JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 1–4 (1995)

# RELATIVE THERMODYNAMIC STABILITIES OF 2-(METHOXYMETHYLENE)TETRAHYDROFURAN AND 5-METHOXYMETHYL-2,3-DIHYDROFURAN

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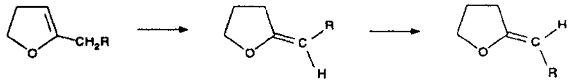
**The relative thermodynamic stabilities of the title compounds were determined by iodine catalyzed chemical equilibration in cyclohexane solution. The main point of interest was a determination of the thermodynamic stability of the –O–C=C–O– moiety found in the exocyclic isomers, i.e. the stabilizing effect of a MeO group on the olefinic linkage of 2-methylenetetrahydrofuran. All three isomeric compounds have essentially similar enthalpy values, which, in comparison with some previous thermodynamic data, shows that the double bond stabilization energy of the MeO group in the exo isomers is only *ca* 3 kJ mol$^{-1}$. The entropy difference between the geometrical isomers is negligible, whereas the endo isomer is favoured by an entropy contribution of *ca* 9 J K$^{-1}$ mol$^{-1}$.**

## INTRODUCTION

5-Methyl-2,3-dihydrofuran and 2-methylenetetrahydrofuran (**1a** and **1b**, respectively) are cyclic vinyl ethers with double bond *endo–exo* isomerism. The *endo* form **1a** has a lower enthalpy by $4{\cdot}7 \pm 0{\cdot}3$ kJ mol$^{-1}$ in diethyl ether solution at 298 K,[1] whereas 1-methylcyclopentene is $16{\cdot}2$ kJ mol$^{-1}$ more stable than methylenecyclopentane in acetic acid solution at 298 K.[2] A major part of the markedly lower difference in thermochemical stability between the *endo–exo* isomeric vinyl ethers than between the corresponding carbocyclic olefins may be explained as follows. In the *exo* → *endo* reaction, the number of alkyl substituents attached to the C=C system increases by one. Since alkyl groups do not stabilize the C=C bond of vinyl ethers as efficiently as they stabilize that of ordinary olefins,[1,3] the *exo* → *endo* reaction is energetically more favourable for the olefins. The weak stabilizing effect of a methyl group on vinyl ethers may be seen from the thermodynamics of the reactions **1a** → **1b** and **2a** → **2b**: for the latter $\Delta H^\circ = 1{\cdot}9 \pm 0{\cdot}2$ kJ mol$^{-1}$ (cyclohexane solution, 298 K),[3] i.e. only 3 kJ mol$^{-1}$ less than that for the former, whereas the corresponding difference is 11 kJ mol$^{-1}$ in related olefins.[2]

**1a** **1b**



**a** **b** **c**

**2**: R = Me
**3**: R = OMe

The primary aim of the present work was to study the thermodynamics of *endo–exo* isomerism in compounds **3a–c** in which the C=C moiety of the *exo* isomers is bonded to a MeO group, thus forming a 1,2-dialkoxyethene (–O–C=C–O–) system. Also of interest was the difference in thermodynamic stability between the geometrical isomers **3b** and **3c**. Thus the relative equilibrium concentrations of **3a–c** were determined in cyclohexane solution at several temperatures. From the equilibrium data the thermodynamic parameters $\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$ at $298{\cdot}15$ K for each isomerization reaction between the title compounds were evaluated.

## RESULTS AND DISCUSSION

The mean values of the relative equilibrium concentrations of the title ethers at various temperatures are given in Table 1. From these data, the values of the equilibrium constant $K$ for each isomerization reaction were calculated, followed by linear least-squares treatment of

