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Proximity effects of oxygen atoms on the enthalpies of formation of simple diethers: a computational G3(MP2)//B3 study

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The enthalpies of formation of a number of acyclic, straight-chain ethers and diethers were determined by G3(MP2)//B3 calculations. The principal aim of the work was to study the magnitude of the O…O proximity effect on the enthalpy contents of diethers as a function of the distance (number of bonds) between the O atoms. 1,4-Diethers and 1,5-diethers were computed to be destabilized by *ca.* 4.5 ($\pm$0.5) and 3.2 ($\pm$0.4) kJ mol^{-1}, respectively, by the O…O proximity effect. The effect was calculated to be negligible in diethers with the O atoms in positions more remote than 1,5 from each other, whereas 1,3-diethers (acetals) are stabilized by *ca.* 22 kJ mol^{-1}, likely on account of the anomeric effect. Calculations on simple monoethers show that the contributions to $\Delta_f H_m^\circ$ of CH$_2$ groups in the β and γ positions (relative to O) are reduced by *ca.* 0.8 and 0.3 kJ mol^{-1}, respectively, relative to those of CH$_2$ groups more remote from the O atom. The computational enthalpies of formation of the studied monoethers and diethers, both cyclic and acyclic, are generally in good agreement with experimental data, another important result of the present work.

Keywords: G3(MP2)//B3 calculations; diethers; ethers; enthalpies of formation; group contributions to enthalpy of formation

INTRODUCTION

In view of our planned studies dealing with the enthalpies of formation of isomeric di- and polyethers in varying chemical surroundings, the aim of the present work was to initially carry out a computational study of the relative enthalpy levels of simple, isomeric straight-chain dioxa-alkanes as a function of the distance (number of bonds) between the O atoms. Possible differences in the enthalpy contents of these compounds may be considered to arise from differences in proximity effects of the O atoms (other effects may also be involved, see later). When the O atoms are widely separated, they may be supposed to behave independently, that is, each of them is likely to have a contribution to molecular enthalpy equal to that of a single O atom in a chemically related environment of a monoether. On closer proximity of the O atoms, the mutual interactions, stabilizing or destabilizing, are expected to become stronger.

Thus, the starting point of the present work was to select a long-chain dioxa-alkane in which the O atoms are far from each other, and then, keeping the position of one of the O atoms fixed, to change that of the other until an acetal moiety, —O—CH$_2$—O—, was achieved. Dioxadecanes were selected as the first molecular system of study. In the 2,9-dioxa isomer, MeO(CH$_2$)$_6$OMe, the distance between the O atoms was assumed to be long enough for negligible O…O proximity effects. Then, with the position of the 2-O atom frozen, that of the other was stepwise reduced down to $n = 4$, where n denotes the position of the 'moving' O atom in these 2,n-dioxadecanes:

$$\mathrm{MeO(CH_2)_6OMe(2,9\text{-}dioxadecane)}$$

$$\mathrm{MeOCH_2O(CH_2)_5Me(2,4\text{-}dioxadecane)}$$

The relative enthalpies of the isomeric diethers were determined by high-level computations using the G3(MP2)//B3 method. As the enthalpies of formation of simple ethers, diethers, and acetals formed another essential goal of this work, the computational enthalpies of formation of the studied compounds were calculated from the computational data.

The results achieved for the 2,n-dioxadecanes prompted a related investigation on the enthalpy contents of α,ω-dimethoxyalkanes MeO(CH$_2$)$_m$OMe as a function of the number of the methylene groups between the O atoms. The calculations were started from $m = 10$ (2,13-dioxatetradecane), in which the O atoms are even more widely separated than those of 2,9-dioxadecane, the starting point of the previous study, and stopped at $m = 1$ (2,4-dioxapentane, an acetal). As these compounds are not isomeric, the proximity effects of the two O atoms on molecular enthalpy are not immediately visible in the enthalpy values, but may be extracted from them by chemical reasoning. These studies gave rise to some further investigations on the enthalpies of formation of other related straight-chain monoethers and acetals.

Besides the acyclic compounds, the enthalpies of formation of some cyclic ethers and acetals were also determined computationally in order to test the reliability of the present computational method as a source of accurate enthalpy of formation data for these oxygenated hydrocarbons.

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RESULTS AND DISCUSSION

Computations

The computations (gas phase, 298.15 K, 1 bar) were carried out using the G3(MP2)//B3 method[1] and the Gaussian 03 package of software.[2] The computational enthalpy values, together with the computational enthalpies of formation calculated by the atomization method,[3] are shown in several tables in the following discussion. For comparison, experimental enthalpies of formation (if available), taken mainly from the data collection of Pedley *et al.*,[4] are also included in the tables. Moreover, the enthalpies of formation of the acyclic compounds, estimated by the group additivity method of Benson using the parameters given by Cohen and Benson[5] and Verevkin,[6] are also shown.

