Thermochemistry of Fluorine Compounds. Part I. The Difluoroiodate Series

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From measurements of the heats of aqueous alkaline hydrolysis at 25 °C the standard enthalpies of formation of the following fluoroiodates are derived: $\Delta H_f^\circ[\mathrm{NaIO_2F_2,cryst.}]_{298} = 202{\cdot}8_5 \pm 0{\cdot}3$ kcal mol^{-1} ($-848{\cdot}7 \pm 1{\cdot}2$ kJ mol^{-1}); $\Delta H_f^\circ[\mathrm{KIO_2F_2,cryst.}]_{298} = -209{\cdot}5 \pm 0{\cdot}3$ kcal mol^{-1} ($-876{\cdot}6 \pm 1{\cdot}2$ kJ mol^{-1}); $\Delta H_f^\circ[\mathrm{RbIO_2F_2,cryst.}]_{298} = -209{\cdot}2 \pm 0{\cdot}3$ kcal mol^{-1} ($-875{\cdot}3 \pm 1{\cdot}2$ kJ mol^{-1}) and $\Delta H_f^\circ[\mathrm{NH_4IO_2F_2,cryst.}]_{298} = -178{\cdot}7 \pm 0{\cdot}3$ kcal mol^{-1} ($-754{\cdot}6 \pm 1{\cdot}2$ kJ mol^{-1}). Estimates of lattice energies and other thermodynamic parameters are also reported.

THE oxyanion chemistry of fluorine is extremely limited: oxyfluoro-ions are very rare and the only example of a charged iodo-oxyfluoro-species is the $IO_2F_2^-$ anion. The preparation of various fluoroiodates MIO_2F_2 (M = Li, Na, and K) is well established[1] and the structure of KIO_2F_2 has been the subject of a single-crystal *X*-ray investigation.[2] No thermodynamic data are available.

EXPERIMENTAL

Preparations.—The compounds MIO_2F_2 (M = Na, K, Rb, and NH_4) were prepared by the established procedure of the appropriate iodate with 40% aqueous hydrogen fluoride in polyethylene beakers at room temperature. Well-formed crystals of fluoroiodates appeared after prolonged standing in a well-ventilated fume cupboard; the supernatant liquid was decanted, the crystals washed with dry diethyl ether, dried in a stream of dry nitrogen, and stored and subsequently manipulated with rigorous protection from moisture. Each sample was analysed for iodine (titrimetrically) and for fluorine (with a selective ion electrode) (Found: I, 57·7; F, 17·3. Calc. for $NaIO_2F_2$: I, 57·7; F, 17·3%; Found: I, 53·8; F, 16·0. Calc. for KIO_2F_2: I, 53·8; F, 16·1%; Found: I, 45·2; F, 13·4. Calc. for $RbIO_2F_2$: I, 44·9; F, 13·5%; Found: I, 59·1; F, 17·4. Calc. for $NH_4IO_2F_2$: I, 59·0; F, 17·7%). The presence of the fluoroiodate ion in each sample was confirmed by analysis of the Raman spectrum of powdered samples obtained by use of a Cary 81 Raman spectrometer equipped with a helium–neon laser and employing the 6328 Å line for excitation.

Calorimeter and Procedure.—The calorimeter has been described,[3] and was operated at 298·15 ± 0·01 K in the isoperibol mode. Duplicate, identical calorimeters were used. All parts were fabricated from borosilicate glass, and vacuum-jacketing employed; thermistors (Standard Telephone and Cable Company Limited, model F 23) were used as sensing elements and results were displayed on a potentiometric recorder. The performance was checked periodically by use of the neutralisation of tris(hydroxymethyl)aminomethane (tham) in excess of aqueous 0·1000N-hydrochloric acid as test reaction. Typical results were: $\Delta H(298\ \mathrm{K},\ 1246 < N < 1441) = 7{\cdot}10 \pm 0{\cdot}01$ kcal mol^{-1} (eleven consecutive runs) [lit.,[4] $\Delta H(298\ \mathrm{K},\ 1180 < N < 1574) = 7{\cdot}109 \pm 0{\cdot}001$ kcal mol^{-1}]. Appropriate amounts of fluoroiodate in glass ampoules were broken into an excess of aqueous 0·1000N-sodium hydroxide (200 ml). The calorimetric reaction was fast, but not violent, and values of the heat of reaction ΔH_{obs} were measured according to the equation (1). In all runs, reaction was carried out

$$\mathrm{MIO_2F_2(cryst.)} + (n + 2)\mathrm{NaOH}(m\mathrm{H_2})\mathrm{O} \longrightarrow$$
$$[\mathrm{MIO_3} + 2\mathrm{NaF} + n\mathrm{NaOH} + (m + 1)\mathrm{H_2O})]\ \Delta H_{\mathrm{obs}} \quad (1)$$

at 298·15 ± 0·01 K with the mole ratio NaOH : H_2O = 1 : 555. Uncertainties are taken as twice the standard deviation of the mean. One kcal is taken as 4·1840 absolute joules.

