Thermochemistry of Fluorine Compounds. Part 5.† Di-μ-oxo-bis[trifluoro-oxoiodine(VII)]

By **Arthur Finch** * and **Peter N. Gates**,* The Bourne Laboratory, Royal Holloway College (University of London), Egham, Surrey TW20 0EX
Anthony J. Edwards * and **Arsein A. K. Hana**, Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

The standard enthalpy of formation of crystalline $(IF_3O_2)_2$ has been determined as −984.0 ± 18.0 kJ mol^{-1} based on enthalpies of reaction with excess of aqueous acidic iodide solution. The stability of $(IF_3O_2)_2$ is considered in terms of this value.

THE structure of di-μ-oxo-bis[trifluoro-oxoiodine(VII)], $(IF_3O_2)_2$, first prepared in 1969,[1] has only very recently been established as a dimer in the crystalline state by low-temperature *X*-ray studies.[2] The dimeric structure persists in the vapour phase below 100 °C,[3] and a value for the enthalpy of sublimation is the only available thermodynamic datum.

Standard enthalpies of formation for iodine oxyfluorides have been reported for the iodine(V) species iodyl fluoride IO_2F, iodine trifluoride oxide, IF_3O,[4] and the (ionic) difluoroiodates, $M[IO_2F_2]$ (M = Na, K, Rb, or NH_4).[5] We now report similar studies on the iodine(VII) species $(IF_3O_2)_2$, measuring enthalpies of reaction in aqueous acidic iodide solution.

EXPERIMENTAL

Preparation of $(IF_3O_2)_2$.—A modification of the previously reported method[1] was used. Tetrafluoro-orthoperiodic acid, HIF_4O_2, was obtained from the reaction of $Ba_3H_4(IO_6)_2$ with a 20-fold excess of fluorosulphuric acid, $HSFO_3$. Sulphur trioxide vapour (from 25% oleum) was condensed into HIF_4O_2 and, on warming under vacuum, pale yellow crystals of $(IF_3O_2)_2$ resulted. These were purified by pumping first through a U tube containing dry potassium sulphate (to remove any fluorosulphuric acid) and then through a P_2O_5 trap. Analysis was by standard titrimetry for iodine and a fluoride-specific ion electrode (Activion) for fluorine [Found: F, 26.4; I, 58.8. Calc. for $(IF_3O_2)_2$: F, 26.4; I, 58.8%].

Due to extreme sensitivity to moisture, samples were sealed into calorimetric ampoules under vacuum, and refrigerated until required for calorimetric experiments.

Calorimeter and Procedure.—The isoperibol calorimeter has been fully described elsewhere.[6] Check experiments on the performance of the system were made before and after $(IF_3O_2)_2$ determinations, using the neutralisation of 2-amino-2-hydroxymethylpropane-1,3-diol with 0.100 mol dm^{-3} aqueous hydrochloric acid. Values for the enthalpy of reaction were −29.77 and −29.79 kJ mol^{-1}; an accepted value[7] is −29.79 ± 0.03 kJ mol^{-1}.

For each of the nine determinations the calorimeter was charged with 200 cm^3 of 0.1 mol dm^{-3} aqueous acidic (0.2 mol dm^{-3} H_2SO_4) potassium iodide solution. The reaction was moderately fast, being complete within 7 min. Post-calorimetric analyses (I_2 + F^-) were consistent with reaction (1).

$$(IF_3O_2)_2(c) + [(8 + m)H^+ + (22 + n)I^-]pH_2O(l) \longrightarrow (8I_3^- + 6F^- + mH^+ + nI^-)(p + 4)H_2O \quad (1)$$

RESULTS

Observed enthalpies of reaction, $\Delta H_R^\ominus$, are listed in the Table. Standard enthalpies of formation of $(IF_3O_2)_2$ were calculated from equation (2) and using the following

$$\Delta H_f^\ominus[(IF_3O_2)_2,c] = 8\Delta H_f^\ominus(I_3^-,aq) + 6\Delta H_f^\ominus(F^-,aq) + 4\Delta H_f^\ominus(H_2O,l) - 8\Delta H_f^\ominus(H^+,aq) - 22\Delta H_f^\ominus(I^-,aq) - \Delta H_R^\ominus \quad (2)$$

ancillary data: $\Delta H_f^\ominus(I_3^-,aq) = -49.79$;[8] $\Delta H_f^\ominus(F^-,aq) = -335.67$;[9] $\Delta H_f^\ominus(H_2O,l) = -285.83$;[9] and $\Delta H_f^\ominus(I^-,aq) = -56.90$ kJ mol^{-1}.[9] Hence $\Delta H_f^\ominus[(IF_3O_2)_2,c] = -984.0 \pm 18.0$ kJ mol^{-1}.

Enthalpies of reaction of $(IF_3O_2)_2$ with aqueous acidic potassium iodide

Mass of $(IF_3O_2)_2$/g	Dilution, *n*	$-\Delta H_R^\ominus$/ kJ mol^{-1}
0.085 70	56 009	1 300.0
0.065 17	73 653	1 304.0
0.081 46	58 924	1 361.2
0.078 76	60 944	1 349.8
0.076 03	63 133	1 282.0
0.040 46	118 636	1 350.4
0.220 21	21 797	1 325.8
0.073 58	65 235	1 322.4
0.060 82	78 921	1 327.2
	Mean =	−1 319.8 ± 17.0

Uncertainties are calculated as 95% confidence limits using a Students' *t* distribution.

