

Thermochemistry of Fluorine Compounds. Part III.¹ Iodine Oxide Trifluoride and Iodyl Fluoride

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From measurements of the heats of aqueous alkaline hydrolysis at 25 °C the following standard enthalpies of formation are derived: $\Delta H_f^\circ[\text{IOF}_3, \text{cryst.}]_{298} = -554.76 \pm 2.51 \text{ kJ mol}^{-1}$ ($-132.59 \pm 0.6 \text{ kcal mol}^{-1}$) and $\Delta H_f^\circ[\text{IO}_2\text{F, cryst.}]_{298} = -246.4 \pm 1.2 \text{ kJ mol}^{-1}$ ($-58.89 \pm 0.29 \text{ kcal mol}^{-1}$).

IODINE OXIDE TRIFLUORIDE, IOF_3 , is well known²⁻⁵ and its structure is now definitely established as a distorted trigonal bipyramid^{6,7} with axial fluorine, and not as $\text{IO}_2^+\text{IF}_6^-$ as previously suggested.³ On being heated,

¹ Part II, Arthur Finch, P. N. Gates, and M. A. Jenkinson, *J.C.S. Dalton*, 1973, 2237.

² O. Ruff and A. Braida, *Angew. Chem.*, 1934, **47**, 480.

³ E. E. Aynsley, R. Nichols, and P. L. Robinson, *J. Chem. Soc.*, 1953, 623.

iodine pentafluoride is evolved and iodyl fluoride, IO_2F , is produced.³ The structure of IO_2F is not settled, although an ionic formulation is discounted, and a covalent, probably polymerised, structure preferred.⁸

⁴ E. E. Aynsley and M. L. Hair, *J. Chem. Soc.*, 1958, 3747.

⁵ E. E. Aynsley, *J. Chem. Soc.*, 1958, 2425.

⁶ J. W. Viers and H. W. Baird, *Chem. Comm.*, 1967, 1093.

⁷ J. W. Viers and H. W. Baird, unpublished results.

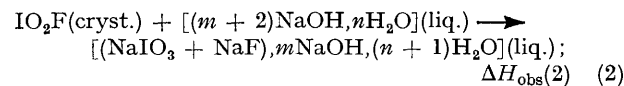
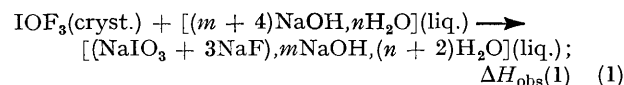
⁸ H. A. Carter and F. Aubke, *Inorg. Chem.*, 1971, **10**, 2296.

Both compounds are quantitatively and rapidly hydrolysed by water.

EXPERIMENTAL

Preparations.—IOF₃ was prepared, following an established procedure,⁹ from I₂O₅ (ca. 2.5 g, 7.5 mmol, B.D.H.) and an excess of IF₅ (30 cm³, 0.51 mol, Matheson Co. Ltd.). The latter was purified by first shaking with mercury, then by trap-to-trap distillation in a grease-free vacuum line. After being stirred for 30 min at 100 °C all solid dissolved, and on subsequent standing at room temperature white needles separated. Excess of IF₅ was removed by prolonged pumping at ambient temperatures, and the remaining crystals were stored in a dry-box and subsequently manipulated under strictly anhydrous conditions. Analysis was by standard titrimetric procedures for iodine and a selective-ion fluoride electrode (Orion, Model 90-00-01), for fluorine (Found: I, 63.6; F, 27.6. Calc. for FIO₃: I, 63.5; F, 28.5%). Iodyl fluoride was obtained by Aynsley's method³ by heating IOF₃ to 110 °C for 1 h under vacuum, evolved IF₅ being trapped. Analyses were as above (Found: I, 71.6; F, 10.8. Calc. for FIO₂: I, 71.3; F, 10.7%).

Calorimeter and Procedure.—These have been fully described.⁹ For each compound the calorimeter was charged with 200 cm³ of 1.000 mol dm⁻³ NaOH. For both IOF₃ and IO₂F reaction was rapid, though not violent, according to equations (1) and (2). With IOF₃ a slight and transient mist formed above the liquid surface, but with no apparent effect on the reaction trace. Separate experiments showed that possible reaction of ampoule glass with the alkaline calorimetric fluid was thermally negligible.



