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Reprint of: The enthalpy of formation of gaseous tetra-*n*-propylammonium cations

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A R T I C L E I N F O

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Dedicated to the memory of the late
Professor Manuel Ribeiro da Silva

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A B S T R A C T

The standard molar enthalpies of formation of crystalline tetraalkylammonium halides, $\Delta_f H^\circ(R_4NX,c)$, R = Me, Et, Pr, Bu and X = Cl, Br, I, and the corresponding lattice energies, $U_L(R_4NX)$ were obtained from the literature as far as available for T = 298.15 K. From consistent values of these two quantities and values for $\Delta_f H^\circ(X^-,g)$ the standard molar enthalpies of formation of the gaseous cations were obtained from $\Delta_f H^\circ(R_4N^+,g) = \Delta_f H^\circ(R_4NX,c) + U_L(R_4NX) + 2RT^\circ - \Delta_f H^\circ(X^-,g)$. The value for the hitherto unreported $\Delta_f H^\circ(Pr_4N^+,g) = (307 \pm 7)$ kJ · mol is here derived. The value for the absolute standard molar enthalpy of hydration is $\Delta_h H^\circ(R_4N^+,aq)$ −210 kJ · mol^{-1}, but may have an appreciable uncertainty, reflecting that of $\Delta_f H^\circ(R_4N^+,aq)$, obtained from interpolation of values for the Me, Et, and Bu analogues.

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1. Introduction

The tetraalkylammonium cations, R_4N^+, have been the subjects of numerous investigations because they show a gradual increase in size as the alkyl chains are lengthened, so that ionic size dependent properties can be studied, see the review [1]. The thermochemistry of their halide and other salts has also been studied by numerous investigators, leading to their enthalpies of formation and lattice energies and to the thermodynamic functions of the gaseous cations and their hydration [1–13]. In addition to the thermochemistry of tetraalkylammonium ions and salts, that of ions and salts with fewer than four alkyl substituents on the nitrogen atom, $NR_nH_{4-n}^+$, have also been studied [2,7–9].

However, it appears that the enthalpy of formation of the isolated tetra-*n*-propyl-ammonium cation has escaped these studies and it is the purpose of this paper to fill this gap. A value, $\Delta_f H^\circ([H(CH_2)_p]_4N^+,g) = (312 \pm 7)$ kJ · mol^{-1} for $p = 3$ was estimated previously by the present author [1] from regressions involving p = 1, 2, and 4, but not involving direct data for p = 3. In order to obtain this information, it is necessary to obtain appropriate enthalpies of formation of tetra-*n*-propylammonium crystalline salts, $\Delta_f H^\circ$, and their lattice energies, U_L, as well as the standard molar enthalpies of formation of the halide anions.

2. The available data

In the following, $\Delta_f H^\circ$ pertains to the molar enthalpy of formation of the compounds in their standard crystalline state from the elements at the standard temperature T° = 298.15 K and pressure P° = 0.1 MPa. Wilson [2] measured the enthalpy of hydrolysis by aqueous hydroxide of crystalline $NMe_nH_{4-n}X$ (n = 1–3, X = Cl, Br, I) salts and derived their $\Delta_f H^\circ$ values. Linear extrapolation to n = 4 then yielded the $\Delta_f H^\circ$ values, for Me_4NX. Nwankwo [3] obtained the enthalpies of formation of the tetraethylammonium halides from the measured enthalpies of solution in water and based the results on $\Delta_f H^\circ(Et_4N^+,aq)$ estimated by Finch *et al.* [4] by extrapolation of values for $NEt_nH_{4-n}^+$, aq. The resulting $\Delta_f H^\circ(Et_4NX,c)$ (X = Cl, Br, I) values have uncertainties of ±5 kJ · mol^{-1}. Finch and Hall [5] again used the hydrolysis by aqueous hydroxide of the $NPr_nH_{4-n}Cl$ (n = 1–3) salts and used linear extrapolation to obtain the $\Delta_f H^\circ(Pr_4NCl,c)$ value. A similar method was used by Derakshman *et al.* [6] to obtain the $\Delta_f H^\circ(Et_4NX,c)$ (X = Cl, Br, I) values. Blazejowski and co-workers [7–9] used thermoanalytical methods (DTA, TG, TGA) to obtain the $\Delta_f H^\circ(NR_nH_{4-n}X,c)$ (R = Me, Et, Pr, Bu, n = 1–3, X = Cl, Br, I) and extrapolation to n = 4 to yield the values for R_4NX. Nagano and co-workers [10,11] used bomb calorimetry to obtain enthalpies of combustion, hence $\Delta_f H^\circ$ values of the tetramethyl-, tetraethyl-, and tetrabutylammonium halides, but for some reason did not extend the study to the tetrapropylammonium salts.

In spite of the divergence of the values reported by various authors that are shown in table 1, the trends are clear: $-\Delta_f H^\circ$

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TABLE 1
The standard molar enthalpies of formation, $-\Delta_f H°/\text{kJ} \cdot \text{mol}^{-1}$, of crystalline tetraalkylammonium halides according to various authors.

