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Standard Enthalpies of Formation and Lattice Energies of Alkylammonium Halides. Part 1. Propylamine Hydrochlorides

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The standard enthalpies of formation of mono-, di-, and tri-propylamine hydrochlorides have been determined by a solution reaction method, leading to values of −354.7 ± 0.4, −389.5 ± 1.0, and −446.4 ± 1.0 kJ mol^{-1} respectively. Using available values of proton affinities, estimates of crystal-lattice energies have been made.

ALKYLAMMONIUM halides $NR_nH_{4-n}X$ ($R = Me, Et, Pr$, *etc.*; $0 \leqslant n \leqslant 4$; $X = Cl, Br$, or I) form a graded series for which thermodynamic data may be determined, and from which properties of large non-spherical ions may be calculated and hence trends explored. Other than for the methyl series ($R = Me$; $X = Cl$, Br, or I) reported by Wilson,[1] very few data are available. Standard enthalpies of formation of such crystalline compounds are important, since in conjunction with increasingly available and reliable experimental high-energy data, *e.g.* for proton affinities, they allow calculation of lattice energies. The results of such calculations may then be used to check estimates made using semi-empirical methods, *e.g.* thermochemical radius calculations.

EXPERIMENTAL

Preparations.—The compound $N(C_3H_7)_3HCl$ (purity 99.8%) was prepared under appropriate conditions from HCl(g) and tri-n-propylamine and recrystallised repeatedly from CCl_4. The compounds $N(C_3H_7)_2H_2Cl$ and $N(C_3H_7)H_3Cl$ (purities 99.5 and 99.92% respectively) were commercial samples (T.C.I., Tokyo) recrystallised from CH_3CCl_3–CCl_4 or CH_3CCl_3 respectively.

Calorimetry.—Enthalpies of solution of samples of crystalline tri-n-propylamine hydrochloride in NaOH (100 cm^3 of 0.1 mol dm^{-3}), and of mono- and di-n-propylamines in NaOH (25 cm^3 of 0.1 mol dm^{-3}), were measured using a commercial isoperibol calorimetric system (L.K.B. model 8700), the performance of which was periodically checked using the enthalpy of neutralisation, $\Delta H_N^\ominus$, of tris(hydroxymethyl)methylamine in an excess of HCl (0.1 mol dm^{-3}) as a test reaction; a typical check result was $\Delta H_N^\ominus = -29.74$ kJ mol^{-1} (lit.,[2] $\Delta H_N^\ominus = -29.790$ kJ mol^{-1}).

For tri- and di-propylamine hydrochloride experiments the calorimetric liquid was pre-saturated with the relevant amine. Mono-n-propylamine is completely miscible with water, hence enthalpy of solution measurements in NaOH (0.1 mol dm^{-3}) were made separately, in two ways. First, the L.K.B. system was used in the normal mode, with samples of amine in the ampoule. Secondly, a direct injection system was constructed as follows: a twin-calorimeter system was arranged such that in the measurement calorimeter a series of injections of amine, *via* fine-bore Teflon tubing connected to a commercial syringe pump (Harvard model 975), was made into NaOH (100 cm^3 of 0.1 mol dm^{-3}). Appropriate volume and enthalpy calibrations and checks were made. Buoyancy corrections were applied to weighings; the vapour pressures of amines were too low to make necessary significant corrections to the observed enthalpies of reaction.

RESULTS

Calorimetric Reaction.—The standard enthalpy of reaction, $\Delta H_R^\ominus$, associated with equation (1) where aq* = H_2O or

$$N(C_3H_7)_nH_{4-n}Cl(c) + OH^-(aq^*) \longrightarrow [N(C_3H_7)_nH_{3-n} + H_2O + Cl^-](aq^*) \quad (1)$$

aqueous saturated amine (see text), was measured. Hence we obtain equation (2) (l† = l or aq* as appropriate).

