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Relationship between Reaction Rates and NMR Chemical Shifts in the Reaction of Cyclic Ketene Acetals with Methanol

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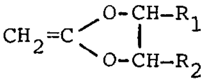
Abstract: The reaction of cyclic ketene acetals with methanol gave the corresponding cyclic orthoacetates in fairly good yield. The linear relationship between their reaction rates and ^1H or ^{13}C NMR chemical shifts of unsaturated methylene groups was obtained from the kinetic studies.

It is known that the unsaturated carbon-carbon double bond of ketene acetals is highly polarized and β-carbon atom has a strong anionoid character because of the electron donating property of the mesomeric effect of oxygen atom. Therefore, most of ketene acetals are susceptible to attack by protic substrates, and undergo the spontaneous polymerization.[1] The kinetics of the hydration of ketene acetals have been studied as the model of acyl transfer reaction through tetrahedral intermediate by several workers.[2-5] From a different view point, cationic[6-7] and radical ring opening polymerizations[8-10] have been also reported.

It is of interest to estimate the reactivities of cyclic ketene acetals by the electronic structure of unsaturated methylene groups, ^1H and ^{13}C NMR chemical shifts of which vary remarkably with their ring size and substituents.

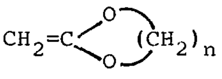
We now report syntheses and methanolysis of cyclic ketene acetals, and the relationship between the reaction rates and the NMR chemical shifts.

Cyclic ketene acetals(I - V) were synthesized by the acetal exchange reaction of chloroacetaldehyde dimethyl acetal with the corresponding glycol, followed by dehydrochlorination of cyclic chloroacetaldehyde acetal with potassium *t*-butoxide. The results are summarized in Table 1.



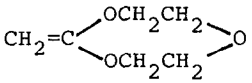
I; $R_1=R_2=CH_3$

II; $R_1=H$, $R_2=CH_2OPh$



III; n=4

IV; n=5



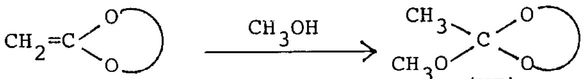
V

Table 1. Preparation and NMR date of cyclic ketene acetals

Compound	Yield(%)	bp(°C/mmHg)	^{1}H and ^{13}NMR spectra(ppm)		
			$C\underline{H}_2=C$	$\underline{CH}_2=C$	$CH_2=\underline{C}$
I	78	76-78/86	3.20	53.02, 53.17	162.88, 163.43
II	68	137-138/4	3.32	53.88	163.5
III	70	68-70/47[a]	3.48	67.35	164.10
IV	82	72-73/30[b]	3.61	69.82	163.82
V	75	67-68/15	3.67	70.52	163.82

a 39-40/8(lit.[11])
b 47-49/9(lit.[11])

The chemical shift of unsaturated methylene group in ketene acetal depends on the extent of p-π conjugation of two oxygen atoms with carbon-carbon double bond.[11] The observed differences in the chemical shifts of ^{1}H and ^{13}C NMR spectra between I and V in unsaturated methylene groups amount to 0.47 ppm and 17.5 ppm, respectively. It can be assumed that the cyclic ketene acetals with a small chemical shift value are more reactive than those with a large one, because the electron density of unsaturated methylene group should increase with the degree of p-π conjugation. In order to clarify a close relationship between the reactivities of cyclic ketene acetals and their chemical shifts of unsaturated methylene groups, equimolar reaction of I-V with methanol was carried out.



(VI)

The reaction products, the cyclic orthoacetates(VI), were isolated to find that the reaction of five membered cyclic ketene acetals with methanol is completed immediately, but the yields in seven- and eight-membered cyclic orthoacetates are 70-90% even after 48 h at room temperature[12], as shown in Table 2. Further, the

Table 2. Reaction of cyclic ketene acetals with methanol[a]

Compound	Time (h)	Orthoester	
		Yield(%)	bp(°C/mmHg)
I	1	98	72-73/110
II	1	98	100-101/1
III	48	92	105-108/110
IV	48	72	85-87/20
V	48	65	54-55/3

[a] Ketene acetal, 0.01 mol; methanol, 0.01 mol; temp., room temp.; solvent, none.

reaction rates(second order) were followed by ^{1}H NMR.[13] The linear relationship between log k_2 and ^{1}H or ^{13}C NMR chemical shifts was obtained, as depicted in Fig.1 and Fig.2, respectively.

