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STANDARD ENTHALPIES OF COMBUSTION AND FORMATION OF PORPHYRIN DERIVATIVES

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ABSTRACT

Using static and moving oxygen bomb calorimeters, the standard enthalpies of combustion at 298.15 K of tetraphenylporphyrin, tetra(*p*-methylphenyl)porphyrin, tetra(*p*-methoxyphenyl)porphyrin, tetra(*o*-aminophenyl)porphyrin, tetra(*p*-nitrophenyl)porphyrin, tetra(3-pyridyl)porphyrin and tetra(*p*-bromophenyl)porphyrin were determined as −22223.2 ±6.3, −24797.8±8.1, −24148.2±7.6, −22647.7±16.2, −21781.4±9.5, −20268.0±6.8 and −21784.4±11.2 kJ mol^{-1} respectively. The corresponding standard enthalpies of formation were 621.3±8.5, 478.6±10.3, −171.1±9.7, 474.2±17.2, 751.0±11.0, 811.8±8.6 and 754.17 ±12.6 kJ mol^{-1}.

INTRODUCTION

Porphyrin compounds have been widely investigated in the past decade with respect to the characteristics of these compounds, such as their use as catalysts to produce hydrogen from water. In analytical chemistry, porphyrin compounds are often used to identify trace metal ions. In medical science, they are used to check for the presence of tumours. Studies of their thermodynamic properties are, however, seldom reported. In this work, the experimental results of the combustion enthalpies of tetraphenylporphyrin (TPP), tetra(*p*-methylphenyl)porphyrin ($T_{p\text{-}CH_3}PP$), tetra(*p*-methoxyphenyl) porphyrin ($T_{p\text{-}OCH_3}PP$), tetra(*o*-aminophenyl)porphyrin ($T_{o\text{-}NH_2}PP$), tetra(*p*-nitrophenyl)porphyrin ($T_{p\text{-}NO_2}PP$), tetra(3-pyridyl)porphyrin (TPyP) and tetra(*p*-bromophenyl)porphyrin ($T_{p\text{-}Br}PP$) are reported and the corresponding standard enthalpies of formation were calculated at 298.15 K.

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EXPERIMENTAL

Materials

Tetraphenylporphyrin (TPP)

Benzaldehyde was added to boiling propionic acid and refluxed for about 30 min at the boil. After cooling to 50–60 °C, alcohol was added, and crystals slowly separated out from the liquid and were filtered off. The resulting violet crude product was washed with methanol, and dissolved in CH_2Cl_2. After adding a benzene solution of 2,3 dichloro-5,6 dinitrilequinone (DDQ), this mixture was refluxed for 30 minutes, the solvent was then evaporated, and the solid product was dissolved in CH_3Cl. The resulting solution was subjected to column chromatography with Al_2O_3 as the solid phase, in order to separate and purify the sample. Pure TPP can be recrystallized from a CH_3Cl–CH_3OH solvent.

Tetra(p-methylphenyl)porphyrin ($T_{p\text{-}CH_3}PP$)

Equal molar quantities of pyrrole and *p*-methylbenzaldehyde were mixed with glacial acetic acid and refluxed for 24 hours. Then, acetic acid was removed by reduced pressure distillation and the resulting solid was dissolved in acetone containing a little pyridine. After the mixture was concentrated, violet crystals precipitated from the liquid and were filtered off. The crude product was washed with acetone and then dissolved in CH_2Cl_2 and the resulting solution was treated by Al_2O_3-column chromatography. $T_{p\text{-}CH_3}PP$ was recrystallized from a mixed acetone–pyridine solvent.

Tetra(p-methoxyphenyl)porphyrin ($T_{p\text{-}OCH_3}PP$)

Crude $T_{p\text{-}OCH_3}PP$ was prepared in a similar manner to TPP. The crude product was dissolved in tetrahydrofuran, DDQ was added, and then the solvent was evaporated. The resulting solid product was dissolved in CH_2Cl_2 and the solution was subjected to column chromatography with Al_2O_3 to separate and purify the sample. $T_{p\text{-}OCH_3}PP$ was recrystallized from CH_3Cl–CH_3OH solvent.

Tetra(o-aminophenyl)porphyrin ($T_{o\text{-}NH_2}PP$)

p-Nitrobenzaldehyde was dissolved in boiling glacial acetic acid, the solution was refluxed for 20 min and pyrrole was added dropwise during the refluxing. Trichloromethane was then added to the hot solution, which was filtered after cooling and the filtered liquid was washed with chloroform until it was colourless. The chloroform layer was separated and the solvent was evaporated yielding, tetra(*p*-nitrophenyl)porphyrin. This was dissolved in concentrated HCl containing $SnCl_2 2H_2O$ and the solution was heated and neutralized with concentrated ammonia. Trichloromethane was added and the mixture was violently stirred. The layer of trichloromethane containing the product was separated using a separating funnel and concentrated by evaporation. The concentrated liquid was washed once with ammonia water and twice with water. After the water was separated out, the solution was dried with anhydrous sodium sulphate. Alcohol and *n*-heptane were added and the mixture was concentrated by evaporation under reduced pressure until the crystals appeared. The crude product was filtered, washed with methanol and then recrystallized from a chloroform–methanol solvent.

Tetra(p-nitrophenyl)porphyrin ($T_{p\text{-}NO_2}PP$)

p-Nitrobenzaldehyde was added to a mixture of propionic acid and a little acetic anhydride. The solution was heated to boiling, pyrrole was added, and the mixture was refluxed for 30 min. After standing for a day, crystals separated out from the liquid mixture, and were filtered and washed in turn with dimethyformamide and $CHCl_3$. The crude product was recrystallized from pyridine three times after drying.

Tetra(3-pyridyl)porphyrin (TPyP)

Equal quantities of 3-pyridylaldehyde and pyrrole were added to a mixture of boiling propionic acid and a little acetic acid. After refluxing for 60 min, the solution was concentrated by evaporation under reduced pressure to 10% of its original volume. The product was diluted with water, adjusted until alkaline with concentrated ammonia and then filtered. The filtered liquid was washed with dilute ammonia and distilled water. Using chloroform–acetone (2 : 1) the carrier and Al_2O_3 as absorbent, the product was treated by column chromatography.

Tetra(p-bromophenyl)porphyrin ($T_{p\text{-}Br}PP$)

A mixture of *p*-bromobenzaldehyde and propionic acid was heated to boiling and then a solution of pyrrole in propionic acid was added dropwise into it. The reaction mixture was refluxed for 30 minutes, alcohol was added after cooling, and the separated crystals were filtered. The crude crystals were dissolved in chloroform containing DDQ, refluxed for 60 min at the boil and filtered after cooling. The filtered liquid was treated by column chromatography using Al_2O_3 as adsorbent.

Characterization

All the samples underwent elemental analyses: the results are given in Table 1. The results of measurements in the visible absorption spectrum, the IR absorption spectrum and nuclear magnetic resonance are in agreement with those in the literature.

The densities of samples were measured and found to be 1.14 (TPP), 0.998 ($T_{p\text{-}CH_3}PP$), 1.02 ($T_{p\text{-}OCH_3}PP$), 1.04 ($T_{o\text{-}NH_2}PP$), 1.36 ($T_{p\text{-}NO_2}PP$), 1.30 (TPyP) and 1.18 ($T_{p\text{-}Br}PP$) g cm^{-3} using the density bottle technique.

Apparatus

A static bomb calorimeter was used for combustion of the following compounds: TPP, $T_{p\text{-}CH_3}PP$, $T_{p\text{-}OCH_3}PP$, $T_{o\text{-}NH_2}PP$, $T_{p\text{-}NO_2}PP$ and TPyP. A

TABLE 1

Results of elemental analysis of the compounds

Compounds	C%		H%		N%	
	expt.	calc.	expt.	calc.	expt.	calc.
TPP	85.70	85.99	4.98	4.89	9.35	9.12
$T_{p\text{-}CH_3}PP$	85.75	85.97	5.35	5.67	8.17	8.36
$T_{p\text{-}OCH_3}PP$	78.22	78.48	5.25	5.18	7.54	7.63
$T_{o\text{-}NH_2}PP$	78.34	78.50	5.05	5.30	16.44	16.60
$T_{p\text{-}NO_2}PP$	66.14	66.50	3.63	3.30	14.40	14.10
TPyP	76.48	77.65	3.89	4.24	17.65	18.11
$T_{p\text{-}Br}PP$	56.10	56.80	2.90	2.82	6.00	6.02

moving bomb calorimeter was used for $T_{p\text{-}Br}PP$, 4-bromobenzoic acid and squalane.

The moving bomb was lined with platinum. The crucible, crucible holder, electrodes and fittings were made of platinum. The temperature of both calorimeters was measured to 1×10^{-5} K with a thermistor and the temperature of the thermostat (jackets) was controlled to ± 0.001 K during the measurement.

The calorimeters were calibrated using standard benzoic acid, for which the current certified value for heat of combustion, distributed by Metrologica Academia Sinica, is 26435 ± 5 J g^{-1} (standard bomb condition). The mean energy equivalent for eleven calibration runs of the static bomb system is $\epsilon^{sf} = 12.6028 \pm 0.0011$ kJ K^{-1}, and for the moving bomb system, $\epsilon^{sf} = 18.6376 \pm 0.0022$ kJ K^{-1}. Because of the difficulty of preparing porphyrin compounds in large quantities, a temperature rise during calibration of only about 1 K resulted.

The Dickinson method was used to evaluate the corrected temperature rises during the calibration and measurement experiments.

The combustion of standard tris(hydroxymethylamino)methane (THAM) was used to check the static bomb calorimeter: $\Delta_c U^{\ominus}$ was found to be -20.0303 ± 0.0060 kJ g^{-1}, in close agreement with published values [1]. The moving bomb calorimeter was tested by measuring the combustion energy of *p*-bromobenzoic acid, the result being $\Delta_c U^{\ominus} = -3091.8 \pm 1.3$ kJ mol^{-1}, in agreement with ref. [2].

All samples were compressed into a pellet.

All calculations were performed on an Apple II computer.

RESULTS

The results of combustion experiments for the seven porphyrin compounds are collected in Tables 2–8. A little benzoic acid was used as a combustion agent in the combustion experiments of the porphyrin com-

TABLE 2

Results for the combustion calorimetry of TPP at 298.15 K

	Run						
	1	2	3	4	5	6	7
m(TPP) (g)	0.370642	0.367949	0.369262	0.366439	0.364826	0.369270	0.366577
m(fuse) (g)	0.001020	0.000900	0.000988	0.000995	0.000987	0.000805	0.001060
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00
$P_i(O_2)$ (101325 Pa)	12.642	11.630	12.722	12.456	11.657	12.722	12.856
ΔT_c (K)	1.06149	1.05358	1.05731	1.04938	1.04496	1.05738	1.05052
ΔU_{ign} (kJ)	0.01724	0.01515	0.01668	0.01683	0.01660	0.01355	0.01785
$\Delta U_{dec}(HNO_3)$ (kJ)	0.00945	0.00808	0.00813	0.00929	0.00951	0.00918	0.01022
ΔU(Washburn (kJ)	0.01448	0.1419	0.01444	0.01427	0.01406	0.01443	0.01434
ΔU(soot) (kJ)	0.00198	0.00393	0.00165	0.00330	0.00099	0.00099	0.00115
ϵ^f(cont.) (kJ K^{-1})	0.04770	0.04744	0.04771	0.04764	0.4744	0.04772	0.04775
ϵ^{sf}(calor.) (kJ K^{-1})	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028
$-\Delta_c U^\ominus$(TPP) (kJ g^{-1}) [a]	36.1243	36.1315	36.1204	36.1262	36.1263	36.1260	36.1408

[a] Mean $\Delta_c U^\ominus(\text{TPP}) = -36.1279 \pm 0.0103$ kJ g^{-1}.

