

Enthalpies of formation of olefinic ethers by G3(MP2)//B3LYP calculations

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The gas-phase enthalpies of formation at 298.15 K of a number of acyclic and cyclic olefinic ethers (mainly α,β -unsaturated ethers), together with those of a few cyclic mono- and dienes, have been estimated by G3(MP2)//B3LYP calculations. In most cases, the computational and experimental data (if available) are in good mutual agreement. Whenever significant deviations between the experimental and computational data were found, the experimental enthalpies of formation arise from a single data source, and it appears that small experimental errors are embedded therein. A marked error was found in the experimental enthalpy of formation of 2-chloroethyl ethyl ether, used in this work as a reagent for estimation of the enthalpy of formation of 2-chloroethyl vinyl ether by an isodesmic reaction. Moreover, significant errors were also found in the literature values for the computational (B3LYP/6-311G^{**}) enthalpies of formation of several Me-substituted derivatives of methyl vinyl ether. The present computational method, besides providing acceptable enthalpies of formation for unsaturated ethers, was also found to give accurate $\Delta_f H_m^o(g)$ values for cyclic mono- and dienes. Thus, the G3(MP2)//B3LYP computational method proved to be a valuable tool for investigating the energetics of olefinic ethers and hydrocarbons. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: enthalpies of formation; G3(MP2)//B3LYP calculations; vinyl ethers; olefinic ethers; olefins

INTRODUCTION

Alkyl vinyl ethers, ROCH=CH₂ and their derivatives form a class of interesting olefinic ethers. The immediate proximity of the C=C bond and O atom allows transfer of negative charge from the O atom to the olefinic linkage by p- π conjugation, a molecule stabilizing factor. The extent of this phenomenon depends on several structural factors (nature, number, and location of substituents at the C=C bond, stereochemistry of the C—O—C=C moiety), making these compounds exciting objects of investigation from e.g., spectroscopic and thermodynamic points of view. In spite of these attractive features, vinyl ethers are characterized by scarcity of fundamental experimentally determined thermochemical data such as gas-phase enthalpies of formation. The experimental $\Delta_f H_m^o(g)$ values of alkyl vinyl ethers appear to be limited to those of R = Et, Pr, Bu, and i-Pr.^[1] In addition, the gas-phase enthalpy of formation of 2-chloroethyl vinyl ether has been reported,^[1] whereas experimental $\Delta_f H_m^o$ values are missing, e.g., for methyl vinyl ether (MVE) and *t*-butyl vinyl ether. On the other hand, the experimental enthalpies of formation of the cyclic vinyl ethers 2,3-dihydrofuran^[2,3] and 3,4-dihydro-2H-pyran^[1] are known in both the liquid and gas phases. In addition, $\Delta_f H_m^o(l)$ values do exist for 2-methoxypropene MeC(OMe)=CH₂ and 1-methoxycyclohexene,^[1] the respective gas-phase values, together with that of 1-methoxycyclopentene, have also been reported,^[4] but these values are not based on pure experimental data. Moreover, the enthalpies of formation of both liquid and gaseous divinyl ether, and those of furan, formally a cyclic divinyl ether, are also available.^[1]

Theoretically, the enthalpy of formation of gaseous MVE has been recently estimated by high level quantum chemical

computations.^[5] For the most stable syn (*s-cis*) conformer of MVE the value of $\Delta_f H_m^o(g)$, 298.15 K) was found to be $-107.1 \text{ kJ mol}^{-1}$, 7.1 kJ mol^{-1} below that of the high-energy anti conformer. In addition, the enthalpies of formation of several methyl-substituted derivatives of MVE (α -Me, (*E*)- β -Me, (*Z*)- β -Me, and β , β -di-Me) have been estimated by B3LYP/6-311G^{**} calculations.^[6]

During the last few decades, the thermodynamic properties of unsaturated ethers have been of great interest to us. Experimentally, the investigations dealing with these compounds have been conducted by means of chemical equilibration, which limits the studies to isomeric compounds for which a thermodynamic equilibrium can be established. However, the scope of these studies would enlarge essentially if, instead of only the differences between the enthalpy levels of certain isomeric compounds, the relative enthalpies of *any* compounds of interest could be estimated by means of an easy (but reliable) method. In fact, we have lately shown^[7] that accurate gas-phase enthalpies of formation of straight-chain saturated ethers and diethers can be obtained by high-level quantum chemical calculations at the G3(MP2)//B3LYP level. In the present work, the usefulness of the same computational method as a source of $\Delta_f H_m^o(g)$ data for unsaturated (mainly vinyl) ethers was tested on available experimental data. In addition to a number of both acyclic and cyclic vinyl ethers, vinyl alcohol, the parent compound of all alkyl vinyl ethers, was included in the present study, together

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Table 1. The isodesmic reactions used in this work^a

