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ENTHALPIES OF SOLUTION OF POTASSIUM HEXAFLUORORHENATE(IV) AND OF POTASSIUM HEXAFLUORORUTHENATE(IV); SINGLE ION HYDRATION ENTHALPIES OF THE HEXAFLUORORHENATE(IV) AND HEXAFLUORORUTHENATE(IV) ANIONS

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SUMMARY

Enthalpies of solution of potassium hexafluororhenate(IV) and of potassium hexafluororuthenate(IV) in water at 298.2K have been determined by direct calorimetry. They are +63.0 ± 0.3 and +59.4 ± 1.5 kJ mol^{-1} respectively. From these results single ion hydration enthalpies of -999 and -967 kJ mol^{-1} have been estimated for the (gaseous) hexafluororhenate(IV) and hexafluororuthenate(IV) anions.

INTRODUCTION

Values of single ion hydration enthalpies are available for a large number of cations, but for a rather smaller number of anions [1]. Hydration enthalpies have been estimated for, e.g., the halide ions, a few oxoanions such as sulphate and nitrate, and miscellaneous anions including thiocyanate [1] and hexahydroxoantimonate(V) [2]. Until recently no values had been estimated for any members of the numerous group of hexahalogenometallate anions, though a value for hexachlororhenate(IV) could be derived from published enthalpy of solution data [3]. We reported values for the single ion hydration enthalpies of the hexachlororhenate(IV) and hexabromorhenate(IV) anions on the basis of enthalpies of solution of their sparingly soluble caesium salts derived from temperature variation of solubilities [4]. We now report an extension of this work to the hexafluororhenate(IV) and hexafluororuthenate(IV) anions. Here the single ion hydration enthalpies are derived from direct calorimetric measurements of the enthalpies of solution of the respective potassium salts in water.

EXPERIMENTAL

Potassium hexafluororhenate(IV) was prepared from potassium hexaiodorhenate(IV) by fusion of the latter with an excess of KF.2HF. After excess of hydrogen fluoride had been driven off at ca. 670K, the hot material was cooled and extracted with water. The potassium hexafluororhenate(IV) remained as an impure solid residue, which was then purified by recrystallisation from hot water [5]. Potassium hexafluororuthenate(IV) was prepared by dissolution of potassium hexafluororuthenate(V) [6] in cold water. After filtration, the potassium hexafluororuthenate(IV) was precipitated from solution by the addition of a saturated solution of potassium fluoride. Both compounds were shown, from their infrared spectra, to be substantially free from fluorosilicate.

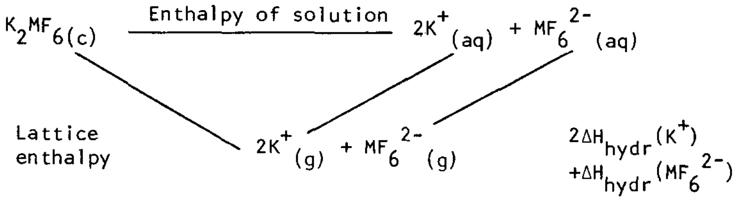
The enthalpies of solution were measured in an LKB 8700 precision calorimeter. This was connected to a Wheatstone bridge circuit, constructed in these laboratories, employing a Kipp-Zonen BD5 recorder as monitor. About 20 to 30 mg of compound were used for each determination; the volume of water used was 100 cm^3. All determinations were carried out at 298.2K.

RESULTS

The enthalpies of solution of potassium hexafluororhenate(IV) and of potassium hexafluororuthenate(IV) in water were found to be +63.0 and 59.4 kJ mol^{-1} respectively. These values represent the means of four and five independent determinations; the 90% confidence limits [7] are 0.3 and 1.5 kJ mol^{-1} respectively.

