Standard Enthalpies of Formation and Thermodynamic Cycle Values of Crystal Lattice Energies of Methylammonium Halides

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The standard enthalpies of formation of the methylammonium halides $[NMe_nH_{4-n}]X$ (n = 1—3; X = Cl, Br, or I) have been derived from calorimetric studies. These values lead to the crystal lattice energies of the salts. Linear relations permit the calculation of $\Delta H_f^\ominus([NMe_4]X,c)$ which are in fair agreement with derived literature values. The values obtained for the crystal lattice energies of the tetramethylammonium halides, however, are in poor agreement with those obtained by extended-calculation procedures.

THIS paper reports derived values for the standard enthalpies of formation of the chloride, bromide, and iodide salts of the methylammonium ion series $[NMe_nH_{4-n}]X$. Such values are of interest because (*i*) they permit trends and variations in a fundamental thermodynamic parameter within a closely related series of compounds to be observed, (*ii*) very little thermodynamic data are available on solid compounds of this type, which contain unsymmetrical polyatomic ions, and (*iii*) such enthalpy data, in conjunction with recent reliable values for amine proton affinities, allow the calculation of crystal lattice energies *via* a thermochemical cycle. These ' indirect ' empirical values will permit methods that employ extended calculation procedures to obtain crystal lattice energies[1] to be perfected for systems involving non-spherical ions.

the solid salts, $\Delta H_f^\ominus([NMe_nH_{4-n}]X,c)$, were derived using literature values for the standard enthalpies of formation of the aqueous hydroxide ion and the relevant products.[2] The results are given in the Table.

$$[NMe_nH_{4-n}]X(c) + [OH]^-(aq) \longrightarrow NMe_nH_{3-n}(aq) + H_2O(l) + X^-(aq) \quad (1)$$

When the enthalpy of formation data were plotted against the number of methyl groups in the cation (n) it was seen that for the chloride and bromide salts there is a gradual decrease in the enthalpy of formation on the introduction of methyl groups which, after the addition of the first group, is linear. The enthalpies of formation of the iodide salts however are virtually independent of the number of methyl groups in the cation. Extrapolation of these plots to $n = 4$ gives the values (Figure). for the standard enthalpies of formation, $\Delta H_f^\ominus([NMe_4]X,c)$, for the tetramethylammonium halides. These values can be compared with those obtained indirectly from thermal-dissociation and enthalpy of solution studies on these compounds.

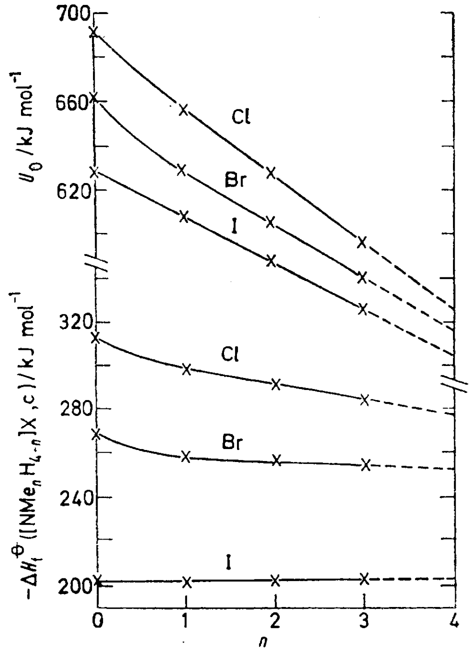
Enthalpies of reaction, ΔH_1, of solid methylammonium halide salts with excess of 0.1 mol dm^{-3} sodium hydroxide solution, standard enthalpies of formation of the solid salts, $\Delta H_f^\ominus([NMe_nH_{4-n}]X,c)$, proton affinities of the amines, p.a., standard enthalpies of formation of the gaseous methylammonium ions, $\Delta H_f^\ominus([NMe_nH_{4-n}]^+,g)$, and the crystal lattice energies of the salts, U_0 (kJ mol^{-1})

Compound	ΔH_1	$\Delta H_f^\ominus([NMe_nH_{4-n}]X,c)$	p.a.	$\Delta H_f^\ominus([NMe_nH_{4-n}]^+,g)$	U_0
$[NH_4]Cl$		−314.4 [a]	866	624	692
$[NH_4]Br$		−270.8 [a]			661
$[NH_4]I$		−201.4 [a]			628
$[NMeH_3]Cl$	5.168 ± 0.062	−298.3 [b]	909	604	656
$[NMeH_3]Br$	11.37 ± 0.07	−258.9			629
$[NMeH_3]I$	17.80 ± 0.46	−200.7			608
$[NMe_2H_2]Cl$	−4.241 ± 0.078	−291.1	936	582	627
$[NMe_2H_2]Br$	7.496 ± 0.064	−257.3			605
$[NMe_2H_2]I$	16.64 ± 0.15	−201.7			587
$[NMe_3H]Cl$	−15.73 ± 0.14	−283.3 [c]	953	559	596
$[NMe_3H]Br$	0.219 ± 0.011	−253.7			579
$[NMe_3H]I$	14.27 ± 0.12	−203.0			565
$[NMe_4]Cl$		−276.0 [d]			566 [d]
$[NMe_4]Br$		−251.5 [d]		536	553 [d]
$[NMe_4]I$		−203.5 [d]			544 [d]

[a] Ref. 2*a*. [b] Ref. 2*a* gives −297.9 kJ mol^{-1}. [c] Ref. 2*a* gives −281.5 kJ mol^{-1}. [d] By extrapolation.

