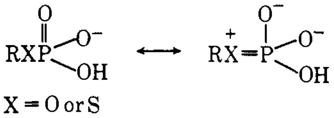
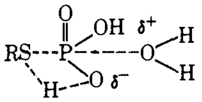
tively facile hydrolysis of these compounds may reside in a smaller resonance interaction between sulfur and phosphorus than between oxygen and phosphorus in the ground state.


(4)

Neutral Species. There is no observable acid catalysis of the hydrolysis of any of the thiolphosphate esters at HCl concentrations up to 6.12 *M*. A similar observation was made for the alkyl ester S-*n*-butyl phosphorothioate.[6] Dittmer, Ramsay, and Spalding[7] found that the rate of hydrolysis of that compound decreased as acid concentration was increased. The value of k_{H_2O}/k_{D_2O} for *p*-NO$_2$ in 6 *M* HCl and DCl is 1.83. Thus hydrolysis of the neutral species also probably involves a slow proton-transfer step not involving hydronium ion. Electron withdrawal in the leaving group does not facilitate the reaction greatly ($k_{NO_2}/k_H = 1.7$). A unimolecular decomposition to metaphosphate with internal protonation in the rate-determining step should proceed more slowly in D$_2$O than in H$_2$O and would be expected to be insensitive to electronic effects, as in the monoanion reaction. The observed ΔS* is, however, −13.2 eu, 21 eu more negative than that for the dianion reaction and 11 eu more negative than for hydrolysis of the monoanion. Thus it seems probable that solvent is involved in the hydrolysis of the neutral species, and that attack by water is taking place. An internal protonation should markedly lower the sensitivity of rate to electron withdrawal in R. For a reaction involving water it might be expected that increasing the ionic strength up to 6 *M* would retard the rate much more strongly than observed as the activity of water is decreased. This objection is, however, not necessarily valid. The rate of hydrolysis of N-(3,3-dimethylbutyryl)-imidazolium ion, which certainly involves water in the transition state, is unaffected by increasing HCl concentration to 6 *M* at 30°.[32]


(5)

Acknowledgment. This work was supported by grants from the National Institutes of Health and the American Cancer Society. Support for Sheldon Milstien was provided by National Institutes of Health Research Training Grant GM 197.

[32] J. A. Fee and T. H. Fife, *J. Phys. Chem.*, 70, 3268 (1966).

Structure and Reactivity of α,β-Unsaturated Ethers. The Acid-Catalyzed Hydrolysis of Alkenyl Alkyl Ethers[1]

T. Okuyama, T. Fueno,[2] H. Nakatsuji, and J. Furukawa

Contribution from the Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto, Japan. *Received April 12, 1967*

Abstract: The rates of the acid-catalyzed hydrolysis of various α,β-unsaturated ethers, R$_1$R$_2$C=CHOR$_3$, in 80% aqueous dioxane have been measured at varying temperatures. The reaction is first order with respect to both ether and acid. The second-order rate constants of ethyl ethers have been found to decrease in the order: vinyl > β-monoalkylvinyl > β,β-dialkylvinyl. Neither *cis*- nor *trans*-β-monoalkylvinyl alkyl ethers suffer geometrical isomerization during the course of hydrolysis. *cis*-β-Monoalkylvinyl alkyl ethers have proved to be several times more reactive than the corresponding *trans* isomers. The heats of activation for the *trans* isomers are greater than those of the *cis* isomers by 1–3 kcal/mole. The activation entropies are positive in sign in the majority of cases. All these results are best interpreted in terms of the rate-determining protonation of the unsaturated bond of the ethers, in which the transition state possesses substantial carbonium ion character.

Alkyl vinyl ethers are known to be readily hydrolyzed in dilute aqueous acids to give acetaldehyde and alcohols[3–7] (eq 1). The course of the reaction must

$$CH_2{=}CHOR + H_2O \xrightarrow{H_3O^+} CH_3CHO + ROH \qquad (1)$$

apparently be different from that of the hydrolysis of saturated ethers.

The mechanism of the unsaturated ether hydrolysis is currently being unraveled by several workers. Kiprianova and Rekasheva[8] first noted that the alkyl–oxygen bond in vinyl ether is not broken during the acid-catalyzed hydrolysis, and thereby established that the unsaturated carbon–carbon bond constitutes a center vulnerable to the primary attack of the hydronium ion. Jones and Wood[9] investigated the hydrolysis of various alkyl vinyl ethers kinetically and suggested on the basis of the

---

[1] Presented in part at the IUPAC International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, Oct 1966.

[2] To whom inquiries concerning this paper should be addressed, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

[3] A. Skrabal and R. Skrabal, *Z. Phys. Chem.*, **A181**, 449 (1938).

[4] R. Skrabal, *ibid.*, **A185**, 81 (1939).

[5] A. Zahorka and K. Weimann, *Monatsh.*, 71, 229 (1938).

[6] R. Paul, *Bull. Soc. Chim. France*, 1, 971 (1934).

[7] E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovskii, *Zh. Obshch. Khim.*, **18**, 1663 (1948).

[8] L. A. Kiprianova and A. F. Rekasheva, *Dokl. Akad. Nauk SSSR*, **142**, 589 (1962).

[9] D. M. Jones and N. F. Wood, *J. Chem. Soc.*, 5400 (1964).

Table I. Boiling Points, Refractive Indices, and Elemental Analysis Data[a] for Alkenyl Ethers

No.[b]	Calcd, %		Found, %		Bp, °C	$n^{25}\text{D}$	Isomeric purity, %
	C	H	C	H			
4c	69.72	11.70	69.22	11.76	68.5	1.3945	97.3
4t					74.5	1.3950	96.6
5c	71.95	12.08	71.00	12.01	93.2–93.5	1.4020	95.5
5t					100.0–100.8	1.4041	96.0
6c	73.63	12.36	73.53	12.15	107.5–108.0	1.4030	96.6
6t					117.5–118.5	1.4072	98.6
7	74.94	12.58	74.77	12.61	128–134	1.4105	1:4[c]
8c	74.94	12.58	74.94	12.32	127	1.4138	99.0
8t					142	1.4148	98.5
9c	76.00	12.76	75.72	12.78	157	1.4221	95.9
9t					175	1.4235	97.2
10c	73.63	12.36	73.54	12.34	110	1.4060	97.5
10t					119	1.4080	95.1
11	71.95	12.08	71.69	12.34	93.8–94.0	1.4030	. . .

[a] Analyses conducted for the *cis* and *trans* mixtures. [b] For numbering, see text and Table III. The suffixes **c** and **t** refer to *cis* and *trans*, respectively. [c] Approximate *cis*/*trans* composition.

observed D_2O solvent isotope effect that the rate-determining step involves transfer of proton from the hydronium ion to the β-carbon of the ethers. Salomaa, *et al.*,[10] concluded the same mechanism for the case of vinyl and isopropenyl ethers. A similar conclusion has been reached by Fife[11] for the acid-catalyzed hydrolysis of 2-ethoxy-1-cyclopentene-1-carboxylic acid. Recently, Kresge and Chiang[12] have taken a closer look at the origin of the D_2O solvent isotope effect in the ethyl vinyl ether hydrolysis and demonstrated that the proton transference is about 60% complete in the transition state of the rate-determining step.

In the present paper, we have undertaken more detailed and systematic investigations of the structure–reactivity relations of the hydrolysis of various unsaturated ethers. Thus, the reaction kinetics of a variety of α,β-unsaturated ethers, $R_1R_2C{=}CHOR_3$, where R_1 and R_2 are an alkyl group or a hydrogen atom, and where R_3 is C_2H_5, n-C_4H_9, or i-C_4H_9, have been compared at various temperatures. Attention has been focused on the difference in reactivity between the *cis* and *trans* isomers. The results obtained seem to show that the reactivities are closely associated with the stabilities of the intermediate carbonium ions relative to the parent ethers. This implication is of particular importance in understanding the mechanisms of reactions of various unsaturated ethers with electrophilic agents as well as the kinetic modes of their stereospecific polymerizations in homogeneous media.

Experimental Section

Materials. Ethyl (**1**), *n*-butyl (**2**), and isobutyl vinyl ethers (**3**) were commercially obtained and distilled from lithium aluminum tetrahydride. Propenyl (**4**), but-1-enyl (**5**), 3-methylbut-1-enyl (**6**), and 2-methylpropenyl ethyl ethers (**11**) and propenyl isobutyl ether (**10**) were prepared by the pyrolysis of appropriate acetals[13] which were obtained from the reactions between aldehydes and alcohols.[14] 3,3-Dimethylbut-1-enyl (**7**), 4-methylpent-1-enyl (**8**), and hept-1-enyl ethyl ethers (**9**) were prepared from the corresponding acylals (1-alkoxyalkyl acetates) which were synthesized from pertinent aldehydes.[15] The *cis* and *trans* isomers of the ethers were separated, whenever required, by fractional distillations through an 80-cm column packed with Raschig rings. Boiling points and refractive indices of all the unsaturated ethers here prepared (**4–11**) are given in Table I, together with their analytical data.

The various aldehydes used for the syntheses of the unsaturated ethers were mostly purchased. Isovaleraldehyde and isobutylacetaldehyde were prepared by the oxidation of alcohol[16] and by the Grignard synthesis,[17] respectively. *t*-Butylacetaldehyde was obtained by the hydrolysis of 1,1-dichloro-3,3-dimethylbutane, which was prepared from *t*-butyl chloride and vinyl chloride.[18]

1,4-Dioxane was dried over calcium dihydride and fractionally distilled, bp 101°. Tetrahydrofuran and other chemicals, which were used as internal standards for the gas–liquid partition chromatographic analysis, were commercially obtained and distilled.

Kinetic Measurements. Hydrolysis was carried out in solutions of 80% aqueous dioxane containing hydrochloric acid. The acid concentrations were in the range 5–20 m*M*. The acidic solutions were prepared by diluting 20.0 ml of hydrochloric acid of appropriate concentrations to 100.0 ml with dioxane.

In a glass-stoppered flask of *ca.* 50-ml content were placed a 20-ml portion of acidic aqueous dioxane and 0.5 ml of internal standard. The mixture was thermostated at a specified temperature. Unsaturated ether (1 ml) was then introduced into the mixture under magnetic stirring, and the reaction started. At specified intervals of time, small portions of the reaction mixture were sampled out with a syringe, and the reaction was stopped by the addition of methanolic potassium hydroxide.

The residual ether was determined by use of a Yanagimoto Model GCG-3DH gas chromatograph with hydrogen as carrier gas. Column packings and internal standards were selected so as to suit the determination of each unsaturated ether. It was found by calibration that the half-height width method fully sufficed for linearly correlating the obtained peak area to the ether concentration. When geometrical isomers exist for an ether, the hydrolysis was started, in most cases, with its isomeric mixture but the kinetic

---

(10) P. Salomaa, A. Kankaanperä, and M. Lajunen, *Acta Chem. Scand.*, 20, 1790 (1966).

(11) T. H. Fife, *J. Am. Chem. Soc.*, **87**, 1084 (1965).

(12) A. J. Kresge and Y. Chiang, *J. Chem. Soc.*, *B*, 58 (1967).

(13) M. Farina, M. Peraldo, and G. Bressan, *Chim. Ind.* (Milan), **42**, 967 (1960).

(14) H. Adkins and B. H. Nissen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p 1.

(15) J. L. E. Erickson and M. Z. Woskow, *J. Org. Chem.*, 23, 670 (1958).

