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The standard enthalpies of formation of the ammonium and silver salts of 3-nitro-1,2,4-triazol-5-one

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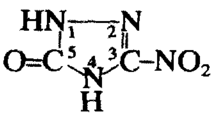
Abstract

The standard enthalpies of formation at 298.15 K of the crystalline silver and ammonium salts of 3-nitro-1,2,4-triazol-5-one have been determined as -269.9 ± 1.1 and -47.1 ± 1.4 kJ mol^{-1}, respectively.

INTRODUCTION

The explosive properties of 3-nitro-1,2,4-triazol-5-one (**I**, HNTO) (throughout this paper HNTO represents 3-nitro-1,2,4-triazol-5-one and NTO^- the corresponding anion) have very recently received attention [1] and the standard enthalpies of formation of this compound, its sodium and potassium salts, and the parent ketone have been determined [2]. This paper reports the determination of the enthalpies of formation of the ammonium and silver salts by solution/reaction calorimetry.



(**I**)

EXPERIMENTAL

Materials

The ammonium salt of HNTO (NH_4NTO, the proton on 4-N is replaced) was prepared from ammonium carbonate and HNTO. The yellow crystals were recrystallized from water, dried at 90°C in vacuo, and

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stored in an evacuated desiccator over P_2O_5. The ammonium content was determined by distillation from aqueous sodium carbonate into standard 0.1 M hydrochloric acid, followed by back-titration against standard 0.1 M NaOH: NH_3 found, 11.60 mass%; calculated for $C_2HN_4O_3 \cdot NH_4$, 11.58 mass%.

The silver salt was prepared by reacting a solution of the ammonium salt with an equimolar quantity of silver nitrate. The initial orange precipitate gradually became yellow after about 10 min. It was filtered, washed with water and methanol, and dried in air at 120°C overnight. The silver content was determined by Volhard's method: Ag found, 45.03 mass%; calculated for $C_2HN_4O_3Ag$, 45.53 mass%.

Calorimetry

Enthalpies of reaction and solution were measured using the calorimeter previously described [3], the performance of which was frequently checked by determinations of the enthalpy of neutralization of tris-(hydroxymethyl)aminomethane (THAM) with excess aqueous 0.1 M HCl.

RESULTS AND DISCUSSION

NH_4NTO

Results for the enthalpy of neutralization of HNTO with 200 cm^3 of 0.01 M aqueous ammonia (reaction (1)) are reported in Table 1, and for the dissolution of NH_4NTO in 200 cm^3 of water (reaction (2)) in Table 2.

$$\mathrm{HNTO(cr)} + \mathrm{NH_3(aq)} = \mathrm{NH_4NTO(aq)} \qquad (1)$$

$$\mathrm{NH_4NTO(cr)} = \mathrm{NH_4NTO(aq)} \qquad (2)$$

TABLE 1

Enthalpy of neutralization of HNTO(cr) with 200 cm^3 of 0.1 M aqueous NH_3 at 298.15 K [a]

m(HNTO) (g)	Moles excess NH_3	$-\Delta H(1)$ (kJ mol^{-1})
0.08749	0.00133	20.59
0.08858	0.00132	20.51
0.12950	0.00100	20.64
0.17876	0.00063	20.69
0.19138	0.00053	20.71
0.24226	0.00014	20.88

[a] Equation (1).

TABLE 2

Enthalpy of solution of $NH_4NTO(cr)$ in 200 cm^3 of water at 298.15 K [a]

$m(NH_4NTO)$ (g)	n [b]	$\Delta H(2)$ (kJ mol^{-1})
0.08337	19590	39.58
0.15127	10800	39.61
0.16883	9670	39.87
0.16992	9610	39.57
0.17378	9400	39.65
0.23538	6940	39.45
		39.62 ± 0.15 [c]

[a] Equation (2). [b] n = mole ratio of H_2O/NH_4NTO. [c] Mean value.

Provided the compositions corresponding to the right-hand sides of eqns (1) and (2) are identical

$$\Delta_f H^{\ominus}(NH_4NTO, cr) = \Delta_f H^{\ominus}(HNTO, cr) + \Delta_f H^{\ominus}(NH_3, aq) + \Delta H(1) - \Delta H(2)$$

The results for the neutralization reaction showed a slight concentration dependence. Linear regression (91% correlation) of the values of $\Delta H(1)$ (kJ mol^{-1}) against the number of moles of excess NH_3 gave the value $\Delta H(1) = (-20.9 \pm 0.1)$ kJ mol^{-1} for zero excess, i.e. for the final state of reaction (2). Using values for ancillary data of $\Delta_f H^{\ominus}(HNTO, cr) = -129.41 \pm 1.07$ kJ mol^{-1} [2] and $\Delta_f H^{\ominus}$(NH_3 in $5550H_2O$) $= -79.97 \pm 0.35$ kJ mol^{-1} (the value in ref. 4 corrected for the difference between the values for $\Delta_f H^{\ominus}(NH_3, g)$ in refs. 4 and 5, and where the uncertainty interval is that of $\Delta_f H^{\ominus}(NH_3, g)$ in ref. 5), $\Delta_f H^{\ominus}(NH_4NTO, cr, 298.15\ K) = -269.9 \pm 1.1$ kJ mol^{-1}. (Throughout this paper uncertainty intervals of reported experimental results denote 95% confidence limits, calculated using Student's t-test at the appropriate number of degrees of freedom.) This result lies within the large uncertainty interval of the value previously reported [6] (-276.6 ± 15.1 kJ mol^{-1}) but is considerably more precise.