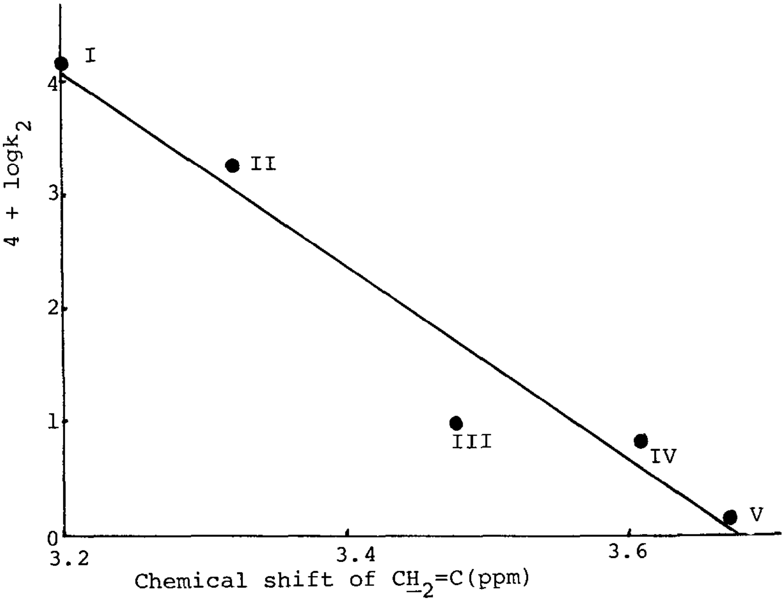


Fig.1. Relationship between log k_2 and ^{1}H NMR chemical shift

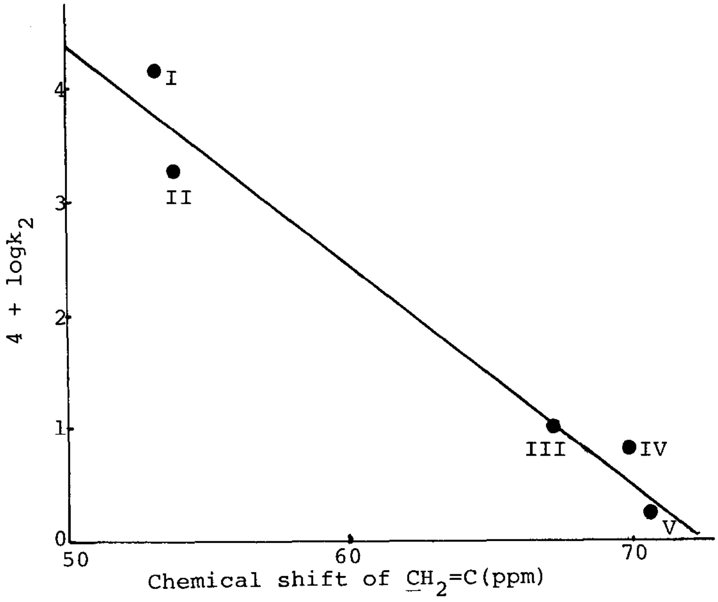


Fig.2. Relationship between log k_2 and ^{13}C NMR chemical shift

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12. Seven- and eight-membered cyclic orthoacetates are relatively unstable and in the absence of a catalyst trimethyl orthoacetate and the corresponding glycol are obtained in the methanolysis if a large excess of methanol is employed.
13. Reaction condition; ketene acetal, 1.67 mol/L; methanol, 1.67 mol/L; temp., 25 °C; solvent, chloroform-d.

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