# The Standard Enthalpy of Formation of Nitrogen Tri-iodide Monoammine and the Nitrogen–Iodine Bond Energy

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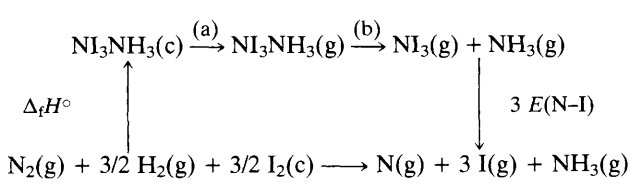
Following three independent solution/reaction calorimetric procedures we report values for the standard enthalpies of formation of $NI_3NH_3$(c) and $NI_3$(g) (+146 ± 6 and +287 ± 23 kJ $mol^{-1}$ respectively) and of the nitrogen–iodine bond energy, $E$(N–I) = 169 ± 8 kJ $mol^{-1}$.

Nitrogen tri-iodide, easily prepared as the crystalline monoammine $NI_3NH_3$, is treacherously unstable, liable to spontaneous explosion, even at 0 °C and under water. Not surprisingly, thermodynamic data are sparse and non-concordant (and have been wrongly transcribed). The monoammine has been the subject of two previous thermochemical studies: a solution/reaction investigation[1] leading to a value of $\Delta_f H^\circ(NI_3NH_3)$ = 146.4 kJ $mol^{-1}$, and a detonation method[2] from which we calculate a value of +130.2 kJ $mol^{-1}$. Using more recently reported ancillary data we re-calculate the




**Scheme 1**

**Table 1.** The standard enthalpy of formation of nitrogen tri-iodide monoammine at 298.15 K.

| $\Delta_fH°$/kJ mol$^{-1}$ | Source |
|---|---|
| +(146.4 ± 5.4) | Ref. 1, original |
| +(157.6 ± 7.5) | Ref. 1, re-analysis of data |
| +(130.2) | Ref. 2 |
| +(145.7 ± 5.0) | Equation (1) (HI) |
| +(147.1 ± 9.0) | Equation (2) ($As_2O_3$) |
| +(175 ± 20) | Equation (3) (synthesis) |
| +(146 ± 6) | Selected value |

former value as +157.6 kJ mol$^{-1}$. Confidence limits are difficult to ascribe but are clearly large.

In this communication we report the results from three independent solution/reaction procedures; two of these are reductive processes and one a direct synthesis. A disadvantage of the latter is that the product is the black amorphous and more sensitive modification, and not the well-defined crystalline form. Manipulative details are given at length elsewhere.[3]

The reductive processes are summarised by the equations (1)—(2). The direct synthesis may be represented by equation (3).

$$NI_3NH_3(c) + 5H^+(aq) + 6I^-(aq) \rightarrow 2NH_4^+(aq) + 3I_3^-(aq) \quad (1)$$

$$NI_3NH_3(c) + 3As(OH)_3(aq) + 3H_2O(l) \rightarrow 2NH_4^+(aq) + 3I^-(aq) + H^+(aq) + 3AsO(OH)_3(aq) \quad (2)$$

$$3I_3^-(aq) + 5NH_3(aq) \rightarrow NI_3NH_3(c) + 3NH_4^+(aq) + 6I^-(aq) \quad (3)$$

Details of the calorimetric system are presented elsewhere,[4] and satisfactory check results, before and after a series of runs, were routinely made using the neutralisation of tris hydroxyaminomethane (THAM) as a standard reaction.

Results are shown in Table 1 and compared with available literature values. Using the cycle shown in Scheme 1, and plausible estimates of the enthalpy changes of processes (a) and (b) [(a) (66 ± 20) kJ mol$^{-1}$; (b) (29 ± 10) kJ mol$^{-1}$, respectively] we further calculate values of $\Delta_fH°(NI_3,g)$ = +(287 ± 23) kJ mol$^{-1}$ and the bond energy term $E$(N–I) = +(169 ± 8) kJ mol$^{-1}$. Computational methods which may be used to generate non-experimental values for these and other parameters are discussed elsewhere.[5]

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