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The Carbon-13 NMR Spectra of Alkyl Vinyl Ethers, and Their Structures and Reactivities

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The ^{13}C NMR spectra of alkyl vinyl ethers were investigated at 22.5°C with neat liquid at 15.09 MHz. When the alkyl group of the ether becomes more electron-donating, the chemical shift of the α-carbon of the vinyl group shifts to a higher field, and that of the β-carbon, to a lower field. From these results, it was concluded that the contribution of the resonance form, $\overset{-}{C}H_2-CH=\overset{+}{O}-R$, in the ether decreases in the order of the increasing electron-repelling power of the alkyl group. Good correlations were obtained between the chemical shifts of the vinyl group and the reactivity of vinyl ether in the cationic reaction. When the ether becomes more reactive, the chemical shift of the α-carbon shifts to a higher field, and that of the β-carbon to a lower field. This fact clearly shows that the attack of the proton on the β-carbon is not the rate determining step in the cationic reaction of the vinyl group. Linear relations were obtained between the chemical shifts of β-methylene protons and of β-carbon, but no correlation was obtained between the chemical shifts of the α-methine proton and of the α-carbon.

Carbon-13 chemical shifts (δ_c) have been reported for several olefinic compounds.[1-3] However, few data have been obtained on alkyl vinyl ethers.[3,4] In our preceding paper[5] we measured the ^1H NMR spectra of alkyl vinyl ethers and studied the resonance contribution in the ether. In this work, we will investigate the ^{13}C NMR spectra of alkyl vinyl ethers and will obtain direct evidence for the previous conclusions. The relationships between the reactivity of alkyl vinyl ether and the ^{13}C chemical shift of the vinyl group were also studied.

Experimental

The methyl vinyl ether was commercially obtained. The other vinyl ethers were prepared from methyl vinyl ether and alcohols by an ether-exchange reaction catalyzed by $Hg(OAc)_2$ in the presence of molecular sieves.[6] All the ethers were purified by refluxing them over lithium aluminum hydride and by subsequent distillation under a high vacuum.

The ^{13}C NMR spectrum was taken at 22.5°C on a JEOL C-60HL spectrometer with a 15.09 MHz RF unit and using a neat liquid in an 8 mmϕ sample tube. The signal to noise ratio of the spectrum was enhanced by the ^{13}C–H noise decoupling. The spectrum of *t*-butyl vinyl ether was also obtained by means of the accumulation over 16 scans using a JEOL JRA-1 accumulator. The chemical shift measurements were done with a nuclear resonance single side band technique;[7] their accuracies were within ±0.2 ppm. Carbon disulfide was used as an external standard, the high field shifts being shown as positive values.

Results and Discussion

^{13}C Chemical Shifts of Alkyl Vinyl Ethers. The chemical shifts of alkyl vinyl ethers are given in Table 1, in which the vinyl ethers are arranged in increasing order of the electron-repelling power of their alkyl groups from the top to the bottom. When the alkyl group becomes more electron-donating, the chemical shift of the α-carbon shifts to a higher field, and that of the β-carbon, to a lower field.

The ^{13}C chemical shift of the vinyl group has been reported to be mainly controlled by the π-electron density and shows an upfield shift when the π-electron density on the carbon atom increases.[3,8] Therefore, the results in Table 1 show that the electron density of the α-carbon is mainly determined

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[1] R. A. Friedel and H. L. Retcofsky, *J. Amer. Chem. Soc.*, **85**, 1300 (1963).

[2] G. B. Savitsky and K. Namikawa, *J. Phys. Chem.*, **68**, 1956 (1964).

[3] G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965).

[4] T. Higashimura, S. Okamura, I. Morishima and T. Yonezawa, *Polymer Lett.*, **7**, 23 (1969).

[5] K. Hatada, M. Takeshita and H. Yuki, *Tetrahedron Lett.*, **1968**, 4621.

[6] H. Yuki, K. Hatada and K. Nagata, This Bulletin, **42**, 3546 (1969).

[7] M. Takeuchi and K. Nakagawa, "Magnetic Resonance and Relaxation," ed. by R. Blinc, North-Holland, Amsterdam, 1967.

