[CONTRIBUTION FROM THE UNIVERSITY OF CHICAGO TOXICITY LABORATORY]

The Volatility and Vapor Pressure of Eight 2-Chloroethyl Alkyl (or Cycloalkyl) Sulfides[1]

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In conjunction with other studies in progress in this Laboratory it was necessary to determine the volatility[4] and vapor pressure of several 2-chloroethyl alkyl (or cycloalkyl) sulfides over the temperature range 0 to 60°. One of these compounds, bis-(2-chloroethyl) sulfide,[5] has been studied before, but other observations had indicated that there might be some considerable error in these data and that a re-evaluation of its volatility was desirable.

The static method of measuring the vapor pressure was unsatisfactory, since for some of these compounds the vapor pressure is only a few thousandths of a millimeter of mercury at 20° and its value needed to be known with considerable accuracy. Of the several dynamic methods the one known as the transpiration method, first described by Regnault[6] but frequently referred to as the method of Walker,[7] was chosen as most suitable. The direct measurement of volatility given by the Regnault procedure was especially desirable for the problem in hand. The apparatus used in these studies was patterned after that of Bent and Francel[8] and will not be described in this report except where important differences are present.

Experimental

Dried tank nitrogen was used as the entrainment gas for all compounds since it avoids possible oxidation of sensitive compounds and is less soluble in most organic compounds than is the oxygen of the air. Six sizes of bottles were used to meter this dry nitrogen before it was passed through the saturator. These bottles were of 1, 2.5, 4, 9, 20 and 50 liters capacity and their volume was determined to closer than ±0.1% by weighing the bottles empty and then filled with distilled water at a known temperature, from which the corrected volume of the bottle was computed.

The spiral condensation traps were cooled by a mixture of solid carbon dioxide and acetone rather than by liquid air as used by Bent and co-workers,[8] since computation indicated that even for a volatile liquid like water under equilibrium conditions at the temperature of solid carbon dioxide the amount of water vapor escaping uncondensed from the trap was far less than the error in weighing the trap when 100–200 mg. of water had been collected. A second cold trap was used in over-night runs, which might finish before the return of the operator, to avoid diffusion of moisture from the atmosphere back into the trap to be weighed.

The 20, 40 and 60° thermostats were of a conventional type with the necessary precautions observed for careful temperature regulation. The temperature was maintained constant to ±0.008° as measured at different points in the bath with a Beckmann thermometer over an extended interval of time. The 0° thermostat was a 1-gallon silvered Pyrex Dewar flask filled with crushed ice and distilled water. In some runs a small electrically driven stirrer was added to this bath, but since it was found to add nothing to the constancy of the temperature it was omitted in later runs.

Vaporizer.—The vaporizer shown in Fig. 1 was patterned after the one described by Bent.[8] It was modified to give more rapid saturation with less liquid[9] by using a coarse sintered glass disk at (A) and indentations at (B). For successful operation the inner spiral should be made from tubing having a bore of 3.5 to 4.0 mm. Both larger and smaller bore tubing are less satisfactory. The vaporizer required 6 to 8 ml. of compound for proper operation. When the vaporizer had been freshly filled with a compound, dry nitrogen was bubbled through the liquid for some hours to remove traces of moisture which may have been picked up during the filling operation. This also served to remove traces of lower boiling impurities in certain cases.

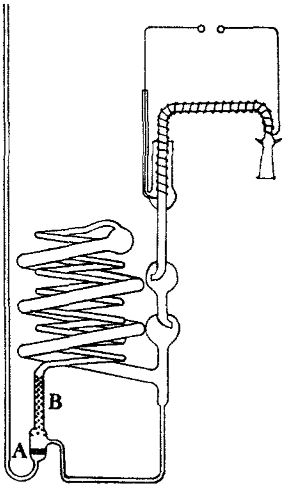

Fig. 1.—Vaporizer.

Presaturator.—In some runs it was considered desirable to approach saturation from both sides. The presaturator shown in Fig. 2 was used to accomplish this. It was connected to the inlet of a regular vaporizer just above the thermostated bath by means of a ground glass joint lightly lubricated on the outer 10 mm. of ground surface. The temperature of the presaturator was maintained about 20° higher than the thermostat bath surrounding the regular vaporizer by applying the proper voltage to the ends of the electrically heated coil by means of a variable transformer.

