Enthalpies of Formation of Some Cyclic 1,3- and 1,4-Di- and Poly-ethers: Thermochemical Strain in the –O–C–O– and –O–C–C–O– Groups

By **Katarina Byström** and **Margret Månsson,*** Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden

Enthalpies of combustion and vaporization at 298.15 K have been measured for five cyclic polyethers. Enthalpies of formation in the liquid and gaseous states have been derived:

	$-\Delta H_f°(l)$/kJ mol^{-1}	$-\Delta H_f°(g)$/kJ mol^{-1}
1,3-Dioxan	377.5 ± 1.1	338.4 ± 1.1
1,4-Dioxan	355.1 ± 0.9	316.5 ± 0.9
1,3,6-Trioxacyclo-octane	516.0 ± 1.2	467.2 ± 1.2
1,4,7,10-Tetraoxacyclododecane	696.8 ± 2.1	631.1 ± 2.1
1,4,7,10,13-Pentaoxacyclopentadecane	879.1 ± 2.0	799.5 ± 2.0

The results for cyclic 1,3- and 1,4-polyethers are discussed in terms of apparent strain energies relative to aliphatic polyethers. It is shown that there is a constant contribution to the apparent strain from each 1,3-dioxa and 1,4-dioxa unit, provided that the reference system consists of compounds which have conformations similar to those of the cyclic polyethers.

In an earlier investigation of straight-chain oxa-compounds it was established that the thermochemical stability of polyethers is strongly dependent on the relative positions of the oxygens.[1] Compared with an aliphatic monoether the 1,4-ether is strained whereas the 1,3-ethers are stabilized. The stabilization energy in the 1,3-ethers is additive, *i.e.* directly proportional to the number of next-nearest-neighbour oxygens.

The large influence upon the energy from the relative positions of the oxygens in straight-chain compounds made it desirable to extend the study to cyclic polyethers. 1,3,5-Trioxan,[2] 1,3,5,7-tetroxocan,[2] and 1,3,5,7,9-pentoxecan [3] have already been studied; the results will be included for discussion in this paper.

In this work energies of combustion and enthalpies of vaporization have been determined for 1,3-dioxan, 1,4-dioxan, 1,3,6-trioxacyclo-octane, 12-crown-4-ether (1,4,7,10-tetraoxacyclododecane), and 15-crown-5-ether (1,4,7,10,13-pentaoxacyclopentadecane). 1,4-Dioxan, 12-crown-4-ether, and 15-crown-5-ether consist of consecutive pairs of next-next-nearest-neighbour oxygens, whereas 1,3,6-trioxacyclo-octane contains both 1,3- and 1,4-dioxa units. Energies of combustion for 1,3-dioxan [4–7] and for 1,4-dioxan [6,8] have been reported; but since there are large discrepancies in the results both compounds were included in this work.

RESULTS AND DISCUSSION

The results from the different series of combustion measurements are summarized in Table 1. The $\Delta u_c°$ values refer to the idealized reaction, where all reactants and products are in their thermodynamic standard states at 298.15 K. The results from the vaporization experiments are listed in Table 2.

Table 3 gives a summary of the standard molar energies, $\Delta U_c°$, and enthalpies, $\Delta H_c°$, of combustion for the five ethers in their liquid state, together with standard enthalpies of vaporization, $\Delta H°_{vap.}$. Also included in Table 3 are derived enthalpies of formation, $\Delta H_f°$, for the liquid and gaseous states.

