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Standard Enthalpies of Formation and Lattice Energies of Alkylammonium Halides. Part 2.[1] Ethylammonium Halides

B. Mokhtar Derakhshan, Arthur Finch, Peter N. Gates, and Michael Stephens
Department of Chemistry, The Bourne Laboratory, Royal Holloway and Bedford Colleges, University of London, Egham, Surrey, TW20 0EX

The standard enthalpies of formation of mono-, di-, and tri-ethylamine hydro-chlorides, -bromides, and -iodides, $NEt_nH_{4-n}X$ (X = Cl, Br, or I; $1 \leqslant n \leqslant 3$) have been determined using a solution-reaction method; extrapolated values for the quaternary salts, NEt_4X (X = Cl, Br, or I) have been estimated. Lattice energies have been computed from these data using semi-empirical methods and also using available proton affinity data and appropriate thermodynamic cycles.

Alkylammonium halides, $NR_nH_{4-n}X$ (R = Me, Et, or Pr; X = Cl, Br, or I; $0 \leqslant n \leqslant 4$) are of considerable synthetic importance, the large cations often being used to effect crystal stabilisation of otherwise unstable complex anions. In addition, their essentially ionic nature, coupled with both aqueous and non-aqueous solubility characteristics, permits their use in diverse solvent systems. Further, in conjunction with increasingly reliable proton affinity data, calculations of lattice energies and associated thermodynamic parameters are possible. Such values may then be used to test estimates made from semi-empirical calculations. Enthalpy of formation data are presently limited to the propylamine hydrochlorides, $NPr_nH_{4-n}Cl$,[1] the methyl series, $NMe_nH_{4-n}X$ (X = Cl, Br, or I),[2] and NEt_2H_2Cl.[3] Since the effect upon the values of enthalpy of formation by successive replacement of H by alkyl groupings is entirely different in the methyl,[4] compared with the propyl (chloride) series, a systematic investigation of the complete ethyl series is timely.

Experimental

Preparations.—Ethylamine hydrobromide was made *via* the gas-phase reaction of HBr and ethylamine at *ca.* −78 °C and the white crystals stored in a vacuum desiccator over $CaCl_2$. Samples were analysed titrimetrically for bromine (Found: Br, 63.5. Calc. for C_2H_8BrN: 63.5%).

Diethylamine hydrobromide was prepared *via* reaction of a dichloromethane solution of diethylamine with HBr (g). The product was recrystallised from ethanol, dried under vacuum and stored as above. Samples were analysed titrimetrically for bromine (Found: Br, 52.0. Calc. for $C_4H_{12}BrN$: 51.9%).

Triethylamine hydrobromide was similarly prepared, recrystallised, stored, and analysed (Found: Br, 43.9. Calc. for $C_6H_{16}BrN$: 43.9%).

Ethylamine hydroiodide was prepared by dissolving HI (g), generated from iodine and tetrahydronaphthalene, in tetrachloromethane and reacting with ethylamine. The white crystalline product was dried under nitrogen, pumped at 50 °C under vacuum, and stored in darkness over $CaCl_2$. Samples were analysed titrimetrically for iodine (Found: I, 73.3. Calc. for C_2H_8IN: 73.4%).

Di- and also tri-ethylamine hydroiodides were similarly prepared, dried, stored, and analysed (Found: I, 62.7. Calc. for $C_4H_{12}IN$: 63.2%. Found: I, 56.0. Calc. for $C_6H_{16}IN$: 55.5%).

Commercial samples of mono-, di-, and tri-ethylamine hydrochlorides were used directly after recrystallisation, drying, and storage as above. Titrimetric analyses for chlorine showed purities of $\geqslant 99.5\%$ for all three compounds.

Calorimetry.—Enthalpies of reaction $\Delta H_R^\ominus$ of the relevant amine hydrohalide in NaOH (100 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 mean result was $\Delta H_N^\ominus = -29.82$ kJ mol^{-1} (lit.,[5] $\Delta H^\ominus = -29.790$ kJ mol^{-1}).

Results

Calorimetric Reactions.—All reactions were rapid and quantitative, being complete within a few minutes. For each compound, $NEt_nH_{4-n}X$ (c) (X = Cl, Br, or I; n = 1—3) the standard enthalpy of reaction, $\Delta H_R^\ominus$, associated with equation (1) was measured. Results are collated in Table 1. Hence we

$$NEt_nH_{4-n}X\,(c) + OH^-\,(aq) \longrightarrow (NEt_nH_{3-n} + H_2O + X^-)\,(aq) \quad (1)$$

obtain equation (2) from which standard enthalpies of formation, $\Delta H_f^\ominus$, of each salt were calculated using appropriate ancillary data.

$$\Delta H_f^\ominus(NEt_nH_{4-n}X,c) = \Delta H_f^\ominus(NEt_nH_{3-n},aq) + \Delta H_f^\ominus(X^-,aq) + \Delta H_f^\ominus(H_2O,l) - \Delta H_f^\ominus(OH^-,aq) - \Delta H_R^\ominus \quad (2)$$

Ancillary Data.—The following data were used: $\Delta H_f^\ominus(NEt_3,aq)$[6] = −174.05, $\Delta H_f^\ominus(NEt_2H,aq)$[6] = −134.30, $\Delta H_f^\ominus(NEtH_2,aq)$[6] = −101.25, $\Delta H_f^\ominus(OH^-,aq)$ = −230.02,[7] $\Delta H_f^\ominus(Cl^-, Br^-, I^-)(aq)$ = −(167.08, 121.50, 56.90, respectively),[7] $\Delta H_f^\ominus(H_2O,l)$ = −285.83[8] (all values in kJ mol^{-1}). Uncertainty levels are as given in original references or were assessed arbitrarily as ten times the last digit quoted. The derived standard enthalpies of formation are included in Table 2.

Discussion

Enthalpies of Formation.—Values of standard enthalpies of formation, $\Delta H_f^\ominus$, of nine ethylammonium halides are listed in Table 2; there is satisfactory agreement with an independent published value of $\Delta H_f^\ominus(NEt_2H_2Cl,c)$.[3] The almost linear change of $\Delta H_f^\ominus$ upon successive replacement of hydrogen by ethyl in each halide series allows confident extrapolation to values of $\Delta H_f^\ominus(NEt_4X,c)$ (X = Cl, Br, or I). These latter values are of interest since, in conjunction with easily measured enthalpies of solution, they enable an estimate to be made of $\Delta H_f^\ominus(NEt_4^+,aq)$.

The variation of $\Delta H_f^\ominus$ of alkylammonium salts with degree

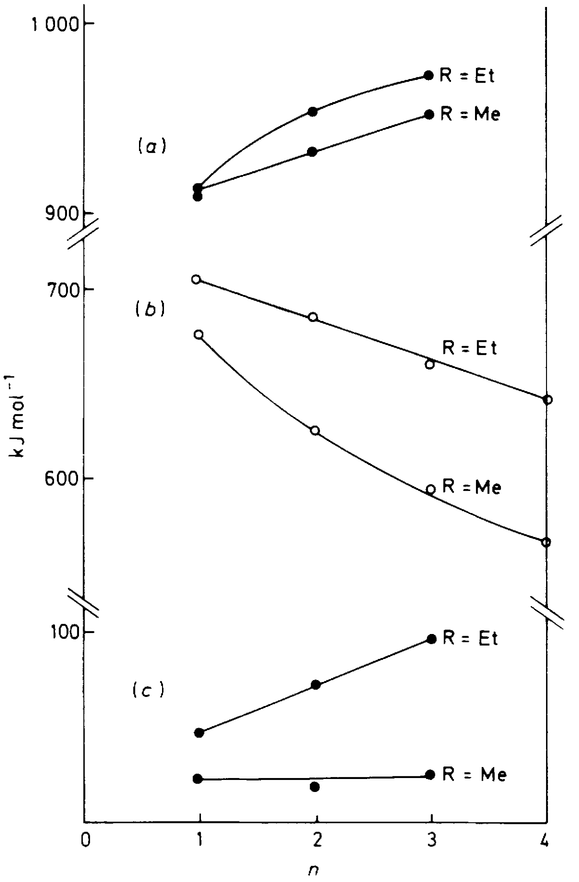

Figure. Plots of (*a*) $P(\mathrm{NR}_n\mathrm{H}_{3-n}, \mathrm{g})$, $1 \leqslant n \leqslant 3$; (*b*) $U(2)(\mathrm{NR}_n\mathrm{H}_{4-n}, \mathrm{Cl}, \mathrm{c})$, $1 \leqslant n \leqslant 4$; and (*c*) $-\Delta H_f^{\ominus}(\mathrm{NR}_n\mathrm{H}_{3-n}, \mathrm{g})$, $1 \leqslant n \leqslant 3$, against n (R = Me or Et)

Table 1. Enthalpies of reaction, $\Delta H_R^{\ominus}$, of ethylammonium halides in excess sodium hydroxide solution (0.1 mol dm^{-3})

