Recent determination of the standard enthalpy of formation of the ammonium azide, $\Delta_f H^\circ(^{15}NH_4N_3,c)$ and the assignment of the viscosity $B$-coefficient for the azide anion, $B(N_3,aq)$, in aqueous solution enable us to estimate the standard enthalpy of formation of the gaseous azide anion, $\Delta_f H^\circ(N_3,g)$, a thermochemical magnitude in some dispute, to be 192 kJ-mol$^{-1}$.

KEY WORDS: $B$-coefficient, enthalpy of formation, azide anion.

1. Introduction

Thermochemical cycles (via lattice energy computations) can provide indirect estimates of the enthalpy of formation of gaseous complex anions.$^{(1,2)}$ Provided a method is available for generating complex anions of a specific type, direct experimentation can be used to obtain the same thermodynamic information.

In the case of the azide anion the experimental work involving the determination of the electron affinity of the azide radical, $A_e(N_3,g)$, and the proton affinity of azide ion, $A_p(N_3,g)$ by Brauman's$^{(3,4)}$ group leads to assignments for $\Delta_f H^\circ(N_3,g)$ of 194.9 kJ-mol$^{-1}$ and 201.0 kJ-mol$^{-1}$, respectively. The electron affinity values measured in these studies are confirmed by recent work by Contimatti et al.$^{(5)}$ and therefore we are led to the expectation that the value for the standard enthalpy of formation of the gaseous azide anion, $\Delta_f H^\circ(N_3,g)$ in the region of 190 - 200 kJ-mol$^{-1}$.

In contrast, the total lattice potential energies of the alkali metal...
azides have been calculated as part of five separate studies\textsuperscript{(6-11)} and are in substantial agreement one study with another, leading (via a thermochemical cycle) to values for $\Delta_f H^0(N_3, g)$ in the region of 144 kJ-mol\textsuperscript{-1}, some 50 kJ-mol\textsuperscript{-1} lower than the estimates made from the experiments above.

SCFMO calculations made by Dewar et al.\textsuperscript{(12)} generate a value for $\Delta_f H^0(N_3, g) = 220$ kJ-mol\textsuperscript{-1}.

In view of the discrepancy between the experimental and cycle values for $\Delta_f H^0(N_3, g)$ this paper utilizes the recent\textsuperscript{(13)} determination of the standard enthalpy of formation of ammonium azide, $\Delta_f H^0(NH_4N_3, c)$ and the assignment\textsuperscript{(14)} of the viscosity $B$-coefficient of the azide anion, $B(N_3, aq)$, in aqueous solution in conjunction with a correlation to generate an estimate for this important quantity, $\Delta_f H^0(N_3, g)$, from an entirely different standpoint.

2. Results and Discussion

A well established correlation\textsuperscript{(15-18)} (having a correlation coefficient 0.9999\textsubscript{6}) which exists between the viscosity $B$-coefficient of the Jones and Dole\textsuperscript{(19)} equation for alkali metal halides (dm\textsuperscript{3} mol\textsuperscript{-1}) and the standard molar enthalpy of hydration of the gaseous alkali metal and halide ions (kJ-mol\textsuperscript{-1}) has been used for the ammonium halides\textsuperscript{(17)} in the analytical form:

$$\left[\Delta_{\text{hyd}} H^0(NH_4^+, g) + \Delta_{\text{hyd}} H^0(X^-, g)\right] = -716.0 - 1193.6 \, B(NH_4X, aq)$$ (1)

The azide ion, being a pseudohalide ion, might be anticipated to obey this relationship and taking a value for $B(NH_4N_3, aq)$ dm\textsuperscript{3} mol\textsuperscript{-1} = -0.029 (derived from the experimental work of Bingham\textsuperscript{(14a,20)} and the value, $B(NH_4^+, aq)$ taken from Marcus\textsuperscript{(21)} we predict a value for $[\Delta_{\text{hyd}} H^0(NH_4^+, g) + \Delta_{\text{hyd}} H^0(N_3, g)] = -681.4$ kJ-mol\textsuperscript{-1}.

A thermochemical cycle links the latter value with the enthalpy of formation of the gaseous azide ion:

$$\Delta_f H^0(N_3, g) = \Delta_f H^0(NH_4N_3, c) + \Delta_{\text{soln}} H^0(NH_4N_3, c)$$
$$- \Delta_f H^0(NH_4^+, g) - [\Delta_{\text{hyd}} H^0(NH_4^+, g) + \Delta_{\text{hyd}} H^0(N_3, g)]$$ (2)

and using the recent value assigned for $\Delta_f H^0(NH_4N_3, c) = 114.4 \pm 0.94$ kJ-mol\textsuperscript{-1}\textsuperscript{(13)} and $\Delta_{\text{soln}} H^0(NH_4N_3, c) = 27.2$ kJ-mol\textsuperscript{-1}\textsuperscript{(13)} with $\Delta_f H^0(NH_4^+, g) = 630.2$ kJ-mol\textsuperscript{-1} leads to the assignment: