# Thermochemistry of Fluorine Compounds. Part II.[1] The Hexafluoroiodate Series

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From measurements of the heats of aqueous alkaline hydrolysis in 0·1M-NaOH at 25 °C the standard enthalpies of formation of the following hexafluoroiodates are derived: $\Delta H_f°[\mathrm{KIF_6}, \text{cryst.}]_{298} = -1492 \pm 2{\cdot}5$ kJ mol$^{-1}$ ($-356{\cdot}5 \pm 0{\cdot}6$ kcal mol$^{-1}$); $\Delta H_f°[\mathrm{RbIF_6}, \text{cryst.}]_{298} = -1473 \pm 2$ kJ mol$^{-1}$ ($-352{\cdot}1 \pm 0{\cdot}5$ kcal mol$^{-1}$); and $\Delta H_f°[\mathrm{CsIF_6}, \text{cryst.}]_{298} = -1466 \pm 2$ kJ mol$^{-1}$ ($-350{\cdot}4 \pm 0{\cdot}5$ kcal mol$^{-1}$). Estimates of lattice energies and of $\Delta H_f[\mathrm{IF_6}^-,\mathrm{g}]_{298}$ are reported.

THE preparation and stoicheiometry of alkali-metal and tetra-alkylammonium hexafluoroiodates by a variety of methods is well established.[2-4] Considerable disagreement concerning the structure of the $\mathrm{IF_6}^-$ moiety as indicated by vibrational[5-7] or Mössbauer studies[8] has been reported. Discrepancies in the reported vibrational spectra have been apparently explained very recently by Christe,[9] and the present indications are that the $\mathrm{IF_6}^-$ moiety does not possess a symmetry higher than $C_{2v}$. No thermodynamic data are available.

## EXPERIMENTAL

*Preparations.*—The compounds $\mathrm{MIF_6}$ (M = K, Rb, and Cs) were prepared by the established procedure[3] summarised in equation (1). Appropriate quantities of the

$$5\mathrm{MI} + 6\mathrm{IF_5} \longrightarrow 5\mathrm{MIF_6} + 3\mathrm{I_2} \qquad (1)$$

relevant iodide (typically *ca.* 5 g) were heated to 100 °C with stirring with an excess (typically *ca.* 30 cm$^3$) of $\mathrm{IF_5}$ in a Pyrex reaction flask incorporated in a conventional high-vacuum line. Iodine and excess of $\mathrm{IF_5}$ were removed by prolonged pumping at *ca.* 50 °C; residues were pure white powders, which were subsequently manipulated under dry-box conditions. Each sample was analysed for iodine (by standard titrimetric procedures) and fluorine with a selective ion electrode) (Found: I, 45·2; F, 40·5. Calc. for $\mathrm{KIF_6}$: I, 45·3; F, 40·7%; Found: I, 39·1; F, 34·8. Calc. for $\mathrm{RbIF_6}$: I, 38·9; F, 34·9%; Found: I, 34·1; F, 30·5. Calc. for $\mathrm{CsIF_6}$: I, 34·0; F, 30·5%).

*Calorimeter and Procedure.*—Appropriate quantities of hexafluoroiodate salts in glass ampoules were broken into an excess of 0·1000N-sodium hydroxide (200 cm$^3$). The calorimetric reaction was fast, being essentially complete within 2 or 3 min, but not violent, and values of the heat of reaction, $\Delta H_{\mathrm{obs}}$, were measured according to equation (2) at 298·15 ± 0·01 K with the mole ratio NaOH : $\mathrm{H_2O}$ = 1 : 556. Uncertainties were taken as twice the standard deviation of the mean. One kcal is taken as 4·1840 absolute joules.

$$\mathrm{MIF_6(cryst.)} + (m + 6)\mathrm{NaOH}(n\mathrm{H_2O}) \longrightarrow [\mathrm{MIO_3} + 6\mathrm{NaF}]\{m\mathrm{NaOH}(n + 3)\mathrm{H_2O}\}\ \Delta H_{\mathrm{obs}} \qquad (2)$$

## RESULTS

Experimental calorimetric results are summarised in Table 1. The measured reaction heat, $\Delta H_{\mathrm{obs}}$, refers to process (2), where M = K, Rb, or Cs. The standard enthalpy of formation of each hexafluoroiodate was calculated by substitution of the experimental value of $\Delta H_{\mathrm{obs}}$ and appropriate ancillary data into the thermochemical