Compound	Dilution [a]	No. of Values	Mean $\Delta H_R^{\ominus}$ [b]/ kJ mol^{-1}
$\mathrm{NEt_3HCl}$ (c)	1 812—4 434	7	-8.62 ± 0.29
$\mathrm{NEt_2H_2Cl}$ (c)	1 663—2 485	7	-1.80 ± 0.04
$\mathrm{NEtH_3Cl}$ (c)	1 002—1 704	7	9.67 ± 0.06
$\mathrm{NEt_3HBr}$ (c)	2 637—4 782	6	-0.88 ± 0.05
$\mathrm{NEt_2H_2Br}$ (c)	2 628—4 336	7	4.92 ± 0.08
$\mathrm{NEtH_3Br}$ (c)	1 370—2 464	7	16.28 ± 0.26
$\mathrm{NEt_3HI}$ (c)	6 160—10 229	6	1.99 ± 0.23
$\mathrm{NEt_2H_2I}$ (c)	5 274—8 896	7	15.90 ± 1.70
$\mathrm{NEtH_3I}$ (c)	2 258—3 593	6	20.10 ± 0.57

[a] Mol ratio, water : compound. [b] Uncertainties are calculated using a Students *t* distribution at the 99.5% level.

Table 2. Standard enthalpies of formation, $\Delta H_f^{\ominus}$(c), and lattice energies, U, of ethylammonium halides, $\mathrm{NEt}_n\mathrm{H}_{4-n}\mathrm{X}$ ($0 \leqslant n \leqslant 4$; X = Cl, Br, or I)

Compound	$-\Delta H_f^{\ominus}$/ kJ mol^{-1}	$U(1)$ [a]/ kJ mol^{-1}	$U(2)$ [b]/ kJ mol^{-1}	ΔU_T/ kJ mol^{-1}
$\mathrm{NEt_4Cl}$	414.0 [c]		641 [c]	
$\mathrm{NEt_3HCl}$	387.5 ± 0.6	607	660	53
$\mathrm{NEt_2H_2Cl}$	355.4 ± 0.7 [d]	617	684	67
$\mathrm{NEtH_3Cl}$	333.9 ± 0.5	659	704	45
$\mathrm{NEt_4Br}$	377.0 [c]		612 [c]	
$\mathrm{NEt_3HBr}$	350.5 ± 0.1	582	633	51
$\mathrm{NEt_2H_2Br}$	316.5 ± 0.7	590	659	69
$\mathrm{NEtH_3Br}$	294.8 ± 0.6	633	677	44
$\mathrm{NEt_4I}$	317.0 [c]		583 [c]	
$\mathrm{NEt_3HI}$	289.0 ± 0.5	558	601	43
$\mathrm{NEt_2H_2I}$	263.0 ± 1.8	580	624	44
$\mathrm{NEtH_3I}$	234.1 ± 0.8	608	640	31

[a] Calculated using proton affinity data (ref. 9). [b] Calculated using the Kapustinskii–Yatsimirskii method (ref. 10). [c] Extrapolated value. [d] Value from ref. 3 is -358.15 ± 0.8 kJ mol^{-1}.

of alkyl substitution, *n*, deserves comment since quite different results are found depending on either the alkyl group or the anion.[4] For the ethyl series presented here, in common with propylammonium chlorides,[1] values of $-\Delta H_f^{\ominus}$ increase smoothly with increasing *n*; similar results are obtained for the ethylammonium tetrachloroiodate series.[4] However, for some methylammonium compounds, *e.g.* chloride and bromide, values of $-\Delta H_f^{\ominus}$ *decrease* with increasing *n*, and for the series $\mathrm{NMe}_n\mathrm{H}_{4-n}\mathrm{X}$ (X = I or $\mathrm{ICl_4}$) all values of $\Delta H_f^{\ominus}$ are constant, within very close limits. Thus, for example, $\Delta H_f^{\ominus}(\mathrm{NH_4I,c}) = \Delta H_f^{\ominus}(\mathrm{NMe_4I,c})$ and $\Delta H_f^{\ominus}(\mathrm{NH_4ICl_4,c}) = \Delta H_f^{\ominus}(\mathrm{NMe_4ICl_4,c})$.

