SHORT COMMUNICATIONS

VAPOUR PRESSURES OF FORMYL FLUORIDE AND CARBONYL CHLOROFLUORIDE*

By G. FISCHER† and A. S. BUCHANAN†

The thermal stability of formyl fluoride has recently been investigated in this laboratory[1] and during the preparation of the compound for kinetic studies it was subjected to careful low-temperature fractionation. Vapour pressures for the pure material were measured following the purification process, as were the vapour pressures of the derived carbonyl chlorofluoride.

Experimental

The vapour pressure apparatus as described in detail previously[2] consisted of a modified Ward–LeRoy low-temperature distillation column connected to a mercury manometer of 1 cm bore. The thermometric fluids employed in the vapour pressure thermometer were ammonia and carbon dioxide, and this system permitted temperatures to be measured with an accuracy of 0·1°. The wide-bore manometer permitted measurement of vapour pressures to an accuracy of 0·2 mm.

The preparation and purification of formyl fluoride will be described elsewhere.[1] The production of carbonyl chlorofluoride involved a novel method in that it was prepared by the photochemical reaction of a small excess of chlorine with formyl fluoride. The following is a possible mechanism for this reaction:

$$Cl_2 \xrightarrow{h\nu} Cl + Cl$$

$$Cl + HCOF \rightarrow HCl + \cdot COF$$

$$\cdot COF + Cl \rightarrow ClCOF$$

The product HCl was removed by fractional distillation from finely divided Celite and excess chlorine was removed quantitatively by reaction with mercury. No significant amounts of phosgene or carbon monoxide were detected in the product. The carbonyl chlorofluoride was further purified by fractionation on the low temperature column and the purity was assessed by the absence of infrared absorptions of possible impurities.

Results

The measured vapour pressures for the two compounds are recorded in Tables 1 and 2.

* Manuscript received September 10, 1963.

† Department of Physical Chemistry, University of Melbourne.

[1] Fischer, G., and Buchanan, A. S., unpublished data.

[2] Creutzberg, F., and Buchanan, A. S., *Aust. J. Chem.*, 1961, **14**, 257.

The following relation was deduced from a least squares treatment of the experimental results for formyl fluoride:

$$\log_{10}p\ (\text{cm}) = 7{\cdot}0740 - 1{\cdot}2734 \times 10^3/T. \qquad (1)$$

This relation yields a latent heat of vaporization of $5{\cdot}83 \pm 0{\cdot}04$ kcal mole^{-1} and a boiling point of $-28{\cdot}0 \pm 0{\cdot}9°$. The Trouton's constant is therefore $23{\cdot}8 \pm 0{\cdot}3$ entropy units.

The corresponding expression for carbonyl chlorofluoride is the following:

$$\log_{10}p\ (\text{cm}) = 7{\cdot}1049 - 1{\cdot}1872 \times 10^3/T. \qquad (2)$$

TABLE 1

MEASURED VAPOUR PRESSURES OF FORMYL FLUORIDE AT VARIOUS TEMPERATURES

Temp.	Pressure (cm)	Temp.	Pressure (cm)	Temp.	Pressure (cm)
−38·0°	42·70	−62·5°	10·30	−74·5°	5·15
−43·5°	33·00	−63·0°	10·40	−75·0°	4·30
−44·8°	30·90	−63·2°	10·30	−77·5°	3·60
−45·5°	31·32	−65·9°	8·90	−78·0°	3·95
−51·5°	21·50	−66·1°	8·30	−78·0°	3·95
−53·5°	18·64	−67·0°	7·66	−78·0°	3·84
−54·3°	18·85	−67·5°	7·60	−85·0°	2·20
−56·5°	16·10	−70·0°	6·17	−87·0°	1·75
−59·7°	13·00	−71·5°	6·30	−89·0°	1·34
−60·5°	11·30	−72·4°	5·26	−91·5°	1·08
−61·6°	11·00	−74·2°	4·51	−94·7°	0·79

TABLE 2

MEASURED VAPOUR PRESSURES OF CARBONYL CHLOROFLUORIDE AT VARIOUS TEMPERATURES

Temp.	Pressure (cm)	Temp.	Pressure (cm)	Temp.	Pressure (cm)
−62·4°	29·04	−74·0°	14·46	−97·4°	2·25
−63·0°	27·83	−75·5°	13·06	−102·6°	1·32
−64·7°	25·60	−77·7°	10·42	−105·8°	0·99
−67·5°	21·41	−87·0°	5·78	−108·9°	0·74
−72·0°	16·38	−90·0°	4·40		

In this case the latent heat of vaporization is $5{\cdot}43 \pm 0{\cdot}18$ kcal mole^{-1} and the boiling point $-46{\cdot}0 \pm 1°$. The Trouton constant is $23{\cdot}9 \pm 0{\cdot}8$ entropy units.

The graphical representations of the relations (1) and (2) are shown in Figure 1.

Discussion

The vapour pressures of formyl fluoride have not been previously reported. The accuracy of the information for the compound as quoted in the present communication is probably most seriously limited by the purity of the sample since this

tends to deteriorate when the compound is manipulated and stored in a glass vacuum system.

Two prior sets of measurements for carbonyl chlorofluoride have been reported.[3,4] Agreement with the present set of observations, which have the advantage of more experimental points, is reasonably good.

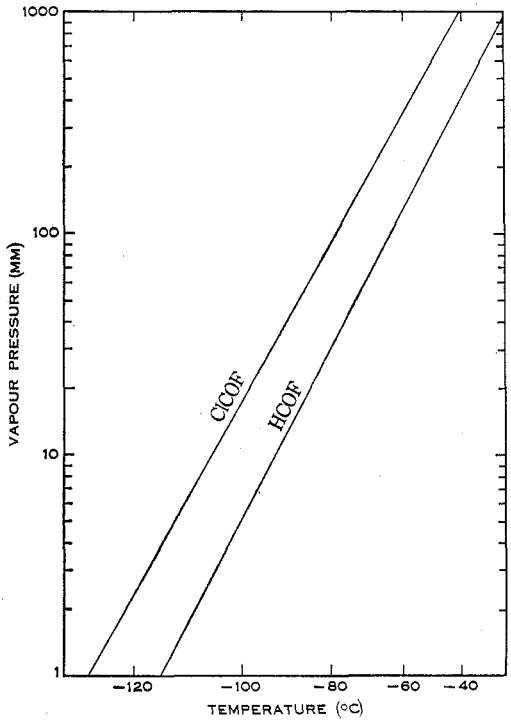

Fig. 1.—Graphical representation of equations (1) and (2)

The values for Trouton's constant of 23·8 and 23·9 for formyl fluoride and carbonyl chlorofluoride respectively may be considered "normal" values. They are significantly less than the value of 26·0 for water where considerable hydrogen bonding occurs in the liquid. The similarity of the values for formyl fluoride and carbonyl chlorofluoride provides some evidence for the absence of hydrogen bonding interaction in the liquid of the former since there can only be dipolar interaction and no hydrogen bonding in the case of the latter compound.

[3] Simons, J. H., Herman, D. F., and Pearlson, W. H., *J. Amer. Chem. Soc.*, 1946, **68**, 1672.
[4] Emeléus, H. J., and Wood, J. F., *J. Chem. Soc.*, 1948, 2185.