Physical Properties and Thermodynamic Functions of Trichloroacetonitrile.

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The density, vapour pressure, refractive index, dielectric constant, and near infra-red and ultra-violet absorption spectra of liquid trichloroacetonitrile have been determined, and values of the thermodynamic functions calculated.

TRICHLOROACETONITRILE is a lachrymatory liquid which has been used as a fumigant. A number of its simpler physical properties have been reported. Its solvent properties, in which capacity as a derivative of acetonitrile it might be expected to offer favourable characteristics, have not been reported. A prerequisite to its use as a solvent in physicochemical studies is adequate characterisation of its physical properties. The present account deals with the properties mentioned in the summary.

EXPERIMENTAL

Preparation and Purification.—The preparation from trichloroacetic acid was as follows:

$$Cl_3C{\cdot}CO_2H + EtOH = Cl_3C{\cdot}CO_2Et + H_2O$$
$$Cl_3C{\cdot}CO_2Et + NH_3 = Cl_3C{\cdot}CO{\cdot}NH_2 + EtOH$$
$$Cl_3C{\cdot}CO{\cdot}NH_2 = Cl_3C{\cdot}CN + H_2O$$

Ethyl trichloroacetate (200 g.) was fractionally distilled and treated with an equal volume of aqueous ammonia (*d* 0·880). Ammonia gas was bubbled through the flask for 0·5 hr. until reaction appeared to be complete. The mixture was kept cool overnight and the amide was filtered off and dried by suspending 100-g. portions in 600 ml. of carbon tetrachloride and removing the water by azeotropic distillation. The amide was filtered off and kept in a desiccator (KOH–paraffin wax).

Dehydration to trichloroacetonitrile was most efficiently done by heating the amide in 150-g. lots with its own weight of phosphoric oxide, the last 40 g. of which were shaken over the well-mixed constituents (McBee, Pierce, and Bolt, *Ind. Eng. Chem.*, 1947, **39**, 391. See also, *Ber.*, 1896, **29**, 2417; 1908, **41**, 2540; 1927, **60**, 1765; 1934, **67**, 1762) : a further 20 g. were added before the nitrile was distilled off. The product was carefully refractionated from phosphoric oxide, the portion boiling at 85·8—86·0°/764 mm. being retained (yield 60% based on the amide).

Infra-red measurements showed that certainly less than 0·02% of the amide was present; a similar figure represents the maximum amount of C–H-containing impurity (assumed to be acetonitrile). Neither N–H nor C–H absorptions could be detected in the liquid by use of a 1-mm. cell. After several months the liquid showed no signs of change even with traces of moisture, provided it was kept in complete darkness.

Another sample, kindly sent to us by the Deutsche Gold- und Silber-Scheideanstalt, had the same properties as our preparation.

Density.—Repeated determinations with a 10-ml. pyknometer having ground stoppers to prevent evaporation gave values (vacuum-corrected) :

$$\text{at } 25{\cdot}00^\circ \pm 0{\cdot}02^\circ : \quad d_4^{25} = 1{\cdot}4403 \pm 5 \times 10^{-4} \text{ g./c.c.}$$

$$\text{at } 35{\cdot}0^\circ \pm 0{\cdot}1^\circ : \quad d_4^{35} = 1{\cdot}4223 \pm 5 \times 10^{-4} \text{ g./c.c.}$$

The mean coefficient of cubical expansion over this range is $12{\cdot}_6 \times 10^{-4}$ per centigrade degree.

Vapour Pressure.—The semimicro-modification of the Smith–Menzies isoteniscope (Steinbach and Devor, *J. Chem. Educ.*, 1945, **22**, 496) has the advantages of requiring small amounts of liquid and of ensuring rapid thermal equilibrium with the bath. The bath was a 2-l. beaker containing water–glycerol which was vigorously stirred mechanically while being heated with a micro-burner. Its temperature was maintained constant within 0·1° for periods of 15 min. The scale of the wide-bore manometer, checked by a cathetometer, was read to 0·5 mm. Exposed-stem corrections were applied to the thermometer whose bulb was close to the vessel in which the liquid boiled : it was read to 0·05° and checked against N.P.L. standards. In four runs the extreme readings for the vapour pressure at 20·0° differed by 1·5 mm. Whilst the plots of $\log_{10} p$ against $1/T$ for each run suggested a slight curvature, the total number of acceptable points did not provide conclusive evidence of a deviation from a straight-line relation. In Table 1 a selection of the observed values are given with, for comparison, the percentage deviations from equation (1) and the Antoine equation, (2).