These effects may be clarified by consideration of the following thermodynamic cycle, where $a = \Sigma\Delta H_f^{\ominus}[\text{amine,g, H}^+\text{,g, X}^-\text{,g}]$, P = proton affinity, and U = lattice energy. Thus, $\Delta H_f^{\ominus}$ (alkylammonium salt) $= a - (P - U)$.

$$\begin{tikzcd}
\text{Alkylammonium salt (c)} \arrow[r, "U"] & \text{amine,H}^+\text{(g)} + \text{X}^-\text{(g)} \arrow[d, "P"] \\
\text{elements (standard states)} \arrow[u, "\Delta H_f^{\ominus}\text{(salt)}"] \arrow[r, "a"] & \text{amine (g)} + \text{H}^+\text{(g)} + \text{X}^-\text{(g)}
\end{tikzcd}$$

Values of $\Delta H_f^{\ominus}$ for methylamines are small (*ca.* 18—24 kJ mol^{-1}) and hence their contribution to $\Delta H_f^{\ominus}$(alkylammonium salt) is slight. For the ethyl and propyl series, however, values of $\Delta H_f^{\ominus}$(amine,g) increase significantly with *n*,[6] with the corresponding effect on the magnitude of $\Delta H_f^{\ominus}$(alkylammonium salt). *Differences*, $\Delta(\Delta H_f^{\ominus})$, in values of $\Delta H_f^{\ominus}$ (alkylammonium salt) in any series are given by equation (3), and

$$\Delta(\Delta H_f^{\ominus}) = \Delta[\Delta H_f^{\ominus}(\text{amine,g})] - (\Delta P + \Delta U) \qquad (3)$$

hence, for the interesting cases (R = Me, X = I or $\mathrm{ICl_4}$) where $\Delta(\Delta H_f^{\ominus}) = 0$, then $\Delta P = \Delta[\Delta H_f^{\ominus}(\text{amine,g})] - \Delta U$. Trends in the parameters P, U, and $\Delta H_f^{\ominus}$(amine,g) as a function of *n* are given in the Figure, inspection of which shows the anomalous behaviour of $\Delta H_f^{\ominus}$(methylamine,g). These latter values are not only small, but essentially constant, whereas P and U vary smoothly and substantially with changes in values of *n*. The invariance of $\Delta H_f^{\ominus}$(alkylammonium salt) in the $\mathrm{NMe}_n\mathrm{H}_{4-n}\mathrm{X}$ (X = I or $\mathrm{ICl_4}$) series is presumably fortuitous, depending on differences between relevant values of lattice energies and proton affinities not being significantly modulated by $\Delta H_f^{\ominus}$(amine,g) values.

Lattice Energies.—Values of ethylammonium halide lattice energies, *U*, may be calculated from proton affinity data (where available) using the relationship (4) (where *n* = 1—3 and X = Cl, Br, or I). Putting $\Delta H_f^{\ominus}(\mathrm{H^+,g}) = 1\,539.9$,[7] $\Delta H_f^{\ominus}(\mathrm{X^-,g}) =$

$$\begin{aligned} U_T = {} & \Delta H_f^{\ominus}(\mathrm{NEt}_n\mathrm{H}_{3-n},\mathrm{g}) + \Delta H_f^{\ominus}(\mathrm{H^+,g}) + \\ & \Delta H_f^{\ominus}(\mathrm{X^-,g}) - \Delta H_f^{\ominus}(\mathrm{NEt}_n\mathrm{H}_{3-n}\mathrm{HX,c}) - P - 2RT \qquad (4) \end{aligned}$$

-246.0, -234, and -197 (Cl^-, Br^-, and I^- respectively),[7] $-\Delta H_f^\ominus$($NEtH_2$, NEt_2H, and NEt_3) (g) $= 47.15$, 71.42, and 95.81 respectively,[6] mean values of $P = 912$, 951.4, and 973 for $NEtH_2$, NEt_2H, and NEt_3 respectively[9] (all values in kJ mol^{-1}), and substituting appropriate values for $\Delta H_f^\ominus$($NEt_nH_{3-n}HX$,c) from Table 2 we calculate values $U(1)$ of the lattice energy (Table 2). These are compared with values, $U(2)$, computed using a standard semi-empirical procedure (Kapustinskii–Yatsimirski thermochemical radius method)[10] using values of 0.125, 0.135, and 0.150 nm respectively for thermochemical radii of $NEtH_3^+$, $NEt_2H_2^+$, and NEt_3H^+. The agreement between such calculated and the essentially experimental values, $U(1)$, is pleasing, the difference being in the region $30 < U < 70$ kJ mol^{-1}, *ca.* 5—12%. This gives credence to the reverse procedure, *i.e.* calculation of values of proton affinities where no direct experimental data exist *via* the semi-empirical computational procedure.

In general, $U \propto 1/d$, where d is the sum of the anionic and cationic radii, and values of U decrease with increasing n as expected; the order with respect to halogen is $U(I) < U(Br) < U(Cl)$, *i.e.* paralleling the decrease in anion size. This is general throughout all alkylammonium compounds studied. Hence there is no reason to attribute any apparent anomalies in the trends in standard enthalpies of formation to crystal or lattice energy effects.

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