The results of previous determinations of the enthalpies of combustion of 1,3- and 1,4-dioxan are listed in Table 4 together with those from this investigation. Our results agree well with those of Snelson and Skinner.[6]

The apparent strain energies, [*S*], referred to in the discussion, were calculated using expression (1) where *m*

$$[S] = \Delta H_f°(\text{g, obs}) - \Delta H_f°(\text{g, ref}) - mRT \quad (1)$$

is the number of rings in the molecule.[9] The enthalpies of formation of the 'normal strain-free' reference compounds were calculated using an Allen bond energy scheme. The Allen scheme $\Delta H_f°(g)$ parameters were those recommended in ref. 10, except for Γ_{OCO} which was taken as -54.2 kJ mol^{-1}.[1]

In Table 5 total strain and strain energies per 1,3-interaction for 1,3-dioxan, trioxan, tetroxocan, and pentoxecan are listed. Compared with straight-chain 1,3-ethers all the cyclic ethers are 'strained', or rather the stabilizing effect from having two ether oxygens in 1,3-positions is reduced. For the three ethers with general formula $(CH_2O)_n$ the strain energy is directly proportional to the number of 1,3-interactions. The strain energy for 1,3-dioxan does not deviate significantly from this constant strain energy increment.

Investigations of the molecular structure in the gas phase of 1,3-dioxan,[11] trioxan,[12] and tetroxocan [13] show that the conformations of the O–C–O units in the different molecules are similar. 1,3-Dioxan and trioxan exist exclusively in a chair conformation, while the tetramer consists of a mixture of two conformers, symmetric crown and boat-chair, where the latter is the most stable in the gas phase. The preferred arrangement of the O–C–O unit in all these conformations is *gauche-gauche*. This arrangement is also found in the gas phase of dimethoxymethane.[14] Thus the comparison of destabilization per O–C–O unit seems meaningful,

TABLE 1

Results of combustion experiments at 298.15 K
[$-\Delta u_c°$/J g^{-1}]

	1,3-Dioxan	1,4-Dioxan	1,3,6-Trioxacyclo-octane	1,4,7,10-Tetraoxacyclododecane	1,4,7,10,13-Pentaoxacyclopentadecane
	26 536.9	26 781.8 [b]	24 371.1	26 849.0	26 797.0
	26 542.4	26 796.0	24 370.0	26 870.3	26 794.4
	26 514.8	26 787.0	24 362.2	26 858.1	26 805.9
	26 511.9	26 776.3	24 359.7	26 856.6	26 801.9
	26 535.1	26 775.5	24 349.0	26 836.7	
	26 520.0	26 782.2	24 363.8	26 858.8	
Mean	26 526.8		24 362.7	26 854.9	26 799.8
Corrected mean	26 529.3 [a]	26 783.1 [b]	24 364.8 [c]	26 859.7 [d]	26 807.6 [e]
Standard deviation of the corrected mean	5.2	3.1	3.8	4.6	2.9

[a] Correction applied for 0.009 mass % H_2O. [b] Correction applied for 0.023 mass % H_2O in the first three results and for 0.036 mass % H_2O in the last three results. [c] Correction applied for 0.028 mass % H_2O, 0.02 mass % tetrahydrofuran, and 0.11 mass % 1,4-dioxan. [d] Correction applied for 0.018 mass % H_2O. [e] Correction applied for 0.029 mass % H_2O and 0.27 mass % 8-chloro-3,6-dioxaoctan-1-ol.

TABLE 2

Results from vaporization experiments at 298.15 K

Compound	$\Delta H°_{vap.}$ kJ mol^{-1}	Number of expts.	pV correction [a] kJ mol^{-1}	Zero correction [b] %
1,3-Dioxan	39.09	5		0.04
1,4-Dioxan	38.64	9		0.04
1,3,6-Trioxacyclo-octane	48.77	6		1.11
1,4,7,10-Tetraoxacyclododecane	65.65	7	0.92	
1,4,7,10,13-Pentaoxacyclopentadecane	79.57	7	0.92	

[a] Defined in ref. 31. [b] Defined in ref. 29.

