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## Internal Rotation II

## The Energy Difference between the Rotational Isomers of 1,2-Dichloroethane

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From the variation of the intensities of infra-red bands with temperature the value of  $\Delta H^0$  for the reaction  $C_{2h}$  dichloroethane  $\rightarrow C_2$  dichloroethane is found to be  $1250 \pm 50$  cal. per mole. The probable energy difference between the isomers is  $1100 \pm 50$  cal. per mole. A tentative assignment of all the fundamentals has been made.

Peak intensities and integrated intensities yield the same results within the limits of the experimental error. The ratio of the number of  $C_2$  molecules to the number of  $C_{2h}$  molecules at room temperature is 0.29.

IT is well known<sup>1</sup> that 1,2-dichloroethane is an equilibrium mixture of two rotational isomers. One isomer has the structure  $C_{2h}$  (a pure *trans*-form)<sup>2</sup> and the other is very likely  $C_2$  or "gauche" in which the azimuthal angle between the C-Cl bonds is  $60^\circ$ .<sup>3</sup> Since at low temperatures the *trans*-form only is present,<sup>2</sup> the  $C_2$  form is the less stable isomer and the potential energy as a function of azimuthal angle is as shown in Fig. 1. The potential barrier corresponds to the ordinate at  $\phi = \pm 60^\circ$  and the ordinate at  $\phi = \pm 120^\circ$  is the energy difference between the isomers, ( $\Delta E_0^0$ ), neglecting the small difference in zero-point vibrational energy between the two forms.

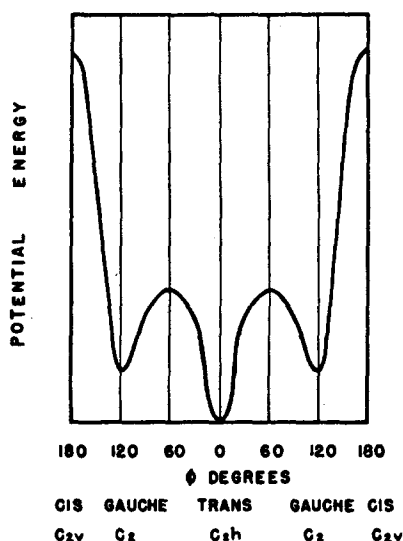


FIG. 1. Potential energy of 1,2-dichloroethane as a function of azimuthal angle.

<sup>1</sup> K. W. F. Kohlrausch, *Ramanspektren* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1945).

<sup>2</sup> S. Mizushima and Y. Morino, *Proc. Ind. Acad. Sci.* **8A**, 315 (1938).

<sup>3</sup> G. Glockler, *Rev. Mod. Phys.* **15**, 111 (1943). The product rule for rotational isomers [See *J. Chem. Phys.* **17**, 256 (1949)] excludes  $C_{2v}$  as the configuration of the other rotational isomer.

A direct method for obtaining  $\Delta E_0^0$  is to study the temperature dependence of the ratio of the intensities of Raman lines<sup>4</sup> or infra-red bands belonging to the two isomers. This method is rigorously true only when applied to the gaseous state, and the previous results<sup>4</sup> obtained in the liquid state are not to be taken as gas values. As Gerding<sup>5</sup> has pointed out, the temperature variation of the intensity ratio of two Raman lines in the liquid may be altogether different from that in the gas, and indeed may be taken as a measure of the molecular interactions in the liquid state. A spectrographic method in the gas phase however can be applied successfully so long as at least two lines or bands corresponding to the two isomers in equilibrium do not overlap.

It was the purpose of this investigation to find the temperature dependence of the ratio of the intensities of two infra-red bands of the isomers of 1,2-dichloroethane in the gas phase; and evaluate  $\Delta H^0$ , for the reaction  $C_{2h}$  dichloroethane  $\rightarrow C_2$  dichloroethane and also  $\Delta E_0^0$ , the difference in energy between the  $C_{2h}$  and  $C_2$  forms.

If  $I_0$  is the intensity of the incident radiation and  $I$  that of the transmitted radiation, the integrated intensity  $A$  over the band width is given by<sup>6</sup>

$$A = \int \ln \frac{I_0}{I} d\nu = \frac{8\pi^3 N \nu |M|^2}{3hc}$$

where  $N$  is the number of molecules per cc,  $\nu$  is the frequency of the band,  $M$  is the dipole moment term, and  $h$  and  $c$  have their usual meaning.