1	(a) $\text{CH}_2=\text{CHOH} + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OH}$
2	(a) $\text{CH}_2=\text{CHOCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_3$
3	(a) $\text{CH}_2=\text{CHOCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_2\text{CH}_3$
4	(a) $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$
5	(a) $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$
6	(a) $\text{CH}_2=\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
7	(a) $\text{CH}_2=\text{CHOCH}(\text{CH}_3)_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}(\text{CH}_3)_2$
8	(a) $\text{CH}_2=\text{CHOC}(\text{CH}_3)_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OC}(\text{CH}_3)_3$
9	(a) $\text{CH}_2=\text{CHOCH}_2\text{CH}=\text{CH}_2 + 2\text{CH}_3\text{CH}_3 \rightarrow 2 \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_2\text{CH}_3$ (b) $\text{CH}_2=\text{CHOCH}_2\text{CH}=\text{CH}_2 + \text{cyclohexane} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 + 1,3\text{-cyclohexadiene}$
10	(a) $\text{CH}_2=\text{CHOCH}=\text{CH}_2 + 2\text{CH}_3\text{CH}_3 \rightarrow 2 \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_3$ (b) $\text{CH}_2=\text{CHOCH}=\text{CH}_2 + \text{cyclohexane} \rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 1,3\text{-cyclohexadiene}$
11	(a) $(E)\text{-CH}_3\text{OCH}=\text{CHCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow (E)\text{-CH}_3\text{CH}=\text{CHCH}_3 + \text{CH}_3\text{OCH}_3$
12	(a) $(Z)\text{-CH}_3\text{OCH}=\text{CHCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow (Z)\text{-CH}_3\text{CH}=\text{CHCH}_3 + \text{CH}_3\text{OCH}_3$
13	(a) $\text{CH}_3\text{OCH}=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{OCH}_3$
14	(a) $\text{CH}_3\text{OC}(\text{CH}_3)=\text{CH}_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_2=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{OCH}_3$
15	(a) $(E)\text{-CH}_3\text{OC}(\text{CH}_3)=\text{CHCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{OCH}_3$
16	(a) $(Z)\text{-CH}_3\text{OC}(\text{CH}_3)=\text{CHCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{OCH}_3$
17	(a) $\text{CH}_3\text{C}(\text{OCH}_3)=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{CH}_3\text{OCH}_2\text{CH}_3$
18	(a) $1\text{-CH}_3\text{O-cyclopentene} + \text{CH}_3\text{CH}_3 \rightarrow 1\text{-CH}_3\text{-cyclopentene} + \text{CH}_3\text{OCH}_3$
19	(a) $1\text{-CH}_3\text{O-cyclohexene} + \text{CH}_3\text{CH}_3 \rightarrow 1\text{-CH}_3\text{-cyclohexene} + \text{CH}_3\text{OCH}_3$
20	(a) $\text{CH}_2=\text{CHCH}_2\text{OCH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{OCH}_2\text{CH}_3$
21	(a) $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3 \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
22	(a) $3\text{-Oxacyclobutene} + \text{CH}_3\text{CH}_3 \rightarrow \text{oxetane} + \text{CH}_2=\text{CH}_2$ (b) $3\text{-Oxacyclobutene} + \text{cyclohexane} \rightarrow \text{oxetane} + \text{cyclohexene}$
23	(a) $\text{Furan} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydrofuran} + 2\text{CH}_2=\text{CH}_2$ (b) $\text{Furan} + \text{cyclohexane} \rightarrow \text{tetrahydrofuran} + 1,3\text{-cyclohexadiene}$
24	(a) $2,3\text{-Dihydrofuran} + \text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydrofuran} + \text{CH}_2=\text{CH}_2$ (b) $2,3\text{-Dihydrofuran} + \text{cyclohexane} \rightarrow \text{tetrahydrofuran} + \text{cyclohexene}$
25	(a) $2,5\text{-Dihydrofuran} + \text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydrofuran} + \text{CH}_2=\text{CH}_2$ (b) $2,5\text{-Dihydrofuran} + \text{cyclohexane} \rightarrow \text{tetrahydrofuran} + \text{cyclohexene}$
26	(a) $4H\text{-Pyran} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydropyran} + 2\text{CH}_2=\text{CH}_2$ (b) $4H\text{-Pyran} + \text{cyclohexane} \rightarrow \text{tetrahydropyran} + 1,3\text{-cyclohexadiene}$
27	(a) $2H\text{-Pyran} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydropyran} + 2\text{CH}_2=\text{CH}_2$ (b) $2H\text{-Pyran} + \text{cyclohexane} \rightarrow \text{tetrahydropyran} + 1,3\text{-cyclohexadiene}$
28	(a) $3,4\text{-Dihydro-}2H\text{-pyran} + \text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydropyran} + \text{CH}_2=\text{CH}_2$ (b) $3,4\text{-Dihydro-}2H\text{-pyran} + \text{cyclohexane} \rightarrow \text{tetrahydropyran} + 1,3\text{-cyclohexadiene}$
29	(a) $3,6\text{-Dihydro-}2H\text{-pyran} + \text{CH}_3\text{CH}_3 \rightarrow \text{tetrahydropyran} + \text{CH}_2=\text{CH}_2$ (b) $3,6\text{-Dihydro-}2H\text{-pyran} + \text{cyclohexane} \rightarrow \text{tetrahydropyran} + 1,3\text{-cyclohexadiene}$
30	(a) $1,3\text{-Dioxole} + \text{CH}_3\text{CH}_3 \rightarrow 1,3\text{-dioxolane} + \text{CH}_2=\text{CH}_2$ (b) $1,3\text{-Dioxole} + \text{cyclohexane} \rightarrow 1,3\text{-dioxolane} + \text{cyclohexene}$
31	(a) $1,4\text{-Dioxin} + 2\text{CH}_3\text{CH}_3 \rightarrow 1,4\text{-dioxane} + 2\text{CH}_2=\text{CH}_2$ (b) $1,4\text{-Dioxin} + \text{cyclohexane} \rightarrow 1,4\text{-dioxane} + 1,3\text{-cyclohexadiene}$
32	(a) $1,4\text{-Dioxene} + \text{CH}_3\text{CH}_3 \rightarrow 1,4\text{-dioxane} + \text{CH}_2=\text{CH}_2$ (b) $1,4\text{-Dioxene} + \text{cyclohexane} \rightarrow 1,4\text{-dioxane} + \text{cyclohexene}$
33	(a) $1,3\text{-Diox-4-ene} + \text{CH}_3\text{CH}_3 \rightarrow 1,3\text{-dioxane} + \text{CH}_2=\text{CH}_2$ (b) $1,3\text{-Diox-4-ene} + \text{cyclohexane} \rightarrow 1,3\text{-dioxane} + \text{cyclohexene}$
44	(a) $\text{Cyclobutadiene} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{cyclobutane} + 2\text{CH}_2=\text{CH}_2$ (b) $\text{Cyclobutadiene} + \text{cyclohexane} \rightarrow \text{cyclobutane} + 1,3\text{-cyclohexadiene}$
45	(a) $\text{Cyclobutene} + \text{CH}_3\text{CH}_3 \rightarrow \text{cyclobutane} + \text{CH}_2=\text{CH}_2$
47	(a) $\text{Cyclopentadiene} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{cyclopentane} + 2\text{CH}_2=\text{CH}_2$ (b) $\text{Cyclopentadiene} + \text{cyclohexane} \rightarrow \text{cyclopentane} + 1,3\text{-cyclohexadiene}$
48	(a) $\text{Cyclopentene} + \text{CH}_3\text{CH}_3 \rightarrow \text{cyclopentane} + \text{CH}_2=\text{CH}_2$
51	(a) $1,3\text{-Cyclohexadiene} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{cyclohexane} + 2\text{CH}_2=\text{CH}_2$ (b) $1,3\text{-Cyclohexadiene} + \text{cyclohexane} \rightarrow 2\text{cyclohexene}$
52	(a) $1,4\text{-Cyclohexadiene} + 2\text{CH}_3\text{CH}_3 \rightarrow \text{cyclohexane} + 2\text{CH}_2=\text{CH}_2$ (b) $1,4\text{-Cyclohexadiene} + \text{cyclohexane} \rightarrow 2\text{cyclohexene}$
53	(a) $\text{Cyclohexene} + \text{CH}_3\text{CH}_3 \rightarrow \text{cyclohexane} + \text{CH}_2=\text{CH}_2$
54	(a) $1\text{-Me-cyclohexene} + \text{CH}_3\text{CH}_3 \rightarrow \text{cyclohexane} + \text{CH}_3\text{CH}_2\text{CH}_3$

^aThe entry numbers refer to the compound numbers of Table 2.

with a few cyclic olefins. The enthalpies of formation were evaluated from the primary computational data by both atomization^[8] and isodesmic reactions (Table 1). In the latter method, the reaction enthalpy is calculated from the computational enthalpies H° of the components of reaction including the molecule with the unknown enthalpy of formation. For this purpose, the computational enthalpies at 298.15 K of a number of simple hydrocarbons and ethers were also calculated. The enthalpy of formation of this molecule is then obtained from the computational reaction enthalpy and experimental^[11] enthalpies of formation of the other species involved in the reaction.

RESULTS AND DISCUSSION

Computations

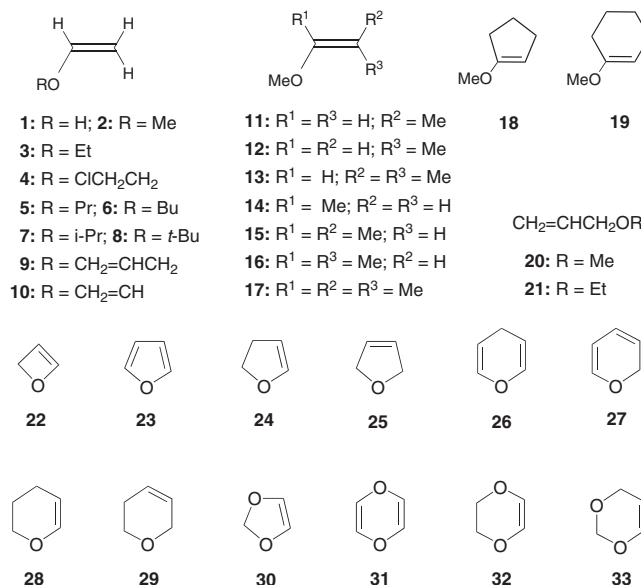
The computations (gas phase, 298.15 K, 1 bar) were carried out using the G3(MP2)//B3LYP method^[9] and the Gaussian 03 package of software.^[10] In this method, molecular geometries and vibrational frequencies are obtained at the B3LYP/6-31G* level, followed by single-point calculations at the QCISD(T)/6-31G* and MP2/G3MP2 large levels with a frozen core approximation.^[9] In addition, an empirical 'high level correction' (HLC) term is included to account for remaining (basis set) deficiencies. The olefinic ethers treated in this work are illustrated in Scheme 1, and the computational enthalpy values, together with the computational enthalpies of formation at 298.15 K calculated by the atomization and isodesmic methods, are shown in Table 2. For several compounds, two isodesmic reactions were used. For the sake of comparison, experimental enthalpies of formation (whenever available), taken mainly from the data collection of Pedley *et al.*,^[11] are also included. Finally, as an average of the computational and experimental data, the most probable values of the gas-phase enthalpy of formation at 298.15 K are given.