TABLE 3

Results and derived quantities at 298.15 K

Compound	$\Delta U_c°$/kJ mol^{-1}	$\Delta H_c°$/kJ mol^{-1}	$\Delta H_f°$(l)/kJ mol^{-1}	$\Delta H°_{vap.}$/kJ mol^{-1}	$\Delta H_f°$(g)/kJ mol^{-1}
1,3-Dioxan	$-2\,337.38 \pm 0.99$	$-2\,339.86 \pm 0.99$	-377.50 ± 1.13	39.09 ± 0.05	-338.4 ± 1.1
1,4-Dioxan	$-2\,359.75 \pm 0.66$	$-2\,362.23 \pm 0.99$	-355.13 ± 0.86	38.64 ± 0.05	-316.5 ± 0.9
1,3,6-Trioxacyclo-octane	$-2\,878.27 \pm 0.99$	$-2\,880.75 \pm 0.99$	-515.95 ± 1.20	48.77 ± 0.21	-467.2 ± 1.2
1,4,7,10-Tetraoxacyclododecane	$-4\,733.01 \pm 1.71$	$-4\,738.07 \pm 1.71$	-696.75 ± 2.05	65.65 ± 0.37	-631.1 ± 2.1
1,4,7,10,13-Pentaoxacyclopentadecane	$-5\,908.10 \pm 1.41$	$-5\,914.30 \pm 1.41$	-879.10 ± 1.96	79.57 ± 0.29	-799.5 ± 2.0

The uncertainties given are twice the final overall standard deviation of the mean.

since what one actually compares is the energy of structurally similar units.

The apparent strain energies calculated for 1,4-dioxan, 12-crown-4-ether, and 15-crown-5-ether, all with the general formula $(CH_2CH_2O)_n$ are 13.8, 32.1, and 30.0 kJ mol^{-1}, respectively. Since an Allen bond energy scheme does not account for interactions between atoms more than two bonds away, the destabilization from the O–C–C–O configurations observed in the open-chain compound is not part of the reference system. In contrast to the 1,3-ethers there does not seem to be a constant contribution to the strain per oxygen–oxygen interaction. In fact, the 12-crown-4-ether exhibits a larger destabilization than does the 15-crown-5-ether. However, the inconstancy of the 'strain increments' can, in fact, be ascribed to differences in the conformations of the structural units that constitute the rings.

TABLE 4

Literature values for the enthalpy of combustion for 1,3-dioxan and 1,4-dioxan

Compound	$-\Delta H_c°$/kJ mol^{-1}	Determination of amount of reaction	Reference
1,3-Dioxan	$2\,331.3 \pm 0.8$	m	4
	$2\,322.1 \pm 5.9$	CO_2	5
	$2\,340.82 \pm 0.59$	CO_2	6
	$2\,332.8 \pm 1.8$	m	7
	$2\,339.9 \pm 1.0$	m	This work
1,4-Dioxan	$2\,345.6 \pm 3.8$	m	8
	$2\,363.92 \pm 0.59$	CO_2	6
	$2\,362.2 \pm 1.0$	m	This work

TABLE 5

Apparent strain energies in cyclic 1,3-ethers

Compound	[S]/kJ mol^{-1}	[S] per 1,3-dioxa unit/ kJ mol^{-1}
1,3-Dioxan	+9.5	9.5
1,3,5-Trioxan	+22.3	7.4
1,3,5,7-Tetroxocan	+31.3	7.8
1,3,5,7,9-Pentoxecan	+35.3	7.1

1,4-Dioxan exists in the chair-form (C_{2h} symmetry). The conceived symmetric crown conformations of 12-crown-4- (C_4) and 15-crown-5-ether (C_5) are adopted only when the ethers form complexes with cations.[15] The uncomplexed ethers have, as a rule, unusual conformations containing pseudo-corners ($g \mp g \pm a$ units), characterized by close 1,5 CH $\cdots$ O interactions. Pseudo-corner formation is found only when solvation of the ether oxygen is excluded, as for example in the gas phase. In ref. 15 the structures shown in the Figure were proposed for the two uncomplexed crown ethers of interest to us. The suggested conformation for the 12-crown-4-ether is for the uncomplexed crystal. The structure for the 15-crown-5 refers to the uncomplexed ether in a CS_2 solution.

