M-2648

J. Chem. Thermodynamics **1991,** 23, 1169–1173

The enthalpies of formation of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one

ARTHUR FINCH, P. J. GARDNER, A. J. HEAD, and
H. S. MAJDI

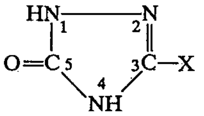
Department of Chemistry, Royal Holloway and Bedford New College
(University of London), Egham, Surrey TW20 0EX, U.K.

(Received 25 April 1991; in final form 20 May 1991)

The standard ($p^\ominus = 0.1$ MPa) molar enthalpies of formation of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one have been determined from measurements of their energies of combustion in oxygen as $-(142.4 \pm 0.7)\ \mathrm{kJ \cdot mol^{-1}}$ and $-(129.4 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$, respectively. From measurements of the enthalpies of neutralization of 3-nitro-1,2,4-triazol-5-one with NaOH(aq) and KOH(aq) the enthalpies of formation of the crystalline sodium and potassium salts have been determined as $-(362.6 \pm 1.2)\ \mathrm{kJ \cdot mol^{-1}}$ and $-(385.1 \pm 1.1)\ \mathrm{kJ \cdot mol^{-1}}$, respectively.

1. Introduction

The use of 3-nitro-1,2,4-triazol-5-one (I, X is NO_2) (NTO) as an explosive, less sensitive than hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), has recently been proposed.$^{(1)}$ This paper reports the enthalpy of formation of this compound, its sodium and potassium salts, and of the parent ketone (I, X is H) (TO), using static-bomb oxygen combustion calorimetry and solution/reaction calorimetry. A value $\Delta_f H_m^\ominus(\mathrm{NTO, cr, 298.15\ K}) = -117\ \mathrm{kJ \cdot mol^{-1}}$ obtained by Stinecipher has been reported as a personal communication in a paper by Ritchie,$^{(2)}$ in which agreement is claimed between this value and an estimate based on an *ab initio* calculation of $\Delta_f H_m^\ominus(\mathrm{g})$ and an estimate of the enthalpy of sublimation. The experimental results for energies of combustion of similar compounds by Lee and Stinecipher$^{(3)}$ are accompanied by large uncertainty intervals and a redetermination of the enthalpy of formation was, therefore, desirable. No values for the other compounds have been previously reported.



(I)

2. Experimental

MATERIALS

TO was prepared by reacting semicarbazide hydrochloride with excess 80 mass per cent aqueous formic acid at the temperature 355 K until all the former had dissolved. The excess formic acid was removed by evaporation and the product crystallized three times from deionized water. After drying at 395 K, the melting temperature and mole-fraction purity were determined by differential scanning calorimetry (d.s.c.) as 507.7_5 K (literature:(4) 507 K to 508 K) and 0.998 to 0.999, respectively.

NTO was prepared by nitration of TO with 70 mass per cent aqueous nitric acid at temperatures from 328 K to 333 K. The precipitated product was filtered, washed with water, and crystallized three times from deionized water (melting temperature: 541 K, decomp.; literature:(4) 543 K to 544 K). The mass-fraction purity was assessed as (0.996 ± 0.001) by h.p.l.c., based on normalization of the chromatograms obtained by isocratic elution of a 5ODS Spherisorb column (Chrompack Ltd) with 70 to 90 volume per cent aqueous methanol containing 1 mass per cent of phosphoric acid; a u.v. detector operated at 200 nm, 250 nm and 300 nm was used.

The acidity of NTO ($pK_a = 3.63$,(4) for ionization of the N-4 proton) permits well defined salts to be obtained. The sodium and potassium salts were prepared by the neutralization of hot aqueous solutions of NTO with the appropriate alkali-metal carbonate. The yellow crystals were recrystallized three times from water and dried at the temperature 363 K *in vacuo*. The potassium content of the potassium salt was determined gravimetrically by precipitation of potassium tetraphenylborate (found: 23.66 mass per cent; required for $C_2HN_4O_3K$: 23.25 mass per cent).