$$\log_{10} p \text{ (mm.)} = 7{\cdot}853 - 1783/T \ (T = {}^\circ\text{K}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\log_{10} p \text{ (mm.)} = 7{\cdot}013 - 1275/(t + 222{\cdot}8) \ (t = {}^\circ\text{C}) \quad . \; . \; . \; . \; . \quad (2)$$

TABLE 1. *Vapour pressures of trichloroacetonitrile.*

Temp.	p (mm.), obs.	Deviation (%) from (1)	Deviation (%) from (2)	Temp.	p (mm.), obs.	Deviation (%) from (1)	Deviation (%) from (2)
16·80°	49·0	−2·4	−0·4	50·15°	222·0	+2·3	+1·6
17·30	51·0	−1·0	+1·0	56·00	273·5	+0·7	−0·7
20·00	58·0	−1·2	+0·4	61·65	340·5	+1·2	+0·3
20·00	58·5	−0·4	+1·2	65·40	388·0	+0·6	0·0
23·40	68·5	−1·1	+0·4	66·90	458·5	+1·7	+1·3
26·55	80·0	0	+0·5	73·65	521·0	+1·4	+0·9
31·00	98·5	+0·8	+1·0	76·65	572·5	+0·6	+0·3
35·05	118·5	+1·5	+0·5	79·75	635·5	+0·7	+0·7
40·40	147·5	+0·9	0·0	83·40	709·5	+0·2	+0·5
47·00	192·5	+0·3	−0·5				

From these results the normal boiling point is 85·7° ± 0·2°/760 mm., the mean latent heat of evaporation is 8160 cal./mole, and the entropy of vaporisation at the boiling point (Trouton constant) is 22·8 cal./mole/°K. The corresponding figures for acetonitrile are 81·2°, 8030 cal./mole and 22·7 cal./mole/°K (Heim, *Bull. Soc. chim. Belg.*, 1933, **42**, 461). On the basis of the Trouton constants these liquids are unassociated.

Refractive Index.—A Pulfrich instrument was used with a sodium lamp and hydrogen discharge tube as sources : the temperature was maintained within ±0·1° by a water stream. The values were: $n_D^{20\cdot0} = 1{\cdot}4409 \pm 0{\cdot}0001$; $n_D^{27\cdot0} = 1{\cdot}4375 \pm 0{\cdot}0001$; $dn/dt = 4{\cdot}9 \times 10^{-4}$ per centigrade degree. The refractive index differences were : $n_D^{20} - n_C^{20} = (248 \pm 5) \times 10^{-5}$, $n_F^{20} - n_D^{20} = (620 \pm 5) \times 10^{-5}$, $n_G^{20} - n_F^{20} = (116 \pm 10) \times 10^{-5}$. The specific dispersion, $10^4(n_F - n_C)/[\text{Density}] = 59{\cdot}9$ ml./g. The addition of 0·2% of trichloroacetamide to the nitrile increased the refractive index by 0·0002. As the amide is produced from the liquid on exposure to light in the presence of moisture, this factor can be used to check the purity of the trichloroacetonitrile.

Ultra-violet Absorption.—The measurements made with a Hilger Uvi-spec spectrometer are shown in Fig. 1 together with the measurements, for comparison for the liquids chloroform and acetonitrile, relative to which (and to carbon tetrachloride) the absorption is shifted towards the visible.

Infra-red Absorption.—This was measured on a Grubb–Parsons S.3 single-beam instrument coupled to a Elliotronic 10-in. chart recorder. A rock-salt prism and cells of 1·0 mm., 0·1 mm., and capillary thickness were used.

The absorptions in the 3μ region were used to check the presence of $-NH_2$ and $-CH$ groups in the purified trichloroacetonitrile. Fig. 2 emphasises the satisfactory nature of the material. Later, a strong absorption was found near 1720 cm.$^{-1}$ in liquid which had been exposed to, *e.g.*, the total radiation from the Nernst filament source. This absorption is probably largely due to carbonyl impurities such as the amide or carbonyl chloride and, as the carbonyl group is one of the most intense absorbers in the infra-red, its presence provides a sensitive criterion of purity in trichloroacetonitrile.

