Unexpected Trends in Standard Enthalpies of Formation of Alkylammonium Salts and Calculation of Amine Proton Affinities

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Positive, negative, and zero variations in values of standard enthalpies of formation of crystalline alkylammonium salts, $NR_nH_{4-n}X$, have all been observed upon substitution of hydrogen by alkyl groups.

We have recently measured the standard enthalpies of formation of numerous alkylammonium salts, $NEt_nH_{4-n}X$ (X = Cl, Br, I; $1 \leqslant n \leqslant 3$); $NR_nH_{4-n}ICl_4$ (R = Me, Et; $0 \leqslant n \leqslant 4$);[1] and $NPr_nH_{4-n}Cl$ ($1 \leqslant n \leqslant 3$)[2]; data for the series $NMe_nH_{4-n}X$ (X = Cl, Br, I; $0 \leqslant n \leqslant 4$) were already available.[3] Two interesting consequences are apparent.

First, the effect of successive substitution of hydrogen by alkyl groups upon the value of the standard enthalpy of formation, ΔH_f°, is surprisingly varied. Remarkably, for at least two anions (I^-, ICl_4^-) in the methyl series, ΔH_f° is, within close limits (± 6 kJ mol^{-1}) independent of the degree of substitution as shown in Figure 1. Thus ΔH_f° $NH_4ICl_4(c)$ = *ca.*

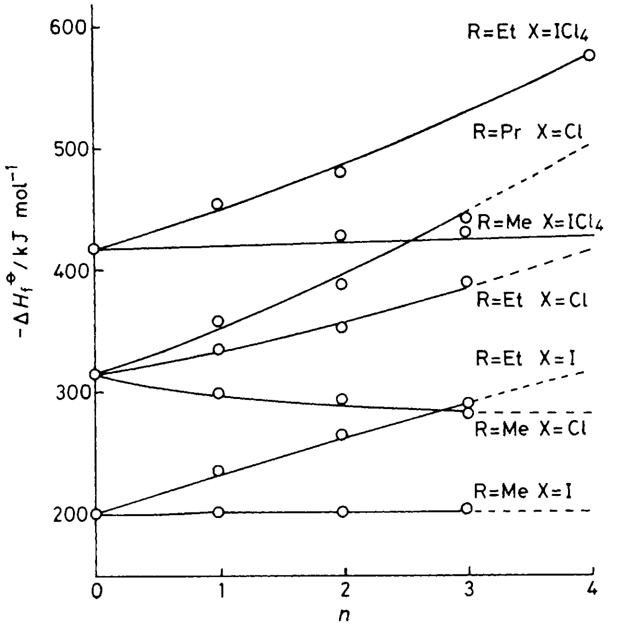

Figure 1. Variation in the values of the standard enthalpies of formation, ΔH_f°, of $R_nH_{4-n}NX$, as functions of *n*.

ΔH_f° NH_3MeICl_4(c) = *ca.* ΔH_f° $NH_2Me_2ICl_4$(c) = *ca.* ΔH_f° $NHMe_3ICl_4$(c) = *ca.* ΔH_f° NMe_4ICl_4(c) and likewise for the $NMe_nH_{4-n}I$ series. Rationalisation of this by considering compensating effects of various parameters involved within appropriate thermochemical cycles may be made, but the choice of cycle is arbitrary. The results are unexpected.

For chlorides there is a decrease in $-\Delta H_f^\circ$ with increasing methyl substitution (paralleled by the bromide) while for both ethyl and propyl compounds there is an increase. For both the iodides and tetrachloroiodates $-\Delta H_f^\circ$ increases with increasing ethyl substitution. Although within each series the change is smooth, the rate of change varies considerably between the methyl, ethyl, and n-propyl series.

Table 1. Calculated and experimental proton affinities (*P*) of mono-, di-, and tri-ethylamines.

		P(expt.)[b]/kJ mol^{-1}	
Amine	*P*(calc.)[a]/kJ mol^{-1}	Range	Mean
Et_3N	920	958.1—986.6	972
Et_2NH	885	939.3—966.1	953
$EtNH_2$	867	895.4—926.3	911

[a] Calculated from the equation, using the Kapustinskii–Yatsimirskii method to obtain lattice energies, U_T. [b] Ref. 5.

Secondly, in Table 1 we compare published, experimental values of proton affinities (*P*) of mono-, di-, and tri-ethylamines, with values calculated using standard enthalpy of formation data for the ethylammonium chloride series. It may be shown that $P = \Delta H_f^\circ(\text{amine, g}) + \Delta H_f^\circ(H^+, g) + \Delta H_f^\circ(Cl^-, g) - \Delta H_f^\circ(\text{amine hydrochloride, c}) - U_T + 2RT$. All quantities are experimentally available with considerable accuracy, except the lattice energies, U_T. These were calculated using the semi-empirical Kapustinskii-Yatsimirskii (K–Y) method,[4] except that values of the thermochemical radius of the cation, *viz.* $NEt_nH_{4-n}^+$, and not of the anion, were computed. The results, collated in Table 1, show reasonable agreement between experimental and calculated values, *i.e.* within *ca.* 5—7% of mean published experimental values of *P*. This in turn gives support to the use of the K–Y method for calculation of lattice energies where values of proton affinities are not available.

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