[Contribution from the University of Chicago Toxicity Laboratory]

The Vapor Pressure of Eleven Organic Compounds[1]

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In order to complete other work in progress in this Laboratory, it was necessary to have accurate data over the temperature range 0 to 60° for the volatility of the compounds reported in this study. The volatility is readily computed from the vapor pressure but a search of the literature revealed that trichloronitromethane (chloropicrin)[4] was the only compound in the group for which data were available. For the remaining compounds data were so scarce as to make it difficult even to estimate their volatility. The volatility was therefore measured for these compounds by the method described in earlier reports.[5] The vapor pressure has been computed from the experimentally measured volatility and is here reported since it is more generally useful than the volatility.

Experimental

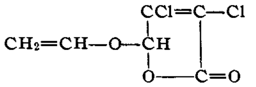
A description of the apparatus used and details of the measurements were reported in an earlier paper.[5b] For each compound at each temperature studied determinations were repeated until a constant reproducible volatility was obtained. If in any series of measurements there was a trend from high values to lower ones this series was continued until the results varied only in a random manner.

All the compounds here reported were prepared in laboratories other than the authors'. The source of each compound is given in a footnote to Table I. The compounds were submitted to our laboratory as pure compounds; however, whenever the sample was large enough to allow further purification it was carefully fractionally distilled in all-glass equipment containing a short Vigreux column before making any measurements upon it. In a few cases the sample submitted was too small to allow any further purification before use. The boiling point (or range), refractive index, and density reported in Table I were those observed for the sample just prior to use. The identity of each compound was assumed to be that stated by the submitter.

Nitrogen was used as the inert carrier gas as in previous studies.[5] No evidence of polymerization or oxidation during any of the studies was observed.

Table I

Constants of the Compounds Studied

Compound	Formula	Boiling point ° C.	Boiling point Mm.	Refractive index n_D	Refractive index ° C.	Density G./ml.	Density ° C.	Constants A	Constants A'	Constants B
Trichloronitromethane[a]	Cl_3CNO_2	109.5–110	755	1.4611[i]	20	1.6558[i]	20	8.27526	11.69636	2054.3
Dimethyl acetylenedicarboxylate[b]	$(CCOOCH_3)_2$							9.20815	12.56598	2941.4
Methyl cyanoformate[c]	$CH_3OCO(CN)$	97	751			1.072[j]	20	8.4433	11.5782	2053.6
Vinyl mucochlorate[d]		115	15	1.5028	25			9.8293	13.3245	3340.3
Phenylcarbylamine chloride[e]	$C_6H_5N{=}CCl_2$	104–105	28	1.5673	25	1.2330[k]	25	8.907	12.353	2820
3-Bromopentanone-2[f]	$CH_3COCH(Br)C_2H_5$	56	21	1.4579	20	1.3406	25	8.4256	11.84841	2359.4
		63–64	32							
1-Chloro-2-triazoethane[f]	$N_3CH_2CH_2Cl$	38–38.5	22	1.4658	20	1.2216[l]	20	8.7112	11.9397	2287.3
2-Nitrobutene-1[g]	$CH_2{=}C(NO_2)C_2H_5$	61	50	1.4373	20	1.0188	20	8.6073	11.8172	2298.7
1-Nitropropene[g]	$NO_2CH{=}CHCH_3$	59–60	34	1.4539[m]	20	1.0650[m]	20	8.4592	11.6041	2306.3
2-Nitropropene[g]	$CH_2{=}CH(NO_2)CH_3$	54	74			1.0660[n]	20	7.9272	11.0721	1993.1
1-Hydroxy-2-pentyne-4-one[h]	$HOCH_2C{\equiv}CCOCH_3$	88.5–89.5	5	1.4571	20	1.0765	20	10.1725	13.3691	3362.6

[a] Eastman Kodak Co. White Label. [b] From Dr. M. S. Kharasch, University of Chicago. The sample was too small to permit further purification before use. [c] From Dr. C. D. Hurd, Northwestern University. [d] From Dr. C. A. Thomas, Monsanto Chemical Co. [e] From Dr. Henry Gilman, Iowa State College. [f] From Dr. G. H. Coleman, University of Iowa. [g] From Dr. Marvin Gold, Visking Corp. [i] Brühl, *Z. physik. Chem.*, **16**, 214 (1895), gave $n^{22.8}_D$ 1.46075 and d^{20}_4 1.6539. [j] Karvonen, *C. A.*, **18**, 1981–1982, gives d^{20} 1.0719. [k] Dyson and Harrington, *J. Chem. Soc.*, 193 (1940), report a density of 1.285 at 15°. [l] Foster and Newman, *ibid.*, **97**, 2576 (1910), give the density as 1.2885 at 24°. [m] Schmidt and Rutz, *Ber.*, **61**, 2146 (1928), give n^{20}_D 1.4527 and d^{20}_4 1.0661. [n] Blomquist, Tapp and Johnson, This Journal, **67**, 1519 (1945), give a density, which corrected to d^{20}_4 is 1.0509, appreciably less than we found. Their boiling range of 48–49° (59.5 mm.) agrees moderately well with the temperature calculated from our equation at which the pressure is 59.5 mm.

