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Combination of ^{17}O and ^{13}C NMR Spectra of Isomeric Allyl and (Z)-Propenyl Ethers with Their Relative Thermodynamic Stabilities

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Abstract: **The ^{17}O NMR spectra of ten allyl ethers $ROCH_2CH{=}CH_2$ and those of the isomeric (Z)-propenyl ethers $ROCH{=}CHMe$, where R is an alkyl group or a MeO-substituted alkyl group, were recorded in $CDCl_3$ solution. The difference in ^{17}O NMR chemical shift between a propenyl ether and the isomeric allyl ether, ca. 50 to 60 ppm, depends primarily on the number of MeO groups attached to the α carbon of the R moiety, and is related to the strength of p-π conjugation in the propenyl ethers. Previous ^{13}C NMR shift data for the β olefinic carbon of the propenyl ethers and the thermodynamic data of isomerization of allyl ethers to propenyl ethers are discussed in view of their relation to the ^{17}O NMR shift data.**

It has been long known[1] that the ^{17}O NMR chemical shifts of alkyl vinyl ethers lie several tens of ppm downfield from those of corresponding saturated ethers. For example, ethyl vinyl ether and diethyl ether absorb at δ 88 and 15 ppm, respectively.[1] The relatively high ^{17}O NMR chemical shift values of alkyl vinyl ethers are likely to arise mainly from p–π conjugation in the vinyloxy system, which decreases electron density on the O atom, and increases it on the β carbon of the vinyl group:

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

The efficiency of this conjugation depends on a number of factors, such as the relative steric orientation of the oxygen lone pair orbitals and the π orbital of the C=C bond, and on the electron releasing character of the alkyl group. The conjugative interaction is also affected by substitution in the vinyl group: electron releasing alkyl groups on the β carbon decrease the strength of conjugation in the vinyloxy moiety.[2]

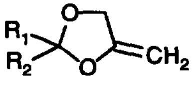
Alkyl propenyl ethers are thermodynamically much more stable than the isomeric alkyl allyl ethers, typical values of ΔG° for the allyl to (*Z*)-propenyl isomerization being -18 to -25 kJ mol^{-1} (298.15 K, DMSO solution).[3] Since the thermodynamic stability of propenyl ethers is promoted by efficient p–π conjugation, revealed by large ^{17}O NMR chemical shift values, it was of interest to study these ethers by this NMR method to see how the thermodynamic results are related to the ^{17}O NMR shift data. For comparison, ^{13}C NMR shift data for the β carbon of the vinyl group from our previous investigations[3,4] were also included.

EXPERIMENTAL

The preparation of the present compounds has been described elsewhere.[3] The ^{17}O NMR spectra were recorded at 21 °C in $CDCl_3$ solution on a Jeol GX-400 NMR spectrometer operating at a frequency of 54.2 MHz. Further details of the experimental procedure are given in Ref. 2. The half-height widths varied from 170 Hz for R = Me to 530 Hz for R = $(MeO)_3C$, generally increasing with increasing molecular mass of the ethers concerned. The chemical shift values, relative to external water, are believed to be accurate within 1–2 ppm.

RESULTS AND DISCUSSION

The ^{17}O NMR chemical shift values, including those for the MeO group(s) of the R moiety, are given in Table 1, together with the differences in chemical shift between propenyl ethers and the isomeric allyl ethers. The magnitude of the differential shift appears to be determined mainly by the number of MeO groups at the α carbon of the R group: for R = Me, Et, i-Pr or *t*-Bu the difference is ca. 59 ppm but on introduction of a single MeO group the differential shift decreases to ca. 56 ppm. An additional MeO group causes a further decrease to ca. 52 ppm whereupon a state of saturation is achieved: the next MeO group has no more effect on the difference in chemical shift. Thus the strength of p-π conjugation in the propenyl ethers decreases on introduction of electron withdrawing MeO groups at the α carbon of the R moiety, which agrees with previous evidence[4] based on ^{13}C NMR chemical shifts of the β carbon of the



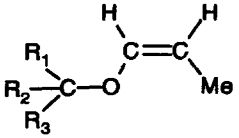


Table 1. ^{17}O NMR Chemical Shifts of Allyl Ethers ($ROCH_2CH{=}CH_2$) and the Corresponding (Z)-Propenyl Ethers ($ROCH{=}CHMe$) in $CDCl_3$ Solution Relative to External Water. The ^{13}C NMR Chemical Shifts of the β-Carbon of the Propenyl Group,[3,4] as well as the Values of $-\Delta G^{\ominus}$ (in kJ mol^{-1}) for the Allyl to (Z)-Propenyl Reaction (298.15 K, DMSO Solution, Ref.3) are Also Given.