Vinyl alcohol and acyclic vinyl ethers

Both vinyl alcohol and the acyclic vinyl ethers have a possibility of rotational isomerism about the O—C(sp^2) bond, leading to one or two stable conformers whose structures are characterized by the value of the torsional angle τ (X—O—C=C), where X = H for vinyl alcohol and X = C for vinyl ethers. Unless sterically hindered by a substituent, *cis* to the O atom, on the β carbon of the vinyl group, the XO moiety mostly prefers the *syn* orientation ($\tau = 0$); otherwise, τ values between 0 and 180° (or -180°) are encountered.

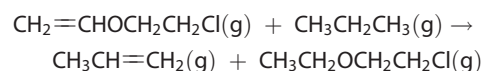
The data of Table 2 show that for vinyl alcohol **1** in its most stable (*syn*) conformation, the mean of the computational $\Delta_f H_m^{\circ}$ (g) values, based on both the atomization and isodesmic methods, falls well within the wide span, -111 to -128 kJ mol⁻¹, of experimental data summarized in reference.^[5] In fact, the mean G3(MP2)//B3LYP enthalpy of formation, -125.2 kJ mol⁻¹, of **1**(*syn*) is in excellent agreement with an experimental $\Delta_f H_m^{\circ}$ (g) value, -125.0 kJ mol⁻¹, of Holmes and Lossing,^[11] as well as with a composite high-level computational value, -125.5 kJ mol⁻¹, of da Silva *et al.*^[5]

Table 2 shows that for alkyl vinyl ethers with R = Et (**3**), Pr (**5**), Bu (**6**), and *i*-Pr (**7**) the computational and experimental $\Delta_f H_m^{\circ}$ (g) values are in good mutual agreement. For R = ClCH₂CH₂ (**4**), a slight disagreement (-5.1 ± 3.6 kJ mol⁻¹) between the experimental and calculated data is suggested, but it should be noted that the experimental enthalpy in question is based on a single



Scheme 1. The olefinic ethers studied in this work.

data source: a reinvestigation might be desirable. For this compound (**4**), the isodesmic reaction (Table 1)



with the reported^[11] enthalpy of formation, -301.3 ± 2.3 kJ mol⁻¹, for gaseous 2-chloroethyl ethyl ether (**66**) gives an enthalpy of formation in marked disagreement with both the computational and experimental one. Obviously, the experimental enthalpy of formation of **66** is significantly erroneous; in fact, our G3(MP2)//B3LYP calculations (using the atomization procedure) give a $\Delta_f H_m^{\circ}$ (g) value of -276.3 kJ mol⁻¹ (which is 25 kJ mol⁻¹ less negative than the literature^[11] value) for the *anti* conformer, the most stable form of **66**. (Here the designation "anti" refers to the relative positions of the Cl and O atoms in the ClCH₂CH₂O moiety of **66**.) The present computational enthalpies of formation of 2-chloroethyl vinyl ether **4** and 2-chloroethyl ethyl ether **66** are further supported by the quite reasonable enthalpy of reaction, -111 kJ mol⁻¹, obtainable from the computational data of Table 2 for the hydrogenation of **4** to **66**. For comparison, the experimental gas-phase enthalpy of hydrogenation of ethyl vinyl ether **3** to diethyl ether **64** is -112 kJ mol⁻¹ at 355 K.^[12]

While the *syn* conformers of most alkyl vinyl ethers are favored by low enthalpy values relative to those of the *anti* forms, the situation is reversed for *t*-butyl vinyl ether **8**: the *anti* conformer with $\tau = 180^\circ$ (for the value of τ in **8** see, however,^[13]) is calculated to be 8.5 kJ mol⁻¹ more stable (on enthalpy basis) than the *syn* form.

It is of interest to compare the relative enthalpies of hydrogenation of alkyl vinyl ethers with increasing branching of the alkyl group at the α -carbon, i.e., those of the reaction $\text{ROCH}=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{ROEt}(\text{g})$. From the mean $\Delta_f H_m^{\circ}$ (g) data of Table 2 one obtains the reaction enthalpies of -109 , -111 , -111 , and -112 kJ mol⁻¹ for R = Me, Et, *i*-Pr, and *t*-Bu, respectively. Only a slight increase in the exothermic character of the hydrogenation reaction with increasing bulkiness of the alkyl group is suggested by the data. Thus, although a marked

Table 2. Computational enthalpies H° and enthalpies of formation^a of the compounds studied in this work