O. . .O proximity effects in 2,n-dioxadecanes

The isomeric 2,*n*-dioxadecanes include five diethers ($n = 5$–9) and an acetal ($n = 4$). If the O atoms of a straight-chain diether, such as 2,*n*-dioxadecane, are sufficiently far from each other (at positions 1,5 or farther away), the molecule prefers an anti arrangement of the heavy atom skeleton, whereas 1,4-diethers may have a significant contribution from a gauche conformation of the —O—C—C—O— moiety.[7] The present computations, however, always pointed to slightly lower ($\leq$1.0 kJ mol^{-1}) enthalpies of formation for the anti conformers of acyclic 1,4-diethers in the gas phase, in line with recent MM4 calculations for 2,5-dioxahexane (1,2-dimethoxyethane).[8] The gauche conformer (a *dl* pair), however, is statistically favoured over the anti. Thus, the gauche form may have a lower Gibbs energy value than the anti conformer around room temperature or at higher temperatures. On the other hand, straight-chain acetals, like 2,4-dioxapentane $CH_3OCH_2OCH_3$, are known to favour gauche–gauche (g^+g^+ and g^-g^-) conformations of the C—O—C—O—C moiety over the anti–anti (aa), anti–gauche (ag) or gauche–anti (ga) conformations.[9,10] Contrary to previous statements,[9,10] the g^+g^- conformation of straight-chain acetals was also found to be a true energy minimum, but significantly less stable than the g^+g^+ and g^-g^- conformations. For the various conformers of the simplest acyclic acetal, 2,4-dioxapentane, the following torsional angles $\tau(C_1—O_2—C_3—O_4)$ and $\tau(O_2—C_3—O_4—C_5)$, as well as relative enthalpies, were calculated:

$$g^+g^+ : \tau(C_1 - O_2 - C_3 - O_4) = \tau(O_2 - C_3 - O_4 - C_5) = 68^\circ (\text{relative enthalpy} = 0)$$

$$g^+g^- : \tau(C_1 - O_2 - C_3 - O_4) = 84^\circ, \tau(O_2 - C_3 - O_4 - C_5) = -84^\circ (\text{relative enthalpy} = +16.0\ \text{kJ mol}^{-1})$$

$$ga : \tau(C_1 - O_2 - C_3 - O_4) = 67^\circ, \tau(O_2 - C_3 - O_4 - C_5) = -176^\circ (\text{relative enthalpy} = +10.9\ \text{kJ mol}^{-1})$$

$$aa : \tau(C_1 - O_2 - C_3 - O_4) = \tau(O_2 - C_3 - O_4 - C_5) = 180^\circ (\text{relative enthalpy} = +23.4\ \text{kJ mol}^{-1})$$

For the other acetals studied, the pattern shown above for 2,4-dioxapentane was closely repeated, but in the case of asymmetric acetals, the ga and ag conformers expectedly do not have strictly equal enthalpies (or respective torsional angles). In view of the favourable enthalpies of the g^+g^+ (g^-g^-) conformers, the contribution of the other conformers to the total enthalpy of gaseous acetals is likely to be small around room temperature.

Table 1 shows that among the 2,*n*-dioxadecanes, the acetal ($n = 4$) has the lowest enthalpy of formation, *ca.* 21.6 kJ mol^{-1} below that of the most stable diether, 2,8-dioxadecane. Moreover, the enthalpies of formation of the 2,*n*-dioxadecanes from $n = 5$ to $n = 8$ show small but significant variations, suggesting varying strengths of proximity effects between the O atoms. For a more illustrative view of these trends, the enthalpies of formation of the 2,*n*-dioxadecanes, relative to that of the 2,9-dioxa isomer, are shown in Table 2. When considering the relative enthalpies of these isomeric dioxa compounds one has to take into account that not all of the variation in $\Delta_f H_m^\circ$ may be ascribed to proximity effects of the O atoms alone: the varying enthalpies partly arise from 'end effects', that is, from different distances of the 'moving' O atom from the end of the hydrocarbon chain. Thus, even for the isomeric mono-oxadecanes (Table 1), the enthalpy of formation is a function of the position of the O atom. Accordingly, relating the enthalpies of formation of the 2,*n*-dioxadecanes with those of structurally related mono-oxadecanes is a more correct way of evaluating the O. . .O proximity effects in the former. This comparison is also shown in Table 2. The enthalpies of formation of the isomeric mono-oxadecanes were first scaled relative to that of the '9-oxa' (= 2-oxa) derivative, and the differences between the scaled enthalpies of the structurally related members in the two series of compounds were then presented as a function of the parameter *n*.