(16) C. M. van Marle and B. Tollens, *Ber.*, **36**, 1342 (1903).

(17) C. E. Wood and M. A. Comley, *J. Soc. Chem. Ind.* (London), **42**, 429 T (1923).

(18) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 1650 (1946).

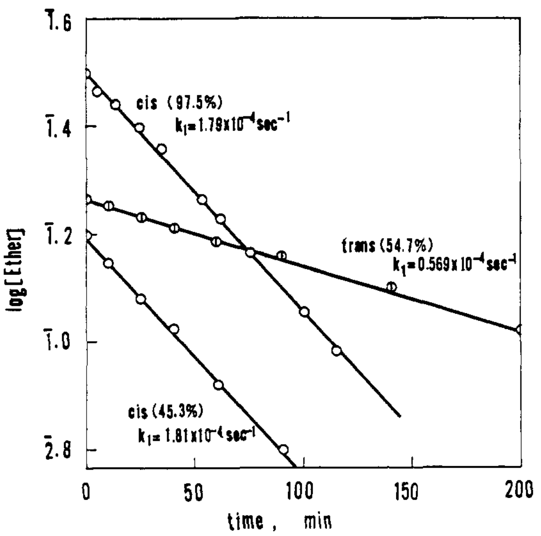


Figure 1. First-order plots for the hydrolysis of propenyl isobutyl ether; [HCl] = 9.30×10^{-3} *M*, 25°.

courses were followed separately. In the case of ethyl vinyl ether (**1**) the course of the ethanol formation was pursued.

Results

It has repeatedly been described by previous workers that for a given acid concentration, the acid-catalyzed hydrolysis of unsaturated ethers is first order with respect to the ether concentration.[7,9–11] We have been able to confirm it for all the alkenyl ethers investigated here; the first-order plots were perfectly linear for the *cis* and *trans* isomers separately in their respective kinetic ranges up to at least 80% conversion. A typical example of such plots is shown in Figure 1.

One notable feature of the alkenyl ether hydrolysis which has first been revealed by the present work concerns the effect of geometrical isomerism on the reactivity. It has been found that, in general, *cis*-alkenyl ethers are several times more reactive than the corresponding *trans* isomers, as can be seen, for example, in Figure 1. This finding constitutes the main body of this paper and will be discussed in detail later.

The fact that the disappearance of each geometrical isomer conforms to the first-order kinetic law may in itself indicate that neither isomeric ether suffers *cis–trans* isomerization during the course of hydrolysis. In order to confirm this point, the rate measurements were performed for mixtures of *cis*- and *trans*-propenyl isobutyl ethers (**10c** and **10t**) of various isomer compositions. The results are summarized in Table II, where it is seen that the first-order rate constants, k_1, for consumptions of the two isomers are independent of the initial isomer compositions. Thus, it is definite that no geometrical isomerization was taking place during the course of hydrolysis. Table II also indicates that the various internal standards added to the reactant mixtures exerted no significant influence upon the hydrolysis rates. Incidentally, gas chromatography showed formation of no other products than the normal hydrolysis products, *i.e.*, aldehyde and alcohol.

The first-order rate constants, k_1, measured as above, were found to be proportional to the acid concentration, as is seen in Figure 2. The proportionality factor, defined as $k_2 = k_1/[\mathrm{HCl}]$, is the second-order rate constant for hydrolysis. For *cis*- and *trans*-propenyl isobutyl ethers, for instance, the values of k_2 at 25° were 1.95×10^{-2} and 6.35×10^{-3} l. mole^{-1} sec^{-1}, respectively.

