346. *The Vapour Pressure and Lattice Energy of Hydrogen-bonded Crystals. Part I. Oxamide, Oxamic Acid, and Rubeanic Acid.*

By R. S. BRADLEY and T. G. CLEASBY.

The vapour pressure and lattice energy of oxamide, oxamic acid, and rubeanic acid have been determined over the respective temperature ranges 80·4—96·45°, 81·6—90·75°, 86·90—105·15° by an effusion method. It has been shown that oxamide is monomeric in the vapour.

OXAMIDE, oxamic acid, rubeanic acid (dithio-oxamide), and anhydrous oxalic acid (discussed in Part II, following paper) form an interesting series of hydrogen-bonded molecular crystals. The structures of the crystals, with the exception of oxamic acid, have been studied, but not all are known in detail; oxamide has been studied by Misch and van der Wyk (*Compt. rend. Soc. Phys. Nat., Genève,* 1938, **55**, 96), rubeanic acid by Jeffrey and Markey (to be published), and oxalic acid by Hendricks (*Z. Krist.*, 1935, **91**, 48), and recently also by Cox, Dougill, and Jeffrey, (*J.*, 1952, 4854). It was hoped to make a comparative study of the lattice energies of these crystals, and to make more detailed calculations later.

EXPERIMENTAL

A pure sample of oxamide, obtained from Professor E. G. Cox, was heated *in vacuo* for a few hours at 100° to remove any volatile impurities. Anhydrous oxamic acid (L. Light and Co. Ltd.), purified by vacuum sublimation at 100°, had m. p. 209° (decomp.), and micro-analysis showed that the nitrogen and carbon content agreed with the theoretical to within 1%. Rubeanic acid was purified by crystallisation from pyridine, followed by vacuum sublimation at 100°.

The method for measuring the vapour pressure was similar to that used by Bradley (*Proc. Roy. Soc.*, 1951, **205**, *A*, 553). The rate of effusion of vapour through a small hole in the platinum window of an effusion vessel was determined by means of the loss of weight recorded on a silica micro-balance. The apparatus, shown in Fig. 1, was modified to operate at 80—100° and also to enable a determination of the molecular weight of the vapour to be made, in a manner similar to that of Volmer (*Z. physikal. Chem.*, Bodenstein Festband, 1931, 863). The effusion vessels *A* consisted of soft-glass bulbs with long necks, and carried platinum windows drilled with holes of diameter approx. 1 mm. Thin discs of aluminium rested on the bulbs to act as radiation shields. The bulbs were joined by a rigid arm and were so disposed that the holes were on opposite sides of the arm, so that on effusion of the vapour a torque was applied to the framework. The framework was suspended from a silica micro-balance *B* by a suspension which carried a small galvanometer mirror *C* so that the reflection of a scale in the mirror could be viewed in a telescope. Most of the suspension consisted of stiff silica fibre; the torsion fibre was that carrying the hook of the balance, *i.e.*, a very short thin fibre. Deflections of the micro-balance due to loss in weight could be followed by means of a travelling microscope. The system could be evacuated to less than 10^{-5} mm. The effusion vessel was heated by a double-walled vapour jacket *D*; the temperature was recorded on the Anschütz thermometer lying near the effusion vessel. Normally, when the runs were done at 80—100°, the effusing vapour condensed on the water-cooled joint *E*, but for runs at lower temperatures, *e.g.*, when benzophenone was used for calibration, a cold finger *F*, cooled by acetone–solid carbon dioxide, was used. *G* is a small piece of aluminium foil hung from the effusion vessel in order to reduce oscillations by the use of a powerful magnet brought up to the apparatus.

It was planned to record the torsion and rate of change of weight at almost the same time, but difficulties due to oscillation were met, and the following procedure was adopted. The effusion vessels were filled through the stem and sealed off, the apparatus was assembled, and the balance load adjusted so that the beam swung freely. The balance beam was then pressed down by the arrestment arm *H*, which could be rotated in the ground joint. The pressure was reduced to 1 mm. of mercury and the zero reading of the torsion was taken at room temperature. The magnet was brought up into position, the boiler was started, and after 30 min. the system was evacuated to less than 10^{-5} mm. of mercury. After 15 min. the magnet was slowly withdrawn by means of a platform carrying a rack and pinion, and after 5 min. the reading of the torsion was taken. There was always a small residual oscillation, the limits of which were recorded. During the whole of this part of the run the beam was held in a fixed position against the arm, so that the torsion hook fibre was always disposed in the same way for repeat runs; the torsional constant of the fibre varied slightly according to the tilt of the beam.

The beam rest was then released, and the oscillations of the beam were damped by suitably moving the beam rest. Deflection–time readings were taken by means of a travelling microscope and a stop-watch, care being taken to read the reference pointer on the balance. The beam was then returned to its fixed position by means of the arrestment; the boiler heater was switched off, 1 mm. of dry air was admitted, and the zero of the torsion checked at room temperature.