Obviously, for $n \geq 7$, the proximity effects between the O atoms of the 2,*n*-dioxadecanes are almost negligible, but they become significant and destabilizing by *ca.* 3 and 4 kJ mol^{-1} for $n = 6$ and $n = 5$, respectively. However, a closer proximity of the O atoms (for $n = 4$, an acetal) leads to a strong stabilization of *ca.* 22 kJ mol^{-1}, relative to that in ordinary diethers (2,*n*-dioxadecanes with $n \geq 7$). The marked stability of acetals has been ascribed to the anomeric effect.[10]

O. . .O proximity effects in α,ω-dimethoxyalkanes

Another way of probing the O. . .O proximity effects in dioxa-alkanes is the evaluation of the enthalpies of formation of α,ω-dimethoxyalkanes $MeO(CH_2)_mOMe$ as a function of the length of the $(CH_2)_m$ moiety. The computational data are shown in Table 3. Insofar as the contribution to $\Delta_f H_m^\circ$ of a CH_2 moiety bonded to two C(sp^3) atoms is independent of the nature of the atoms attached to these two C atoms, the enthalpies of formation of α,ω-dimethoxyalkanes are expected to change by a constant amount (= that found in straight-chain alkanes) for each change of m by unity. For a compound with $m = 10$, the longest α,ω-dimethoxyalkane in this study, the proximity effects between the O atoms are likely to be negligible, even smaller than those in 2,9-dioxadecane, the reference compound in the earlier treatment of the O. . .O proximity effects.

In the group additivity scheme, the contribution of the C—(C)$_2$(H)$_2$ group increment to the enthalpy of formation has been evaluated as -20.92 kJ mol^{-1} from experimental data on straight-chain alkanes.[5] To find out the computational value of this parameter, the enthalpies of formation of the nine alkanes from ethane to decane were calculated (Table 3). On going from propane to decane, the average change in $\Delta_f H_m^\circ$ was calculated to be -21.14 kJ mol^{-1} for each CH_2 group introduced. The value of this group increment shows no significant or systematic variation with increasing length of the alkane chain. (However, on

Table 1. Computational enthalpy data (g, 298.15 K) for mono- and dioxadecanes by the G3(MP2)//B3 method, including enthalpies of formation calculated by the group additivity method[a]

Compound	H (a.u.)	$\Delta_f H_m^\circ$ (comp)	$\Delta_f H_m^\circ$ (GAV)	$\Delta(\Delta_f H_m^\circ)$ (GAV-comp)
2-Oxadecane	−429.422963	−343.8	−342.9	0.9
3-Oxadecane	−429.428054	−357.2	−355.6	1.6
4-Oxadecane	−429.427550	−355.9	−355.6	0.3
5-Oxadecane	−429.427288	−355.2	−355.6	−0.4
2,4-Dioxadecane (gg)	−465.328488	−469.9	−465.3	4.6
2,4-Dioxadecane (g^+g^-)	−465.322756	−454.8		
2,4-Dioxadecane (ag)	−465.324429	−459.2		
2,4-Dioxadecane (ga)	−465.324377	−459.1		
2,4-Dioxadecane (aa)	−465.319654	−446.7		
2,5-Dioxadecane (a)	−465.318282	−443.1	−447.4	−4.3
2,5-Dioxadecane (g)	−465.318033	−442.4		
2,6-Dioxadecane	−465.318712	−444.2	−447.4	−3.2
2,7-Dioxadecane	−465.320012	−447.6	−447.4	0.2
2,8-Dioxadecane	−465.320266	−448.3	−447.4	0.9
2,9-Dioxadecane	−465.315419	−435.6	−434.8	0.8
3,5-Dioxadecane (gg)	−465.333500	−483.0	−478.0	5.0
3,5-Dioxadecane (g^+g^-)	−465.327891	−468.3		
3,5-Dioxadecane (ag)	−465.329361	−472.2		
3,5-Dioxadecane (ga)	−465.329422	−472.3		
3,5-Dioxadecane (aa)	−465.324644	−459.8		
3,6-Dioxadecane (a)	−465.323209	−456.0	−460.1	−4.1
3,6-Dioxadecane (g)	−465.322952	−455.3		
3,8-Dioxadecane	−465.325409	−461.8	−460.1	1.7
3,7-Dioxadecane	−465.323874	−457.8	−460.1	−2.3
4,6-Dioxadecane (gg)	−465.332964	−481.6	−478.0	3.6
4,6-Dioxadecane (g^+g^-)	−465.327576	−467.5		
4,6-Dioxadecane (ag)	−465.328895	−470.9		
4,6-Dioxadecane (ga)	−465.328893	−470.9		
4,6-Dioxadecane (aa)	−465.324275	−458.8		
4,7-Dioxadecane (a)	−465.323008	−455.5	−460.1	−4.6
4,7-Dioxadecane (g)	−465.322687	−454.6		

[a] Enthalpies of formation in kJ mol^{-1}.