No.	Compound	H° (a.u.)	$\Delta_f H_m^\circ$ (g), computational			$\Delta_f H_m^\circ$ (g), exp.	$\Delta_f H_m^\circ$ (g) (mean)
			(atomization)	(isod. a)	(isod. b)		
1	HOCH=CH ₂ ($\tau = 0^\circ$)	-153.586211	-126.1	-124.3		-111 to -128 ^b	-125.2 ^c
	HOCH=CH ₂ ($\tau = 180^\circ$)	-153.584561	-121.8	-120.0			-120.9
2	MeOCH=CH ₂ ($\tau = 0^\circ$)	-192.806664	-109.2	-106.6			-107.9
	MeOCH=CH ₂ ($\tau = 169^\circ$)	-192.803251	-100.2	-97.7			-99.0
3	EtOCH=CH ₂ ($\tau = 0^\circ$)	-232.046574	-143.4	-138.8		-140.8 (0.9)	-141.0
	EtOCH=CH ₂ ($\tau = 172^\circ$)	-232.043386	-135.0	-130.5			-132.8
4	ClCH ₂ CH ₂ OCH=CH ₂ ($\tau = 0^\circ$, anti Cl-CH ₂ CH ₂ -O-)	-691.205839	-164.9	[-186.8]		-170.1 (3.6)	-167.5
	ClCH ₂ CH ₂ OCH=CH ₂ ($\tau = 167^\circ$, anti Cl-CH ₂ CH ₂ -O-)	-691.202513	-156.2	-152.3			-154.3
5	PrOCH=CH ₂ ($\tau = 0^\circ$)	-271.281125	-163.5	-160.7		-161.6 (2.3)	-161.9
	PrOCH=CH ₂ ($\tau = 171^\circ$)	-271.277927	-155.1	-152.3			-153.7
6	BuOCH=CH ₂ ($\tau = 0^\circ$)	-310.515919	-184.3	-180.6		-184.5 (2.7)	-183.1
	BuOCH=CH ₂ ($\tau = 170^\circ$)	-310.512745	-176.0	-172.3			-174.2
7	i-PrOCH=CH ₂ ($\tau = 0^\circ$, $\tau(C_\alpha-O-C-H) = 40^\circ$)	-271.286019	-176.4	-173.9		-173.8 (2.3)	-174.7
	i-PrOCH=CH ₂ ($\tau = 163^\circ$, $\tau(C_\alpha-O-C-H) = 42^\circ$)	-271.284990	-173.7	-171.2			-172.5
8	t-BuOCH=CH ₂ ($\tau = 180^\circ$)	-310.524806	-207.6	-203.0			-205.3
	t-BuOCH=CH ₂ ($\tau = 0^\circ$)	-310.521581	-199.2	-194.5			-196.9
9	CH ₂ =CHCH ₂ OCH=CH ₂ ($\tau_1 = \tau_2 = 0^\circ$) ^d	-270.066287	-34.3	-26.8	-29.3		-30.1
	CH ₂ =CHCH ₂ OCH=CH ₂ ($\tau_1 = 163^\circ$, $\tau_2 = 128^\circ$) ^d	-270.062743	-25.0	-17.5	-20.0		-20.8
10	CH ₂ =CHOCH=CH ₂ ($\tau_1 = 18^\circ$, $\tau_2 = -150^\circ$)	-230.832825	-17.0	-11.5	-12.0	-13.6 (1.0)	-13.5
	CH ₂ =CHOCH=CH ₂ ($\tau_1 = \tau_2 = 180^\circ$)	-230.832449	-16.1	-10.6	-11.1		-12.6
11	(E)-MeOCH=CHMe ($\tau = 0^\circ$)	-232.042731	-133.3	-132.1			-132.7
12	(Z)-MeOCH=CHMe ($\tau = 159^\circ$)	-232.040964	-128.7	-127.5			-128.1
13	MeOCH=CMe ₂ ($\tau = 154^\circ$)	-271.280371	-161.6	-161.3			-161.5
14	MeC(OMe)=CH ₂ ($\tau = 0^\circ$)	-232.050047	-152.5	-150.9		[-148.6], -151.2 ^e	-151.5
15	(E)-MeC(OMe)=CHMe ($\tau = 0^\circ$)	-271.283644	-170.1	-169.9			-170.0
16	(Z)-MeC(OMe)=CHMe ($\tau = 140^\circ$)	-271.280305	-161.4	-161.1			-161.3
17	MeC(OMe)=CMe ₂ ($\tau = 130^\circ$)	-310.516797	-186.6	-184.4			-185.5
18	1-MeO-cyclopentene ($\tau = 0^\circ$)	-309.330125	-131.3	-130.4			-130.9
19	1-MeO-cyclohexene ($\tau = 0^\circ$)	-348.572703	-172.5	-171.9		[-121.9]	-170.6
20	CH ₂ =CHCH ₂ OMe	-232.033928	-110.2	-105.6		[-161.0], -167.6 ^e	-107.9
21	CH ₂ =CHCH ₂ OEt	-271.274039	-144.9	-142.0			-143.5
22	3-Oxacyclobutene	-191.579919	51.3	54.0	53.1		-52.8
23	Furan	-229.674811	-37.0	-31.9	-34.6	-34.9 (0.7)	-34.6
24	2,3-Dihydrofuran	-230.855799	-77.4	-76.0	-76.9	-72.3 (0.4)	-76.7
25	2,5-Dihydrofuran	-230.851079	-65.0	-63.7	-64.5		-64.4

(Continues)

Table 2. (Continued)

No.	Compound	H^0 (a.u.)	ΔH_m^0 (g), computational			ΔH_m^0 (g), exp.	ΔH_m^0 (g) (mean)
			(atomization)	(isod. a)	(isod. b)		
26	4H-pyran	-268.892869	-13.8	-7.0	-9.7		-10.2
27	2H-pyran	-268.889555	-5.1	1.7	-1.0		-1.5
28	3,4-Dihydro-2H-pyran	-270.098858	-119.8	-116.8	-117.6	-112.8 (0.9)	-116.8
29	3,6-Dihydro-2H-pyran	-270.092221	-102.4	-99.2	-100.2		-100.6
30	1,3-Dioxole	-266.752562	-180.4	-178.3	-179.2		-179.3
31	1,4-Dioxin	-304.778565	-87.8	-78.8	-81.5		-82.7
32	1,4-Dioxene	-305.993195	-216.5	-211.3	-212.1		-213.3
33	1,3-Diox-4-ene	-305.998797	-231.2	-229.0	-229.9		-230.0
34	Ethene	-78.434950	49.4			52.5 (0.4)	51.0
35	Ethane	-79.651026	-83.1			-83.8 (0.4)	-83.5
36	Propene	-117.673875	17.8			20.0 (0.8)	18.9
37	Propane	-118.885808	-103.8			-104.7 (0.5)	-104.3
38	1-Butene	-156.908221	-1.8			0.1 (1.0)	-1.0
39	(E)-2-Butene	-156.912205	-12.2			-11.4 (1.0)	-11.8
40	(Z)-2-Butene	-156.910334	-7.3			-7.1 (1.0)	-7.2
41	Isobutene	-156.914446	-18.1			-16.9 (0.9)	-17.5
42	2-Methyl-1-butene	-196.148681	-37.4			-35.3 (1.0)	-36.4
43	2-Methyl-2-butene	-196.150302	-41.7			-41.8 (1.1)	-41.8
44	Cyclobutadiene	-154.414680	424.3	432.0	429.0	428 (16) ^f	428.3
45	Cyclobutene	-155.680618	161.0			156.7 (1.5)	158.9
46	Cyclobutane	-156.896604	28.7			28.4 (0.6)	28.6
47	Cyclopentadiene	-193.753705	129.9	137.6	132.5	134.3 (1.5)	133.6
48	Cyclopentene	-194.955957	33.7			33.9 (1.4)	33.8
49	1-Methylcyclopentene	-234.197354	-4.4			-3.8 (0.7)	-4.1
50	Cyclopentane	-196.162618	-74.0			-76.4 (0.8)	-75.7
51	1,3-Cyclohexadiene	-232.990938	102.8	108.9	107.3	106.2 (0.9)	106.3
52	1,4-Cyclohexadiene	-232.990870	102.9	109.1	107.4	104.8 (0.6) ^g	106.1
53	Cyclohexene	-234.198168	-6.5	-4.2		-5.0 (0.7)	-5.2
54	1-Methylcyclohexene	-273.439151	-43.5			-43.3 (0.8)	-43.4
55	Cyclohexane	-235.407738	-121.9			-123.4 (0.8)	-122.7
56	MeOH	-115.553224	-200.3			-201.5 (0.3)	-200.9
57	MeOMe	-154.773781	-183.7			-184.1 (0.5)	-183.9
58	MeOEt	-194.013730	-218.0			-216.4 (0.7)	-217.2
59	MeOPr	-233.248248	-238.1			-238.2 (0.7)	-238.2
60	MeOi-Pr	-233.253376	-251.5			-252.0 (1.0)	-251.8
61	MeOBu	-272.483039	-258.8			-258.1 (1.2)	-258.5

62	MeO <i>i</i> -Bu	-272.486647	-268.3		-268.3
63	MeO <i>t</i> -Bu	-272.493093	-285.2		-284.4
64	EtOEt	-233.253607	-252.1		-252.1 (0.8)
65	EtOPr	-272.488147	-272.2		-272.2 (1.1)
66	EtOCH ₂ CH ₂ Cl (anti Cl-CH ₂ CH ₂ -O-)	-692.413877	-276.3		-276.3 ^c
	EtOCH ₂ CH ₂ Cl (gauche Cl-CH ₂ CH ₂ -O-)	-692.413143	-274.4		-274.4
67	EtO <i>i</i> -Pr	-272.493272	-285.7		-285.7
68	EtO <i>t</i> -Bu	-311.732938	-319.2		-317.0
69	Oxetane	-192.795295	-79.4		-80.0
70	Tetrahydrofuran	-232.061154	-181.7		-183.0
71	Tetrahydropyran	-271.303622	-222.6		-223.0
72	1,3-Dioxolane	-267.962299	-296.2		-297.1
73	1,3-Dioxane	-307.206094	-340.6		-341.5
74	1,4-Dioxane	-307.197161	-317.1		-316.5

^a Gas phase, 298.15 K (in kJ mol⁻¹). The experimental values of $\Delta_f H_m^\circ$ (g), unless otherwise indicated, are from reference [1]. The values shown in brackets (from reference [4]) are not based on pure experimental data, and thus they are not included in the mean value of $\Delta_f H_m^\circ$ (g).