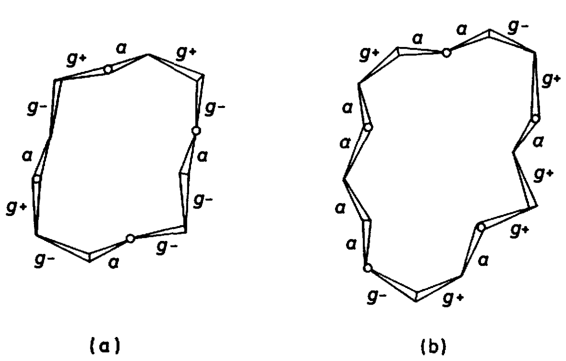

FIGURE (a) Crystal structure of 12-crown-4-ether in the uncomplexed state. (b) Conformation for uncomplexed 15-crown-5-ether in CS_2 solution

When apparent strain energy is calculated the reference is a hypothetical isomer to the actual compound with the same sequence of atoms but with all bonds *anti*. A carbon–carbon *gauche* bond will lead to steric 1,4 O $\cdots$ O interactions and an oxygen–carbon *gauche* bond will give rise to steric 1,4 CH $\cdots$ HC interactions. According to ref. 16 both types of interactions are unfavourable and an O–C–C–O configuration having any bond *gauche* will have a higher energy than the corresponding *anti* configuration, *i.e.* any *gauche* bond will result in an apparent strain. This is in agreement with the variation of the strain in the series of 1,4-ethers assuming that gas-phase conformations for the crown ethers are similar to those in the Figure. The most destabilized compound, the 12-crown-4-ether, has the largest number of *gauche* bonds.

A different choice of reference system is one consisting of hypothetical isomers not only with the same sequence of atoms but also with the same conformations of the different O–C–C–O units. The contributions to the strain from conformational differences between the actual compounds and the reference compounds will be reduced and a situation similar to that for the 1,3-ethers would be expected.

Attempts to calculate the gaseous enthalpies of formation of these hypothetical isomers were made using an Allen bond energy scheme together with the results obtained by Podo *et al.*[16] They made theoretical analyses of the conformational equilibria of 1,2-dimethoxyethane and calculated the energies of each stable rotamer. From their computations the energy for the *trans* to *gauche* transition can be estimated to be 4.6 kJ mol^{-1} for a CH_2–O bond and 0.4 kJ mol^{-1} for a CH_2–CH_2 bond. A sequence of $g \pm g \mp$ for the OCH_2CH_2 group will result in a 1,5-CH $\cdots$ O interaction. Podo's estimate for this interaction is an unfavourable energy of 1.3—2.1 kJ mol^{-1}.

Calculating the apparent strain energy for the ethers relative to this reference system gives the following results. 1,4-Dioxan has two 1,4-$CH_2 \cdots H_2C$ interactions and one 1,4-O $\cdots$ O interaction. Thus, a reference system with the same conformation will have an increased energy of 9.6 kJ mol^{-1}. Similar reasoning for the reference to the 12-crown-4-ether, with four *gauche* CH_2–O bonds, four *gauche* CH_2–CH_2 bonds, and two sequences of g^+g^- bonds, shows that it has an energy of 23.4 kJ mol^{-1} above the *trans*-form. The 15-crown-5-ether has three *gauche* CH_2–O bonds, four *gauche* CH_2–CH_2 bonds, and two pairs of g^+g^- bonds, which in terms of energy corresponds to 18.8 kJ mol^{-1}.

Table 6 gives the reduced apparent strain energy $[S_{red.}]$, together with the same quantity per 1,4-dioxa unit relative to this new reference system. As in the case of the 1,3-ethers a constant 'strain increment' is obtained, which seems reasonable since comparisons in both cases are now made between structurally similar units.

