determined from the data for the three pentafluoroethyl derivatives of benzene reported in this paper and the dipole moment of 4-pentafluoroethyl trifluoromethylbenzene reported by Brown and De Vries.[4] The group moment 2.65 D is 0.11 unit larger than the moment for the trifluoromethyl group on benzene.

A comparison of the dipole moments of the ether derivatives of trifluoromethylbenzene discloses some anomalous results. The moment of the trifluoromethyl group is 2.54, that of the methoxy group in anisole is 1.23, yet the moment of 4-methoxy trifluoromethylbenzene was found to be 3.28 and that of 5-methoxy-1,3-bis-(trifluoromethyl)-benzene is 3.23. A vector addition of the moments involved gives 1.31 D.

From the value 2.10 found for 1,3-bis-(trifluoromethyl)-benzene and 3.74 found for 2-methoxy-1,3-bis-(trifluoromethyl)-benzene, the moment of the methoxy group, when ortho to a trifluoromethyl group, seems to be 1.64. This makes the value 1.72 found for 2-methoxy-1,4-bis-(trifluoromethyl)-benzene seem reasonable. However, for 4-methoxy 1,3-bis-(trifluoromethyl)-benzene the observed value 4.01 is considerably larger than the value 1.91 calculated by vector addition from the value 1.64 for the methoxy group and 2.10 for the moment of 1,3-bis-(trifluoromethyl)-benzene.

Both the Hedestrand and Guggenheim methods of calculating dipole moments agree well with each other and appear to be applicable for moments above 1.0 D. Both methods are subject to relatively high percentage errors when the dipole moment is small.

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WEST LAFAYETTE, INDIANA RECEIVED AUGUST 11, 1950

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Internal Rotation. VI. A Dilute Solution Method for the Spectroscopic Determination of the Energy Difference between Rotational Isomers[1]

BY J. POWLING[2] AND H. J. BERNSTEIN

A liquid phase technique for the determination of rotational isomerization energies using infrared analytical methods is presented in which the effect of solvent is adequately eliminated. The isomerization energies of some substituted ethanes have been determined and the values agree with the gas values within the experimental error.

Rotational isomerism in organic compounds was first investigated spectroscopically (Raman effect) by Kohlrausch.[3a,b] The nature of hindered rotation in symmetrical dihalogenoethanes was then extensively investigated by Mizushima[4a,4b,5] who demonstrated the existence of a solvent effect[4a] and showed that only the *trans* form existed in the solid state but the liquid and gaseous phases contained both a *trans* and a *gauche* form in thermal equilibrium.[6]

A quantitative estimation of the isomerization energy, ΔH, in liquid 1,1,2,2-tetrachloroethane was made by Langseth and Bernstein[7] assuming that the relation

$$K = \frac{\text{concn. of the less stable isomer}}{\text{concn. of the more stable isomer}} = \text{const. } e^{-\Delta H/RT} \quad (1)$$

was valid.

The ΔH value obtained in the liquid phase was 1100 cal./mole whereas a more recent investigation[8] of this molecule in the gas phase by the variation of electric moment with temperature yielded a value of $\Delta H_{\text{gas}} = 0 \pm 200$ cal./mole. The apparent anomaly is entirely due to the environment in the condensed phase[4a] and has been observed also in the cases of 1,2-dichloroethane[3a,9,10,11] and 1,2-dibromoethane.[12] The liquid phase value for 1,2-dichloroethane was found to be ~0 cal./mole (Raman effect[11]), compared with the gas value of ~1250 cal./mole (infrared[13,14]). Recent values for liquid 1,2-dibromoethane are in good agreement but differ greatly from the gas values. Rank, *et al.*,[10] found $\Delta H_{\text{liquid}} = 740$ cal./mole using the Raman effect and Mizushima and co-workers[12] found $\Delta H_{\text{liquid}} = 760$ cal./mole (Raman effect). The latter workers using an infrared technique found $\Delta H_{\text{liquid}} = 680$ cal./mole. These liquid values are to be compared with the infrared gas phase results of Bernstein[15] and Mizushima, *et al.*,[13] which give isomerization energies of 1770 cal./mole and 1450 cal./mole, respectively.

The true energy difference can be obtained directly only from gas phase measurements and indeed the values of ΔE_0^0 may be evaluated when the dimensions and vibrational assignments of the

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[1] Presented at the Symposium on Molecular Structure held at Columbus, Ohio, June, 1950.

[2] National Research Laboratories Post-doctorate Fellow, 1949–1951.

[3] (a) K. W. F. Kohlrausch, *Z. physik. Chem.*, **B18**, 61 (1932); (b) K. W. F. Kohlrausch and F. Koppl, *ibid.*, **B26**, 209 (1934).

