms involved in the long chlorine-chlorine distances are at an angle of 120° with respect to each other. The peaks at 3.36 and 4.30 Å. correspond to distances between chlorine atoms separated by angles of about 70° and 180° , respectively. These immediately are seen to be the angles involved in a model for which ϕ is about 130° . The radial distribution function shows, therefore, that the most stable configura-

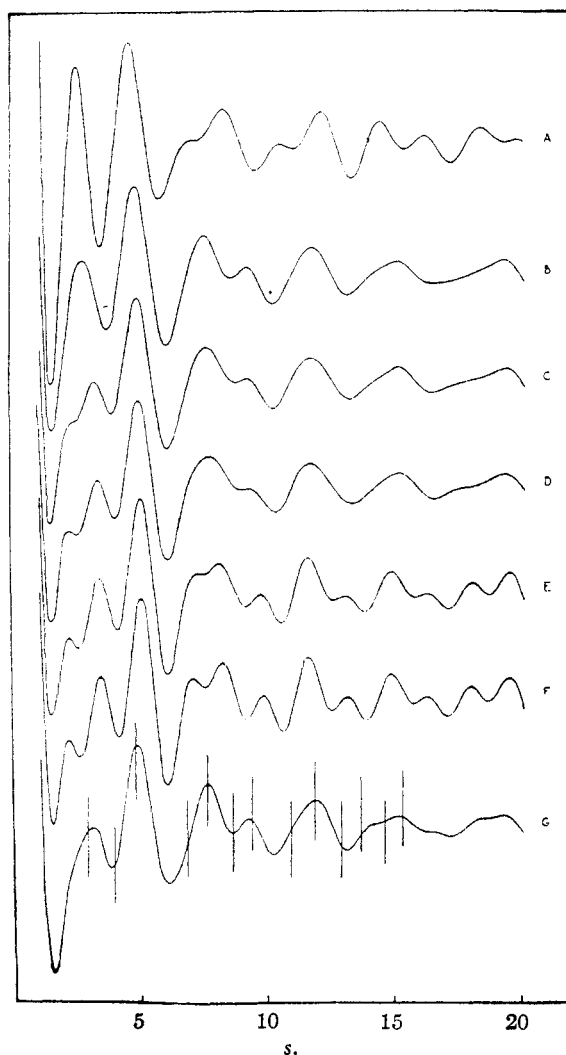


Fig. 2.—Theoretical intensity curves for 1,1,2-trichloroethane. Curve A, *cis* model. Curve B, freely rotating model. Curve C, model having a sinusoidal potential barrier of 5 kcal./mole, the *trans* configuration being the most stable. Curve D, same as for C except that the barrier is 10 kcal./mole. Curve E, same as for C except that the barrier is 20 kcal./mole. Curve F, *trans* model. Curve G, calculated for a model in which the potential barrier is taken to be the sum of the electrostatic interactions and the exchange repulsions.

tion of the molecule is not the *trans* but is *rotated about 50°* from the *trans* configuration. In making this argument it was assumed that the interatomic distances in the molecule are those given by the table of covalent radii,^{9,10} and that the bond angles on the carbon atoms are tetrahedral.

In interpreting the photographs by the usual visual method, theoretical intensity curves were first calculated for a rigid *cis* and a rigid *trans* model. These curves are shown in Fig. 2, curves A and F, respectively. In calculating these curves and curves for the other models considered, the interatomic distances in the molecule were taken to be those given by the table of covalent radii.⁹ All the bond angles were assumed to be tetrahedral except the Cl-C-Cl angle which was taken to be 111°, the value found in chloroform.¹¹ Other values for this angle were tried but gave unsatisfactory results. The *cis* curve shows the fourth maximum to be higher than the third or fifth, while the photographs show it to be weaker than the third or fifth. The *cis* model is, therefore, ruled out. The *trans* curve does not resemble the photographs in that it shows extra maxima that are not observed on the photographs. This is easily seen by examining the positions of the observed maxima and minima and curve F in Fig. 2.

If the interaction of the chlorine atoms on the two ends of the molecule is assumed to produce a sinusoidal potential barrier, then the two such interactions in 1,1,2-trichloroethane, when added together, will give again a sinusoidal potential barrier, the stable configuration being the *trans*. Although this result has been shown to be not valid by the radial distribution function, we shall consider it in calculating theoretical intensity curves. Theoretical curves were calculated for sinusoidal potentials having heights of zero, 5, 10 and 20 kcal./mole. These curves are shown in Fig. 2. The curve for zero barrier corresponds to completely free rotation. This curve is unsatisfactory because it shows only one maximum instead of the sixth and seventh. The 5 and 10 kcal./mole curves are unsatisfactory for the same reason. The 20 kcal./mole curve resembles the *trans* curve in showing too many maxima and therefore is not acceptable. We have thus

reached the same conclusion as was reached by examination of the radial distribution function—the most stable configuration is not the *trans* configuration.

In calculating these curves the same procedure was followed as in the case of the disubstituted ethanes.^{2,3} For the disubstituted ethanes curves were calculated for molecules having all possible configurations differing by 30°. These curves were then added together using the Boltzmann factor as a weighting factor. For 1,1,2-trichloroethane it was found necessary to include molecules having values of ϕ differing by 10° instead of by 30°, except for the steeper barriers.

