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Thermochimica Acta 375 (2001) 85–91

thermochimica acta

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Thermochemical properties of crown ether compounds

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Received 15 November 2000; received in revised form 15 March 2001; accepted 16 March 2001

Abstract

The constant-volume combustion energies have been determined for three kinds of crown ether (CE) using a precision rotating-bomb calorimeter (RBC). The standard enthalpies of combustion, $\Delta_c^{CE}H^{\theta}$, and standard enthalpies of formation, $\Delta_f^{CE}H^{\theta}$, have been calculated for these CE. Two empirical formulas have been proposed about the standard combustion enthalpies of aromatic CE.

Keywords: Benzo-15-crown-5; Di-benzo-18-crown-*b*; Di-benzo-24-crown-8; Standard enthalpy of formation; Empirical formula

1. Introduction

The use of crown ethers (CE) and related macrocyclic and macropolycyclic molecules as a class of complexing agents has been investigated extensively during the past 20 years [1–4]. This class of complexing agents has exhibited potential significance not only in co-ordination chemistry but also in biological systems, particularly with respect to ion transport and antibiotics, as well as in organic synthesis and catalysis. However, CE and complexes of CE with rare-earths have rarely been investigated by thermo-chemical methods. Thus, there are few thermo-chemical data available in the literature concerning CE and theirs complexes with rare-earths.

In this paper, as part of a systematic investigation on the thermo-chemical properties of the CE and theirs complexes with rare-earths, combustion energies have been determined for several CE using a rotating-bomb calorimeter (RBC). The standard enthalpies of combustion, $\Delta_c^{CE}H^{\theta}$, and standard enthalpies of formation$\Delta_f^{CE}H^{\theta}$, have been calculated for these CE. Two empirical formulas have been proposed about the standard combustion enthalpies of aromatic CE.

2. Experimental

2.1. Reagents

All three CE: benzo-15-crown-5, di-benzo-18-crown-6 and di-benzo-24-crown-8, which were obtained from Tuo jiang chemical plant, are chromatographic purity, which were checked by HPLC, and the purity of three crown ethers is greater than 99.9%. The IR and NMR spectra of three CE samples show the absence of any impurities in these CE samples. Hereafter, the above crown ethers are named B15C5, DB18C6 and DB24C8, respectively.

2.2. Apparatus and experimental procedure

The constant-volume combustion energy for a compound is determined using the precision RBC-type 1

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0040-6031/01/$ – see front matter
PII: S0040-6031(01)00513-5

[5], and the basic experimental procedure used in this investigation is described as follows:

- Regulate the room temperature to 25 ± 1°C.
- Control the constant-temperature water bath of outer casing of the rotating-bomb to 25.0000± 0.0005°C.
- Adjust the water temperature in the caloritube lower than that of the water bath of outer casing and make sure that the range of the temperature is equal to half the total temperature rise of the calorimeter or so.
- Add the known amount of pure water to the caloritube.
- Lay the sample into the crucible which is fixed on the support in the rotating-bomb and does not drop into the solution.
- Fix the combustion wire in the bomb and inject the initial bomb-solution into the rotating-bomb.
- Fill of 2533.125 kPa oxygen after sealing the bomb.
- Set up the calorimeter well. Begin the experiment and keep up a constant-rate of temperature change for the calorimeter.
- In the experimental initial stage, read once the temperature every 30 s; record 10 readings. After the eleventh reading begin heating.
- Record the temperature every 1 min up to the constant-rate of temperature change. This marks the main period of combustion reaction.
- Later, read the temperature every 30 s; record 10 readings at the later stage of the experiment. After the experiment is over, analyse the final products of the combustion reaction.

2.2.1. Calibration of the energy equivalent for the calorimeter

The calorimetric system was calibrated by benzoic acid of purity 99.999%. Benzoic acid has an isothermal heat of combustion at 25°C of −26476.0± 3.6 J g^{-1}. The accuracy is ±0.0136%. The energy equivalent of RBC-type 1 calorimeter was calculated according to the equation

$$W = \frac{Qa + Gb + 5.983c}{\Delta T} \quad (1)$$

where W is the energy equivalent of the RBC-type 1 calorimeter (in J K^{-1}), Q the combustion enthalpy of benzoic acid (in g), a the mass determined benzoic acid (in J g^{-1}), G the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm^{-1}), b the length of actual Ni–Cr wire consumed (in cm), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^3 of 0.1000 mol dm^{-3} solution of NaOH (in J cm^{-3}), c the volume (in cm^3) of consumed 0.1000 mol dm^{-3} solution of NaOH, and ΔT the correct value of the temperature rise. The average energy equivalent of RBC-type 1 calorimeter, W (obtained from nine runs) is equal to 17.9487 ± 0.00884 kJ K^{-1}. The accuracy is 0.0491%.The expression method of data is

$$x = \overline{x} \pm 2\sigma_a, \qquad \sigma_a = \sqrt{\frac{\sum_i (x_i - \overline{x})^2}{n(n-1)}}.$$