[4] (a) Mizushima, Morino and Higasi, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **25**, 153 (1934); (b) Mizushima, Morino and Noziri, *ibid.*, **29**, 63, 188 (1936).

[5] Mizushima, Morino and Kubo, *ibid.*, **38**, 459 (1937).

[6] S. Mizushima and Y. Morino, *Bull. Chem. Soc. Japan*, **17**, 94 (1942).

[7] A. Langseth and H. J. Bernstein, *J. Chem. Phys.*, **8**, 410 (1941).

[8] W. D. Gwinn and J. R. Thomas, THIS JOURNAL, **71**, 2785 (1949).

[9] H. Gerding and P. C. Meerman, *Rec. trav. chim.*, **61**, 523 (1942).

[10] D. H. Rank, R. E. Kagarice and D. W. E. Axford, *J. Chem. Phys.*, **17**, 1354 (1949).

[11] I. Watanabe, S. Mizushima and Y. Masiko, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **40**, 425 (1943).

[12] Mizushima, Morino, Kuratani and Katayama, *J. Chem. Phys.*, **18**, 754 (1950).

[13] T. Simanouti, H. Turuter and S. Mizushima, *Sci. Pap. Inst. Phys. Chem. Res.* (*Tokyo*), **42**, 165 (1945).

[14] H. J. Bernstein, *J. Chem. Phys.*, **17**, 256 (1949).

[15] H. J. Bernstein, *J. Chem. Phys.*, **18**, 897 (1950).

isomeric forms are known[11,14] since

$$K = \frac{\text{concn. of less stable isomer}}{\text{concn. of more stable isomer}}$$

$$= \text{const.}\ \frac{\text{optical density of a band belonging to less stable isomer}}{\text{optical density of a band belonging to more stable isomer}}$$

$$= n\sqrt{\frac{(\mathrm{I_A I_B I_C})_l}{(I_A I_B I_C)_m}}\ \frac{\Pi\left(1 - e\,\frac{-h\nu}{kT}\right)_m}{\Pi\left(1 - e\,\frac{-h\nu}{kT}\right)_l}\ e\,\frac{-\Delta E_0^0}{kT} \qquad (2)$$

where

$$n = \frac{\text{number of minima corresponding to the less stable isomer}}{\text{number of minima corresponding to the more stable isomer}}$$

in the potential energy of the molecule for one complete revolution, and the other symbols have their usual significance.

Very often it is not possible to work in the gas phase because of thermal decomposition or because the gas spectrum is too overlapped owing to the rotational wings.

A liquid phase method for the evaluation of the true isomerization energy would be invaluable in many such cases. This energy evaluated from equation (1) would have to be corrected for the interactions of the environment before the gas value could be obtained. Such a correction is discussed in the consideration of the solvent effect.

Solvent Effect.—The intensity ratio of two Raman lines belonging to the *gauche* and *trans* forms of 1,2-dichloroethane were observed to be different in solutions of different dielectric constant.[4a] Mizushima, *et al.*, recognized that the solvent effect was complicated and probably would be correctly interpreted by a relation between the intensity ratio and μ/V where μ is the dipole moment and V the molecular volume. Mizushima and co-workers[11] did succed in accounting for the difference between ΔH_{gas} and ΔH_{liquid} for 1,2-dichloroethane on the basis of an energy term arising from Onsager's[16] considerations of the reaction field. Onsager established that if a rigid dipole of moment μ is introduced into a cavity of radius a in an unpolarized medium of dielectric constant ϵ, dipoles are induced in the medium which, in turn, subject the original dipole to a field, the strength of which is given by

$$F = \frac{2(\epsilon - 1)}{2\epsilon + 1} \times \frac{\mu}{a^3} \qquad (3)$$

The interaction energy, δE, involved was taken by Mizushima, *et al.*,[11] to be

$$\delta E = \int_0^{\mu} - F\,\mathrm{d}\mu = -\frac{\epsilon - 1}{2\epsilon + 1}\frac{\mu^2}{a^3} \qquad (4)$$

= gain in energy of the dipole in medium of dielectric constant ϵ

Assuming that a *gauche* molecule of 1,2-dichloroethane may be represented by a sphere of volume $4/3\pi\, a^3 = M/\rho N$ where

M = molecular weight
ρ = liquid density
N = the Avogadro number

and that the medium may be represented by the liquid, the change in energy of the *gauche* molecule due to the electrostatic interaction with its surroundings can be estimated by equation (4). Thus

$$E_{\text{gauche(gas)}} = E_{\text{gauche(liquid)}} - \delta E$$

where E is the internal energy. Since the *trans* molecule has a very small permanent moment such interactions are negligible and

$$E_{\text{trans(gas)}} = E_{\text{trans(liquid)}} - 0$$

Now

$$\Delta E_{\text{gas}} = (E_{\text{gauche}} - E_{\text{trans}})_{\text{gas}}$$

and

$$\Delta E_{\text{liquid}} = (E_{\text{gauche}} - E_{\text{trans}})_{\text{liquid}}$$