[8] M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

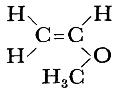
TABLE 1. ^{13}C NMR SPECTRA OF ALKYL VINYL ETHERS ($H_2C_\beta{=}C_\alpha HOR$)

R	Chemical shift from CS_2 (ppm)					
	α	β	c	d	e	f
$-C_cH_3$	40.5	109.6	141.2			
$-C_cH_2C_dH_3$	39.7	108.5	131.4	180.7		
$-C_cH_2C_dH_2C_eH_2C_fH_3$	40.6	108.1	126.8	162.8	174.9	180.7
$-C_cH_2C_dH(C_eH_3)_2$	40.8	108.7	120.5	167.0	175.8	
$-C_cH(C_dH_3)_2$	42.3	106.2	123.3	172.7		
$-C_c(C_dH_3)_3$	46.9	103.5	118.9	166.7		

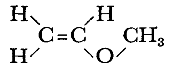
by the electron-repelling power of the alkyl group.

On the contrary, the electron density of the β-carbon decreases when the electron-repelling power of alkyl group becomes stronger. Alkyl vinyl ether takes the following resonance form: $\bar{C}H_2-CH=\overset{+}{O}-R$.9) Our inspection of ^1H NMR spectra of alkyl vinyl ethers suggested that the resonance contribution decreases in the order of the arrangement shown in Table 1, from the top to the bottom.5) The contribution of such a resonance form would lead to an increase in the π-electron density of β-carbon. Therefore, the results in Table 1 are considered to be direct evidence for the above suggestion.

The resonance will be most favorable when the olefinic π-orbital and the lone-pair p-orbital on the oxygen atom overlap. Therefore, the degree of this resonance contribution is considered to depend on the conformation of alkyl vinyl ether. If the oxygen atom is assumed to have essentially sp^3 hybridization and, hence, a tetrahedral disposition of its bonds and lone-pair electrons, the probable conformations are *cis*, *trans* and *gauche* forms. From the inspection of molecular models, the *cis* and *trans* forms are most favorable for the resonance,



cis



trans

while in the *gauche* form the resonance is almost entirely hindered. Infrared study10) showed that, in methyl vinyl ether, the *cis* form is more stable at room temperature. As the alkyl group of vinyl ether is bulkier, the *cis* and *trans* forms become unstable because of the steric interaction between the alkyl group and α- or β-hydrogen of the vinyl group and the proportion of the gauche form gradually increases. Therefore, the degree of resonance contribution in alkyl vinyl ether is mainly controlled by the steric effect and decreases with an increase in the bulkiness of its alkyl group.

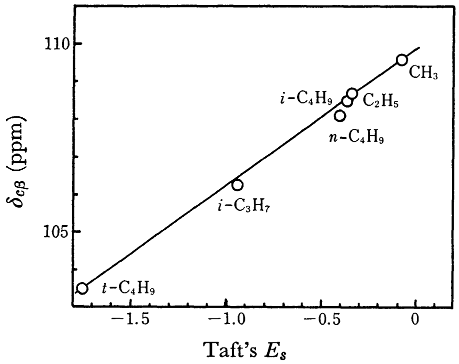


Fig. 1. Plots of $\delta_{c\beta}$ *vs.* E_s.

The order of the arrangement of the ether shown in the table is also in accordance with the increasing order of bulkiness of the alkyl group. By plotting the ^{13}C chemical shifts of β-carbon ($\delta_{c\beta}$) against the Taft steric parameter, E_s, of the alkyl group, a good linear relation was obtained; it is shown in Fig. 1, where the E_s value for R in the ether is that for the RCH_2 of RCH_2COOR'. These results clearly indicate the validity of the above theory.

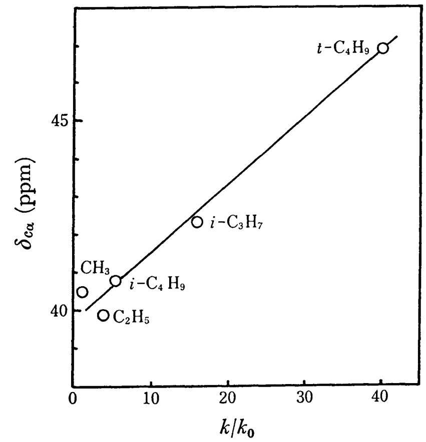


Fig. 2. Plots of $\delta_{c\alpha}$ *vs.* the relative rate of hydrolysis. The hydrolysis was carried out in acetone-water mixture (95/5 vol/vol) at 25°C using HCl catalyst.11) The relative rate is represented by the ratio of the rate coefficient of respective vinyl ether to that of methyl vinyl ether.

