Internal Rotation in Ethylene Chloride

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The electron diffraction method of investigation has been used to determine the nature of the potential barrier restricting the rotation about the carbon-carbon single bond in ethylene chloride ($CH_2Cl - CH_2Cl$). Assuming that the shape of the barrier is given by a cosine function, the height of the barrier is between 5 kcal./mole and infinity. This potential barrier is compared with the barrier resulting from the exchange repulsions and the electrostatic repulsions of the two ends of the molecule. Eyring's method was used for calculating the exchange repulsions. The repulsions between the chlorine atoms must be calculated differently from the repulsions between hydrogen and chlorine atoms in order to obtain agreement between theory and experiment. Duplicate experiments were done at Princeton and at Pasadena.

THE electron diffraction photographs of ethylene chloride vapor from which these results are deduced were taken at Pasadena and at Princeton. Both compounds were Eastman products, fractionally distilled in three-foot columns on which the reflux ratio could be controlled. The first photographs were taken by both of us at Pasadena. The Pasadena apparatus has been described by Brockway.[1] The Princeton apparatus is similar to the Pasadena apparatus and has been used previously.[2] The Pasadena and Princeton photographs were made with electrons having wave-lengths of 0.0611A and 0.0590A, respectively. The two sets of photographs, which are identical except for the effect of electron wave-length, and lead to identical results, will not be discussed separately.

We did not attempt to determine by electron diffraction all the bond distances and bond angles in the molecule in addition to the shape of the potential barrier. The carbon-hydrogen distance was assumed to be 1.09A, the carbon-hydrogen distance in methane.[3] The carbon-carbon distance was assumed to be 1.54A, the carbon-carbon distance in diamond[4] and a large number of saturated hydrocarbons.[5] All the bond angles on the carbon atoms were assumed to be tetrahedral. This assumption is made reasonable by the fact that in methylene chloride and chloroform, where the chlorine-chlorine distances are only about 2.90A, the bond angles are but slightly (about 3°) distorted from the tetrahedral value.[6]

The observed values of $s(s_{obs} = (4\pi \sin \theta/2)/\lambda)$ for the maxima and minima and the intensities of the maxima of the electron diffraction photographs are tabulated in Table I. The heavier photographs show up to nine maxima. The last two cannot be measured with much accuracy. The first three maxima are of approximately equal intensity. The fourth and fifth are much weaker. The sixth is strong. The seventh, eighth and ninth are progressively weaker.

The data have been treated by the radial distribution method[7] and by the modified radial distribution method.[8] Both radial distribution curves are shown in Fig. 1. The modified radial distribution curve differs from the ordinary radial distribution curve in that the peaks are sharper. The positions of the maxima are practically identical. The average positions of the maxima on the two curves are 1.73A, 2.70A and 4.29A. The first two peaks represent carbon-chlorine distances, and the third peak represents the chlorine-chlorine distance. 4.29A is just the value of the chlorine-chlorine distance for the *trans*-configuration of the molecule if the carbon-