Therefore

$$\Delta E_{\text{gas}} = \Delta E_{\text{liquid}} - \delta E$$
$$= \Delta E_{\text{liquid}} + \frac{\epsilon - 1}{2\epsilon + 1}\frac{\mu^2}{a^3} \qquad (5)$$

It is evident that μ and ϵ must be known before ΔE_{gas} may be evaluated from (5). The moment of the *gauche* form μg may be evaluated when $P_E + P_A$, and the rotational and vibrational partition functions are known, from the relations for the mean moment and the square of the mean moment.[11] Evaluation of ΔE therefore required dielectric measurements of the gas and of the liquid and complete vibrational assignments of the isomers. The results obtained for 1,2-dichloroethane were in fair agreement with the gas values.[11]

It may be shown, however, that determinations of equilibria in dilute solutions with non-polar solvents can give equally accurate values of ΔH_{gas} without the elaborate experimentation required to determine variable dielectric constants and the dipole moments of each configuration of a molecule. Equation (5) may be extended to solutions, with ΔH assumed to be approximately equal to ΔE so that

$$\Delta H_{\text{gas}} = \Delta H_{\text{solution}} - \delta E \qquad (6)$$

If at infinite dilution the values of ϵ and $a^3 = M/\rho \times 3/4\pi N$ for the solvent may be used and since for non-polar solvents these quantities do not vary appreciably with temperature, then the expression for δE may be modified to

$$\delta E = -\left\{\frac{\epsilon - 1}{(2\epsilon + 1)a^3}\right\}_{\text{solvent}} \mu^2 \qquad (7)$$

In the gas phase molecular interactions are negligible so that $\delta E = 0$; also if the solvent property, $(\epsilon - 1)/(2\epsilon + 1)a^3$, is vanishingly small $\delta E = 0$ under which conditions $\Delta H_{\text{solution}} = \Delta H_{\text{gas}}$. A plot of $\Delta H_{\text{solution}}$ *vs.* $(\epsilon - 1)/(2\epsilon + 1) \times \rho/M$ should give a straight line, the slope of which is proportional to μ^2 and the intercept at the $\Delta H_{\text{solution}}$ axis is equal to ΔH_{gas}. Not only is the knowledge of the variable dielectric constant and the moment of the polar isomer not necessary for application of this method, but this method yields some measure of the moment.

The choice of the effective "cavity" is still open to question but the use of $a^3{}_{\text{solvent}}$ in equation (7) is justified by the correlation of the experimental data given below. To the degree of accuracy of this work satisfactory interpretation of results was obtained with a^3 proportional to the molecular volume of the solvent whether the solvent molecules were larger or smaller than the solute mole-

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(16) L. Onsager, THIS JOURNAL, 58, 1486 (1936).

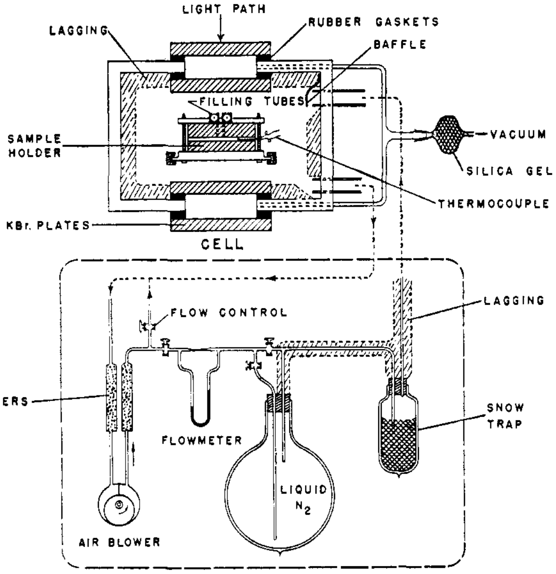
cules. Use of a^3_{solute} leads to quite unsatisfactory results. The validity of the assumption must be judged by the agreement between the "gas" values of ΔH determined in this way and those determined by a true gas technique (see below).

Experimental

Values of ΔH for 1,2-dichloroethane, 1,2-dibromoethane, 1-chloro-2-bromoethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane have been obtained by a dilute solution technique.

