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Note

Thermochemistry of polyhalides. IV. Anhydrous and hydrated potassium tetrachloroiodates

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Previous measurements on $MICl_4$[1] and $MICl_2$[2] (M = Cs, Rb) and simple thermodynamic arguments leading to predictions of numerical values of enthalpies of formation and of dissociation suggest that $KICl_4$ should be of marginal stability at ambient temperatures. In the course of spectroscopic investigations of salts containing the ICl_4^- anion it has been shown in this laboratory[3] that both $KICl_4$ and $KICl_4 \cdot H_2O$ may be prepared as pure crystalline compounds although the internal vibrations of the anion differ in the two compounds. A direct thermochemical investigation hence seemed appropriate since the factors governing the formation and relative stabilities of hydrated salts are little discussed[4].

EXPERIMENTAL

Materials and syntheses

$KICl_4 \cdot H_2O$. KIO_3 (15 g, B.D.H. reagent-grade material) was slowly added, with continuous stirring, to concentrated aqueous HCl (50 cm^3). Yellow crystals of $KICl_4 \cdot H_2O$ were filtered on a glass sinter and dried over $CaCl_2$ in a desiccator. Potentiometric halogen analysis gave the following results: Cl, 42.98%; I, 38.56% (calculated, Cl, 43.00%; I, 38.94%).

$KICl_4$. $KIBr_2$, prepared as described previously[5], was reacted with sulphuryl chloride. Sulphur dioxide and bromine were formed, and yellow, crystalline $KICl_4$ was stored in a desiccator over $CaCl_2$ and in an atmosphere of chlorine. Potentiometric halogen analysis gave the following results: Cl, 46.18%; I, 40.80% (calculated, Cl, 46.06%; I, 40.96%).

Solid-state Raman spectra (Coderg PHO Raman spectrometer) using 647.1 nm exciting radiation confirmed the presence of ICl_4^- species.

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Calorimetry

The isoperibol calorimeter used is fully described elsewhere[6]; check experiments using the neutralisation of 2-amino-2-hydroxymethylpropane-1,3 diol (THAM) in aqueous 0.100 mole dm^{-3} hydrochloric acid gave results typically of $\Delta H^0 = -29.87 \pm 0.05$ kJ mole^{-1} (literature value[7], $\Delta H^0 = -29.79 \pm 0.031$ kJ mole^{-1}).

The thermochemical reaction was that discussed previously[1], viz. reaction with aqueous silver nitrate, according to:

$$3\mathrm{KICl_4(c)} + [(p+15)\mathrm{AgNO_3}]m\mathrm{H_2O(l)} + (q+6)\mathrm{H_2O(l)} \rightarrow 12\,\mathrm{AgCl}(c) + \mathrm{AgI(c)} + 2\mathrm{AgIO_3(c)} + (p\,\mathrm{AgNO_3} + 3\mathrm{KNO_3} + 12\mathrm{HNO_3})(m+q)\mathrm{H_2O(l)} \quad (1)$$

Pre-saturation of the calorimetric liquid with silver iodate ensured complete precipitation of $AgIO_3$.

RESULTS

Standard enthalpies of reaction, ΔH_R°, according to eqn. (1) were measured using 100 cm^3 of $AgNO_3$ (0.025 mole dm^3) in the calorimeter, and are displayed in Table 1. Reactions were moderately fast, being complete within ca. 5 min. Considerable care was taken to ensure adequate and uniform stirring of the dense precipitates of silver halides and iodate.

Using the following ancillary data, respectively

ΔH_f°[AgI, AgCl, and $AgIO_3$](c) $= -[61.84 \pm 0.1^8, 127.07 \pm 0.1^8$ and $166.2 \pm 0.7^9]$
ΔH_f°[KNO_3, aq (3000 H_2O), $AgNO_3$, aq (2000 H_2O) and HNO_3, aq (4000 H_2O)]
(liq) $= -[457.67 \pm 0.5, 101.73 \pm 0.1$ and $207.00 \pm 0.46]^{10}$, and
$\Delta H_f^\circ[H_2O](l) = -285.83 \pm 0.04^{11}$.

TABLE 1

ENTHALPY OF REACTION OF $KICl_4$(c) AND $KICl_4 \cdot H_2O$(c) WITH SILVER NITRATE IN WATER AT 298.15 K

Uncertainties are calculated as 95% levels using Student's *t*-distribution table at the appropriate number of degrees of freedom.

