J. Chem. Thermodynamics 1989, 21, 265-274

## Enthalpies of combustion of 1,4-naphthoquinone, 9,10-anthraquinone, 9,10-phenanthraquinone, 1,4,9,10-anthradiquinone, 5,8-dihydroxy-1,4-naphthoquinone, and 1,4-dihydroxy-9,10-anthraquinone

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(Received 24 November 1988)

The standard ( $p^{\circ} = 0.1$  MPa) molar enthalpics of combustion in oxygen at 298.15 K were measured by static-bomb calorimetry for some quinones and dihydroxyquinones. The standard molar enthalpies of sublimation at 298.15 K were measured by microcalorimetry for 1,4-naphthoquinone and 9,10-phenanthraquinone; values were selected from the literature for the remaining compounds in order to derive the standard molar enthalpies of formation in the gaseous state.

	$-\Delta_{\rm c} H_{\rm m}^{\circ}({\rm cr})/({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta_{\rm f} H^{\circ}_{\rm m}({\rm g})/({\rm kJ}\cdot{\rm mol}^{-1})$
1,4-Naphthoquinone	$4604.1 \pm 1.1$	$-97.5 \pm 1.9$
9,10-Anthraquinone	$6464.0 \pm 2.1$	$-75.7 \pm 2.9$
9,10-Phenanthraquinone	$6497.8 \pm 1.6$	$-49.3\pm2.8$
1,4,9,10-Anthradiquinone	$6033.6 \pm 2.4$	$-209.0 \pm 4.0$
5,8-Dihydroxy-1,4-naphthoquinone	$4196.8 \pm 0.5$	$-499.1 \pm 3.2$
1,4-Dihydroxy-9,10-anthraquinone	$6057.4 \pm 1.0$	-471.7 + 2.3

The energies of the intramolecular hydrogen bonds in the dihydroxyquinones were assessed as  $(25 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$ . 1,4,9,10-Anthradiquinone is apparently considerably strained, and although its reaction with water produces 1,4-dihydroxy-9,10-anthraquinone, a concomitant formation of hydrogen peroxide is shown to be thermodynamically improbable.

#### 1. Introduction

Quinones are an important group of compounds and although their reduction to hydroquinones can be carried out reversibly, there are many conflicting thermodynamic data for these reactions.<sup>(1,2)</sup> Thermodynamic quantities for the reduction-

oxidation reaction of 1,4-benzoquinone and 1,4-dihydroxybenzene were reported by Pilcher and Sutton.<sup>(3)</sup> Magnus<sup>(4)</sup> reported enthalpies of combustion for a series of quinones but his values for 1,4-benzoquinone and 9,10-anthraquinone differ from others reported in the literature.<sup>(5)</sup> To resolve some of these discrepancies we now report the standard molar enthalpies of combustion of 1,4-naphthoquinone, 9,10anthraquinone, and 9,10-phenanthraquinone. The reaction of 1,4,9,10-anthradiquinone (green) with water is of interest in that it results in the formation of 1,4-dihydroxy-9,10-anthraquinone (red), *i.e.* the diquinone is reduced, and analytical tests of the reaction mixture have suggested the presence of hydrogen peroxide.<sup>(6,7)</sup> Although the overall reaction is complex, the question arises as to whether it is thermodynamically possible for 1,4,9,10-anthradiquinone to oxidize water to hydrogen peroxide. To resolve this question we report the standard molar enthalpies of combustion of 1,4,9,10-anthradiguinone, 1,4-dihydroxy-9,10-anthraguinone, and, for comparison purposes, 5,8-dihydroxy-1,4-naphthoquinone. 1,4,5,8-Naphthodiquinone reacts very rapidly with water to form 5.8-dihydroxy-1,4-naphthoquinone, and traces of hydrogen peroxide have been detected in the reaction products.<sup>(7)</sup> However, this reaction with water is so rapid that we were unable to prepare a sample of this diquinone suitable for combustion measurements.

To derive enthalpies of formation in the gaseous state, the standard molar enthalpies of sublimation of 1,4-naphthoquinone and 9,10-phenanthraquinone were measured by microcalorimetry. Values were selected from the literature for the remaining compounds except for 1,4,9,10-anthradiquinone; because of the difficulty of handling this compound in a dry atmosphere, measurement was not attempted but an estimate was made.