TABLE 1

Experimental data for aqueous alkaline hydrolyses of some Group 1A hexafluoroiodates

| Compound | $w$/g | $-\Delta H_{\mathrm{obs.}}$/kJ mol$^{-1}$ |
|---|---|---|
| $\mathrm{KIF_6}$(cryst.) | 0·1912 | 445·9 |
| | 0·1560 | 445·7 |
| | 0·1751 | 440·0 |
| | 0·1085 | 449·3 |
| | 0·1835 | 443·5 |
| | 0·1683 | 441·1 |
| | 0·1285 | 444·9 |
| | 0·1405 | 438·3 |
| | 0·1849 | 442·3 |
| | 0·1593 | 448·4 |
| $\Delta H_{\mathrm{obs.}}$(mean) = $-443{\cdot}9 \pm 2{\cdot}2$ kJ mol$^{-1}$ | | |
| $\mathrm{RbIF_6}$(cryst.) | 0·1559 | 455·1 |
| | 0·1460 | 460·2 |
| | 0·1570 | 456·6 |
| | 0·1888 | 460·0 |
| | 0·1865 | 459·9 |
| | 0·1843 | 458·0 |
| | 0·1511 | 453·0 |
| | 0·1826 | 460·3 |
| | 0·1855 | 456·1 |
| | 0·1444 | 460·0 |
| | 0·1473 | 462·0 |
| $\Delta H_{\mathrm{obs.}}$(mean) = $-458{\cdot}3 \pm 1{\cdot}7$ kJ mol$^{-1}$ | | |
| $\mathrm{CsIF_6}$(cryst.) | 0·1610 | 460·2 |
| | 0·2551 | 457·1 |
| | 0·1859 | 458·2 |
| | 0·2185 | 457·2 |
| | 0·2227 | 456·1 |
| | 0·1801 | 457·3 |
| | 0·2056 | 456·6 |
| | 0·1854 | 461·3 |
| | 0·1702 | 463·1 |
| $\Delta H_{\mathrm{obs.}}$(mean) = $-458{\cdot}0 \pm 1{\cdot}7$ kJ mol$^{-1}$ | | |

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equation (3). Values for the dilution coefficients ($n$, and $p$, and $q$), are available from the detailed results; heats of mixing were disregarded. Ancillary data are from accepted sources.

$$\Delta H_f^\circ[\mathrm{MIF_6(cryst.)}] = \Delta H_f^\circ[\mathrm{MIO_3}(n\mathrm{H_2O})] + 6\Delta H_f^\circ[\mathrm{NaF}(p\mathrm{H_2O})] + 3\Delta H_f^\circ[\mathrm{H_2O(liq.)}] - 6\Delta H_f^\circ[\mathrm{NaOH}(q\mathrm{H_2O})] - \Delta H_{\mathrm{obs}} \quad (3)$$

DISCUSSION

As with the corresponding difluoroiodate salts,[1] the substantial negative values obtained for the $\Delta H_f^\circ$ values (Table 2) are consistent with their apparent thermodynamic stability with respect to storage at ambient temperatures. Adopting the 'thermochemical radii' treatment of the Kapustinskii equation, as detailed in Part I, we can calculate approximate but self-consistent lattice energies as $\mathrm{KIF_6}$, 807; $\mathrm{RbIF_6}$, 774; and $\mathrm{CsIF_6}$, 728 kJ mol$^{-1}$. These values are necessarily approximate, owing to, *inter alia*, uncertainties in the value adopted for the thermochemical radius of the hexafluoroiodate ion (133 pm), an uncertainty of 10 pm in which causes a change of *ca.* 27 kJ mol$^{-1}$ in $U_{298}$. As before,[1] however, *differences* in $U_{298}$ values are certainly much more precise. Similarly, consistent values for the standard enthalpy of formation of any ionic hexafluoroiodate salt can be obtained by appropriate substitution in equation (4) where $T = 298$ K. A value for $U_T[\mathrm{M}_x(\mathrm{IF_6})_y]$ can be estimated by the Kapustinskii–Yatsimirskii procedure [1] employing a value of 133 pm for the thermochemical radius of the $\mathrm{IF_6}^-$ ion. The value of $\Delta H_f^\circ[\mathrm{IF_6}^-, \mathrm{g}]_{298}$ can be calculated from the experimental values of $\Delta H_f^\circ[\mathrm{MIF_6, c}]_{298}$.

$$\Delta H_f^\circ[\mathrm{M}_x(\mathrm{IF_6})_y,\mathrm{cryst.}]_T = -\{U_T[\mathrm{M}_x(\mathrm{IF_6})_y] + (x+y)RT\} + x\Delta H_f^\circ[\mathrm{M^+, g}]_T + y\Delta H_f^\circ[\mathrm{IF_6^-, g}]_T \quad (4)$$

TABLE 2

Derived standard enthalpies of formation

| Compound | $\Delta H_f^\circ$(298 K) / kJ mol$^{-1}$ | $\Delta H_f^\circ$(298 K) / kcal mol$^{-1}$ |
|---|---|---|
| $\mathrm{KIF_6}$ | −1492 ± 2·5 | −356·5 ± 0·6 |
| $\mathrm{RbIF_6}$ | −1473 ± 2 | −352·1 ± 0·5 |
| $\mathrm{CsIF_6}$ | −1466 ± 2 | −350·4 ± 0·5 |

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