RESULTS

Experimental calorimetric results are summarised in Table 1. The measured reaction heat, ΔH_{obs}, refers to process (1), where M = Na, K, Rb, or NH_4, as appropriate. The standard enthalpy of formation of each fluoroiodate was calculated by substitution of the observed value of ΔH_{obs} and appropriate ancillary data (Table 2) into the thermochemical equation (2). Results are in Table 3.

$$\Delta H_f^\circ\mathrm{MIO_2F_2(cryst.)} = \Delta H_f^\circ\mathrm{MIO_3(5000H_2O)} + 2\Delta H_f^\circ\mathrm{NaF(3000H_2O)} + \Delta H_f^\circ\mathrm{H_2O(liq.)} - 2\Delta H_f^\circ\mathrm{NaOH(500H_2O)} - \Delta H_{\mathrm{obs}} \quad (2)$$

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[1] R. F. Weinland and O. Lauenstein, *Z. anorg. Chem.*, 1899, **20**, 30.

[2] L. Helmholz and M. T. Rogers, *J. Amer. Chem. Soc.*, 1940, **62**, 1537.

[3] R. L. Coley, Ph.D. Thesis, University of London, 1971.

[4] J. O. Hill, G. Öjelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

TABLE 1

Experimental data for aqueous alkaline hydrolysis of some Group IA fluoroiodates

Compound	w/g	$-\Delta H_{obs}$ kcal mol^{-1}
$NaIO_2F_2$(cryst.)	0·6042	25·26
	0·3806	25·23
	0·7676	25·86
	0·6762	25·98
	0·6975	25·38
	0·8802	25·46
	0·5423	25·19
	0·9015	24·97
	0·5190	25·30
	0·7176	24·86
	0·4873	24·95
	ΔH_{obs}(mean) = −25·31 ± 0·22 kcal mol^{-1}	
KIO_2F_2(cryst.)	0·3334	21·95
	0·5178	21·16
	0·3653	22·54
	0·5521	21·70
	0·5589	20·56
	0·5393	21·77
	0·6956	20·43
	0·5985	21·24
	0·6400	21·31
	0·5490	21·33
	0·7270	21·24
	0·7267	20·87
	ΔH_{obs}(mean = −21·34 ± 0·34 kcal mol^{-1}	
$RbIO_2F_2$(cryst.)	0·7756	20·66
	0·7736	20·70
	0·6864	20·80
	0·6961	20·74
	0·5204	21·18
	0·5379	20·77
	0·7693	20·42
	0·7390	20·55
	0·6263	20·74
	0·8083	20·66
	ΔH_{obs}(mean) = −20·72 ± 0·12 kcal mol^{-1}	
$NH_4IO_2F_2$(cryst.)	0·3903	24·97
	0·3682	24·63
	0·5253	24·62
	0·4932	24·44
	0·3378	24·81
	0·4767	24·83
	0·3440	24·97
	ΔH_{obs}(mean) = −24·75 ± 0·16 kcal mol^{-1}	

TABLE 2

Ancillary heat of formation data (298 K)

Compound	ΔH_f° kcal mol^{-1}	Compound	ΔH_f° kcal mol^{-1}
NaOH($500H_2O$)	−112·12	$NaIO_3$($5000H_2O$)	−112·28
NaF($3000H_2O$)	−135·90	KIO_3($5000H_2O$)	−114·98
RbF($5000H_2O$)	−137·57	NH_4F($5000H_2O$) [a]	−111·17
H_2O(liq.) [a]	−68·31$_5$		

[a] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, ' Selected Values of Chemical Thermodynamic Properties,' Technical Note 270—3, 1968, U.S. Govt. Printing Office. All other data from F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, National Bureau of Standards Circular 500, Part I, 1952, U.S. Govt. Printing Office.

TABLE 3

Derived standard enthalpies of formation

Compound	ΔH_f°(298 K) kcal mol^{-1}	ΔH_f°(298 K) kJ mol^{-1}
$NaIO_2F_2$(cryst.)	−202·8$_5$ ± 0·3	−848·7 ± 1·2
KIO_2F_2(cryst.)	−209·5 ± 0·4	−876·6 ± 1·6
$RbIO_2F_2$(cryst.)	−209·2 ± 0·3	−875·3 ± 1·2
$NH_4IO_2F_2$(cryst.)	−178·7 ± 0·3	−754·6 ± 1·2

DISCUSSION

The substantial negative values obtained for the standard enthalpies of formation of the fluoroiodates, *ca.* -10^2 kcal mol^{-1}, are consistent with their apparent stability on storage for long periods. A more useful thermodynamic parameter for ionic crystals, however, is that of the lattice energy, U°, which may be equated, without significant error, with the internal energy change U_{298} accompanying the dissociation of the crystal into gas ions, *viz*, equation (3). Only for

$$MIO_2F_2(\text{cryst., 298 K}) \longrightarrow [M^+ + IO_2F_2^-](\text{g., 298 K})\ U_{298} \quad (3)$$