The choice of non-polar solvents was very narrow and only bromine, carbon disulfide, stannic chloride and tetrachloroethylene were found generally useful for very dilute solutions, in the region from 1100 to 1300 cm.$^{-1}$. The bromine and stannic chloride made the analytical technique difficult but the solvents offered a usefully wide range of molecular volume.

The higher temperature determinations were carried out in a cell previously described[15] and the low temperature determinations in another especially designed cell. This cell and the cooling system are shown in Fig. 1. The infrared beam passes through the cold sample by way of double salt windows. The space between each pair of windows is evacuated so that the outer windows do not cool and condense moisture from the atmosphere. Refrigeration is effected by means of a controlled stream of cold dry nitrogen which passes around the sample holder. The latter is filled while in position with thin filling tubes extending to the outside of the cold box.



Low temperature cell and layout.

Fig. 1.

Materials

1,2-Dichloroethane was Eastman Kodak Co. redistilled, b.p. 83.0–83.5°, 760 mm.

1,2-Dibromoethane was Eastman Kodak Co. redistilled, b.p. 131.5–132°, 760 mm.

1-Chloro-2-bromoethane was prepared by equilibrating equimolar quantities of 1,2-dichloroethane and 1,2-dibromoethane over anhydrous aluminum chloride[17] for about 48 hours followed by fractional distillation in a 1-meter Stedman column, b.p. 107° 760 mm.

1,1,2-Trichloroethane was prepared from 1,2-dichloroethane and SO_2Cl_2 after the method of Kharasch and Brown[18]; b.p. 113° 760 mm.

1,1,2,2-Tetrachloroethane was Eastman Kodak Co., redistilled, b.p. 146° 760 mm.

For infrared analysis of these compounds complete assignments of the vibrational spectra to their isomeric forms were not necessary. Observations of alternations in band densities with temperature only were necessary to indicate the bands belonging to the more or less stable isomer. Frequently only one form, the more stable, existed in the crystalline state and a comparison of the liquid and solid spectra was sufficient to associate the spectrum with its isomeric form. Even when more than one form was present in all phases (*e.g.*, 1,1,2,2-tetrachloroethane) considerable intensity alternation of the bands occurred with change of phase.

The equilibrium was followed according to the relation

$$\text{equilibrium constant} = \frac{\text{concn. of less stable isomer}}{\text{concn. of more stable isomer}}$$

$$= \text{constant} \cdot \left(\frac{d_{\text{less stable}}}{d_{\text{more stable}}}\right)_{c \to 0}$$

where

d is the optical density $= \ln I_0/I = \alpha c L$

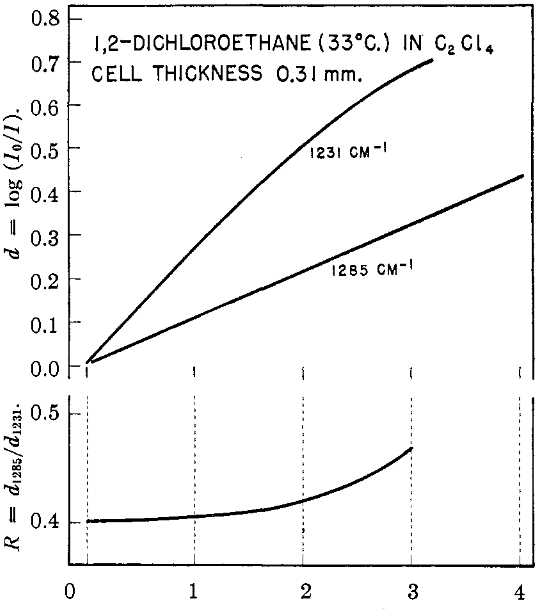
and

α is the extinction coefficient

c is the concentration

L is the cell length

Peak intensities are used throughout the solution work and the optical density ratios extrapolated to infinite dilution. Figure 2 shows a plot of the optical densities of the 1231 and 1285 cm.$^{-1}$ bands of 1,2-dichloroethane (belonging to the *trans* and *gauche* forms, respectively) against total concentration. The ratio $R = d_{1285}/d_{1231}$ is shown on the same concentration scale below. It is seen that R reaches its limiting value only at very low optical densities and since extrapolation is not linear the accuracy of determination of $R_{c \to 0}$ is somewhat restricted.



Total concentration $C_2H_4Cl_2$ (% vol.).

Fig. 2.

The false values[19] of ΔH arising from the use of ratios obtained at concentrations greater than zero are shown in Figs. 3 and 4. Figure 3 gives an example of the R *vs.* concentration plots over a range of temperatures as generally used for a ΔH determination and Fig. 4 shows the false ΔH values from a log R against $1/T$ plot arising from different concentrations in a cell of constant length. The correct value is only obtained toward the limit $c = 0$.

