$$B_2H_6(\text{liq.}) + xNH_3(s) = B_2H_6{\cdot}xNH_3(s);\ \Delta H = -15.9 \pm 1.2 \text{ kcal./mole.}$$

Summary

Freezing point depression measurements for diborane in ammonia (at approximately 195° K.) show the diborane to be present in a two boron formula, $B_2H_6{\cdot}xNH_3$. No sign of either dissociation or association was noted.

The heat evolved on reaction of diborane with solid ammonia is 15.9 ± 1.2 kcal, per mole of B_2H_6.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Rotational Configuration and Dipole Moments of 1,1,2-Trichloroethane and 1,1,2,2-Tetrachloroethane[1]

BY J. R. THOMAS[2] AND WILLIAM D. GWINN

The rotational configurations of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane have been previously investigated. From the electron diffraction investigation of the former compound Beach and Turkevich[3] were able to show that the stable configurations were staggered rather than eclipsed. These authors suggested that the skew configuration formed by rotating one-half of the molecule 120° out of the *cis* position was the most important form. By similar means Schomaker and Stevenson[4] showed that 1,1,2,2-tetrachloroethane existed in staggered rather than eclipsed forms. They suggested that both possible configurations were relatively stable. Hassel and Viervoll,[5] however, interpreted the same type of data as showing that only the configuration oscillating about the *trans* position was of importance. From the number of Raman lines observed in the liquid spectrum it has been concluded that at least two configurations exist.[6,7] Langseth and Bernstein[7] from the Raman spectrum of the liquid and its variation with temperature concluded that the two forms differed in energy by 1100 cal./mole. These investigators assigned an eclipsed configuration to one of the forms, a possibility which is definitely excluded by the electron diffraction data. Mizushima and his co-workers[6] showed from the Raman spectrum that at least two forms probably existed in the solid state. From gaseous dipole moment determinations over a limited temperature range Smyth and McAlpine[8] showed a configuration other than the *trans* to be present. These authors also suggested that both staggered configurations existed and that the two were of comparable stability.

While the electron diffraction investigations show definitely that these compounds exist in staggered rather than eclipsed configurations, the method does not give reliable information about the relative abundance of the staggered forms. The Raman spectra of the liquid and solid states of 1,1,2,2-tetrachloroethane indicate that more than one configuration exists in these phases. However, the extrapolation of these data to the gaseous state seems questionable, since the intermolecular forces in condensed systems are comparable to the intramolecular forces determining the rotational configuration of an isolated molecule. While the gaseous dipole moment investigations of Smyth and McAlpine definitely show that 1,1,2,2-tetrachloroethane does not exist exclusively as the *trans* form, the restricted temperature range over which they were able to work prohibits any further conclusions.

In order to extend the information concerning the rotational configuration of these compounds, we have determined their gas dipole moments over an extended range of temperature. As an aid in the interpretation of these results the dipole moment of pentachloroethane also has been determined.

Experimental

The determinations of dielectric constants were made using the heterodyne beat method. A stainless steel gas cell with a capacity of 970 micromicrofarads was incorporated in the resonant grid circuit of a Hartley type electron coupled oscillator operating at 200 kc. An electron coupled crystal oscillator, operating at 100 kc., was used as a frequency standard. A high degree of frequency stability in both oscillators was obtained by proper choice of circuit elements and constructional details. In order to facilitate tuning, and to reduce inter-oscillator coupling, both oscillator tubes were followed by two wide band-pass buffer stages. The balance point was determined by applying the output of the two oscillators to the deflection plates of an oscilloscope tube and observing the ap-

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[1] Presented before the General, Physical and Inorganic Division of the American Chemical Society at Portland, Oregon, September 13, 1948. Abstracted from a thesis by J. R. Thomas, presented to the Graduate Division of the University of California in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

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(3) A. Turkevich and J. Y. Beach, THIS JOURNAL, **61**, 3127 (1939).

(4) V. Schomaker and D. P. Stevenson, *J. Chem. Phys.*, **8**, 637 (1940).

(5) O. Hassel and H. Viervoll, *Arch. Math. Naturvidenskab*, 165 (1944).