2.2.2. Correction of the heat exchange

The correct value of the heat exchange was calculated by the equation [6]

$$\Delta(\Delta T) = nV_0 + \frac{V_n - V_0}{\overline{T}_n - \overline{T}_0}\left(\frac{T_0 + T_n}{2} + \sum_{i=1}^{n-1} T_i - n\overline{T}_0\right) \quad (2)$$

where $\Delta(\Delta T)$ denotes the correct value of the heat exchange, n is the number of readings for the main (or reaction) period, V_0 and V_n are the rate of temperature change at the initial and final stage, respectively (V is positive when temperature decreases), $\overline{T}_0$, $\overline{T}_n$ the average temperatures of the calorimeter at the initial and final stages, respectively (average temperature for first and last reading), T_0 is the last reading of the initial stage, T_n the first reading of the final stage. $\sum_{i=1}^{n-1} T_i$ is the sum of all the readings except the last one of the main period. $(V_n - V_0)/(\overline{T}_n - \overline{T}_0)$ must be constant.

2.2.3. Analysis of final gas products

The gases formed in the combustion reaction were collected in a gas-collecting bag. The amounts of gas were measured by a gas meter, which was joined between the bag and the instrument of gas determination.

2.2.3.1. The analytical principle and technique of carbon dioxide. The gaseous CO_2 formed in the combustion reaction was absorbed by a weighted absorption pipe with alkali asbestos. The amount of CO_2 can be determined through the weight increment

of the pipe after sucked up carbon dioxide. The amount of CO_2 dissolved in the final acidic solution was ignored.

Each measurement had four absorption pipes connected with each other. The first one was filled with P_4O_{10} and $CaCl_2$ (anhydrous) to absorb the water vapour in gases; the second one was filled with active MnO_2 in order to absorb the nitrogen oxides; the third one was filled with alkali asbestos to absorb the CO_2 for evaluation; the fourth one was also filled with P_4O_{10} and $CaCl_2$ to absorb the water formed in the process of determination.

2.2.3.2. The analytical principle and technique of nitrogen oxides (NO_x). Azo dye forms when the NO_2 is absorbed by the absorption solution in the first flask. The NO does not react with the absorption solution but becomes NO_2 when it passes through an oxide pipe. The formed NO_2 is absorbed by the absorption solution in the second flask. The amount of NO_2 and NO can be got by determination of the absorbency at wavelength between 540 and 545 nm (Saltzman calorimetric analysis method).

2.2.4. Analysis of the final solution

The fittings and inside wall of the bomb were washed using quadratic distilled water, then the bomb solution transferred completely (including the washing solution) to a cone bottle, and heated to boiling to remove CO_2. The solution after neutralisation was cooled to room temperature in a volumetric flask. The amount of HNO_3 was determined by using the Derarda's alloy method. Then, the corrected heat of nitric acid containing nitrogen was obtained based on the result.

The analytical results of the final products show that the combustion reactions was complete, neither carbon deposits or carbon monoxide was formed during the combustion reaction, the amount of NO_x in the final gas phase was insignificant.

3. Results and discussion

3.1. Thermochemical property of CE

3.1.1. Combustion energy of CE

The method of combustion energy determining for B15C5, DB18C6 and DB24C8 is the same as that for the calorimeter with benzoic acid. The sample weights were determined in vacuo. The combustion energies of the samples of B15C5, DB18C6 and DB24C8 were calculated by the following formula

$$\Delta_c^{CE(s)}E = \frac{W\,\Delta T - Gb - 5.983V}{m} \quad (3)$$

where $\Delta_c^{CE(s)}E$ (in J g^{-1}) denotes the constant-volume combustion energies of the sample of B15C5, DB18C6 and DB24C8, and m the mass (in g) of the determined sample. The other symbols are the same as in Eq. (1). The results of calculations for B15C5, DB18C6 and DB24C8 are given in Tables 1–3, respectively.