Table 2. Computational enthalpies of formation (in kJ mol^{-1}) of n-oxadecanes and 2,n-dioxadecanes, relative to those of the 9-oxa isomers[a]

	n					
Compound	4	5	6	7	8	9
n-Oxadecane	−12.1	−11.4	−11.4	−12.1	−13.4	0
2,n-Dioxadecane	−34.3	−7.5	−8.6	−12.0	−12.7	0
Difference	−22.2	3.9	2.8	0.1	0.7	0

[a] Gas phase, 298.15 K.

going from ethane to propane, the change in $\Delta_f H_m^\circ$ −20.7 kJ mol^{-1}, is slightly exceptional).

In the following treatment, the enthalpy of formation, −520.3 kJ mol^{-1}, of 2,13-dioxatetradecane $MeO(CH_2)_{10}OMe$ (assumed to be devoid of O...O proximity effects) was taken as a reference value from which the enthalpies of formation of the other ($m = 1$–9) α,ω-dimethoxyalkanes were estimated, assuming each decrement of m by unity to increase the enthalpy of

Table 3. Computational enthalpies *H* and enthalpies of formation[a] (computational, group additivity method, and experimental[b]) of 2,*n*-dioxa-alkanes and alkanes

Compound	*H* (298.15 K) (a.u.)	$\Delta_f H^\circ_m$ (comp)	$\Delta_f H^\circ_m$ (GAV)	$\Delta_f H^\circ_m$ (exp)	$\Delta(\Delta_f H^\circ_m)$ (GAV-comp)	$\Delta(\Delta_f H^\circ_m)$ (exp-comp)
2,5-Dioxahexane (a)	−308.373840	−346.2	−351.1		−4.9	
2,5-Dioxahexane (g)	−308.373477	−345.2				
2,6-Dioxaheptane	−347.609289	−368.7	−372.0		−3.3	
2,7-Dioxaoctane	−386.845441	−393.0	−392.9		0.1	
2,8-Dioxanonane	−426.080210	−413.7	−413.8		−0.1	
2,9-Dioxadecane	−465.315419	−435.6	−434.8		0.8	
2,10-Dioxaundecane	−504.550256	−456.4	−455.7		0.7	
2,11-Dioxadodecane	−543.785309	−477.9	−476.6		1.3	
2,12-Dioxatridecane	−583.020235	−499.0	−497.5		1.5	
2,13-Dioxatetradecane	−622.255235	−520.3	−518.4		1.9	
Ethane	−79.651026	−83.1	−83.7	−83.8 (0.4)	−0.6	−0.7 (0.4)
Propane	−118.885808	−103.8	−104.6	−104.7 (0.5)	−0.8	−0.9 (0.5)
Butane	−158.120741	−124.9	−125.5	−125.6 (0.7)	−0.6	−0.7 (0.7)
Pentane	−197.355642	−146.0	−146.4	−146.9 (0.9)	−0.4	−0.9 (0.9)
Hexane	−236.590624	−167.2	−167.4	−167.1 (0.8)	−0.2	0.1 (0.8)
Heptane	−275.825504	−188.2	−188.3	−187.7 (1.3)	−0.1	0.5 (1.3)
Octane	−315.060516	−209.6	−209.2	−208.6 (1.4)	0.4	1.0 (1.4)
Nonane	−354.295409	−230.6	−230.1	−228.2 (0.7)	0.5	2.4 (0.7)
Decane	−393.530381	−251.8	−251.0	−249.5 (1.3)	0.8	2.3 (1.3)

[a] Gas phase, 298.15 K (in kJ mol^{-1}).
[b] Reference [4].

formation by the previously mentioned computational amount of 21.14 kJ mol^{-1}. The computational and estimated enthalpies of formation of α,ω-dimethoxyalkanes, together with the differences therein, $\Delta(\Delta_f H^\circ_m)$ (comp-est), are shown in Table 4.

From $m = 9$ to $m = 4$, the differences $\Delta(\Delta_f H^\circ_m)$, ≤0.9 kJ mol^{-1}, suggest only small (if any) proximity effects between the O atoms. Noteworthy, the difference is only 0.1 kJ mol^{-1} for $m = 6$, that is for 2,9-dioxadecane, used as the reference compound in the previous discussion of the 2,*n*-dioxadecanes. For both $m = 5$ and $m = 4$, the presence of slight destabilizing interactions is obvious, particularly for $m = 5$. The higher destabilization for $m = 5$ (2,8-dioxanonane), though unexpected, is in line with the previous data (Table 2) for 2,8-dioxadecane, in which the O…O distance is comparable to that in 2,8-dioxanonane. For $m = 9$–6, the differences $\Delta(\Delta_f H^\circ_m)$ (comp-est) are small and positive, suggesting weak destabilizing O…O proximity effects in these compounds. On the other hand, they may simply arise from the inherent inaccuracies of the computed $\Delta_f H^\circ_m$ values: a $\Delta_f H^\circ_m$ value 0.2 kJ mol^{-1} less negative than the present one for the reference compound gives rise to both positive and negative differences $\Delta(\Delta_f H^\circ_m)$ for *m* ranging from 6 to 9.