(6) S. Mizushima, Y. Morino and K. Kozima, *Sc. Pap. I. P. C. R. (Tokyo)*, **29**, 111 (1936).

(7) A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 1410 (1940).

(8) C. P. Smyth and K. B. McAlpine, THIS JOURNAL, **57**, 979 (1935).

pearance of a stationary Lissajous figure on the screen. These considerations reduced the error due to frequency instability, coupling, and balance point determination to a negligible value.

The instrument was calibrated with nitrogen at 25°, the dielectric constant being taken as 1.0005800 (N. T. P.) from the data of Hector and Woernley.[9] A number of check determinations of air freed of carbon dioxide and water gave a value of $1.0005682 \pm 5 \times 10^{-7}$ (N. T. P.), whereas the above authors report $1.0005669 \pm 1 \times 10^{-7}$ (N. T. P.) as the most likely value.

Frequently the thermal decomposition of the material being studied limits the temperature range over which measurements can be made.[8] In order to minimize the effect of a small amount of decomposition a flow method of handling the gases was used rather than the usual static method. This was accomplished by incorporating the gas cell in the flow stream of a boiler-condenser circulatory system in which the pressure was regulated by a barostat. By greatly reducing the fraction of the total sample which was held at an elevated temperature, the extent of decomposition of the compound being studied was reduced to essentially zero. Calibrated platinum resistance thermometers, good to ±0.1°, placed in the gas stream as it entered and as it left the gas cell, were used to determine the gas temperature. The gas cell was contained in a thermostated oil-bath. The gas pressure was determined by reading a closed end mercury manometer with a cathetometer, the manometer being placed between the water condenser and the boiler of the circulatory system. Although this arrangement was capable of giving pressure measurements of ±0.1 mm., the use of the flow system resulted in a certain sacrifice in precision due to the difficulty of maintaining a completely even boiling rate of the liquid sample. This factor is primarily responsible for the experimental uncertainty in the data given in Table I.

The compounds studied in this work were Eastman Kodak Co. products of technical grade. They were purified by repeated washings with concentrated sulfuric acid, steam distillation, and a final distillation in a thirty-plate column. The central portions were taken over a 0.2° range, and the compounds were then stored over anhydrous calcium sulfate until they were used.

TABLE I

MOLAR POLARIZABILITY OF 1,1,2-TRICHLOROETHANE

T, °K.	Pressure range, mm.	Detns. at dif. pressures	P, cc.
339.7	39.6 to 110.6	4	60.5 ± 0.20
354.7	89.2 to 132.6	5	58.8 ± 0.20
376.7	71.0 to 147.1	6	57.6 ± 0.30
394.9	78.0 to 164.5	7	56.1 ± 0.10
427.7	78.0 to 147.3	6	54.9 ± 0.25
450.4	75.7 to 148.5	6	53.55 ± 0.08
472.7	65.5 to 149.9	5	52.5 ± 0.26
516.6	97.3 to 152.0	6	51.1 ± 0.20
MOLAR POLARIZABILITY OF 1,1,2,2-TETRACHLOROETHANE			
362.4	38.0 to 88.4	7	62.5 ± 0.20
377.5	67.9 to 112.5	4	60.8 ± 0.40
387.3	39.0 to 128.4	7	59.5 ± 0.13
401.3	75.6 to 126.5	6	58.35 ± 0.15
426.8	64.7 to 140.1	6	56.7 ± 0.12
443.4	67.4 to 125.7	7	56.2 ± 0.20
459.4	91.5 to 137.8	5	55.5 ± 0.20
480.9	83.2 to 152.7	7	54.4 ± 0.26
500.7	85.9 to 147.8	7	53.5 ± 0.30
MOLAR POLARIZABILITY OF PENTACHLOROETHANE			
399.6	47.9 to 107.0	7	49.1 ± 0.25
412.2	68.8 to 114.2	6	48.7 ± 0.23
439.8	76.4 to 134.5	7	47.6 ± 0.15
473.1	91.9 to 137.5	6	46.8 ± 0.20
493.9	99.1 to 134.0	5	46.7 ± 0.20
516.6	84.4 to 121.9	5	45.9 ± 0.30