<sup>4</sup> A. Langseth and H. J. Bernstein, *J. Chem. Phys.* **8**, 410 (1940).

<sup>5</sup> H. Gerding and P. G. Meerman, *Rec. Trav. Chim.* **61**, 523 (1942).

<sup>6</sup> E. B. Wilson, Jr., *J. Chem. Phys.* **14**, 578 (1946). As pointed out in this paper  $\int \ln(I_0/I) d\nu$  is the integrated intensity at infinite resolution. In this work slit widths of the order of  $5 \text{ cm}^{-1}$  are used so there is a small correction for finite slit widths to be applied to the experimental  $A$ 's. However, since the ratio of two band intensities is always used, these corrections tend to cancel one another and measured intensity ratio is not appreciably different from the absolute ratio.

For a particular band  $A$  is proportional to  $N\nu$ , and for a band belonging to the  $C_2$  isomer  $AC_2 = K_{C_2} N_{C_2} \nu_{C_2}$ , and for one belonging to the  $C_{2h}$  isomer  $AC_{2h} = K_{C_{2h}} N_{C_{2h}} \nu_{C_{2h}}$ . The ratio of the intensities of the two bands is

$$\frac{AC_2}{AC_{2h}} = \text{const.} \frac{N_{C_2}}{N_{C_{2h}}} \quad (1)$$

when the same two bands are always compared.

Since the *trans*-form is more stable the equilibrium constant is

$$K = \frac{N_{C_2}}{N_{C_{2h}}} = \text{const.} \exp(-\Delta H^0/RT) \quad (2)$$

where  $\Delta H^0$  is positive and  $R$  is the gas constant, and both are measured in cal./mole.

Substituting from Eq. (1) in (2)

$$\frac{AC_2}{AC_{2h}} = \text{const.} \exp(-\Delta H^0/RT). \quad (3)$$

When the L.H.S. is known for several temperatures a least square method for  $\log AC_2/AC_{2h}$  and  $1/RT$  gives the best value of  $\Delta H^0$ .

The methods of statistical thermodynamics<sup>7</sup> show moreover that for an isomeric equilibrium of the type *trans*- $\rightleftharpoons$ *cis*- that

$$K = \frac{N_{cis-}}{N_{trans-}} = \frac{f_{cis-}}{f_{trans-}} \cdot \exp(-\Delta E_0^0/RT)$$

where  $f_{cis-}$ ,  $f_{trans-}$  are the partition functions of the *cis*- and *trans*-molecules respectively.

In the case of 1,2-dichloroethane where the isomeric forms are  $C_{2h}$  and  $C_2$  with twice as many potential minima for the  $C_2$  as for the  $C_{2h}$  the equilibrium constant is given by

$$K = \frac{N_{C_2}}{N_{C_{2h}}} = \frac{2f_{C_2}}{f_{C_{2h}}} \cdot \exp(-\Delta E_0^0/RT). \quad (4)$$

$\Delta E_0^0$  is the energy difference at 0°K between the two isomers. Assuming the rigid rotator and harmonic oscillator approximations<sup>8</sup>

$$\frac{f_{C_2}}{f_{C_{2h}}} = \left[ \frac{(I_A I_B I_C)_{C_2}}{(I_A I_B I_C)_{C_{2h}}} \right]^{\frac{1}{2}} \frac{\Pi_{C_{2h}}}{\Pi_{C_2}}$$

where  $(I_A I_B I_C)_{C_2}$  is the product of the principal moments of inertia of the  $C_2$  molecule and

$(I_A I_B I_C)_{C_{2h}}$  that for the  $C_{2h}$  molecule; and

$$\Pi_{C_{2h}} = (1 - \exp(-h\nu_1/kT)) \times (1 - \exp(-h\nu_2/kT)) \cdots (1 - \exp(-h\nu_{18}/kT))$$

where  $\nu_1 \nu_2 \cdots \nu_{18}$  are the frequencies of the fundamental modes of vibration of the  $C_{2h}$  molecule; and

$$\Pi_{C_2} = (1 - \exp(-h\omega_1/kT)) \times (1 - \exp(-h\omega_2/kT)) \cdots (1 - \exp(-h\omega_{18}/kT))$$

where  $\omega_1 \omega_2 \cdots \omega_{18}$  are the frequencies of the fundamentals of the  $C_2$  molecule.