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9) J. Feeney, A. Ledwith and L. H. Sutcliffe, *J. Chem. Soc.*, **1962**, 2021.

10) N. L. Owen and N. Shepherd, *Trans. Faraday Soc.*, **60**, 634 (1964).

^{13}C Chemical Shift and Reactivity of Alkyl Vinyl Ether. The carbon-13 NMR spectrum of alkyl vinyl ether may also give important information concerning its reaction mechanism. Therefore, let us now briefly discuss the mechanism of the cationic reaction of alkyl vinyl ether.

Alkyl vinyl ether is readily hydrolysed by dilute aqueous acids, and the relative rate of hydrolysis falls in the sequence;

$$CH_2{=}CHOR + H_2O \xrightarrow{H^+} ROH + CH_3CHO$$

$R = t\text{-}C_4H_9 > i\text{-}C_3H_7 > i\text{-}C_4H_9 > C_2H_5 > CH_3$. From their inspection of the ^1H NMR spectra of alkyl vinyl ethers, Ledwith and Woods[11] suggested that the electron release to the double bond of alkyl vinyl ether falls in the sequence: $CH_3 > i\text{-}C_3H_7 > t\text{-}C_4H_9$ and that, therefore, a simple, slow proton transfer to the terminal methylene group cannot be the rate-determining step in the acid-catalyzed hydrolysis.

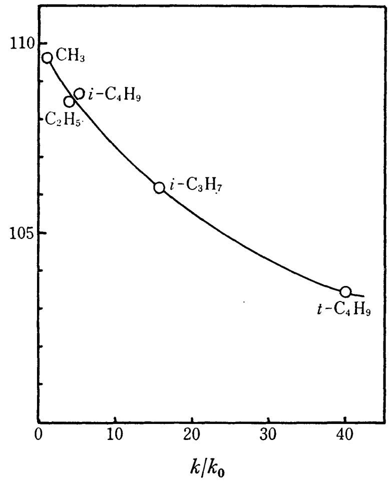

Fig. 3. Plots of $\delta_{c\beta}$ *vs.* the relative rate of hydrolysis.

As is shown in Figs. 2 and 3, a good correlations was obtained between the relative rate of hydrolysis[11] and the ^{13}C chemical shift of α- or β-carbon. These results show that the lower the electron density of β-carbon, and the higher that of α-carbon, the higher the reactivity in acid hydrolysis. This clearly indicates that the attack of the proton on the β-carbon is not the rate-determing step in this reaction. The π-electron density of α-carbon may play an important role in the rate-determining process in the hydrolysis.

The relative reactivity of alkyl vinyl ether in the cationic polymerization falls in the same order as that in the acid-catalyzed hydrolysis. In Figs. 4 and 5 the α- and β-carbon resonances are plotted against the relative reactivities of the ethers. Linear relations similar to those in Figs. 2 and 3 were obtained. The reactivities are represented by $1/r_1$, which was determined in the copolymerization of the respective vinyl ether (M_2) with n-butyl vinyl ether (M_1) at $-78°C$ in toluene by the use of an $EtAlCl_2$ catalyst.[12]

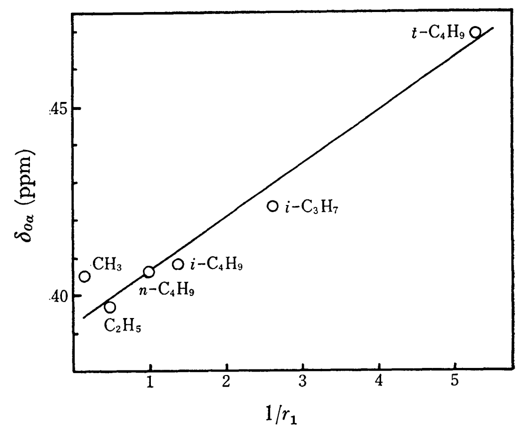

Fig. 4. Plots of $\delta_{c\alpha}$ *vs.* $1/r_1$ for alkyl vinyl ether.