### 2. Experimental

1,4-Naphthoquinone (NQ), 9,10-anthraquinone (AQ), and 9,10-phenanthraquinone (PQ) were purified from commercial samples (Janssen Chimica) by repeated sublimation *in vacuo*. The purification process was continued until the combustion results were consistent and the carbon-dioxide recovery ratios were satisfactory.

1,4-Dihydroxy-9,10-anthraquinone (quinizarin:  $ADQH_2$ ) (Aldrich) was purified by chromatography on silica gel with dichloromethane as the eluant. The main fraction was sublimed *in vacuo*, the sublimate recrystallized from toluene, and this product then resublimed *in vacuo*. 1,4,9,10-Anthradiquinone (ADQ) was prepared from quinizarin using a modification of the method reported by Dimroth *et al.*<sup>(8)</sup> Purified quinizarin, 4 g in 450 cm<sup>3</sup> dichloromethane, was oxidized to ADQ by a solution of 9.7 g of lead tetraacetate in 500 cm<sup>3</sup> of dichloromethane. The mixture was stirred at room temperature for 1 h and then filtered through Celite. The green filtrate was diluted with cyclohexane and then evaporated under reduced pressure; the cyclohexane facilitated removal of acetic acid. The residue was crystallized from toluene to give the diquinone as pale-green felted needles of melting temperature 483.2 K. The product was stored in the dark over  $P_4O_{10}$ . 5,8-Dihydroxy-1,4-naphthoquinone (naphthazarin, NDQH<sub>2</sub>) was prepared by a method similar to that described by Fierz-David and Stockar.<sup>(9)</sup> 1,5-Dinitronaphthalene (50 g) was dissolved in 540 cm<sup>3</sup> of 10 mass per cent oleum and a solution of 25 g of sulphur in 300 cm<sup>3</sup> of 20 mass per cent oleum was added slowly, the temperature being kept at 320 K. The mixture was stirred until a test portion dissolved completely in water to give a blue solution. The reaction mixture was poured on to 2 kg of ice, the solution filtered, and, after boiling, the naphthazarin separated. The product was washed with water and then purified by chromatography on calcium carbonate with benzene as eluant. The naphthazarin was recrystallized from benzene and sublimed *in vacuo* giving red crystals of melting temperature 516 K. The density,  $\rho = 1.54 \text{ g} \cdot \text{cm}^{-3}$ , was determined but carbon-dioxide recoveries were not measured. *n*-Hexadecane (Aldrich Gold Label) stored under nitrogen was used as the combustion auxiliary aid for some of the measurements.

The average ratios of carbon dioxide observed to those calculated from the masses of the samples, together with the densities of the samples, were NQ( $\rho = 1.422 \text{ g} \cdot \text{cm}^{-3}$ ), 0.9996 ± 0.0003; AQ( $\rho = 1.419 \text{ g} \cdot \text{cm}^{-3}$ ), 0.9999 ± 0.0001; PQ( $\rho = 1.405 \text{ g} \cdot \text{cm}^{-3}$ ), 1.0001 ± 0.0001; ADQ( $\rho = 1.35 \text{ g} \cdot \text{cm}^{-3}$ ), 1.0002 ± 0.0003; and ADQH<sub>2</sub>( $\rho = 1.533 \text{ g} \cdot \text{cm}^{-3}$ ), 1.0000 ± 0.0001.

The enthalpies of combustion of NQ, AQ, and PQ were measured using the staticbomb calorimeter in Porto. This calorimeter, subsidiary apparatus, and technique have been described.<sup>(10, 11)</sup> The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples—CRM190n) having a specific energy of combustion under standard bomb conditions of (26433.9 ± 3.9) J · g<sup>-1</sup>. The calibration results were corrected to give the energy equivalent  $\varepsilon$ (calor) corresponding to the average mass of water added to the calorimeter: 3119.6 g. From six calibrations,  $\varepsilon$ (calor) = (15902.5 ± 1.0) J · K<sup>-1</sup>, where the uncertainty quoted is the standard deviation of the mean. ADQ and ADQH<sub>2</sub> were measured using the static-bomb calorimeter in Manchester.<sup>(12)</sup> The energy equivalent was determined from the combustion of benzoic acid (NBS standard reference sample 39i) having a specific energy of combustion under standard bomb conditions of (26434±3) J · g<sup>-1</sup>. From eight calibrations,  $\varepsilon$ (calor) = (15293.14±0.67) J · K<sup>-1</sup>, where the uncertainty quoted is the standard deviation of the mean, for an average mass of water added to this calorimeter of 2897.0 g.

