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THERMODYNAMICS OF VINYL ETHERS—XVII†

THERMODYNAMIC STABILITY OF 1,2-DIALKOXYETHYLENES

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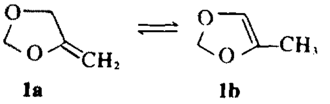
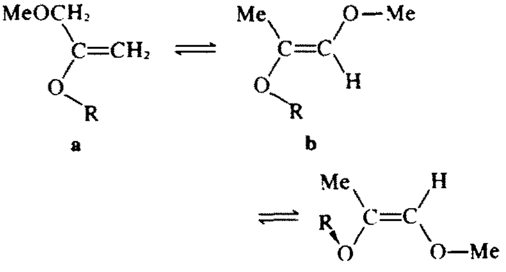
Abstract—The relative thermodynamic stability of the monoalkoxy- and 1,2-dialkoxyethylene systems [O–C=C–H(C) and O–C=C–O, respectively] has been studied by chemical equilibration of suitable isomeric compounds. Although a single alkoxy substituent stabilizes the C=C bond by about 25 kJ mol^{-1}, the 1,2-dialkoxyethylene system is no more stable than the monoalkoxyethylene ("ordinary" vinyl ether) system. On the contrary, the MeO–C=C–OMe system was found to be about 4 kJ mol^{-1} (on an enthalpy basis) less stable than the system MeO–C=C–H.

The standard enthalpies of hydrogenation (gas phase, 355 K) of ethylene,[1] 1-butene[2] and (E)-2-butene[2] to the corresponding saturated hydrocarbons are −137.3, −126.9 and −115.6 kJ mol^{-1}, respectively. These examples show that (in the absence of mutual steric interactions between the substituents) the stabilizing effect of alkyl groups on a C=C bond is additive and amounts to 10–11 kJ mol^{-1} per alkyl group. In ethyl vinyl ether (EtOCH=CH$_2$) the ethoxy substituent lowers the standard enthalpy of hydrogenation of the ethylenic linkage to −111.9 kJ mol^{-1},[3] i.e. the stabilizing effect of the ethoxy group is about 25 kJ mol^{-1} (14–15 kJ mol^{-1} more than that of an alkyl group). The higher stabilizing ability of the ethoxy group is to be ascribed to the $p-\pi$ resonance between the lone electron pairs of the oxygen atom and the π electrons of the C=C bond.

Now it may be asked whether the stabilizing effect of alkoxy groups on a C=C bond is additive, too, especially if we are dealing with a 1,2-dialkoxysubstituted ethylene. This problem was previously encountered in a study of the relative stabilities of 4-methylene-1,3-dioxolane **1a** and 4-methyl-1,3-dioxole **1b**.[4] The results suggested that the stability of the O–C=C–O system in **1b** is in fact lower than that of a β-alkylsubstituted vinyl ether system (O–C=C–C). However, since the relative stability of **1a** and **1b** is also affected by ring strain effects, hard to estimate for each isomer, the relative stability of the two systems in question has now been studied in acyclic compounds and in simple cyclic compounds where both isomers at equilibrium can be assumed to have equal ring strain energies. The following equilibria have been investigated.

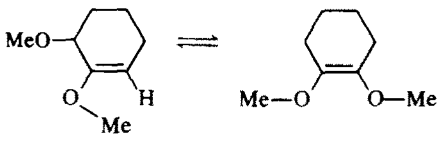


1a **1b**

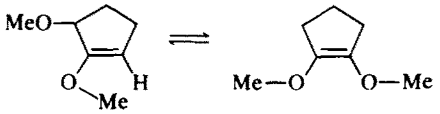


a **b** **c**

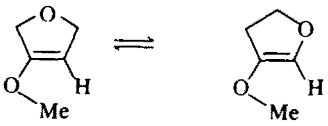
2, R = Me; **3**, R = CH(Et)$_2$



4a **4b**



5a **5b**



6a **6b**

RESULTS AND DISCUSSION

The results of the equilibration experiments are given in Table 1. The essential feature of reaction **2a**→**2b** is the substitution of a methoxy group for one of the β hydrogen atoms of the vinyl group. An attractive cis interaction of about 3 kJ mol^{-1} can be assumed to exist between the Me and MeO groups of **2b** (this figure is obtained from the difference in the standard enthalpies of gaseous (E)- and (Z)-t-butyl propenyl ether[5]). Despite this stabilizing interaction in **2b** the enthalpy change for the reaction in question is slightly positive (=0.6 kJ mol^{-1}). Thus the system MeO–C=C–OMe is in fact about $3+0.6=3.6$ kJ mol^{-1} less stable than the system MeO–C=C–H, i.e. the second methoxy group in the former system leads to a destabilization of about 4 kJ mol^{-1} (relative to a hydrogen atom as the β substituent). Similarly, in reaction **6a**→**6b** the system O–C=C–C is replaced by the system O–C=C–O, and since the stabilizing effect of a β alkyl group in vinyl ethers has been shown[6,7] to be about 4.3 kJ mol^{-1}, an enthalpy change of about $3.6+4.3\cong 8$ kJ mol^{-1} might be

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†Part XVI: E. Taskinen and H. Kalva, *Finn. Chem. Lett.* 208 (1975).