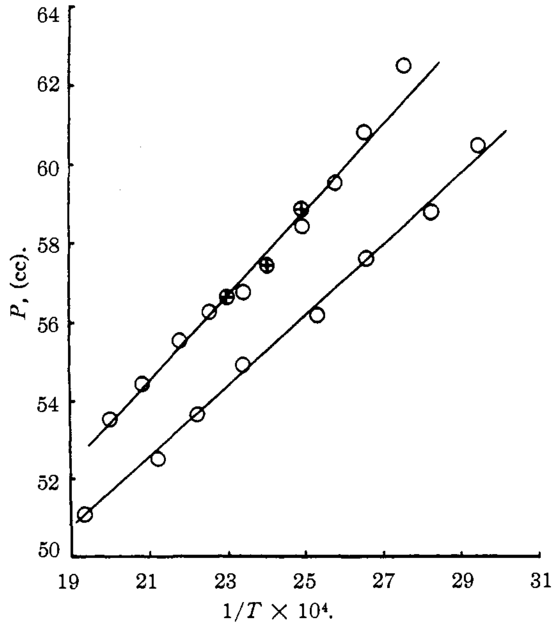

Fig. 1.—The molar polarizabilities of 1,1,2-trichloroethane (lower curve) and 1,1,2,2-tetrachloroethane (upper curve) as a function of the reciprocal of the absolute temperature: ⊕, Smyth and McAlpine; ○, this research.

Results

The results of the measurements of 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and pentachloroethane are given in Table I. A plot of the molar polarizability *versus* the reciprocal of the absolute temperature is shown in Fig. 1 for the first two compounds. In the case of 1,1,2,2-tetrachloroethane the data of Smyth and McAlpine[4] are also shown. It is particularly important to notice from Fig. 1 that these plots give straight lines within experimental error.[10] In the case of tetrachloroethane the lowest temperature point, at 362° K., is probably affected by adsorption of gas on the condenser plates. Using the slope of the plot of molar polarizability

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(9) L. G. Hector and D. L. Woernley, *Phys. Rev.*, **69**, 101 (1946).

(10) In a recent letter to the editor Oriani and Smyth, *J. Chem. Phys.*, September, 1948, report that the dipole moment of 1,1,2-trichloroethane is much more temperature dependent than our data indicate. The dipole moment they report is also considerably higher than that which we find. Personal communication with Professor Smyth reveals that the two sets of polarizability measurements are essentially in agreement at temperatures above 430°K. Their group of points at 385°K. are somewhat higher than our polarizability values in that region. The primary source of the discrepancy is found in the method of estimating the atomic polarizability. The atomic polarizability will be discussed in the last part of this paper. However, regardless of the value of the atomic polarizability used, our data give no minimum in the dipole moment *vs.* temperature curve, as do the data of Oriani and Smyth.

versus the reciprocal of the absolute temperature the dipole moments of 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and pentachloroethane are found to be 1.25 × 10^{-18} e. s. u.,[11] 1.29 × 10^{-18} e. s. u., and 0.92 × 10^{-18} e. s. u., respectively. The uncertainty in the absolute values is probably not more than ±0.01 × 10^{-18} e. s. u. The average deviation of the dipole moments calculated from the individual polarizability measurements for 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and pentachloroethane are ±0.005 × 10^{-18}, ±0.005 × 10^{-18} and ±0.006 × 10^{-18} e. s. u., respectively.

Discussion

In 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane, as in 1,2-dichloroethane, the dipole moment changes with the angle of internal rotation, and consequently depends upon the potential barrier for internal rotation. The potential barrier to internal rotation in 1,2-dichloroethane has been discussed extensively by Gwinn and Pitzer,[12] who have concluded that its dipole moment is determined primarily by the relative energies of the three minima of the potential energy curve for internal rotation. In 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane we expect a similar situation. There will be a three-fold potential barrier with two equivalent minima corresponding to the skew configuration of each compound. The third minimum will correspond to the *trans* configuration in 1,1,2,2-tetrachloroethane and to the *cis* configuration in 1,1,2-trichloroethane.