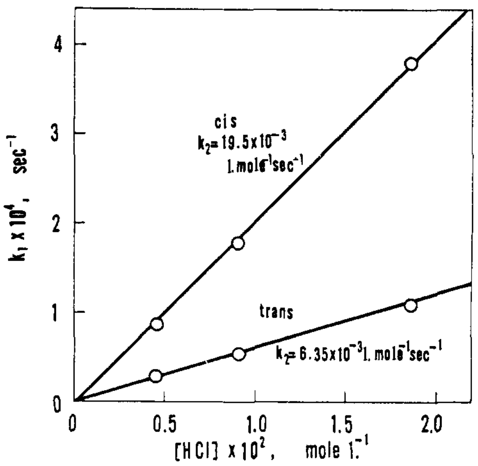


Figure 2. Linear dependence of the hydrolysis rate of propenyl isobutyl ether on the acid concentration at 25°.

Table II. The First-Order Rate Constants, k_1, of the Hydrolysis of Propenyl Isobutyl Ether[a]

Isomeric composition, %		Intern std	$k_1 \times 10^5$, sec^{-1}	
cis	*trans*		*cis*	*trans*
73.3	26.7	THF	5.23[b]	...
44.9	55.1	THF	5.30[b]	1.54[b]
97.5	2.5	THF	17.9[c]	...
88.5	11.5	THF	18.6[c]	...
88.5	11.5	CCl_4	18.1[c]	...
88.5	11.5	Toluene	17.7[c]	...
45.3	54.7	THF	18.1[c]	5.69[c]
21.9	78.1	THF	...	6.11[c]
71.9	28.1	THF	60.6[d]	19.3[d]
58.6	41.4	THF	58.6[d]	19.8[d]

[a] [HCl] = 9.30×10^{-3} *M*. The initial total concentration of the *cis* and *trans* ethers was *ca.* 0.31 *M*. [b] At 15°. [c] At 25°. [d] At 35°.

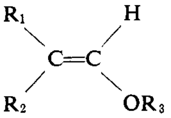
Measurements of the hydrolysis rates were conducted for various alkenyl ethers at varying temperatures. The values of k_2 obtained are summarized in Table III. It can be seen in Table III that at any temperature selected the reactivitives of *cis* isomers are several times as great as those of the corresponding *trans* isomers. This effect of the geometrical isomerism on the reactivity is even greater than that of the variation in alkyl groups attached to the β-carbon atom. Also noticeable is the trend that the reactivity diminishes with increasing number of the alkyl substitutions on the β position.

From the k_2 values listed in Table III, the heats and entropies of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were evaluated in a usual manner. Linearities of the plots of $\log (k_2/T)$ against $1/T$ were satisfactory for all the compounds studied. All the activation parameters obtained are listed in Table III. It should be noted that the activation entropies are positive in sign in all the cases except for ethyl vinyl ether (**1**).

Discussion

A. Rate-Determining Protonation. It is well established that in the hydrolysis of alkyl vinyl ethers, the primary reaction takes place at the carbon–carbon

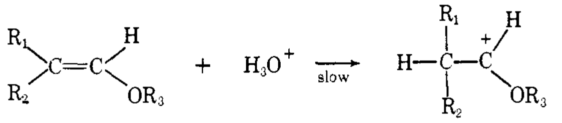
Table III. The Rate Constants and Activation Parameters for the Hydrolyses of Alkenyl Ethers