TABLE 3

Results for the combustion calorimetry of $T_{p\text{-}CH_3}PP$ at 298.15 K

	Run							
	1	2	3	4	5	6	7	8
$m(T_{p\text{-}CH_3}PP)$ (g)	0.360356	0.356837	0.356877	0.360661	0.359785	0.358347	0.355611	0.354990
m(fuse) (g)	0.001060	0.001090	0.000930	0.001105	0.000855	0.000982	0.001010	0.000930
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
$P_i(O_2)$ (101325 Pa)	21.114	14.294	15.600	15.360	14.960	14.774	15.680	15.307
ΔT_c (K)	1.05615	1.04435	1.04536	1.05626	1.05338	1.04947	1.04137	1.03935
ΔU_{ign} (kJ)	0.01783	0.01836	0.01563	0.01857	0.01443	0.01649	0.01700	0.01565
$\Delta U_{dec.}(HNO_3)$ (kJ)	0.01664	0.00954	0.01176	0.01232	0.01054	0.01010	0.01087	0.01054
ΔU(Washburn) (kJ)	0.01507	0.01405	0.01423	0.01435	0.01427	0.01418	0.01420	0.01412
ΔU(soot) (kJ)	0.00297	0.00181	0.00130	0.00050	0.00033	0.00020	0.00033	0.00033
ϵ^f(cont.) (kJ K^{-1})	0.04919	0.04959	0.04992	0.04988	0.04977	0.04972	0.04994	0.04984
ϵ^{sf}(calor.) (kJ K^{-1})	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028
$-\Delta_c U^{\ominus}(T_{p\text{-}CH_3}PP)$ (kJ g^{-1}) [a]	36.9519	36.9171	36.9492	36.9316	36.9361	36.9415	36.9349	36.9322

[a] Mean $\Delta_c U^{\ominus}(T_{p\text{-}CH_3}PP) = -36.9368 \pm 0.0120$ kJ g^{-1}.

TABLE 4

Results for the combustion calorimetry of $T_{p\text{-OCH}_3}PP$ at 298.15 K

	Run					
	1	2	3	4	5	6
$m(T_{p\text{-OCH}_3}PP)$(g)	0.383956	0.402541	0.402549	0.0400082	0.401809	0.401989
m(fuse) (g)	0.000744	0.00870	0.000855	0.000875	0.000860	0.00900
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00	10.00	10.00
$P_i(O_2)$(101325 Pa)	15.759	16.345	15.812	15.572	15.732	15.705
ΔT_c (K)	0.99985	1.04811	1.04862	1.04159	1.04597	1.04667
$\Delta U_{\text{ign.}}$ (kJ)	0.01251	0.01464	0.01443	0.01473	0.01445	0.01516
$\Delta U_{\text{dec.}}(HNO_3)$ (kJ)	0.01598	0.01712	0.01739	0.01571	0.01544	0.01592
ΔU(Washburn) (kJ)	0.01418	0.01500	0.01491	0.1479	0.01488	0.01488
ΔU(soot) (kJ)	0.00693	0.00561	0.00497	0.00429	0.00528	0.00660
ϵ^{f}(cont.) (kJ K^{-1})	0.04855	0.04875	0.04862	0.04855	0.04859	0.04859
ϵ^{sf}(calor.) (kJ K^{-1})	12.6028	12.6028	12.6028	12.6028	12.6028	12.6028
$-\Delta_c U^{\ominus}(T_{p\text{-OCH}_3}PP)$ (kJ g^{-1}) [a]	32.8520	32.8391	32.8526	32.8347	32.8352	32.8428

[a] Mean $\Delta_c U^{\ominus}(T_{p\text{-OCH}_3}PP) = -32.8427 \pm 0.0104$ kJ g^{-1}.

TABLE 5

Results for the combustion calorimetry of $T_{o\text{-}NH_2}PP$ at 298.15 K

	Run			
	1	2	3	4
m(ba) (g) [a]	0	0	0	0.016019
$m(T_{o\text{-}NH_2}PP)$ (g)	0.405415	0.398683	0.395474	0.383823
m(fuse) (g)	0.001062	0.000865	0.000585	0.000910
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00
$P_i(O_2)$ (101325 Pa)	30.652	30.253	30.572	29.800
ΔT_c (K)	1.11053	1.09099	1.08254	1.08408
$\Delta U_{ign.}$ (kJ)	0.01743	0.01424	0.00966	0.01495
$\Delta U_{dec}(HNO_3)$ (kJ)	0.03919	0.03888	0.03976	0.03925
ΔU(Washburn) (kJ)	0.01658	0.01625	0.01610	0.01619
ΔU(soot) (kJ)	0.00419	0.00525	0.00421	0.00624
ϵ^f(cont.) (kJ K^{-1})	0.05167	0.05155	0.05162	0.05143
ϵ^{sf}(calor.) (kJ K^{-1}) [b]	12.2644	12.2644	12.2644	12.2644
$-\Delta_c U^\ominus(T_{o\text{-}NH_2}PP)$ (kJ g^{-1}) [c]	33.5665	33.5416	33.5579	33.5154

[a] ba, benzoic acid.