TABLE 6

Apparent strain energies for 1,4-ethers

Compound	$[S]$/kJ mol^{-1}	$[S_{red.}]$/ kJ mol^{-1}	$[S_{red.}]$ per 1,4-dioxa unit/ kJ mol^{-1}
1,4-Dioxan	13.8	4.2	2.1
12-Crown-4-ether	32.1	8.7	2.2
15-Crown-5-ether	30.0	11.2	2.2

Cyclohexane, tetrahydropyran, 1,3-dioxan, and trioxan form a series where carbons are successively replaced by ether oxygens. All four compounds exist exclusively in the chair form.[11,12,17] In Table 7 gaseous enthalpies of formation are listed together with the change in enthalpy of formation Δ, for the replacement of a methylene group by an ether oxygen. The ether increment, *i.e.* the difference in enthalpy of formation between tetrahydropyran and cyclohexane is —100.0 kJ mol^{-1}, which is 4.8 kJ mol^{-1} less negative than the open-chain increment. The apparent strain energies in the cyclic polyethers can partly be attributed to this difference in ether increment.

TABLE 7

Enthalpy of formation change for the successive replacement of CH_2 by O

Compound	$\Delta H_f°(g)$/kJ mol^{-1}	Δ/kJ mol^{-1}
Cyclohexane	−123.4	
Tetrahydropyran	−223.4	−100.0
1,3-Dioxan	−338.4	−115.0
1,3,5-Trioxan	−465.8	−127.4

Relative to the cyclic monoether both six-membered cyclic polyethers are stabilized. The stabilization energy amounts to 15.0 and 42.4 (14.1 per 1,3-interaction) kJ mol^{-1}, respectively. The stabilization energy per 1,3-interaction in an open-chain polyether is 17.6 kJ mol^{-1}, which means that the stabilizing effect is reduced by an average of 3.3 kJ mol^{-1}. Thus, there are two factors contributing to the apparent strain energy in cyclic 1,3-ethers; the stabilization from two oxygens in 1,3-position is reduced by 3.3 kJ mol^{-1} and the cyclic ether increment is 4.8 kJ mol^{-1} less negative than the aliphatic one.

The change in enthalpy of formation when a methylene group in tetrahydropyran is replaced by an ether oxygen to form 1,4-dioxan is −93.1 kJ mol^{-1}, *i.e.* 1,4-dioxan is 'strained' by 6.9 kJ mol^{-1} relative to the cyclic monoether. The apparent strain energy from having two oxygens in the 1,4-positions is thus *ca.* 3.5 kJ mol^{-1} per OCCO unit in addition to the 4.8 kJ mol^{-1} per oxygen.

1,3,6-Trioxacyclo-octane contains both OCO and OCCO units. The apparent strain energy relative the Allen bond energy scheme is 26.6 kJ mol^{-1}. The total strain can be divided into three major contributions, the strain associated with the ether increment, the reduced stabilization of the OCO unit, and the destabilization of the OCCO unit.

In ref. 18 the structure of trioxacyclo-octane was proposed to be a mixture of a crown and a boat-chair conformer. Both conformations have all bonds *gauche*, which means that each OCO and OCCO unit has a similar configuration to that in the six-membered rings. An estimate of the strain energy associated with having three oxygens, one reduced 1,3-interaction, and two 1,4-destabilizations, using the results from the six-membered rings, gives a total destabilization of 24.7 kJ mol^{-1}. This is in fair accord with the observed strain energy of 26.6 kJ mol^{-1} considering the simple model.

Molecular mechanics calculations for ethers containing more than one oxygen atom have been made,[19,20] but since no predictions are made for the compounds studied in this work, there is no possibility of comparisons of results.

EXPERIMENTAL

Compounds.—All five ethers were of commercial origin. The various samples were purified by distillation in a spinning-band column. Some of the samples were further purified by preparative g.l.c. Before distillation the ethers were tested for the presence of peroxides by mercury.[21] Removal of peroxides was made with cerium(III) hydroxide.[22] The purity was checked by g.l.c. using at least two different columns with different stationary phases. N.m.r. spectra were run on the pure samples to ascertain the identity of the sample and also to give a further proof of the absence of any impurities. Tests were performed to make sure that the drying agent used did not cause any decomposition of the samples, and these were then dried directly before filling the ampoules for the combustion experiments.[23] The water content in some of these ampoules was measured using a g.l.c. method.[24] Corrections for water content were applied if the analysis indicated more than 0.003 mass % H_2O.