Mass $KICl_4$ (g)	*$-\Delta H_R$ (kJ mole^{-1})*	*Mass $KICl_4 \cdot H_2O$ (g)*	*$-\Delta H_R$ (kJ mole^{-1})*
0.1492	307.4	0.1397	282.3
0.1335	300.0	0.1415	283.0
0.1386	302.5	0.1407	288.0
0.1405	302.2	0.1259	287.4_5
0.1493	292.3_5	0.1781	271.4
0.1338	295.1	0.1551	282.1
		0.1283	295.5
$\Delta H_R = -299.9 \pm 5.7$ kJ mole^{-1}		$\Delta H_R = -284.3 \pm 6.8$ kJ mole^{-1}	

(all values in kJ mole^{-1}), the following standard enthalpies of formation were calculated

$\Delta H_f^\circ[\mathrm{KICl_4(c)}] = -545.2 \pm 6.1$
$\Delta H_f^\circ[\mathrm{KICl_4 \cdot H_2O(c)}] = -846.6 \pm 7.1$ kJ mole^{-1}.

DISCUSSION

In a previous communication[1], based on calculations of lattice energies, a value of $\Delta H_f^\circ[\mathrm{KICl_4(c)}] = -538$ kJ mole^{-1} was predicted, in excellent agreement with the experimental value of -545 kJ mole^{-1} given above. This gives support to the model used, and, in particular, to the values derived for $\Delta H_f^\circ[\mathrm{ICl_4^-(g)}]$ and the thermochemical radius of the $\mathrm{ICl_4^-}$ anion, viz. -631 kJ mole^{-1} and 412 pm, respectively. The thermal stability of $\mathrm{KICl_4}$, however, is better considered in relation to the dissociation process, $\mathrm{KICl_4 \rightleftharpoons KICl_2 + Cl_2}$, for which the relevant enthalpy value, ΔH_D°, has been shown to be calculable from the relationship $\Delta H_D^\circ \simeq \Delta U(\mathrm{KICl_4} - \mathrm{KICl_2}) + 26$ kJ mole^{-1}, whence $\Delta H_D \simeq +6.1$ kJ mole^{-1}. Assuming, as before, that entropy contributions from $\mathrm{KICl_4}$ and $\mathrm{KICl_2}$ will largely cancel, and that the $T\Delta S$ term for $\mathrm{Cl_2}$ is ~ 67 kJ mole^{-1} at ambient temperatures[1], then the free energy of dissociation, ΔG_D°, $\simeq -6$ kJ mole^{-1}, and the dissociation constant, $K_p \simeq 11$. The observed stability is hence not unreasonable, since activation barriers to ionic mobility in the solid state are doubtless high. Thermal stability will be strongly temperature-dependent, not only due to the loss of chlorine, but also since the $\mathrm{KICl_2 \rightleftharpoons KCl + ICl}$ dissociation will become significant.

Comparison of increment values of ΔH_f° for anhydrous and hydrated crystals suggests a value of ca. 310 kJ mole^{-1} for $\Delta H(_f^\circ\mathrm{KICl_4 \cdot H_2O}) - \Delta H_f^\circ(\mathrm{KICl_4})$, in excellent agreement with the observed difference of 301 kJ mole^{-1}. This again gives confidence in the predictive procedure based on lattice energy and thermochemical radii calculations. The observed enhanced stability of the hydrated, compared with the anhydrous, crystal presumably results from the differences in crystal structure[12]; this is discussed in detail elsewhere[3] but it is clear from the vibrational spectra that the environment of the $\mathrm{ICl_4^-}$ ion differs in the two compounds. A simple, three-band Raman spectrum of $\mathrm{KICl_4}$ (bands at 286 (ν_1, A_{1g}), 260 (ν_4, B_{2g}) and 128 (ν_2, B_{1g}) cm^{-1}) may be readily interpreted in terms of D_{4h} point group symmetry whereas the more complex pattern from the distorted $\mathrm{ICl_4^-}$ ion in $\mathrm{KICl_4 \cdot H_2O}$ (together with some coincident IR bands) illustrates the effect of the lower site symmetry. The splittings in the Raman spectrum follow closely those in $\mathrm{SCl_3^+ICl_4^-}$ (Form I)[13] in which the $\mathrm{ICl_4^-}$ ion has recently been shown to have a similar distortion[14].

In conclusion, standard enthalpies of formation of crystalline potassium tetrachloroiodate and potassium tetrachloroiodate monohydrate have been determined as -545.2 ± 6.1 and -846.6 ± 7.1 kJ mole^{-1}, respectively. These and derived quantities are discussed in relation to predicted values and stabilities of tetrachloroiodates.

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