Dipole moment data will give no information as to the height of the potential barriers, but will enable us to determine the energy difference between the minima. The dipole moment may be approximated by the following equation, obtained in the usual manner[13]

$$\mu^2 = (\mu_1^2 + 2\mu_2^2 \exp.(\Delta E/RT))/(1 + 2 \exp.(-\Delta E/RT)) \qquad (1)$$

where μ_1 is the dipole moment of the *cis* form in 1,1,2-trichloroethane, and of the *trans* form in 1,1,2,2-tetrachloroethane, and μ_2 is the dipole moment of either of the two equivalent skew forms.

The invariance of the dipole moment of these two compounds with respect to temperature shows, either that for each molecule only one configuration exists to any appreciable extent, or that both configurations exist with equal energy.[14]

In order to distinguish between the above two possibilities it is necessary to estimate the magnitude of the bond moments in these compounds. For this purpose the apparent C–Cl bond moments for a series of chlorinated compounds are listed in Table II. Figure 2 shows graphically the change in the apparent C–Cl moments as a function of molecular composition. The points represented by open circles correspond to the experimental values of Table II.

TABLE II

C–Cl BOND MOMENTS[g]

Compound	$\mu_{\text{molecular}}$ × 10^{18} e. s. u.	Method	μ^g C-Cl Bond Moment × 10^{18} e. s. u.
CH_3Cl[a]	1.86	P–$1/T$ (gas)	1.86
CH_2Cl_2[b]	1.60	P–$1/T$ (gas)	1.39
$CHCl_3$[b]	0.95	P–$1/T$ (gas)	0.95
CH_3CH_2Cl[a]	2.03	P–$1/T$ (gas)	2.03
CH_3CHCl_2[c]	2.05	P–$1/T$ (gas)	1.78
CH_3CCl_3[d]	1.77	P–MR_{NaD}(gas)	1.77
CH_2ClCCl_3[e]	1.39	P–$1/T$ (gas)	1.24
$CHCl_2CCl_3$[f]	0.92	P–$1/T$ (gas)	0.92

[a] R. Sanger, *Helv. phys. acta*, **3**, 161 (1930). [b] R. Sanger, *Physik Z.*, **27**, 556 (1926). [c] P. M. Ghosh, P. C. Mahanti and S. C. Mukherjee, *Z. physik. Chem.*, **58**, 711 (1929). [d] R. H. Wiswall, Jr., and C. P. Smyth, *J. Chem. Phys.*, **9**, 356 (1939). [e] J. E. Roberts, University of California, unpublished data. [f] This research. [g] The apparent C-Cl bond moments are calculated assuming C-H bond to be zero, so that the real C-Cl moment is the C-Cl moment given in the table plus a constant additive term for the C-H moment. It is further assumed in this calculation that all bond angles have the normal tetrahedral value.

The general decrease in the individual bond moments shown in Fig. 2 results primarily from the mutual inductive interaction of adjacent polar bonds. An empirical discussion of this effect seems adequate for our purposes.[15] The inductive lowering of the bond moments of two bonds involving the same central carbon atom will be somewhat greater than that of bonds on adjacent carbon atoms, and the induced dipole effects in polarizable parts of the molecule will be less, the more symmetrical the distribution of polar bonds. Consequently, it is to be expected that the values of the apparent bond

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(11) The value of 1.25 × 10^{-18} for 1,1,2-trichloroethane leads to a high value of the atomic polarizability (6.7 cc.). If a lower value of the atomic polarizability is used, a higher and slightly temperature dependent dipole moment is obtained. This alternate interpretation alters the following conclusions only slightly, and is presented at the end of the discussion.

(12) W. D. Gwinn and K. S. Pitzer, *J. Chem. Phys.*, **16**, 303 (1948).