	Allyl ether		Propenyl ether		Difference (prop. − allyl)		δ(C–β) (prop.)	$-\Delta G^{\ominus}$	$\Delta(-\Delta G^{\ominus})$[b]
R	δ(O-1)	δ(O-2)	δ(O-1)	δ(O-2)	Δδ(O-1)	Δδ(O-2)			
Me	-24		35[a]		59		101.0	19.94	
Et	9		67[a]		58		101.0	21.33	1.4
i-Pr	31		91[a]		60		101.1	23.14	1.8
t-Bu	44		104[a]		60		102.4	24.90	1.8
$MeOCH_2$	32	9	87	15	55	6	103.1	18.91	
MeOCHMe	47	22	103	30	56	8	102.5	20.70	1.8
$MeOCMe_2$	50	27	106	31	56	4	102.9	21.47	0.8
$(MeO)_2CH$	54	29	105	31	51	2	104.1	18.34	
$(MeO)_2CMe$	60	35	113	37	53	2	103.8	20.24	1.9
$(MeO)_3C$	57	31	109	35	52	4	104.1	18.32	

[a] Ref. 2. [b] Increase in $-\Delta G^{\ominus}$ from the previous entry.

vinyloxy group in 2-substituted-4-methylene-1,3-dioxolanes and (Z)-propenyl ethers. In the former compounds, the effect of polar factors on the chemical shift of C-β may be expressed as

$$\delta(\text{C-}\beta)/\text{ppm} = (77.27 \pm 0.10) + (1.12 \pm 0.09)\cdot\Sigma\sigma^{*}_{R}$$

where $\Sigma\sigma^{*}_{R}$ represents the sum of the Taft's polar substituent constants for the two atoms or groups attached to C-2 of the 1,3-dioxolane ring. For the present compounds, (Z)-propenyl ethers, the corresponding equation was obtained as

$$\delta(\text{C-}\beta)/\text{ppm} = (99.76 \pm 0.32) + (1.34 \pm 0.14)\cdot\Sigma\sigma^{*}_{R}$$

where $\Sigma\sigma^{*}_{R}$ represents the sum of the substituent constants for the three atoms/groups attached to the α carbon of the RO moiety. In the 4-methylene-1,3-dioxolane ring system, with a relatively fixed ring conformation, the relationship between ^{13}C NMR chemical shift and polar character of substituents is remarkably linear; in the open-chain propenyl ethers, where the torsional angle C–O–C=C, and hence the strength of p-π conjugation, are more easily affected by the bulkiness of R, clear deviations from linearity were found (see below).

Although a moderately smooth linear correlation between the polar character of R and δ(C-β) of the vinyloxy group in ROCH=CHMe was thus observed, the present findings of the differential ^{17}O NMR shift values falling into separate categories according to the number of MeO groups attached to the α carbon of the R moiety suggest that a similar trend might also be discernible in the ^{13}C NMR chemical shifts. This expectation is confirmed by the data of Table 1, which is a strong indication of a common origin of the observed variations in both the ^{13}C NMR and ^{17}O NMR shift data.

For R = *t*-Bu, the ^{13}C NMR shift value is slightly larger than the shift values for R = Me, Et or i-Pr (though the opposite might be expected on the basis of the polar characters of these substituents), indicating that the C–O–C=C skeleton of the *t*-Bu derivative is less planar than those of the other alkyl derivatives. However, the slight decrease in conjugation for R = *t*-Bu does not emerge from the differential ^{17}O NMR shift data, which is reasonable in view of their lower accuracy relative to the ^{13}C NMR data.

It is worth noting that the state of saturation achieved in both the differential ^{17}O NMR data and the ^{13}C NMR shift data of the propenyl ethers after introduction of two MeO groups at the α carbon of the R moiety is also evident in the 4-methylene-1,3-dioxolane series, cf. the ^{13}C NMR shift values of 79.6 and 79.5 ppm, respectively, for the β carbons of the 2-methoxy- and 2,2-dimethoxy-derivatives.[4]

Since the NMR shift data, discussed above, are related to the strength p–π conjugation, and hence to molecular stability, and may be divided into subgroups according to the number of MeO substituents at the α carbon of the R moiety, it was of interest to classify our previous thermodynamic data for the allyl to propenyl isomerization in the same sequence (Table 1). Considering the values of $-\Delta G^{\circ}$ for the first members of the four subgroups of compounds [R = Me, MeOCH$_2$, (MeO)$_2$CH and (MeO)$_3$C], it is seen that the decreasing strength of conjugation in the propenyl ethers, as revealed by the NMR shift data, is also seen in the diminishing $-\Delta G^{\circ}$ values of isomerization. Once again, the saturation effect appears: within experimental error, the values of ΔG° for R = (MeO)$_2$CH and R = (MeO)$_3$C are equal. The thermodynamic data of Table 1 also include the effect of increasing methyl substitution at the α carbon [the term $\Delta(-\Delta G^{\circ})$]: in most cases the effect is ca. 1.8 kJ mol^{-1} for each Me group introduced.