A potential barrier to internal rotation can be calculated in the following manner. The nine electrostatic interactions can be evaluated by the use of the individual bond moments. These moments have been tabulated by Smyth.¹² In making this calculation it was assumed that the bond moments were due to charges at the centers of the atoms involved in the bond. The sums of these interactions are tabulated in Table II as a function of the angle ϕ . The exchange repulsions also must be considered. We have evaluated the nine exchange repulsions by the method of Eyring.¹³ The Morse curve was assumed to be 20% coulombic in each case. These totals are tabulated in Table II as a function of ϕ . The sums of the electrostatic and exchange interactions are tabulated in Table II and shown in Fig. 3, curve A. It is seen that the stable configuration of the molecule is about 60° removed from the *trans* configuration. This is in agreement with the result deduced from the radial distribution function.

TABLE II

ELECTROSTATIC AND EXCHANGE INTERACTIONS AS A FUNCTION OF THE INTERNAL CONFIGURATION, KCAL./MOLE							
Interactions	0°	30°	60°	90°	120°	150°	180°
Electrostatic	2.64	2.60	2.43	1.83	1.15	0.55	0.34
Exchange	13.31	14.28	15.56	14.83	14.25	15.36	16.11
"Corrected" exchange	16.09	17.42	19.19	17.53	15.78	16.16	16.70
Electrostatic plus exchange, $E(\phi) - E(\text{min.})$	0.55	1.48	2.59	1.26	0	0.51	1.05
Electrostatic plus "Corrected" exchange, $E(\phi) - E(\text{min.})$	2.02	3.31	4.91	2.65	0.22	0	0.3

In treating the disubstituted ethanes,^{2,3} it was found necessary to apply a correction to the halogen-halogen exchange repulsions to obtain agreement with the photographs.² When this method is used to get the chlorine-chlorine exchange re-

(9) L. Pauling and M. L. Huggins, *Z. Krist.*, **87A**, 205 (1934).

(10) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 1223 (1937).

(11) L. E. Sutton and L. O. Brockway, *THIS JOURNAL*, **57**, 473 (1935).

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

(13) H. Eyring, *THIS JOURNAL*, **54**, 3191 (1932).

pulsions in 1,1,2-trichloroethane, we obtain the "corrected" exchange repulsions collected in Table II. The sums of the "corrected" exchange repulsions and the electrostatic interactions are given in Table II and shown in Fig. 3, curve B.

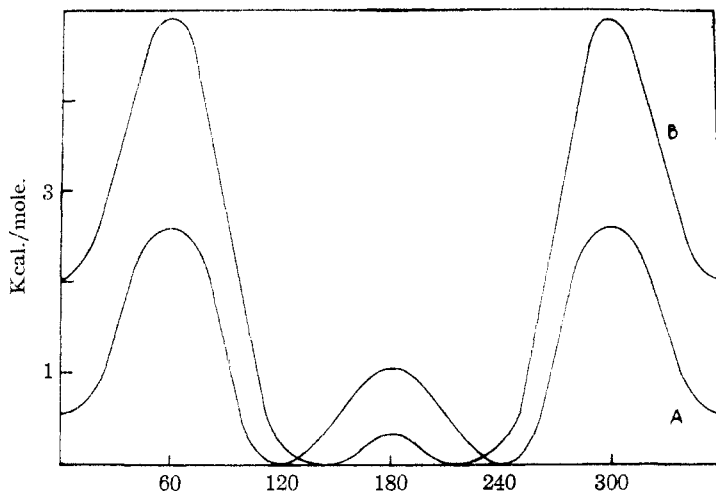


Fig. 3.—The potential barrier to internal rotation. Curve A, the electrostatic interactions plus the exchange interactions, assuming the Morse curve to be 20% coulombic. Curve B, the electrostatic interactions plus the "corrected" exchange interactions.

The shape of the potential curve is changed somewhat but the most stable configuration is essentially the same.

Theoretical intensity curves were calculated for the potential functions shown in Fig. 3. These two curves are practically indistinguishable to the eye so only one of them (curve G) has been included in Fig. 2.

Both curves are quantitatively compared with the photographs in Table I. Curve G resembles the photographs more closely than any other curve calculated. The vertical lines represent

the positions of the observed maxima and minima. The incomplete resolution of the sixth and seventh maxima would probably be remedied if the temperature factor had been included and the Z approximation had not been made.

The vertical lines in Fig. 1 indicate the position and importance in the scattering function of the finally determined interatomic distances. The values shown for the long chlorine-chlorine distances are those for a model in the most stable configuration—when ϕ is 130° . The oscillation about this position will, of course, smear these points to some extent.

The radial distribution function and the qualitative and quantitative comparison of the photographs with the calculated intensity curves lead to the final results.

Summary

From an electron diffraction investigation it has been shown that 1,1,2-trichloroethane is not a rigid molecule in the *cis* or the *trans* configuration, nor does it have a sinusoidal potential barrier to internal rotation with the *trans* configuration the most stable. The most stable configuration is rotated about 50° from the *trans* position. A potential barrier calculated from electrostatic (dipole) and exchange interactions is in agreement with the experiments. The C-Cl distance is $1.75 \pm 0.03 \text{ \AA}$. The Cl-C-Cl angle is $111^\circ 30' \pm 2'$. The C-C and C-H distances were assumed to be 1.54 and 1.09 \AA , respectively.

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