(13) Since the reduced moment of inertia for internal rotation and the vibrational frequencies both vary with the angle of internal rotation, as does the energy, the exact expression would contain all of these. However, Pitzer (*J. Chem. Phys.*, **14**, 239 (1946)) has shown in general that the effect of the changing moment of inertia just cancels the effect of the changing vibrational frequencies. This has been verified in detail by Gwinn and Pitzer (ref. 12) for 1,2-dichloroethane. Therefore the moment of inertia and vibrational frequencies have been omitted in eq. 1. Neglecting the variation of E with the angle of internal rotation amounts to assuming very high barriers between the various isomers. In 1,2-dichloroethane, where more precise calculations have been made, eq. 1 would underestimate the energy by several hundred calories. In 1,1,2-trichloroethane, which would be similar to 1,2-dichloroethane, only the lower limit to the energy is given. Hence eq. 1 will give an overly conservative estimate of this limit. In 1,1,2,2-tetrachloroethane eq. 1 is used only to establish experimental errors.

(14) Similar behavior would be noted if the rotation were completely free; however, it is certain that free internal rotation is impossible in these compounds.

(15) See also H. M. Smallwood and K. F. Herzfeld, THIS JOURNAL, **52**, 1919 (1930); L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

moments in 1,2-dichloroethane[12] and 1,1,2-trichloroethane will lie between those for ethyl chloride and 1,1,1,2-tetrachloroethane; and that the bond moment of 1,1,2-trichloroethane will be less than that of 1,2-dichloroethane. Similarly, the bond moment of 1,1,2,2-tetrachloroethane will be expected to lie between that of 1,1,2-trichloroethane and pentachloroethane.

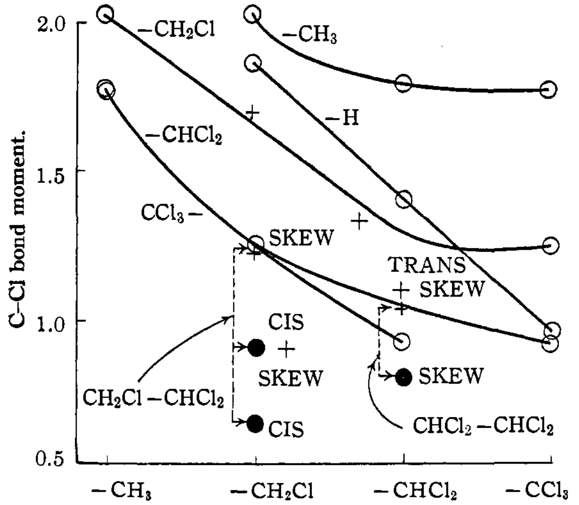

Fig. 2.—The C–Cl bond moments of a number of chlorinated hydrocarbons as a function of molecular composition. When the bond moment is influenced by internal rotation, its value for the most logical interpretation (see text) is represented by a cross; alternate interpretations give values represented by solid circles.

In the event that 1,1,2-trichloroethane consists entirely of the *cis* form, it is seen that the C–Cl bond moment would have to be 0.65 × 10^{-18} e. s. u. to account for the observed molecular moment of 1.25 × 10^{-18} e. s. u. If the energy difference between the *cis* and the skew forms were zero, it is apparent from equation 1 that the C–Cl moment would have to be 0.90 × 10^{-18} e. s. u. to account for the observed molecular moment. However, if the skew form alone were present, the C–Cl moment would have to be 1.25 × 10^{-18} e. s. u. to account for the observed molecular moment. Since this is the only value which is consistent with the above, it may be concluded that the vapor of 1,1,2-trichloroethane consists almost entirely of the skew form. In Fig. 2, the bond moment values of 0.65 × 10^{-18} e. s. u. and 0.90 × 10^{-18} e. s. u. are shown as solid circles, while the value of 1.25 × 10^{-18} e. s. u. is represented by a cross. The bond moment of 1.25 × 10^{-18} e. s. u. has been calculated, assuming that the angle between the projections of the adjacent C–Cl bonds on a plane perpendicular to the C–C axis is 60° in the skew configuration. Actually, for reasons to be discussed later, this angle is probably closer to 70°, so that the bond moment in this compound is somewhat larger than is shown in Fig. 2.