* Part of these results were presented to the American Physical Society at New York City, February, 1938.
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[1] Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[2] Beach and Stevenson, J. Am. Chem. Soc. **60**, 475 (1938); J. Chem. Phys. **6**, 75 (1938).
[3] Ginsburg and Barker, J. Chem. Phys. **3**, 668 (1935).
[4] *Strukturbericht.*
[5] Pauling and Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[6] Sutton and Brockway, J. Am. Chem. Soc. **57**, 473 (1935).
[7] Pauling and Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).
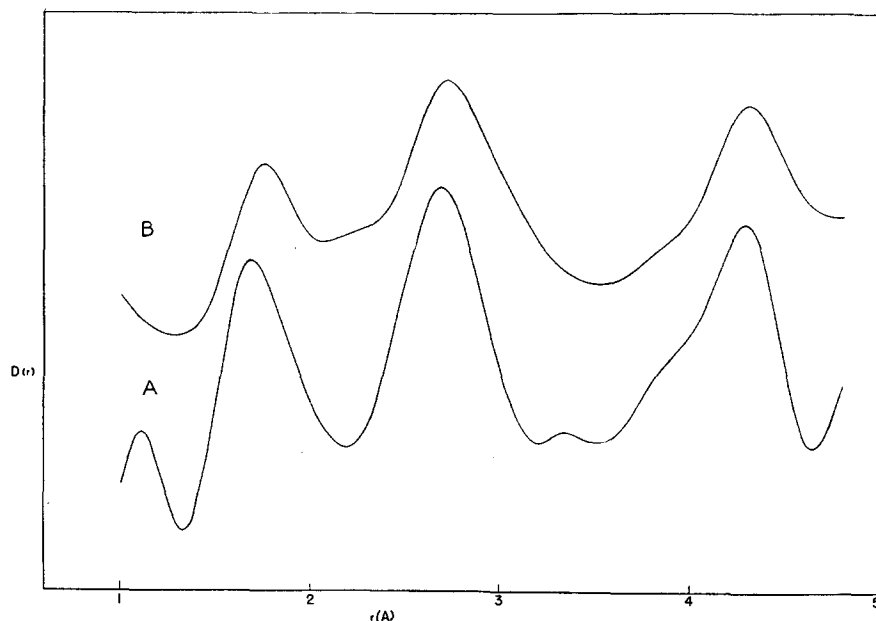[8] Schomaker, to be published.

FIG. 1. Curve A, modified radial distribution function. Curve B, ordinary radial distribution function.

chlorine distance is assumed to be 1.76A, the radius table value[9] for the carbon-chlorine single bond distance. The dissymmetry in the chlorine-chlorine peak on the modified radial distribution curve indicates that some of the molecules are oscillating from the *trans*-configuration to intermediate configurations having shorter chlorine-

TABLE I. *Ethylene chloride.**

Max.	Min.	I	s_{obs}	s_a	s_a/s_{obs}	s_b	s_b/s_{obs}
1		12	3.160	3.26	1.032	3.31	1.047
	2		4.136	3.97	0.960	4.01	0.970
2		15	4.936	4.84	0.981	4.87	0.987
	3		6.668	6.68	1.002		
3		13	7.679	7.72	1.005	7.79	1.014
	4		8.594	8.58	0.998	8.70	1.012
4		4	9.194	9.14	0.994	9.23	1.004
	5		9.964	9.98	1.002	10.09	1.013
5		3	10.591	10.78	1.018		
	6		11.302	11.12	0.984		
6		8	12.041	12.02	0.998	12.10	1.005
	7		13.183	13.02	0.988	13.14	0.997
7		4	14.815	14.95	1.009	14.90	1.006
				Av. $\overline{0.998}$		Av. $\overline{1.005}$	
				C—Cl=1.76		C—Cl=1.77	

Final results C—Cl=1.76±0.02A.
5 kcal./mole $=\leqq V_0 \leqq$ infinity.

* (a) From *trans* curve. (b) From 6 kcal./mole curve. The first maximum and the second minimum were omitted in the averaging.

[9] Pauling and Huggins, Zeits. f. Krist. **87A**, 205 (1934).

chlorine distances. While doubtless such motion occurs, the radial distribution function is not sufficiently accurate to make a quantitative estimate of the extent of the motion possible.

To arrive at more definite results regarding the oscillation about the *trans*-configuration the electron diffraction data have been treated by the visual method.[10] The relation $V = V_0(\cos \phi + 1)$ is assumed to represent the potential barrier to internal rotation. ϕ is the angle between the plane containing one chlorine atom and the two carbon atoms and the plane containing the other chlorine atom and the two carbon atoms. V_0 is the height of the barrier and limits will be placed on its value from the electron diffraction data. This form for the potential function has been shown to be a fairly satisfactory approximation to the actual potential function by a study of the consistency of the V_0 values obtained from dipole moments using different potential functions.[11]