DISCUSSION

Calorimetric Reaction.—Initial separation of elemental iodine, followed by rapid dissolution to give a brown solution, is clearly visible. The reactions involved are hence sequential, *viz.* $(IF_3O_2)_2 + 14I^- + 8H^+ \longrightarrow 6F^- + 8I_2 + 4H_2O$ followed by formation of tri-iodide from iodide and iodine.

Stability of $(IF_3O_2)_2$.—This merits special consideration in view of the assumption that its thermal and photolytic stability at ambient temperatures is sufficient to justify its use in ampoules equilibrated at 298 K for considerable periods. It is known from two independent sources[1,10] that at temperatures above 97 °C decomposition occurs, according to $(IF_3O_2)_2 \longrightarrow 2IF_3O + O_2$. Using the values $\Delta H_f^\ominus(IF_3O,c) = -554.76$ kJ mol^{-1} (ref. 4) and $\Delta H_f^\ominus[(IF_3O_2)_2,c] = 984.0$ kJ mol^{-1} (see above) we derive a value of −125.5 kJ mol^{-1} for the standard enthalpy

---

† Part 4, A. Finch, P. N. Gates, and S. J. Peake, *Thermochim. Acta*, 1974, **10**, 203.

change of this decomposition reaction at 298 K. If we assume that the major entropy contribution arises from the production of $O_2(g)$ then $\Delta G^\ominus \ll 0$, leading to a correspondingly very large positive value for the equilibrium constant. The apparent thermal stability at ambient temperatures is hence unexpected. Confidence that decomposition has not occurred during storage and equilibration at 298 K in the calorimeter comes from the results of the calorimetric reaction, *viz.* $-1\,319.8 \pm 17.0$ kJ mol^{-1} (nine samples with differing masses and storage and equilibration periods). Further, calculation shows that the very different value (*ca.* -437 kJ mol^{-1}) is expected for reaction of the putative decomposition product under identical calorimetric conditions, *i.e.* $IF_3O + 2H^+ + 8I^- \longrightarrow 3F^- + H_2O + 3I_3^-$. The results of elemental analyses, based on both fluoride-ion and iodine measurements, give additional strong support to the (kinetic) stability at ambient temperatures.

The enthalpy of sublimation of $(IF_3O_2)_2$ is independently available[10] as 45.7 kJ mol^{-1} and this, together with our measured value for the crystal, leads to $\Delta H_f^\ominus[(IF_3O_2)_2,g, 298\text{ K}] = -938.3$ kJ mol^{-1}. Since reliable thermochemical data are only available for the iodine(VII) species IO_4^- [11] and IF_7,[9] estimation of bond energies is not possible, as the dimeric structure contains both terminal and bridging oxygen bonds. Further, transference of a mean I–F bond energy derived from measurements on IF_7 only is unrealistic. A key quantity in such bond-energy calculations is a value for $\Delta H_f^\ominus$-(IF_5O,c), but the physical properties[12] of IF_5O render a calorimetric determination very difficult.

[9/743 *Received*, 14*th May*, 1979]

REFERENCES

[1] A. Engelbrecht and P. Peterfy, *Angew. Chem.*, 1969, **8**, 768.
[2] L. E. Smart, *J.C.S. Chem. Comm.*, 1977, 519.
[3] M. J. Vasile, W. E. Falconer, F. A. Stevie, and I. R. Beattie, *J.C.S. Dalton*, 1977, 1233.
[4] A. Finch, P. N. Gates, and M. A. Jenkinson, *J.C.S. Dalton*, 1973, 2725.
[5] A. Finch, P. N. Gates, and M. A. Jenkinson, *J.C.S. Dalton*, 1972, 2044.
[6] A. Finch, P. N. Gates, and S. J. Peake, *J.C.S. Dalton*, 1977, 397.
[7] E. J. Prosen and M. V. Kilday, *J. Res. Nat. Bur. Stand.*, 1973, **A77**, 581.
[8] C. H. Wu, M. M. Birky, and L. G. Hepler, *J. Phys. Chem.*, 1963, **67**, 1202.
[9] J. D. Cox, ' Halogen Compounds,' Catch Tables, University of Sussex, 1972.
[10] I. R. Beattie, R. Crocombe, A. German, P. Jones, C. Marsden, G. Van Schalkwyk, and A. Bukovszky, *J.C.S. Dalton*, 1976, 1380.
[11] G. K. Johnson, P. N. Smith, E. H. Appelman, and W. N. Hubbard, *Inorg. Chem.*, 1970, **9**, 119.
[12] N. Bartlett and L. E. Levchuk, *Proc. Chem. Soc.*, 1963, 342; J. H. Holloway, H. Selig, and H. H. Claassen, *J. Chem. Phys.*, 1971, **54**, 4305.