3.1.2. Standard combustion enthalpy of CE

The standard combustion enthalpy of B15C5, DB18C6 and DB24C8, $\Delta_c^{CE(s)}H^\theta$, refers to the combustion enthalpy changes of the following ideal combustion reactions at 298.15 K and 101.325 kPa,

Table 1
Combustion energy standard combustion enthalpy and standard formation enthalpy of B15C5 (in kJ mol^{-1})

Number	Mass of B15C5 (m g^{-1})	ΔT (K)	Heat of q_N (J)	Heat of q_c (J)	$-\Delta_c^{B15C5(s)}E$	$-\Delta_c^{B15C5(s)}H^{\theta}$ [a]	$-\Delta_f^{B15C5(s)}H^{\theta}$
1	1.24875	1.9876	21.74	9.90	7658.46	7664.66	702.78
2	1.04590	1.6643	12.75	12.15	7653.72	7659.92	707.52
3	0.98260	1.5618	9.60	11.70	7648.71	7654.91	712.53
4	1.05485	1.6774	13.15	12.15	7648.48	7654.68	712.76
5	1.15370	1.8339	13.50	12.15	7649.17	7655.37	712.07
6	1.04235	1.6585	14.59	8.10	7656.68	7662.88	704.56
Average					7652.54 ± 3.58	7658.74 ± 3.58	708.70 ± 3.58

[a] Accuracy ± 0.0468%.

Table 2
Combustion energy, standard combustion enthalpy and standard formation enthalpy of DB18C6 (in kJ mol^{-1})

Number	Mass of DB18C6 (m g^{-1})	ΔT (K)	Heat of q_N (J)	Heat of q_c (J)	$-\Delta_c^{DB18C6(s)}E$	$-\Delta_c^{DB18C6(s)}H^{\theta}$ [a]	$-\Delta_f^{DB18C6(s)}H^{\theta}$
1	0.92480	1.4898	9.50	8.10	10414.16	10421.60	878.56
2	1.00425	1.6188	13.45	12.15	10418.34	10425.78	874.38
3	1.03160	1.6612	14.46	12.15	10408.00	10415.44	884.72
4	1.00035	1.6123	13.40	11.70	10417.10	10424.54	875.62
5	0.89930	1.4491	11.47	12.15	10414.27	10421.71	878.45
6	1.10055	1.7716	12.50	12.15	10405.33	10412.77	887.39
Average					10412.87 ± 4.18	10420.32 ± 4.18	879.85 ± 4.18

[a] Accuracy ± 0.0401%.

respectively.

$$C_{14}H_{20}O_5\ (s) + \tfrac{33}{2}O_2\,(g) \rightarrow 14CO_2\,(g) + 10H_2O\,(\ell) \quad (4)$$

$$C_{20}H_{24}O_6\,(s) + 23O_2\,(g) \rightarrow 20CO_2\,(g) + 12H_2O(\ell) \quad (5)$$

$$C_{24}H_{32}O_8\,(s) + 28O_2\,(g) \rightarrow 24CO_2\,(g) + 16H_2O\,(\ell) \quad (6)$$

The standard combustion enthalpies of the B15C5, DB18C6 and DB24C8 was calculated from the combustion energies by the equation

$$\Delta_c^{CE(s)}H^{\theta} = \Delta_c^{CE(s)}E + \Delta n\,RT \quad (7)$$

The results of the calculations for B15C5, DB18C6 and DB24C8 are also given in Tables 1–3, respectively.

3.1.3. Standard formation enthalpy of CE

The standard formation enthalpy of CE was calculated by Hess's law according to the following thermochemical equations

$$\Delta_f^{B15C5(s)}H^{\theta} = 14\Delta_f^{CO_2(g)}H^{\theta} + 10\Delta_f^{H_2O(\ell)}H^{\theta} - \Delta_c^{B15C5(s)}H^{\theta} \quad (8)$$

$$\Delta_f^{DB18C6(s)}H^{\theta} = 20\Delta_f^{CO_2(g)}H^{\theta} + 12\Delta_f^{H_2O(\ell)}H^{\theta} - \Delta_c^{DB18C6(s)}H^{\theta} \quad (9)$$

$$\Delta_f^{DB24C8(s)}H^{\theta} = 24\Delta_f^{CO_2(g)}H^{\theta} + 16\Delta_f^{H_2O(\ell)}H^{\theta} - \Delta_c^{DB24C8(s)}H^{\theta} \quad (10)$$

The results of the calculations are also given in Tables 1–3, respectively.

According to [7], the final uncertainty of the obtained average value for crown ethers is composed of three parts, the final uncertainty of the obtained average value for B15C5 should be $[(0.0468)^2+$

Table 3
Combustion energy, standard combustion enthalpy and standard formation enthalpy of DB24C8 (in kJ mol^{-1})

Number	Mass of DB24C8 (m g^{-1})	ΔT (K)	Heat of q_N (J)	Heat of q_c (J)	$-\Delta_c^{DB24C8(s)}E$	$-\Delta_c^{DB24C8(s)}H^{\theta}$ [a]	$-\Delta_f^{DB24C8(s)}H^{\theta}$
1	1.05645	1.6823	13.73	12.15	12808.17	12818.09	1199.43
2	1.00470	1.5983	13.16	12.15	12795.06	12804.98	1212.54
3	1.08155	1.7222	14.35	9.90	12808.23	12818.15	1199.37
4	1.10030	1.7499	14.30	10.08	12792.93	12802.85	1214.67
5	0.97650	1.5529	12.70	12.15	12790.54	12800.46	1217.06
6	0.86975	1.3837	11.70	12.15	12795.06	12804.98	1212.54
Average					12798.33 ± 6.28	12808.25 ± 6.28	1209.27 ± 6.28

[a] Accuracy ± 0.0490%.

$(0.0491)^2 + (0.0136)^2]^{1/2} = \pm 0.069\%$; the one for DB18C6, $\pm[(0.0401)^2 + (0.0491)^2 + (0.0136)^2]^{1/2} = \pm 0.065\%$; the one for DB24C8, $\pm[(0.0490)^2 + (0.0491)^2 + (0.0136)^2]^{1/2} = \pm 0.071\%$.

3.2. Thermochemical properties of crown ethers $C_nH_{2n}O_{n/2}$

The $C_nH_{2n}O_{n/2}$ denotes 12-crown-4 ($n = 8$), 15-crown-5 ($n = 10$), 18-crown-6 ($n = 12$) and 24-crown-8 ($n = 16$), etc. Hereafter, the above crown ethers are named 12C4, 15C5, 18C6 and 24C8.

3.2.1. Standard formation enthalpy of $C_nH_{2n}O_{n/2}$

The reported standard formation enthalpies, $-\Delta_f^{18C6\,(s)}H^\theta$ [8] and $-\Delta_f^{C_4H_8O_2\,(g)}H^\theta$, $-\Delta_f^{12C4\,(\ell)}H^\theta$ and $-\Delta_f^{15C5\,(\ell)}H^\theta$ [9], are 1388.7 kJ mol^{-1} and 316.5, 696.8 and 879.1 kJ mol^{-1} (Table 4), respectively. The standard formation enthalpies, $-\Delta_f^{15C5\,(\ell)}H^\theta$ and $-\Delta_f^{24C8\,(s)}H^\theta$, which were estimated using data of $\Delta_f^{B15C5\,(s)}H^\theta$, $\Delta_f^{DB24C8\,(s)}H^\theta$ and $\Delta_f^{C6H6\,(\ell)}H^\theta$ and bond enthalpy data and bond lengths of C–H and C–O(C=O) bonds [10–14], are 942.65 and 1735.84 kJ mol^{-1} (Table 4), respectively. The average standard formation enthalpies of different O–CH_2–CH_2–O units, $-\Delta_f^{O-(CH_2)_2-O}H^\theta$, for 1,4-dioxane, 12C4, 15C5, 18C6 and 24C8 were easily obtained from the above corresponding standard formation enthalpies and the number of O–$(CH_2)_2$–O units in theirs CE cycles, and theirs values are 158.2, 174.2, 188.53, 231.45 and 216.98 kJ mol^{-1} (Table 4), respectively. Fig. 1 shows the relationship of $-\Delta_f^{O-(CH_2)_2-O}H^\theta$ with the numbers of O–CH_2–CH_2–O units in the CE cycles.