The trichloroacetonitrile molecule is assumed to have the same symmetry as methyl chloride, *i.e.*, C_{3v}. Accordingly its twelve fundamental vibrational modes consist of four symmetric ones (class A_1) and four doubly-degenerate (class E) vibrations, all of which should be Raman-active. Mecke (Landolt–Börnstein, " Tabellen," 6th edn., Vol. I, Part 2, Springer Verlag, Berlin, 1951) assigned the eleven Raman frequencies reported by Cheng (*Z. physikal. Chem.*, 1934, **26**, *B*, 288) and if $r(CCl_3)$, the degenerate rocking frequency of the CCl_3-group is added at 350 cm.$^{-1}$ (which is suggested by combination bands in the infra-red), most of the observed frequencies can be accounted for. The symbols ν, b, s, and a refer to fundamental stretching, bending, symmetric, and antisymmetric modes respectively; the values are :

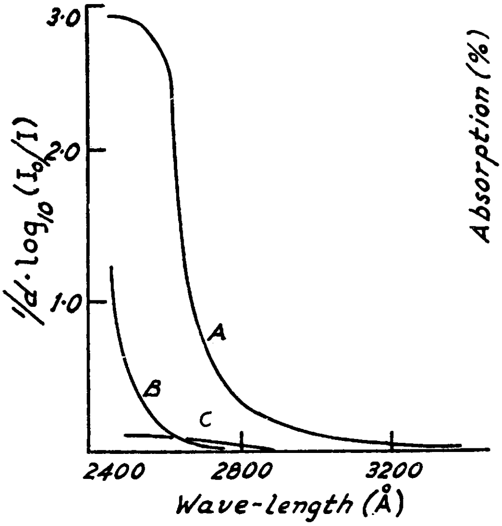

FIG. 1. *Absorptions in the near ultra-violet.*

A, Trichloroacetonitrile. *B*, Chloroform. *C*, Acetonitrile.

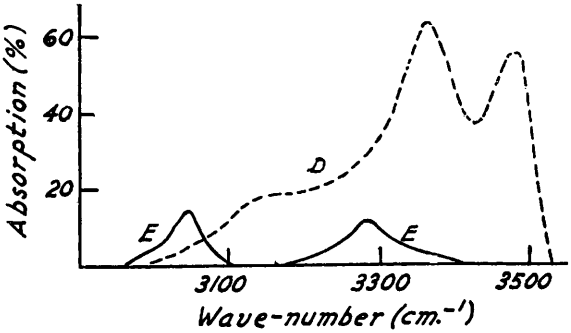

FIG. 2. *Infra-red absorptions* (1·0 *mm. cell*).

D, Trichloroacetamide (0·5% in trichloroacetonitrile).
E, Pure trichloroacetonitrile.

Class A_1 *vibrations*		*Class* E *vibrations*	
$\nu_s(CCl_3) = 487$ cm.$^{-1}$	$b_s(CCl_3) = 316$ cm.$^{-1}$	$b_a(CCl_3) = 265$ cm.$^{-1}$	$r(CCl_3) = 350$ cm.$^{-1}$
$\nu(CN) = 2250$ cm.$^{-1}$	$\nu(CC) = 1030$ cm.$^{-1}$	$\nu_a(CCl_3) = 792$ cm.$^{-1}$	$b(CCN) = 163$ cm.$^{-1}$

Table 2 shows the absorption centres measured and the intensities observed with the liquid in a 0·10-mm. cell: the absence of an entry in the 2nd and 5th columns means that the absorption was only observed in a longer (1·0 mm.) cell. Between 640 and 1400 cm.$^{-1}$, Cheng and Lecomte (*Ann. Physik*, 1936, **5**, 427) reported absorption maxima for trichloroacetonitrile in solution at 742, 790, 962, and 1010 cm.$^{-1}$. Clearly, in the pure liquid the weaker peak at 742 cm.$^{-1}$ is not resolved in the intense absorption from 750 to 814 cm.$^{-1}$.

