for two hours, then cooled and poured into 1 liter of water containing 30 g. of sodium hydroxide. The mixture was steam distilled, the product separated from the aqueous layer and dried over anhydrous magnesium sulfate and redistilled at reduced pressure to obtain 184 g. (77.5%) of 3-trifluoromethyl diphenyl ether, b.p. 81° (1 mm.), $n^{20}_{\rm D}$ 1.5118.

Anal. Calcd. for $C_{13}H_9F_3O$: C, 65.53; H, 3.81. Found: C, 65.18, 65.04; H, 3.86, 3.98.

Three other trifluoromethyl substituted ethers were prepared as above.

3-Trifluoromethyl 4′-Chlorodiphenyl Ether.—From 169 g. (0.75 mole) of *m*-bromobenzotrifluoride and 121 g. (0.94 mole) of *p*-chlorophenol was obtained 75 g. (36.8%) of 3-trifluoromethyl 4′-chlorodiphenyl ether, b.p. 94–95° (1 mm.), $n^{20}_{\rm D}$ 1.5278.

Anal. Calcd. for $C_{13}H_8F_3ClO$: C, 57.30; H, 2.96. Found: C, 56.85, 57.04; H, 3.00, 3.10.

3-Trifluoromethyl 3′-Ethyldiphenyl Ether.—From 118 g. (0.525 mole) of *m*-bromobenzotrifluoride and 64 g. (0.525 mole) of *m*-ethylphenol was obtained 106 g. (76%) of 3-trifluoromethyl-3′-ethyl diphenyl ether, b.p. 89° (1 mm.), $n^{20}_{\rm D}$ 1.5100.

Anal. Calcd. for $C_{15}H_{13}F_3O$: C, 67.68; H, 4.92. Found: C, 67.32, 67.50; H, 5.16, 4.89.

3-Trifluoromethyl Phenyl-α-naphthyl Ether.—From 232 g. (1.03 moles) of *m*-bromobenzotrifluoride and 240 g. (1.87 moles) of α-naphthol was obtained 52.5 g. (17.7%) of 3-trifluoromethyl phenyl-α-naphthyl ether, b.p. 157–158° (3 mm.), $n^{20}_{\rm D}$ 1.5784, with recovery of half the *m*-bromobenzotrifluoride unchanged.

Anal. Calcd. for $C_{17}H_{11}F_3O$: C, 70.08; H, 3.85. Found: C, 70.65, 70.48; H, 3.85, 3.98.

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RECEIVED NOVEMBER 16, 1951

Internal Rotation. VII. The Energy Difference between the Rotational Isomers of Some Halogen Substituted Ethanes

BY F. E. MALHERBE[1] AND H. J. BERNSTEIN

Liquid 1,1,2-tribromoethane is considered to consist of different isomeric forms.[2] This view is supported by the fact that certain bands, *e.g.*, those at 1183 and 1001 cm.$^{-1}$ which are present in the infrared spectrum of the liquid are absent in the spectrum of the solid tribromoethane (see Table III). In the course of an investigation, by the dilute solution method,[3] of the temperature dependence of the intensity of bands belonging to different rotational isomers anomalous results were obtained, and it was in fact possible to obtain a spurious value for ΔH by investigating a pair of bands belonging to the same isomeric species. This apparent temperature dependence led us to reinvestigate 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane which had been done previously by the dilute solution method.[3] An attempt was made also to determine a value for the energy difference between the isomeric forms in liquid 1,1,2-trichloroethane, 1,1,2-tribromoethane and 1,1,2,2-tetrabromoethane.

Experimental

The infrared spectra were obtained on a Perkin–Elmer Model 12c infrared spectrometer with a Brown electronic recorder. Absorption bands at frequencies above 2000 cm.$^{-1}$ were recorded with a LiF prism, frequencies between 2000 and 660 cm.$^{-1}$ with a NaCl prism, frequencies between 660 and 420 cm.$^{-1}$ with a KBr prism and those below 420 cm.$^{-1}$ with a KRS-5 prism. In the region below 420 cm.$^{-1}$ the liquids only were investigated. The experimental technique and principles of the method have been described previously.[3] Here, a new furnace capable of more accurate temperature control, was used.

The 1,1,2,2-tetrachloroethane was an Eastman Kodak product, distilled through a Stedman column, of 40 theoretical plates, b.p. 146 ± 0.2° at 760 mm.

The 1,1,2,2-tetrabromoethane and 1,1,2-tribromoethane were also Eastman Kodak products, redistilled; b.p. 151 ± 0.2°, 188.4 ± 0.2°, respectively.

