348. *The Vapour Pressure and Lattice Energy of Hydrogen-bonded Crystals. Part III.* 2-Thenoic, 2-Furoic, and Pyrrole-2-carboxylic Acids.*

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The vapour pressures of these three acids (thiophen-, furan-, and pyrrole-2-carboxylic acids) have been determined by a Knudsen effusion method over the respective temperature ranges 41·8—50°, 44—55°, and 76·6—80·4°. The lattice energies are respectively 23·17, 25·92, and 30·31 kcal. mole^{-1}, and the entropies of vaporisation 48·71, 58·28, and 62·76 cal. degree^{-1} mole^{-1}.

THE three acids mentioned in the title differ only in the presence in the ring of S, O, and NH respectively, and a comparison of the structures and thermodynamic properties is therefore of interest. The structure of 2-thenoic acid has been studied by Care and Cox and will be reported elsewhere.

EXPERIMENTAL

Preparation and Purification of Materials.—(a) *2-Thenoic acid.* The preparation was based on that of Voermann (*Rev. Trav. chim.*, 1907, **26**, 297). Thiophen was acetylated and sodium permanganate was added slowly, with stirring, to a mixture of acetylthiophen and aqueous sodium hydroxide. The solution was kept overnight and then heated on a water-bath until brown hydrated manganese dioxide was precipitated; this was filtered off, and dilute hydrochloric acid added to the filtrate until the solution was feebly alkaline. The filtrate was cooled, hydrogen peroxide added, and after a few hours' standing the solution was heated and stirred for a few minutes on a water-bath. 2-Thenoic acid was then precipitated by addition of hydrochloric acid, and the remainder was extracted from the solution by means of ether. The resulting brown crystals were recrystallised first from ethyl alcohol (charcoal) and then from hot water to give colourless needles, m. p. 126—127°, d_4^{18} 1·42 (from flotation in aqueous sulphuric acid).

(b) *2-Furoic acid.* This was obtained commercially and purified by sublimation; d_4^{18} 1·47.

(c) *Pyrrole-2-carboxylic acid.* McKay and Schmidt's method (*J. Amer. Chem. Soc.*, 1926, **48**, 192) gave only a poor yield, so the following method was devised. To ethylmagnesium iodide (from magnesium, 8·5 g.; ethyl iodide, 33 ml.; dry ether, 80 ml.), freshly distilled pyrrole (3·5 ml.) was added dropwise, with stirring, the container being cooled by ammonium nitrate, ice, and water to which solid carbon dioxide was added occasionally. The resulting solution was poured into a thick suspension of solid carbon dioxide in ether (*ca.* 1 l.) contained in a 2-l. flask. The contents of the flask set into a semi-solid mass and when all the carbon dioxide had evaporated the solid residue was separated from the ether, and the magnesium

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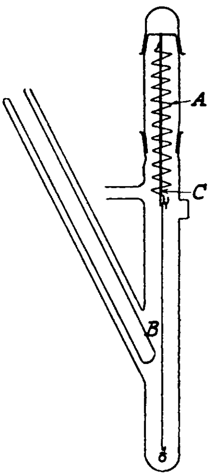
* Part II, preceding paper.

salt decomposed by dilute hydrochloric acid. White crystals slowly settled on standing. These were separated and the solution was extracted with ether. The crystals became grey in air and were purified by treatment in hot ether with charcoal, filtration, and evaporation of the ether. The product was kept in a sealed tube in the dark; m. p. 191—191·5° (decomp.) (Found: C, 53·65; H, 4·5. Calc. for $C_5H_5O_2N$: C, 54·0; H, 4·5%), d_4^{18} 1·30.



