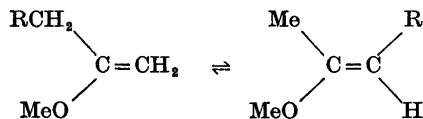


Thermodynamics of Vinyl Ethers. VI. The Stabilizing Effect of Methoxymethyl and (Methoxycarbonyl)methyl Groups on the Ethylenic Linkage of Vinyl Ethers

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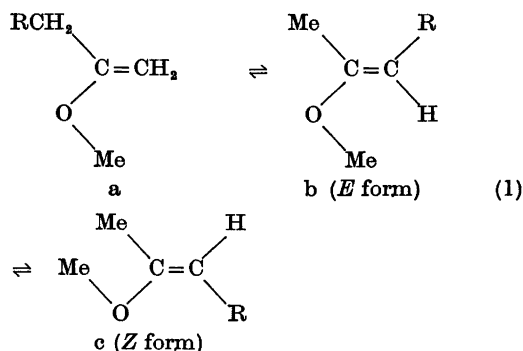
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Thermodynamics of the following isomerization reaction have been studied by means of chemical equilibration:



The values of ΔH° (g, 298.15 K) (0.53 ± 0.47 kJ mol⁻¹ for R=CH₂OCH₃ and 0.77 ± 0.39 kJ mol⁻¹ for R=CH₂OCOCH₃) show that the stabilizing effect of a methoxymethyl or (methoxycarbonyl)methyl group on the double bond of a vinyl ether is equal within experimental error to that of an unsubstituted alkyl group, such as Me, Et, or i-Pr.

In part III of this series,¹ thermodynamics of the following isomerization reaction were studied:



(R = Me, Et, i-Pr)

The values of ΔH° for the a \rightleftharpoons b isomerization were found to be practically independent of the

alkyl group R, ΔH° (g, 298.15 K) = 0.45 ± 0.38 , 0.78 ± 0.39 , and 0.60 ± 0.37 kJ mol⁻¹ for the Me, Et and i-Pr derivatives, respectively, which shows that the stabilizing effect of the alkyl group on the double bond of the b isomer was practically independent of R. Excluding destabilizing steric interactions, the stabilizing energy of the alkyl group was evaluated as *ca.* 4.3 kJ mol⁻¹, which is considerably less than the stabilization, *ca.* 11 kJ mol⁻¹, brought about by R on the double bond of a corresponding olefinic hydrocarbon. This was assumed to be due to electron delocalization in vinyl ethers, which leads to a shift of negative charge to the β carbon of the double bond. Electropositive alkyl groups, when attached to the β carbon, were assumed to oppose this electron delocalization by their inductive effect, and thus their stabilizing effect on vinyl ethers is considerably weaker than on olefins.

However, it might be expected that if the alkyl group R were essentially less electropositive than Me, Et or i-Pr, electron delocalization in b would be restored and thus the group R should stabilize the double bond more effectively. To test the validity of this assumption, thermodynamics of reaction (1) were studied in cases R=CH₂OCH₃ and R=CH₂OCOCH₃. Both of these groups are noticeably more electronegative than Me, Et, or i-Pr.

EXPERIMENTAL

Materials. 2,4-Dimethoxy-1-butene (Ia) and isomers (Ib, Ic). 2-Methoxyethyl methyl ketone was prepared from methyl vinyl ketone and

methanol in the presence of mercuric oxide and boron trifluoride etherate.² The yield of the product boiling at 410–411 K/101.8 kPa was 60%. It was converted to its dimethyl acetal by means of trimethyl orthoformate in methanol.³ The yield of the acetal, b.p. 335–336 K/2.7 kPa, was 62%. The acetal was distilled slowly from Al₂O₃ to give a mixture of methanol and the desired vinyl ethers.⁴ The product was washed with water and dried over CaCl₂. After redistillation from metallic sodium the yield of the mixture of the isomeric vinyl ethers (b.p. ca. 401 K/101.6 kPa) was about 20%.

Methyl 4-methoxy-4-pentenoate (IIa) and isomers (IIb, IIc). Levulinic acid (0.86 mol), methanol (2.7 mol), benzene (250 cm³), and concentrated sulfuric acid (24 cm³) were refluxed for 24 h, after which the mixture was poured into water and the organic layer was washed with sat. NaHCO₃ solution and water. After drying over CaSO₄, the product was distilled to give a 22% yield of the methyl ester of levulinic acid, b.p. 362–364 K/2.1 kPa. The ester was converted to its dimethyl acetal, as described above for I. However, the acetal was not isolated but the crude acetal was distilled slowly from a small amount of *p*-toluenesulfonic acid. After a forerun of methanol, a 72% yield of the isomeric vinyl ethers could be collected at 350–359 K/2.3 kPa.