In accordance with equation (1) the observed dipole moment of 1,1,2-trichloroethane would vary 0.012 × 10^{-18} e. s. u. from 340 to 516° K., if the skew form were 4000 cal./mole more stable than the *cis* form. If the energy difference were 3000 cal./mole the observed dipole moment would vary 0.04 × 10^{-18} e. s. u. over this temperature interval. Since the experimental uncertainty in the observed dipole moment over this range of temperature is ±0.005 × 10^{-18} e. s. u., it may be concluded that the *cis* form of 1,1,2-trichloroethane is at least 4000 cal./mole less stable than the skew form.

In 1,1,2,2-tetrachloroethane it is apparent that the *trans* form alone cannot account for the observed moment of 1.29 × 10^{-18} e. s. u., since its moment must be close to zero. However, the skew configuration cannot account for the observed molecular moment, since this would lead to a C–Cl bond moment of 0.80 × 10^{-18} e. s. u. (solid circle in Fig. 2) which is too low for this compound. Consequently, it must be concluded that both forms exist with equal energy. This leads to a value of 1.03 × 10^{-18} e. s. u. as the C–Cl bond moment, which is represented in Fig. 2 by a cross, and which is seen to be a reasonable value. Calculation of the temperature variation of the observed dipole moment over the temperature range 377 to 501°K. leads to the result that the dipole moment would vary 0.012 × 10^{-18} e. s. u. if the skew from were 200 cal./mole more stable than the *trans* form, or would vary 0.017 × 10^{-18} e. s. u. if the *trans* form were 200 cal./mole more stable than the skew form. For an energy separation of 300 cal./mole these values are 0.017 × 10^{-18} e. s. u. and 0.027 × 10^{-18} e. s. u., respectively. Since the experimental uncertainty over this temperature range amounts to ±0.005 × 10^{-18} e. s. u., it may be concluded that the energy difference between the staggered configurations of 1,1,2,2-tetrachloroethane is zero ±200 cal./mole. The difference between this value and the value of 1100 cal./mole obtained by Langseth and Bernstein[7] can be attributed to the fact that these investigators worked with the liquid rather than the gaseous phase. The effect of intermolecular forces in condensed phases influencing the rotational isomeric distribution may be seen from the data of Van Arkel and Snoek[16] and of Mizushima and his co-workers.[6] These investigators found that the dipole moments of these compounds in solution were markedly affected by the particular solvent being used.

In addition to these results concerning 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane, it is known from the work of Gwinn and Pitzer[12] that the *trans* configuration of 1,2-dichloroethane is 1400 cal./mole more stable than the skew configuration. The results pertaining to these three compounds are summarized in Fig. 3.

(16) A. E. van Arkel and J. L. Snoek, *Z. physik. Chem.*, **B18**, 159 (1932).

Usually the forces which are thought to give rise to the potential barriers restricting internal rotation are those due to electrostatic interactions, steric repulsive forces, and London's attractive forces.

If there were no steric hindrance and the bond angles and charge distributions in the bonds were the same in these compounds, we would expect the energy differences between the staggered configurations of 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane to be the same (*i. e.*, about 1400 calories). Consequently, the variance in the energy values found experimentally must be attributed to the variance in these molecular parameters and to steric hindrance. The bond moments are known to decrease in the order 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane as discussed above. The energy differences between the staggered configurations of these compounds would decrease in the same order if the dipole interaction terms were of critical importance. Since this order of configurational stability is not experimentally observed, it is concluded that bond dipole interactions are not of paramount importance in determining the configurational stability of these compounds.

Probably the most important interactions which determine the relative stability of the two forms of 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane are those due to steric repulsions. It has been shown in the work on 1,2-dichloroethane[12] that the potential energy rises steeply when the angle between the projections of the two C–Cl bonds in a plane perpendicular to the C–C axis becomes less than 50 to 60°. The electron diffraction study of 1,1,2-trichloroethane by Turkevich and Beach[3] showed that the angle between the adjacent C–Cl bonds was probably 70° instead of 60°. Both of these results indicate that steric repulsions become important when this angle is near 60 or 70°.