^b For a summary of the experimental data, see reference [5].

^c The mean does not include the experimental values.

^d $\tau_1 = \angle(\text{C}-\text{O}-\text{C}=\text{C})$, $\tau_2 = \angle(\text{O}-\text{C}-\text{C}=\text{C})$.

^e The gas-phase data involve estimated enthalpies of vaporization of the liquid compounds, based on experimental boiling temperatures.

^f Reference [29].

^g Reference [3].

^h Doubtful, not included in the mean.

ⁱ Reference [30].

^j Reference [31].

increase of strain is expected in the reactant ROCH=CH₂ on going from R = Me to R = *t*-Bu (note the syn → anti change in conformation), there appears to occur a simultaneous and almost equal increase of strain in the product ROEt on account of the nonbonded interactions between the alkyl groups in *t*-butyl ethyl ether **68**.

Experimental $\Delta_f H_m^\circ(\text{g})$ data are unavailable for allyl vinyl ether **9**; the mean $\Delta_f H_m^\circ(\text{g})$ values for the two conformers of this compound are based entirely on computational data. The mean $\Delta_f H_m^\circ(\text{g})$ data of Table 2 for **9** and allyl ethyl ether **21** suggest an enthalpy of hydrogenation of -113 kJ mol^{-1} for the vinyloxy moiety of **9**; similarly, hydrogenation of the allyl moiety of **9** to a propyl group (leading to propyl vinyl ether **5**) is calculated to be exothermic by 132 kJ mol^{-1} . Accordingly, these hydrogenation reactions appear to be slightly (3 kJ mol^{-1}) more exothermic than the related reactions propyl vinyl ether **5** → ethyl propyl ether **65** (-110 kJ mol^{-1}) and allyl ethyl ether **21** → ethyl propyl ether **65** (-129 kJ mol^{-1}). Thus, the two C=C bonds of **9** seem to give rise to a destabilization of 3 kJ mol^{-1} in this compound. However, this conclusion may be erroneous, because if the two enthalpies of hydrogenation of **9** are calculated directly from the computational enthalpies H° of **5**, **9**, and **21** (thus neglecting the contribution of the isodesmic reactions to the mean enthalpy of formation), the suggested destabilization, 3 kJ mol^{-1} , vanishes from **9**.

The computational and experimental $\Delta_f H_m^\circ(\text{g})$ values for divinyl ether **10** are also in good mutual agreement. As a whole, it may be summarized that for **1–10** (excluding 2-chloroethyl vinyl ether **4**), the experimental $\Delta_f H_m^\circ(\text{g})$ values are generally slightly more positive than the computational ones. In principle, this is an expected trend, because the computational $\Delta_f H_m^\circ(\text{g})$ values are those of the most stable conformers, not those of a Boltzmann distribution of conformers of different stabilities like the experimental ones. However, unless the less stable conformers are markedly favored by entropy (relative to that of the most stable conformer), the effect on $\Delta_f H_m^\circ$ of the Boltzmann distribution of conformers is rather small.

As mentioned above (see Introduction), the experimental values of $\Delta_f H_m^\circ(\text{l})$ at 298.15 K are known for 2-methoxypropene **14** and 1-methoxycyclohexene **19**,^[1] but the respective gas-phase values, in the absence of experimental enthalpies of vaporization, are missing. However, the latter may be estimated from the normal boiling temperatures θ of the compounds in question using, e.g., an equation derived previously^[14] for olefinic compounds:

$$\begin{aligned} \Delta_{\text{vap}} H_m^\circ(298.15 \text{ K}) / \text{kJ mol}^{-1} \\ = (20.51 \pm 0.25) + (0.161 \pm 0.003) \times \theta / ^\circ\text{C} \end{aligned}$$

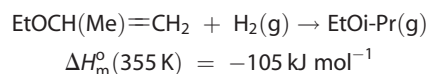
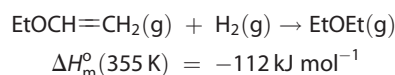
Thus, for liquid 2-methoxypropene **14** ($\theta = 35^\circ\text{C}$ ^[4]) and 1-methoxycyclohexene **19** ($\theta = 141^\circ\text{C}$ ^[4,15]) the enthalpies of vaporization at 298.15 K are estimated to be 26.1 and 43.2 kJ mol^{-1} , respectively. (Alternatively, the enthalpy of vaporization at 298.15 K of **14** might be equated with that, 26.6 kJ mol^{-1} ,^[1] for the isomeric ethyl vinyl ether **3**, which has a similar normal boiling temperature.) Accordingly, from the liquid phase enthalpies of formation of **14** and **19** (-177.3 ± 0.9 and $-210.8 \pm 2.3 \text{ kJ mol}^{-1}$,^[1] respectively) one obtains the respective $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ values of ca. -151.2 and $-167.6 \text{ kJ mol}^{-1}$. The former of these values is in good agreement with the present computational enthalpy of formation of $-152.5 \text{ kJ mol}^{-1}$, while the latter is 5 kJ mol^{-1} less negative than the computational one,

$-172.5 \text{ kJ mol}^{-1}$. Although true experimental gas-phase enthalpies of formation have not previously been reported for **14** and **19**, the 'semi-empirical' $\Delta_f H_m^\circ(\text{g}, 298.15 \text{ K})$ data, -148.6 (**14**) and $-161.0 \text{ kJ mol}^{-1}$ (**19**), of Hine and Arata^[4] for these compounds are noteworthy. The former of these values is not far from those of the present study for **14**, while the latter is somewhat less negative in comparison with the present data for **19**. The positive divergence of the $\Delta_f H_m^\circ(\text{g})$ data of Hine and Arata^[4] from the results of the present work is found to apply also to the enthalpy of formation of 1-methoxycyclopentene **18**, for which the authors^[4] report $\Delta_f H_m^\circ(\text{g}) = -121.9 \text{ kJ mol}^{-1}$, a value 9 kJ mol^{-1} less negative than the computational one, $-130.9 \text{ kJ mol}^{-1}$, of Table 2.

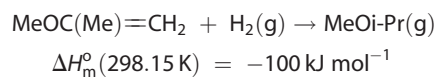
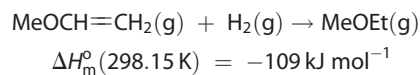
On the other hand, the present estimated and computational (G3(MP2)//B3LYP) values of $\Delta_f H_m^\circ(\text{g})$ for 2-methoxypropene **14** (Table 2) differ markedly (ca. -16 kJ mol^{-1}) from a previous computational (B3LYP/6-311G**) result of $-136.2 \text{ kJ mol}^{-1}$.^[6] The latter value of $\Delta_f H_m^\circ(\text{g})$ would require the enthalpy of vaporization at 298.15 K of liquid **14** to be ca. 41 kJ mol^{-1} , a value certainly too high.