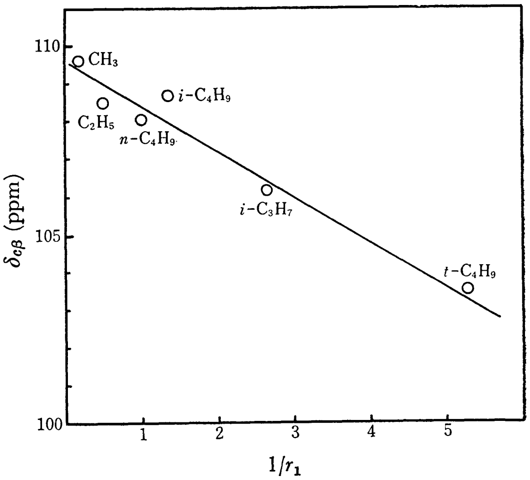

Fig. 5. Plots of $\delta_{c\beta}$ *vs.* $1/r_1$ for alkyl vinyl ether.

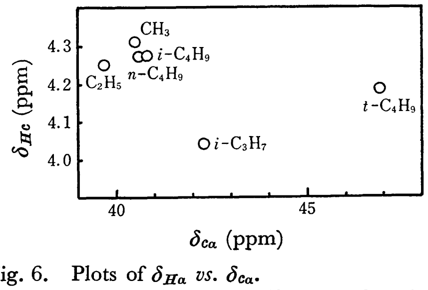

Fig. 6. Plots of $\delta_{H\alpha}$ *vs.* $\delta_{c\alpha}$.
The proton chemical shift was referred to the methyl signal of solvent toluene, low field shift being shown as positive value.

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[11] A. Ledwith and H. J. Woods, *J. Chem. Soc., B*, **1966**, 753.

[12] H. Yuki, K. Hatada and M. Takeshita, *J. Polym. Sci., Part A*-1, **7**, 667 (1969).

Higashimura and his collaborator[13] studied the ^{13}C NMR spectra of *n*-butyl, isopropyl, and 2-chloroethyl vinyl ethers and found that the reactivity of vinyl ethers is not related to their chemical shifts. From this results, they concluded that the attack of the carbonium ion on the β-carbon is not the rate-determining step in the cationic polymerization of vinyl ether.

The results in Figs. 4 and 5 may give a strong evidence for Higashimura's suggestion, and may also suggest that the interaction of the carbonium ion with the α-carbon is an important consideration in determining the transition state of the rate-determining step.

Correlation of ^1H Chemical Shifts with ^{13}C Chemical Shifts. The chemical shift of the α-methine proton of alkyl vinyl ether has been reported to be independent of the electron-repelling power of the alkyl group.[5] No correlation was obtained between the chemical shifts of the α-methine proton and of the α-carbon (Fig. 6). These facts suggest that the chemical shift of this proton is controlled not only by the electron density at the α-carbon, but also by the diamagnetic shielding effect of an O–C bond in the OR group. On the other hand, linear relations were obtained between the chemical shifts of β-methylene protons and of the β-carbon, as is shown in Fig. 7. These relations show that the chemical shifts of β-methylene protons shift to a higher field when the π-electron density of β-carbon increases. The diamagnetic shielding may have little effect on these protons; the chemical shifts are mainly controlled by the electron density at the β-carbon.

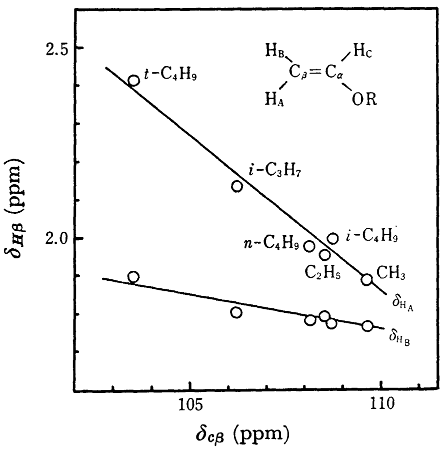

Fig. 7. Plots of $\delta_{H\beta}$ *vs.* $\delta_{C\beta}$.

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[13] T. Higashimura, S. Okamura, I. Morishima and T. Yonezawa, *Polymer Lett.*, **7**, 23 (1969).