This complete set of vibrational frequencies enables the thermodynamic factors for trichloroacetonitrile to be calculated by way of the standard partition functions. The values so obtained refer to an assumed ideal gas state at a pressure of one atmosphere and are based on the rigid-rotator, harmonic-oscillator model. The vibrational contributions were evaluated by using Torkington's tables (*J. Chem. Phys.*, 1950, **18**, 1373); for the other modes the relations given by

Wagman *et al.* (*J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) were used. Assuming that the CCl_3-group had the same structure as in chloroform (Unterberger, Trambarulo, and Smith, *J. Chem. Phys.*, 1950, **18**, 565) and that the other bond lengths were : C–C, 1·48 Å, and C≡N, 1·16 Å (cf. Table 38, Stuart, " Die Struktur des Freien Moleküls," Springer Verlag, Berlin, 1952), then $I_1I_2I_3$, the product of the moments of inertia (Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431), $= 1{\cdot}1632 \times 10^{-112}$ g.^{3} cm.^{6}; σ, the symmetry number, = 3, and M, the molecular weight, = 144·40.

TABLE 2. *Infra-red absorptions of trichloroacetonitrile.*

Absorption, cm.$^{-1}$	% absorption 0·1-mm. cell	Assignment	Absorption, cm.$^{-1}$	% absorption 0·1-mm. cell	Assignment
680	—	1026 − 350 = 674 *or*	1368	—	1026 + 350 = 1376
		350 × 2 = 700	1469	—	2250 − 792 = 1458
750 to 814	100	792	1580	30	792 × 2 = 1584
861	30	1026 − 163 = 863	1735	10	C = O of impurity
914	—	2250 − (1026 + 316)	1816	10	1026 + 792 = 1818
		= 908	2090	—	2250 − 163 = 2087
968 to 980	100	487 × 2 = 974	2205	extremely weak	—
1025 to 1035	100	1030	2250	70	2250
1100	5	792 + 316 = 1108	2402	15	2250 + 163 = 2413
1133	—	792 + 350 = 1142	2502	—	2250 + 265 = 2515
1186	10	1026 + 163 = 1189	2728	—	2250 + 487 = 2737
1225	—	2250 − 1026 = 1224	3043	—	2250 + 792 = 3042
1274	20	792 + 487 = 1279	3278	—	2250 + 1026 = 3276

TABLE 3. *Thermodynamic functions calculated for trichloroacetonitrile in ideal gas state at* 1 *atmosphere* (cal./mole/°K).

T° K	273·15	298·15	300	400	600	800	1000
$C°_p$	22·22	22·95	23·00	25·17	27·59	28·90	29·70
$(H° - H_0°)/T$	15·16	15·79	15·83	17·92	20·79	22·67	24·00
$-(G° - H_0°)/T$	63·16	64·52	64·62	69·48	77·33	83·91	89·08
$S°$	78·32	80·31	80·45	87·40	98·12	106·58	113·08

Dielectric Constant.—The dielectric constant was measured for the liquid in a Hartshorn–Ward resonance circuit apparatus (*J. Inst. Elect. Eng.*, 1936, **79**, 597). The auxiliary cell, of rhodium-flashed stainless steel, in which the dielectric constant was measured, held approx. 10 ml. of liquid and had an air capacity of 80 μμF. Owing to the limits in the calibration of the variable condenser the capacity of the auxiliary cell had to be measured in series with a fixed silver–mica capacitor. This condition and the fact that the apparatus was originally designed to measure dielectric absorption markedly reduced the accuracy attainable in the measurement of the dielectric constant. From measurements at 210 kc./sec. a generous estimate of the uncertainty gave the value at 19°, $\varepsilon = 7{\cdot}85 \pm 0{\cdot}2$. When the Onsager relation (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) for the dipole moment (μ) in terms of dielectric constant (ε), refractive index (n), and density (d) of a pure polar liquid of molecular weight (M) is used, *i.e.*,

$$\mu^2 = \frac{9MkT(\varepsilon - n^2)(2\varepsilon + n^2)}{4\pi N \,.\, d\varepsilon(n^2 + 2)^2}$$

the value $\mu = 1{\cdot}93$ D is evaluated. On the simplest assumptions for constancy of group moments, this value should be equal to the difference between the moments for acetonitrile and chloroform, which is 2·1 D. The agreement is not unreasonable.

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