The formula for the intensity of scattered electrons is

$$I = \sum_i \sum_j Z_i Z_j \frac{\sin s l_{ij}}{s l_{ij}}.$$

[10] Pauling and Brockway, J. Chem. Phys. **2**, 867 (1934).
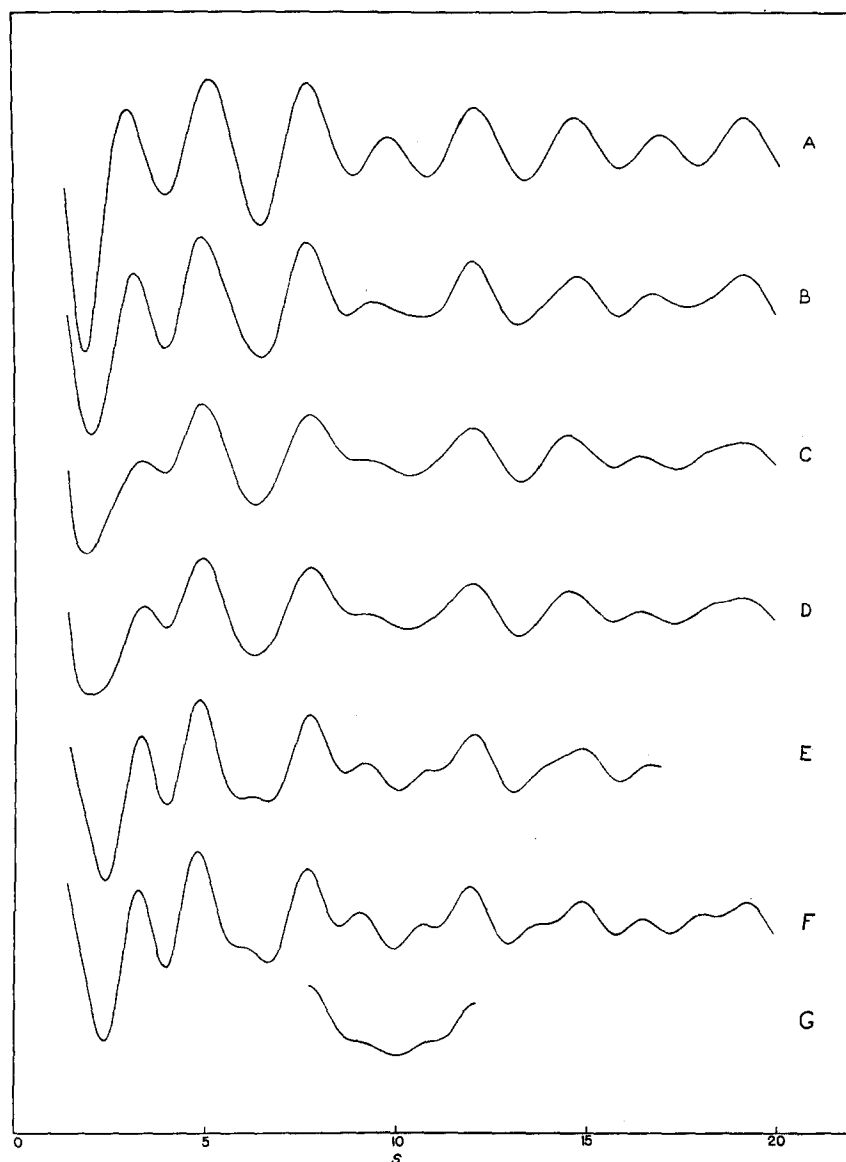[11] Beach and Stevenson, J. Chem. Phys. **6**, 635 (1938).

FIG. 2. Theoretical intensity curves. Curve A, *cis* model. Curve B, half-*cis* and half-*trans*. Curve C, free rotation. Curve D, $V_0=0.6$ kcal./mole. Curve E, $V_0=6.0$ kcal./mole. Curve F, $V_0=$infinity, *trans* model. Curve G, segment of curve for potential function shown in Fig. 4, Curve A.

l_{ij} is the distance from the ith to the jth atom; Z is atomic number. Intensity curves were calculated for ethylene chloride for values of V_0 ranging from zero to infinity. When V_0 equals infinity all the molecules are in the *trans*-position. When V_0 equals zero all the molecules rotate freely, and there are equal numbers of molecules in all configurations. For intermediate values of V_0 the number of molecules possessing a given configuration is found from the Boltz-

mann factor, $\exp(-V(\phi)/RT)$. The electron diffraction curves are calculated by adding the intensity formulas for molecules having values of $\phi=0°$, $30°$, $\cdots$ $180°$ weighted by the appropriate Boltzmann factor. The Boltzmann factors and the final curves are determined by the value given to V_0.