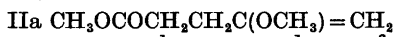
NMR spectra. The NMR spectra were recorded in CCl₄ solutions (ca. 20 vol %) at 307 K with TMS as internal standard. NMR spectra could not be obtained for the *Z* isomers because of their low concentration in the synthesis products. For the spectra of Ia and Ib, the isomers were separated by preparative GLC; the spectra of IIa and IIb were recorded on a mixture containing equimolar amounts of IIa and IIb. Peak positions and some coupling constants:



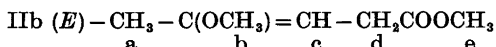
τ 6.72 (a), 6.56 (b), 7.71 (c), 6.48 (d), 6.14 (ef); $J_{bc}=6.9$ Hz.



τ 8.21 (a), 6.50 (b), 5.47 (c), 6.16 (d), 6.80 (e); $J_{bd}=7.5$ Hz.



τ 6.39 (a), 7.62 (bc), 6.50 (d), 6.18 (ef); $J_{bc}=0.0$ Hz.



τ 8.25 (a), 6.50 (b), 5.54 (c), 7.08 (d), 6.39 (e); $J_{cd}=7.4$ Hz.

Procedure. The details of the equilibration procedure have been described previously.^{1,5,6} The equilibrations were carried out in cyclo-

hexane solutions with iodine as catalyst. The column used in the gas chromatographic analyses was a 4 m column containing 10% Carbowax 1500 on Chromosorb G. The isomers were eluted in alphabetical order. Of the geometric isomers b and c, the one with the higher thermodynamic stability (b) was taken as the *E* isomer.^{1,6} Because of the relatively poor resolution of the peaks of IIb and IIc, the amount of the latter in the equilibrium mixtures could not be determined with sufficient accuracy. Hence isomerization data involving this compound have not been included in this work. However, the error in the area of the peak of IIb, caused by the poor resolution of the peaks of the geometric isomers, was negligible because of the low concentration of IIc. Peak areas, which were considered to be proportional to the molar concentrations of the isomers,⁵ were determined by the cut-and-weigh method.

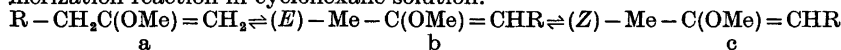
In the case R=CH₂OCOCH₃, the position of equilibrium could be approached from both sides. However, in the case R=CH₂OCH₃, only Ia was used for the equilibrations, for sufficient amounts of IIb could not be separated owing to the low yield of the synthesis. In the latter case, the progress of isomerization was followed by GLC and after the isomer composition ceased to change, the position of equilibrium was considered having been attained. To be sure that true equilibrium had been reached, the following samples of the equilibration mixture were analyzed over sufficiently extended periods of time to detect possible changes in the isomer ratios.

*Determination of normal boiling points.*⁶ Ia, Ib, and Ic: Reference curve (compound, b.p. at 101.3 kPa, relative retention time): isobutyl vinyl ether, 356.2 K, 0.228; isobutylidene ethyl ether, 366.7 K, 0.279; 1-methoxycyclopentene, 387.0 K, 0.485; 1-ethoxycyclopentene, 409.0 K, 0.780; 1-methoxycyclohexene, 417.1 K, 1.000. The relative retention times of Ia, Ib, and Ic were 0.543, 0.745, and 0.745 leading to normal b.p.'s of 392.7 K, 406.2 K, and 406.2 K, respectively. IIa, IIb, and IIc: Reference curve: 1-methoxycyclopentene, 387.0 K, 0.294; 1-ethoxycyclopentene, 409.0 K, 0.391; 1-methoxycyclohexene, 417.1 K, 0.473; 1-ethoxycyclohexene, 435.0 K, 0.648; 1-propoxycyclohexene, 455.9 K, 1.000. The relative retention times of IIa, IIb, and IIc were 0.668, 0.793, and 0.812 leading to normal b.p.'s of 436.8 K, 444.9 K, and 446.1 K, respectively.

RESULTS

Table 1 shows the mean values of the equilibrium constant *K* and its standard error at different temperatures. Table 2 gives the values of ΔG° , ΔH° , and ΔS° of isomerization at 298.15 K, which were calculated from the variation of the mean equilibrium constant with

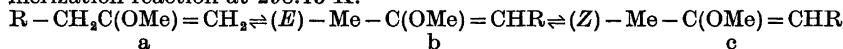
Table 1. Values of the mean equilibrium constant K and its standard error for the following isomerization reaction in cyclohexane solution:



Catalyst (I_2) concentration/mol dm⁻³: 0.004 (R = CH₃OCH₂), 0.008 (R = CH₃OCOCH₂); substrate concentration ca. 2.0 mol dm⁻³; n denotes the number of independent determinations.

