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

By **Arthur Finch,* Peter N. Gates,** and **Michael A. Jenkinson,** Department of Chemistry, Royal Holloway College, University of London, Egham, Surrey TW20 0EX

From measurements of the heats of aqueous alkaline hydrolysis at 25 °C the following standard enthalpies of formation are derived: $\Delta H_f^\circ[\mathrm{IOF_3,cryst.}]_{298} = -554{\cdot}76 \pm 2{\cdot}51$ kJ mol^{-1} ($-132{\cdot}59 \pm 0{\cdot}6$ kcal mol^{-1}) and $\Delta H_f^\circ[\mathrm{IO_2F,cryst.}]_{298} = -246{\cdot}4 \pm 1{\cdot}2$ kJ mol^{-1} ($-58{\cdot}89 \pm 0{\cdot}29$ kcal mol^{-1}).

IODINE OXIDE TRIFLUORIDE, IOF_3, is well known [2-5] and its structure is now definitely established as a distorted trigonal bipyramid [6,7] with axial fluorine, and not as $IO_2^+IF_6^-$ as previously suggested.[3] On being heated, 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]

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[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.

[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[7] J. W. Viers and H. W. Baird, unpublished results.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.—IOF_3 was prepared, following an established procedure,[3] from I_2O_5 (*ca.* 2·5 g, 7·5 mmol, B.D.H.) and an excess of IF_5 (30 cm^3, 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 IF_5 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 FIO_3: I, 63·5; F, 28·5%). Iodyl fluoride was obtained by Aynsley's method [3] by heating IOF_3 to 110 °C for 1 h under vacuum, evolved IF_5 being trapped. Analyses were as above (Found: I, 71·6; F, 10·8. Calc. for FIO_2: I, 71·3; F, 10·7%).

Calorimeter and Procedure.—These have been fully described.[9] For each compound the calorimeter was charged with 200 cm^3 of 1·000 mol dm^{-3} NaOH. For both IOF_3 and IO_2F reaction was rapid, though not violent, according to equations (1) and (2). With IOF_3 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.

$$\begin{aligned}\mathrm{IOF_3(cryst.)} + [(m+4)\mathrm{NaOH},n\mathrm{H_2O}](\mathrm{liq.}) \longrightarrow \\ [(\mathrm{NaIO_3} + 3\mathrm{NaF}),m\mathrm{NaOH},(n+2)\mathrm{H_2O}](\mathrm{liq.}); \\ \Delta H_{\mathrm{obs}}(1)\end{aligned} \tag{1}$$

$$\begin{aligned}\mathrm{IO_2F(cryst.)} + [(m+2)\mathrm{NaOH},n\mathrm{H_2O}](\mathrm{liq.}) \longrightarrow \\ [(\mathrm{NaIO_3} + \mathrm{NaF}),m\mathrm{NaOH},(n+1)\mathrm{H_2O}](\mathrm{liq.}); \\ \Delta H_{\mathrm{obs}}(2)\end{aligned} \tag{2}$$

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

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

IOF_3(cryst.)		IO_2F(cryst.)	
w/g	$-\Delta H_{\mathrm{obs}}(1)$ / kJ mol^{-1}	w/g	$-\Delta H_{\mathrm{obs}}(2)$ / 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

$\Delta H_{\mathrm{obs}}(1) = -315{\cdot}47 \pm 1{\cdot}00$ kJ mol^{-1}; $\Delta H_{\mathrm{obs}}(2) = -139{\cdot}61 \pm 0{\cdot}62$ kJ mol^{-1} whence $\Delta H_f^\circ[\mathrm{IOF_3,cryst.}]_{298} = -554{\cdot}76 \pm 2{\cdot}51$ kJ mol^{-1} and $\Delta H_f^\circ[\mathrm{IO_2F,cryst.}]_{298} = -246{\cdot}40 \pm 1{\cdot}2$ kJ mol^{-1}.

$$\begin{aligned}\Delta H_f^\circ[\mathrm{IOF_3,cryst.}] = {} & \Delta H_f^\circ[\mathrm{NaIO_3},n\mathrm{H_2O},\mathrm{liq.}] \\ & + 3\Delta H_f^\circ[\mathrm{NaF},n\mathrm{H_2O},\mathrm{liq.}] \\ & + 2\Delta H_f^\circ[\mathrm{H_2O},\mathrm{liq.}] \\ & - 4\Delta H_f^\circ[\mathrm{NaOH},n\mathrm{H_2O}] \\ & - \Delta H_{\mathrm{obs}}(1)\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta H_f^\circ[\mathrm{IO_2F,cryst.}] = {} & \Delta H_f^\circ[\mathrm{NaIO_3},n\mathrm{H_2O},\mathrm{liq.}] \\ & + \Delta H_f^\circ[\mathrm{NaF},n\mathrm{H_2O},\mathrm{liq.}] \\ & + \Delta H_f^\circ[\mathrm{H_2O},\mathrm{liq.}] \\ & - 2\Delta H_f^\circ[\mathrm{NaOH},n\mathrm{H_2O},\mathrm{liq.}] \\ & - \Delta H_{\mathrm{obs}}(2)\end{aligned} \tag{4}$$

When IOF_3 is heated it forms IO_2F, 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 value [11] for $\Delta H_f^\circ[\mathrm{IF_5,g}] = 840{\cdot}27 \pm 1{\cdot}67$ kJ mol^{-1}, shows that the synthetic reaction $2IOF_3 \longrightarrow IO_2F + IF_5$ is close to athermal, being endothermic by only *ca.* 23 ± 6 kJ (5·5 ± 1·4 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 IO_2F the driving force is clearly the continuous removal of IF_5.

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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.