No.	R_1	R_2	R_3	$k_2 \times 10^3$, l. mole^{-1} sec^{-1} 15°	25°	35°	45°	$\Delta H^{\ddagger}$,[a] kcal/mole	$\Delta S^{\ddagger}$,[b] eu	Intern std
1[c]	H	H	C_2H_5	25.0	75.1			17.5	−4.9	THF[f]
2	H	H	n-C_4H_9	19.6[d]	68.7[d]	216[d]		20.6	+5.4	THF[f]
3	H	H	i-C_4H_9	16.8	60.8[e]	188		20.7	5.6	THF[f]
4c	H	CH_3	C_2H_5	8.40	29.3	90.9		20.4	2.9	C_6H_6
4t	CH_3	H	C_2H_5	2.26	9.03	29.9		22.2	6.5	C_6H_6
5c	H	C_2H_5	C_2H_5	7.67	26.3	85.9		20.7	3.7	CCl_4
5t	C_2H_5	H	C_2H_5	1.83	6.86	23.4		21.9	5.0	CCl_4
6c	H	i-C_3H_7	C_2H_5	7.57	22.9	76.5		19.8	0.5	$(i$-$C_3H_7)_2O$
6t	i-C_3H_7	H	C_2H_5	1.14	4.00	15.9		22.6	6.5	$(i$-$C_3H_7)_2O$
7c	H	t-C_4H_9	C_2H_5		35.5	100.4	303	19.6	0.5	n-C_8H_{18}
7t	t-C_4H_9	H	C_2H_5		4.99	18.2	54.8	22.0	4.7	n-C_8H_{18}
8c	H	i-C_4H_9	C_2H_5		10.9	37.9	116	21.6	5.0	n-C_9H_{20}
8t	i-C_4H_9	H	C_2H_5		2.77	9.95	33.7	22.9	6.7	n-C_9H_{20}
9c	H	n-C_5H_{11}	C_2H_5	3.78	13.11	40.3		20.3	0.9	TL[g]
9t	n-C_5H_{11}	H	C_2H_5	0.949	3.33	12.0		21.8	3.2	TL[g]
10c	H	CH_3	i-C_4H_9	5.66	19.5	64.1		20.8	3.5	THF[f]
10t	CH_3	H	i-C_4H_9	1.66	6.35	21.0		21.8	4.4	THF[f]
11	CH_3	CH_3	C_2H_5		2.21	8.89	28.8	23.6	8.5	CCl_4

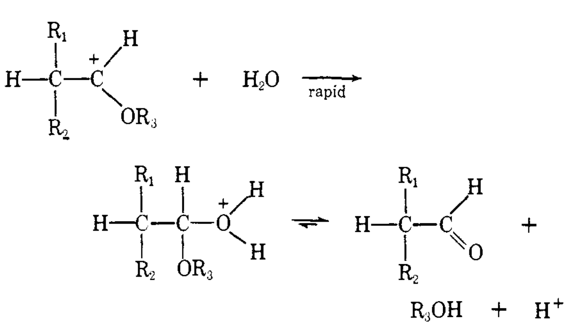
[a] Probable error of each entry does not exceed 0.2 kcal/mole. [b] Accurate to within ±0.3 eu. [c] $k_2 = 15.0 \times 10^{-3}$ l. mole^{-1} sec^{-1} at 10°. [d] Reference 5 reports values of 21.7×10^{-3}, 65.0×10^{-3}, and 173×10^{-3} l. mole^{-1} sec^{-1} at 15, 25, and 35°, respectively. [e] A value of 56×10^{-3} l. mole^{-1} sec^{-1} is reported in ref 9. [f] Tetrahydrofuran. [g] Tetralin.

double bond.[8–11] On the basis of rather indirect information regarding D_2O solvent isotope effects[9–12] a proposal has been made that the rate-determining step of the ether hydrolysis is the proton transfer from hydronium ion to the unsaturated bond of the ethers.



(2)

In the present study, we have observed that neither *cis*- nor *trans*-alkenyl ethers suffer geometrical isomerization during the course of hydrolysis. This observation may be taken, to the best of our knowledge, as a *first* and *direct* proof that the proton-transfer process is indeed rate determining. The resultant carbonium ions must then suffer a rapid attack of water to complete the reaction.



(3)

Putting the effect of geometrical isomerism out of consideration for a moment, one may notice in Table III that the reactivities of ethyl ethers diminish in the order: vinyl (**1**) > β-monoalkylvinyl (**4–9**) > β,β-dialkylvinyl (**11**). In addition, α-methylvinyl ethyl ether has been reported to hydrolyze *ca.* 2 × 10^4 times faster than ethyl vinyl ether (**1**).[9] These orders of reactivity are explainable by the concept of the hyperconjugative stabilities of the carbonium ions formed. That is, the greater the number of the hydrogen atoms linked with the α-carbon or -carbons (with respect to the charged center), the more stable are the carbonium ions on account of the hyperconjugation and, hence, the more reactive are the parent unsaturated ethers.[19,21] This view is compatible with the concept that the formation of carbonium ions is rate determining (Chart I).