[b] Weight of water in the can was changed.

[c] Mean $\Delta_c U^\ominus(T_{o\text{-}NH_2}PP) = -33.5453 \pm 0.0240$ kJ g^{-1}.

pounds. The oxygen pressure in the bomb was tested in order to achieve complete combustion of the samples; the best oxygen pressure was 13 atm for TPP, 15 atm for $T_{p\text{-}CH_3}PP$, 16 atm for $T_{p\text{-}OCH_3}PP$, 20 atm for TPyP and 14–16 atm for $T_{p\text{-}NO_2}PP$ (1 atm = 101325 Pa).

TABLE 6

Results for the combustion calorimetry of $T_{p\text{-}NO_2}PP$ at 298.15 K

	Run					
	1	2	3	4	5	6
$m(T_{p\text{-}NO_2}PP)$ (g)	0.368522	0.370996	0.370371	0.373998	0.371612	0.368991
m(DBP) (g) [a]	0.098657	0.099089	0.098676	0.097491	0.102981	0.105668
m(fuse) (g)	0.000839	0.000881	0.000754	0.000932	0.000778	0.000720
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00	10.00	10.00
$P_i(O_2)$ (101325 Pa)	14.51	14.08	16.86	15.10	16.27	16.16
ΔT_c (K)	1.04381	1.05065	1.04834	1.05214	1.06155	1.06252
$\Delta U_{ign.}$ (kJ)	0.01485	0.01564	0.01348	0.01462	0.01561	0.01282
$\Delta U_{dec.}(HNO_3)$ (kJ)	0.01983	0.01692	0.02071	0.01257	0.01870	0.02062
ΔU(Washburn) (kJ)	0.01509	0.01512	0.01561	0.01542	0.01571	0.01567
ϵ^f(cont.) (kJ K^{-1})	0.04788	0.04777	0.04847	0.04801	0.04833	0.04832
ϵ^{sf}(calor.) (kJ K^{-1}) [b]	12.5823	12.5823	12.5823	12.5823	12.5823	12.5823
$-\Delta_c U^\ominus(T_{p\text{-}NO_2}PP)$ (kJ g^{-1}) [c]	27.3994	27.4190	27.4170	27.3950	27.4170	27.4232

[a] DBP, dibutyl phthalate.

[b] Weight of water in can was different from Tables 2–5.

[c] Mean $\Delta_c U^\ominus(T_{p\text{-}NO_2}PP) = -27.412 \pm 0.012$ kJ g^{-1}.

TABLE 7

Results for the combustion calorimetry of TPyP at 298.15 K

	Run						
	1	2	3	4	5	6	7
$m(\mathrm{TP_yP})$ (g)	0.347668	0.350723	0.351040	0.347949	0.344700	0.344574	0.343235
$m(\mathrm{ba})$ (g) [a]	0.081983	0.071467	0.069775	0.072496	0.076072	0.075860	0.075867
$m(\mathrm{fuse})$ (g)	0.001018	0.000960	0.001169	0.00898	0.000891	0.000992	0.001055
$m(H_2O)$ (g)	10.00	10.00	10.00	10.00	10.00	10.00	10.00
$P_i(O_2)$ (101325 Pa)	19.310	19.284	19.977	17.310	19.737	20.750	19.177
ΔT_c (K)	1.07587	1.06214	1.05935	1.05729	1.05598	1.05601	1.05261
$\Delta U_{\mathrm{ign.}}$ (kJ)	0.01708	0.01603	0.01956	0.01603	0.01488	0.01661	0.01770
$\Delta U_{\mathrm{dec.}}(\mathrm{HNO_3})$ (kJ)	0.01114	0.01414	0.01148	0.01845	0.02091	0.02282	0.02042
ΔU(Washburn) (kJ)	0.01649	0.01619	0.01629	0.01573	0.01611	0.01625	0.01596
ΔU(soot) (kJ)	0.00191	0.00139	0.00815	0.00766	0.00881	0.00322	0.00700
ϵ^{f}(cont.) (kJ K^{-1})	0.04898	0.04896	0.04912	0.04849	0.04910	0.04935	0.04895
ϵ^{sf}(calor.) (kJ K^{-1})	12.5823	12.5823	12.5823	12.5823	12.5823	12.5823	12.5823
$-\Delta_c U^{-}$(TPyP) (kJ g^{-1}) [b]	32.7326	32.7408	32.7552	32.7532	32.7620	32.7429	32.7596