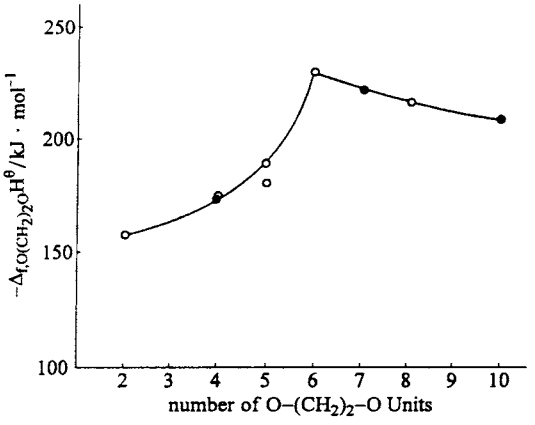

Fig. 1. $-\Delta_f^{O-(CH_2)_2-O}H^\theta$ values against the number of O–CH_2–CH_2–O units atom in crown ether cycle.

The average standard formation enthalpies of O–CH_2–CH_2–O unit, $-\Delta_f^{O-(CH_2)_2-O}H^\theta$, for 12C4, 21C7 and 30C10 can also be estimated using interpolation and extrapolation according to the above curve, so than, the obtained standard formation enthalpies of 12C4, 21C7 and 30C10 are 696.0, 1561.0 and 2095.0 kJ mol^{-1}.

3.2.2. Standard combustion enthalpy of $C_nH_{2n}O_{n/2}$

The standard combustion enthalpy of $C_nH_{2n}O_{n/2}$, $\Delta_c^{C_nH_{2n}O_{n/2}}H^\theta$, refers to the combustion enthalpy change of the following combustion reaction at 298.15 K and 101.325 kPa:

$$C_nH_{2n}O_{n/2}\,(s) + \frac{5n}{4}O_2\,(g) \rightarrow nCO_2\,(g) + nH_2O \quad (11)$$

Table 4
Standard combustion enthalpy and standard formation enthalpy of crown ethers $C_nH_{2n}O_{n/2}$ (in kJ mol^{-1})

Crown ether	Composition of crown ether	$-\Delta_f^{C_4H_8O_2\,(g)}H^\theta$	$-\Delta_f^{C_nH_{2n}O_{n/2}\,(s)}H^\theta$	$-\Delta_c^{C_nH_{2n}O_{n/2}\,(s)}H^\theta$
12C4	$C_8H_{16}O_4$	174.2	696.8[a]	4737.9[a]
15C5	$C_{10}H_{20}O_5$	188.53	942.65[a]	5850.8[a]
18C6	$C_{12}H_{24}O_6$	231.45	1388.7	6705.3
21C7	$C_{14}H_{28}O_7$	223.0	1561.0	7949.8
24C8	$C_{16}H_{32}O_8$	216.98	1735.84	9133.6
30C10	$C_{20}H_{40}O_{10}$	209.5	2095.0	11491.8
Dioxane	$C_4H_8O_2$	158.2	316.5[b]	2400.9[b]

[a] $-\Delta_f^{C_nH_{2n}O_{n/2}\,(\ell)}H^\theta$, $-\Delta_c^{C_nH_{2n}O_{n/2}\,(\ell)}H^\theta$.
[b] $-\Delta_f^{C_4H_8O_2\,(g)}H^\theta$, $-\Delta_c^{C_4H_8O_2\,(g)}H^\theta$

for example,

$$C_{10}H_{20}O_5\,(\ell) + \frac{25}{2}O_2\,(g) \rightarrow 10CO_2\,(g) + 10H_2O\,(\ell)$$

$$C_{16}H_{32}O_8\,(s) + 20O_2\,(g) \rightarrow 16CO_2\,(g) + 16H_2O\,(\ell)$$

The standard combustion enthalpy of $C_nH_{2n}O_{n/2}$ was calculated by Hess's law according to the thermochemical equation

$$\Delta_c^{C_nH_{2n}O_{n/2}\,(s)}H^\theta = n\Delta_f^{CO_2\,(g)}H^\theta + n\Delta_f^{H_2O\,(\ell)}H^\theta - \Delta_c^{C_nH_{2n}O_{n/2}\,(s)} \quad (12)$$

The results of the calculations are also given in Table 4.