KIO_2F_2 is it possible, even in principle, to calculate a value for the Madelung constant, but no value for the repulsive coefficient is available. Hence it is more reasonable to compute a self-consistent set of lattice energies by use of the Born–Mayer form of the Kapustinskii equation,[5] which can be written as (4) where ν =

$$U_{298}\ (\text{kcal mol}^{-1}) = \frac{287{\cdot}2\nu z_1 z_2}{r(M^+) + r(IO_2F_2^-)}\left[1 - \frac{0{\cdot}345}{r(M^+) + r(IO_2F_2^-)}\right] + 2{\cdot}5\nu z_1 z_2 \quad (4)$$

number of ions in ' molecule ' [*i.e.*, 2] and z_1,z_2, are the charges on the cation and anion respectively [*i.e.* each 1]. Values for the crystal ion radii, $r(M^+)$ and $r(IO_2F_2^-)$, are required; the former are readily available and the latter is best calculated by the well-established Yatsimirskii ' thermochemical radius ' procedure.[6] For two crystalline compounds, M′X and M″X, we have equation (5) where $\Delta H_L'$, $\Delta H_L''$ are the lattice enthalpies

$$\Delta H_L' - \Delta H_L'' = U_T' - U_T'' = \Delta H_f^\circ M'^+(\text{g.}) - \Delta H_f^\circ M''^+(\text{g.}) - \Delta H_f^\circ M'X(\text{cryst.}) + \Delta H_f^\circ M''(\text{cryst.}) \quad (5)$$

of the M′X and M″X respectively. Since the quantity $[U_T' - U_T'']$ can be expressed in terms of the Kapustinskii equation (4) written for each compound, a value for $r(IO_2F_2^-)$ can be calculated. This calculation was performed for $NaIO_2F_2$ and KIO_2F_2, by use of the ancillary data in Table 4, and solving the appropriate

TABLE 4

Data used to compute a value for the thermochemical radius of the $IO_2F_2^-$ ion

Species	Standard enthalpies of formation 298 K kcal mol^{-1}	Ion radius (cryst.)/Å
$NaIO_2F_2$	−203(cryst.)	
KIO_2F_2	−210(cryst.)	
Na^+	−146(g.) [a]	1·00 [a]
K^+	−123(g.) [a]	1·33 [a]

[a] D. A. Johnson, ' Some Thermodynamic Aspects of Inorganic Chemistry,' Cambridge University Press, 1968.

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[5] A. F. Kapustinskii, *Quart. Rev.*, 1956, **10**, 283; see also T. C. Waddington, ' Advances in Inorganic and Radiochemistry,' eds. H. J. Emeléus and A. G. Sharpe, vol. 1, Academic Press, 1959, p. 157.

[6] K. B. Yatsimirskii, *Russ. J. Inorg. Chem.*, 1961, **6**, 265; see also T. C. Waddington, ref. 5.

quartic equation for $r(IO_2F_2^-)$ whence $r(IO_2F_2^-) = 1{\cdot}8_3$ Å. This was adopted for subsequent lattice-energy computations, results for 1 : 1 crystals are shown in Table 5. It is probably not meaningful to attempt to ascribe precise error limits to these values. A major uncertainty is the validity of the value of $r(IO_2F_2^-)$, a change of 0·1 Å in which is reflected by a lattice-energy value change of *ca.* 10 kcal mol^{-1}. *Differences* in values of lattice energies are clearly much more precise than the absolute values. Using the relationship (6) we can, using known values for the standard heats of formation of $NaIO_2F_2$, KIO_2F_2, and $RbIO_2F_2$,

TABLE 5

Calculated values of lattice energies of some 1 : 1 fluoroiodate crystals, MIO_2F_2

M	Li	Na	K	Rb	Cs	Ag	NH_4
U_{298}/kcal mol^{-1}	202	183	167	161	152	176	162

$$\Delta H_f^\circ MIO_2F_2(\text{cryst.}) = \Delta H_f^\circ IO_2F_2(\text{g.}) - U_T - 2RT + \Delta H_f^\circ M^+(\text{g.}) \quad (6)$$

calculate a value for $\Delta H_f^\circ IO_2F_2^-(\text{g.})$ of $-164{\cdot}8 \pm 0{\cdot}6$ kcal g-ion^{-1}, the error limits referring solely to the precision of the three calculated results. Substitution of this value in equation (3) with appropriate literature values of $\Delta H_f^\circ M^+(\text{g.})$ and calculated values of $U_T MIO_2F_2$ now enables the estimation of the standard heats of formation of other 1 : 1 metal fluoroiodate crystals. A simple extrapolation method, based on comparing the differences between experimental values for the standard heats of formation of pairs of alkali-metal salts, *e.g.*, sodium and potassium chloride, sodium and potassium bromide, *etc.*, leads to a value of $\Delta H_f^\circ CsIO_2F_2$(cryst.) = -210 kcal mol^{-1}. This, while not an independent check of the calculation from equation (6), lends support to this method as realistic. Further extension to calculations of lattice energies and standard heats of formation of Group IIA fluoroiodates, $M^{2+}(IO_2F_2^-)_2$, leads to values of reasonably predictable magnitudes. The apparent non-existence of these compounds may hence depend on the insolubility of the parent Group IIA iodates, which presumably precludes their use as synthetic precursors.

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