Table 1. Thermodynamic data for the reactions studied in this work. Solvent: cyclohexane, temperature 298.15 K. The errors are twice the standard errors unless otherwise noted.

Reaction	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
2a → 2b^{a}	-0.32 ± 0.05	0.6 ± 0.4	3.2 ± 1.0
2b → 2c	4.04 ± 0.10	5.6 ± 0.8	5.2 ± 2.5
2a → 2c	3.72 ± 0.15	6.2 ± 1.1	8.4 ± 3.5
3a → 3b^{a}	-0.32 ± 0.10	0 ± 1	1 ± 3
3b → 3c^{a}	0.55 ± 0.10	0 ± 1	-2 ± 3
3a → 3c^{a}	0.24 ± 0.10	0 ± 1	-1 ± 3
4a → 4b	7.75 ± 0.03	11.4 ± 0.2	12.1 ± 0.7
5a → 5b	9.81 ± 0.04	11.9 ± 0.2	6.9 ± 0.6
6a → 6b	5.13 ± 0.07	7.4 ± 0.4	7.6 ± 1.1

^{a}Estimated errors.

predicted for **6a** → **6b**, in agreement with the experimental value. The agreement shows that the ring strain energies of the 2,5-dihydrofuran (in **6a**) and 2,3-dihydrofuran (in **6b**) rings are equal, in line with the corresponding sulfur compounds.[8] The data of the present study thus confirm that the stabilizing effect of alkoxy groups on a C=C bond is not additive.

The values of ΔH° for reactions **4a** → **4b** and **5a** → **5b** involving a transfer of a MeO group to a cis position with respect to the other MeO group are unexpectedly positive in comparison with that for the related reaction **2a** → **2c**. Previously,[9] the reaction 6 - chloro - 1 - methoxycyclohexene → 2 - chloro - 1 - methoxy - cyclohexene, which is analogous to **4a** → **4b**, was studied and the value of ΔH° was even in this case more positive than could be expected. It is possible that relatively strong attractive (stabilizing) forces exist between the two methoxy groups in **4a** and **5a** as well as between the chlorine atom and the methoxy group of 6 - chloro - 1 - methoxycyclohexene.

By comparing the values of the thermodynamic parameters for equilibria **2a** → **2c** in the cases R = Me and R = CH(Et)$_2$, it is seen that the effect of the bulkier alkoxy group is as found previously for reactions $MeCH_2C(OR){=}CH_2 \rightarrow MeC(OR){=}CHMe$[10] and $ClCH_2C(OR){=}CH_2 \rightarrow MeC(OR){=}CHCl$,[9] i.e. bulky alkoxy groups favor the relative stability of the Z isomer.

In considering the values of ΔS° for **4a** → **4b** and **5a** → **5b** it should be noted that the **a** isomers have an asymmetric carbon atom and, in addition, they are statistically favored at equilibrium by a factor of 2. To eliminate these effects, the term $2 R \ln 2 = 11.5$ J K^{-1} mol^{-1} should be added to the experimental ΔS°-values.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded in CCl_4 with TMS as internal reference. The chemical shifts are given in τ value (ppm) and the coupling constants in Hz. The spectra were recorded on a mixture of isomers because of experimental difficulties in separating the isomers.

Preparation of **2**. Methoxyacetonitrile[11] was treated with methylmagnesium iodide in diethyl ether[12] to give methoxymethyl methyl ketone b.p. 388–389 K at 100.0 kPa (lit.[12] 387.8 K at 99.4 kPa). The yield was 20%. The keto ether was converted[13] into its dimethyl acetal (b.p. 406–409 K at 100.0 kPa, yield 80%), and the acetal was decomposed to methanol and a mixture of the three isomers (42% **2a**, 37% **2b**, and 21% **2c**, b.p. 382–384 K at 100.0 kPa) by fractionation from a small amount of p-toluenesulfonic acid. The yield was 35%. NMR: **2a**: 6.73 ($\underline{Me}OCH_2$), 6.47 ($\underline{Me}OC{=}C$), 6.28 (OCH_2), 6.02 (H–C=C, trans to oxygen, J_{gem} 1.8), 5.93 (H–C=C, cis to oxygen); **2b**: 8.28 (Me–C=C, $J_{allylic}$ 1.0), 6.61 and 6.59 (2 MeO), 4.41 (H–C=C); **2c**: 8.47 (Me–C=C, $J_{allylic}$ 1.0), 6.57 and 6.35 (2 MeO), 4.84 (H–C=C).

