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THERMOCHEMISTRY OF FLUORINE COMPOUNDS

IV. RUBIDIUM TETRAFLUOROIODATE

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ABSTRACT

From measurement of the heat of hydrolysis, at 25 °C, the enthalpy of formation of rubidium tetrafluoroiodate is derived: $\Delta H_f^\circ[\mathrm{RbIF_4}, \text{cryst.}]_{298} = -191.12 \pm 4.43$ kJ mol^{-1}. Heat capacity measurements for $RbIF_4$ over the range 273–303 K are also reported.

INTRODUCTION

The preparation of alkali-metal tetrafluoroiodates by various methods is well established[1-3]. Vibrational spectra of $CsIF_4$ reported by Christe[4] indicate that the IF_4^- anion has a square-planar structure of D_{4h} symmetry and not C_{2v} symmetry as first reported[5]. No thermodynamic data are available for these salts.

EXPERIMENTAL

Preparations

$RbIF_4$ was prepared, by the method of Hargreaves and Peacock[1], from RbI (5 g, 23.5 mmol, B.D.H.) and an excess of IF_5 (30 cm^3, 0.51 mol, Matheson Co. Ltd.). IF_5 was purified by shaking with mercury followed by trap-to-trap distillation using a grease-free vacuum line. The reaction mixture was stirred for 20 min at 20 °C. Excess IF_5 and iodine were removed by prolonged pumping at room temperature. Residues were pure white powders, which were subsequently manipulated under dry-box conditions. The change in weight of the pyrex reaction vessel was found to be identical with the theoretical increase (based on RbI).

Several attempts were made to prepare $CsIF_4$ using the same method. In each case the experimental weight change and fluorine analysis indicated that $CsIF_4$:$CsIF_6$ mixtures were produced.

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Analysis and determination of hydrolysis stoichiometry

Aqueous hydrolysis was rapid (about 2 min) but not violent, resulting in the separation of elemental iodine. Qualitative tests on the aqueous hydrolysate gave the following indications: fluoride ions (calcium chloride test), iodate ions (5% aqueous thiocyanate and starch paper), and the absence of iodide ions (aqueous silver nitrate followed by aqueous ammonia).

Quantitative determination of fluoride ion after hydrolysis (Orion selective ion fluoride electrode) gave the following result: found 26.4%; calc. for $RbIF_4$, 26.35%.

Quantitative determinations of iodate and iodine in the aqueous hydrolysate were made as follows:

(a) Two samples of $RbIF_4$ (ca. 0.2 g, 0.7 mmol) were hydrolysed in water (25 cm^3) and the liberated iodine removed by vigorous boiling for 30 min. The residual iodate was analysed titrimetrically (addition of iodide followed by titration of liberated iodine against 0.1M thiosulphate) giving the results $RbIF_4:IO_3 = 1.67$, 1.65:1.

(b) After a similar hydrolysis, iodine was separated by repeated extractions with carbon tetrachloride and the iodine content of the combined extracts determined titrimetrically (0.1 M thiosulphate). The aqueous portion was titrated for iodate as in (a). Found: $RbIF_4:IO_3 = 1.67:1$ and $RbIF_4:I_2 = 5.02:1$.

The overall stoichiometry is hence quantitatively represented by the following equation:

$$5RbIF_4 + 9H_2O \rightarrow 5RbF + 15HF + 3HIO_3 + I_2.$$

Calorimeter and calorimetric procedure

The calorimeter used has been fully described elsewhere[6]. 200 cm^3 of distilled water were used as the calorimetric fluid. The calorimetric reaction was fast but not violent, being complete within 2 min. The measured heat of reaction, ΔH_R, refers to the process summarised in eqn (1).

$$5RbIF_4(\text{cryst}) + (n+9)H_2O(\text{liq}) \rightarrow [(5RbF + 3HIO_3 + 15HF)nH_2O(\text{liq})] + I_2(\text{cryst}) \quad (1)$$

DSC and heat capacity measurements

The heat capacity of $RbIF_4$ was measured using a Perkin-Elmer differential scanning calorimeter (Model DSC 1), with encapsulation in sealed aluminium pans, at a scan speed of 4 K min^{-1}. Sapphire was used as calibrant, and temperature measurement was checked using n-octacosane (m.p. 61.2°C) supplied as a standard from the National Physical Laboratory, Teddington, and n-tridecane (m.p. −5.5°C). $RbIF_4$ was also scanned in the direct mode over the range −100 to +180°C. A single exotherm (165°C) was observed which appeared to correspond with decomposition of the sample.

RESULTS

Experimental calorimetric results are in Table 1. The standard heat of formation of $RbIF_4$ was calculated by substitution of appropriate ancillary data (Table 2) into eqn (2).

$$5\Delta H_f^\circ[\mathrm{RbIF_4,\ cryst.}]_{298} = 5\Delta H_f^\circ[\mathrm{RbF,\ 2000\ H_2O}] + 3\Delta H_f^\circ[\mathrm{HIO_3,\ 4000\ H_2O}] + 15\Delta H_f^\circ[\mathrm{HF,\ 750\ H_2O}] - 9\Delta H_f^\circ[\mathrm{H_2O,\ liq}] - 5\,\Delta H_R \quad (2)$$

Heats of mixing and heat of solution of iodine were disregarded; weights were not corrected to vacuo. Uncertainty intervals in ΔH_R are expressed as twice the standard deviation of the mean.

TABLE 1

EXPERIMENTAL DATA FOR HYDROLYSIS OF RUBIDIUM TETRAFLUOROIODATE

Mean $\Delta H_R = -41.25 \pm 0.22$ kJ mol^{-1}; hence ΔH_f° [$RbIF_4$ (cryst.)]$_{298} = -191.12 \pm 4.43$ kJ mol^{-1}.

w (g)	$-\Delta H_R$ (*kJ mol*$^{-1}$)
1.5833	41.71
1.5370	41.17
1.5109	40.25
1.4753	41.80
1.4454	42.05
1.3861	42.13
1.3814	39.45
1.2362	41.50

TABLE 2

ANCILLARY HEAT OF FORMATION DATA

Compound	ΔH_f° (*kJ mol*$^{-1}$)
H_2O (liq.)[7]	-285.829 ± 0.04
RbF (2,000 H_2O)[8]	-575.513 ± 0.4
HIO_3 (4,000 H_2O)[9]	-221.785 ± 0.4
HF (750 H_2O)[10]	-12.761 ± 0.004

TABLE 3

HEAT CAPACITY OF RUBIDIUM TETRAFLUOROIODATE

T (K)	273	278	283	288	293	298	303
C_p (JK^{-1} mol^{-1})	120.2	124.0	127.7	135.0	138.8	144.5	148.3

Heat capacity data are collected in Table 3, and are represented, following a least-squares procedure, by the following equation:

$$C_p = 0.975T - 146.6$$

The overall accuracy is estimated to be ±2%.

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