In the skew form of 1,1,2-trichloroethane the two substituted methyl groups can rotate about their axes and relieve the steric repulsions. However, there would be large steric repulsions in the *cis* form, which would tend to make this form unstable with respect to the skew form. This is the same direction as the electrostatic term, and together they may well account for the observed energy of something greater than 4000 calories.

In 1,1,2,2-tetrachloroethane the chlorine atoms are so arranged that there are large steric repulsions in both forms. However, in the skew form the strains would be relieved if the Cl–C–Cl angle were greater than a tetrahedral angle.[17] There may be a permanent increase in the angle, because of the repulsion between the two chlorines attached to the same carbon atom, as is observed in methylene chloride.[18] There would also be additional distortion of the Cl–C–Cl angle in the skew configuration, leading to a large reduction in the steric repulsions, at the expense of introducing some strain into the Cl–C–Cl bond. The analogous effect of a decreased Cl–C–Cl angle in the *trans* configuration would take place to a far smaller extent because of the repulsion of the two chlorine atoms in the $CHCl_2$ group. These effects would tend to stabilize the skew form with respect to the *trans* form. This stabilization may be sufficient to counteract the electrostatic energy which favors the *trans* form, so that both forms are of equal energy, as observed.

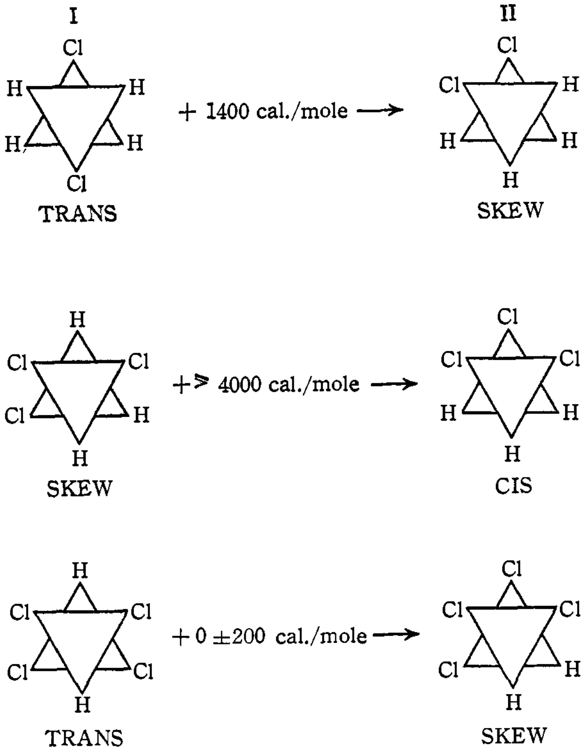

Fig. 3.—The equilibrium rotational configurations of 1,2-dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane.

In 1,1,2-trichloroethane an alternate interpretation of the data results by assuming an atomic polarizability. In Table III the data are calculated for various values of the atomic polarizability, along with the difference in energy. Since the difference in energy between the two forms should be constant, the dipole moments plotted against $1/T$ should be nearly a straight line. For all values of the atomic polarizability other than 6.7 cc. the experimental dipole moment curves have too much curvature. This curvature is sufficient to eliminate from consideration the possibility of Pa = 0.0, but it is not sufficient to eliminate Pa = 3.0 or 4.5 cc., where the deviations are only about the same order of magnitude as the experimental error. It would also be unreasonable to assume that Pa = 0, since in all

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[17] This was originally proposed by Mizushima and co-workers in reference 6.

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

similar compounds where data are available, the atomic polarizability is at least several cubic centimeters.

TABLE III

DIPOLE MOMENT OF 1,1,2-TRICHLOROETHANE CALCULATED USING:

T, °K.	*Pa* = 0	*Pa* = 3.0	*Pa* = 4.5	*Pa* = 6.7
339.7	1.39	1.33	1.30	1.25
354.7	1.39	1.32	1.29	1.24
376.7	1.40	1.33	1.30	1.24
394.9	1.40	1.33	1.29	1.24
427.7	1.43	1.35	1.31	1.25
450.4	1.43	1.35	1.31	1.25
472.7	1.44	1.36	1.31	1.25
516.6	1.46	1.38	1.33	1.25
ΔE, cal./mole	(2100)	2400	3000	$\geqslant$4000
$\mu_0 \times 10^{18}$ e. s. u.	(1.37)	1.30	1.28	1.25

It is impossible to calculate the atomic polarizability, because the shape of the potential barrier to internal rotation is unknown, and internal rotation contributes heavily to the atomic polarizability.[19]

Fortunately this alternate interpretation of the data alters our conclusion only slightly. The skew form of 1,1,2-trichloroethane is the low energy form, as before. The energy difference between the two forms is at least 2300 cal./mole, instead of 4000 cal./mole, as before. This affects no other conclusions concerning this molecule.