Preparation of **3**. Equimolar amounts of methoxyacetone dimethyl acetal and 3-pentanol were heated in the presence of toluene p-sulfonic acid in a distillation apparatus. After the evolution of methanol ceased, a 70% yield of **3** (the three isomers were present in practically equal amounts, b.p. 359–363 K at 5.2 kPa) could be obtained by fractional distillation. NMR: **3a**: 6.74 (MeO), 6.31 (OCH_2), 6.11 (H–C=C, trans to oxygen), 5.94 (H–C=C, cis to oxygen), 9.1 (2 $\underline{Me}$–CH_2), about 8.5 (2 C–CH_2–C); **3b**: 8.31 (Me–C=C, $J_{allylic}$ 1.1), 6.60 (MeO), 4.31 (H–C=C), the signals of the 3-pentoxy group as in **3a**; **3c**: 8.48 (Me–C=C, $J_{allylic}$ 1.3), 6.60 (MeO), 4.89 (H–C=C), the signals of the 3-pentoxy group as in **3a**.

Preparation of **4**. Trans-2-Methoxycyclohexanol, prepared from cyclohexene oxide (Aldrich) in 80% yield,[14] was oxidized to 2-methoxycyclohexanone as described by Adkins *et al.*[15] The yield of the product, b.p. 337–338 K at 1.2 kPa (lit.[15] 331–332 K at 1.1 kPa), was 36%. The ketone was then converted into **4** (90% **4a**, 10% **4b**, b.p. 341 K at 1.2 kPa, yield 30%) as described above for **2**. NMR: **4a**: 6.69 (MeO–C(sp^3)), 6.55 (MeO–C(sp^2)), 5.38 (H–C=C, J_{vic} 3.9), 7.8–8.7 (ring protons, the proton bound to the same carbon as the first MeO group was not detected); **4b**: 6.49 (2 MeO), 7.8–8.7 (ring protons).

Preparation of **5**. A treatment of 2-chlorocyclopentanone (Aldrich) with trimethyl orthoformate, methanol and a small amount of toluene p-sulfonic acid gave an about 25% yield of a mixture of **5a** and **5b** (in a ratio of about 10:1), b.p. 354–355 K at 6.1 kPa, instead of the expected 5-chloro-1-methoxycyclopentene and its isomer. NMR: **5a**: 6.72 (MeO–C(sp^3)), 6.43 (MeO–C(sp^2)), 5.9 ($\underline{H}$–C–OMe), 5.43 (H–C=C), 7.6–8.4 (other ring protons); signals of **5b** were not detected.

Preparation of **6**. 3-Hydroxytetrahydrofuran was oxidized to 3-oxotetrahydrofuran by the method of Adkins *et al.*[15] The yield of the product b.p. 412–413 K at 99kPa, was 17%. The ketone was converted into **6** (85% **6a**, 15% **6b**) as described for **2**. The yield of **6**, b.p. 327–331 K at 5.8 kPa, was 35%. NMR: **6a**: 6.37 (MeO), 5.5 (H–C=C + CH_2), 5.7 (CH_2); **6b**: the olefinic proton appeared as a triplet with J = 1.7 at τ 4.23.

Configurational assignment of the geometric isomers of **2** *and* **3**. The two oxygen atoms of **6b** are of necessity trans to each other, and the olefinic proton was found at τ 4.23. The olefinic protons of the geometric isomers of **2** absorbed at τ 4.41 and 4.84. Thus it is obvious that the former signal belongs to the E isomer **2b**. Moreover, the olefinic protons of (E)- and (Z)-1,2-dimethoxyethylene absorb at τ 3.85 and 4.28, respectively.[16] The signal of the E isomer is thus found 0.43 ppm to a lower field. The difference between τ 4.84 and 4.41 is also 0.43 ppm, and hence the latter shift value should be ascribed to the E isomer (**2b**). Further, on going from **2** to **3** the relative stability of the geometric isomer with the higher τ value increased, and thus it should be the Z form (see Discussion).

Equilibrations. Cyclohexane was used as solvent and iodine as catalyst. The equilibrated samples were analyzed by NMR (**2** and **3**) or by GLC (**4** – **6**). The GLC method could not be used for **2** and **3**, since the retention times of the isomers were too similar. The relative concentrations of the isomers of **2** were determined from the integrated intensities of the signals of their olefinic protons. For **3** the signals at τ 6.31 (**a**, OCH_2), 4.31 and 4.89 (the olefinic protons of **b** and **c**, respectively) were used. In the GLC analyses, a Carbowax 20 M column was used for **4** and **5** (order of elution: **b**, **a**) and an SE-30 column for **6** (order of elution: **b**, **a**). Prior to equilibrations the mixtures of isomers were separated from impurities by preparative GLC. The temperatures at which the equilibrations were carried out were: 271, 300, 323 and 373 K for **2**; 300, 323 and 373 K for **3**; 273, 282, 294, 297, 312, 326, 338, 353, 373 and 404 K for **4**; 298, 323, 373 and 403 K for **5**, and 271, 298, 323, 373 and 403 K for **6**. The equilibration procedure has been described in more detail previously.[17]

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