Table 4. Computational and estimated (see text) enthalpies of formation of α,ω-dimethoxyalkanes (in kJ mol^{-1}) in the gas phase at 298.15 K

Compound	$\Delta_f H^\circ_m$ (comp)	$\Delta_f H^\circ_m$ (est)	$\Delta(\Delta_f H^\circ_m)$ (comp-est)
$MeOCH_2OMe$	−352.1	−330.0	−22.1
$MeO(CH_2)_2OMe$	−346.2	−351.2	5.0
$MeO(CH_2)_3OMe$	−368.7	−372.3	3.6
$MeO(CH_2)_4OMe$	−393.0	−393.5	0.5
$MeO(CH_2)_5OMe$	−413.7	−414.6	0.9
$MeO(CH_2)_6OMe$	−435.6	−435.7	0.1
$MeO(CH_2)_7OMe$	−456.4	−456.9	0.5
$MeO(CH_2)_8OMe$	−477.9	−478.0	0.1
$MeO(CH_2)_9OMe$	−499.0	−499.2	0.2
$MeO(CH_2)_{10}OMe$	−520.3	−520.3[a]	0.0

[a] Set as the reference value.

Summarizing, destabilizing O…O proximity effects of *ca.* 5.0 and 3.6 kJ mol^{-1} were computed to exist in the 1,4- and 1,5-dioxa systems of 2,5-dioxahexane and 2,6-dioxaheptane, respectively. For comparison, the data of Table 2 point to destabilization energies of 3.9 and 2.8 kJ mol^{-1} for the related dioxa systems of 2,5-dioxadecane and 2,6-dioxadecane, respectively. Accordingly, the destabilization energies obtained by the two different methods are in good mutual agreement. On the other hand, from an experimental enthalpy of formation the 1,4-dioxa system of 3,6-dioxaoctane $EtOCH_2CH_2OEt$ has been estimated by Månsson[11] to be destabilized, relative to aliphatic monoethers, by *ca.* 11 kJ mol^{-1}. This estimate exceeds the present computational values of the 1,4-dioxa destabilization energy by 6–7 kJ mol^{-1}. In line with the significant disagreement between these computational and experimental destabilization energies, the present computational enthalpy of formation, −415.2 kJ mol^{-1}, for 3,6-dioxaoctane (Table 5) is 7 kJ mol^{-1} more negative than the experimental one, −408.2 ± 1.0 kJ mol^{-1}.[11] In the absence of additional experimental enthalpy of formation

Table 5. Computational enthalpies H and enthalpies of formation[a] (computational, group additivity method, and experimental[b]) of 3,6- and 3,7-dioxa-alkanes

Compound	H (298.15 K) (a.u.)	$\Delta_f H_m^\circ$ (comp)	$\Delta_f H_m^\circ$ (GAV)	$\Delta_f H_m^\circ$ (exp)	$\Delta(\Delta_f H_m^\circ)$ (GAV-comp)	$\Delta(\Delta_f H_m^\circ)$ (exp-comp)
3,6-Dioxaoctane (a)	−386.853881	−415.2	−418.3	−408.2 (1.0)	−3.1	7.0 (1.0)
3,6-Dioxaoctane (g)	−386.853603	−414.4				
3,7-Dioxanonane	−426.089347	−437.7	−439.1	−436.2 (1.5)	−1.4	1.5 (1.5)

[a] Gas phase, 298.15 K (in kJ mol^{-1}).
[b] References [11] and [12].

data for acyclic diethers containing a 1,4-dioxa system, it remains uncertain whether the significant difference between the computational and experimental data arises from experimental error or shortcomings of the computational method. The computational value of the enthalpy of formation of 3,6-dioxaoctane is supported by the fact that 1,4-dioxane, which has two —O—C—C—O— systems, gives a computational $\Delta_f H_m^\circ$ value in excellent agreement with the experimental one (see below). Moreover, Månsson reported some problems in the purification of their sample of 3,6-dioxaoctane. In view of these divergent results, new experimental data on the enthalpies of formation of 1,4-diethers are highly welcome.

