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THERMOCHEMISTRY OF PICRATES. II. THE STANDARD ENTHALPY OF FORMATION OF PICRIC ACID

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ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion at 298.15 K of picric acid has been determined as -2571.92 ± 1.74 kJ mole^{-1}. This gives rise to a value for the standard enthalpy of formation of -217.88 ± 1.99 kJ mole^{-1}. These results are compared with previous combustion values and also with values calculated from solution calorimetric studies.

INTRODUCTION

Although picric acid [2,4,6-trinitrophenol, $C_6H_2(NO_2)_3OH$] is an important commercial compound readily available in a state of purity, reported thermodynamic properties are surprisingly discrepant. In particular, the standard enthalpy of formation derived from combustion experiments apparently differs from values calculated from solution-reaction processes; literature combustion experiments themselves exhibit poor precision. In this paper we report a re-determination of enthalpies of combustion and formation.

EXPERIMENTAL

Materials and synthesis

Picric acid

Picric acid (B.D.H., AnalaR grade) was recrystallised four times from ethanol and dried in air at ca. 105–110°C for several hours. The melting point was 121.5–122°C; literature values range from 120 to 122°C.

Acetanilide

A commercial sample (B.D.H., OAS grade) was used as supplied after drying overnight at 110°C.

Benzoic acid

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

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Combustion calorimeter

A commercial instrument (Gallenkamp Automatic Bomb Calorimeter Model CB-110) was used with modifications given in detail in a previous paper [6].

The system was calibrated using benzoic acid and the performance checked using acetanilide as a test substance. Experimental details and the calculation procedure are as given before [6].

ϵ_{sf} value and acetanilide

The mean of 11 calibration experiments using benzoic acid gave the energy equivalent of the uncharged calorimeter as 8.6186 ± 0.0026 kJ K^{-1} and the mean of seven experiments using acetanilide as a test substance gave a value of $\Delta u_c^0 = -31.221 \pm 0.013$ kJ g^{-1}, in very good agreement with the recommended value, viz. -31.2300 ± 0.0069 kJ g^{-1} [5].

RESULTS AND DISCUSSION

The energy of combustion of picric acid at 298.15 K was found to be -11.2717 ± 0.0076 kJ g^{-1}. Using the equation

$$C_6H_3N_3O_{7(c)} + 13/4\ O_{2(g)} = 6\ CO_{2(g)} + 3/2\ H_2O_{(l)} + 3/2\ N_{2(g)}$$

the standard enthalpy of formation, $\Delta H_f^0[C_6H_2(NO_2)_3OH, (c)]$ at 298 K $= -217.88 \pm 1.91$ kJ $mole^{-1}$. Relevant details of the combustion experiments are listed in Table 1.

TABLE 1

Combustion calorimetry results for picric acid

Ref no	A	B	C	D	E	F
m (sample) (g) [a]	2 465541	1 939664	1 962406	2 412313	2 472575	2 355853
m (fuse) (g)	0 00511	0 00474	0 00499	0 00439	0 00388	0 00469
m (Pt wire) (g)	0 00619	0 00563	0 00615	0 00620	0.00647	0 00594
m (silica crucible) (g)	4 638936	4 449560	4 449830	4 449730	4.638856	4 449650
m (soot) (g)	0 00000	0 00020	0 00000	0.00000	0 00000	0 00000
m (H_2O) (g)	10 8	10 8	10 8	10 8	10 8	10 8
q_i (kJ)	0 091204	0 084732	0 089105	0 078611	0 069691	0 083858
q_n (kJ)	0 081816	0 063900	0 059123	0 066289	0 067842	0 068081
q_c (kJ)	0 00000	0 00660	0 00000	0 00000	0 00000	0 00000
q_w (kJ)	0 065324	0 050484	0 051188	0 063985	0 065718	0 062323
$\Delta\theta$ (K)	3 2290	2 5421	2 5740	3 1541	3 2356	3.0829
ϵ_f (kJ K^{-1})	8 6792	8 6786	8 6786	8 6790	8 6793	8 6790
ϵ_{cf} (kJ K^{-1})	0 060636	0 059956	0 059980	0 060438	0 060643	0.060380
$-\Delta u_c^0$ (298 15 K) (kJ g^{-1})	11 2701	11 2748	11 2817	11 2613	11 2754	11 2665

Mean $= -11\ 2717 \pm 0\ 0076$ kJ g^{-1}

[a] Density of picric acid taken as 1 76 g cm^{-3} for buoyancy correction purposes

TABLE 2

Enthalpies of combustion and formation of picric acid

$-\Delta H_c^0$ (kJ mole^{-1})	$-\Delta H_f^0$ (kJ mole^{-1})	Ref
2575.46±1 34	214 35±1.38	1
2569 10±2 55	220.71±2.59	2
2578 60±2 51	211 29±2 51	3
2567 64±2 51	222 17±2 59	4
2571 92±1 74	217 88±1 99	This work

Table 2 summarises values of $\Delta H_f^0[C_6H_2(NO_2)_3OH, (c)]$, ranging from ca. −211 to ca. −222 kJ mole^{-1}. The value reported in this work, ca. −218.0 kJ mole^{-1}, is coincidentally very close to the mean of all four values and the early value of ca. −211 kJ mole^{-1} is clearly too low. Since the bomb system used was satisfactorily checked using acetanilide, we have additional confidence in the value of −217.9 ± 2 kJ mole^{-1}.

However, this is apparently inconsistent with a value derived from solution-reaction experiments. A very recent [6] combustion study of ammonium picrate essentially confirms an earlier study. Combination of a value of the standard enthalpy of formation, calculated from these results, with precision enthalpy of solution and enthalpies of neutralisation measurements appear to suggest a value of $\Delta H_f^0[C_6H_2(NO_2)_3OH, (c)] \approx -229$ kJ mole^{-1}. This is not only well outside the experimental error of this study, but is anomalously high compared with results from all reported combustion studies. However, the constitution of picric acid in aqueous solution is known to be concentration-dependent and further solution-calorimetric studies will be reported later.

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