The true $\Delta H_{\text{solution}}$ values, derived from $R_{c \to 0}$, observed for each solvent were plotted against the solvent

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[17] G. Dougherty, THIS JOURNAL, **51**, 579 (1929).

[18] M. S. Kharasch and M. C. Brown, *ibid.*, **61**, 2142 (1939).

[19] The increase in R as the concentration increases over the limited range from 0 to 4% by volume may be shown to be due only to deviation from Beer's law and not to any change in equilibrium with concentration since an equivalent increase in the path length with constant concentration has the same effect.

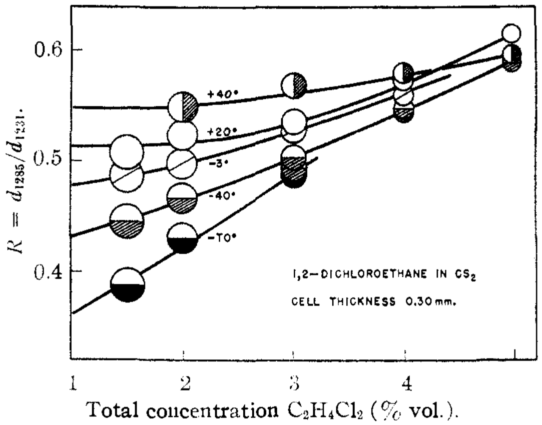

Fig. 3.

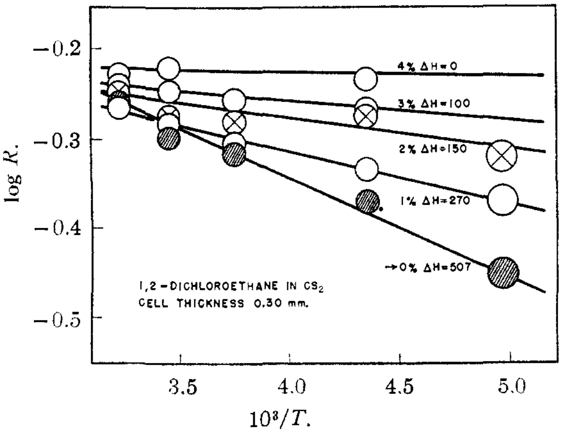

Fig. 4.

property, $\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}$[20] and extrapolated to $\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M} = 0$. The solvents giving the observed ΔH values may be identified in the graphs from their values along the abscissa which are 2.09, 2.27, 4.24 and 5.55 all $\times\ 10^{-3}$ for C_2Cl_4, $SnCl_4$, CS_2 and Br_2, respectively. The intercept on the $\Delta H_{obs.}$ axis is then a value free from solvent interaction, that is, the gas value. The curves for the materials studied are given in Figs. 5, 7, 9, 11 and 13.

Results and Discussion

1,2-Dichloroethane.—The ratio of the optical densities of the *trans* band at 1231 cm.$^{-1}$ and the *gauche* band at 1285 cm.$^{-1}$ were measured at various concentrations in different[9] solvents. The value of 1480 ± 160 cal./mole, obtained from the dilute solution values in bromine, carbon disulfide, stannic chloride and tetrachloroethylene and extrapolated to zero solvent interaction (Fig. 5) is in fair agreement with gas values from other sources. (For a general comparison of results with other values from the literature see Table I.) From the slope of the curve the moment of the polar isomer was found to be 2.53×10^{-18} e.s.u. which is in good agreement with 2.55×10^{-18} e.s.u. calculated by Mizushima[21] from dielectric measurements. If the moments of the polar isomers are known or can be estimated a gas value of ΔH may be calculated from one solution determination only.

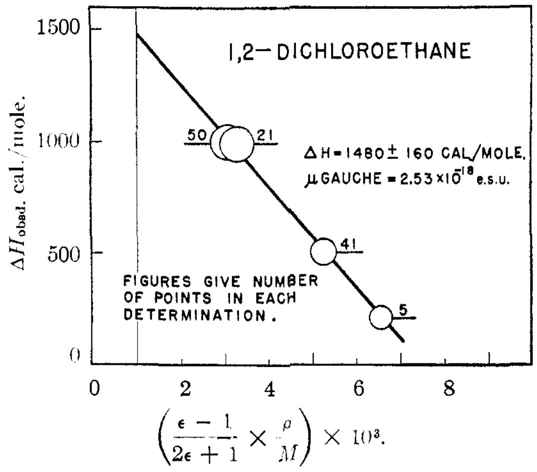

Fig. 5.