RESULTS AND DISCUSSION

Experimental calorimetric results are in the Table. The measured reaction heats, ΔH_{obs} , refer to processes summarised by equations (1) and (2). Standard enthalpies of formation were calculated by substitution of appropriate ancillary data into (see ref. 10) equations (3) and (4) as appropriate. Heats of mixing were disregarded; weights were not corrected to vacuo; un-

Experimental data for aqueous alkaline hydrolysis of iodine oxide trifluoride and iodyl fluoride

IOF ₃ (cryst.)		IO ₂ F(cryst.)	
w/g	$-\Delta H_{\text{obs}}(1)$ kJ mol ⁻¹	w/g	$-\Delta H_{\text{obs}}(2)$ kJ mol ⁻¹
0.1240	316.35	0.2720	139.20
0.2109	314.22	0.2134	140.75
0.1796	317.02	0.1829	138.49
0.1700	314.64	0.1956	138.91
0.2006	316.60	0.2960	140.12
0.1380	316.48	0.2917	140.71
0.1944	313.01	0.4573	138.78
		0.3578	139.91

$$\Delta H_{\text{obs}}(1) = -315.47 \pm 1.00 \text{ kJ mol}^{-1}; \quad \Delta H_{\text{obs}}(2) = -139.61 \pm 0.62 \text{ kJ mol}^{-1} \text{ whence } \Delta H_f^\circ[\text{IOF}_3, \text{cryst.}]_{298} = -554.76 \pm 2.51 \text{ kJ mol}^{-1} \text{ and } \Delta H_f^\circ[\text{IO}_2\text{F}, \text{cryst.}]_{298} = -246.40 \pm 1.2 \text{ kJ mol}^{-1}.$$

certainty intervals in ΔH_{obs} are expressed as twice the standard deviation of the mean.

$$\Delta H_f^\circ[\text{IOF}_3, \text{cryst.}] = \Delta H_f^\circ[\text{NaIO}_3, n\text{H}_2\text{O}, \text{liq.}] + 3\Delta H_f^\circ[\text{NaF}, n\text{H}_2\text{O}, \text{liq.}] + 2\Delta H_f^\circ[\text{H}_2\text{O}, \text{liq.}] - 4\Delta H_f^\circ[\text{NaOH}, n\text{H}_2\text{O}] - \Delta H_{\text{obs}}(1) \quad (3)$$

$$\Delta H_f^\circ[\text{IO}_2\text{F}, \text{cryst.}] = \Delta H_f^\circ[\text{NaIO}_3, n\text{H}_2\text{O}, \text{liq.}] + \Delta H_f^\circ[\text{NaF}, n\text{H}_2\text{O}, \text{liq.}] + \Delta H_f^\circ[\text{H}_2\text{O}, \text{liq.}] - 2\Delta H_f^\circ[\text{NaOH}, n\text{H}_2\text{O}, \text{liq.}] - \Delta H_{\text{obs}}(2) \quad (4)$$

When IOF₃ is heated it forms IO₂F, which under ambient conditions has negligible vapour pressure. Enthalpies of vaporisation, and thus values for I-O and I-F bond energies, are hence inaccessible. It is noteworthy that use of the standard enthalpies of formation obtained in this study, and a value¹¹ for $\Delta H_f^\circ[\text{IF}_5, \text{g}] = 840.27 \pm 1.67 \text{ kJ mol}^{-1}$, shows that the synthetic reaction $2\text{IOF}_3 \longrightarrow \text{IO}_2\text{F} + \text{IF}_5$ is close to athermal, being endothermic by only ca. $23 \pm 6 \text{ kJ}$ ($5.5 \pm 1.4 \text{ kcal}$). Since the number of formal I-F and I-O bonds remains constant, this presumably implies little profound change in bond order. Under appropriate conditions the reaction may be reversed. During the synthesis of IO₂F the driving force is clearly the continuous removal of IF₅.

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⁹ R. L. Coley, Ph.D. Thesis, Univ. of London, 1971.

¹⁰ A. Finch, P. N. Gates, and M. A. Jenkinson, *J.C.S. Dalton*, 1972, 2044.

¹¹ J. L. Settle, J. H. E. Jeffes, P. A. G. O'Hare, and W. N. Hubbard, presented at the 23rd Calorimetry Conference, Midland, Michigan, August 1968.