Results were the same when equilibrium was approached from both sides only if the rate of gas flow was sufficiently low when approaching equilibrium from the unsaturated side. This required rates of flow as low as 0.5 to 1.5 liters/hr. for those compounds which reached equilibrium most slowly. In general the compounds of low viscosity produced more rapid saturation of the nitrogen stream than was produced by the more viscous liquids.

Flow Regulator.—The needle valve used by Bent[8] to regulate the rate of flow of water from the reservoir into the metering bottle, displacing the contained nitrogen,

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[4] Volatility is defined as the mass of the volatile substance per unit volume of air (or nitrogen) saturated with the substance. In this report the unit of volatility is milligrams per liter.

[5] (a) Lamb, Carleton, Hughes and Nichols, THIS JOURNAL, **42**, 79 (1920); (b) Herbst, *Kolloidchem. Beih.*, **23**, 313 (1926); (c) Mumford, Phillips and Ball, *J. Chem. Soc.*, 589 (1932); (d) Jackson, *Chem. Rev.*, **15**, 425 (1934); (e) Holst and Melander, *Svensk Kem. Tid.*, **55**, 131 (1943).

[6] Regnault, *Ann. chim. phys.*, [3] **15**, 129 (1845).

[7] Walker, *Z. physik. Chem.*, **2**, 602 (1888).

[8] Bent and Francel, THIS JOURNAL, **70**, 634 (1948).

[9] A saturator requiring only a very small amount of liquid was necessary since for certain of the compounds studied only very small samples were submitted.

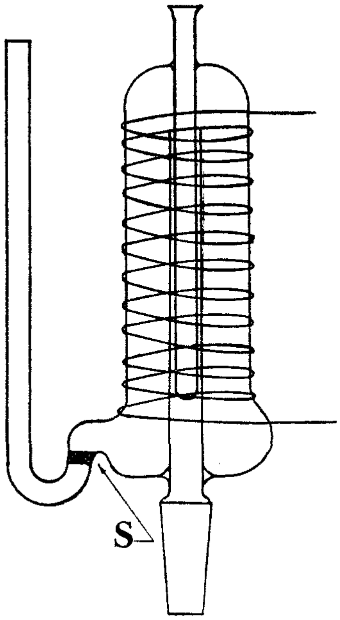

Fig. 2.—Presaturator: S, sintered glass disk.

was advantageously replaced by a calibrated flow regulator of the form shown in Fig. 3. The by-pass on the side of the regulator was opened when the water was forced back into the reservoir from the metering bottle. A series of these regulators was prepared having flow rates varying from 0.8 l./hr. to 6.0 l./hr. It was customary to use a different flow rate for each determination at a given temperature. If the results with different rates of flow checked, equilibrium was assumed to have been established; if the higher rate of flow gave a lower volatility than the slower rate of flow, it was assumed that the higher flow rate was too great and that saturation had not been secured. Only rates of flow slow enough to give concordant results were used.

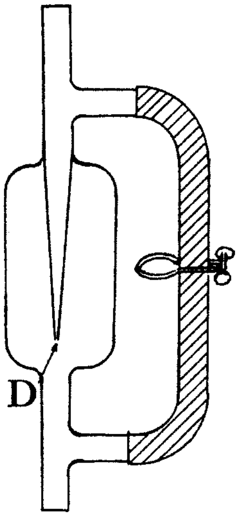

Fig. 3.—Flow regulator: D, diameter 0.5 to 0.1 mm.

Purification of Compounds.—As indicated in Table I all compounds studied were prepared in laboratories other than that of the authors. Samples were generally furnished in a purified form. Nevertheless, each sample was carefully fractionally distilled under reduced pressure from all-glass apparatus just prior to use. A fraction having an essentially constant boiling point was used for these measurements. The boiling range, refractive index and density of the fraction used are recorded in Table I. The refractive index of the material in the vaporizer was checked at the completion of a series of runs, in some cases, to make certain that no change in composition had occurred during the determination. Two samples of bis-(2-chloroethyl) sulfide, one made by the Levinstein[10] and one by the thiodiglycol[11] process, were each purified highly and run separately, thus giving an indication of the reproducibility of the method and the purity of the samples.