Results

In Table I are recorded, in addition to the physical constants of the compounds, the three constants A, A' and B for the two equations

$$\log p = A - B/T \qquad (1)$$

$$\log WT = A' - B/T \qquad (2)$$

computed by the method of least squares from the experimental points. These constants apply when the pressure is expressed in millimeters of mercury, the temperature, T, is the absolute tem-

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(4) (a) Baxter, Bezzenberger and Wilson, This Journal, **42**, 1388 (1920); (b) Herbst, *Kolloid Beihefte*, **23**, 330 (1927); (c) Blaszkowska-Zakrzewska, *Roczniki Chem.*, **8**, 210 (1928); **8**, 219 (1928); (d) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(5) (a) Bent and Francel, This Journal, **70**, 634 (1948); (b) Redemann, Chaikin and Fearing, *ibid.*, **70**, 631 (1948).

perature and the volatility, *W*, is expressed in milligrams of agent per liter of nitrogen (or air). From these equations it is possible to calculate the vapor pressure, volatility, mean molar heat of vaporization, etc.

In Table II are recorded data pertaining to the precision of measurements for each compound described in this report. While these data would indicate a precision of about 1% for most of the measurements, the vapor pressure, as computed by the equations given, may have an error somewhat larger than this amount since the vapor pressures calculated from the volatility in an inert gas stream are too large according to Gerry and Gillespie.[6] The values from which the constants given in Table I were determined were not corrected for this factor since the volatility in an inert gas was the quantity desired at the time the experimental work was done and consequently no additional measurements were made by which these corrections could be made.

TABLE II

PRECISION OF EXPERIMENTAL DATA

	Percentage deviation from smoothed curve of			
	Experimental points		Points calculated from least squares equation	
Compound	Maximum	Mean	Maximum	Mean
Trichloronitromethane	0.99	0.46	0.36	0.24
Dimethyl acetylenedicarboxylate	1.7	.57	.52	.23
Methyl cyanoformate	0.89	.53	.47	.33
Vinyl mucochlorate	1.8	.98	.68	.27
Phenylcarbylamine chloride	2.43	1.24	.63	.38
3-Bromopentanone-2	1.34	0.54	.24	.18
1-Chloro-2-triazoethane	1.05	.66	.22	.21
2-Nitrobutene-1	1.84	.99	.12	.07
1-Nitropropene	1.60	.80	.18	.09
2-Nitropropene	1.07	.67	.49	.33
1-Hydroxy-2-pentyne-4-one	0.35	.18	.17	.11

Discussion

Since considerable data[4] were available for trichloronitromethane, redetermination of its vapor pressure was primarily for comparison of results. In Table III the results of several workers are compared at four temperatures. Blaszkowska-Zakrzewska[4c] also give two different values for the vapor pressure at 100° from direct measurements by two different methods, 532.0 and 524.3 mm. From the above Table and these data, the Hertz equation would appear best for the entire temperature range. Both Baxter's equation and ours are satisfactory at lower temperatures where the measurements were made, but give values which are too large at elevated temperatures by 9–11%. In the range 0 to 40° the first three equations give values agreeing within 2%.

TABLE III

COMPARISON OF VAPOR PRESSURES COMPUTED FOR CHLOROPICRIN FROM VARIOUS EQUATIONS

	Pressure in millimeters at ° C.			
Equation	0	20	40	100
Our	5.70	18.57	52.02	590
Hertz[4c]	5.68	18.56	51.31	530
Baxter[4a]	5.64	18.30	51.32	579
Blaszkowska-Zakrzewska[4c]	6.88	20.75	54.40	527

The generalizations for chloropicrin probably are also approximately true for all the compounds reported here, namely: within the temperature range 0 to 60° the results are good to 1 to 2%, but outside this range the error may become much larger.

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Summary

1. The volatility of eleven organic compounds has been measured by a dynamic method.

2. The corresponding vapor pressures have been computed from the volatilities, and the constants for logarithmic equations for both the volatility and vapor pressure have been calculated.

3. The vapor pressure found for trichloronitromethane has been compared with measurements made by previous workers.

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(6) Gerry and Gillespie, *Phys. Rev.*, **40**, 269 (1932).