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THERMOCHEMISTRY OF PICRATES. I. THE STANDARD ENTHALPY OF FORMATION OF AMMONIUM PICRATE

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ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion at 298.15 K of the yellow crystalline modification of ammonium picrate has been determined as —2833.11 ± 2.83 kJ mole^{-1}. The standard enthalpy of formation is —385.44 ± 2.94 kJ mole^{-1}. These results are discussed in relation to previous values and also in connexion with solution calorimetric studies involving picric acid and metal picrates.

INTRODUCTION

Ammonium picrate [2,4,6-$(NO_2)_3C_6H_2ONH_4$], long known and with an extensive history in the explosives industry [1], is a key compound in the thermochemistry of metal picrates. For these compounds, consistent and reliable values of standard enthalpies of formation may be calculated from solution-reaction calorimetric measurements. An essential input datum is a value for the standard enthalpy of formation of the aqueous picrate ion, which derives from precise enthalpy of solution experiments involving either picric acid or ammonium picrate. Surprisingly, agreed values of standard enthalpies of formation for neither of these compounds are apparently available [2—9]. Since ammonium picrate is far more easily soluble in aqueous media than is picric acid, and is hence more suitable for solution-reaction experiments, we have measured its enthalpy of combustion using conventional static-bomb oxygen calorimetry.

EXPERIMENTAL

Materials and synthesis

Ammonium picrate

Picric acid (B.D.H., AnalaR grade) in an acetone—water mixture (1 : 1) was carefully neutralised using aqueous ammonium carbonate (B.D.H., AnalaR grade). The yellow product was recrystallised four times from water, dried in air at ca. 120°C for ca. 7 h, and stored over anhydrous magnesium perchlorate. Under these conditions the red modification is not formed [10]. Analysis was based on distillation from aqueous sodium carbonate into standard aqueous HCl to collect NH_3, followed by titration using standard NaOH. Results were: NH_3, 6.91% (calcd. 6.907%). A Karl Fischer titration indicated that the water content was negligible.

Acetanilide

A commercial sample (B.D.H., OAS grade) was used as supplied after drying overnight at ca. 110°C. A purity of ca. 99.95% was indicated using differential scanning calorimetry [11].

Benzoic acid

Certified material (B.C.S. Thermochemical Standard No. 190j, 99.97%) was used directly, as recommended, without further treatment.

Combustion calorimeter

This was a commercial instrument (Gallenkamp Automatic Bomb Calorimeter, Model CB-110) modified as follows: the thermometer supplied was replaced by a digital quartz thermometer (Hewlett-Packard, Model 2801 A); the bomb supplied was replaced by a twin-valve bomb (Parr Instrument Company, Bomb No. 1101) of internal volume 360 cm^3; the supplied stainless-steel calorimeter can was replaced by a unit fabricated in copper (0.1 cm thick) to improve thermal response and a double stirrer was used within the calorimeter can.

TABLE 1

Combustion calorimetry results for ammonium picrate

Ref. No.	A	B	C	D	E
m(sample)(g) *	2.738639	1.104000	2.45520	2.451683	2.597862
m(fuse)(g)	0.00447	0.00430	0.00381	0.00326	0.00427
m(Pt wire)(g)	0.00622	0.00565	0.00642	0.00575	0.00512
m(silica crucible)(g)	4.651442	4.638626	4.638646	4.638726	4.638616
m(soot)(g)	0.00000	0.00020	0.00023	0.00021	0.00003
$m(H_2O)$(g)	10.80000	10.80000	10.80000	10.80000	10.80000
q_i(kJ)	0.080010	0.077037	0.068470	0.058847	0.076512
q_n(kJ)	0.099016	0.073754	0.097821	0.073336	0.101404
q_c(kJ)	0.00000	0.00660	0.00759	0.00693	0.00099
q_w(kJ)	0.066904	0.025039	0.059280	0.059511	0.063061
$\Delta\theta$(K)	3.6677	1.4854	3.2919	3.2795	3.4839
ϵ_f(kJ K^{-1})	8.6804	8.6782	8.6801	8.6801	8.6802
ϵ_{cf}(kJ K^{-1})	0.061849	0.059627	0.061464	0.061460	0.061658
$-\Delta u_c^0$(298.15 K) (kJ g^{-1})	11.5354	11.5230	11.5493	11.5356	11.5484

Mean = −11.5504 ± 0.0115 kJ g^{-1}.

* Density of ammonium picrate was taken as 1.72 g cm^{-1} for buoyancy correction purposes.

The system was calibrated using benzoic acid, and the performance checked using acetanilide as a test material: detailed results are given below. All samples were pelleted, contained in a silica crucible, and fired by a weighed cotton fuse (ca. 3—4 mg) ignited electrically by a weighed platinum wire (ca. 6 mg, diameter 0.0089 cm, electrical energy input 0.0018 kJ). Weighings were buoyancy corrected, and accurate to ±0.5 × 10^{-5} g.

