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Enthalpies of formation of hydrazinium salts of some fluoro anions

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Abstract

The enthalpies of solution of the salts $N_2H_6SiF_6$, $N_2H_6ZrF_6$, $N_2H_6(BF_4)_2$ and $(N_2H_5)_2GeF_6$ have been measured and the enthalpies of formation of $N_2H_6SiF_6$, $N_2H_6(BF_4)_2$ and $(N_2H_5)_2GeF_6$ estimated.

Introduction

Few enthalpies of formation of hydrazinium salts have been reported; these include, however, those of N_2H_5F and $N_2H_6F_2$ [1]. The title compounds have been isolated in a pure state over recent years; they are white salts which dissolve endothermally in water. Since hydrolysis appears to be negligible on the time scale of solution calorimetry measurements (cf. salts of SbF_6^-) [2], the enthalpies of solution may be measured directly; from the results, enthalpies of formation may be calculated using known ancillary data.

Experimental

Compounds

Hydrazinium (2+) hexafluorometallates of silicon and zirconium were prepared from aqueous solutions of H_2SiF_6 or H_2ZrF_6 with hydrazinium (2+) fluoride – $N_2H_6F_2$ [3, 4].

The compound $N_2H_6(BF_4)_2$ was synthesised by the reaction between $N_2H_6F_2$ and boron trifluoride in anhydrous hydrogen fluoride [5].

Hydrazinium (1+) hexafluorogermanate(IV) was prepared by neutralisation of fluorogermanic acid with a 50% solution of $N_2H_4 \cdot H_2O$ at a pH value of 5. The colourless crystals were separated out by the addition of 95% ethanol [6].

Each compound was characterised by chemical analysis and X-ray powder photography.

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TABLE 1.

Enthalpies of solution of compounds and estimated enthalpies of formation (kJ mol^{-1})

Compound	No. of determinations	ΔH (soln.)	ΔH^0_f
$N_2H_6SiF_6$	8	40.32 ± 0.93	-2437 ± 1
$N_2H_6ZrF_6$	6	40.79 ± 2.11	
$N_2H_6(BF_4)_2$	7	28.74 ± 0.76	-3186 ± 1
$(N_2H_5)_2GeF_6$	10	65.37 ± 4.6	-2096 ± 5

TABLE 2

Ancillary data[a] (kJ mol^{-1})

ΔH^0_f		ΔH^0_f	
SiF_6^{2-}(aq.)	−2389.1	BF_4^-(aq.)	−1574.9
H_2GeF_6(aq.)	−2015.4	$N_2H_5^+$(aq.)	−7.5

[a] Values taken from ref. 10. Values for H_2GeF_6(aq.) and GeF_6^{2-}(aq.) are assumed to be identical. In this paper $\Delta H^0_f F^-$(aq.) is taken to be −332.63 kJ mol^{-1} [10].

Calorimetric measurements

These were made using a LKB 8700 calorimeter as described previously [7]. Samples of between 50 and 100 mg were used with 30 ml of water. As all compounds were isolated in the form of crystals, they were ground into a fine powder prior to filling them into frangible bulbs. Owing to a moderate sensitivity to moisture, $N_2H_6(BF_4)_2$ and $(N_2H_5)_2GeF_6$ samples were loaded in a dry-box. The ranges of error reported in Tables 1 and 2 refer to 90% confidence limits for the mean values given.

Results and discussion

These compounds dissolved smoothly in water, and their enthalpies of solution are close to those of related alkali or alkaline earth salts (Table 1). It has not been possible to estimate an enthalpy of formation for $N_2H_6ZrF_6$ because of the absence of reliable data for ΔH_f $(ZrF_6)^{2-}$(aq.). (There is a literature reference [8] to this quantity without an associated value; it is in reality impossible to use the other data in ref. 8 to calculate$\Delta H_f(ZrF_6)^{2-}$(aq.) because of the doubtful nature of aqueous zirconium chemistry.) The three calculated enthalpies of formation are within the expected range, and indicate the salts are formed exothermally from the parent fluorides plus the appropriate hydrazinium fluoride (−115, −205 and −212 kJ mol^{-1} for $N_2H_6SiF_6$, $N_2H_6(BF_4)_2$ and $(N_2H_5)_2GeF_6$, respectively).

The lattice enthalpy of $N_2H_6SiF_6$ may be calculated, using ΔH^0_f $(SiF_6)^{2-}(g) = -2295$ kJ mol^{-1} [9] and a newly calculated value [11] of 2115 kJ mol^{-1} for $\Delta H_f N_2H_6^{2+}(g)$. The figure obtained, -2290 kJ mol^{-1}, is close to that of $BaSiF_6$ (-2323 kJ mol^{-1}) [9].

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