R	T/K	n	$K_1(\text{a} \rightleftharpoons \text{b})$	$10K_2(\text{a} \rightleftharpoons \text{c})$	$10K_3(\text{b} \rightleftharpoons \text{c})$
CH ₃ OCH ₂	303.2	3	1.162 ± 0.010	0.332 ± 0.008	0.285 ± 0.007
	323.2	5	1.128 ± 0.006	0.445 ± 0.009	0.394 ± 0.008
	340.2	5	1.061 ± 0.006	0.547 ± 0.011	0.514 ± 0.011
	361.2	3	1.032 ± 0.002	0.655 ± 0.008	0.634 ± 0.009
	373.2	4	1.035 ± 0.006	0.748 ± 0.013	0.723 ± 0.013
	397.2	4	1.014 ± 0.006	0.955 ± 0.017	0.943 ± 0.017
	415.2	4	0.961 ± 0.007	1.076 ± 0.013	1.121 ± 0.016
CH ₃ OCOCH ₂	297.2	8	0.839 ± 0.004
	323.2	6	0.848 ± 0.006		
	348.2	4	0.834 ± 0.011		
	369.2	4	0.827 ± 0.012		
	398.2	6	0.802 ± 0.004		
	420.2	3	0.799 ± 0.006		

Table 2. Values of the standard free energy, enthalpy, and entropy changes for the following isomerization reaction at 298.15 K:



The errors are twice the standard errors.

State	R	Reaction	$\Delta G^\circ/\text{kJ mol}^{-1}$	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
Liquid	CH ₃ OCH ₂	a ⇌ b	-0.395 ± 0.071	-1.65 ± 0.36	-4.2 ± 1.0
		a ⇌ c	8.599 ± 0.085	10.94 ± 0.43	7.8 ± 1.2
		b ⇌ c	9.002 ± 0.084	12.63 ± 0.42	12.1 ± 1.2
Gaseous	CH ₃ OCOCH ₂	a ⇌ b	0.393 ± 0.051	-0.53 ± 0.25	-3.1 ± 0.7
		a ⇌ c	...	0.53 ± 0.47	-1.7 ± 1.1
	CH ₃ OCH ₂	a ⇌ c	...	13.11 ± 0.52	10.3 ± 1.1
		b ⇌ c	...	12.63 ± 0.52	12.1 ± 1.3
	CH ₃ OCOCH ₂	a ⇌ b	...	0.77 ± 0.39	-1.8 ± 0.8

temperature, as described previously.⁵ The values of ΔH° and ΔS° in the ideal gas state at 298.15 K were evaluated as shown in part II of this series.⁶

DISCUSSION

According to Table 2, the values of ΔH° (g, 298.15 K) for the reaction a ⇌ b, in cases R = CH₃OCH₂ and R = CH₃OCOCH₂, are very similar and moreover, comparable to those for

the same reaction in cases R = Me, Et, or i-Pr, as is seen from Table 3.

As it is apparent that steric repulsions between the two *cis* alkyl groups in the b isomer are very similar in each case, the results of this work reveal the rather unexpected fact that the stabilizing effect of a methoxymethyl or (methoxycarbonyl)methyl group on the double bond of a vinyl ether does not noticeably differ from that of an unsubstituted alkyl group. Thus one might be tempted to draw the conclusion

Table 3.

R	σ^* (Ref. 7)	$\Delta H^\circ(\text{g}, 298.15 \text{ K})/\text{kJ mol}^{-1}$	Ref.
CH_3OCH_2	0.52	0.53 ± 0.47	This work
$\text{CH}_3\text{OCOCH}_2$	0.73 ^a	0.77 ± 0.39	This work
CH_3	0.00	0.45 ± 0.38	1
CH_3CH_2	-0.10	0.78 ± 0.39	1
$(\text{CH}_3)_2\text{CH}$	-0.19	0.60 ± 0.37	1

^a Obtained by dividing the σ^* -value of the methoxycarbonyl group by 2.8, the factor that approximately corresponds to the attenuation of the inductive effect by one methylene group.

that the inductive effect of the group R has no effect on its stabilizing power. However, the similar stabilization energies may be due to a fortuitous compensation of two opposing effects. Damico⁸ has found that in methyl octenoates, equilibrium distribution of the double bond disfavors the 3-octenoate with respect to the 4-, 5-, or 6-octenoates, the equilibrium ratio of the 3-isomer to any of the other isomers mentioned being about 0.3 (at 398 K). Similarly, in methyl pentenyl ethers, the ratio of the 2-pentenyl isomer to the 3-pentenyl isomer was about 0.6 (at 293 K). Thus methoxymethyl and (methoxycarbonyl)methyl groups do not stabilize the double bond of an ordinary olefin so effectively as unsubstituted alkyl groups. As the σ^* -values of the methoxymethyl and (methoxycarbonyl)methyl groups do not significantly differ from that of a hydrogen atom (0.49),⁷ it might be thought that these groups restore the electron delocalization that is present in vinyl ethers with no substituents on the β carbon of the vinyl group, but because of their weaker "intrinsic" ability to stabilize olefinic double bonds, the net stabilization on vinyl ethers is comparable to that caused by an unsubstituted alkyl group. However, it seems amazing that the two opposite effects should completely compensate each other in both cases.

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