Treatment of Results

In the interest of economy of space the experimental points are not given, three to twelve measurements having been made at each temperature for each compound. Values agreeing within 1 to 3%, the lower limit for moderately volatile compounds and the upper limit for compounds of very low volatility, were used. The study of 2-chloroethyl 2-chlorocyclohexyl sulfide was made with somewhat less precision, but is included here for completeness. Exceptionally large values at the beginning of a run, due to traces of more volatile impurities, and points of obvious experimental error were discarded. Measurements were made for each compound at 20, 40 and 60° wherever possible, in some cases at 0, 20 and 40°, and in a few instances at 40 and 60° only because of the very low vapor pressure of the compound. The arithmetic mean of all points at any given temperature was taken for each compound. A smoothed curve was fitted to these mean points by the method of least squares.

The Clausius–Clapeyron equation was used in deriving appropriate relationships between the several variables since it was believed that over the small temperature range 0 to 60° these assumptions were justified: (1) the molal latent heat of vaporization remains essentially constant, (2) the vapor at these low partial pressures obeys the laws of ideal gases and (3) the volume of unit mass of the liquid phase is negligible in comparison with the volume of the same mass of the vapor at these temperatures and pressures. These assumptions allow the three equations used to be related quantitatively.

$$W = \frac{wT_1(p_2 - p)}{vT_2p_1} \qquad (1)$$

W = volatility expressed in mg./liter of nitrogen (or air) saturated with the compound.

w = increase in the weight of the trap in mg.

v = corrected volume, in liters, of the bottle metering out the dry nitrogen

T_1 = initial temperature of the gas in the metering bottle °K.

T_2 = temperature of the thermostat bath, °K.

p = vapor pressure of liquid under study, found by successive approximations, mm.

p_1 = barometric pressure when the bottle was closed after filling with dry nitrogen and equalizing to atmospheric pressure, mm.

p_2 = mean barometric pressure during the determination of mm.

$$\log p = A - B/T \qquad (2)$$

$$\log WT = A' - B/T \qquad (3)$$

in which $A' = A + \log M + 1.20520$. A, A', and B are constants and M is the molecular weight of the compound under study. In equations (2) and (3) pressure was expressed in mm., and temperature in ° K.

In Table II are shown the mean and the maxi-

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[10] M. Sartori, "The War Gases," 1st English ed., J. and A. Churchill, Ltd., London, 1939, p. 223.

[11] *Ibid.*, p. 220.

TABLE I

CONSTANTS OF THE 2-CHLOROETHYL ALKYL SULFIDES USED

Alkyl group	Formula	Boiling point °C.	Mm.	Refractive index n_D	°C.	Density G./cc.	°C.	Constants for equations A	A'	B
Methyl[a]	$ClC_2H_4SCH_3$	138.0–138.7	744			1.1155[e]	20	8.28937	11.53837	2215.7
Ethyl[a]	$ClC_2H_4SC_2H_5$	71–72	40	1.4878	20	1.0664[g]	20	8.29455	11.59502	2318.8
2-Chloroethyl[b] (Levinstein)	$(ClC_2H_4)_2S$	105, M. p. 14.2–14.4	14	1.5220[d]	30	1.2684[d]	25	9.31448	12.72119	3061.5
2-Chloroethyl[c] (Thiodiglycol)	$(ClC_2H_4)_2S$	110 M. p. 14.4	20	1.5220[d]	30	1.2681[d]	25	9.31768	12.72439	3062.5
Allyl[a]	$ClC_2H_4SCH_2CH{=}CH_2$	66–67[h]	14	1.5071	20	1.0761[h]	20	8.88346	12.22408	2619.9
Benzyl[a,f]	$ClC_2H_4SCH_2C_6H_5$	145	13	1.571	20	1.1477[g]	25	7.37666	10.85044	2733.4
2-Chlorocyclopentyl[a]	$ClC_2H_4SC_5H_8Cl$	125–127	10	1.5322	25	1.2370	25	9.72886	13.23306	3444.6
2-Chlorocyclohexyl[a]	$ClC_2H_4SC_6H_{10}Cl$	139–143	7	1.5369	25	1.2168	20	8.7460	12.28018	3265.5
Bis-(2-chloroethyl) trisulfide[a,i]	$(ClC_2H_4)_2S_3$	M. p. 28–29		1.6050	30	1.3940	30	9.23029	12.78410	3565.7