It has been shown by Altar[12] that this procedure is not rigorously correct. The weighting

[12] Altar, J. Chem. Phys. **3**, 460 (1935).

factors are not exactly equal to the Boltzmann factors. The entropy of the molecule varies with ϕ and the statistical weights are not constant when V_0 equals zero. This is true for this type of molecule even if the product of inertia is independent of ϕ. However, these effects are small at all angles near 180°, which is the region occupied by most of the molecules, and will be neglected.

The electron diffraction intensity curves are plotted in Fig. 2. The *trans*-curve corresponds most closely to the photographs. The 6 kcal./ mole curve is less satisfactory because the fifth maximum on it is not sufficiently prominent. The other curves are unsatisfactory from a qualitative inspection, none of them showing the fourth and fifth maxima correctly. Quantitative comparisons of the photographs with curves E and F are made in Table I. The curves in Fig. 2 are all calculated for molecular models having a carbon-chlorine distance of 1.76A. This does not predetermine the carbon-chlorine distance because if the value had been incorrect a value for the carbon-carbon distance different from the assumed 1.54A would have been obtained when quantitative comparisons of curves and photographs were made. The final results are: $C-Cl = 1.76 \pm 0.02A$ and 5 kcal./mole $\leqq V_0 \leqq$ infinity.

Wierl,[13] from electron diffraction photographs showing only three maxima, reported that the chlorine-chlorine distance in ethylene chloride is 4.5A. He also stated that ethylene chloride could be an approximately equimolal mixture of *cis* and *trans*-molecules. The theoretical intensity curve for this mixture is curve B, Fig. 2. It is unsatisfactory because it possesses only one

maximum between the prominent third and sixth maxima, Wierl assumed a carbon-chlorine bond distance of 1.82A. Debye[14] reported a chlorine-chlorine distance of 4.4A from x-ray photographs.

DISCUSSION

There are several contributions to the potential barrier to internal rotation, the more important ones being the exchange steric repulsion between all atoms not bonded to each other, the electrostatic interaction of the bond dipoles, and the interaction between the bond orbitals on the carbon atoms. The magnitude of this last effect in H_2O_2 has been calculated by Penney and Sutherland.[15] They find that the potential energy of the molecule due to this interaction has maxima of about 2 kcal./mole in the *cis*- and *trans*-positions and minima when ϕ is $\pm 90°$. This effect in ethane or ethylene chloride would lead to three approximately equal potential minima at angles of 120°. The depth of the minima should be less for several reasons. The carbon atoms are separated by a greater distance than the oxygen atoms. The orbitals on the carbon atoms make a larger angle (109° 28′) with the carbon-carbon bond than the oxygen orbitals make with the oxygen-oxygen bond (90°). The potential humps are separated by only 120° instead of 180° and the nine repulsions will tend to cancel. To show how this might occur we have calculated the exchange repulsions[16] between hydrogen atoms for the hypothetical molecule H_2OOH_2. The H_2OO groups are assumed to be planar and the $H-O-O$ angles tetrahedral. The hydrogen atoms are located approximately on the loops of the oxygen orbitals, the interaction between which has been calculated by Penney and Sutherland. Taking 0.94A and 1.32A for the hydrogen-oxygen and oxygen-oxygen distances, the steric repulsions between hydrogen atoms is greater by 1.9 kcal./ mole when $\phi = 0°$ than for the configuration with $\phi = 90°$. Comparing this with the steric repulsion potential barrier of 0.3 kcal./mole, obtained by Eyring[16] for ethane, it is seen that the nine interactions tend to cancel out. If an analogy exists between orbital interactions and steric