1-Chloro-2-bromoethane.—The bands of frequencies 1203 cm.$^{-1}$ (form (a)) and 1250 cm.$^{-1}$ (form (b)) were used (see Fig. 6). The value found for ΔH_{gas} was 1850 ± 150 cal./mole (Fig. 7) and is higher than the gas value of 1430 ± 100 cal./mole which, for comparison, was determined in the gas phase after a method already described.[14] The areas under the absorption bands, rather than the peak intensities were used to follow the equilibrium in the gas. The plot of log R_{areas} *vs.* $1/T$ for gaseous 1-chloro-2-bromoethane is shown in Fig. 8. If the peak intensities were used instead of areas a higher value of ΔH_{gas} was obtained (~1600 cal./mole).

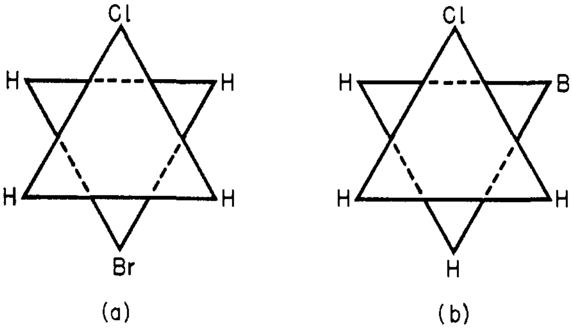

Fig. 6.—1-Chloro-2-bromoethane.

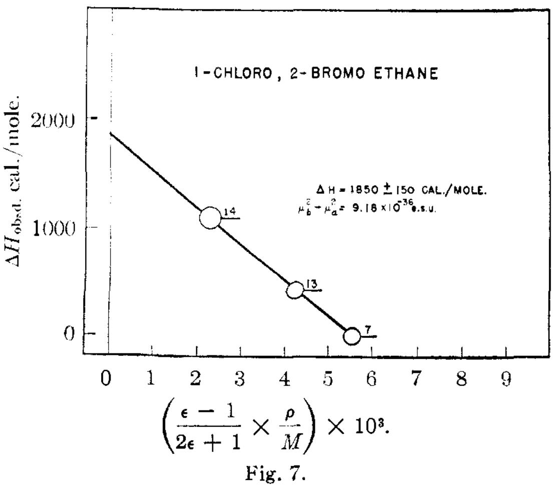

Fig. 7.

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[20] For the best relative values of molecular volumes of the solvents their densities at the boiling points were used.

[21] I. Watanabe, S. Mizushima and Y. Morino, *Sci. Pap. Inst. Phys. Chem. Res. (Tokyo)*, **39**, 401 (1942).

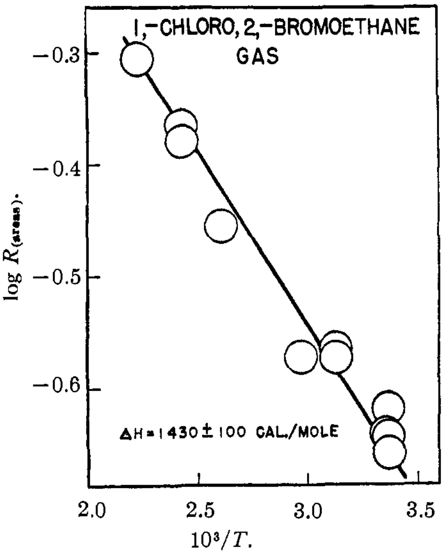


Fig. 8.

Where both forms possess a dipole moment, the slope of the curve will give only the difference between the squares of each moment ($\mu_b^2 - \mu_a^2$).

The value of ($\mu_b^2 - \mu_a^2$) for 1-chloro-2-bromoethane (Fig. 7) is 9.18×10^{-36} e.s.u. If the moment of isomer (a) is taken to be the difference between the C–Cl and C–Br bond moments, *i. e.*, 0.46×10^{-18} e.s.u., then the dipole moment of the form (b) becomes 3.0×10^{-18} e.s.u. This is high compared with 1,2-dichloroethane.

1,2-Dibromoethane.—The bands employed were 1188 cm.$^{-1}$ for the *trans* form and 1245 cm.$^{-1}$ for the *gauche* form. ΔH_{gas} from the observed solution values is about 2000 cal./mole (Fig. 9). Again this is higher than the value determined in the gas phase but considering both experimental errors the value of 1770 observed by Bernstein[15] may not be significantly different. The error is not considered big enough to include the results of Mizushima, *et al.*,[18] for this compound (1450 cal./mole). The results for the above three compounds do, however, appear to be consistently higher by about 300 cal./mole than those obtained in the gas phase although the experimental error might account for the discrepancy.