Determination of Vapour Pressures.—The vapour pressures were determined by Knudsen's method, *i.e.*, measurement of the rate of effusion of vapour through a small hole in the wall of a bulb containing the solid. The effusion vessel (Bradley and Waghorn, *Proc. Roy. Soc.*, 1950, *A*, **206**, 65; Bradley and Shellard, *ibid.*, 1949, *A*, **198**, 239) consisted of a soft-glass bulb with a platinum-foil window which was pierced by a hole of the order of 0·5 mm. in diameter The rate of loss of vapour was followed by a McBain–Bakr balance, in a manner similar to that of Hopke and Sears (*J. Chem. Phys.*, 1951, **19**, 1345) and others, except that a fused-silica helical spring was used. The apparatus is shown in the Figure. The helical spring *A* had a sensitivity of $(1—2{\cdot}5) \times 10^{-3}$ g. mm.$^{-1}$, and was calibrated for the load appropriate to the vapour-pressure experiments by means of small weights which were weighed on a Kuhlmann micro-analytical balance. The calibration plot of load versus extension was linear. Extensions could be read to 0·001 mm. Vapour effusing from the bulb under conditions of high vacuum was condensed on the surface *B*, which was cooled by means of acetone–solid carbon dioxide. Vibrational difficulties were avoided by the use of a *thick* rod *C* terminating in the reference pointer, by supporting the oil-pump on rubber mats and by making the connection to the apparatus by thick pressure-tubing. The temperature of the balance case was controlled by thermostat to ±0·03°. Benzophenone, recrystallised from alcohol, was used as a calibrating substance.

Precautions were taken to reduce errors as described in Parts I and II (preceding papers). One defect of the method is that only a small range of temperature is available, since too high a temperature causes self-cooling and too low a temperature gives rates which are too small for study with a silica spring. The micro-balance method used in Parts I and II allows the study of a wider range of temperature, but involves more difficult experimentation.

Results.—2-Thenoic (*α-thiophenic or thiophen-2-carboxylic*) *acid.*

T	41·82°	41·93°	42·79°	45·15°	46·82°	50·02°
V. p. (cm. of Hg) × 10^5	27·9	28·8	31·6	40·5	49·9	72·3

Whence $\log_{10} p = -5065/T + 12{\cdot}53$; lattice energy = 23,170 cal. mole^{-1}; entropy of vaporisation = 48·71 cal. degree^{-1} mole^{-1}.

2-Furoic (*furan-2-carboxylic*) *acid.*

T	44·06°	46·70°	49·65°	53·13°	55·05°
V. p. (cm. of Hg) × 10^5	62·3	80·4	115·8	178·3	227·2

Whence $\log_{10} p = -5667/T + 14{\cdot}62$; lattice energy = 25,920 cal. mole^{-1}; entropy of vaporisation = 58·28 cal. degree^{-1} mole^{-1}.

Pyrrole-2-carboxylic (*α-pyrrolic*) *acid.*

T	76·58°	78·52°	79·08°	80·42°	81·97°	83·44°	85·61°
V. p. (cm. of Hg) × 10^5	42·68	54·0	58·1	68·7	81·7	98·5	127·2

Whence $\log_{10} p = -6633/T + 15{\cdot}60$; lattice energy = 30,310 cal. mole^{-1}; entropy of vaporisation = 62·76 cal. degree^{-1} mole^{-1}.

In 2-thenoic acid there is one hydrogen bond per molecule, since the molecules are arranged in a helix with the carbonyl group of one molecule linked to the hydroxyl group of the next (Care and Cox, to be published). This implies that the contribution to the lattice energy of intermolecular forces, that of the hydrogen bond being omitted, is approx. 16 kcal. mole^{-1}, a value much greater than the latent heat of vaporisation of liquid thiophen (8·2 kcal. mole^{-1}) or methylthiophen (8·6 kcal. mole^{-1}). This is presumably due to the attraction between the carboxyl group of one molecule and the ring of another, and possibly to inductive effects of the carboxyl group on the ring (which will affect the action of one ring on another). A similar comparison can be made between benzene (latent heat of sublimation 10 kcal. mole^{-1}) and benzoic acid (lattice energy 21 kcal. mole^{-1}). The structures of the remaining acids have not been calculated in detail, although pyrrole-2-carboxylic and 2-thenoic acids have the same space-group. It is hoped to publish a more detailed analysis when the structures have been established in detail.

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