Substituting for  $f_{C_2}/f_{C_{2h}}$  in Eq. (4)

$$\frac{N_{C_2}}{N_{C_{2h}}} = 2 \left[ \frac{(I_A I_B I_C)_{C_2}}{(I_A I_B I_C)_{C_{2h}}} \right]^{\frac{1}{2}} \frac{\Pi_{C_{2h}}}{\Pi_{C_2}} \cdot \exp(-\Delta E_0^0/RT). \quad (5)$$

Since we are interested only in the temperature dependent terms, from (1) and (5)

$$\frac{AC_2}{AC_{2h}} = \text{const.} \frac{\Pi_{C_{2h}}}{\Pi_{C_2}} \cdot \exp(-\Delta E_0^0/RT). \quad (6)$$

Again a least squares solution for

$$\log \left( \frac{AC_2}{AC_{2h}} \cdot \frac{\Pi_{C_2}}{\Pi_{C_{2h}}} \right)$$

and  $1/RT$  gives the best value of  $\Delta E_0^0$ .

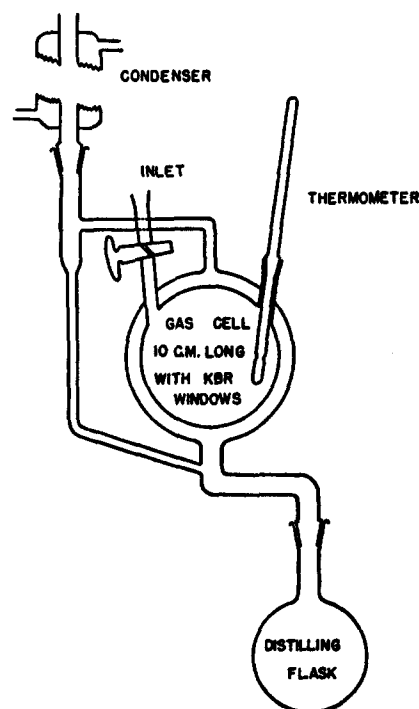


FIG. 2.

<sup>7</sup> Fowler and Guggenheim, *Statistical Thermodynamics* (The MacMillan Company, New York, 1939), p. 157.

<sup>8</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, New York, 1945).

## EXPERIMENTAL AND RESULTS

The 1,2-dichloroethane was the Eastman Kodak product distilled through a 60 cm Stedman column: b.p. =  $82.9 \pm 0.1^\circ\text{C}$  at normal pressure. The infra-red spectra were obtained in the laboratory of Dr. R. N. Jones on a Perkin Elmer spectrometer with a Brown recorder, by Dr. D. A. Ramsay and Mr. D. Keir. A 10-cm long absorption cell with KBr windows was used. Vapor from a constant boiling liquid condensing on the walls of the cell served to heat the contents. In this way the temperature was kept quite steady ( $\pm 1^\circ$ ) and was read from a thermometer (which penetrated the cell). See Fig. 2.

A preliminary run showed that two bands at  $1235\text{ cm}^{-1}$  and  $1291\text{ cm}^{-1}$  whose intensity ratio  $A_{1235}/A_{1291}$  decreased with temperature, would be suitable because of practically no overlapping.

Figure 3 shows a  $\log I_0/I/\text{cm}^{-1}$  plot for the two bands at room temperature and  $424^\circ\text{K}$ .

In Table I the complete I. R. spectrum of 1,2-dichloroethane at room temperature (10-cm cell at 80 mm Hg) is given. The assignment is given in the last column where  $\nu$ 's are for the  $C_{2h}$  form and the  $\omega$ 's for the  $C_2$  form. The intensity is designated in column 2 in the ordinary way and in column 3 the separations between peaks are given, where measured. Column 4 indicates the contour of the band.

In Table II the integrated intensities  $A$  of the bands in arbitrary units at 5 different temperatures are given. At each of the first 3 temperatures 3 runs were taken and at the last 2 only 2 runs were obtained. The last column gives the material used in the distilling flask to obtain the various temperatures.