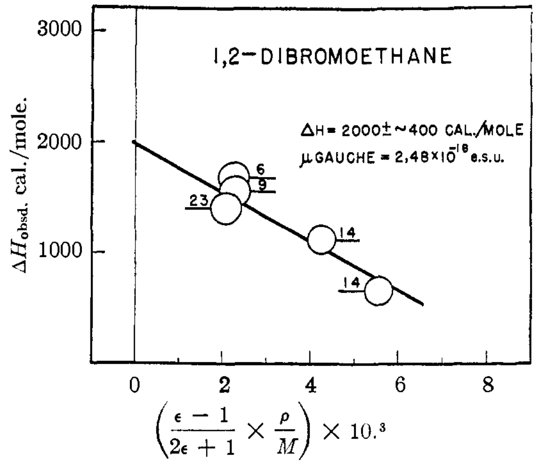


Fig. 9.

1,1,2-Trichloroethane.—Two pairs of bands were available for this material; 1049 cm.$^{-1}$ from the more stable form (a) (see Fig. 10) with 1008 cm.$^{-1}$ from the less stable form (b), and also 547 cm.$^{-1}$ (a) with 524 cm.$^{-1}$ (b). The only solvent suitable for the pair of bands at the lower frequencies was CS_2. The ΔH for this solvent has been determined for both pairs of bands and the agreement was within the experimental error (see Fig. 11, the points at $(\epsilon - 1)/(2\epsilon + 1)\cdot\rho/M)\cdot 10^3 = 4.24$).

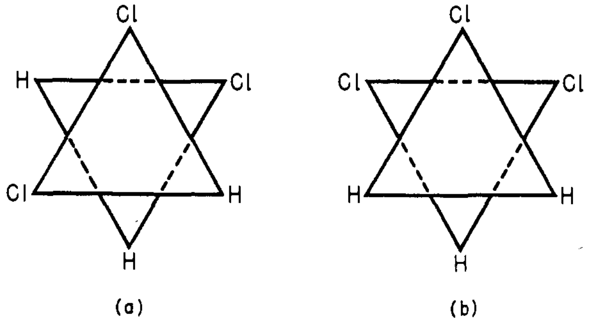


Fig. 10.—1,1,2-Trichloroethane.

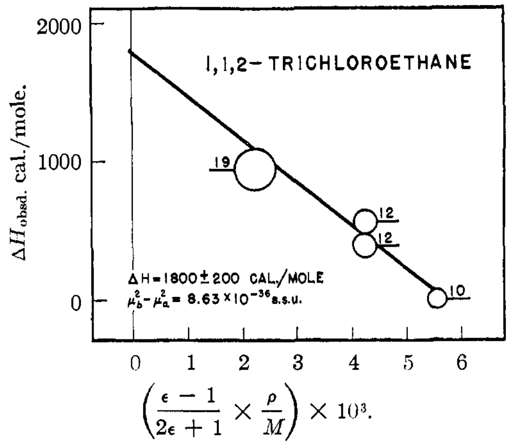
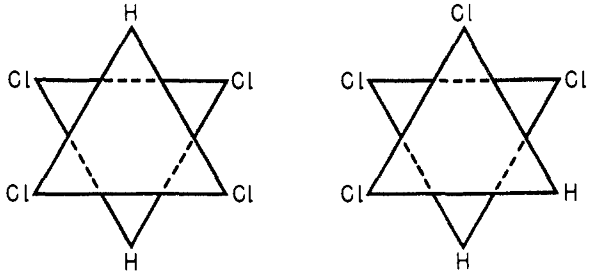


Fig. 11.

The ΔH_{gas} value for 1,1,2-trichloroethane obtained from the dilute solution determinations (Fig. 11) cannot be compared with an infrared gas phase measurement since the bands are overlapped in the vapor. Thomas and Gwinn[8] have obtained a value of the isomerization energy from gas phase polarizability measurements but there was some uncertainty concerning the atomic polarizability of the molecule. Because of this uncertainty the isomerization energy was quoted by them to be greater than 2300 cal./mole and probably greater than 4000 cal./mole. The figure obtained in this work, 1800 cal./mole, is lower than their minimum but the difference may not be significant if both errors are taken into account. The higher value, however, seems to be definitely excluded.

1,1,2,2-Tetrachloroethane.—The spectrum of this material was crowded and all suitable bands were overlapped to some extent. The best resolved were those at 1279 cm.$^{-1}$ (isomer (a) less stable in solution) and 1243 cm.$^{-1}$ (isomer (b) more stable in solution). The structures of the isomers (a) and (b) are shown in Fig. 12. Figure 13 indicates that there is only a small energy difference between the isomers (280 cal./mole) as was found also by Thomas and Gwinn.[8] The dipole moment of form (b) is found to be 2.51×10^{-18} e.s.u., assuming that of form (a) to be zero as in the case of 1,2-dichloroethane.