The observed close relationship between the NMR shift data and the thermodynamic data of isomerization for the lowest members of the four subgroups (i.e. for compounds in which steric effects on the relative thermodynamic stabilities are likely to be at a minimum) prompted a more detailed analysis of the type of correlation. If the ^{17}O NMR and ^{13}C NMR chemical shifts are linearly related to the strength of conjugation in the propenyl ethers, and if the observed trend in the $-\Delta G^{\circ}$ values results only from changes in p–π conjugation, a linear relationship should exist between the NMR shift data and the Gibbs energy of isomerization. This appears to be the case: if the differential ^{17}O NMR shifts and the ^{13}C NMR shifts of the propenyl ethers are plotted against $-\Delta G^{\circ}$, good linear correlations are observed (Fig. 1). Linear least-squares treatments of the shift data against $-\Delta G^{\circ}$ lead to the equations

$$\Delta\delta(\text{O-1})/\text{ppm} = -33.9 + 4.667\cdot(-\Delta G^{\circ}/\text{kJ mol}^{-1}) \quad (r = 0.986)$$

$$\delta(\text{C}-\beta)/\text{ppm} = 139.4 - 1.923\cdot(-\Delta G^{\circ}/\text{kJ mol}^{-1}) \quad (r = -0.999).$$

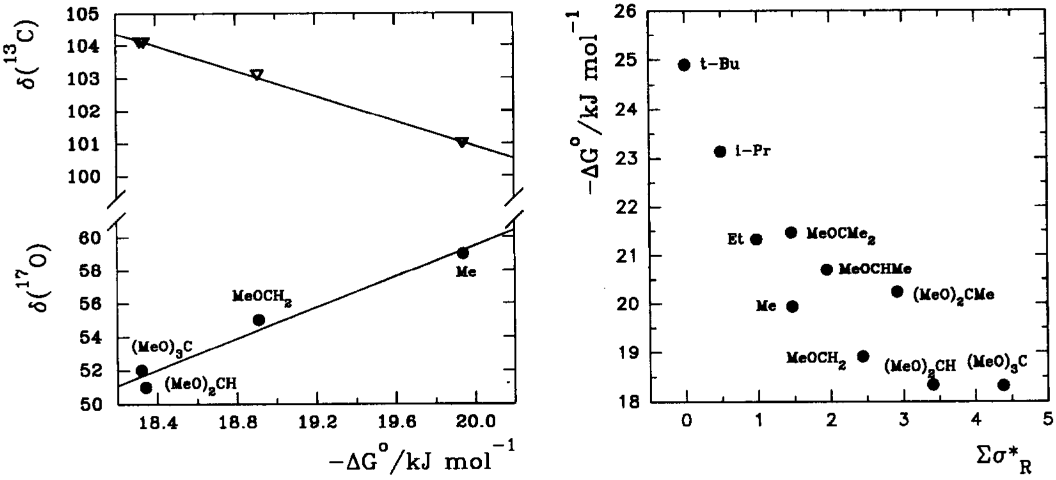


Fig. 1. (*left*) The ^{13}C NMR chemical shifts of C–β of propenyl ethers and the differential ^{17}O NMR shifts against $-\Delta G^{\circ}$ of isomerization, (*right*) values of $-\Delta G^{\circ}$ against the sum of the σ* values for the groups attached to the α carbon of the R moiety in ROCH=CHMe.

On the other hand, however, the remarkably good linear relationship between the NMR and thermodynamic ΔG° data seems puzzling, and possibly fortuitous, since the linear relationship might actually be expected only if the entropy contributions to ΔG° of isomerization were equal in the four reactions concerned; however, for R = $(MeO)_2CH$ and R = $(MeO)_3C$, the values of ΔS° are ca. 4 J K^{-1} mol^{-1} lower than those for R = Me and R = $MeOCH_2$.[3]

In an earlier article[3] it was shown that the relative enthalpies of isomerization of allyl ethers to propenyl ethers could be predicted with moderate success by force-field calculations, which suggested that these values were determined mainly by steric factors. The previous discussion of the correlation between the NMR shift data and Gibbs energy of isomerization proposes that part of the observed variatiations in energy functions may be ascribed to electronic factors. Thus it was of interest to plot the values of ΔG° (which could be measured with higher accuracy than the enthalpy values) against the Taft's σ^* values[5] of the groups attached to the α carbon of (*Z*)-propenyl ethers (Fig. 1). The correlation between these quantities is far from linear: with increasing number of Me groups attached to the α carbon the Gibbs energy of isomerization rises steeply, which points to a higher increase in steric strain in the allyl ethers.

The chemical shifts of the O atom(s) of the R moiety (O-2), shown in Table 1, increase on going from allyl ethers to propenyl ethers. The incremental shifts $\Delta\delta$(O-2) appear to be related to the strength of conjugation in the vinyloxy moiety as judged from the δ(O-1) values; this sounds reasonable since the decrease of negative charge on the O atom, due to conjugation, has an attractive effect on the electrons of the neighboring oxygen atom(s). It is also possible, however, that the decreasing trend in the $\Delta\delta$(O-2) values with increasing number of MeO substituents in the R moiety is, at least in part, a consequence of distribution of the electron-attracting power of the vinyloxy group among several oxygen atoms of R in the lower entries of Table 1.

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