CALORIMETRY

The energies of combustion of TO and NTO were determined using the static-bomb calorimeter previously described(5) in the isoperibol mode.(6) The calorimeter was calibrated by combustion of thermochemical standard benzoic acid (Bureau of Analysed Samples Batch 190k) for which the certified value (under standard bomb conditions) was $-(26.4344 \pm 0.0025)\ \mathrm{kJ \cdot g^{-1}}$. The energy equivalent of the calorimeter (13 determinations) was $(9.3708 \pm 0.0014)\ \mathrm{J \cdot K^{-1}}$;† this value differs from that given in reference 6 because a new bomb (Model 1108, Parr Instrument Company, volume $0.346\ \mathrm{dm^3}$) was used. Calorimetric procedures were the same as previously described in reference 6. Both compounds were non-hygroscopic and encapsulation of the tablets was unnecessary: clean combustions were obtained using an initial oxygen pressure of approximately 3.0 MPa.

The enthalpies of neutralization of NTO(cr) with aqueous sodium and potassium hydroxides and the enthalpies of solution in water of the sodium and potassium salts of NTO were measured using a twin-vessel isoperibol reaction calorimeter(7) operated at the temperature (298.15 ± 0.05) K. The experimental precision and

---

† Throughout this paper uncertainty intervals of reported experimental results denote 95 per cent confidence limits, calculated using values of Student's t at the appropriate number of degrees of freedom.

accuracy were frequently successfully checked by measurements of the molar enthalpy of neutralization of tris(hydroxymethyl)aminomethane (THAM) with excess 0.1 $\mathrm{mol \cdot dm^{-3}}$ HCl.

The specific heat capacities of TO and NTO were determined over the temperature range 320 K to 420 K using d.s.c. (Perkin-Elmer DSC-2) with sapphire as reference material for calibration, and the results are represented by the equations:

$$c_p(\mathrm{TO, cr})/(\mathrm{J \cdot g^{-1} \cdot K^{-1}}) = 0.00214(T/\mathrm{K}) + 0.125,$$
$$c_p(\mathrm{NTO, cr})/(\mathrm{J \cdot g^{-1} \cdot K^{-1}}) = 0.00386(T/\mathrm{K}) - 0.278.$$

3. Results

The results of typical combustion experiments are reported in table 1, where q denotes the total measured energy change, and q_i, q_n, q_{ss}, and q_c the energy corrections for, respectively, the electrical energy of ignition and combustion of the cotton fuse, the formation of nitric acid, the reduction to standard states, and a small residue of carbon (<0.2 mg) in the combustions of TO. The mean values of seven runs for TO and eight for NTO, together with the derived molar quantities for the reactions:

TO: $\mathrm{C_2H_3N_3O(cr) + 2.25O_2(g) = 2CO_2(g) + 1.5H_2O(l) + 1.5N_2(g)}$,

NTO: $\mathrm{C_2H_2N_4O_3(cr) + O_2(g) = 2CO_2(g) + H_2O(l) + 2N_2(g)}$,

and the molar enthalpies of formation are listed in table 2. The enthalpies of formation of $\mathrm{CO_2(g)}$ and $\mathrm{H_2O(l)}$ were taken from reference 8.

The enthalpies of neutralization of NTO with (a) 0.005 $\mathrm{mol \cdot dm^{-3}}$ NaOH(aq) and (b) 0.007 $\mathrm{mol \cdot dm^{-3}}$ KOH(aq) are reported in table 3, where r denotes the mole ratio

TABLE 1. Typical results for the combustion of TO and of NTO

	TO	NTO
m(cpd)/g[a]	2.24924	3.76990
q/J	28711.5	27816.4
q_i/J	41.5	66.5
q_n/J	157.7	140.3
q_{ss}/J	50.9	79.9
q_c/J	-3.3	0
$-\Delta_c u^\ominus/(\mathrm{J \cdot g^{-1}})$	12655.3	7302.5

[a] Corrected for buoyancy using $\rho(\mathrm{TO}) = 1.22\ \mathrm{g \cdot cm^{-3}}$; $\rho(\mathrm{NTO}) = 1.92\ \mathrm{g \cdot cm^{-3}}$.