TABLE II. *Repulsions in ethylene chloride, kcal./mole.*

ϕ	0°	30°	60°	90°	120°	150°	180°
Electrostatic interactions	1.80	1.46	0.85	0.18	-0.29	-0.59	-0.65
Exchange repulsions	14.03	13.30	12.83	13.83	14.58	14.38	13.75
Total	15.83	14.76	13.68	14.01	14.29	13.79	13.10
$E(\phi)-E(\pi)$	2.73	1.66	0.58	0.91	1.77	0.69	0.0
Corrected exchange repulsions	17.37	15.82	14.22	14.45	14.87	14.56	13.89
Corrected exchange plus electrostatic	19.17	17.28	15.07	14.63	14.58	13.97	13.24
$E(\phi)-E(\pi)$	5.93	4.04	1.83	1.39	1.34	0.73	0.0

[13] Wierl, Ann. d. Physik **13**, 453 (1932).

[14] Debye, Physik. Zeits. **31**, 142 (1930).
[15] Penney and Sutherland, J. Chem. Phys. **2**, 492 (1934).
[16] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

repulsions, which does not seem unreasonable, the orbital interaction in ethane, ethylene chloride, etc., would be expected to give rise to a small potential barrier, 0.3 or 0.4 kcal./mole.

The dipole interaction of the two CH_2Cl groups has been calculated by Smyth, Dornte and Wilson.[17] They used the formula for the interaction of dipoles at large distances, placing the dipole at a point along the carbon-chlorine bond. Changing the position of the dipole on the carbon-chlorine bond altered the shape of the potential curve but did not change the difference in energy between the cis- and trans-configurations. We have repeated the calculations assuming that the dipoles are due to charges located at the center of the atoms. This is true insofar as the charge distributions on the atoms are spherically symmetric. The magnitudes of the charges are found by dividing the bond moments[18] by the interatomic distances. Summing the nine electrostatic interactions gives a slightly higher potential barrier, 2.4 kcal./mole. This potential curve is tabulated in Table II and is shown in Fig. 3, curve A.

The van der Waals attractions have not been calculated as the present methods of calculating them yield abnormally large interaction at small interatomic distances.

The largest interactions between the two CH_2Cl groups are the exchange repulsions. These can be calculated by the method of Eyring.[16] We have calculated and summed the nine repulsions as a function of the angle ϕ. The Morse curve was assumed to be 20 percent coulombic. The sum is tabulated in Table II and is shown in Fig. 3, curve B. The exchange plus the electrostatic interactions are tabulated in Table II and shown in Fig. 4, curve A.

To see if this potential curve is compatible with the electron diffraction data we have calculated the theoretical intensity formula for it. A segment of it is shown in Fig. 2, curve G. It is unsatisfactory in the region shown. It does not show the fourth and fifth maxima. If the potential curve A, Fig. 4, were correct the radial distribution function would show a peak at 3.2A roughly equal in height to the one at 4.29A.

[17] Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).
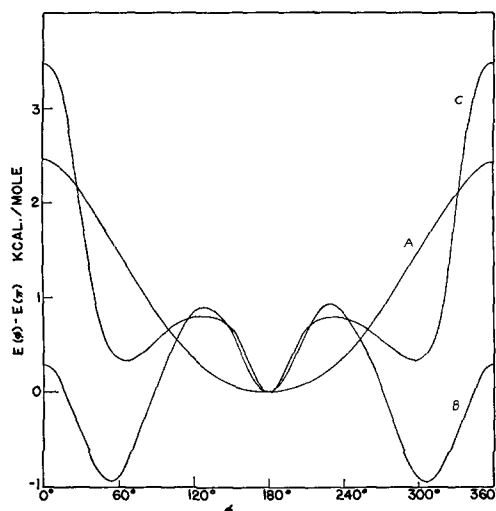[18] Smyth, J. Phys. Chem. **41**, 209 (1937).

FIG. 3. Curve A, electrostatic interaction. Curve B, exchange repulsion. Curve C, corrected exchange repulsion.

That this peak is not present is easily seen in Fig. 1. If the repulsions between the chlorine atoms were greater at the cis-position by about 2.5 kcal./mole, the theoretical potential curve would be brought into agreement with the electron diffraction data.

