

NMR SPECTRA OF ALKYL VINYL ETHER AND ITS STRUCTURES

Koichi Hatada, Masatoshi Takeshita and Heimei Yuki
Department of Chemistry, Faculty of Engineering Science,
Osaka University,
Toyonaka, Osaka, Japan

(Received in Japan 20 June 1968; received in UK for publication 6 August 1968)

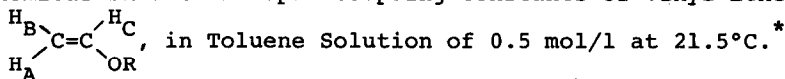
The NMR spectra of some vinyl ethers at 16.2 and 40.0 MHz have been obtained by Feeney at room temperature (1) and correlated with the degree of resonance contributions in vinyl ethers (2). In this work we have measured the NMR spectra of alkyl vinyl ethers at various temperatures using 100 MHz spectrometer and studied on the resonance and the molecular conformation in alkyl vinyl ether.

The spectral parameters of vinyl ethers are given in Table I, in which the vinyl ethers are arranged in increasing order of their reactivities in cationic polymerization (3) from top to the bottom. This order is generally in accordance with the increasing order of bulkiness of alkyl group in alkyl vinyl ether. From top to the bottom in this Table the geminal coupling constant of vinyl ether, J_{AB} , generally increases and the chemical shifts of H_A and H_B , δ_A and δ_B , are to lower field and the difference, $\delta_A - \delta_B$, increases.

It has been suggested that alkyl vinyl ethers may take a following resonance form (1,4). $\bar{C}H_2-CH=O^+-R$ Pople (5) has shown that the coupling constant between geminal hydrogen atoms increases as the s-character of the carbon atom between them increases. So the J_{AB} value of alkyl vinyl ether can be used as an indication of the degree of resonance. Thus the contributions of the resonance form are greatest in methyl vinyl ether and least in t-butyl vinyl ether. On the other hand, the resonance in alkyl vinyl ether must lead to a reduction in the olefinic character of the vinyl group and consequently the terminal methylene protons will become more equivalent. The values of δ_A , δ_B and $\delta_A - \delta_B$ shows that the resonance contribution in alkyl vinyl ether decreases from top to the bottom in Table 1, that is, in the increasing order of the bulkiness of its

TABLE 1

Chemical Shifts and Spin Coupling Constants of Vinyl Ethers,



R	Chemical shift (p.p.m.)				Coupling constant (cps)		
	δ_A	δ_B	δ_C	$\delta_A - \delta_B$	J_{AB}	J_{BC}	J_{AC}
CH ₃	1.88	1.76	4.31	0.12	-2.4	7.0	14.6
C ₂ H ₅	1.95	1.79	4.25	0.16	-1.7	6.9	14.8
n-C ₃ H ₇	1.96	1.77	4.27	0.19	-1.7	6.9	14.5
n-C ₄ H ₉	1.97	1.78	4.27	0.19	-2.0	7.4	13.3
n-C ₆ H ₁₃	2.00	1.79	4.29	0.21	-1.7	6.9	14.6
i-C ₄ H ₉	1.99	1.77	4.27	0.22	-1.8	7.4	13.3
C ₆ H ₅ CH ₂	2.06	1.83	4.28	0.23	-1.9	6.5	13.8
i-C ₃ H ₇	2.13	1.80	4.04	0.33	-1.3	6.8	14.1
C ₆ H ₁₁	2.19	1.83	4.08	0.36	-1.3	6.7	14.2
t-C ₄ H ₉	2.41	1.90	4.18	0.51	0.0	6.3	13.7

alkyl group, since the diamagnetic shielding effect of a O-C bond in OR group is thought to be almost constant for all the alkyl groups.

The resonance will be most favorable when the olefinic π -orbital and the lone-pair p-orbital on the oxygen atom overlap each other. So the degree of this resonance contribution is considered to depend on the conformation of alkyl vinyl ether. By an infrared spectroscopic study Owen (6) has shown that for methyl vinyl ether the cis form is more stable at room temperature and the second form appeared at elevated temperatures. If the oxygen atom is assumed to have essentially sp³ hybridization and hence a tetrahedral disposition of its bonds and lone-pair electrons, the probable conformations could be represented as shown in Fig. 1. Among these conformations the cis and trans forms are most favorable for the resonance and in the gauche form the resonance is almost hindered.

* The spectra were taken by the use of a JNM-4H-100 spectrometer at 100 MHz referring the chemical shifts to the methyl signal of solvent toluene and analysed by means of an ABX type analysis. The accuracies of the measurements of δ and J lie within the deviation of 0.005 p.p.m. and 0.2 cps, respectively.