TABLE 2. Standard ($p^\ominus = 0.1$ MPa) energies and enthalpies of combustion and formation of TO and NTO

	$-\Delta_c u^\ominus/(\mathrm{J \cdot g^{-1}})$	$-\Delta_c U^\ominus_m/(\mathrm{kJ \cdot mol^{-1}})$	$-\Delta_c H^\ominus_m/(\mathrm{kJ \cdot mol^{-1}})$	$-\Delta_f H^\ominus_m/(\mathrm{kJ \cdot mol^{-1}})$
TO	12654.3 ± 7.0	1076.44 ± 0.59	1073.34 ± 0.59	142.4 ± 0.7
NTO	7310.9 ± 8.0	950.88 ± 1.04	943.44 ± 1.04	129.4 ± 1.1

TABLE 3. Enthalpies of neutralization of NTO with (a) 0.005 $\text{mol}\cdot\text{dm}^{-3}$ NaOH(aq) and (b) 0.007 $\text{mol}\cdot\text{dm}^{-3}$ KOH(aq)

$m(\text{NTO})/\text{g}$	r	$-\Delta_r H_m/\text{kJ}\cdot\text{mol}^{-1}$	$m(\text{NTO})/\text{g}$	r	$-\Delta_r H_m/\text{kJ}\cdot\text{mol}^{-1}$
	(a) NaOH(aq)			(b) KOH(aq)	
0.09700	14900	20.87	0.12993	11120	20.95
0.10268	14070	20.87	0.14085	10260	20.97
0.10700	13510	20.84	0.14106	10250	20.87
0.11389	12690	20.90	0.15420	9370	20.83
0.12100	11940	20.80	0.16614	8700	20.94
0.12614	11450	20.90		Mean:	20.91 ± 0.07
0.12623	11450	20.89			
	Mean:	20.87 ± 0.03			

TABLE 4. Enthalpies of solution of the (a) sodium and (b) potassium salts of NTO in water

$m(\text{salt})/\text{g}$	r	$\Delta_{\text{sln}} H_m/\text{kJ}\cdot\text{mol}^{-1}$	$m(\text{salt})/\text{g}$	r	$\Delta_{\text{sln}} H_m/\text{kJ}\cdot\text{mol}^{-1}$
	(a) Sodium salt			(b) Potassium salt	
0.07405	22810	28.00	0.13413	13930	38.65
0.07916	21340	28.02	0.13722	13620	38.55
0.08096	20860	28.02	0.14332	13040	38.57
0.08271	20420	27.93	0.15235	12260	38.67
0.10759	15700	27.97	0.16311	11460	38.55
0.12218	13820	27.97	0.17238	10840	38.60
	Mean:	27.98 ± 0.04		Mean:	38.60 ± 0.05

$n(\text{H}_2\text{O})/n(\text{NTO})$. The enthalpies of solution in water of the sodium and potassium salts of NTO are reported in table 4, where r denotes the mole ratio $n(\text{H}_2\text{O})/n(\text{salt})$.

The enthalpies of formation of the sodium and potassium salts of NTO have been derived from their enthalpies of solution in water, the enthalpies of neutralization of NTO(cr), and the enthalpies of formation of NTO(cr), (H_2O, l), NaOH in $11100\text{H}_2\text{O}$: $-(470.13 \pm 0.07)\ \text{kJ}\cdot\text{mol}^{-1}$, and KOH in $7930\text{H}_2\text{O}$: $-(482.01 \pm 0.09)\ \text{kJ}\cdot\text{mol}^{-1}$. The last two values were calculated from $\Delta_f H_m^\circ(\text{OH}^-, \text{aq}, \infty)$, $\Delta_f H_m^\circ(\text{Na}^+, \text{aq}, \infty)$, and $\Delta_f H_m^\circ(\text{K}^+, \text{aq}, \infty)$ taken from reference 8, and enthalpies of dilution from reference 9. The following values were obtained:

$$\Delta_f H_m^\circ(\text{C}_2\text{HN}_4\text{O}_3\text{Na}, \text{cr}, 298.15\ \text{K}) = -(362.6 \pm 1.2)\ \text{kJ}\cdot\text{mol}^{-1},$$

$$\Delta_f H_m^\circ(\text{C}_2\text{HN}_4\text{O}_3\text{K}, \text{cr}, 298.15\ \text{K}) = -(385.1 \pm 1.1)\ \text{kJ}\cdot\text{mol}^{-1}.$$

