

Short Communication

Thermodynamic and spectroscopic properties of the fluoroiodate ion

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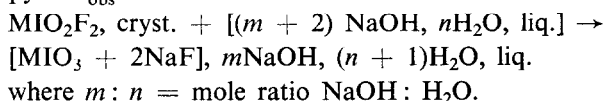
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(Received February 26, 1972)

Oxy-fluorine anions are extremely rare, the only example of any oxy-fluorine iodine anion being that afforded by the fluoroiodate system, $[\text{IO}_2\text{F}_2]^-$. This ion is hence apparently unique, and whilst X-ray structural data are well-established¹, and the syntheses^{2,3} of several alkali metal and other salts are well known, no thermodynamic data exist. In this Communication we report preliminary measurements for the standard heats of formation of potassium and sodium fluoroiodates and also an estimation of the lattice energies of these crystals.

Potassium and sodium fluoroiodates were made by the established method of crystallisation from a 40% aqueous HF solution of the appropriate iodate. The crystals were gently dried and stored with rigorous exclusion of water. Fluorine and iodine analyses were as follows: Found: (i) I, 57.7; F, 17.3%. NaIO_2F_2 requires I, 57.7; F, 17.3%. Found: (ii) I, 53.8; F, 16.0%. KIO_2F_2 requires I, 53.8; F, 16.1%. Infrared and Raman frequencies for the potassium salt are listed in Table 1 together with assignments to fundamental modes. The observed spectra are substantially in agreement with those recently reported for KIO_2F_2 ⁴. The pattern of frequencies is entirely consistent with a C_{2v} formulation as required by the X-ray data. The pattern of the spectra for the Na^+ and K^+ compounds are very similar and it is thus reasonable to infer a common shape for the IO_2F_2^- ion in both of these compounds.

Calorimetric measurements were performed using aqueous alkaline hydrolysis in a solution-reaction calorimeter⁵ operated at 25° in the isoperibol mode. Reactions were rapid, being typically completed within *ca.* 2 min. The reaction enthalpy $\Delta H_{\text{obs}}^\circ$ refers to the reaction:



Hence

$$\begin{aligned} \Delta H_f^\circ[\text{MIO}_2\text{F}_2, \text{cryst.}] = & \Delta H_f^\circ[\text{MIO}_3, 5000\text{H}_2\text{O}] + 2\Delta H_f^\circ[\text{NaF}, 5000\text{H}_2\text{O}] \\ & + \Delta H_f^\circ[\text{H}_2\text{O}, \text{liq.}] - 2\Delta H_f^\circ[\text{NaOH}, 500\text{H}_2\text{O}] - \Delta H_{\text{obs}}^\circ \end{aligned}$$

In all runs, reaction was carried out at $25.0 \pm 0.01^\circ$ with the mole ratio $\text{NaOH} : \text{H}_2\text{O} = 1 : 555$.

Values for $\Delta H_{\text{obs}}^\circ$ for NaIO_2F_2 and KIO_2F_2 were -25.31 ± 0.11 and

TABLE 1

INFRARED AND RAMAN SPECTRA OF KIO_2F_2 IN THE SOLID STATE

Raman (cm^{-1})	Infrared (cm^{-1})	Assignments
194 (vw)	197 (s)	ν_4 (a_1)
—	220 (m, sh)	ν_5 (a_2)
323 (s)	—	ν_9 (b_2)
346 (w)	345 (s)	ν_7 (b_1)
	351 (w, sh)	
360 (m)	360 (s)	ν_3 (a_1)
	407 (m)	
456 (vw)	440 (m)	ν_8 (b_2)
479 (s)	485 (vs)	ν_2 (a_1)
804 (w, sh)	805 (w, sh)	
817 (vs)	819 (vs)	ν_1 (a_1)
838 (w)	845 (m)	
—	851 (m)	ν_6 (b_1)

s, strong; m, medium; w, weak; v, very; sh, shoulder.

-21.34 ± 0.17 kcal mol $^{-1}$, respectively. Hence, using accepted values for ancillary data⁶ we derive: $\Delta H_f^\circ[\text{NaIO}_2\text{F}_2, \text{cryst.}]_{298} = -202.85 \pm 0.23$ kcal mol $^{-1}$; $\Delta H_f^\circ[\text{KIO}_2\text{F}_2, \text{cryst.}]_{298} = -209.52 \pm 0.27$ kcal mol $^{-1}$. The thermodynamic stability of these compounds is further reflected in the magnitude of their lattice energies, U_{298} . These may be estimated from the Kapustinskii equation⁷, using either a circumcising radius derived from known structural parameters or by the thermochemical radius approach⁸. Values are as follows: NaIO_2F_2 , $U_{298} = 184$ kcal mol $^{-1}$; KIO_2F_2 , $U_{298} = 167$ kcal mol $^{-1}$. It is probably not meaningful to give definite error limits for the lattice energy values, but it is certainly reasonable to assume that the above values are correct to within 10 kcal mol $^{-1}$. Since the value of the thermochemical radius used is a major uncertainty, and is common, then *differences* in lattice energies do not reflect the above large uncertainty.

From the above values of the standard heats of formation and of the derived estimations of lattice energies, similar parameters for other alkali metal fluoroiodates and Group II fluoroiodates may be estimated by simple extrapolation.

We thank the Science Research Council for a maintenance grant (to M.A.J.).

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