[a] ba, benzoic acid.

[b] Mean $\Delta_c U^{\ominus}(\mathrm{TPyP}) = -32.749 \pm 0.011$ kJ g^{-1}.

TABLE 8

Results for the combustion calorimetry of $T_{p\text{-Br}}PP$ at 298.15 K

	Run					
	1	2	3	4	5	6
$m(T_{p\text{-Br}}PP)$ (g)	0.285228	0.283386	0.280473	0.290422	0.260158	0.275644
$m(\text{Auxi.})$ (g) [a]	0.214965	0.214045	0.213584	0.216144	0.235992	0.238953
$m(\text{fuse})$ (g)	0.001050	0.001110	0.001301	0.001212	0.000969	0.001281
ΔT_c (K)	0.90742	0.90432	0.89826	0.91731	0.93043	0.95786
$\Delta U_{\text{ign.}}$ (kJ)	0.01885	0.01996	0.02338	0.02181	0.01742	0.02306
$\Delta U_{\text{dec.}}(HNO_3)$ (kJ)	0.00068	0.00149	0.00173	0.00093	0.00065	0.00143
$-\Delta U(HBr)$ (kJ)	0.02687	0.02670	0.02642	0.02737	0.02450	0.02596
$\Delta U(As_2O_5)$ (kJ)	0.07935	0.10445	0.07742	0.08224	0.11062	0.10930
$\Delta U(\text{Auxi.})$ (kJ)	10.04766	10.00464	9.98307	10.10275	11.03047	11.16887
$\Delta U(\text{Washburn})$ (kJ)	0.05232	0.05199	0.05171	0.05292	0.05259	0.05438
$\epsilon^f(\text{cont.})$ (kJ K^{-1})	0.13336	0.13339	0.13333	0.13346	0.13357	0.13366
$-\Delta_c U^\ominus(T_{p\text{-Br}}PP)$ (kJ g^{-1}) [b]	23.4042	23.4052	23.4099	23.4025	23.3929	23.4082

[a] Auxi., squalane.

[b] Mean $\Delta_c U^\ominus(T_{p\text{-Br}}PP) = -23.4038 \pm 0.0121$ kJ g^{-1}.

When $T_{p\text{-}NO_2}PP$ was burned, dibutyl phthalate was used for delaying combustion. Its combustion energy was measured in the same static bomb calorimeter and yielded $\Delta_c U^\ominus$ (1, 298.15 K) $= -30.778 \pm 0.015$ kJ g^{-1}, in good agreement with ref. 3.

The weight loss of dibutyl phthalate under combustion conditions was tested before the combustion experiment was undertaken. A sample of known mass was put into the crucible and equilibrated for 2 h; there was no detectable mass change as chemical interaction between dibutyl phthalate and $T_{p\text{-}NO_2}PP$ is not believed to occur. Therefore, liquid dibutyl phthalate was dropped directly onto a sample pellet placed in the crucible.

Squalane was used as combustion agent for $T_{p\text{-Br}}PP$, its standard enthalpy of combustion being -19801.3 ± 4.9 kJ mol^{-1}.

In the experiment with the bromine compound, arsenous oxide solution was used to reduce free bromine formed during the combustion reaction to bromide ion. The test for free bromine was negative with levels of H_2PtBr less than 10^{-6} g. A suitable oxygen pressure for combustion of $T_{p\text{-Br}}PP$ is 30 atm.