CCC 0894–3230/95/010004–04

*Received 10 March 1994*
*Revised 18 August 1994*

Table 1. Values of the mean percentage equilibrium concentrations of **3a–c** in cyclohexane solution at various temperatures, together with the thermodynamic parameters of isomerization at 298·15 K[a]

| | Concentration (%) | | |
|---|---|---|---|
| Temperature (°C) | **3a** | **3b** | **3c** |
| 25 | 60·7 | 19·5 | 19·8 |
| 40 | 61·3 | 19·0 | 19·7 |
| 60 | 61·3 | 19·5 | 19·2 |
| 80 | 62·0 | 19·6 | 18·4 |
| 100 | 61·5 | 20·0 | 19·5 |
| 120 | 61·1 | 20·1 | 18·8 |
| 150 | 60·1 | 19·9 | 20·0 |
| 170 | 60·3 | 19·9 | 19·8 |
| Reaction | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J K$^{-1}$ mol$^{-1}$) |
| **3a** → **3b** | 2·88 ± 0·05 | 0·4 ± 0·3 | −8·3 ± 0·7 |
| **3b** → **3c** | −0·01 ± 0·12 | −0·3 ± 0·6 | −0·9 ± 1·7 |
| **3a** → **3c** | 2·87 ± 0·05 | 0·1 ± 0·7 | −9·2 ± 1·9 |

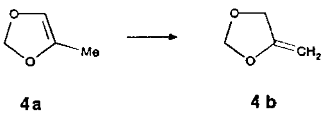
[a] The errors are twice the standard errors.

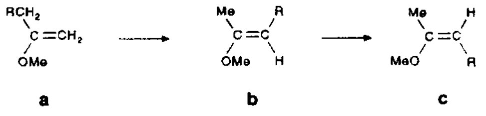
ln $K$ vs $T^{-1}$ according to the van't Hoff equation to give the values of the thermodynamic parameters of isomerization at 298·15 K (Table 1).

The *endo* isomer **3a** is the most abundant species at all temperatures covered by the measurements. Moreover, both geometrical isomers have a content of *ca* 20% in the equilibrium mixtures. Remarkably, the relative composition remains essentially unchanged throughout the temperature range investigated, which shows that the three isomeric species have essentially equal enthalpy values. Thus the higher thermodynamic stability of the *endo* isomer is an entropy effect.

In comparison with the enthalpy change for **1a** → **1b**, 4·7 kJ mol$^{-1}$, the value of $\Delta H^\circ$ for **3a** → **3b** (0·4 kJ mol$^{-1}$) suggests that the MeO substituent of **3b** has a stabilizing effect of *ca* 4·3 kJ mol$^{-1}$ on the olefinic system. However, part of this effect probably arises from an attractive *cis* interaction between the O atom of the MeO group and the H atoms of the 3-methylene group of the tetrahydrofuran ring. Assuming this interaction to be equal to the stabilizing *cis* interaction energy of about 1·5 kJ mol$^{-1}$ between a MeO group and an Et group in an olefinic system,[4] the true double bond stabilization energy of the MeO group in **3b** is thus obtained as *ca* 3 kJ mol$^{-1}$.

The figure obtained is far from the value of 22 kJ mol$^{-1}$ usually ascribed to the double bond stabilization energy of a MeO group.[5] However, we found many years ago[6] that a 1,2-dialkoxyethene system is much less stable than expected assuming additivity of the double bond stabilization energies of alkoxy groups. This was shown by an enthalpy change of −1·1 kJ mol$^{-1}$ in dioxane solution[6] for **4a** → **4b**: in comparison with the $\Delta H^\circ$ value of +4·7 kJ mol$^{-1}$ for **1a** → **1b** the *endo* isomer **4a** containing the –O–C=C–O– system is thus destabilized by 5.8 kJ mol$^{-1}$ relative to **1a**. The same phenomenon was also encountered in the reaction **5a** → **5b**, for which $\Delta H^\circ = 0{\cdot}6 \pm 0{\cdot}4$ kJ mol$^{-1}$ (cyclohexane solution, 298 K).[7] Taking into account the presence of a stabilizing Me...OMe *cis* interaction energy, about 2.9 kJ mol$^{-1}$,[4] in the reaction product, it follows that in **5b** the MeO group attached to C-$\beta$ of the vinyl moiety has an actual double bond *destabilizing* effect of *ca* 3·5 kJ mol$^{-1}$.