$$\Delta H_f^\ominus[N(C_3H_7)_nH_{4-n}Cl,c] = \Delta H_f^\ominus[N(C_3H_7)_nH_{3-n},l\dagger] + \Delta H_f^\ominus(Cl^-,aq) + \Delta H_f^\ominus(H_2O,l) - \Delta H_f^\ominus(OH^-,aq) - \Delta H_R^\ominus \quad (2)$$

Reactions were quantitative and rapid, being complete within a few min. Results are collated in Table 1; the values for the enthalpy of solution, $\Delta H_S^\ominus$, of mono-n-propylamine in 0.1 mol dm^{-3} NaOH using the differential injection method lay in the range $22.4 \leqslant -\Delta H_S^\ominus \leqslant 25.8$ kJ mol^{-1}, in satisfactory agreement with the value of -24.28 ± 0.13 kJ mol^{-1} obtained using the isoperibol calorimeter. Using additional literature data, values for the standard enthalpies of formation of the three hydrochlorides were calculated, using equation (2), and are collated in Table 2.

TABLE 1

Enthalpies of reaction, $\Delta H_R^\ominus$ (or solution, $^*\Delta H_S^\ominus$), of propylammonium chlorides (or propylamine *) in excess of sodium hydroxide solution (0.1 mol dm^{-3})

Compound	Dilution †	No. of values	$\Delta H_R^\ominus$ (or $^*\Delta H_S^\ominus$)/ kJ mol^{-1}
NPr_3HCl,c	6 800—10 200	6	13.92 ± 0.11
NPr_2H_2Cl,c	759—1 354	10	8.03 ± 0.10
$NPrH_3Cl,c$	555—827	6	3.04 ± 0.03
$NPrH_2,l$	472—971	8	*—24.28 ± 0.13

† Mole ratio of water to compound.

TABLE 2

Standard enthalpies of formation, $\Delta H_f^\ominus$(c), and lattice energies, U_T, of n-propylammonium chlorides, $NPr_nH_{4-n}Cl$

Compound	$-\Delta H_f^\ominus$/kJ mol^{-1}	U_T/kJ mol^{-1}
NH_4Cl	217	692 [a]
$NPrH_3Cl$	354.7 ± 0.4	639
NPr_2H_2Cl	389.5 ± 1.0	593
NPr_3HCl	446.4 ± 1.0	575
NPr_4Cl	500 [b]	550 [b]

[a] Ref. 1. [b] Extrapolated value.

Ancillary Data.—The following data were used: $\Delta H_f^\ominus$(NPr$_3$,l)[3] = −207.15, $\Delta H_f^\ominus$(NPr$_2$H,l)[4] = −156.1, $\Delta H_f^\ominus$(N-PrH$_2$,l)[3] = −101.50, $\Delta H_f^\ominus$(NaOH,aq, 0.1 mol dm^{-3})[5] = −469.57, $\Delta H_f^\ominus$(NaCl,aq, 0.1 mol dm^{-3})[5] = −409.07, and $\Delta H_f^\ominus$(H$_2$O,l)[6] = −285.83 (all values in kJ mol^{-1}). Unless stated in the original references, uncertainties are arbitrarily assessed as ten times the last given digit; a major uncertainty (*ca.* 1 kJ mol^{-1}) apparently lies in reported values for enthalpies of formation of the amines.

The standard enthalpies of formation are listed in Table 2, together with estimates of relevant lattice energies.

