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Note

STANDARD ENTHALPIES OF FORMATION OF TETRAMETHYL- AND TETRAETHYLAMMONIUM HEXACHLOROPHOSPHATES

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Tetraalkylammonium cations are of considerable synthetic importance as a means of stabilising a variety of anions in salts which would be unstable if smaller monatomic cations were involved. Thermochemical data on such systems are comparatively sparse, with studies mainly limited to stable salts with monatomic cations. However, salts of the type $M^+PCl_6^-$ (M = Na, K, Rb, Cs) are not known. In this paper, we report the preparation, enthalpy of aqueous alkaline hydrolysis, and standard enthalpies of formation of $R_4N^+PCl_6^-$(c) where R = CH_3 and C_2H_5. From these and other ancillary data, values for the lattice energies of these salts are estimated.

EXPERIMENTAL

Preparations

$(C_2H_5)_4NPCl_6$

$(C_2H_5)_4NCl$, (6.98 g, 0.042 mole) in CH_2Cl_2 was added slowly with stirring to a solution of PCl_5 (7.03 g, 0.034 mole) in CH_2Cl_2 under a nitrogen atmosphere. The resulting white precipitate was filtered in the absence of air, washed with CH_2Cl_2 and pressed dry. Found: Cl, 56.4%. Calcd. for $(C_2H_5)_4NCl_6$: Cl, 56.9%.

$(CH_3)_4NPCl_6$

$(CH_3)_4NPCl_6$ was prepared by the addition of PCl_5 (10.26 g, 0.042 mole) in CH_2Cl_2 to a slurry of $(CH_3)_4NCl$ (5.35 g, 0.049 mole) followed by stirring (two days) when the white crystals which separated were filtered, washed with CH_2Cl_2, and dried. Found: Cl, 67.5%. Calcd. for $(CH_3)_4NPCl_6$: Cl, 66.9%.

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Calorimetry

Enthalpies of aqueous alkaline hydrolysis were measured at 298.15K using a LKB 8700-1 Precision Calorimetry System equipped with a 100 cm^3 reaction vessel. The system was checked using the neutralisation of 2-amino-2-hydroxymethylpropane-1,3-diol (THAM) in aqueous 0.100 mole dm^{-3} hydrochloric acid, for which we obtained $\Delta H^0 = -29.69 \pm 0.03$ kJ $mole^{-1}$ (literature value [1], $\Delta H^0 = -29.79 \pm 0.031$ kJ $mole^{-1}$).

Accurately weighed amounts of the salts (5—11 × 10^{-5} mole) contained in glass ampoules were broken into an excess of aqueous 0.100 mole dm^{-3} sodium hydroxide solution (100 cm^3). The exothermic hydrolysis was reasonably fast, with most of the heat evolution in the first 60 sec. Reaction was complete after ca. 15 min.

RESULTS AND DISCUSSION

The standard enthalpies of hydrolysis were calculated on the basis of the equation

$$R_4NPCl_6(c) + 8\ NaOH(n\ H_2O) \rightarrow (5\ NaCl + Na_3PO_4 + R_4NCl)(n + 4)H_2O \quad (1)$$

The results are given in Table 1.

Assuming the ancillary data listed in Table 2, standard enthalpies of formation of the two hexachlorophosphates were calculated from

$$\Delta H_f^0[(CH_3)_4NPCl_6,\ c] = 6\ \Delta H_f^0[Cl^-,\ (aq)] + \Delta H_f^0[PO_4^{3-}.\ (aq)]$$
$$+ 4\ \Delta H_f^0[H_2O,\ (l)] + \Delta H_f^0[(CH_3)_4N^+,\ (aq)] - 8\ \Delta H_f^0[OH^-,\ (aq)] - \Delta H_h^0 \quad (2)$$