In all solutions, except those with a very low value of $\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}$ $(< \sim 1.0)$ the form (b) is the more stable. In the gas phase, however, the *trans* isomer (a) appears to be slightly more stable. The slope of the curve in Fig. 13 is seen to be reversed compared with all previous examples of $\Delta H_{\text{obsd.}}$ *vs.* $\frac{\epsilon - 1}{2\epsilon + 1} \times \frac{\rho}{M}$. Only in the case of 1,1,2,2-tetrachloroethane does the energy difference between the isomer in solution increase with increasing polarizability of the solvent. In previous cases the energy of the more polar form in the gas phase has been considerably higher than that of the less polar form and the effect of solvent has been to lower the energy of the more polar form and consequently reduce the energy difference. In the case of 1,1,2,2-tetrachloroethane the energies of the two forms are little different in the gas phase and the effect of solvent in lowering the energy of the polar form is to increase the energy difference according to the degree of electrostatic interaction with the particular solvent. The different behavior is shown by the comparison of the potential energy diagrams of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane in Fig. 14.



(a) (b)

Fig. 12.—1,1,2,2-Tetrachloroethane.

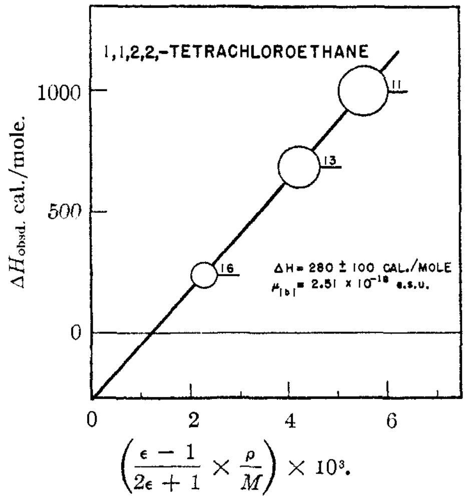


Fig. 13.

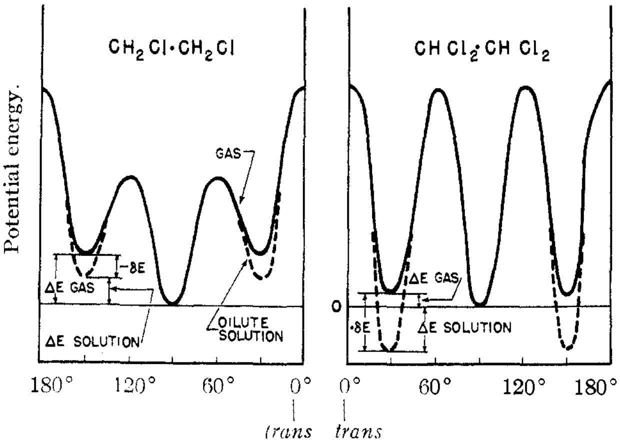


Fig. 14.—Angle of rotation about C—C axis.

Table I summarizes the rotational isomerization energies determined by the dilute solution method and gives for comparison those at present available in the literature. Liquid phase values, which are not comparable with those from the gas phase, are in parentheses.

Table I

Rotational Isomerization Energies

Isomerization energy (cal./mole)	Method	Author
	$CH_2Cl \cdot CH_2Cl$	
1320	Infrared, gas	Bernstein[14]
1030	Infrared, gas	Mizushima, *et al.*[12]
1210	Raman and dipole moment	Mizushima, *et al.*[11]
1400	Gas heat capacity	Gwinn and Pitzer[22]
1480	Dil. soln. infrared	This work
(~0)	Raman, liquid	See refs. 9, 10, 11, 21
	$CH_2Br \cdot CH_2Br$	
1450	Infrared, gas	Mizushima, *et al.*[13]
1400	Dipole moment	Mizushima, *et al.*[13]
1770	Infrared, gas	Bernstein[15]
2000	Dil. soln. infrared	This work
(740)	Raman, liquid	Rank, *et al.*[10]
(760)	Raman, liquid	Mizushima, *et al.*[12]
(2420)	Raman, liquid	Aronov, *et al.*[23]
	$CH_2Cl \cdot CH_2Br$	
1430	Infrared, gas	This work
1850	Dil. soln. infrared	This work
(~0)	Raman, liquid	Aronov, *et al.*[23]
	$CH_2Cl \cdot CHCl_2$	
$\gtrsim$4000 or >2300	Dipole moment	Gwinn and Thomas[8]
1800	Dil. soln. infrared	This work
	$CHCl_2 \cdot CHCl_2$	
(1100)	Raman, liquid	Langseth and Bernstein[7]
~0	Dipole moment	Gwinn and Thomas[8]
~280	Dil. soln. infrared	This work

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