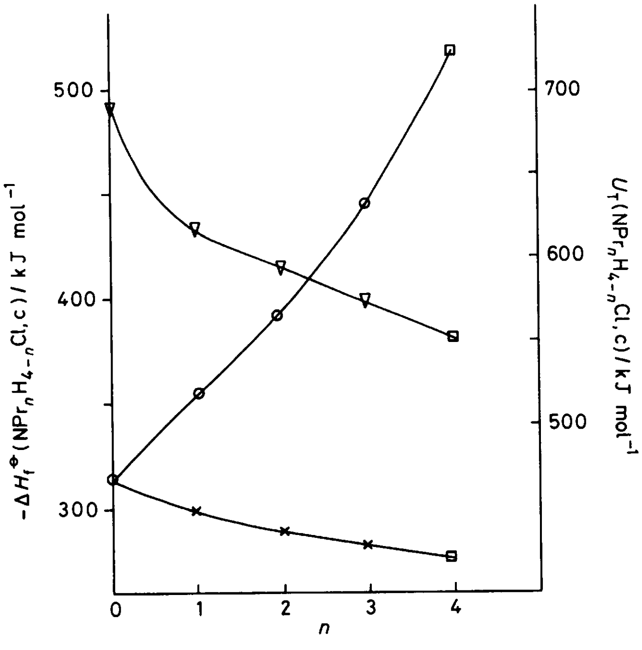
DISCUSSION

Enthalpies of Formation.—These decrease smoothly from *ca.* −355 to *ca.* −446 kJ mol^{-1} upon progressive replacement of H by CH$_2$CH$_2$CH$_3$ groupings. Although entirely reasonable, this contrasts sharply with the behaviour of the analogous methylammonium series, where there is a slight trend for the enthalpies of formation to increase[1] with increasing substitution, *i.e.* −298, −291, −283 kJ mol^{-1} respectively for NMeH$_3$Cl, NMe$_2$H$_2$Cl, and NMe$_3$HCl. The situation is paralleled by the parent amines, NR$_{3-n}$H$_n$, for which values of the standard enthalpies of formation[3] are, in order of increasing alkyl substitution, −11, −10, −10.9 (Me) and −101, −156, −207 (Pr) kJ mol^{-1} respectively. This has important implications for possible extrapolations to obtain estimates of the standard enthalpy of formation of the tetra-alkylammonium chloride, NPr$_4$Cl, for which the experimental calorimetric method is not applicable. However, an estimate in the range $-480 < \Delta H_f^\ominus < -520$ kJ mol^{-1} appears reasonable. This quantity is important, since, in conjunction with relatively simple enthalpy of solution measurements, a value for $\Delta H_f^\ominus$(NPr$_4$$^+$,aq) may be estimated. For this, comparable measurements on other halides are relevant, and further experimental results will be reported.

Lattice Energies.—An interesting extension is a calculation of lattice-energy values for the propylammonium series. It may be shown that the lattice energy, U_T, is given by equation (3) where P is the

$$U_T = P + \Delta H_f^\ominus(\mathrm{H^+,g}) + \Delta H_f^\ominus(\mathrm{Cl^-,g}) + \Delta H_f^\ominus(\mathrm{NPr}_n\mathrm{H}_{3-n},\mathrm{g}) - \Delta H_f^\ominus(\mathrm{NPr}_n\mathrm{H}_{4-n}\mathrm{Cl,c}) - 2RT \quad (3)$$

proton affinity of the relevant amine. This calculation neglects heat-capacity contributions and thermal effects arising from polymorphism, *e.g.* order–disorder transitions or internal rotations; these, however, are unlikely to amount to more than a few per cent of the lattice-energy values. Putting $\Delta H_f^\ominus$(Cl$^-$,g)[7] = −246.02, $\Delta H_f^\ominus$(H$^+$,g)[8] = 1 535.9, $-\Delta H_f^\ominus$(NPrH$_2$, NPr$_2$H, and NPr$_3$,g)[9] = 70, 115, and 161 respectively, the proton affinities[10] of NPrH$_2$, NPr$_2$H, and NPr$_3$ = 931, 966, and 994.5 respectively (all values in kJ mol^{-1}), and using values of $\Delta H_f^\ominus$(NPr$_n$H$_{4-n}$Cl,c) from Table 2, we derive the values of lattice energies given in Table 2. As expected these decrease with increasing cationic size, and are substantially less than corresponding values calculated for the analogous methylammonium chlorides, which range from 596 to 656 kJ mol^{-1}. Extrapolation of the smooth decrease (see Figure) leads to an estimate of U_T(NPr$_4$Cl) of *ca.* 5.50 kJ mol^{-1}.



Plots of enthalpies of formation of methylammonium (×) and propylammonium chlorides (○), and crystal lattice energies (▽) of propylammonium chlorides against the number of alkyl groups (n) in the cation. Extrapolated values are denoted by □

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