1,3-*Dioxan* (I). The sample was distilled at 22.5 kPa, the main fractions boiling at 335 K. G.l.c. analysis indicated small amounts of ethanol. The sample was dried first with KOH and then with molecular sieves. During the second drying all traces of impurities disappeared. The water content was 0.009 mass %.

1,4-*Dioxan* (II). The sample was distilled at 24.3 kPa. G.l.c. analysis of the main fractions, taken at 328 K, did not show the presence of any foreign material. The sample was dried with KOH and molecular sieves. Water analysis of two different ampoules from two different filling tubes yielded 0.023 and 0.036 mass %. Thus, different corrections for water content were applied depending on which tube the ampoule was taken from.

1,3,6-*Trioxacyclo-octane* (III). The compound was distilled at 6.7 kPa and the main fractions were collected at 352 K. G.l.c. measurements indicated the presence of small amounts of two impurities. These were identified as tetrahydrofuran (0.20 mass %) and 1,4-dioxan (0.11 mass %). The water content was 0.028 mass %.

1,4,7,10-*Tetraoxacyclododecane* (12-*crown*-4-*ether*) (IV). The sample was purified by distillation at 5.3 kPa followed by preparative g.l.c. No impurities could be detected by g.l.c. The water content was 0.018 mass %.

1,4,7,10,13-*Pentaoxacyclopentadecane* (15-*crown*-5-*ether*) (V). During the distillation, performed at 3.1 kPa, the temperature difference between pot and head was *ca.* 10 K, which could indicate decomposition of the sample in the pot. The main fractions collected from the distillation contained a total of 2% of two impurities. By preparative g.l.c. one of them was removed and the other was reduced to 0.27 mass %. The remaining impurity was identified as 8-chloro-3,6-dioxaoctan-1-ol by mass spectrometry. The water content was 0.029 mass %.

Combustion Calorimetry. Apparatus and Procedure.—The rotating bomb calorimeter TKL-3 was used with the platinum-lined bombs 3C [(IV), (V)] and 3B [(I)—(III)][25] having the internal volumes 0.2620 and 0.2609 dm^3, respectively. Details of the calorimetric procedure are described in ref. 1. All combustions were carried out according to standard procedure with 0.79 cm^3 of water in the bomb and an initial pressure of oxygen of 3.04 MPa at 298.15 K. The ignition energy was measured in each experiment. Paraffin oil, designated TKL-66A,[26] was used as an auxiliary material. All experiments were designed to have a minimum of 35% of the total combustion energy from the oil, since polyethers tend to deposit soot in the glass if the amount of oil is less. Whenever the compound did not burn properly the experiment was rejected.

Calibrations were made by burning benzoic acid (National Bureau of Standards SRM 39i) under certificate conditions. A Hewlett–Packard quartz thermometer was used in its 100 s mode (resolution 10^{-5} K).

The compounds were transferred in vacuum to a receiver containing the glass ampoules for the combustion experiments. All ampoules were made out of Pyrex glass.

All weighings were reduced to masses and molar masses were calculated using the 1977 table of atomic weights.[27]

TABLE 8

Auxiliary quantities used in the calculations

Compound	ρ/g cm^{-3}	$\left(\frac{\partial v}{\partial T}\right)_p$/ mm^3 K^{-1} g^{-1}	c_p/ J K^{-1} g^{-1}
1,3-Dioxan	1.03	1.1	1.7
1,4-Dioxan	1.03	1.1	1.7
1,3,6-Trioxacyclo-octane	1.05	1.2	2.0
12-Crown-4-ether	1.10	1.0	2.0
15-Crown-5-ether	1.10	1.0	2.0

TABLE 9

Summary of typical combustion experiments. $\Delta u_c°$(oil) $-(46\ 044.3 \pm 2.0)$ J g^{-1}; $\Delta u_c°$(fuse) $-(16\ 807 \pm 4)$ J g^{-1}. The standard deviations of the mean for the calibration series were 0.6 J K^{-1} [(I)—(III)] and 0.9 J K^{-1} [(IV), (V)]