The computational (B3LYP/6-311G**) enthalpy of formation, $-107.4 \text{ kJ mol}^{-1}$, reported by Sebbar *et al.*^[6] for gaseous allyl methyl ether **20** is in line with the data, $-107.9 \text{ kJ mol}^{-1}$, of Table 2. However, the computational enthalpies of formation of several methyl-substituted derivatives of MVE, given by the same authors, do not agree with the data of the present study. As shown above, 2-methoxypropene **14**, an α -Me-substituted derivative of MVE, is reported^[6] to have a $\Delta_f H_m^\circ(\text{g})$ value ca. 16 kJ mol^{-1} too high. On the other hand, for the β -mono-Me (**11**, **12**) and β,β -di-Me (**13**) derivatives of MVE the B3LYP/6-311G** calculations^[6] suggest enthalpies of formation which are markedly more negative than those found in the present study. Thus, for **11** and **12** the values of $\Delta_f H_m^\circ$, -143.5 and $-151.6 \text{ kJ mol}^{-1}$, respectively,^[6] are too negative by 10.9 (**11**) and 23.5 kJ mol^{-1} (**12**), in comparison with the data of Table 2. Similarly, the B3LYP/6-311G** enthalpy of formation, $-182.9 \text{ kJ mol}^{-1}$, of **13** is 21 kJ mol^{-1} more negative than that, $-161.5 \text{ kJ mol}^{-1}$, found in the present study.

The dubious character of the enthalpy of formation data for the methyl-substituted methyl vinyl ethers, given by the B3LYP/6-311G** calculations,^[6] is confirmed by calculation of the enthalpies of hydrogenation of the unsaturated ethers in question from the data given. From early experimental thermochemical data of Kistiakowsky *et al.*^[12] one obtains

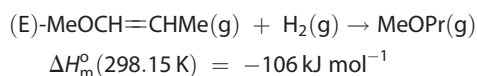
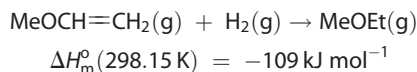


i.e., an α -Me substitution decreases the exothermicity of the hydrogenation reaction of ethyl vinyl ether by ca. 7 kJ mol^{-1} . For comparison, from the data of Table 2 for the respective methyl vinyl ethers one obtains



i.e., a Me substituent attached to C- α of MVE decreases the exothermicity of the hydrogenation reaction by a comparable amount of ca. 9 kJ mol⁻¹. On the other hand, from the B3LYP/6-311G** enthalpy of formation, -136.2 kJ mol⁻¹,^[6] for **14** one obtains an enthalpy of hydrogenation of -116 kJ mol⁻¹, suggesting that, instead of an expected stabilization of ca. 9 kJ mol⁻¹, the α -Me group of **14** leads to a destabilization of the C=C bond by ca. 7 kJ mol⁻¹.

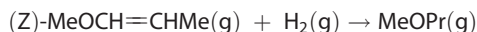
A related reasoning shows that the B3LYP/6-311G** enthalpies of formation^[6] of the β -Me and β,β -di-Me derivatives of MVE are also markedly erroneous. Thus, from the data of Table 2 one obtains



i.e., a β -Me substitution (in the *E* position where it has no interfering steric effect on the orientation of the MeO group) decreases the enthalpy of hydrogenation of MVE by 3 kJ mol⁻¹. For comparison, from the B3LYP/6-311G** enthalpy of formation, -143.6 kJ mol⁻¹,^[6] of (*E*)-MeOCH=CHMe **11** one obtains an enthalpy of hydrogenation of ca. -95 kJ mol⁻¹ for this compound, which suggests a double bond stabilization effect of ca. 14 kJ mol⁻¹ for the β -Me group of **11**. Although this value is not far from the double bond stabilization effect (ca. 11 kJ mol⁻¹) of alkyl groups on the C=C bonds of ordinary olefins,^[16] it has been shown^[17-20] that in β -alkyl-substituted vinyl ethers with sterically unhindered p- π conjugation (like that in the -O-C=C moiety of **11**) the alkyl group stabilizes the C=C bond by only a few kJ mol⁻¹. Similarly, for the reaction



the data of Table 2 give a reaction enthalpy of -107 kJ mol⁻¹ (instead of the -85 kJ mol⁻¹ from the data of Sebbar *et al.*^[6] for the reagent), which is quite reasonable in comparison with that, -110 kJ mol⁻¹ (from the data of Table 2), for the reaction



(it is preferable to compare the enthalpy of hydrogenation of MeOCH=CMe₂ (**13**) with that of the *Z* isomer (**12**) of MeOCH=CHMe, because in these compounds the MeO moieties have almost equal spatial orientations, see the respective τ values given in Table 2).

That the enthalpies of formation reported for the Me-substituted methyl vinyl ethers by the B3LYP/6-311G** calculations^[6] are markedly erroneous is further confirmed by consideration of the relative enthalpies of the geometrical isomers **11** and **12**. For the *E* \rightarrow *Z* isomerization in the gas phase the reported B3LYP/6-311G** data lead to an enthalpy change of -8 kJ mol⁻¹, contrary to that of +4 kJ mol⁻¹ found in the present G3(MP2)//B3LYP calculations. The claimed B3LYP/6-311G** enthalpy difference between **12** and **11** appeared suspicious enough for us to repeat the B3LYP/6-311G** calculations with the results $H^{\circ}(298.15 \text{ K}) = -232.380552 \text{ a.u.}$ for **11**, -232.379414 a.u. for **12**. Thus, for the *E* \rightarrow *Z* isomerization of MeOCH=CHMe, $\Delta H_{\text{m}}^{\circ}$ (B3LYP/6-311G**) = +3.0 kJ mol⁻¹ (i.e., not -8 kJ mol⁻¹), in line with our G3(MP2)//B3LYP value of +4.0 kJ mol⁻¹. Experimentally, we have found an *E* \rightarrow *Z* isomerization enthalpy of

+1.26 \pm 0.12 kJ mol⁻¹ for MeOCH=CHMe in the neat liquid, corresponding to +0.43 \pm 0.32 kJ mol⁻¹ in the gas phase.^[19]

For the *E* \rightarrow *Z* isomerization of 2-methoxy-2-butene (compounds **15** and **16**, respectively), the data of Table 2 give a computational reaction enthalpy of 8.7 kJ mol⁻¹, not far from our experimental gas-phase value of 9.9 \pm 0.4 kJ mol⁻¹.^[20] For comparison, our previous DFT calculations at the B3LYP/6-31G* and B3LYP/6-311 + G(2d,p) levels have given *E* \rightarrow *Z* isomerization enthalpies of 8.5 and 8.8 kJ mol⁻¹, respectively, for 2-methoxy-2-butene.^[21]

Cyclic ethers

In addition to the computational enthalpies of formation of acyclic vinyl ethers, related studies were also carried out for a number of unsaturated 4- to 6-membered ring compounds, including both ethers and hydrocarbons. In the case of cyclic olefinic ethers, comparison of the computational enthalpies of formation with experimental data is rarely possible. For gaseous furan **23**, however, the experimental^[1] enthalpy of formation, -34.9 \pm 0.7 kJ mol⁻¹, is in good agreement with the mean (-34.5 kJ mol⁻¹) of the computational data (including the two isodesmic reactions). For 2,3-dihydrofuran^[2,3] **24** and 3,4-dihydro-2*H*-pyran^[1] **28** the experimental $\Delta H_{\text{m}}^{\circ}$ values are 4-7 kJ mol⁻¹ less negative than the mean computational values. In the absence of several experimental determinations of the enthalpies of formation of these 5- and 6-membered vinyl ethers the source of the slight disagreement between the computational and experimental data is uncertain. However, the enthalpies of hydrogenation of 2,3-dihydrofuran **24** and 3,4-dihydro-2*H*-pyran **28** to the respective saturated ethers have been measured in dilute hexane solution at 298 K with the results -107.1 and -103.3 kJ mol⁻¹, respectively.^[22] For comparison, from the computational data of Table 2 one obtains the respective $\Delta H_{\text{m}}^{\circ}$ values of -106.2 and -104.9 kJ mol⁻¹, in line with the experimental solution data. On the other hand, from the experimental gas-phase enthalpies of formation (Table 2) for 2,3-dihydrofuran **24** and tetrahydrofuran **69**, and for 3,4-dihydro-2*H*-pyran **28** and tetrahydropyran **70**, one arrives at gas-phase enthalpies of hydrogenation of -111.9 and -110.6 kJ mol⁻¹ for **24** and **28**, respectively, in slight disagreement with the solution and computational data. Thus, the experimental gas-phase enthalpies of formation of **24** and **28** seem to be slightly too high.