**5**: R = OMe

**6**: R = Me

Summarizing, a single MeO substituent at the C=C bond of simple olefins is usually ascribed a strong stabilization energy of 22 kJ mol$^{-1}$, whereas the stabilization is only about 3 kJ mol$^{-1}$ in **3b**, and a destabilization of *ca* 3·5 kJ mol$^{-1}$ is found in **5b**. How are these widely varying stabilization energies explainable? Obviously, the clue to these findings arises from the phenomenon of p–$\pi$ conjugation in alkoxyolefins:

$$-\mathrm{O}-\mathrm{C}{=}\mathrm{C} \leftrightarrow -\overset{+}{\mathrm{O}}{=}\mathrm{C}-\overset{-}{\mathrm{C}}$$

In monoalkoxyethenes, under favourable mutual steric orientation of the lone pair orbitals on oxygen and the $\pi$ orbital of the C=C bond, the stabilization due to p–$\pi$ conjugation is strong. However, in 1,2-dialkoxyethenes the conjugative effects of the two oxygen atoms tend to push the $\pi$ electrons of the olefinic linkage in opposite directions. Thus, if both oxygen atoms have an equal chance of conjugation with the C=C bond, as in symmetrically substituted 1,2-dialkoxyethenes, the stabilizing conjugative effects of the two oxygen atoms are partially cancelled so that the system is no more stable, possibly even less stable, than a monoalkoxysubstituted ethene. On the other hand, if we consider a monoalkoxyolefin in which the O atom, for steric or electronic reasons, is unable to conjugate efficiently with the C=C bond, the introduction of a second alkoxy substituent at the neighbouring olefinic carbon may give rise to a marked increase in stability if the substituent introduced has a good chance for conjugation with the olefinic linkage. Accordingly, the stabilization brought about by the second alkoxy group in 1,2-dialkoxyethenes is likely to be highly dependent on the stabilization due to the first alkoxy group.

Seemingly, in **3b** and **5b** the MeO groups attached to C-$\beta$ of the vinyl group have equal chances of p–$\pi$ conjugation with the olefinic linkage. However, since the MeO group of **3b** leads to a slight increase in stability whereas the reverse is true for that of **5b**, it appears that the ring oxygen of **3b** conjugates less efficiently with the C=C bond than the MeO group attached to C-$\alpha$ of **5b**. This is reasonable since in **5b** the MeO group attached to C–$\alpha$ may assume the planar *s-cis* conformation with a maximum p–$\pi$ overlap whereas the mutual orientation of the ring oxygen p orbitals and the adjacent $\pi$ orbital in **3b** is less favourable for conjugation owing to the probable non-planar character of the five-membered ring (cf. the non-planar structures of methylenecyclopentane[8] and $\gamma$-butyrolactone[9]).

Accordingly, the change in thermodynamic stability on introduction of a second alkoxy group to a monoalkoxyolefin may serve as a probe of the strength of p–$\pi$ conjugation in the original compound. Of course, the stabilization due to the second alkoxy group depends also on *its* ability to conjugate with the C=C bond. Considering **3b** and **5b**, it appears that in each compound the MeO group on C-$\beta$ of the vinyl moiety may similarly assume either a planar *s-trans* or a non-planar *gauche* structure (cf. the discussion of the conformations of methyl vinyl ether in Ref. 10); thus the MeO groups in question are likely to have equal steric possibilities for conjugation with the olefinic system.