The contribution of different types of conformations will depend on the temperature. The NMR spectra of alkyl vinyl ether were measured at various temperatures* (Fig. 2). The $\delta_A - \delta_B$ value of methyl vinyl ether increases as the temperature increases. This clearly shows that the degree of resonance contribution in methyl vinyl ether decreases with increasing temperature. The proportion of more stable conformation will decrease at higher temperature and the second form of conformation will appear. From the result above mentioned this second conformation is considered to be an unfavorable form to the resonance, that is, the gauche form. In the case of alkyl vinyl ether, in which the α -carbon of its alkyl group is primary, the $\delta_A - \delta_B$ value changes with temperature as that of methyl vinyl ether does. So the change in conformation with temperature may be similar to that of methyl vinyl ether, although the proportion of gauche form will gradually increase as the alkyl group of vinyl ether is bulkier.

* There may be some weak interaction between solvent toluene and vinyl ether. However, this will not affect the following conclusion because the similar results were obtained in CCl_4 at various temperatures.

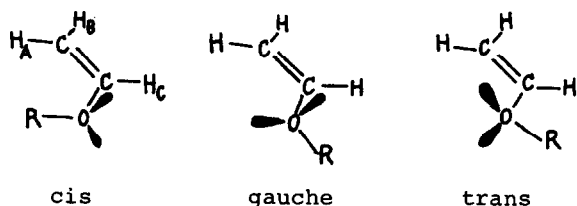
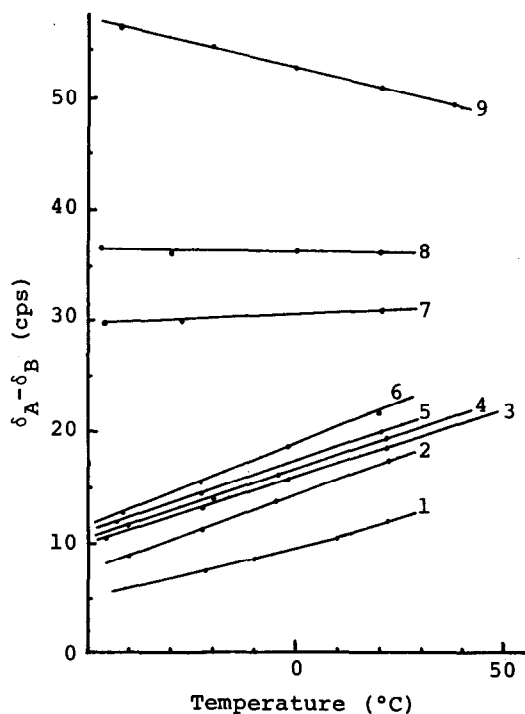


FIG. 1

A Diagrammatic Representation of Possible Conformations of Alkyl Vinyl Ether



- 1 CH₃, 2 C₂H₅, 3 n-C₃H₇, 4 i-C₄H₉,
 5 n-C₆H₁₃, 6 C₆H₅CH₂, 7 i-C₃H₇,
 8 C₆H₁₁, 9 t-C₄H₉,

FIG. 2

$\delta_A - \delta_B$ of Alkyl Vinyl Ether
 at Various Temperatures

On the contrary, the $\delta_A - \delta_B$ value of t-butyl vinyl ether increases as the temperature decreases, indicating that the resonance contribution in this ether decreases with decreasing temperature. The inspection of molecular models suggests that both the cis and trans form of t-butyl vinyl ether are sterically hindered because of the bulkiness of t-butyl group and the gauche form is more stable. The above observation shows that in this ether the contribution of gauche form is predominant. It increases, and consequently the degree of resonance decreases, gradually as the temperature decreases.

In the case of isopropyl or cyclohexyl vinyl ether, in which the α -carbon of alkyl group is secondary, the $\delta_A - \delta_B$ value lies between that of t-butyl vinyl ether and those of alkyl vinyl ethers, in which the α -carbon of alkyl group is primary, and is almost constant at various temperatures. These results suggest that in these two ethers the energy difference between the gauche form and another one is so small that the contribution of conformations does not vary with the change of temperature, and consequently the degree of resonance is almost constant at various temperatures. The conformation other than the gauche form will probably be trans, because the cis form is sterically hindered.

It may be given as a conclusion that in alkyl vinyl ether the conformational contribution of gauche form increases gradually as the alkyl group is bulkier; in methyl vinyl ether the cis form is more stable and in t-butyl vinyl ether the contribution of gauche form is predominant.

References

- (1) J. Feeney, A. Ledwith, L. H. Sutcliffe, J. Chem. Soc., 1962, 2021
- (2) A. Ledwith, H. J. Woods, J. Chem. Soc. (B), 1966, 753
- (3) H. Yuki, K. Hatada, M. Takeshita, to be submitted to J. Polymer Sci.
- (4) P. H. Plesch, The Chemistry of Cationic Polymerization p. 378. Pergamon Press, London (1963)
- (5) J. A. Pople, A. A. Bothner-By, J. Chem. Phys., 42, 1339 (1965)
- (6) N. L. Owen, N. Shepherd, Trans. Farad. Soc., 60, 634 (1964)