	1,3-Dioxan	1,4-Dioxan	1,3,6-Trioxacyclo-octane	1,4,7,10-Tetraoxacyclododecane	1,4,7,10,13-Pentaoxapentadecane
m'(comp)/g	0.356 730	0.368 239	0.462 830	0.512 478	0.469 894
m''(oil)/g	0.246 085	0.236 005	0.205 299	0.156 134	0.179 219
m'''(fuse)/g	0.001 145	0.001 706	0.001 307	0.001 189	0.001 256
m(Pt)/g	9.193	11.169	11.169	11.565	9.245
$\Delta\theta$/K	0.728 173	0.726 439	0.726 111	0.733 917	0.729 868
$\epsilon°$(calor)/J K^{-1}	28 672.2	28 672.1	28 672.2	28 674.0	28 673.9
m^i(cont)/g	21.00	22.98	23.05	23.48	21.13
ϵ^i(cont)/J K^{-1}	13.38	13.64	13.88	13.95	13.60
ΔU_Σ/J	7.93	7.93	8.64	8.69	8.47
$-\Delta u_c°$(comp)/J g^{-1}	26 535.1	26 796.0 [a]	24 362.2	26 858.8	26 797.0

[a] Correction for water included.

The corrected temperature rise $\Delta\theta$ and the energy equivalent $\varepsilon°$(calor) of the system were calculated as described in ref. 28.

Vaporization Calorimetry.—The enthalpies of vaporization for compounds (I)—(III) were measured using the Wadsö-type calorimeter.[29] Corrections were applied as described in ref. 29. The so-called zero-effect (caused mainly by gas expansion and friction), which varies with pressure and capillary tube for the inlet carrier gas, amounted to 1.11% in the experiments on (III), whereas for (I) and (II) it was only 0.04%. As a correction of the order of 1% is undesirably large the vaporization technique has since been modified.[30] As a test both the old and the new technique was used in determinations on some alkyl-substituted benzenes with complete agreement between the results in all cases. It was thus considered unnecessary to rerun compound (III).

The enthalpies of vaporization of the crown ethers (IV) and (V) were measured with the Morawetz-type calorimeter.[31] In these measurements the pressure–volume work is reduced and to get the enthalpy of vaporization a correction must be applied. The correction was 0.92 kJ mol^{-1} for both compounds.

Calculations.—All symbols used are those of Hubbard *et al.*[32] but with U representing internal energy. A computer program based on the procedure in ref. 32 was used to calculate the Washburn correction ΔU_Σ. Some auxiliary data used in the calculations are given in Table 8. The final overall precision of the $\Delta u_c°$ mean values was estimated as outlined by Bjellerup.[33]

Results from typical combustion experiments are listed in Table 9. Corrections for water and other impurities were applied. For 1,3,6-trioxacyclo-octane the corrections for the content of 1,4-dioxan (0.11 mass %) and tetrahydrofuran (0.02 mass %) were made using $\Delta u_c°$ equal to $-(26\ 783 \pm 3)$ J g^{-1} and $-(35\ 130 \pm 5)$ J g^{-1}, respectively. The total correction for the two impurities amounts to (4.8 ± 1.8) J g^{-1}. The correction for presence of 8-chloro-3,6-dioxaoctan-1-ol in 15-crown-5-ether was made using an estimated value for $\Delta u_c°$ equal to $-(21.20 \pm 0.12)$ kJ g^{-1}. It was assumed that during combustion 20% of the impurity reacted to form Cl_2 and the rest to form HCl. The correction amounts to $-(15.1 \pm 1.2)$ J g^{-1}. The largest contribution to the uncertainty in the correction is the uncertainty in the determination of the amount of impurity. This was estimated to be ± 0.02 mass %.

Values for the enthalpy of formation for gaseous carbon dioxide and liquid water used in the derivations of the enthalpies of formation of the compounds were taken from ref. 34.