The samples weights were corrected to their weights in a vacuum.

The static bomb was initially charged with 10.00 g water. In the moving bomb experiment, 30 cm^3 of 0.0547 mol L^{-1} and 0.1176 mol L^{-1} arsenous oxide solution, respectively, were placed in the bomb for the combustion of *p*-bromobenzoic acid and $T_{p\text{-Br}}PP$.

The Washburn correction to reduce the heat of combustion in the bomb process to the standard heat of combustion was evaluated for those com-

TABLE 9

Standard enthalpies of combustion and formation of porphyrin compounds (s, 298.15 K)

Compounds	$-\Delta_c H^\ominus$ (kJ mol^{-1})	$\Delta_f H^\ominus$ (kJ mol^{-1})
TPP	22223.2 ± 6.3	621.3 ± 8.5
$T_{p\text{-}CH_3}PP$	24797.8 ± 8.1	478.6 ± 10.3
$T_{p\text{-}OCH_3}PP$	24148.2 ± 7.6	−171.1 ± 9.7
$T_{o\text{-}NH_2}PP$	22647.7 ± 16.2	474.2 ± 17.2
$T_{p\text{-}NO_2}PP$	21781.4 ± 9.5	751.0 ± 11.0
TPyP	20268.0 ± 6.8	811.8 ± 8.6
$T_{p\text{-}Br}PP$	21784.4 ± 11.2	754.2 ± 12.6

pounds containing carbon, hydrogen, oxygen and nitrogen, as described in ref. 4, but for the halogenated compounds the correction was performed by the method described in ref. 5.

By combining the standard enthalpies of combustion of the porphyrin compounds with the enthalpies of formation for $CO_2(g)$ (-393.51 ± 0.13 kJ mol^{-1} and $H_2O(l)$(-285.830 ± 0.042 kJ mol^{-1}) [6], the enthalpies of formation of the compounds of interest were calculated and are given in Table 9.

The uncertainties are "uncertainty intervals" defined as twice the final overall standard deviation of the mean.

DISCUSSION

The standard enthalpies of combustion and vaporization of the compounds of several *meso*-substituting groups in porphyrin compounds are given in Table 10.

The "group enthalpies" in porphyrin compounds and benzene compounds were calculated from the heats of combustion in Tables 9 and 10 and are given in Table 11.

Apart from the $-CH_3$ group, the absolute values of all "group enthalpies" of benzene compounds are larger than those of the porphyrin compounds as

TABLE 10

Standard enthalpies of combustion and vaporization of benzene compounds (l, 298.15 K)

Compounds	$-\Delta_c H^\ominus$ (kJ mol^{-1})	$\Delta_{vap} H^\ominus$ (kJ mol^{-1})	Ref.
C_6H_6	3267.6	33.85	7
$C_6H_5CH_3$	3910.2	37.90	7
$C_6H_5OCH_3$	3778.9	46.78	7
$C_6H_5NH_2$	3393.0	55.77	7
$C_6H_5NO_2$	3092.0	50.91	8
C_6H_5Br	3136.3	43.80	7

TABLE 11

"Group enthalpies" in porphyrin and benzene compounds

Groups	$\Delta H^{\ominus}$ [a] (kJ mol^{-1})	$\Delta H^{\ominus}$ [b] (kJ mol^{-1})	$\Delta(\Delta H^{\ominus})$ (kJ mol^{-1})
4($-CH_3$)	2574.6	2568.8	−5.3
4($-OCH_3$)	1925.0	1968.4	43.4
4($-NH_2$)	424.5	514.0	89.5
4($-NO_2$)	−441.8	−702.8	−261.0
4(−Br)	−438.8	−525.6	−86.8

[a] Group enthalpies in porphyrin compounds.

[b] Group enthalpies in benzene compounds.

can be seen from Table 11. The differences of both absolute values are largest for $-NO_2$ and smallest for $-CH_3$, which may possibly relate to the ability of the groups to attract electrons.