Salt	Wilson	Nwankwo	Finch&Hall	Derakshnan	Blazejowski	Nagano
			$-\Delta_f H°/kJ \cdot mol^{-1}$			
Me_4NCl	276.0				272	276.4
Me_4NBr	251.5				268	251.0
Me_4NI	203.5				190	203.9
Et_4NCl		400.8		414.0	401	369.4
Et_4NBr		374.1		377.0	360	342.7
Et_4NI		331.5		317.0	316	300.2
Pr_4NCl			500		475	
Pr_4NBr					442	
Pr_4NI					395	
Bu_4NCl					534	564.8
Bu_4NBr					415	540.3
Bu_4NI					460	498.6

increases as the alkyl chains become longer and diminishes as the halide anions become heavier.

In the following, the lattice energy of a salt, U_L, is the energy that has to be invested in the crystalline salt at $T = 0$ K to separate its ions to infinite distance in the ideal gas phase at the same temperature. The correction from $T = (0 \text{ to } 298.15)$ K is of the order of $2 \text{ kJ} \cdot \text{mol}^{-1}$ [2] and conversion to lattice enthalpies at $T = 298.15$ K adds $2RT = 5.0 \text{ kJ} \cdot \text{mol}^{-1}$ to the lattice energies. Boyd [12] was among the first who calculated the lattice thermodynamics of tetra-*n*-alkylammonium halides. He realised the importance of taking account of the non-electrostatic interactions in the crystals of these salts in addition to the electrostatic ones. Ladd [13] used different expressions for taking account of these interactions and obtained significantly smaller values. Johnson and Martin [14] averaged the previously published values of Boyd and Ladd, but did not add any new information in the set of lattice energies they reported. Wilson [2] measured calorimetrically the enthalpies of formation of methylammonium halides: $NMe_nH_{4-n}X$ ($n = 1$–$3, X = Cl, Br, I$) leading to their lattice energies. He then resorted to linear extrapolation of the values against n to obtain the values for $n = 4$, the tetraalkylammonium halides (in the case of the iodide, the linearity extended to NH_4I). The values are somewhat larger than Boyd's. Nwankwo [3] calculated the lattice energies of tetramethyl- and tetraethylammonium halides according to the Kapustinskii–Yatsimirskii expression [15,16] and obtained for Et_4NI a value lower than that of Ladd (and Boyd). Finch and Hall [5] used an extrapolation similar to Wilson's for the *n*-propylammonium chlorides, $NPr_nH_{4-n}Cl$ ($n = 1$–3), and obtained the rather large value of $550 \text{ kJ} \cdot \text{mol}^{-1}$ for Pr_4NCl. Blazejowski and co-workers [7–9] again used the extrapolation method for $NR_nH_{4-n}X$, ($R = Me$, Et, Pr, Bu, $X = Cl, Br, I, n = 1$–3) as well as the Kapustinskii–Yatsimirskii expression and obtained two values for each R_4NX salt. For the bromides the two modes of calculation agreed only for the ethyl and propyl salts, whereas for the iodides the extrapolation was non-linear and could not be carried out satisfactorily. Nagano *et al.* [10,11] determined the enthalpies of formation of tetramethyl-, tetraerthyl, and tetrabutylammoniumm iodides by bomb calorimetry and derived some of the lattice energies.

In spite of the divergence of the values reported by various authors and shown in table 2, the trends are clear: U_L diminishes as the alkyl chains become longer and as the halide anions become heavier.

3. The enthalpy of formation of gaseous tetraalkylammonium cations

The standard molar enthalpy of formation of the gaseous tetraalkylammonium cations at $T° = 298.15$ K is obtained from:

$$\Delta_f H°(R_4N^+, g) = \Delta_f H°(R_4NX, c) + U_L(R_4NX) + 2RT° - \Delta_f H°(X^-, g), \tag{1}$$

where $\Delta_f H°(X^-, g)$ is the standard molar enthalpy of formation of the gaseous halide anions at $T°$. These values are available from the compilation of Wagman *et al.* [17] as $-(233.13, 219.07, \text{ and } 197) \text{ kJ} \cdot \text{mol}^{-1}$ for $X = Cl^-$, Br^-, and I^-, respectively. However, in order to apply equation (1), it is necessary to employ consistent values of $\Delta_f H°(R_4NX, c)$ and $U_L(R_4NX)$. These are available from the work of Blazejowski and co-workers [7–9], albeit the reported values are estimates based on linear extrapolation of experimental data for $NR_nH_{4-n}X$ salts with $n = 1$–3 and $X = Cl^-$, Br^-, and I^-. The resulting values of $\Delta_f H°(R_4N^+, g)$ are shown in table 3 and within small uncertainties are independent of the nature of the halide anion as they should be. Their averages with values obtained for

TABLE 2
The lattice energies, $U_L/\text{kJ} \cdot \text{mol}^{-1}$, of tetraalkylammonium halides according to various authors.

Salt	Boyd	Ladd	Wilson	Nwankwo	Finch&Hall	Blazejowski[a]	Nagano
				$U_L/kJ \cdot mol^{-1}$			
Me_4NCl	552.7	502	566			576	584
Me_4NBr	544.3	494	553			587, 558	573
Me_4NI	518.0	477	544			531	548
Et_4NCl				422		575	
Et_4NBr				412		555, 556	
Et_4NI	458.6	448		396		530	522
Pr_4NCl					550	546	
Pr_4NBr	493.3	423				532, 530	
Pr_4NI						505	
Bu_4NCl						521	
Bu_4NBr						453, 506	
Bu_4NI						484	

[a] The first entries are from extrapolation of $NR_nH_{4-n}X$ data, the second ones from application of the Kapustinskii–Yatsimirskii expression.

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