The enthalpy of mixing of the products was assumed to be zero. Hence

$$\Delta H_f^0[(CH_3)_4NPCl_6,\ c] = -736.0 \pm 5.0\ kJ\ mole^{-1}$$

and

$$\Delta H_f^0[(C_2H_5)_4NPCl_6,\ c] = -879.2 \pm 15.0\ kJ\ mole^{-1}$$

Using these values, an attempt was made to calculate the lattice energies of these species via the thermochemical radius approach of Kapustinskii and Yatsimirskii [2], Unfortunately, the quartic equation did not yield a meaningful root for the thermochemical radius. However, lattice energies, U, have been calculated on the basis of the following equations

$$U \simeq \Delta H + 2RT$$

and

$$R_4NPCl_6(c) \overset{U}{\rightarrow} R_4N^+(g) + PCl_6(g)$$

Using the values of standard enthalpies of formation $(CH_3)_4N^+$,g = 536 [7], $(C_2H_5)_4N^+$,g = 463 [8], and PCl_6^-,g = —876 [9] (all values in kJ $mole^{-1}$) we

TABLE 1

Enthalpy of aqueous alkaline hydrolysis, ΔH_h^0, of R_4NPCl_6(c) at 298.15 K ($R = CH_3$, C_2H_5)

Mass $(CH_3)_4NPCl_6$ (g)	Dilution (n)	$-\Delta H_h^0$ (kJ $mole^{-1}$)	Mass $(C_2H_5)_4PCl_6$ (g)	Dilution (n)	$-\Delta H_h^0$ (kJ $mole^{-1}$)
0.02124	79 514	958.72	0.04448	44 963	913.11
0.02406	70 194	946.84	0.03316	60 313	904.27
0.02153	78 443	952.74	0.04120	48 543	914.57
0.03541	47 695	958.55	0.02982	67 069	945.92
0.02086	80 962	957.42	0.02513	79 586	914.41
0.02343	72 082	952.11	0.03670	54 496	861.93 *
0.01859	90 849	955.19	0.02063	96 946	910.44
0.02032	83 114	968.14			
0.03521	47 966	960.83			
Mean $\Delta H_h^0 = -956.73 \pm 4.63$ kJ $mole^{-1}$ **			Mean $\Delta H_h^0 = -917.12 \pm 14.60$ kJ $mole^{-1}$ **		

* Value excluded from mean.

** Uncertainties are calculated as 95% levels, using a student's *t* distribution with the appropriate number of degrees of freedom.

TABLE 2

Ancillary enthalpy of formation data (298.15 K)

Species	ΔH_f^0 (kJ $mole^{-1}$)	Ref.
Cl^-(aq)	-167.08 ± 0.09	3
OH^-(aq)	-230.03 ± 0.05	3
H_2O (l)	-285.8 ± 0.04	3
PO_4^{3-}(aq)	-1284.0 ± 1.0	4
$(C_2H_5)_4N^+$(aq)	-246.5 ± 5.0 *	
$(CH_3)_4N^+$(aq)	-103.3 ± 3.0	6

* Extrapolated from data [5] for aqueous NH_4^+, $(C_2H_5)NH_3^+$, $(C_2H_5)_2NH_2^+$ and $(C_2H_5)_3NH^+$.

derive $U[(CH_3)_4NPCl_6] \simeq 401$ and $U[(C_2H_5)_4NPCl_6] \simeq 471$ kJ $mole^{-1}$. In view of the nature of the estimates of the enthalpies of formation of the gas phase ions, confidence limits are unrealistic: differences in lattice energies, however, are presumably much more precise. It is interesting to note that the larger value attaches to the compound with the larger anion, reflecting the apparently anomalous values of enthalpies of formation for the $(CH_3)_4N^+$,g and $(C_2H_5)_4N^+$,g species.

CONCLUSION

Measured enthalpies of aqueous alkaline hydrolysis of tetramethyl- and tetraethylammonium hexachlorophosphates have been used to calculate

$\Delta H_f^0[(CH_3)_4NPCl_6,c] = -736.0 \pm 5.0$ kJ mole^{-1} and $\Delta H_f^0[(C_2H_5)_4NPCl_6,c] = -879.2 \pm 15.0$ kJ mole^{-1} and to estimate lattice energies.

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