The present G3(MP2)//B3LYP enthalpies of formation for **24** and **28** are also supported by reasonable enthalpies of isomerization of these vinyl ethers to their allylic counterparts, 2,5-dihydrofuran **25** and 3,6-dihydro-2*H*-pyran **29**, respectively. For **24** \rightarrow **25** one obtains computationally $\Delta H_{\text{m}}^{\circ} = +12.4 \text{ kJ mol}^{-1}$ (exp. +12.6 \pm 0.5 kJ mol⁻¹ in DMSO solution^[23]), and for **28** \rightarrow **29** $\Delta H_{\text{m}}^{\circ} = +17.5 \text{ kJ mol}^{-1}$ (exp. +18.9 \pm 1.1 kJ mol⁻¹ in DMSO solution^[23]).

Another interesting pair of isomeric cyclic vinyl ethers is formed by the 4*H*- and 2*H*-pyrans, **26** and **27**, respectively. The former is a cyclic divinyl ether, whereas the latter contains a conjugated 1,3-butadiene moiety. Experimental enthalpies of formation are unavailable for these compounds, but the computational data of Table 2 suggest **26** to be ca. 8.7 kJ mol⁻¹ more stable than **27**. Accordingly, the reaction **26** \rightarrow **27** is calculated to be ca. 9 kJ mol⁻¹ more favorable than the related double-bond migration reaction **28** \rightarrow **29** for which $\Delta H_{\text{m}}^{\circ}$ (comp.) = +17.5 kJ mol⁻¹. The decreased endothermicity of

the former reaction might be ascribed to the expected stabilizing effect of the C=C—C=C moiety in the reaction product **27**. On the other hand, such an effect is not found in the related reaction involving the carbocyclic compounds 1,4-cyclohexadiene **52** and 1,3-cyclohexadiene **51**, which both computationally (Table 2) and experimentally^[3,24] lay on almost the same enthalpy level.

The data of Table 2 allow the enthalpies of hydrogenation of the two C=C bonds of 4*H*-pyran **26** to be studied stepwise. Thus, the enthalpies of formation of **26** (−10.2), 3,4-dihydro-2*H*-pyran **28** (−116.8), and tetrahydropyran **70** (−223.0 kJ mol^{−1}) reveal that essentially equal amounts of heat, 106–107 kJ mol^{−1}, are released in both reactions, **26** → **28** and **28** → **70**. This is in marked contrast to the separate enthalpies of hydrogenation of the two C=C bonds of the acyclic divinyl ether **10**: the enthalpies of formation of Table 2 for **10** (−13.5), ethyl vinyl ether **3** (−141.0), and diethyl ether **64** (−252.1 kJ mol^{−1}) suggest that ca. 128 kJ mol^{−1} of heat is released in the hydrogenation of **10** to **3**, but only 111 kJ mol^{−1} in that of **3** to **64**. The marked development of heat in the hydrogenation of **10** to **3** shows that the total p-π (π-p-π) conjugation energy of **10**, despite its two C=C bonds, is not twice of that of **3** but preferably comparable to that of **3** with only a single C=C bond. This fact, well known since the early thermochemical measurements of Kistiakowsky *et al.*,^[12] is likely to arise from the steric nature of the C=C—O—C=C moiety of **10**, which, according to previous^[25] and present computational results, is nonplanar (contrary to that of 4*H*-pyran **26**), and thus less favorable for efficient p-π interaction for each C=C bond than the planar^[26] C—O—C=C moiety of ethyl vinyl ether **3**.

The individual enthalpies of hydrogenation of the two C=C bonds of 2*H*-pyran **27** are also of interest. From the data of Table 2, hydrogenation of the pure olefinic C=C bond (between C-3 and C-4) of **27** releases 115 kJ mol^{−1} of heat, 7 kJ mol^{−1} less than hydrogenation of the olefinic C=C bond of 3,6-dihydro-2*H*-pyran **29** (122 kJ mol^{−1}). Similarly, hydrogenation of the —O—C=C moiety of 2*H*-pyran **27** to its saturated counterpart is calculated to be exothermic by 99 kJ mol^{−1}, i.e., 7 kJ mol^{−1} less exothermic than hydrogenation of the similar C=C bond of 3,4-dihydro-2*H*-pyran **28**. Thus, the conjugated 1,3-diene system of **27** appears to give rise to a stabilization energy of 7 kJ mol^{−1}. On the other hand, the 1,3-diene system of 1,3-cyclohexadiene seems to be devoid of conjugative stabilization, as shown by the similar enthalpies of formation of the 1,3- and 1,4-cyclohexadienes. This view is supported by the total enthalpy of hydrogenation, −229 kJ mol^{−1}, of 1,3-cyclohexadiene **51** to cyclohexane **55**, exceeding that, −221 kJ mol^{−1}, of 2*H*-pyran to tetrahydropyran by −8 kJ mol^{−1}.

The enthalpies of formation of 1,4-dioxin **31** (−82.7), 1,4-dioxene **32** (−213.3), and 1,4-dioxane **73** (−316.5 kJ mol^{−1}) show the hydrogenation of **31** to **32** to be markedly (−131 kJ mol^{−1}) exothermic, no doubt because of the antiaromatic character of the former, whereas only 103 kJ mol^{−1} of heat is released in the hydrogenation of **32** to **73**. The latter figure is comparable to that (106 kJ mol^{−1}) evolved in the hydrogenation of 3,4-dihydro-2*H*-pyran **28** to tetrahydropyran **70**. Noteworthy, hydrogenation of the C=C bond of the 5-membered 1,3-dioxole **30** leads to evolution of ca. 118 kJ mol^{−1} of heat, 11 kJ mol^{−1} more than hydrogenation of that, 107 kJ mol^{−1}, of 2,3-dihydrofuran **24**. For comparison, gas-phase hydrogenations (at 355 K) of cyclohexene **53** and cyclopentene **48** are exothermic by −119.6 and −112.6 kJ mol^{−1}, respectively,^[27,28] i.e., hydrogenation of the 6-membered olefin is 7 kJ mol^{−1} more exothermic

than that of the 5-membered one. This is in marked contrast to the properties of the respective ethers containing an —O—C=C—O— moiety: hydrogenation of 1,4-dioxene **32** to 1,4-dioxane **73** is 15 kJ mol^{−1} less exothermic than that of 1,3-dioxole **30** to 1,3-dioxolane **72**. The unsaturated ethers, contrary to olefins, have a possibility for stabilizing p-π interaction, but it is impossible in cyclic compounds to separate the contribution of this stabilizing agent from molecule destabilizing agents such as ring strain. Thus the origin of the marked difference between the enthalpies of hydrogenation of the cyclic olefins and cyclic vinyl ethers discussed above cannot be settled.

