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Relative Thermodynamic Stabilities of Isomeric Alkyl Allyl and Alkyl (Z)-Propenyl Ethers

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The relative thermodynamic stabilities of ten allyl ethers ($ROCH_2CH=CH_2$) and the corresponding isomeric (*Z*)-propenyl ethers (where R is an alkyl group, or a methoxysubstituted alkyl group) have been determined by chemical equilibration in DMSO solution with *t*-BuOK as catalyst. From the variation of the equilibrium constant with temperature, the values of the thermodynamic parameters ΔG°, ΔH° and ΔS° of isomerization at 298.15 K were evaluated. The propenyl ethers are highly favored at equilibrium, the values of both ΔG° and ΔH° for the allyl → propenyl reaction being ca. -18 to -25 kJ mol^{-1}. The favor of the propenyl ethers is increased by bulky alkyl substituents, and decreased by methoxysubstituted alkyl groups. In most cases the entropy contribution is negligible; however, for R = $(MeO)_2CH$ and R = $(MeO)_3C$ the values of ΔS° are ca. -5 J K^{-1} mol^{-1}.

In some previous works,[1-3] we have studied the relative thermodynamic stabilities of geometrical isomers of the type ROCH=CHMe, where R is an alkyl group or a methoxysubstituted alkyl group. In most cases, these compounds were prepared from the respective allyl ethers by isomerization with *t*-BuOK in DMSO solution.[4] In each case the conversion of allyl ethers to propenyl ethers appeared to go to completion, with the *Z* isomer forming about 90 to 95 % of the reaction product in a kinetically controlled reaction. (Though the equilibrium between alkyl allyl and alkyl (*Z*)-propenyl ethers is readily established, the true thermodynamic equilibrium including the *E* isomer is attained only after prolonged heating of the reaction mixture whereby the amount the *E* form may increase to about 50 %). The aim of the present study was to clarify how complete the conversion of allyl ethers to the corresponding (*Z*)-propenyl ethers actually is, how it depends on the structure of the alkyl group, and to what extent it is determined by enthalpy as well as entropy contributions. For that purpose the equilibrium isomer ratios of the following reaction were determined at several temperatures, and the values of the thermodynamic parameters of isomerization were evaluated from the van't Hoff equation.

$$\underset{\textbf{(a)}}{\mathrm{ROCH_2CH{=}CH_2}} \rightarrow \underset{\textbf{(b)}}{(Z)\text{-}\mathrm{ROCH{=}CHMe}} \qquad (1)$$

1 $R = Me$
2 $R = Et$
3 $R = i\text{-}Pr$
4 $R = t\text{-}Bu$
5 $R = MeOCH_2$
6 $R= (MeO)_2CH$
7 $R = (MeO)_3C$
8 $R = MeOCHMe$
9 $R = (MeO)_2CMe$
10 $R = MeOC(Me)_2$

The mean values of the experimental equilibrium constant K at various temperatures are given in Table 1. From these values the thermodynamic parameters $\Delta G^\ominus$, $\Delta H^\ominus$, and $\Delta S^\ominus$ at 298.15 K were obtained by linear least-squares treatment of lnK *vs.* T^{-1} (Table 2). From the values of $\Delta G^\ominus$ at 298.15 K, the values of the equilibrium constant at this temperature were calculated (Table 2). The latter data show that for all practical purposes, the extent of conversion of allyl ethers to propenyl ethers at equilibrium may be regarded as quantitative. However, there is a more than 14-fold ratio between the highest K value, 23000 for $R = t$-Bu, and the lowest K value, 1620 for $R = (MeO)_3C$.

Expectedly, the extent of reaction is controlled by reaction enthalpy, and in most cases the entropy contribution is negligible. Interestingly, for $R = (MeO)_2CH$ and $R = (MeO)_3C$ the values of $\Delta S^\ominus$ are similar, about -5 J K^{-1} mol^{-1}, and clearly different from those for the other reactions. The observed differences in $\Delta S^\ominus$ are difficult to explain but they possibly point to variations in the number of conformers present in the reagents and the products.