The 1,1,2-trichloroethane was a Carbide and Carbon Chemicals product redistilled; b.p. 113 ± 0.2° whereas the sample used in the earlier work[2] had been prepared by a well known method.[4]

Results

1,1,2,2-Tetrachloroethane.—Reinvestigation of the temperature dependence of the pairs of bands at 1279 and 1243 cm.$^{-1}$, respectively, which had been used in the previous work,[3] as well as their behavior on freezing the liquid, led to the conclusion that they belong to the same isomeric form. The apparent temperature dependence of the bands, giving the straight line of Fig. 13 in the earlier paper,[3] is due largely to underestimating the experimental error and perhaps, also to temperature effects which are being investigated in more detail at the present moment in this Laboratory. No suit-

TABLE I

INFRARED SPECTRA OF 1,1,2-TRICHLOROETHANE

Frequencies in cm.$^{-1}$; relative spectral densities in parentheses; (sh) indicates shoulder; frequencies of prominent bands in liquid spectrum which are absent in the solid spectrum are underlined

Liquid (0.025 mm. cell)	Solid (approx. 0.005 mm. layer)	Vapor (10 cm. cell, 100 mm.)
2998 (3)		2943 (3)
2873 (1)		2810 (1)
1430 (7)	1424 (3)	1437 (7)
1308 (5)	1305 (1)	1306 (5)
1264 (7)	1259 (2)	1260 (9)
1237 (5)		
1212 (9)	1212 (5)	1204 (10) doublet
1162 (3)	1162 (1)	1161 (3)
1124 (2)	1120 (1)	
1086 (sh)	1058 (1)	
1050 (3)	1050 (1)	1050 (3)
1010 (2)		
940 (sh)		941 (10)
933 (9)	932 (9)	932 (10)
890 (1)	887 (0)	890 (0)
875 (2)	873 (1)	881 (0)
857 (0)		
849 (0)		
785 (sh)	781 (sh)	796 (10)
777 (7)	770 (8)	787 (10)
730 (10)	727 (10)	736 (10)
700 (5)		
662 (7)	667 (8)	668 (10)
640 (3)	637 (sh)	
613 (0)	613 (0)	
586 (0)	586 (sh)	
569 (0)		
545 (sh)		
524 (3)		
(0.2 mm. cell)		
388 (6)		
330 (3)		

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[1] N. R. C. Post-doctorate Fellow 1950–1951.

[2] L. Kahovec and J. Wagner, *Z. physik. Chem.*, **B47**, 48 (1940).

[3] J. Powling and H. J. Bernstein, THIS JOURNAL, **73**, 1815 (1951).

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

able pair of bands was found so that there is no value for ΔH by the dilute solution method forthcoming for this molecule.

1,1,2-Trichloroethane.—The sample of trichloroethane used in this work was found to be different from that used in the previous investigation[8] in one important respect, namely, that one of the bands (at 547 cm.$^{-1}$), whose temperature dependence relative to the band at 524 cm.$^{-1}$ had been measured, was absent in the infrared spectra of the liquid and solid material. The other pair of bands (at 1050 and 1010 cm.$^{-1}$) was present, however, in the spectrum of the liquid and it was confirmed that they belonged to different species, since of the pair only the band at 1050 cm.$^{-1}$ is present in the spectrum of the solid trichloroethane. The temperature dependence of this pair of bands was measured in the liquid and the plot of log (ratio of peak heights) *vs.* $1/T$ is shown in Fig. 1; the value found for ΔH was approximately 0.1 cal. The infrared spectra of 1,1,2-trichloroethane in the liquid, solid and vapor state are given in Table I.

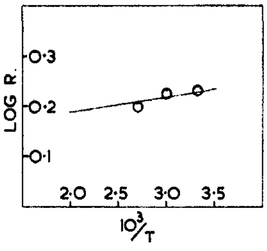

Fig. 1.

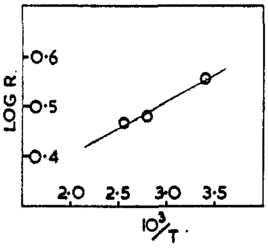

Fig. 2.

1,1,2,2-Tetrabromoethane.—No suitable pair of bands was found in the infrared spectrum of liquid tetrabromoethane. The spectrum of the liquid shows three bands at 636, 614 and 584 cm.$^{-1}$, respectively, whereas of these only the band at 614 cm.$^{-1}$ is present in the spectrum of the solid. The attempt to investigate the temperature dependence of the pair of bands at 614 and 584 cm.$^{-1}$ in the pure liquid and in solution proved unsatisfactory, owing to the large amount of overlap of the bands. The spectra of 1,1,2,2-tetrabromoethane in the liquid and solid states are given in Table II.