[a] Supplied by Dr. R. C. Fuson. [b] Supplied by Edgewood Arsenal. [c] Supplied by Dr. R. Norris Shreve. [d] According to Mumford's equations (ref. 5c) the refractive index at 30° is 1.5226 and at 25° the density is 1.2693. [e] Kirner (THIS JOURNAL, **50**, 2446 (1928)) gives d^{20}_{20} 1.1245. [f] This compound behaved as if it were undergoing decomposition during the determination. Results may not be closer than ±10% for this compound. However, Kilmer and du Vigneaud (*J. Biol. Chem.*, **154**, 247 (1944)) report the b. p. as 105–108° (1.5 mm.). The value calculated from our equation is 106.6° (1.5 mm.). [g] Dawson (THIS JOURNAL, **55**, 2070 (1933)) gives d^{25}_4 1.0663 for the ethyl derivative and d^{25}_4 1.1479 for the benzyl compound. [h] Sherlin and Vasilevksii (*J. prakt. Chem.*, **121** 173 (1929)) report the boiling point as 67.5–69° (12 mm.) and the density as d^{20}_{20} 1.0768. [i] R. C. Fuson, *et al.*, *J. Org. Chem.*, **11**, 484–498 (1946).

mum percentage deviation from the smoothed curve of the experimental points. For all the compounds except the 2-chlorocyclohexyl 2-chloroethyl sulfide the mean deviation is less than 2%. The mean and the maximum deviation are also included for the points calculated, using the least squares equation, from the smoothed curve values. The small percentage deviations of these points indicates that the equation describes the curve accurately over the temperature range studied.

TABLE II

PRECISION OF DATA

Alkyl group	Percentage deviation from the smoothed curve of Experimental points Mean	Maximum	Points calculated from least squares equation Mean	Maximum
Methyl	0.5	1.1	0.2	0.3
Ethyl	0.9	1.5	.02	.05
2-Chloroethyl	1.5	3.8	.3	.7
Allyl	0.6	0.9	.2	.4
Benzyl	1.8	2.2	.1	.3
2-Chlorocyclopentyl	1.9	2.9	.1	.2
2-Chlorocyclohexyl	3.5	6.1	1	.3
Bis-(2-chloroethyl) trisulfide	1.5	2.7	3	.8

A consideration of the known sources of error involved in these determinations would indicate a probable error of ±1 to 2%, depending upon the size of the sample collected in the weighing trap. However, since several of the systemic errors tend to cause low results, it is almost certain that the results herein reported will tend to be low, if in error.

The two samples of bis-(2-chloroethyl) sulfide, prepared by different methods, gave vapor pressure determinations which were in excellent agreement as shown by a percentage deviation from the mean of only 0.5% at both ends of the temperature range, and since the sign of the deviation was the same at both limits, the curves were parallel. This speaks well for the reproducibility of the method. Balson, Denbigh and Adams[12] have recently reported their study of the vapor pressure of bis-(2-chloroethyl) sulfide made concurrently with our study. Their results over the temperature range common to both studies are in quite good agreement with our own.

The equations reported are supposed to apply quite precisely between 0 and 60°, but they may be used over a much larger temperature range if somewhat larger errors can be permitted. It must also be borne in mind that these equations are for the liquid phase only.

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Summary

1. The volatility of eight 2-chloroethyl alkyl (or cycloalkyl) sulfides has been measured between 0 and 60° by a transpiration method.

2. Vapor pressures have been calculated from the volatility measurements, and using these values logarithmic equations have been calculated for both the volatility and the vapor pressure of these compounds.

3. The mean molar latent heat of evaporation has been calculated from the derived vapor pressure equation for each compound.

4. The probable error of these determinations over the temperature range 0 to 60° is estimated to be ±1 to 2%. The equations may be used for extrapolating to temperatures outside these limits with somewhat larger errors.

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(12) Balson, Denbigh and Adams, *Trans. Farad. Soc.*, **43**, 42 (1947).