The value of $\Delta S^\circ$ for **3a** → **3b**, $-8{\cdot}3 \pm 0{\cdot}7$ J K$^{-1}$ mol$^{-1}$, is in close agreement with the reaction entropies of $-8{\cdot}0 \pm 1{\cdot}0$, $-7{\cdot}0 \pm 0{\cdot}4$ and $-9{\cdot}6 \pm 1{\cdot}3$ J K$^{-1}$ mol$^{-1}$ for the **1a** → **1b**,[1] **2a** → **2b**[3] and **4a** → **4b**[6] reactions, respectively. Note especially that the values of $\Delta S^\circ$ for these *endo* → *exo* isomerization reactions are essentially independent of whether the group attached to C-$\beta$ of the *exo* isomer is a MeO group (**3b**) or a Me group (**2b**). However, for **5a** → **5b** the entropy change, $3{\cdot}2 \pm 1{\cdot}0$ J K$^{-1}$ mol$^{-1}$ in cyclohexane solution,[7] is significantly more positive than that, $-4{\cdot}7 \pm 0{\cdot}7$ J K$^{-1}$ mol$^{-1}$ (also in cyclohexane solution),[11] for the related reaction **6a** → **6b**. The origin of the marked difference in these reaction entropies is obscure.

The enthalpy difference between the geometrical isomers **3b** and **3c** is negligible, which suggests that the *cis* interaction energies between the MeO group and the respective ring moieties (a $CH_2$ group and an O atom) are similar (unless the thermodynamic stability of the O–C=C–O system is inherently dependent on its configuration). For comparison, the reaction **5b** → **5c** is endothermic by $5{\cdot}6 \pm 0{\cdot}8$ kJ mol$^{-1}$.[7] The positive enthalpy change in this reaction is understandable in view of the probable conformational change experienced by the MeO group bonded to C-$\alpha$: the dominating planar *s-cis* conformer of the reactant is no more feasible for the product, owing to the steric requirements of the other MeO group in the *cis* position. The reduction in molecular stability due to decreased conjugation in the MeO–$C_\alpha$=$C_\beta$ moiety is not fully compensated for by increased conjugation in the $C_\alpha$=$C_\beta$–OMe group, since energetically this change may be considered to correspond roughly to rotation of the *s-cis* conformer of methyl vinyl ether to the second stable (*gauche* or *s-trans*) conformer, which requires *ca* 7 kJ mol$^{-1}$ of energy in the gas phase.[10]

The negligible entropy change in **3b** → **3c** agrees with that for **2b** → **2c**, $-0{\cdot}7 \pm 0{\cdot}7$ J K$^{-1}$ mol$^{-1}$.[3] This suggests that the former reaction involves no change in the number of conformers available for the MeO group. On the other hand, the entropy of **5c** is $5{\cdot}2 \pm 2{\cdot}5$ J K$^{-1}$ mol$^{-1}$ higher than that of **5b**,[7] which points to a presence of additional conformers of the MeO–$C_\alpha$=$C_\beta$ moiety in **5c**, in addition to those present in the reactant **5b**. For comparison, the reaction **6b** → **6c** is also accompanied by a marked increase in entropy: $\Delta S^\circ = 13{\cdot}9 \pm 0{\cdot}8$ J K$^{-1}$ mol$^{-1}$.[11]

In conclusion, it appears that in 1,2-dialkoxyethenes and related compounds, the presence of two O atoms at vicinal olefinic carbons does not lead to a particularly stable system in the thermodynamic sense. On the contrary, the thermodynamic stability of this system is roughly comparable to that of a monoalkoxysubstituted ethene. The two oxygen atoms are competing for conjugation with the $\pi$ electrons of the olefinic linkage: in a symmetrically substituted ethene the two conjugative forces are in balance, whereas in an unsymmetrically substituted ethene the two O atoms conjugate with different efficiencies with the olefinic system.

