[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Vapor Pressures of *cis* and *trans* Disubstituted Ethylenes

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Preliminary to the study of some gas phase reactions of the dibromo- and diiodoethylenes, the vapor pressures of the isomers of these compounds were measured. Since for each of these compounds both the heat and the entropy of vaporization of the *cis* isomer were greater than those of the *trans*, previously reported vapor pressure measurements on other pairs of isomers were examined to ascertain the generality of this effect.

Experimental

Materials.—The dibromoethylenes were prepared by reducing technical tetrabromoethylene with granular zinc and alcohol.[1] After the mixture was steam distilled, the distillate was separated with sulfuric acid, washed, and dried with calcium chloride. A solution of the dibromoethylene in absolute alcohol was fractionally distilled, and the separated isomers were then washed free of alcohol and dried. Infrared absorption spectra showed that each sample contained not more than 3% of the other isomer. Refractive indices for the sodium D line at 25° were 1.5370 for *cis*-dibromoethylene and 1.5440 for the *trans* isomer.

trans-Diiodoethylene was prepared, as reported previously,[2] by passing commercial tank acetylene into a solution of iodine in 95% ethyl alcohol, and was purified by repeated crystallizations from alcohol. The resulting crystals were dried over calcium sulfate, since drying over sulfuric acid led to decomposition of the crystals.

cis-Diiodoethylene was prepared by isomerization of crude *trans*-diiodoethylene at 160°.[2] The crystals of the *trans* isomer in the equilibrium mixture were separated from the *cis* isomer by filtration and centrifugation at successively lower temperatures. Traces of the iodine catalyst were removed from the liquid by washing with sulfite, then with water, and finally drying. The solid isomer melted between −14 and −13°.

Procedure.—The method of Gould, Holzman and Niemann[3] was used to determine the vapor pressures of the separated isomers within the range between 1 and 286 mm. In this method the sample was sealed in a capillary tube above a small air pocket, and, at different temperatures, measurements were made of the pressure at which the mixture of air and vapor in this pocket occupied a specified volume. The temperature was measured with small calibrated immersion thermometers graduated to 0.5° and suspended near and parallel to the capillary tube. The original method was modified in that the bottom of the column of liquid was adjusted to the same mark in each measurement so that corrections could be made for volume changes due to evaporation of the sample during a run. Since samples were used over a considerable temperature range, they were initially chosen to occupy about 10 mm. of the capillary.

Since *trans*-diiodoethylene melts at 73°, some difficulty was encountered in collecting and measuring this substance. A melted sample, sucked into the warmed capillary, was kept liquid until the capillary had been sealed at the tip. When the sample was to be measured, the capillary was attached to the manometer–vacuum system and again warmed until the diiodoethylene had become liquid. The system was evacuated to a point where the whole sample, interspersed with air pockets, was drawn into the larger neck of the capillary, and all but the bottom air pocket was drawn off. The sample was then allowed to settle back in the capillary, and measurements were made.

Results

The vapor pressure data appear in Table I. Other points determined for *cis*-dibromoethylene fit the calculated relation equally well. Two additional runs were made using mixtures of *cis*- and *trans*-dibromoethylene, and a vapor pressure curve intermediate between that of the two pure isomers was obtained.

TABLE I

VAPOR PRESSURES OF DIHALOETHYLENES

Temp., °K.	Obs. P, mm.	Temp., °K.	Obs. P, mm.
cis-$C_2H_2Br_2$		*cis*-$C_2H_2I_2$	
299.4	20.8	314.2	4.7
307.8	32.0	317.2	6.6
316.6	50.0	334.5	6.9
325.7	75.3	342.7	11.0
334.0	110.6	347.4	16.1
337.7	127.3	358.6	24.4
343.5	164.0	361.7	25.5
344.4	168	367.2	33.0
349.0	202	371.8	44.4
350.8	215	378.6	52.3
trans-$C_2H_2Br_2$ (2 runs)		385	70.3
277.0	12.2	392.9	99.9
292.9	26.6	405.5	147
299.2	31.4	406	148.5
307.5	54.5	410	175.6
314.8	74.4	418	214
322.5	100.0	425	286
324.6	105.3	*trans*-$C_2H_2I_2$ (2 runs)	
330.9	138.3	350.4	20.8
335.5	160	362.8	32.9
338.1	181.7	375.2	52.7
343.6	208	379.1	62.9
cis-$C_2H_2I_2$ (2 runs)		385.6	76.9
302.1	1.3	391.7	94.6
299.3	1.6	403.2	136.5
321.4	4.2		

The data were fitted to equations of the type $\log P = -A/T + B$, where P is the vapor pressure in mm. and T is in °K. The average deviation of pressures above 10 mm. is about 1% for *cis*-dibromoethylene and *trans*-diiodoethylene and is about 4% for *trans*-dibromoethylene and *cis*-diiodoethylene. The constants obtained are recorded in Table II, together with similar constants calculated from data reported for other *cis* and *trans* substituted ethylenes.

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* Harvard College A.B. 1939.

[1] H. van der Walle, *Bull. soc. chim. Belg.*, **27**, 209–217 (1913).

[2] R. M. Noyes, R. G. Dickinson and V. Schomaker, THIS JOURNAL, **67**, 1319–1329 (1945).

[3] C. Gould, G. Holzman and C. Niemann, *Ind. Eng. Chem., Anal. Ed.*, **19**, 204 (1947).