Using the notation of Coops et al. [14] values for the internal energy change on combustion were calculated from

$$-\Delta u_c^\theta = [(\epsilon_{sf} + \epsilon_{cf})\Delta\theta - q_i - q_n - q_w + q_c]/m_s$$

where ϵ_{sf} is the energy equivalent of the standard final system, i.e. the bomb less the oxygen and water charges, the combustion products, the platinum firing wire and the crucible. The energy equivalent of these components is contained in the ϵ_{cf} term. The correction for nitric acid formed during combustion, q_n, was calculated using $\Delta u_f^\theta(HNO_3, 500\ H_2O) = -59.72$ kJ $mole^{-1}$ [12] and for the combustion of the unburnt soot residue, 33 kJ g^{-1} was used. The abbreviated procedure of Prosen [13] was used to evaluate the Washburn correction, q_w. The fore and after periods are not exactly parallel (as would be the case in a perfect adiabatic system) and the corrected temperature rise, $\Delta\theta$, was calculated by back-extrapolation to a point corresponding to 0.63 of the observed temperature change.

The mean of 11 calibration experiments using benzoic acid gave the energy equivalent of the uncharged calorimeter as $\epsilon_{sf} = 8.6186 \pm 0.0026$ kJ K^{-1}, and the mean of six experiments using acetanilide as a test substance gave a value of $\Delta u_c^\theta = -31.218 \pm 0.011$ kJ g^{-1}, in satisfactory agreement with the recommended value, viz. -31.2300 ± 0.0069 kJ g^{-1} [15]. Uncertainty intervals are quoted as 95% confidence limits throughout.

F	G	H	I	J	K
2.514827	2.239838	2.491305	2.330267	2.019368	2.134050
0.00433	0.00382	0.00357	0.00380	0.00432	0.00405
0.00632	0.00642	0.00604	0.00683	0.00625	0.00618
4.638666	4.638606	4.638646	4.766064	4.638736	4.766024
0.00018	0.00020	0.00021	0.00012	0.00016	0.00018
10.80000	10.80000	10.80000	10.80000	10.80000	10.80000
0.077737	0.068642	0.064269	0.068292	0.077387	0.072665
0.100986	0.092387	0.094716	0.093880	0.091312	0.092304
0.00594	0.00660	0.00693	0.00396	0.00528	0.00594
0.060834	0.053637	0.060287	0.056008	0.047882	0.050850
3.3714	3.0037	3.3414	3.1311	2.7145	2.8717
8.6802	8.6797	8.6801	8.6800	8.6795	8.6797
0.061546	0.061172	0.061514	0.061391	0.060872	0.061124
11.5438	11.5470	11.5568	11.5711	11.5626	11.5816

RESULTS AND DISCUSSION

The energy of combustion at 298.15 K of ammonium picrate was found to be —11.5504 ± 0.0115 kJ g^{-1}. Using the equation

$$C_6H_6N_4O_7(c) + 4\ O_2(g) = 6\ CO_2(g) + 2\ N_2(g) + 3\ H_2O(l)$$

the standard enthalpy of combustion is hence —2833.11 ± 2.83 kJ $mole^{-1}$ and the standard enthalpy of formation, $\Delta H_f^\theta[2,4,6\text{-}(NO_2)_3C_6H_2ONH_4,\ c]$ at 298.15 K is —385.44 ± 2.94 kJ $mole^{-1}$. Detailed experimental results are collated in Table 1.

Ammonium picrate may be prepared in either of two coloured modifications, red or yellow, at ambient temperatures. However, the red form is metastable with respect to the yellow, and is not expected to result from the procedure adopted here.

Table 2 lists reported values of $\Delta H_f^\theta[C_6H_2(NO_2)_3ONH_4,\ c]$ with values ranging from ca. —350 kJ $mole^{-1}$ to —399 kJ $mole^{-1}$. The value reported by Urbanski and Soroka in 1938 [9], besides being much lower than any other, is coupled with a difference of ca. 42 kJ $mole^{-1}$ between the standard enthalpies of formation of the red and yellow forms. This may be compared with a difference of only ca. 5 kJ $mole^{-1}$ reported by Médard and Thomas [6]. This latter difference seems very much more likely, and is consistent with exploratory differential scanning calorimetric (DSC) measurements made in this laboratory although it is not possible to quantify the DSC results.

Recalculation of the results obtained by Médard and Thomas, using more recent values of $\Delta H_f^\theta[CO_2,\ g]$ and $\Delta H_f^\theta[H_2O,\ g]$ leads to a value which agrees very satisfactorily within experimental error to that reported here. The considerable difference between these values, and that of Vorob'ev et al. [2], viz. ca. 16 kJ $mole^{-1}$ is difficult to explain. Vorob'ev's procedure is based on solution calorimetry involving enthalpies of neutralisation of picric acid by ammonium, lithium, sodium and potassium hydroxides. Calculation of a value of $\Delta H_f^\theta[C_6H_2(NO_2)_3ONH_4,\ c]$ from these measurements

TABLE 2

Values of standard enthalpies of formation, ΔH_f^θ, of ammonium picrate at 298.15 K

$-\Delta H_f^\theta$ (kJ $mole^{-1}$)	Method	Ref.
396.64 ± 2.7	Combustion (y)	6
399.15 ± 2.5	Combustion (r)	7
384.1 ± 2.7	y *	
350.2	Combustion (y)	9
392.04	Combustion (r)	9
369.95	Solution (y)	2
385.44 ± 2.94	Combustion (y)	This work

r = Red form; y = yellow form.

* Recalculated from ref. 6.

depends upon a value for the standard enthalpy of formation of picric acid, derived from combustion experiments. The agreement between the independent, collated combustion values of Médard and Thomas, and Clift and Féderoff [8], with those reported here suggest that a re-examination of the value for the standard enthalpy of formation of picric acid may be appropriate.

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