We thank Kungl. Fysiografiska Sällskapet for financial support of this work. The assistance of G. Gräntz, who performed the vaporization experiments, is gratefully acknowledged.

[1/1391 *Received*, 4*th September*, 1981]

REFERENCES

[1] M. Månsson, *J. Chem. Thermodyn.*, 1969, **1**, 141.

[2] M. Månsson, E. Morawetz, Y. Nakase, and S. Sunner, *Acta Chem. Scand.*, 1969, **23**, 56.

[3] M. Månsson, *Acta Chem. Scand.*, 1974, **B28**, 895.

[4] S. M. Skuratov, A. A. Strepikheev, S. M. Shtekher, and A. V. Volokina, *Dokl. Akad. Nauk SSSR*, 1957, **117**, 263.

[5] S. E. Fletcher, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 1959, 580.

[6] A. Snelson and H. A. Skinner, *Trans. Faraday Soc.*, 1961, **57**, 2125.

[7] K. Pihlaja and S. Louma, *Acta Chem. Scand.*, 1968, **22**, 2401.

[8] W. A. Roth and I. Mayer, *Z. Electrochem.*, 1933, **39**, 35.

[9] B. Nelander and S. Sunner, *J. Chem. Phys.*, 1966, **44**, 2476.

[10] J. D. Cox and G. Pilcher, ' Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London, 1970, ch. 7.

[11] Gy. Schultz and I. Hargittai, *Acta Chim. Acad. Sci. Hung.*, 1974, **83**, 331.

[12] A. H. Clark and T. G. Hewitt, *J. Mol. Struct.*, 1971, **9**, 33.

[13] E. E. Astrup, *Acta Chem. Scand.*, 1980, **A34**, 85.

[14] E. E. Astrup, *Acta Chem. Scand.*, 1973, **27**, 3271.

[15] J. Dale, *Isr. J. Chem.*, 1980, **20**, 3.

[16] F. Podo, G. Némethy, P. I. Indovina, L. Radics, and V. Viti, *Mol. Phys.*, 1974, **27**, 521.

[17] H. E. Breed, G. Gundersen, and R. Seip, *Acta Chem. Scand.*, 1979, **A33**, 225.

[18] J. Dale, T. Ekeland, and J. Krane, *J. Am. Chem. Soc.*, 1972, **94**, 1389.

[19] N. L. Allinger, S. H. M. Chang, D. Hindman Glaser, and H. Hönig, *Isr. J. Chem.*, 1980, **20**, 51.

[20] M. J. Bovill, D. J. Chadwick, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1529.

[21] K. Hess and H. Frahm, *Chem. Ber.*, 1938, **71**, 2627.

[22] J. B. Ramsey and F. T. Aldridge, *J. Am. Chem. Soc.*, 1955, **77**, 2561.

[23] M. Månsson and S. Sunner, *Acta Chem. Scand.*, 1962, **16**, 1863.

[24] P. Sellers, *Acta Chem. Scand.*, 1971, **25**, 2295.

[25] M. Månsson and S. Sunner, to be published.

[26] M. Månsson, *J. Chem. Thermodyn.*, 1974, **6**, 1153.

[27] *Pure Appl. Chem.*, 1979, **51**, 405.

[28] L. Bjellerup, *Acta Chem. Scand.*, 1959, **13**, 1511.

[29] I. Wadsö, *Acta Chem. Scand.*, 1966, **20**, 536.

[30] M. Månsson, unpublished results.

[31] E. Morawetz, *Chem. Scr.*, 1971, **1**, 103.

[32] W. N. Hubbard, D. W. Scott, and G. Waddington, in Experimental Thermochemistry,' ed. F. D. Rossini, Interscience, New York, 1956, ch. 5.

[33] L. Bjellerup, *Acta Chem. Scand.*, 1961, **15**, 121.

[34] CODATA key values for thermodynamics, *J. Chem. Thermodyn.*, 1976, **8**, 603.