The experimental conditions were similar for both calorimeters. Samples were ignited at  $(298.150 \pm 0.001)$  K in oxygen at 3.04 MPa with 1 cm<sup>3</sup> of water added to the bomb. The electrical energy for ignition was determined from the change in potential difference across a capacitor when discharged through the platinum ignition wire. For the cotton-thread fuse, empirical formula CH<sub>1.686</sub>O<sub>0.843</sub>,  $-\Delta_c u^\circ = 16250$  J · g<sup>-1</sup>. The corrections for nitric-acid formation were based on -59.7 kJ · mol<sup>-1</sup> for the energy of formation of 0.1 mol · dm<sup>-3</sup> HNO<sub>3</sub>(aq) from N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O(l).<sup>(14)</sup> Corrections for carbon formation were based on  $-\Delta_c u^\circ = 33$  kJ · g<sup>-1</sup>.<sup>(13)</sup> The amount of substance used in each experiment was determined from the total mass of carbon dioxide produced after allowance for that formed from the cotton-thread fuse, Melinex, and *n*-hexadecane, and that lost due to carbon formation. For each compound,  $(\partial u/\partial p)_T$  at 298.15 K was assumed to be -0.1 J · g<sup>-1</sup> · MPa<sup>-1</sup>, a value typical for most organic solids. For each compound,  $\Delta_c u^\circ$  was calculated by the procedure given by Hubbard *et al.*<sup>(13)</sup> The relative atomic masses used were those recommended by the IUPAC Commission.<sup>(15)</sup>

Combustion of the quinones NQ, AQ, and PQ posed unexpected difficulties because of the occurrence of explosions on ignition in some of the measurements. A greater number of experiments than is customary was carried out and in some of these, hexadecane was used as the auxiliary combustion aid. The results when using hexadecane were in agreement with the other values. The specific energy of combustion of the hexadecane was measured in the Porto calorimeter: from six experiments,  $-\Delta_c u^{\circ} = (47151.4 \pm 1.5) \text{ J} \cdot \text{g}^{-1}$  in agreement with the value reported by Fraser and Prosen.<sup>(16)</sup>

The substances ADQ and ADQH<sub>2</sub> were burned in Melinex bags, to protect ADQ from attack by water prior to ignition. For ADQH<sub>2</sub> it was not possible to manipulate the pellets for weighing because they were friable. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032).<sup>(17)</sup> The specific energy of combustion of dry Melinex is  $-\Delta_c u^\circ = (22902 \pm 5) \text{ J} \cdot \text{g}^{-1}$  and the mass of carbon dioxide produced from the Melinex was calculated using the factor previously reported.<sup>(18)</sup>

The measurements on NDQH<sub>2</sub> were made using an aneroid bomb calorimeter,<sup>(19)</sup> and the original results<sup>(20)</sup> were recalculated using more recent auxiliary quantities. The experimental conditions were similar to those for the Porto and Manchester calorimeters except that the electrical energy for ignition was measured by an integrator circuit, the fuse for ignition was filter paper for which  $-\Delta_c u^{\circ} = 17230 \text{ J} \cdot \text{g}^{-1}$ , and recovery of the carbon dioxide was not attempted. The calorimeter was calibrated using benzoic acid (B.D.H. Thermochemical Standard) with a specific energy of combustion under standard bomb conditions of  $(26433.8 \pm 3.6) \text{ J} \cdot \text{g}^{-1}$ . From 14 calibration experiments,  $\varepsilon(\text{calor}) = (7399.6 \pm 0.5) \text{ J} \cdot \text{K}^{-1}$ , where the uncertainty quoted is the standard deviation of the mean.