Assuming that the bond energy of the individual chemical bonds in the porphyrin compounds is equal to that of the corresponding bonds in porphin and benzene derivatives (though clearly this is not the case) in terms of suitable combinations of heats of combustion, we have $\Delta_c H^{\ominus}$(porphyrin compds.) $= \Delta_c H^{\ominus}$(porphin) $+ 4\Delta_c H^{\ominus}$(benzene compds.)

$$-4\Delta_f H^{\ominus}(\mathrm{H_2O, l}) + \Delta_{\mathrm{sub}} H^{\ominus}(\text{porphyrin compds.}) - \Delta_{\mathrm{sub}} H^{\ominus}(\text{porphin})$$
$$-4\Delta_{\mathrm{vap}}\, H^{\ominus}(\text{benzene compds.}) + 4\big[D(\mathrm{C_{ph'}}{-}{-}{-}\mathrm{C_{b'}}) - D(\mathrm{C_{ph}}{-}{-}{-}\mathrm{H})$$
$$-D(\mathrm{C_b}{-}{-}{-}\mathrm{H}) + D(\mathrm{H}{-}{-}{-}\mathrm{H})\big] \qquad (1)$$

where $D(\mathrm{C_{ph'}}{-}{-}{-}\mathrm{C_{b'}}$ are the bond energies of the bonds formed between the carbon of the porphin ring and the carbon on the benzene ring in porphyrin compounds and are taken as 331 kJ mol^{-1}, $D(\mathrm{H}{-}{-}{-}\mathrm{H}) = 436$ kJ mol^{-1} and $D(\mathrm{C_b}{-}{-}{-}\mathrm{H}) = 461$ kJ mol^{-1} [8]. Because the conjugated structure in the porphin ring is similar to that in benzene, we have assumed the following approximate values: $D(\mathrm{C_{ph}}{-}{-}{-}\mathrm{H})$ (porphin) 461 kJ mol^{-1}; $\Delta_c H^{\ominus}(\text{porphin}) = -8764.14 \pm 11.8$ kJ mol^{-1} and $\Delta_{\mathrm{sub}} H^{\ominus}(\text{porphin}) = 108.8$ kJ mol^{-1} [9].

Inserting the above data in eqn. (1), the heats of sublimation of the porphyrin compounds can be calculated as follows: $\Delta_{\mathrm{sub}} H(\mathrm{TPP}) = -667$ kJ mol^{-1}, $\Delta_{\mathrm{sub}} H(\mathrm{T_{\mathit{p}\text{-}CH_3}PP}) = -657$ kJ mol^{-1}, $\Delta_{\mathrm{sub}} H(\mathrm{T_{\mathit{p}\text{-}OCH_3}PP}) = -572$ kJ mol^{-1}, $\Delta_{\mathrm{sub}} H(\mathrm{T_{\mathit{o}-NH_2}PP}) = -490$ kJ mol^{-1}, $\Delta_{\mathrm{sub}} H(\mathrm{T_{\mathit{p}\text{-}NO_2}PP}) = -860$ kJ mol^{-1} and $\Delta_{\mathrm{sub}} \mathrm{H}(\mathrm{T_{\mathit{p}\text{-}Br}PP}) = -711$ kJ mol^{-1}.

The negative values indicate that the above assumption that the bond energy values are equal is contrary to endothermal law during the sublimation process of the substance. However, in terms of this incorrect assumption, we can also roughly evaluate the extent of the difference in the bond energies between the porphyrin compounds and the porphin plus benzene compounds. Assuming that the enthalpies of sublimation of the porphyrin compounds can be approximately considered to approach to within 108.8 kJ mol^{-1} of the heat of sublimation of porphin, the total difference in bond energies between the individual porphyrin compounds and porphin plus corresponding benzene compound is at least larger than 776 kJ mol^{-1} (TPP), 766 kJ mol^{-1}($T_{p\text{-}CH_3}PP$), 681 kJ mol^{-1}($T_{p\text{-}OCH_3}PP$), 599 kJ mol^{-1}($T_{o\text{-}NH_2}PP$), 969 kJ mol^{-1}($T_{p\text{-}NO_2}PP$) and 816 kJ mol^{-1}($T_{p\text{-}Br}PP$).

Because it is not easy to experimentally measure the heats of sublimation of porphyrin compounds which have a large ring structure, the bond energy of these compounds can be approximated from the enthalpy of formation of the gaseous substance.

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