If NH_4NTO were completely dissociated in aqueous solution, the enthalpy of solution in water (to infinite dilution) would be given by

$$\begin{aligned}\Delta_{sol} H^{\ominus}(NH_4NTO, cr, \infty) &= \Delta_f H^{\ominus}(NTO^-, aq, \infty) + \Delta_f H^{\ominus}(NH_4^+, aq, \infty) \\ &\quad - \Delta_f H^{\ominus}(NH_4NTO, cr) \\ &= (-94.3 \pm 2.1) + (-133.26 \pm 0.25) \\ &\quad - (269.9 \pm 1.1) \\ &= 42.3 \pm 0.5 \text{ kJ mol}^{-1}\end{aligned}$$

The uncertainty interval associated with this value is only ±0.5 kJ mol^{-1} because $\Delta_f H^{\ominus}(HNTO, cr)$ occurs in the expressions for both

$\Delta_f H^\ominus(\mathrm{NTO}^-, \mathrm{aq}, \infty)$ and $\Delta_f H^\ominus(\mathrm{NH_4NTO, cr})$ and therefore cancels. The experimental values of $\Delta_{sol}H(\mathrm{NH_4NTO, cr})$ showed no dependence on concentration in the range 0.003–0.008 M (Table 2), but the mean experimental value differs by 2.7 ± 0.5 kJ mol^{-1} from the value of $\Delta_{sol}H^\ominus(\mathrm{NH_4NTO, cr}, \infty)$ calculated above. Although endothermic enthalpies of infinite dilution are well known for both strong electrolytes and hydrolysing electrolytes, the magnitude of the present effect from a 0.002 M solution is considerably greater than in other examples [7]. Another possible contributing effect, the dissociation of $\mathrm{NH_4^+(aq)}$, has been shown to be very small (about 0.05 kJ mol^{-1}) in the case of ammonium nitrate [8].

AgNTO

The enthalpy of formation of AgNTO(cr) was derived from measurements of the enthalpy of its precipitation from aqueous solutions of excess $\mathrm{NH_4NTO}$ and solid $\mathrm{AgNO_3}$ (Table 3). The stoichiometry was established by carrying out the reaction under conditions identical to those which obtained during the calorimetric measurements. After ten minutes' reaction the precipitate was filtered, weighed, and dried at 120°C; the mean ratio of the mass found to the calculated mass (two determinations) was 0.97. The filtrate was examined for silver ion by Volhard's method: none was detected. Using values for ancillary data of $\Delta_f H^\ominus(\mathrm{AgNO_3, cr}) = -124.39$ kJ mol^{-1} [4], $\Delta_f H^\ominus(\mathrm{NH_4NTO, aq}) = -230.3 \pm 1.1$ kJ mol^{-1} (from the sum of $\Delta_f H^\ominus(\mathrm{NH_4NTO, cr})$ and $\Delta_{sol} H^\ominus(\mathrm{NH_4NTO, cr})$ reported above), and $\Delta_f H^\ominus(\mathrm{NH_4NO_3}$ in $10\,000\ \mathrm{H_2O}) = -340.0 \pm 0.4$ kJ mol^{-1} (the value in ref. 4 corrected for the difference between $\Delta_f H^\ominus(\mathrm{NH_4NO_3, aq}, \infty)$ in refs. 4 and 5), gives $\Delta_f H^\ominus(\mathrm{AgNTO, cr, 298.15\ K}) = -47.1 \pm 1.4$ kJ mol^{-1}. The uncertainty interval has been calculated from the

TABLE 3

Enthalpies of the reaction (at 298.15 K) $\mathrm{AgNO_3(cr)} + [(p+1)\mathrm{NH_4NTO} + n\mathrm{H_2O}](\mathrm{sln}) = \mathrm{AgNTO(cr)} + [\mathrm{NH_4NO_3} + p\mathrm{NH_4NTO} + n\mathrm{H_2O}](\mathrm{sln})$ (3)

$m(\mathrm{AgNO_3})$ (g)	n	$-\Delta H(3)$ (kJ mol^{-1})
0.12164	10520	32.71
0.15900	11810	31.37
0.16304	11520	31.74
0.17858	10270	32.48
0.18278	15440	32.32
0.19697	9530	33.47
		32.35 ± 0.78 [a]

[a] Mean value.

precision of the experimental results and estimated uncertainties of ±0.2 and ±0.4 kJ mol^{-1} in the literature values of the enthalpies of formation of $AgNO_3$(cr) and NH_4NO_3(aq), respectively.