RESULTS AND DISCUSSION

Enthalpies of Formation.—The enthalpy change ΔH_1 for reaction (1) was measured in an isoperibol calorimeter at 298.15 K. The standard enthalpies of formation of



Plots of enthalpies of formation and crystal lattice energies of the methylammonium halides against the number of methyl groups (n) in the cation.

Smith and Calvert[3] measured the dissociation pressures for reaction (2) over the temperature range 463—503 K

$$[NMe_4]X(c) \longrightarrow NMe_3(g) + MeX(g) \quad (X = Cl \text{ or } I) \quad (2)$$

for the chloride and 513—580 K for the iodide. Analysis of their data [least-squares fit of log (P/mmHg) against $1/T$] * gives values for the enthalpy change for reaction (2) of 162.7 kJ mol^{-1} for the chloride at 483 K and 169.4 kJ mol^{-1} for the iodide at 546 K. The values at 298 K of 168.5 and 195.3 kJ mol^{-1} respectively were obtained by using the following molar heat-capacity data in J K^{-1} (temperature range, correlation coefficient for the least-squares fit) directly or by assuming that the same

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] N. N. Greenwood, ' Ionic Crystals, Lattice Defects and Nonstoicheiometry,' Butterworths, London, 1968, p. 27.

[2] (*a*) Nat. Bur. Stand., Technical Note 270-3, Washington D.C., 1968; (*b*) CODATA Recommended Key Values for Thermodynamics, 1973, *J. Chem. Thermodynamics*, 1975, **7**, 1.

[3] A. Smith and R. P. Calvert, *J. Amer. Chem. Soc.*, 1914, **36**, 1363.

expression holds over the appropriate temperature range:

$[NMe_4]Cl(c),\ C_P = 39.196 + 0.3955T$ (260—350 K, 1.0000)[4]

$[NMe_4]I(c),\ C_P = 50.033 + 0.3730T$ (200—300 K, 0.9996)[5]

$NMe_3(g),\ C_P = 19.807 + 0.2425T$ (298.15—500 K, 0.9997)[6]

$MeCl(g),\ C_P = 18.749 + 0.0736T$ (298.15—500 K, 1.0000)[6]

$MeI(g),\ C_P = 23.394 + 0.0700T$ (298.15—500 K, 0.9995)[6]

Using literature data for the enthalpies of formation of the products[2a] gives $\Delta H_f^\ominus([NMe_4]Cl,c) = -273.6$ kJ mol^{-1} and $\Delta H_f^\ominus([NMe_4]I,c) = -206.6$ kJ mol^{-1}. These values together with enthalpy of solution data[7,8] and ancillary data[2b] give $\Delta H_f^\ominus([NMe_4]^+,aq) = -101.9$ and -107.9 kJ mol^{-1} respectively. Taking the mean value of -104.9 ± 3.0 kJ mol^{-1}, the enthalpy of solution of $[NMe_4]Br$,[9] and $\Delta H_f^\ominus(Br^-,aq)$[2b] gives $\Delta H_f^\ominus([NMe_4]Br,c) = -251.1$ kJ mol^{-1}. The derived standard enthalpies of formation of the tetramethylammonium salts are in fair agreement with those obtained by extrapolation (Table). The latter values give a mean value for $\Delta H_f^\ominus([NMe_4]^+,aq)$ of -104.8 ± 0.6 kJ mol^{-1}.

Crystal Lattice Energies.—Two independent pulsed-ion cyclotron resonance studies on the intrinsic gas-phase basicities of amines at 298 K have produced comparable values for the proton affinities of methylamines.[10] These values are based on the absolute value for ammonia[11] of 866 ± 13 kJ mol^{-1}. The value of 866 kJ mol^{-1} is supported by preliminary results of other workers.[10b] The mean values for the two sets are given in the Table together with the standard enthalpies of formation of the corresponding gaseous amine cations calculated using ancillary literature data.[2a] The crystal lattice energies at absolute zero, U_0, are obtained from a thermochemical cycle which can be expressed by equation (3). The term $\Sigma\Delta H_T$ arises from any polymorphic transitions which these salts may undergo between 0 and 298 K.[12] Such transitions can amount to 4 kJ mol^{-1},[13] but are usually of the order 1 kJ mol^{-1} or less.[4,14] They have been ignored in this work. The magnitude and sign of the heat-capacity term is more difficult to assess in the absence of values for most of the salts and all the gaseous cations. It has been assumed to be zero. Some idea of the validity of this assumption can be gauged from what data are available. Values of $\int_0^{298} C_P\,dT$ are available for $[NH_4]Cl$ and $[NH_4]Br$ (15.4 ± 0.9 kJ mol^{-1}),[14b,c] $[NMeH_3]Cl$ (17.5 kJ mol^{-1}),[13] and the tetramethylammonium halides (28.4 ± 0.6 kJ mol^{-1}).[4,5] Such values are not available for the gaseous cations, but are available for the corresponding isoelectronic and structurally similar hydrocarbons methane (10.03 kJ mol^{-1}),[15] ethane (11.95 kJ mol^{-1}),[15] and 2,2-dimethylpropane (21.06 kJ mol^{-1}).[15] If the theoretical value for a monatomic gas (6.20 kJ mol^{-1}) is used for the halide ions, then the heat-capacity term is of the order ± 2 kJ mol^{-1}. Boyd[16] reached the same conclusion for the tetramethylammonium salts using a more sophisticated vibrational-analysis method.

$$U_0 = \Delta H_f^\ominus([NMe_nH_{4-n}]^+,g) + \Delta H_f^\ominus(X^-,g) - \Delta H_f^\ominus([NMe_nH_{4-n}]X,c) + \Sigma\Delta H_T + \int_0^{298} \{C_P([NMe_nH_{4-n}]X,c) - C_P([NMe_nH_{4-n}]^+,g) - C_P(X^-,g)\}dT \quad (3)$$

The crystal lattice energies obtained by this approach are given in the Table. Plots of U_0 against the number of methyl groups in the cation (n) were similar to the plots of the standard enthalpy of formation but with greater gradients (Figure). Extrapolation to $n = 4$ gives values for the tetramethylammonium halides. These give the mean value $\Delta H_f^\ominus([NMe_4]^+,g) = 536 \pm 1$ kJ mol^{-1}, which is consistent with the values obtained for the other methylammonium ions.

The cycle values obtained for the ammonium compounds are in good agreement with extended-calculation studies[17] which give 698 (Cl), 665 (Br), and 634 (I) kJ mol^{-1}. However, the cycle values for the tetramethylammonium compounds are greater than those obtained by calculations. Ref. 16 gives 553 (Cl), 544 (Br), and 518 (I) kJ mol^{-1}, whereas ref. 18 gives 502 (Cl), 494 (Br), and 477 (I) kJ mol^{-1}. Such differences are usually explained by invoking the presence of non-ionic contributions to the bonding. (Good discussions on this point are provided by Johnson[19] and Adams.[20]) In this context it should be noted that i.r. studies on these tetramethylammonium salts indicate the presence of $C-H \cdots X^-$ hydrogen bonding in all cases.[21] Some $N-H \cdots X^-$ hydrogen bonding is therefore to be

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expected for the salts of unsymmetrically methyl-substituted cations.

It should be noted that for the tetramethylammonium salts the values of the enthalpy of formation and crystal lattice energy are obtained by simple extrapolations of observed empirical relations. The values are therefore only semiempirical. The fact that the enthalpies of formation so obtained agree fairly well with values obtained using an entirely different approach appears to give some justification for the extrapolations.

EXPERIMENTAL

The salts were prepared by adding a slight excess of an aqueous solution of the amine to the stoicheiometric amount of aqueous acid. Water was removed on a rotary evaporator and the product recrystallised several times from ethanol. The well formed crystals were pumped dry *in vacuo*. Because of the hygroscopic nature of some of the compounds, and the fact that the iodides are light sensitive, they were all stored in brown glass bottles in a dry-box. Subsequent manipulations were carried out in the dry-box or on a vacuum line. All the compounds were analytically pure with respect to halide ion as shown by volumetric analysis using the adsorption-indicator method [22] (dichlorofluorescein for chlorides and bromides, eosin for iodides).

The calorimeter and experimental procedures have been described elsewhere.[23] The calorimetric solvent used in all measurements was 0.1 mol dm^{-3} sodium hydroxide solution. Uncertainty intervals for the calorimetric measurements are twice the standard deviation of the mean obtained from at least five measurements. The uncertainties in data from ref. 2*a* are not available. Errors in data derived from the calorimetric results cannot therefore be quoted, but it is unlikely that they will be much greater than twice those observed for the calorimetric measurements. Whilst the value for the proton affinity of ammonia is now known with some degree of accuracy, the precision of the most recent measurements [10b] has yet to be published. The uncertainties in data derived from the proton-affinity values are therefore unknown but are likely to be less than ±5 kJ mol^{-1}. Regression analyses of the data shown in the Figure give the uncertainties in the enthalpies of formation and crystal lattice energies for the tetramethylammonium salts as ±5 kJ mol^{-1} for the chlorides and bromides and ±2 kJ mol^{-1} for the iodides.

[5/1934 *Received, 6th October*, 1975]

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