The standard enthalpies of sublimation of NQ and PQ were measured by the "vacuum sublimation" drop-microcalorimetric method.<sup>(21)</sup> Samples (about 5 mg) of each compound contained in a small thin glass capillary tube sealed at one end were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter held at 480 K and then removed from the hot-zone by vacuum sublimation. The observed standard molar enthalpies of sublimation  $\{H_m^{\circ}(g, 480 \text{ K}) - H_m^{\circ}(cr, 298.15 \text{ K})\}$  were corrected to 298.15 K using  $\Delta_{298.15 \text{ K}}^{480.00 \text{ K}} H_m^{\circ}(g)$  estimated by a group method based on the values of Stull *et al.*<sup>(22)</sup> The micro-calorimeter was calibrated *in situ* for these experiments at 480 K by making use of the reported enthalpies of sublimation of naphthalene,<sup>(22)</sup> and of 9,10-anthraquinone.<sup>(23.24)</sup>

#### 3. Results

Results for a typical combustion experiment on each compound are given in table 1;  $\Delta m(H_2O)$  is the deviation of the mass of water added to the calorimeter from the average mass assigned to  $\varepsilon(\text{calor})$ . Samples were ignited at 298.15 K so that  $-\Delta U(\text{IBP}) = \{\varepsilon(\text{calor}) + c_p(H_2O, 1)\Delta m(H_2O) + \varepsilon_f\}\Delta T_{ad} - \Delta U(\text{ign.}); \Delta U_{\Sigma}$  is the correction to the standard state: the remaining terms are as previously defined.<sup>(13)</sup> The individual values of  $\Delta_c u^\circ$  together with the mean and its standard deviation are given

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	NQ	AQ	PQ	ADQ	ADQH <sub>2</sub>	NDQH2
$m(CO_2, total)/g$	2.00598	2.04886	1.86624	2.70807	2.75695	
m(cpd)/g	0.71858	0.69016	0.62862	1.00025	1.02634	0.59774
m(Melinex)/g		-	Reference -	0.05057	0.05242	
m(fuse)/g	0.00395	0.00408	0.00376	0.00307	0.00272	0.00299
$\Delta T_{\rm ad}/{\rm K}$	1.31909	1.35099	1.23657	1.73613	1.77359	1.78917
$\varepsilon_{\rm f}/({\rm J}\cdot{\rm K}^{-1})$	15.2	16.0	15.9	14.2	14.5	13.9
$\Delta m(H_2O)/g$	0.5	0.0	0.1	0.1	-0.1	
$-\Delta U(\mathbf{IBP})/\mathbf{J}$	20998.6	21504.6	19684.0	26574.4	27148.3	13256.9
$\Delta U(HNO_3)/J$	2.5	3.6	2.3	10.7	5.1	1.5
$\Delta U(ign.)/J$	1.0	1.2	1.0	0.3	0.4	7.1
$\Delta U(\text{carbon})/J$	0.0	0.0	0.0	0.0	4.2	5.4
$\Delta U_{\Sigma}/J$	15.8	15.8	14.2	24.8	24.7	12.8
$-m\Delta u^{\circ}$ (Melinex)/J	_			1158.3	1200.4	
$-m\Delta_{c}u^{\circ}(\text{fuse})/\text{J}$	64.2	66.3	61.1	49.9	44.1	51.6
$-\Delta_{\rm c} u^{\circ}({\rm cpd})/({\rm J}\cdot{\rm g}^{-1})$	29107.5	31034.7	31189.6	25324.4	25214.1	22077.2

TABLE 1. Typical combustion results at 298.15 K ( $p^{\circ} = 0.1$  MPa)

TABLE 2. Values of  $-\Delta_c u^\circ$  at 298.15 K ( $p^\circ = 0.1$  MPa)

NQ	AQ	PQ	ADQ	$ADQH_2$	NDQH2
		$-\Delta_{\rm c} u^{\circ}$	$(J \cdot g^{-1})$		
29107.5	31051.1	31196.4	25332.9	25219.6	22079.8
29113.8	31037.5	31198.9	25324.4	25212.8	22077.2
29091.3	31030.0	31205.7	25347.5	25218.5	22076.3
29099.0	31027.6	31199.3	25336.0	25219.0	22073.2
29095.2	31034.7	31189.6		25214.0	
29108.7	31015.0	31181.2			
29112.4	31033.6	31188.3			
29102.3		31191.3			
29106.5		31180.5			
29098.0		31206.4			
		31198.0			
		31206.4			
		$-\langle \Delta_{\rm c} u^{\circ} \rangle$	$\rangle/(\mathbf{J}\cdot\mathbf{g}^{-1})$		
$29103.5\pm2.4$	$31032.8 \pm 4.1$	$31195.2 \pm 2.6$	$25335.2 \pm 4.8$	$25216.8 \pm 1.4$	$22076.6 \pm 1.4$