Professor Eyring has suggested to us that because of the large number of nonbonding electrons in Cl_2 a deeper Morse curve than the actual one should be used in calculating the exchange repulsions. We have adopted the following procedure for doing this. The Morse curve for Cl_2 is multiplied by 14/8, the ratio of the total number of valence electrons to the number of electrons on the valence shell of one atom. This will not affect the Morse curve of a bond involving a hydrogen atom. Assuming that 20 percent of this Morse curve is coulombic and calculating the chlorine-chlorine repulsions leads to the corrected repulsions. When these repulsions are used the potential barrier becomes higher. It is tabulated in Table II and plotted in Fig. 4, curve B. The electron scattering curve calculated for this potential barrier is identical with the one calculated for $V_0 = 6.0$ kcal./mole, curve E, Fig. 2. The agreement between theoretical and experimental potential barriers requires that the chlorine-chlorine repulsions be calculated by this or some analogous method. The same results can be reached by assuming
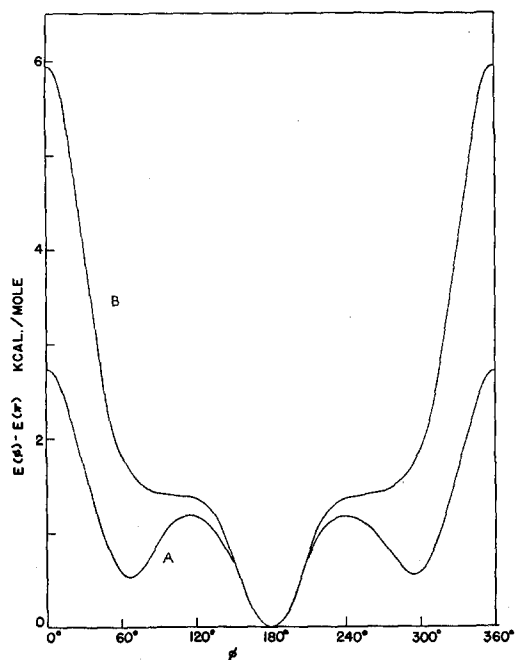
FIG. 4. Curve A, exchange repulsion plus electrostatic interaction. Curve B, corrected exchange repulsion plus electrostatic interaction.

that the coulombic part of the Cl_2 Morse curve is different (smaller) from the 20 percent used for the other calculations of exchange repulsions. The procedure above seems to us more justifiable.

The strongest justification for the above procedure is that it leads to results in agreement with the electron diffraction data on ethylene chloride. This calculation does not change the values previously calculated for the hydrogen-hydrogen repulsion in ethane. Our estimate of the orbital interaction when added to the hydrogen-hydrogen repulsions gives a value of about 0.6

kcal./mole for the potential barrier in ethane. The methods we find satisfactory for calculating the barrier in ethylene chloride do not lead to the high barrier (3 kcal./mole) which has been reported for ethane. It is possible that the analogy on which our estimate of the orbital interaction is based is not sufficiently good. However, it is difficult to understand why it should be as bad as is indicated by the existing data on ethane.

Altar[12] has obtained a potential barrier for ethylene chloride from the temperature variation of the dipole moment. The theoretical intensity curve from Altar's potential function is identical with curve E, Fig. 2, for which V_0 is 6 kcal./mole. The shape of his curve near the *trans*-position is the same as the shape of a cosine curve having an amplitude of 5 kcal./mole. The difference between the two potential curves at small values of ϕ cannot be detected in the electron diffraction curves because of the small fraction of the molecules having small values of ϕ. It must be emphasized that in putting limits on V_0, the height of the barrier, we have assumed a certain shape for the potential curve. We have really only determined the shape of the potential curve near the *trans*-position of the molecule. At small values of ϕ the shape of the barrier may be quite different from that of a cosine function. If the actual barrier is steeper than the cosine function at small values of ϕ, our V_0 is small. If the actual barrier is flatter than the cosine function at small values of ϕ, our V_0 is too high. In any event, the barrier is high at small angles.

We wish to thank Professor Henry Eyring, Professor Linus Pauling and Professor Charles P. Smyth for many valuable discussions on this subject.