DISCUSSION

Two pieces of information are required for the derivation of single ion hydration enthalpies for these hexafluoroanions from our calorimetric results. These are the lattice enthalpies of the salts, and the single ion hydration enthalpy for the potassium ion:



Lattice energies for potassium hexafluororhenate(IV) and hexafluororuthenate(IV) have been calculated on the assumption of spherical anions, using the method of Ewald for the electrostatic interactions [8] and the Born-Mayer approach for the repulsive terms [9]. The salts have trigonal unit cells, dimensions $\underline{a}_o = 5.86_5$, $\underline{c}_o = 4.60_7$ Å for potassium hexafluororhenate(IV) and $\underline{a}_o = 5.76$, $\underline{c}_o = 4.64$ Å for potassium hexafluororuthenate (IV) [10]. The value used for ρ in the Born-Mayer expression was 0.345×10^{-10}m [9]. From these data and assumptions we calculate lattice energies of -1634 and -1661 kJ mol^{-1} for potassium hexafluororhenate(IV) and hexafluororuthenate(IV). Hence the respective lattice enthalpies are -1641 and -1668 kJ mol^{-1}.

From these calculated lattice enthalpies and our measured enthalpies of solution, the sums of the enthalpies of hydration of the (gaseous) constituent ions are -1571 and -1609 for potassium hexafluororhenate(IV) and potassium hexafluororuthenate(IV). These sums of ion hydration enthalpies can only be separated into their single ion constituents by making some reasonable but essentially empirical assumption. We choose to use the assumption that the single ion hydration enthalpy for the proton is -1091 kJ mol^{-1} [11]. On this assumption the single ion hydration enthalpy for K^+ is -321 kJ mol^{-1}, and hence the single ion hydration enthalpies for the ReF_6^{2-} and RuF_6^{2-} anions are -999 and -967 kJ mol^{-1} respectively. These values are compared with hydration

TABLE 1

Single Ion Hydration Enthalpies (SIHE) for Selected Anions

Anion	SIHE/kJ mol^{-1}	Ref.
ReF_6^{2-}	-999	This work
RuF_6^{2-}	-967	This work
$ReCl_6^{2-}$	-827, -845	[4]
$ReBr_6^{2-}$	-784	[4]
SO_4^{2-}	-1109	[1]
ReO_4^-	-172	[4]
F^-	-485	[1]

TABLE 2

Estimates for the ionic radii of Re^{4+} and Ru^{4+}

Radius of Re^{4+}/Å	Radius of Ru^{4+}/Å	Source
0.63	0.58	[12]
0.72	0.63	[13]
0.72	0.65	[14]
0.77	0.76	[15]

enthalpies reported for a selection of other anions in Table 1. These anion hydration enthalpies correlate qualitatively with anion charge (z) and size (radius r). It would not be fruitful to attempt a quantitative correlation with z^2/r or with z/r in view of the assumptions involved in estimating r for polyatomic ions. It is interesting that the hydration enthalpy for the ReF_6^{2-} anion is more negative than that for the RuF_6^{2-} anion, despite the smaller size of Ru^{4+} (Table 2). This order of values is presumably determined by slightly different charge distributions and metal-fluorine distances within the anions.

It is impossible to cite statistically meaningful uncertainties for the anion hydration enthalpies reported here. The uncertainties in the measured enthalpies of solution (see Results section) are considerably smaller than the uncertainties introduced in the derivation of the single ion values. Thus there is an uncertainty of several kJ mol^{-1} in the absolute value for the enthalpy of hydration of the proton [11], which will be reflected directly in our cited anion hydration enthalpies. Different authors use different assumptions in the derivation of single ion values; reference to the original assumptions is needed when comparing single ion values from different sources. However the uncertainty arising from this is smaller than those arising in the course of calculating lattice energies for salts containing polyatomic ions. Thus values ranging from -1506 to -1419 kJ mol^{-1} have been obtained for the lattice energy of potassium hexachlororhenate(IV) according to the method used. The former value is that obtained from a simple Born-Mayer calculation [9]. The latter value is obtained by the direct minimisation method of Jenkins and Pratt [16], which is based on the Huggins and Mayer potential approach [17], using a value of -0.56 for the effective charge on each chlorine atom [18]. This range of lattice energies results in an equal range for the estimates of anion hydration enthalpies, which will be from -827 to -740 kJ mol^{-1} for $ReCl_6^{2-}$. Until the calculation of lattice energies for this type of compound has been improved there will remain uncertainties of this order of magnitude in single ion hydration enthalpies for polyatomic ions. Fortunately the values given in Table 1 have all been derived using similar lattice energy calculations, so they may be intercompared safely.

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