TABLE II

VAPOR PRESSURE CONSTANTS. HEATS AND ENTROPIES OF VAPORIZATION OF SUBSTITUTED ETHYLENES

Compound	Isomer	*A*	*B*	ΔH, cal./mole	ΔS cal./mole deg.
Dichloroethylene[4]	*cis*	1748	8.18	8,000	26.0
	trans	1701	8.22	7,780	26.3
Dibromoethylene	*cis*	2120	8.40	9,720	26.8
	trans	1840	7.71	8,380	23.5
Diiodoethylene	*cis*	2430	8.18	10,950	25.0
	trans	2210	7.62	10,200	22.9
(Solid)[5]	*trans*	2130	5.86	(9,760)	(21.9)
Butene-2[6]	*cis*			5,870	23.4
	trans			5,670	22.9
Stilbene[7]	*cis*	3474	9.484	15,920	30.2
	trans	3290	8.56	15,100	26.7
Diethyl maleate[4]	*cis*	2865	8.66	13,110	27.4
Diethyl fumarate[4]	*trans*	2805	8.60	12,840	27.1
Dimethyl maleate[8]	*cis*	2715	8.655	12,430	26.4
Dimethyl fumarate[8]	*trans*	2807	8.830	12,880	27.2
Diethyl citraconate[4]	*cis*	2864	8.60	13,110	27.0
Diethyl mesaconate[4]	*trans*	2927	8.72	13,390	27.6
Dimethyl citraconate[9]	*cis*	2830	8.72	12,930	27.7
Dimethyl mesaconate[9]	*trans*	2730	8.61	12,480	27.2
Citraconic nitrile[9]	*cis*	3030	8.73	13,890	27.6
Mesaconic nitrile[9]	*trans*	2560	8.56	11,730	27.1

The heats of vaporization in cal./mole were determined from the relation, $\Delta H = 2.303\ RA$. The entropies of vaporization in cal./mole deg., were calculated at constant molal volume[10] from the relation, $\Delta S = \Delta H/T_m$, where T_m is the temperature at which V_m, the molal volume of the vapor, is 62.36 liters.

Discussion

Measurements of the vapor pressures of solid *trans*-diiodoethylene between −8 and 20°, as determined by Broadway and Fraser[5] by a molecular effusion method, give calculated heats and entropies of vaporization which are even less than those for the liquid observed in this investigation. An extrapolation of their data not only fails to intersect our curves near the melting point, but suggests a vapor pressure less than 25 mm. at the known boiling point of the liquid.

The compounds listed in Table II are chiefly disubstituted ethylenes in which the two substituting groups are identical. We have also included derivatives of citraconic and mesaconic acids because the methyl group is less polar than the other groups. We have omitted data on other pairs of isomers[11] in which the more polar substituting groups are not identical and in which the *cis* isomers are not necessarily more polar than the *trans*.

The data in Table II suggest that for compounds of this type the heat and entropy of vaporization of the *cis* isomer are greater than those of the *trans*. Small reversals of this generalization are shown by two of the pairs of esters, and for the entropies of vaporization of the dichloroethylenes. For all other pairs the values of ΔS for the *cis* form are from 0.3 to 3.5 entropy units greater than for the *trans*, and the value of ΔH is from 200 to 2100 cal. greater.

The precision of the data warrants only a qualitative discussion of the isomeric differences. Since the *cis* isomers are the more polar, it is not surprising that the additional dipole–dipole interaction should increase the energy of vaporization. The fact that the entropy of vaporization of the *cis* liquid to a specified molal volume of vapor is greater than the corresponding quantity for the *trans* liquid suggests that the *cis* form has a greater degree of order when the substituting groups are the same. It may be that the greater range of orienting forces due to the dipoles of the *cis* molecules favors larger or more frequent regions of semi-crystallinity than exist in the liquid *trans* isomer.

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Summary

The vapor pressures of the *cis* and *trans* isomers of dibromo- and diiodoethylene have been measured. A comparison of data for these compounds and for eight other pairs of isomers indicate that, for symmetrically disubstituted pairs, both the heat of vaporization and the entropy of vaporization of the liquid *cis* isomer are usually greater than those of the *trans* isomer. A qualitative explanation of these differences is suggested.

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(4) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517-550 (1947).

(5) L. F. Broadway and R. G. J. Fraser, *J. Chem. Soc.*, 429-431 (1933).

(6) R. W. Wackher, C. B. Linn and A. V. Grosse, *Ind. Eng. Chem.*, **37**, 464 (1945).

(7) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1946, Vol. III, p. 390.

(8) J. de Wolf and L. VandeStraete, *Bull. classe sci. Acad. roy. Belg.*, **21**, 216-225 (1935). These authors list additional measurements by other investigators which scatter rather badly and have been excluded from these calculations.

(9) L. VandeStraete, *ibid.*, **21**, 226-235 (1935).

(10) For reasons for using this method see J. H. Hildebrand, THIS JOURNAL, **37**, 970 (1915), and J. H. Hildebrand and T. S. Gilman, *J. Chem. Phys.*, **15**, 229-231 (1947).

(11) Crotonitrile, crotonic acid, 1-bromo-1-butene, 2-bromo-2-butene, tiglo- and angelonitriles, erucic and brassidic acids, and oleic and elaidic acids. See Stull, ref. 4. No conclusions can be drawn from data for these compounds.