The computational results suggest the 1,5-dioxa systems of 2,6-dioxadecane and 2,6-dioxaheptane to be destabilized by 2.8 and 3.5 kJ mol^{-1}, respectively, by the O...O proximity effects. This is not far from the experimental findings of Månsson[12] for the 1,5-dioxa system of 3,7-dioxanonane $EtOCH_2CH_2CH_2OEt$, which point to a strain of *ca.* 2 kJ mol^{-1} in this compound. In line with this result, the experimental enthalpy of formation, −436.2 ± 1.5 kJ mol^{-1}, of the latter compound is supported by the present computational value of −437.7 kJ mol^{-1} (Table 5).

Effect of the O atom on the increment values of nearby CH$_2$ groups in monoethers and acetals

The destabilization energies derived above for close proximity of the O atoms in dioxa-alkanes were referenced relative to thermochemical stability of monoethers, or alternatively, relative to that of diethers in which the O atoms may be assumed to behave independently. This gives rise to a question of the thermochemical role of the O atom in straight-chain monoethers: do CH_2 groups of monoethers, excluding the first to oxygen, at varying distances from the O atom have the same (constant) contribution to the enthalpy of formation as CH_2 groups of straight-chain alkanes? This assumption is involved in the value of group additivity parameter C—(C)$_2$(H)$_2$. To study this question, the relation between $\Delta_f H_m^\circ$ and the number of CH_2 groups in the alkyl group R′ of monoethers ROR′ was studied for R = Me, Et, and Pr, allowing the C—(C)$_2$(H)$_2$ group increments for methylene groups at different distances from the O atom to be evaluated. It was also of interest to study the same problem in acetals $MeOCH_2OR'$ and $CH_2(OR')_2$.

The results of the computations are given in Tables 6 and 7. For the sake of interest, the contribution of the first (α) CH_2 group, corresponding to the change R′ = Me to R′ = Et, is also included in the data. The contribution of the C—(C)(O)(H)$_2$ group increment is seen (Table 7) to be almost constant, *ca.* −34.1 kJ mol^{-1}, in each of these compounds. For comparison, Cohen and Benson[5] and Verevkin[6] report experimental values of −33.9 and −33.6 ± 0.4 kJ mol^{-1}, respectively, for this parameter. On the other hand, the computational C—(C)$_2$(H)$_2$ group increment for the change from R′ = Et to R′ = Pr is calculated to be −20.2 ± 0.1 kJ mol^{-1} in both ethers and acetals. This value is significantly different from the experimental and computational ones of −20.92 and −21.14 kJ mol^{-1}, respectively, for the respective group increment in alkanes. Increasing the length of R′ from Pr to Bu leads to changes of *ca.* −20.8 kJ mol^{-1} in the computational values of $\Delta_f H_m^\circ$ for both ethers and acetals, that is, to contributions also slightly smaller than the CH_2 group increment in alkanes. Extending the length of R′ from Bu to Am and from Am to Hex gives rise to changes in the computational enthalpy of formation which, on average, are slightly higher, viz. from −21.3 to −21.4 kJ mol^{-1}, than the computational reference value in alkanes. Only extending the length of the group R′ from Hex to longer alkyl groups does the value of the CH_2 group increment become comparable to that in alkanes.

Summarizing, in both straight-chain monoethers and acetals the effect of the O atom(s) is to decrease the absolute values of the contributions to $\Delta_f H_m^\circ$ of the CH_2 groups β and γ away from the O atom(s), relative to their value in simple alkanes. Slightly enhanced contributions appear to exist for the next two (δ and ε) CH_2 groups, but the evidence is not conclusive. Methylene groups more remote than ε from the O atom(s) have their normal (alkane) contributions, −21.1 kJ mol^{-1}, to $\Delta_f H_m^\circ$.

The slightly reduced contributions to $\Delta_f H_m^\circ$ of the β and γ CH_2 groups of ethers may be thought to originate from the effect of the O atom on the charges on nearby C atoms. Calculations at the B3LYP/6-31G* level for 2-oxadecane point to *excess* Mulliken charges of +0.248, −0.018, and −0.010 |*e*| on C-3 (α), C-4 (β), and C-5 (γ), respectively, relative to the charges on C-6 and C-7, which are the same (−0.252 |*e*|) as those on the central carbons of decane, an alkane. For comparison, AIM[14–22] calculations (at the MP2/6-31G* level) suggest markedly different excess charges of +0.506, +0.010, and −0.003 |*e*| on C-3, C-4, and C-5, respectively. It is well-known that distribution of atomic charges among the atoms of a molecule is a difficult task, but obviously there are small excess charges on C-β and C-γ of ethers, possibly responsible for the reduced contributions to $\Delta_f H_m^\circ$ of the respective CH_2 groups. Further, both the Mulliken and AIM methods point to marked accumulations of positive excess charge on C-α of ethers. This is likely to be the main source of the destabilizing proximity effects found in 1,4- and 1,5-diethers: in the former, the positive excess charges are located on vicinal