## DISCUSSION

From the data in Table II and Eq. (3) a least squares solution gives  $\Delta H^\circ = 1250 \pm 50$  cal. per mole. In order to evaluate  $\Delta E_0^\circ$  the frequencies of the fundamentals have to be known. In the temperature range investigated, frequencies greater than  $1000\text{ cm}^{-1}$  contribute very little to the vibrational parti-

tion function and can be neglected in evaluating the  $\Pi$ 's.

The assignment made in Table I is comparatively straightforward. The modes of vibration in the  $B_u$  class of the  $C_{2h}$  molecules give rise to bands which are doublets<sup>9</sup> and those in the  $A_u$  class give singlets.<sup>9</sup> Since the variation in electric moment is not parallel to any of the principal axes of inertia of a  $C_2$  molecule, the bands are hybrid. However, since the gauche form is only  $60^\circ$  out of plane from the  $C_{2v}$  form, the modes antisymmetric with respect to the two-fold axis would be expected to give triplets;<sup>10</sup> the modes symmetric with respect to the two-fold axis would be expected to give doublets. The latter seem to appear very weakly in the infra-red.

In Table III the Raman and infra-red data are collected and a tentative assignment of all fundamentals is given. In the table  $\nu_1$  to  $\nu_6$  inclusive are  $A_g$  vibrations,  $\nu_7$  to  $\nu_{11}$  inclusive are  $B_u$  vibrations,  $\nu_{12}$  to  $\nu_{15}$  inclusive are  $A_u$  vibrations,  $\nu_{16}$  to  $\nu_{18}$  inclusive are  $B_g$  vibrations, and  $\omega_1$  to  $\omega_6$  and  $\omega_{12}$  to  $\omega_{15}$  are  $A$  vibrations, and  $\omega_7$  to  $\omega_{11}$  and  $\omega_{16}$  to  $\omega_{18}$  are  $B$  vibrations.

On the whole this assignment seems probable and is consistent with the Raman and infra-red data in all points except one (see reference c to Table III). Whether the line at  $124\text{ cm}^{-1}$  is polarized or depolarized however only affects the assignment and not the determination of  $\Delta E_0^\circ$  for which only the magnitude of the frequency is significant.\*

TABLE I. Infra-red spectrum of 1,2-dichloroethane (10-cm path, 80 mm of Hg).

Absorption band in $\text{cm}^{-1}$	Intensity	Separation in $\text{cm}^{-1}$	Contour	Assignment
543	m.			$\nu_1 + \nu_7$
695	m.	13	triplet	$\omega_7$
*728	s.	9	doublet	$\nu_8$
772	w.		singlet	$\nu_{13}$
832	v.w.			$\nu_2 + \nu_{12}$
890	m.	15	triplet	$\omega_8$
946	m.	13	doublet	$\nu_9$
993	w.			$\nu_2 + \nu_7$
1027	w.			$\omega_4$
1124	w.			$\omega_9$
1235	s.	10	doublet	$\nu_{10}$
1291	s.	12	triplet	$\omega_{10}$
1319	w.			$\nu_{14}$
1460	m.	11	doublet	$\omega_{14}$
1531	w.			$\nu_1 + \nu_{10}$
2881	m.			$\omega_6$
3029	s.			$\nu_{11}$

\* This band was resolved at a pressure of 5 mm of Hg.

<sup>9</sup> T. Y. Wu, J. Chem. Phys. 5, 392 (1937).

<sup>10</sup> T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, Michigan, 1946), p. 122.

\* Recently W. D. Gwinn and K. S. Pitzer, J. Chem. Phys. 16, 303 (1948), have estimated the vibrational heat capacity using Wu's (see reference 10) choice of fundamentals. These authors also consider the line at  $124\text{ cm}^{-1}$  to be polarized. They use Raman data of Mizushima *et al.*, Bull. Chem. Soc. (Japan) 17, 94 (1942), for  $\nu_7 = 223\text{ cm}^{-1}$ .

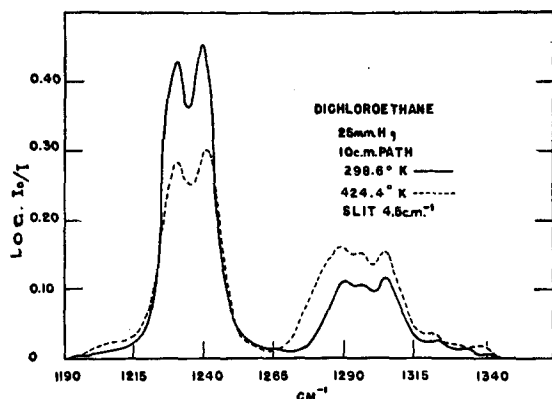


FIG. 3.