## EXPERIMENTAL

The title compounds were prepared by pyrolysis of tetrahydrofurfural dimethyl acetal [b.p. 63–64 °C/11 Torr (1 Torr = 133·3 Pa)] over $Al_2O_3$ at 330 °C. This acetal was obtained from furfural dimethyl acetal (b.p. 56 °C/10 Torr) in a yield of >90% by hydrogenation over Raney nickel in MeOH solution (100 atm, 100 °C). As a major side-product of the hydrogenation reaction, the saturated ether 2-(methoxymethyl)tetrahydrofuran (b.p. 51 °C/20 Torr) was formed; its relative amount could be reduced to a few per cent by adding two drops of diethylamine to the reaction mixture (150 ml; substrate to solvent volume ratio = 2 : 1). The isomer mixture obtained from the pyrolysis reaction typically consisted of 64% **3a**, 20% **3b** and 16% **3c**. In addition, variable amounts of the unchanged reagent were recovered. The reaction product was further fractionated by distillation. The pure *endo* isomer **3a** was collected at 77 °C/54 Torr, a 70 : 30 mixture of **3a** and **3b** at 78–79 °C/54 Torr and 95% pure **3c** at 83 °C/54 Torr (pure **3b** could not be obtained, owing to its similar volatility to **3a**). The total yield of the pyrolysis reaction was *ca* 30%.

*$^{1}H$ NMR (399·8 MHz, $CDCl_3$, TMS).* **3a**: 4·38 (tr, 9·5 Hz, 2H), 2·64 (m, 2H), 4·90 (m, 1H), 3·92 (m, 2H), 3·36 (s, 3H). **3b**: 4·11 (tr, 6·7 Hz, 2H), 1·98 (m, 2H), 2·51 (tr, 7·1 Hz, 2H), 6·02 (tr, 2·2 Hz, 1H), 3·48 (s, 3H). **3c**: 4·11 (tr, 6·7 Hz, 2H), 1·98 (m, 2H), 2·46 (tr, 7·3 Hz, 2H), 5·32 (tr, 1·5 Hz, 1H), 3·56 (s, 3H). Tetrahydrofurfural dimethyl acetal: 3·73 (m, 1H), 3·81 (m, 1H), 3·91 (m, 1H), 4·17 (d, 5·8 Hz, 1H), 3·37 (s, 3H), 3·38 (s, 3H), 1·7–2·0 (m, 4H).

*$^{13}C$ NMR (100·5 MHz, $CDCl_3$, TMS).* **3a**: 70·2 (C-2), 29·8 (C-3), 98·3 (C-4), 154·6 (C-5), 67·1 ($CH_2$), 58·3 (Me). **3b**: 147·0 (C-2), 23·9 (C-3), 24·6 (C-4), 70·3 (C-5), 124·7 (CH), 59·3 (Me). **3c**: 140·4 (C-2), 25·7 (C-3), 25·1 (C-4), 70·7 (C-5), 121·5 (CH), 60·0 (Me).

*Equilibration experiments.* The equilibration experiments were carried out in cyclohexane solution (*ca* 20 vol.% of substrate) with $I_2$ as catalyst (0·01 M).[12] After destroying the catalyst by addition of diethylamine, the equilibrium mixtures were analysed by GLC (50 m XE-60 capillary column at 100 °C; retention times 6·2, 7·0 and 13·7 min for **3a**, **3b** and **3c**, respectively). Both **3a** and **3c** were used as the initial reagents in the equilibration experiments; the same equilibrium composition was readily obtained from both directions.

*Configurational assignment.* The configurations of the geometrical isomers were deduced from their NMR spectra and other data as follows. The chemical shift of the olefinic proton of the more volatile isomer was found at $\delta$ 6·02, 0·70 ppm downfield from that of the other geometrical isomer; the higher shift value for the more volatile isomer suggests a *cis* juxtaposition of the olefinic proton and ring oxygen atom. The values of the allylic coupling constant of the olefinic proton with the ring 3-$CH_2$ group were 2·2 and 1·5 Hz for the more volatile and less volatile compounds, respectively; the larger coupling constant points to a *trans* allylic coupling. Further, the $^{13}C$ NMR chemical shifts of the olefinic carbons are several ppm higher for the more volatile geometrical isomer, in agreement with related data for the *E* form of several 1,2-dialkoxyethenes for which the configuration can be determined unequivocally from the value of the coupling constant between the olefinic protons.[13] Finally, the lower boiling point and the markedly shorter retention time of the more volatile compound through the XE-60 column in the GLC analysis suggest a significantly smaller polar character for this isomer; this agrees with a *trans* juxtaposition of the two O atoms.

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