3.3. Thermochemical properties of aromatic CE

3.3.1. Standard combustion enthalpy of aromatic CE

Two empirical formulas for standard combustion enthalpies of aromatic CE have been proposed as follows:

$$\Delta_c^{DBCE\,(s)}H^\theta = 2\Delta_c^{C_6H_6\,(\ell)}H^\theta + \frac{n-4}{n}\Delta_c^{C_nH_{2n}O_{n/2}}H^\theta - 2\Delta_C^{H_2\,(g)}H^\theta \quad (13)$$

$$\Delta_c^{BCE\,(s)}H^\theta = 2\Delta_c^{C_6H_6\,(\ell)}H^\theta + \frac{n-2}{n}\Delta_c^{C_nH_{2n}O_{n/2}}H^\theta - \Delta_C^{H_2\,(g)}H^\theta \quad (14)$$

where in Eqs. (13) and (14) DBCE denotes di-benzo-CE, $\Delta_c^{C_6H_6\,(\ell)}H^\theta = -3265$ kJ mol^{-1}, $\Delta_c^{H_2\,(g)}H^\theta = -285.83$ kJ mol^{-1}, BCE denotes benzo-CE.

The standard combustion enthalpies of di-benzo-*p*-crown-*q* ($p = 12$, 18, 21, 24, 30; $q = 4$, 6, 7, 8, 10) $\Delta_c^{DBCE\,(s)}H^\theta$, were calculated using Eq. (13), and the results of the calculations are given in Table 5. The standard combustion enthalpies of benzo-*s*-crown-*t* ($s = 12$, 15, 18; $t = 4$, 5, 6), $\Delta_c^{BCE\,(s)}H^\theta$, were calculated using the Eq. (14), and the results of the calculations are also given in Table 5, for example,

$$\Delta_c^{DB24C8\,(s)}H^\theta = 2\Delta_c^{C_6H_6\,(\ell)}H^\theta + \frac{16-4}{16}\Delta_c^{C_{16}H_{32}O_8\,(s)}H^\theta - 2\Delta_c^{H_2\,(g)}H^\theta$$

$$= 2(-3265) + \frac{3}{4}(-9133.6) - 2(-285.83)$$

$$= -12808.7\ \text{kJ mol}^{-1}$$

$$\Delta_c^{B15C5\,(s)}H^\theta = \Delta_c^{C_6H_6\,(\ell)}H^\theta + \frac{10-2}{10}\Delta_c^{C_{10}H_{20}O_5\,(\ell)}H^\theta - \Delta_c^{H_2\,(g)}H^\theta$$

$$= -3265 - \frac{4}{5}(5850.8) + 285.83$$

$$= -7659.8\ \text{kJ mol}^{-1}$$

3.3.2. Standard formation enthalpy of aromatic CE

The standard formation enthalpies of di-benzo-*p*-crown-*q* $p = 12, 18, 21, 24, 30$; $q = 4, 6, 7, 8, 10$) were calculated by Hess's law according to the thermochemical equation

$$\Delta_f^{DBCE\,(s)}H^\theta = (p-q+8)\Delta_f^{CO_2\ \ (g)}H^\theta + (p-q)\Delta_f^{H_2O\,(\ell)}H^\theta - \Delta_c^{DBCE\,(s)}H^\theta \quad (15)$$

The results of the calculations are also given in Table 5.

The standard formation enthalpies of benzo-*s*-crown-*t* ($s = 12$, 15, 18; $t = 4$, 5, 6), $\Delta_f^{DBCE\,(s)}H^\theta$, were calculated by Hess's law according to the thermo-chemical equation

$$\Delta_f^{BCE\,(s)}H^\theta = (s-t+4)\Delta_f^{CO_2\,(g)}H^\theta - (s-t)\Delta_f^{H_2O\,(\ell)}H^\theta - \Delta_c^{BCE\,(s)}H^\theta \quad (16)$$

The results of the calculations are also given in Table 5.

Table 5
standard combustion enthalpy and standard formation enthalpy of aromatic crown ethers (in kJ mol^{-1})

DBCE	$-\Delta_c^{DBCE\,(s)}H^\theta$	$-\Delta_f^{DBCE\,(s)}H^\theta-$	BCE	$-\Delta_c^{BCE\,(s)}H^\theta$	$-\Delta_f^{BCE\,(s)}H^\theta$
DB12C4	8327.3	255.5	B12C4	6532.6	476.2
DB18C6	10428.5	871.6	B15C5	7659.8	707.6
DB21C7	11635.0	1023.8	B18C6	8603.2	1122.9
DB24C8	12808.7	1208.8			
DB30C10	15216.9	1518.0			

Comparisons of the calculation and experimental results (Tables 1–3) for DB18C6, DB24C8 and B15C5 show that both the proposed formulas conform to reality.

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