TABLE II.

T°K	A cm <sup>-1</sup>		Av. value of $\frac{A_{1291}}{A_{1295}}$	Distilling material
	A <sub>1295</sub>	A <sub>1291</sub>		
298.6	27.95	10.83	0.387	Carbon tetra- chloride
	29.12	10.74	0.369	
	27.92	10.35	0.371	
347.7	27.30	13.31	0.488	Carbon tetra- chloride
	27.24	13.38	0.491	
	27.05	13.00	0.481	
368.3	27.30	15.32	0.561	H <sub>2</sub> O
	28.69	16.03	0.559	
	27.89	15.42	0.553	
387.4	26.46	15.98	0.604	C <sub>2</sub> Cl <sub>4</sub>
	25.17	14.33	0.569	
	23.25	16.90	0.727	
424.4	21.61	15.29	0.708	C <sub>2</sub> HCl <sub>6</sub>

With the above fundamentals the II's of Eq. (6) may be calculated and  $\Delta E_0^0$  evaluated, whence  $\Delta E_0^0 = 1100 \pm 50$  cal. per mole. Of course the value of  $\Delta E_0^0$  is dependent on the frequencies chosen for the unobserved fundamentals  $\nu_1$ ,  $\nu_{12}$  and  $\nu_{13}$  of Table III. To make  $\Delta E_0^0$  very different from 1000 cal. the values of these frequencies would indeed have to be extreme. In no case, however, can the value of  $\Delta E_0^0$  exceed its upper limit of  $\Delta H^0 = 1250$  cal.

Using the electron diffraction data<sup>11</sup> for the dimensions of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> and assuming tetrahedral angles the product of the principal moments of inertia for the C<sub>2h</sub> and C<sub>2</sub> forms may be evaluated. It is found<sup>12</sup> that

$$\left[ \frac{(I_A I_B I_C)_{C_2}}{(I_A I_B I_C)_{C_{2h}}} \right]^{\frac{1}{2}} = 1.355.$$

Using this value of 1.355 for the moment of inertia factor and the II's computed for the above choice of fundamentals the ratios  $N_{C_2}/N_{C_{2h}}$  at 298.6°K,

<sup>11</sup> L. R. Maxwell, J. Opt. Soc. Am. **30**, 374 (1940).

<sup>12</sup> See reference 8, p. 509.

TABLE III. Vibrational assignment of C<sub>2</sub> and C<sub>2h</sub> 1,2-dichloroethane.

$\nu$	Trans C <sub>2h</sub>		$\omega$	C <sub>2</sub>	
	Raman*	I. R.**		Raman*	I. R.**
1	301		1	264	
2	753		2	653	
2	991		3	943	
4	1054		4	1032	1027
5	1302		5	1205	
6	2956		6	2873	2881
7		243 <sup>a</sup>	7	676	696
8		725	8	881	890
9		950	9	1143	1124
10		1235	10		1291
11		3029	11		3000
12		80 <sup>b</sup>	12	124 <sup>c</sup>	
13		772	13	454	
14		1319	14		1460
15		3000	15	3000	3000
16	1263		16	410	
17	1442		17	1428	
18	3002		18	3000	

\* Raman data from Kohlrausch (liquid) (reference 1).

\*\* Infra-red data from this work (gas).

<sup>a</sup> Obtained from the observed band at 544 by difference.  $544 = 243 + 301$ .

<sup>b</sup> Obtained from the observed band at 833,  $833 = 80 + 753$ .

<sup>c</sup> This line is given as depolarized in the literature whereas in its present assignment it should be polarized. Measurements of depolarization in the region close to the exciting line are very difficult, however, and it is possible that the data have been misinterpreted.

347.7°K, 368.3°K, 387.4°K, and 424.4°K are found to be 0.290, 0.374, 0.417, 0.451, 0.574 respectively.

If peak intensities are used throughout instead of areas it is found that  $\Delta H^0 = 1325 \pm 50$  cal. per mole and  $\Delta E_0^0 = 1140 \pm 50$  cal. per mole. There seems to be no significant difference in the results obtained whether peak intensities or integrated intensities are used.

#### ACKNOWLEDGMENT

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