4. Discussion

The value obtained for $\Delta_c H_m^\circ(\text{NTO}, \text{cr}, 298.15\ \text{K})$ differs by $12\ \text{kJ}\cdot\text{mol}^{-1}$ from that quoted in reference 2, for which the uncertainty is probably large.

The acid strength of NTO is sufficient to ensure that the sodium and potassium salts are completely ionized in aqueous solution. Moreover, the dilutions of the final state of the neutralization experiments ($9000 < r < 15000$) is high enough to approximate closely to infinite dilution and, therefore, to enable $\Delta_f H_m^\ominus(C_2HN_4O_3^-, aq, \infty)$ to be calculated from the equation:

$$\Delta_f H_m^\ominus(C_2HN_4O_3^-, aq, \infty) = \Delta_f H_m^\ominus(NTO, cr) - \Delta_f H_m^\ominus(H_2O, l) - \Delta_f H_m^\ominus(M^+, aq, \infty) + \Delta_f H_m^\ominus(MOH, aq) + \Delta_r H_m, \qquad (1)$$

where $\Delta_r H_m$ denotes the molar enthalpy of neutralization of NTO(cr) with MOH(aq) (M = Na, K). A simpler expression is

$$\Delta_f H_m^\ominus(C_2HN_4O_3^-, aq, \infty) = \Delta_{sln} H_m(C_2HMN_4O_3, cr) - \Delta_f H_m^\ominus(M^+, aq, \infty) + \Delta_f H_m^\ominus(C_2HMN_4O_3, cr), \qquad (2)$$

which yields the same result but appears to indicate that the value obtained is dependent on the experimental value for the enthalpy of solution of ($C_2HMN_4O_3$, cr), which is not, in fact, true. Two independent values for the sum of the last three terms in equation (1) may be obtained from the results reported in table 3: $-(250.66 \pm 0.10)\ kJ \cdot mol^{-1}$ (M = Na) and $-(250.78 \pm 0.14)\ kJ \cdot mol^{-1}$ (M = K), from which the weighted mean: $-(250.70 \pm 0.08)\ kJ \cdot mol^{-1}$, is derived. Thus

$$\Delta_f H_m^\ominus(C_2HN_4O_3^-, aq, \infty) = -(94.3 \pm 2.1)\ kJ \cdot mol^{-1},$$

where the uncertainty interval has been doubled to allow for the assumption that the measurement conditions yielded the results for infinite dilution.

One of us (H.S.M.) gratefully acknowledges financial support from the Government of Iraq.

REFERENCES

1. Lee, K.-Y.; Chapman, L. B.; Coburn, M. D. *J. Energetic Materials* **1987,** 5, 27.
2. Ritchie, J. P. *J. Org. Chem.* **1989,** 54, 3553.
3. Lee, K.-Y.; Stinecipher, M. M. *Propellants, Explosives, Pyrotechnics* **1989,** 14, 241.
4. Schmidt, J.; Gehlen, H. *Z. Chem.* **1965,** 5, 304.
5. Finch, A.; Gardner, P. J.; Smith, A. *Thermochim. Acta* **1981,** 49, 281.
6. Finch, A.; Gardner, P. J.; Head, A. J.; Wu Xiaoping *J. Chem. Thermodynamics* **1990,** 22, 301.
7. Peake, S. J. Ph.D. Thesis, University of London, **1976.**
8. *CODATA Key Values for Thermodynamics.* Cox, J. D.; Wagman, D. D.; Medvedev, V. A.: editors. Hemisphere, New York. **1989.**
9. *NBS Tables of Chemical Thermodynamic Properties.* Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982,** 11, Supplement No. 2.