The runs using oxamide were calibrated by means of very pure sulphur at 62—63°, with reference to Neumann's data (*Z. physikal. Chem.*, 1934, *A*, **171**, 416). With oxamic and rubeanic acids, for which the vapour pressure alone was studied, benzophenone was used at 38—44°, with reference to Neumann and Volker's data (*ibid.*, 1932, *A*, **161**, 33). In addition, an absolute determination was made by finding the hole area and thickness photomicrographically. Agreement was obtained with the indirect determination to within 1% after allowance for the tube resistance of the effusion hole by Clausing's method (*Ann. Physik*, 1932, **12**, 961).

FIG. 1.

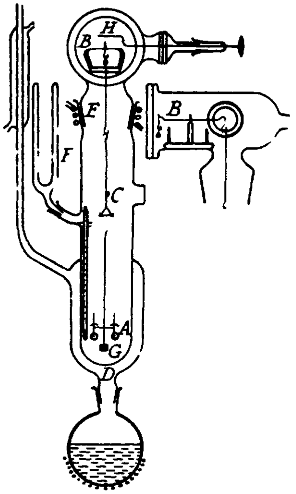
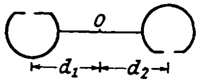


FIG. 2.



Errors arising from an incorrect ratio of hole size to mean free path and from self-cooling were shown to be negligible by the consistent results obtained with effusion vessels of different hole size. This consistency also covers a further possible error due to incorrect ratio of hole size to the surface of the solid in the effusion vessel, for the measured vapour pressure p is always slightly less than the true saturation pressure p_0. The rate of effusion through the hole of area A is equal to the net rate of supply of the vapour in the effusion vessel, or

$$Ap = \alpha A_s p_0 - \alpha A_s p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where A_s is the area of the solid, and α the evaporation coefficient. Hence $p/p_0 = \alpha A_s/(A + \alpha A_s)$. Under the conditions of this research the difference between p_0 and p is negligible. Theoretical calculations of the self-cooling and of the resistance factor due to the balance-case tubing showed that errors due to these factors were negligible. The cooling due to radiation losses from the hot region at 100° to the cold region at room temperature was calculated to be rather less than 1°, but was not allowed for since the temperatures were read on the thermometer inside the case.

Vapour pressures p may be calculated from the rate of loss of mass, $\mathrm{d}w/\mathrm{d}t$, since

$$p = (-\,\mathrm{d}w/\mathrm{d}t)(2\pi \mathbf{R}T/M)^{\frac{1}{2}}/A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where M is the molecular weight, and $\mathbf{R}$ the gas constant. This equation may be written

$$p = (-\,\mathrm{d}w/\mathrm{d}t)T^{\frac{1}{2}}K_1/M^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where K_1 is an apparatus constant determined by calibration by means of sulphur or benzophenone.

The molecular weight may be calculated from the consideration that the recoil force at the holes of effective area A_1 and A_2 is $\frac{1}{2}pA_1$ and $\frac{1}{2}pA_2$ respectively, and that there will be a torque about the axis of rotation O (Fig. 2). This torque will be $2(\frac{1}{2}pA_1d_1)$ or $2(\frac{1}{2}pA_2d_2)$, whichever is the smaller; any lack of balance between the two torques acting on the separate effusion vessels will act as a force at the fulcrum O, and will not cause rotation about the axis. If the angle of torsion is θ and the torsional constant c, then $c\theta = pA_1d_1$ (the first alternative being taken for the torques), and

$$p = K_2\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where K_2 can be found by calibration. Hence

$$M = (-\mathrm{d}w/\mathrm{d}t)^2TK_1^2/(K_2\theta)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Results for oxamide are given in Table 1, and the values of the lattice energy and entropy of vaporisation for the three compounds now examined, together with those for anhydrous oxalic acid (from Part II, for comparison), are summarised in Table 4.

TABLE 1. *Vapour pressures* (*cm.* Hg) *of oxamide.*

Effusion vessel 1.				Effusion vessel 1.				Effusion vessel 2.			
	Angle of torsion,	V. p. × 10^5 from			Angle of torsion,	V. p. × 10^5 from			Angle of torsion,	V. p. × 10^5 from	
T	radians	torsion	$-\mathrm{d}w/\mathrm{d}t$	T	radians	torsion	$-\mathrm{d}w/\mathrm{d}t$	T	radians	torsion	$-\mathrm{d}w/\mathrm{d}t$
92·75°	0·175	2·90	2·94	88·60°	0·111	1·88	1·84	96·45°	0·201	4·14	4·09
92·50	0·175	2·90	2·77	88·45	0·112	1·90	1·85	96·40	0·200	4·11	4·14
92·30	0·171	2·84	2·77	88·45	0·111	1·89	1·90	92·05	0·125	2·57	2·59
91·40	0·152	2·58	2·60	80·45	0·0469	0·800	0·802	90·10	0·108	2·21	2·26
90·65	0·145	2·47	2·45	80·40	0·0469	0·800	0·807	88·80	0·093	1·92	1·93
88·70	0·112	1·90	1·88	80·40	0·0487	0·837	0·796	88·55	0·090	1·86	1·89