Thermochemical radius of the NTO$^-$ anion

The lattice energies of ionic crystals containing polyatomic ions are readily estimated [9] using the Kapustinskii procedure [10]. This involves calculating a "thermochemical radius" [11] for the complex ion involved, a calculation requiring values of the standard enthalpies of formation of two salts containing the common polyatomic ion. All six possible pairs from the Na^+, K^+, Ag^+, and NH_4^+ salts of HNTO were treated thus to obtain a thermochemical radius for NTO$^-$. For combinations involving Ag^+, unrealistic results were obtained, possibly suggesting that the Ag^+ salts are significantly covalent. For the remaining cases, a mean value of 2.5 Å for the thermochemical radius of NTO$^-$ was obtained. This value was used to calculate the lattice energies ($-U_0$) of the sodium, potassium, and ammonium salts of HNTO as 560, 550, and 512 kJ mol^{-1}, respectively. Figure 1 illustrates how these calculated lattice energies depend on the choice of the thermochemical radius of the anion and, consequently, gives a clear indication of the sensitivity of the estimation procedure.

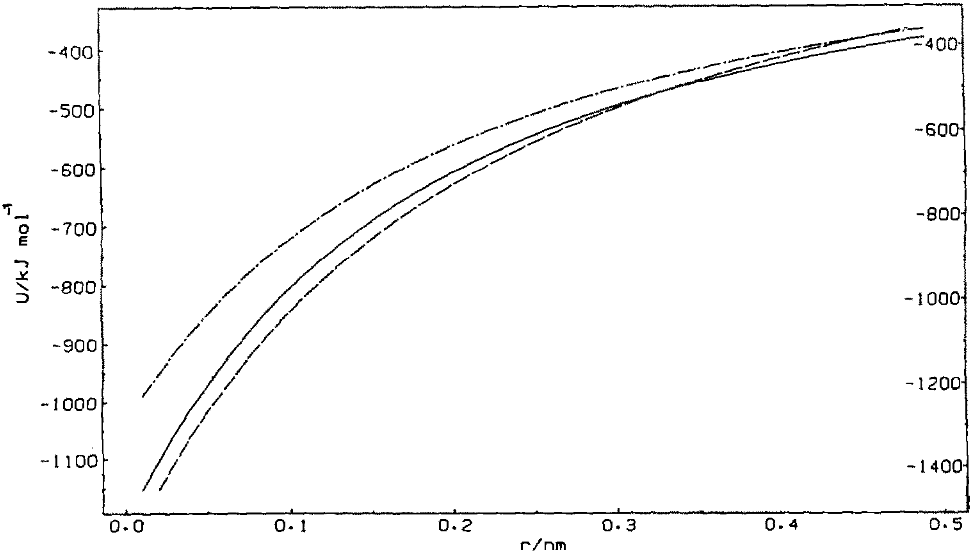

Fig. 1. Variation of calculated lattice energy [10] with anion thermochemical radius for the ammonium (– · – · –), potassium (———) and sodium (– – –) salts of HNTO.

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REFERENCES

1 Xie Yi, Hu Rongzu, Wang Xiyou and Fu Xiayun, Proc. 17th Int. Pyrotechnics Seminar and 2nd Beijing Int. Symp. on Pyrotechnics and Explosives, Beijing, China, 1991, Vol. 1, Beijing Institute of Technology Press, Beijing, 1991, p. 509.
2 A. Finch, P.J. Gardner, A.J. Head and H.S. Majdi, J. Chem. Thermodyn., 23 (1991) 1169.
3 S.J. Peake, Ph.D. Thesis, University of London, 1976.
4 NBS Tables of Chemical Thermodynamic Properties, D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, Suppl. 2, 11 (1982).
5 J.D. Cox, D.D. Wagman and V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989.
6 K.-Y. Lee and M.M. Stinecipher, Propellants Explos. Pyrotech., 14 (1989) 241.
7 E. Lange, in W.J. Hamer (Ed.), The Structure of Electrolytic Solutions, Wiley, New York, 1959, Chapter 9.
8 C.E. Vanderzee, D.H. Waugh and N.C. Haas, J. Chem. Thermodyn., 12 (1980) 21.
9 T.C. Waddington, Adv. Inorg. Radiochem., 1 (1959) 157.
10 A.F. Kapustinskii, Q. Rev. Chem. Soc., 10 (1956) 283.
11 H.D.B. Jenkins and K.P. Thakur, J. Chem. Educ., 56 (1979) 576.