Table 6. Computational enthalpies H and enthalpies of formation[a] (computational, group additivity method, and experimental[b]) of mono-oxa-alkanes and acetals

Compound	H (298.15 K) (a.u.)	$\Delta_f H^\circ_m$ (comp)	$\Delta_f H^\circ_m$ (GAV)	$\Delta_f H^\circ_m$ (exp)	$\Delta(\Delta_f H^\circ_m)$ (GAV-comp)	$\Delta(\Delta_f H^\circ_m)$ (exp-comp)
Mono-oxa-alkanes						
2-Oxapropane	−154.773781	−183.7	−183.8	−184.1 (0.5)	−0.1	−0.4 (0.5)
2-Oxabutane	−194.013730	−218.0	−217.4	−216.4 (0.7)	0.6	1.6 (0.7)
2-Oxapentane	−233.248248	−238.1	−238.3	−238.2 (0.7)	−0.2	−0.1 (0.7)
2-Oxahexane	−272.483039	−258.8	−259.2	−258.1 (1.2)	−0.4	0.7 (1.2)
2-Oxaheptane	−311.718004	−280.0	−280.1		−0.1	
2-Oxaoctane	−350.953008	−301.4	−301.1		0.3	
2-Oxanonane	−390.187993	−322.6	−322.0		0.6	
2-Oxaundecane	−468.657884	−364.9	−363.8		1.1	
2-Oxadodecane	−507.892874	−386.2	−384.7	−381.1 (1.6)	1.5	5.1 (1.6)
3-Oxapentane	−233.253607	−252.1	−251.0	−252.1 (0.8)	1.1	0.0 (0.8)
3-Oxahexane	−272.488147	−272.2	−271.9	−272.2 (1.1)	0.3	−0.3 (1.1)
3-Oxaheptane	−311.722936	−293.0	−292.8		0.2	
3-Oxaoctane	−350.958008	−314.5	−313.7		0.8	
3-Oxanonane	−390.193111	−336.1	−334.7		1.4	
3-Oxaundecane	−468.662986	−378.3	−376.5		1.8	
4-Oxaheptane	−311.722673	−292.3	−292.8	−292.9 (1.1)	−0.5	−0.6 (1.1)
4-Oxaoctane	−350.957454	−313.0	−313.7		−0.7	
4-Oxanonane	−390.192500	−334.5	−334.7		−0.2	
4-Oxaundecane	−468.662557	−377.2	−376.5		0.7	
4-Oxadodecane	−507.897399	−398.1	−397.4		0.7	
Acetals						
2,4-Dioxapentane (gg)	−269.149204	−352.1	−348.1	−348.4 (0.8)	4.0	3.7 (0.8)
2,4-Dioxahexane (gg)	−308.389048	−386.1	−381.7		4.4	
2,4-Dioxaheptane (gg)	−347.623671	−406.4	−402.6		3.8	
2,4-Dioxaoctane (gg)	−386.858458	−427.2	−423.5		3.7	
2,4-Dioxanonane (gg)	−426.093472	−448.5	−444.4		4.1	
3,5-Dioxaheptane (gg)	−347.628966	−420.3	−415.3	−414.8 (0.8)	5.0	5.5 (0.8)
4,6-Dioxanonane (gg)	−426.098202	−460.9	−457.1		3.8	
5,7-Dioxaundecane (gg)	−504.567798	−502.5	−499.9	−501.3 (3.1)	2.6	1.2 (3.1)

[a] Gas phase, 298.15 K (in kJ mol^{-1}).
[b] Reference [4].

Table 7. Contributions (in kJ mol^{-1}) of a CH_2 group to the enthalpy of formation (g, 298.15 K) of acyclic ethers ROR′ and of acetals $MeOCH_2OR'$ and $CH_2(OR')_2$ as a function of the increasing length of the alkyl group R′

	R′								
	Me → Et	Et → Pr	Pr → Bu	Bu → Am	Am → Hex	Hex → Hep	Hep → Oct	Oct → Non	Non → Dec
Ethers									
R = Me	−34.3	−20.1	−20.7	−21.2	−21.4	−21.2	−20.9	−21.1	−21.3
R = Et	−34.1	−20.1	−20.8	−21.6	−21.1	−21.1	−21.1		
R = Pr	−34.1	−20.1	−20.7	−21.5	−21.4	−21.3	−20.9		
Acetals									
$MeOCH_2OR'$	−34.0	−20.3	−20.8	−21.3	−21.4				
$CH_2(OR')_2$	−34.1[a]	−20.3[a]	−20.8[a]						

[a] Contribution of a single CH_2 group.