in table 2. Table 3 lists the derived standard molar enthalpies of combustion and of formation in the crystalline and gaseous states. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion and of formation are twice the overall standard deviations of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive  $\Delta_f H_m^{\circ}$  from  $\Delta_c H_m^{\circ}$  the standard molar enthalpies of formation of H<sub>2</sub>O(l):  $-(285.83\pm0.04)$  kJ·mol<sup>-1</sup>, and of CO<sub>2</sub>(g):  $-(393.51\pm0.13)$  kJ·mol<sup>-1</sup>, were used.<sup>(25)</sup>

The microcalorimetric value for the enthalpy of sublimation of NQ agrees with that reported by de Kruif *et al.*:<sup>(26)</sup> (90.7  $\pm$  2.0) kJ·mol<sup>-1</sup>, but not with the Magnus value:<sup>(4)</sup>

_	$\frac{-\Delta_{\rm c}U_{\rm m}^{\circ}({\rm cr})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{-\Delta_{\rm c}H_{\rm m}^{\circ}({\rm cr})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{\rm f} H_{\rm m}^{\circ}({\rm cr})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}}{\rm kJ\cdot mol^{-1}}$	$\frac{\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})}{{\rm kJ}\cdot{\rm mol}^{-1}}$
NQ	$4602.9 \pm 1.1$ 6461 5 ± 2 1	$4604.1 \pm 1.1$ $6464.0 \pm 2.1$	$-188.5 \pm 1.7$ -188.5 + 2.8	$91.0 \pm 0.8$ 112.8 ± 0.5 (23, 24)	$-97.5 \pm 1.9$
PQ ADO	$6495.3 \pm 1.6$ $60348 \pm 2.4$	$6497.8 \pm 1.6$ $6033.6 \pm 2.4$	$-154.7 \pm 2.4$ $-333.0 \pm 3.0$	$112.8 \pm 0.5$ $108.1 \pm 1.5$ $124 \pm 21$	$-49.3 \pm 2.8$ $-209 \pm 4$
$ADQH_2$ NDQH_2	$6054.8 \pm 2.4$ $6057.4 \pm 1.0$ $4198.0 \pm 0.5$	$6053.0 \pm 2.4$ $6057.4 \pm 1.0$ $4196.8 \pm 0.5$	$-595.0 \pm 3.0$ $-595.1 \pm 2.1$ $-595.8 \pm 1.4$	$ \begin{array}{c} [124 \pm 2] \\ 124.1 \pm 0.9^{(28)} \\ 96.7 \pm 2.9^{(30)} \end{array} $	$-209 \pm 4$ -471.7 ± 2.3 -499.1 ± 3.2

TABLE 3. Derived standard molar values at 298.15 K ( $p^{\circ} = 0.1$  MPa)

 $(72.4 \pm 3.8)$  kJ·mol<sup>-1</sup>. For AQ, 14 values of the enthalpy of sublimation were reported between 1952 and 1982 ranging from 108.0 to 136.6 kJ·mol<sup>-1</sup>; we select the weighted mean of the values from the very careful studies by Bardi *et al*.:<sup>(23)</sup> (113.0 ± 0.8) kJ·mol<sup>-1</sup> and by Murata *et al*.:<sup>(24)</sup> (112.4 ± 1.2) kJ·mol<sup>-1</sup>. For PQ, the microcalorimetric value disagrees with those reported by Magnus.:<sup>(4)</sup> (91.6 ± 4.8) kJ·mol<sup>-1</sup> and by Hoyer and Peperle:<sup>(27)</sup> (132 ± 6) kJ·mol<sup>-1</sup>. For ADQH<sub>2</sub> we select the value of Malaspina *et al*.<sup>(28)</sup> which agrees with that of Hoyer and Peperle:<sup>(27)</sup> (124.8 ± 4.8) kJ·mol<sup>-1</sup> but not with that of Beynon and Nicholson:<sup>(29)</sup> (105.3 ± 1.3) kJ·mol<sup>-1</sup>. The value for ADQ was assumed to be the same as that for ADQH<sub>2</sub>.