Since the atomic polarizability of 1,1,2,2-tetrachloroethane is only 2.7 cc., there is no alternate interpretation of the data.

Acknowledgment.—The authors wish to express their appreciation to Professor Richard E. Powell for reading this manuscript and for his helpful suggestions.

Summary

The dipole moments of gaseous 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane and of pentachloroethane have been determined from the slope of the polarizability *vs.* $1/T$ curves to be 1.25×10^{-16}, 1.29×10^{-18} and 0.92×10^{-18} e. s. u., respectively. Within experimental error the dipole moments are independent of temperature. This leads to a high atomic polarizability for 1,1,2-trichloroethane (6.7 cc.). If smaller atomic polarizabilities are assumed, the dipole moment becomes somewhat larger and slightly temperature dependent. From these data and a survey of the C–Cl bond moments for a number of chlorinated compounds it is concluded that the *cis* configuration of 1,1,2-trichloroethane is at least 4000 cal./mole (or at least 2300 cal./mole if a smaller atomic polarizability is assumed) less stable than the skew configuration, while the energy difference between the *trans* and skew configurations of 1,1,2,2-tetrachloroethane is concluded to be 0 ± 200 cal./mole. The dipole moments of these compounds give no information as to the heights of the potential barrier to internal rotation. These results are compared with existing data on 1,2-dichloroethane. It is proposed that in these compounds the steric interactions between chlorine atoms are important factors determining the relative stability of the equilibrium rotational configurations.

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[19] An over-simplified calculation of the atomic polarization, using only bending force constants, no cross terms, and a force constant for internal rotation of 0.7×10^{-12} ergs/rad.^{2} molecule (a 2500 cal./mole threefold cosine barrier), gives 3 cc. for the atomic polarizability. It is quite conceivable that the minimum in 1,1,2-trichloroethane may be flatter, and internal rotation may contribute much more to atomic polarizability.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

The Theory and Kinetics of Specific Oxidation. III. The Cerate–2,3-Butanediol Reaction in Nitric Acid Solution

BY FREDERICK R. DUKE[1] AND ARLINGTON A. FORIST

Previous work involving the trivalent manganese–oxalate reaction[2] and the periodate–glycol reaction[3] has supported the theory that specific oxidations of glycols and related compounds proceed through the disproportionation of coördination complexes. To further test this theory, a study of the cerate oxidation of 2,3-butanediol in nitric acid solution was undertaken.[4] The butanediol was used instead of ordinary glycol because tetravalent cerium attacks the product (formaldehyde) of ethylene glycol oxidation at a rate comparable to that of the main reaction.

Theory

Since tetravalent cerium is known to have a coördination number of six, the reaction between cerate and 2,3-butanediol presents the possibility of the formation of mono-, di- and tri-glycolated coördination intermediates, as indicated

$$\mathrm{Ce(X)_6 + G \rightleftarrows CeG(X)_4 + 2X} \tag{1}$$

$$\mathrm{CeG(X)_4 + G \rightleftarrows CeG_2(X)_2 + 2X} \tag{2}$$

$$\mathrm{CeG_2(X)_2 + G \rightleftarrows CeG_3 + 2X} \tag{3}$$

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[2] (a) Duke, THIS JOURNAL, **69**, 2885 (1947); (b) Taube, *ibid.*, **69**, 1418 (1947); **70**, 1216 (1948).

[3] Duke, *ibid.*, **69**, 3054 (1947).

[4] See Smith and Duke, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 120 (1943), for a discussion of cerium oxidations of this type.