Table 8. Computational enthalpies *H* and enthalpies of formation[a] (computational, group additivity method, and experimental[b]) of some cyclic ethers and acetals

Compound	*H* (298.15 K) (a.u.)	$\Delta_f H_m^\circ$ (comp)	$\Delta_f H_m^\circ$ (exp)	$\Delta(\Delta_f H_m^\circ)$ (exp-comp)
Oxirane	−153.558137	−52.4	−52.6 (0.6)	−0.2 (0.6)
Oxetane	−192.795295	−79.4	−80.5 (0.6)	−1.1 (0.6)
Tetrahydrofuran	−232.061154	−181.7	−184.2 (0.8)	−2.5 (0.8)
Tetrahydropyran	−271.303622	−222.6	−223.4 (1.0)	−0.8 (1.0)
1,3-Dioxolane	−267.962299	−296.2	−298.0 (1.4)	−1.8 (1.4)
1,3-Dioxane	−307.206094	−340.6	−342.3 (4.3)	−1.7 (4.3)
1,4-Dioxane	−307.197161	−317.1	−315.8 (0.8)	1.3 (0.8)

[a] Gas phase, 298.15 K (in kJ mol^{-1}).
[b] Reference [4].

carbons, in the latter on carbons separated by a CH_2 group from each other. In 1,6- and other diethers the electrostatic repulsion between these charges is too weak for significant destabilization.

Additional remarks on the enthalpies of formation of acyclic ethers, acetals, and diethers

There are no experimental enthalpies of formation available for the mono-oxa- and dioxadecanes, and scarcity of thermochemical data is typical also of the other compounds of this study. The computational data may, however, be compared with the enthalpies of formation calculated by the group additivity method. Generally, the agreement between the $\Delta_f H_m^\circ$ data obtained by these different methods is very good, excluding the inability of the group additivity method to make a difference between enthalpies of formation of isomeric compounds composed of the same number of similar group equivalents.

In the few cases where the computational data may be compared with experiment, the agreement is generally good. Acetals, however, appear to be slightly exceptional. 5,7-Dioxaundecane (dibutoxymethane), 3,5-dioxaheptane (diethoxymethane), and 2,4-dioxapentane (dimethoxymethane), shown in Table 6, are reported to have experimental gas-phase enthalpies of formation of −501.3, −414.8, and −348.4 kJ mol^{-1}, respectively, at 298.15 K.[4] While the first of these values is in good agreement with the computational value of −502.5 kJ mol^{-1}, the latter two experimental values are 4–5 kJ mol^{-1} less negative than the respective computational ones. The scarcity of experimental data for the acetals does not allow a critical evaluation of possible systematic errors in the computational values for acetals.

Finally, the experimental standard enthalpy of formation of 2-oxadodecane (methyl decyl ether) is reported to be −381.1 ± 2.1 kJ mol^{-1} (Table 6).[13] Both our computational result (−386.2 kJ mol^{-1}) and the group additivity value (−384.7 kJ mol^{-1}) suggest that the experimental result is in error (too positive) by 4–5 kJ mol^{-1}.

Cyclic ethers and acetals

Besides the acyclic compounds treated above, several cyclic ethers and acetals are included in the present study (Table 8). The agreement between the thermochemical data obtained experimentally and computationally for these compounds is very good. Noteworthy, the computational enthalpies of formation of the cyclic acetals, 1,3-dioxolane and 1,3-dioxane, are also in agreement with experiment, which supports the computational values of the enthalpies of formation of the acyclic acetals diethoxymethane and dimethoxymethane discussed above.

Summary

The computational results show that proximity effects of the O atoms increase the enthalpies of formation of straight-chain 1,4-diethers by 4.5 (±0.5) kJ mol^{-1}, and those of 1,5-diethers by 3.2 (±0.4) kJ mol^{-1}. If the O atoms are more widely separated, the proximity effects are negligible, contrary to those in 1,3-diethers (acetals), which are stabilized by *ca.* 22 kJ mol^{-1}, apparently through the anomeric effect. Computations on monoethers reveal the contributions of the β and γ CH_2 groups to $\Delta_f H_m^\circ$ to be slightly smaller than those for CH_2 groups more remote from the O atom, contrary to the markedly strong contribution of the α CH_2 group. Calculation of the Mulliken and AIM atomic charges point to a presence of small excess charges on the β and γ carbons of ethers, possibly responsible for the reduced contributions to $\Delta_f H_m^\circ$ of the respective CH_2 groups. Moreover, the destabilizing proximity effects of O atoms in 1,4- and 1,5-diethers are likely to arise mainly from electrostatic repulsion between the marked positive excess charges on C-2 and C-3 of 1,4-diethers and on C-2 and C-4 of 1,5-diethers.

Finally, the present computational method, G3(MP2)//B3, was shown to provide accurate enthalpy of formation data for both acyclic and cyclic ethers, diethers, and acetals. In certain acyclic acetals, however, some divergence between experimental and computational data was found, but the disagreement is small, and possibly ascribable to experimental error.

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