TABLE 4. Comparison with previous values at 298.15 K

	$-\Delta_{\rm c} H_{\rm m}^{\circ}({ m cr})/({ m kJ\cdot mol^{-1}})$	reference
NQ	4604.1 ± 1.1	this work
	$4609.2 \pm 1.8$	4
AQ	$6464.0 \pm 2.1$	this work
-	6444.9 + 3.1	4
	6467.6+3.3	31
PQ	$6497.8 \pm 1.6$	this work
-	$6421.6 \pm 1.3$	4

Comparison with previous measurements is given in table 4. Large disagreements with the values reported by Magnus<sup>(4)</sup> are apparent. Discrepancies greater than  $30 \text{ kJ} \cdot \text{mol}^{-1}$  are also found between the values of Magnus<sup>(4)</sup> and those of Pilcher and Sutton<sup>(3)</sup> for 1,4-benzoquinone and 1,4-dihydroxybenzene.

#### 4. Discussion

The following increments in  $-\Delta_f H_m^{\circ}(g)/(kJ \cdot mol^{-1})$  were calculated using the values reported in this paper, in reference 5, and with  $\Delta_f H_m^{\circ}(1,4\text{-dihydroxy-naphthalene}, g)/(kJ \cdot mol^{-1}) = -(197.0 \pm 1.8):^{(32)}$ 

1,2,4,5-Tetramethylbenzene					
<i>m</i> '(compound)/g	0.56980	0.63437	0.56874	0.57858	0.55235
m"(polyethene)/g	0.07334	0.07149	0.06974	0.06606	0.07018
$\Delta t_{\rm c}/{\rm K} = (t_{\rm f} - t_{\rm i} + \Delta t_{\rm corr})/{\rm K}$	1.96780	2.15775	1.95297	1.97079	1.90464
$\varepsilon(\text{calor})(-\Delta t_{c})/\text{kJ}$	28.0730	-30.7828	-27.8614	-28.1156	-27.1720
$\varepsilon(\text{cont.})(-\Delta t_{c})/\text{kJ}$	-0.0323	0.0359	-0.0320	-0.0323	-0.0311
$\Delta U_{ m ign}/ m kJ$	0.0477	0.0484	0.0492	0.0467	0.0478
$\Delta U_{\rm dec}({\rm HNO}_3)/{\rm kJ}$	0.0017	0.0009	0.0015	0.0012	0.0010
$\Delta U$ (corr. to std. states)/kJ	0.0103	0.0116	0.0102	0.0104	0.0099
$-m''\Delta_{\rm c}u^{\circ}({\rm polyethene})/{\rm kJ}$	3.4009	3.3151	3.2339	3.0633	3.2543
$\Delta_{\rm c} u^{\circ}({\rm compound})/({\rm kJ}\cdot{\rm g}^{-1})$	-43.2515	-43.2598	-43.2511	-43.2548	-43.2518
$\langle \Delta_{\rm c} u^{\circ}(298.15 \text{ K}) \rangle / (\text{kJ} \cdot \text{g}^{-1})$	$-43.2538 \pm 0$	.0016			
	Per	ntamethylbenzer	ie		
m'(compound)/g	0.63856	0.63642	0.64044	0.63512	0.64064
$\Delta t_{\rm s}/{\rm K} = (t_{\rm f} - t_{\rm i} + \Delta t_{\rm corr})/{\rm K}$	1.95127	1.94454	1.95721	1.94055	1.95762
$\varepsilon(\text{calor})(-\Delta t_{c})/\text{kJ}$	-27.8556	-27.7596	-27.9405	-27.7026	-27.9462
$\varepsilon(\text{cont.})(-\Delta t_{\rm c})/\text{kJ}$	-0.0322	-0.0321	-0.0323	-0.0320	-0.0323
$\Delta U_{ign}/kJ$	0.0500	0.0497	0.0485	0.0478	0.0501
$\Delta U_{\rm dec}({\rm HNO}_3)/{\rm kJ}$	0.0021	0.0014	0.0017	0.0014	0.0014
$\Delta U(\text{corr. to std. states})/kJ$	0.0106	0.0105	0.0106	0.0105	0.0106
$\Delta_{\rm c} u^{\circ}({\rm compound})/({\rm kJ}\cdot{\rm g}^{-1})$	-43.5750	-43.5719	-43.5824	-43.5743	-43.5758
$\langle \Delta_{\rm c} u^{\circ}(300.15 \text{ K}) \rangle / (\text{kJ} \cdot \text{g}^{-1})$	$-43.5759 \pm 0$	.0018			