TABLE II

INFRARED SPECTRA OF 1,1,2,2-TETRABROMOETHANE (*cf.* TABLE I)

Liquid	Solid	Liquid	Solid
2986 (8)	2986 (9)	925 (0)	927 (0)
2430 (1)		895 (1)	903 (0)
2260 (2)	2264 (3)	828 (4)	831 (2)
1932 (1)	1938 (0)	788 (4)	794 (1)
1355 (1)	1358 (1)	761 (4)	766 (2)
1304 (1)	1310 (1)		748 (sh)
1275 (sh)		707 (9)	707 (8)
1240 (9)	1243 (9)	636 (6)	
1194 (6)	1198 (5)	614 (8)	614 (8)
1135 (10)	1135 (9)	584 (4)	
1073 (1)	1065 (0)		562 (1)
1006 (8)	1009 (6)	536 (4)	533 (8)
		449 (2)[a]	449 (3)

[a] 0.2 mm. cell.

1,1,2-Tribromoethane.—In the infrared spectrum of liquid tribromoethane there is a pair of bands at 1041 and 1000 cm.$^{-1}$, respectively, which belong to different isomeric forms, since again, of this pair, only the band at 1041 cm.$^{-1}$ is present in the spectrum of the solid tribromoethane. The temperature dependence of this pair of bands was measured in the liquid state, and the plot of log (ratio of peak heights) *vs.* $1/T$ is shown in Fig. 2; the value of ΔH for the liquid is approximately 0.5 cal. The infrared spectra of the 1,1,2-tribromoethane in the liquid and solid state are given in Table III.

Discussion

TABLE III

INFRARED SPECTRA OF 1,1,2-TRIBROMOETHANE (*cf.* TABLE I)

Liquid	Solid	Liquid	Solid
	3548 (1)	1142 (10)	1145 (8)
3021 (10)		1119 (9)	1124 (6)
3002 (9)		1041 (4)	1042 (4)
2960 (6)	2979 (3)		1022 (sh)
2924 (sh)		1000 (1)	
2821 (1)			895 (sh)
2773 (1)		879 (10)	880 (10)
2534 (0)			847 (0)
2484 (0)		812 (1)	812 (0)
2456 (0)		769 (0)	767 (0)
2420 (0)		752 (0)	
2290 (2)		720 (0)	
2094 (0)	2130 (sh)		695 (sh)
2073 (0)	2062 (0)	686 (8)	682 (5)
1413 (9)	1415 (5)		642 (sh)
1315 (sh)	1306 (0)	609 (8)	605 (8)
1269 (9)	1272 (10)	562 (8)	560 (8)
1258 (8)		525 (2)	547 (1)
	1245 (1)	479 (0)	
1213 (10)	1214 (10)	426 (1)	
1181 (9)		334 (3) 0.2 mm. cell	

It is apparent that the latitude of error in the infrared methods for measuring the energy difference between the isomeric forms is wider than previously reported.[3] In making measurements on pure liquids the greatest difficulty is the correct positioning of the background, since the scattering in an empty cell is greater than in one containing liquid between the plates. Furthermore, the effect of temperature and solvent on the shapes of bands requires further investigation and work along these lines is in progress in this Laboratory. In the previous dilute solution technique,[3] the peak heights of bands have been taken as a measure of their concentrations and further investigation is in progress to determine whether this is adequate or not.

In obtaining the infrared spectra of compounds in the solid state extreme care has to be taken to ensure that one has the true crystalline solid, rather than a glassy solid, the formation of which has been previously reported.[5,6] In many cases, especially for volatile liquids, the most satisfactory solids are obtained by condensation of the vapor in a Hornig-type cell,[6] and allowing the glassy solid to heat up slowly until it crystallizes.

(5) J. K. Brown and N. Sheppard, *Discus. Farad. Soc.*, **9**, 144 (1950); *J. Chem. Phys.*, **19**, 976 (1951); F. E. Malherbe and H. J. Bernstein, *ibid.*, **19**, 1607 (1951).

(6) E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

DIVISION OF CHEMISTRY
NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

RECEIVED DECEMBER 10, 1951

The Infrared Spectra of Some Allenic Compounds

BY JOHN H. WOTIZ AND WALTER D. CELMER

The characteristic allenic bond (C=C=C) absorption band is usually listed near 1970 cm.$^{-1}$.[1] This bond is of considerable analytical value as it is

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(1) R. B. Barnes, R. C. Gore and R. W. Stafford, *Anal. Chem.*, **20**, 402 (1948).