TABLE 2. *Vapour pressures* (*cm.* Hg) *of oxamic acid.*

	Effusion vessel 3.								Effusion vessel 4.		
T	90·00°	88·90°	82·55°	81·60°	78·65°	77·30°	76·00°	75·80°	90·75°	89·90°	82·15°
V. p. × 10^5	11·3	11·1	5·37	4·86	3·52	3·04	2·65	2·65	12·1	11·3	4·95

TABLE 3. *Vapour pressures* (*cm.* Hg) *of rubeanic acid.*

	Effusion vessel 5.						Effusion vessel 6.		
T	104·15°	103·75°	102·05°	102·00°	101·60°	98·20°	105·15°	104·25°	98·05°
V. p. × 10^4	12·2	11·8	10·4	10·3	10·2	7·52	14·0	12·8	7·16
T	98·15°	98·05°	94·45°	94·75°	93·35°	86·90°			
V. p. × 10^4	7·56	7·35	5·13	5·35	4·59	2·44			

TABLE 4.

Substance	Lattice energy (cal. mole^{-1})	Entropy of vaporisation (cal. degree^{-1} mole^{-1})
Oxamide	27,000	44·4
Oxamic acid	25,800	44·4
Rubeanic acid	25,200	45·0
Oxalic acid (α) (cf. Part II)	23,400	47·0
Oxalic acid (β) (cf. Part II)	22,300	44·3

Instead of calculating M for oxamide, we have given the vapour pressures calculated from the torsion and loss of weight, the value of M being assumed. The vapour pressure is well represented by the equation $\log_{10}p$(cm. of Hg) $= -5893/T + 11{\cdot}568$. If the molecular weight is calculated from equation (5) a mean value of 87·1 is obtained, in good agreement with the actual value, 88·05, although a scatter of $\pm 5\%$ was observed. It should be remembered, however, that this molecular weight was determined on vapours at very low pressures, and that errors in the determination of θ or $(-\mathrm{d}w/\mathrm{d}t)$ are doubled in the calculation of the molecular weight. (Owing to the low vapour pressure the latent heat of vaporisation may be equated to the lattice energy.)

The vapour pressure of oxamic acid (Table 2) is well represented by the equation $\log_{10} p$ (cm. of Hg) $= -5639/T + 11{\cdot}580$. Results for rubeanic acid are given in Table 3; the vapour pressures are given by $\log_{10} p$ (cm. of Hg) $= -5515/T + 11{\cdot}713$.

Discussion.—The lattice energy of molecular crystals such as oxamide, etc., may be split into the quantum-mechanical dispersion energy, electrostatic interaction energy, and energy of repulsion. Part of this energy may be attributed to the so-called hydrogen bonding between nearest neighbours, but it is not easy to calculate or even define such a contribution in the solid state where the contribution of non-nearest neighbours may be appreciable, especially to the electrostatic term. The (O···H–O) hydrogen bond energy has usually been estimated for carboxylic acids from the heat of dimerization of the vapours to be approximately 8 kcal. Similarly the N···H–N bond has been estimated from the virial coefficient of ammonia to be 3·8 kcal. (Lambert and Strong, *Proc. Roy. Soc.*, 1950, *A*, **200**, 566), but this dimerization energy involves a general electrostatic and dispersive interaction between the two molecules, as well as repulsive energy and reorganisation energy of the fragment after the dimer has split into monomers. The danger of neglecting repulsive energy is brought out by Searcy's calculation for ice (*J. Chem. Phys.*, 1947, **17**, 210), this energy amounting to 42% of the lattice energy of the solid.

It is clear on the basis of two hydrogen bonds per molecule, and the assumption that the " hydrogen bond energy " deduced from the vapour applies to the solid state, that there is a considerable " background energy." The proper analysis awaits a detailed knowledge of the structures, but it is noteworthy that the replacement of CO·OH by $CO{\cdot}NH_2$ increases the lattice energy (cf. oxamic acid and oxamide), which is contrary to what might be expected. The replacement of O by S causes a decrease in lattice energy, in accordance with expectations (cf. oxamide and rubeanic acid). It is possible that part of the lattice energy arises from the presence of some kind of zwitterion, *e.g.*, $NH_3^+\ CO{\cdot}CO_2^-$, with the possibility of proton transfer from one potential trough to another, *e.g.*, a CO_2H group of one molecule adjacent to the NH_2 group of another molecule could lose a proton to the NH_2 group; such zwitterions, which might have a transient existence, would increase the electrostatic energy and the melting point, although the so-called resonance energy due to proton transfer would be negligible.

We thank the Shropshire Education Committee and the University of Leeds for grants to one of us (T. G. C.), and Professor E. G. Cox for his interest and encouragement.

THE UNIVERSITY OF LEEDS. [*Received, December* 11*th*, 1952.]