TABLE 2. Results of combustion experiments

recalculated values of our previously published standard molar enthalpy of combustion.<sup>(1)</sup> The uncertainties in table 3 are twice the final overall standard deviations of the mean and were estimated as outlined by Olofsson.<sup>(11)</sup> The values for the standard molar enthalpies of formation of H<sub>2</sub>O(l) and CO<sub>2</sub>(g) at 298.15 K:  $-(285.830\pm0.042)$  kJ·mol<sup>-1</sup> and  $-(393.51\pm0.13)$  kJ·mol<sup>-1</sup>, respectively, were taken from reference 12.

The results of our Knudsen effusion experiments with the three compounds are summarized in table 4, which collects values of temperature, time, and mass of sublimed substance. The vapour pressures were calculated by mean of the equation:

$$p = (\Delta m/W_a at)(2\pi RT/M)^{1/2},$$
 (1)

The symbols of this equation have the same meaning as in reference 5. The highest percentage error for the vapour pressure in table 4 is 0.7, and has been computed as the sum of the estimated errors of all quantities in equation (1).

TABLE 3. Standard molar energies and enthalpies of combustion and formation ( $p^\circ = 101.325$  kPa)

Compound	T/K	$\frac{\Delta_{\rm c} U_{\rm m}(T)}{\rm kJ\cdot mol^{-1}}$	$\frac{\Delta_{\rm c}H_{\rm m}^{\circ}(300.15{\rm K})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{\rm e}H_{\rm m}^{\circ}(298.15{\rm K})}{{\rm kJ}\cdot{\rm mol}^{-1}}$	$\frac{\Delta_{\rm f} H_{\rm m}^{\circ}({\rm cr, 298.15  K})}{\rm kJ\cdot mol^{-1}}$
1,2,4,5-Tetramethyl- benzene Pentamethylbenzene Hexamethylbenzene	298.15 300.15 300.15	$-5805.6 \pm 1.4$ -6460.0 ± 1.6 -7120.1 ± 1.9	$-6470.0 \pm 1.6$ -7131.4 ± 1.9	$-5814.2 \pm 1.4$ -6470.6 ± 1.6 -7132.2 ± 1.9	$-121.7 \pm 1.9$ $-144.6 \pm 2.2$ $-162.4 \pm 2.5$

	$\frac{\Delta_{\rm f} H^{\circ}_{\rm m}({\rm quinone, g})}{{\rm kJ} \cdot {\rm mol}^{-1}}$	$\frac{E_{\rm a}}{\rm kJ\cdot mol^{-1}}^{(35)}$	$\frac{\Delta_{\rm f} H^{\circ}_{\mathfrak{m}}({\rm radical ion, g})}{{\rm kJ}\cdot{\rm mol}^{-1}}$
BQ	$-122.9 \pm 3.5$	184.5±4.2	$-307.4 \pm 5.5$
NQ	$-97.5 \pm 1.9$	$174.9 \pm 4.2$	$-272.4\pm4.6$
AQ	$-75.7 \pm 2.9$	$153.6 \pm 4.2$	$-229.3 \pm 5.1$

TABLE 5. Electron affinities  $E_a$  and  $\Delta_f H_m^\circ$  (radical ions) at 298.15 K ( $p^\circ = 0.1$  MPa)

The electron affinities of a series of quinones were determined from gas-phase equilibria measurements by Heinis *et al.*,<sup>(35)</sup> who showed that the energy of the electron-attachment reaction was virtually temperature independent. Table 5 lists the electron affinities and the derived enthalpies of formation of the gaseous radical ions. Table 6 lists the increments in  $\Delta_f H^{\circ}_m(g)$  due to the fusion of a benzene ring to the quinone, its radical ion, the hydroquinone, and the parent aromatic hydrocarbon. From these increments it is apparent that the increase in the  $\pi$ -delocalization stabilization energy resulting from the fusion of the benzene ring is in the sequence: quinone > radical ion > hydroquinone = parent aromatic hydrocarbon.