Table 2 shows that if Me groups are substituted for the H atoms of the Me group of methyl allyl ether, the values of the enthalpy as well as Gibbs energy of isomerization become more negative by ca. 1-2 kJ mol^{-1} for each Me group introduced. Thus the propenyl ethers are favored thermodynamically by bulky alkyl groups. This agrees with previous ^{13}C NMR shift data[5] of alkyl (*Z*)-propenyl ethers which show that the strength of p-π conjugation in the –O–C=C moiety, and hence molecular stability, increases with the bulkiness of the alkyl group. However, at least part of the increased favor of the propenyl ethers in this series may also be due to increased destabilization of the allyl ethers by steric factors. On the other hand, a similar substitution with

Table 1. Mean Values of the Equilibrium Constant K at Different Temperatures

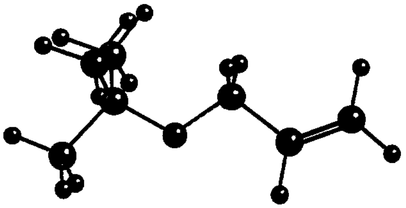
	Temperature /°C						
R	25	50	75	100	125	150	170
Me			967	602	399	279	216
Et		2733	1612	1001	623	432	320
i-Pr			2890	1738	1044	699	516
t-Bu			5180	2950	1850	1100	793
$MeOCH_2$		1112	666	446	292	205	160
$(MeO)_2CH$		900	500	328	215	154	119
$(MeO)_3C$	1590	906	510	314	219	151	
MeOCHMe		2170	1240	737	495	332	252
$(MeO)_2CMe$		1860	1100	686	462	315	
$MeOC(Me)_2$		2970	1760	1047	693		

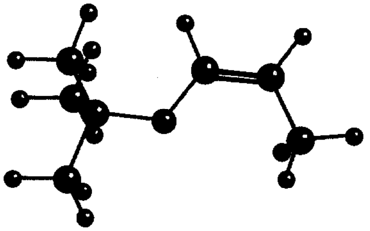
Table 2. Thermodynamic Data for Reaction (1) in DMSO Solution at 298.15 K. The Errors are Twice the Standard Errors.

R	$\Delta G^{\ominus}$/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}	K
Me	-19.94 (0.03)	-20.2 (0.2)	-1.0 (0.3)	3110
Et	-21.33 (0.14)	-21.4 (0.6)	0.0 (1.6)	5470
i-Pr	-23.14 (0.14)	-23.4 (0.6)	-0.8 (1.4)	11300
t-Bu	-24.90 (0.30)	-25.4 (1.2)	-1.6 (3.0)	23000
$MeOCH_2$	-18.91 (0.11)	-19.3 (0.5)	-1.2 (1.3)	2050
$(MeO)_2CH$	-18.34 (0.12)	-19.9 (0.5)	-5.2 (1.4)	1635
$(MeO)_3C$	-18.32 (0.10)	-19.9 (0.5)	-5.3 (1.5)	1620
MeOCHMe	-20.70 (0.07)	-21.4 (0.3)	-2.2 (0.8)	4235
$(MeO)_2CMe$	-20.24 (0.07)	-20.1 (0.3)	0.3 (0.9)	3510
$MeOC(Me)_2$	-21.47 (0.14)	-20.9 (0.8)	1.9 (2.2)	5770

MeO groups instead of Me groups leads to no marked change in reaction enthalpy, and the changes in $\Delta G^{\ominus}$ are also small, but slightly positive. Further, if the substitution is carried out with both Me and MeO groups (the last three entries in Table 2), the values of $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ either show no significant change or become slightly more negative. As a whole, the range of variation in the $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ values is relatively small, 5 to 6 kJ mol^{-1}.

For comparison, the effect of the structure of the alkyl group R on the energetics of reaction (1) was studied by molecular mechanics calculations using the COSMIC force-field.[6] Steric energies were calculated for all compounds of the present study, and using the change in steric energy for **1a** → **1b** (R = Me) as a standard, the corresponding changes in other reactions were referenced against it to obtain the relative reaction enthalpies for these reactions. As an example, the energy minimized structures of the two compounds for R = *t*-Bu are shown below.





In general, the calculated relative reaction enthalpies were in good agreement with the experimental ones (Table 3). Especially, the increasingly negative $\Delta H^{\ominus}$ values for R = Et, i-Pr, and *t*-Bu were nicely predicted by the force field calculations. This suggests that the observed trend in $\Delta H^{\ominus}$ arises mainly from steric, instead of electronic, factors. The highest disagreements were found for reactions with R = $(MeO)_3C$ and R = $MeOC(Me)_2$, which were predicted to be 2.6 kJ mol^{-1} more exothermic than the experimental values.