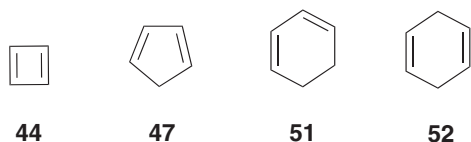
Finally, the enthalpy of hydrogenation, −112 kJ mol^{−1}, of 1,3-diox-4-ene **33** to 1,3-dioxane **73** reveals a reaction about 6 kJ mol^{−1} more exothermic than the related reaction 3,4-dihydro-2*H*-pyran **28** → tetrahydropyran **70**. The higher exothermicity of the former reaction may possibly be ascribed to the additional O atom in the ring, which through its electron-withdrawing effect decreases the strength of p-π conjugation in the reactant, relative to that in **28**. Alternatively, since 1,3-diox-4-ene **33** contains an allyl ether moiety (—O—CH₂—C=C) in place of the —CH₂CH₂C=C moiety of **28**, hydrogenation of the former is expected to be more exothermic than that of the latter, cf. (from the data of Table 2) the enthalpies of hydrogenation of −130 and −123 kJ mol^{−1} of allyl methyl ether **20** and propene **36**, respectively. The latter explanation is in almost quantitative agreement with the data observed. This, however, may be fortuitous since the enthalpy of hydrogenation is affected by the difference in strain between the product and the reactant, and it seems unlikely that this difference is the same in the two pairs of compounds compared.

Cyclic dienes

The mean computational enthalpy of formation, 428 kJ mol^{−1} (Table 2), of cyclobutadiene **44** (Scheme 2) is in good agreement with the experimental one.^[29] The same holds for 1,3-cyclopentadiene **47**, 1,3-cyclohexadiene **51**, and 1,4-cyclohexadiene **52**. Good agreement between computational and experimental data is also found for cyclic mono-olefins and saturated cyclanes. From the data of Table 2 the enthalpies of hydrogenation of cyclobutadiene **44**, 1,3-cyclopentadiene **47**, and 1,3-cyclohexadiene **51** to the respective mono-olefins are calculated to be −269, −100, and −112 kJ mol^{−1}, respectively, illustrating the high strain in **44**. For comparison, the enthalpies of hydrogenation of cyclobutene **45**, cyclopentene **48**, and cyclohexene **53** to the respective saturated cyclanes are −130, −110, and −118 kJ mol^{−1}, respectively.

SUMMARY

The gas-phase enthalpies of formation of a number of both acyclic and cyclic olefinic ethers, mainly α,β-unsaturated (vinyl) ethers, have been estimated by G3(MP2)//B3LYP calculations, and compared with experimental data whenever possible. In most cases, agreement between the computational and experimental data is good, sometimes even excellent. For the unsaturated ethers **3–33** the average absolute deviation |Δ| between experiment and the mean (atomization and isodesmic) computational enthalpies of formation was obtained as 2.3 kJ mol^{−1} with a standard deviation σ_{n−1} = 2.2 kJ mol^{−1}. A marked error was found in the experimental enthalpy of formation of



Scheme 2. The cyclic dienes studied in this work.

2-chloroethyl ethyl ether, used in this work as a reagent for determination of the enthalpy of formation of 2-chloroethyl vinyl ether by an isodesmic reaction. Moreover, significant errors have also been found in the literature values for the computational (B3LYP/6-311G**) enthalpies of formation of several Me-substituted derivatives of methyl vinyl ether. The present computational method, besides providing acceptable enthalpies of formation of unsaturated ethers, was also found to give accurate $\Delta_f H_m^0$ (g) values for cyclic mono- and dienes. In summary, the G3(MP2)//B3LYP computational method turned out to be a valuable tool for investigating the energetics of olefinic ethers and hydrocarbons.

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REFERENCES

- [1] J. B. Pedley, R. D. Naylor, S. P. Kirby, *Thermochemical Data of Organic Compounds* (2nd edn), Chapman and Hall, London, **1986**.
- [2] W. V. Steele, R. D. Chirico, A. Nguyen, I. A. Hossenlopp, N. K. Smith, (1989), *Determination of Some Pure Compound Ideal-Gas Enthalpies of Formation*. NTIS Report No. DE-89000748. DOE Fossil Energy, Bartlesville Project Office, OK.
- [3] W. V. Steele, R. D. Chirico, A. Nguyen, I. A. Hossenlopp, N. K. Smith, *AIChE Symp. Ser.* **1989**, *85*, 140–162.
- [4] J. Hine, K. Arata, *Bull. Chem. Soc. Japan* **1976**, *49*, 3089–3092.
- [5] G. da Silva, C.-H. Kim, J. W. Bozzelli, *J. Phys. Chem. A* **2006**, *110*, 7925–7934.
- [6] N. Sebbar, H. Bockhorn, J. W. Bozzelli, *Phys. Chem. Chem. Phys.* **2002**, *4*, 3691–3703.
- [7] E. Taskinen, A. Taskinen, *J. Phys. Org. Chem.* **2008**, *21*, 449–456.
- [8] J. W. Ochterski, *Thermochemistry in Gaussian, Gaussian Technical Support Information*, **2006**.
- [9] A. G. Baboul, L. A. Curtiss, P. C. Redfern, K. Raghavachari, *J. Chem. Phys.* **1999**, *110*, 7650–7657.
- [10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, **2004**.
- [11] J. L. Holmes, F. P. Lossing, *J. Am. Chem. Soc.* **1982**, *104*, 2648–2649.
- [12] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, W. E. Vaughan, *J. Am. Chem. Soc.* **1938**, *60*, 440–450.
- [13] I. S. Ignatyev, M. Montejo, T. Sundius, F. P. Urena, J. J. L. Gonzalez, *Chem. Phys.* **2007**, *333*, 148–156.
- [14] E. Taskinen, *J. Chem. Thermodyn.* **1974**, *6*, 271–280.
- [15] E. Taskinen, *Tetrahedron* **1994**, *50*, 795–806.
- [16] C. T. Mortimer, *Reaction Heats and Bond Strengths*, Pergamon Press, Oxford, **1962**.
- [17] E. Taskinen, *Relative Stabilities and the Kinetics of Hydrolysis of Endo-Exo Isomeric Five- and Six-Membered Cyclic Vinyl Ethers*. *Annales Academiae Scientiarum Fennicae, Series A2: Chemica*, No. 163, **1972**.
- [18] E. Taskinen, *J. Chem. Thermodyn.* **1973**, *5*, 783–791.
- [19] E. Taskinen, P. Liukas, *Acta Chem. Scand.* **1974**, *B28*, 114–120.
- [20] E. Taskinen, *J. Chem. Thermodyn.* **1974**, *6*, 345–353.
- [21] E. Taskinen, *Struct. Chem.* **2000**, *11*, 185–191.
- [22] N. L. Allinger, J. A. Glaser, H. E. Davis, D. W. Rogers, *J. Org. Chem.* **1981**, *46*, 658–661.
- [23] E. Taskinen, T. Alanko, J. F. Liebman, *Struct. Chem.* **2006**, *17*, 323–326.
- [24] E. Taskinen, K. Nummelin, *J. Org. Chem.* **1985**, *50*, 4844–4847.
- [25] K. Sohlberg, B. L. Baker, S. P. Leary, N. L. Owen, J. C. Facelli, B. A. Trofimov, *J. Mol. Struct.* **1995**, *354*, 55–69.
- [26] N. L. Owen, G. O. Sørensen, *J. Phys. Chem.* **1979**, *83*, 1483–1488.
- [27] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, W. E. Vaughan, *J. Am. Chem. Soc.* **1936**, *58*, 137–145.
- [28] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, *J. Am. Chem. Soc.* **1937**, *59*, 831–841.
- [29] A. Fattahi, L. Lis, X. Tian, S. R. Kass, *Angew. Chem. Int. Ed.* **2006**, *45*, 4984–4988.
- [30] K. G. Sharonov, A. M. Rozhnov, A. V. Koro'kov, S. Y. Karaseva, *J. Chem. Thermodyn.* **1995**, *27*, 751–753.
- [31] M. Iborra, J. F. Izquierdo, J. Tejero, F. J. Cunill, *J. Chem. Eng. Data* **1989**, *34*, 1–5.