TABLE 6.  $\Delta \{\Delta_f H_m^{\circ}(g)\}\$  for benzene-ring attachment at 298.15 K ( $p^{\circ} = 0.1$  MPa)

	Crystallin	ne state	Gaseous state		
	$\Delta_{\rm r} G_{\rm m}^{\circ}/({\rm kJ}\cdot{\rm mol}^{-1})$	$E^{\circ}/\mathbf{V}$	$\Delta_{\rm r} G^{\circ}_{\rm m}/({\rm kJ}\cdot{\rm mol}^{-1})$	$E^{\circ}/V$	
$BQ + H_2 = BQH_2$	$-132.6 \pm 2.3$	$0.687 \pm 0.012$	$-94.9 \pm 5.0$	$0.492 \pm 0.025$	
$NQ + H_2 = NQH_2$	$-82.7 \pm 2.0$	$0.429 \pm 0.010$	$-51.9 \pm 3.6$	$0.269 \pm 0.018$	
$ADQ + H_2 = ADQH_2$	$-215.9 \pm 3.9$	$1.119\pm0.020$	$-215.1 \pm 5.2$	$1.115 \pm 0.027$	

TABLE 7. Standard molar Gibbs energy changes and standard electromotive force of quinone reduction reactions at 298.15 K ( $p^\circ = 0.1$  MPa)

For the reduction of 1,4-benzoquinone (BQ) to 1,4-dihydroxybenzene (BQH<sub>2</sub>) by hydrogen, Pilcher and Sutton<sup>(3)</sup> deduced that for this reaction in the crystalline state,  $\Delta_r S^{\circ}_m/(J \cdot K^{-1} \cdot mol^{-1}) = -(154.8 \pm 4.2)$ , and in the gaseous state,  $\Delta_r S^{\circ}_m/(J \cdot K^{-1} \cdot mol^{-1}) = -(159.8 \pm 8.4)$  (estimated uncertainty). Assuming the standard molar entropy change to be constant for the reduction of quinone systems, standard molar Gibbs energy changes and the standard electromotive forces of the reduction reactions can be derived at 298.15 K and are listed in table 7.

The standard electromotive force for  $BQ/BQH_2$  in the crystalline state was reported by Conant and Fieser<sup>(36)</sup> as  $(0.681 \pm 0.001)$  V. Some values of the standard electromotive force for these reduction reactions have been reported for the components in solution.<sup>(37)</sup> These values are not comparable with those in table 7 but they are expected to be of roughly the same size, *e.g.*  $BQ/BQH_2$ , 0.711 V;  $NQ/NQH_2$ , 0.484 V;  $AQ/AQH_2$ , 0.154 V, and for  $PQ/PQH_2$ , 0.460 V. As expected the values for  $NQ/NQH_2$  and  $PQ/PQH_2$  are similar.

For the reduction of the anthradiquinone,  $E^{\circ} = (1.119 \pm 0.020)$  V, is too small for this compound to be able to oxidize water to hydrogen peroxide. At 298.15 K, for

$$H_2O_2(l) + H_2(g) = 2H_2O(l),$$

 $\Delta_r G_{nn}^{\circ}/(kJ \cdot mol^{-1}) = -(339.2 \pm 4.2), E^{\circ} = (1.758 \pm 0.021)$  V. Thus the quinizarin and any hydrogen peroxide detected in the products of the reaction of anthradiquinone with water, will not be formed in the initial reaction step but must arise by an alternative route. Phthalic acid has been found in the reaction products<sup>(7)</sup> in sufficient amount to propose as a possible overall reaction scheme:

$$5ADQ(cr) + 7H_2O(l) = 3ADQH_2(cr) + 2C_6H_4(CO_2H)_2(soln) + CO_2(g) + CH_3OH(l),$$

for which  $\Delta_r H_m^{\circ} \approx -675 \text{ kJ} \cdot \text{mol}^{-1}$ , *i.e.* this overall reaction is energetically favourable and may be the main one producing ADQH<sub>2</sub>, but its overall complexity suggests that it is likely to be accompanied by side reactions.

We acknowledge financial support from INIC to Centro de Investigação em Quimica (U.P.), Research Project L.5, and the award of an SERC CASE studentship to P.M.G.

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