To see how the present findings agree with available thermodynamic data, let us consider the reaction **2a** → **2b**, for convenience in two steps *via* the *E* isomer. An estimate of the magnitude of reaction enthalpy in the first step may be obtained by consideration of the double-bond stabilizing abilities of the groups attached to the olefinic bonds. Thus the reactant is stabilized by an $EtOCH_2$ group, and the product by a Me group and an EtO group. Since the double-bond stabilizing ability of an $EtOCH_2$ group is likely to be similar to that of a $MeOCH_2$ group, which is known to be some 2.5 kJ mol^{-1} less than that of a Me group,[7] reaction enthalpy of the first step might be thought to correspond to the stabilization due to an EtO group, corrected by the afore-

Table 3. Values of Relative Reaction Enthalpies (in kJ mol^{-1}) for Reaction (1) from the COSMIC Force Field and Experiment

Method	Et	i-Pr	*t*-Bu	$MeOCH_2$	$(MeO)_2CH$	$(MeO)_3C$	MeOCHMe	$(MeO)_2CMe$	$MeOC(Me)_2$
COSMIC	-0.2	-2.5	-4.3	-0.1	-0.3	-2.3	-0.1	-0.5	-3.3
Exp.	-1.2	-3.2	-5.2	0.9	0.3	0.3	-1.2	0.1	-0.7

mentioned amount. The stabilization given by an EtO group is obtained as -25.5 kJ mol^{-1} from the difference between the enthalpies of hydrogenation of ethene and ethyl vinyl ether.[8,9] However, it must be taken into account that in vinyl ethers, like the product of the first step, the double-bond stabilizing ability of alkyl groups is ca. 7 kJ mol^{-1} smaller than that in alkyl-substituted olefins.[10] Thus the reaction enthalpy of the first step might be estimated to be ca. -25.5-2.5+7 = -21.0 kJ mol^{-1}. Finally, since the value of $\Delta H^{\circ}(1)$ for the E → Z reaction is -0.7 kJ mol^{-1}, reaction **2a** → **2b** is calculated to be exothermic by -21.7 kJ mol^{-1} ≅ -22 kJ mol^{-1}, in agreement with the experimental ΔH° value of -21.4 kJ mol^{-1}.

EXPERIMENTAL

Materials. Allyl ethyl ether (**2a**) was obtained from Aldrich Co., and the well-known allyl Me and allyl i-Pr ethers were prepared from allyl bromide and the respective sodium alkoxides; **1a** bp 42 °C (lit.[11] 42°C/752 torr), **3a** bp 80-82 °C (lit.[12] 82-83 °C/730 torr). For the other compounds, excluding **7a** and **7b**, see Refs. 1-3. Compound **7a**, bp 72-73°C/45 torr, was prepared from $(MeO)_4C$ and allyl alcohol, with p-TsOH as catalyst. It was converted to **7b**, bp 65-66°C/30 torr, by treatment with *t*-BuOK in DMSO. Prior to the equilibration experiments the compounds were purified by distillation on a Perkin-Elmer Auto Annular Still. ^1H NMR ($CDCl_3$): **7a** 3.31 (s, 9H), 4.06 (d, 2H, *J* 5.2), 5.93 (m, 1H), 5.16 (d, 1H, *J* 10.4), 5.32 (d, 1H, *J* 17.1); **7b** 3.33 (s, 9H), 6.24 (d, 1H, *J* 6.4), 4.62 (m, 1H), 1.64 (d, 3H, *J* 7.0). ^{13}C NMR ($CDCl_3$): **7a** 50.4 ($\underline{C}H_3O$), 120.5 ($\underline{C}$-O), 63.9 (O-$\underline{C}H_2$), 133.8 ($\underline{C}H$), 116.2 (=$\underline{C}H_2$); **7b** 50.6 ($\underline{C}H_3O$), 120.5 ($\underline{C}$-O), 136.7 (O-$\underline{C}H$), 104.1 (=$\underline{C}H$), 9.2 ($\underline{C}H_3$).

Equilibrations. The equilibrium investigations were carried out in dry DMSO solution, with substrate concentrations of 20 vol-%, and catalyst concentrations of 50-100 mg/ml. The reaction mixtures were closed in ampoules, which were kept at the appropriate temperatures until the attainment of thermodynamic equilibrium. Then the samples were quickly cooled by immersion into crushed ice, after which they were diluted with diethyl amine (to facilitate GLC analysis), followed by analysis using 50 m capillary colums of types SE-30, Carbowax 20M, and Silar 9 C. To check whether the presence of catalyst in the injected samples could cause any change in isomer ratio during the GLC analysis, a few equilibrated samples were extracted with cyclohexane (which does not dissolve the catalyst, or appreciable amounts of DMSO), and the cyclohexane solutions were analyzed. However, the isomer ratios determined by both methods were indistinguishable. To facilitate attainment of the thermodynamic equilibrium, the initial isomer ratios in the reaction mixtures were adjusted to be relatively close to the final equilibrium values (which were approached from both sides at most temperatures). At the highest temperatures used, the thermodynamic equilibribrium was achieved within a few tens of minutes while several weeks, or months, were required at the lowest temperatures. Generally, the mean values of the equilibrium constant at each temperature are based on 5-10 independent determinations.

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