The above argument implicitly assumes that the carbonium ion intermediates as formed by reaction 2 would have stabilities parallel to those of the transition state of the same reaction. Kresge and Chiang[12] have shown that the proton transfer from the hydronium ion to ether is only half complete by the time the transition state is reached. This point, however, will not invalidate our argument because the transition state probably possesses substantial carbonium ion character. This is synonymous to stating that the assumption of a free carbonium ion is a useful extrapolation of the transition state in discussing the relative reactivities of different ethers semiquantitatively.[23]

(19) This is in accord with the so-called Baker–Nathan order. In the acid-catalyzed hydrolysis of acetals, $R_1R_2C(OC_2H_5)_2$, relative reactivities were quantitatively explained in terms of the polar substituent constants for R_1 and R_2 and of the number of α-hydrogen atoms in the groups R_1 and R_2. The latter is assumed to be proportional to the relative hyperconjugative stabilization in the carbonium ions formed in the rate-determining step.[20]

(20) M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 5590 (1955).

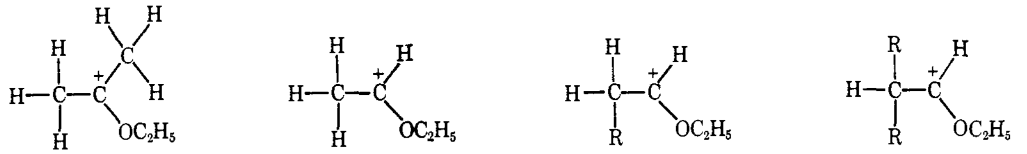
(21) Ehrenson and co-workers[22] have made theoretical considerations of the possible effects of hyperconjugation on the rates of reactions involving carbonium ion-like transition states. The acid-catalyzed hydration of olefins was chosen as a typical case.

(22) S. Ehrenson, *J. Am. Chem. Soc.*, **86**, 847 (1964); S. Ehrenson, S. Seltzer, and R. Diffenbach, *ibid.*, **87**, 563 (1965).

(23) Such an extrapolation has been found to be plausible to interpret the effect of the ring substituents on the hydrolysis rate of phenyl vinyl ether, which was observed to fit the Hammett equation with a negative reaction constant.[24]

(24) T. Fueno, I. Matsumura, T. Okuyama, and J. Furukawa, to be published.

Chart I



No. of α-hydrogens	6	3	2	1
relative rate	2×10^4	1	0.1–0.4 (*cis*) 0.04–0.1 (*trans*)	0.03

When the conjugative stabilizing effects in the transition state are the same for different ethers, their relative rates of hydrolysis must be determined by the relative stabilities of their ground states. As may be seen in Table III, the reactivities of β-monoalkylvinyl ethyl ethers, whether *cis* or *trans*, decrease roughly in the order of an increasing number of the carbon atoms constituting the β-alkyl groups. For this class of alkenyl ethers, the hyperconjugative stabilities of the intermediate carbonium ions will be approximately the same, inasmuch as the numbers of the α-hydrogen atoms in the carbonium ions are the same, *i.e.*, 2. Naively, the observed effect of alkyl substituents on the reactivity may be related with the inductive effects of the alkyl groups opposing the polarization of the vinyl linkage in the ground state. Interpretation of the substituent effect in terms of an adverse steric effect of bulkier alkyl groups in the activation process seems to be inadequate on grounds which will be presented later. Relatively great reactivity of *cis*-β-*t*-butyl compound **7c** may probably be due to the relief of its steric strain on forming the carbonium ion.

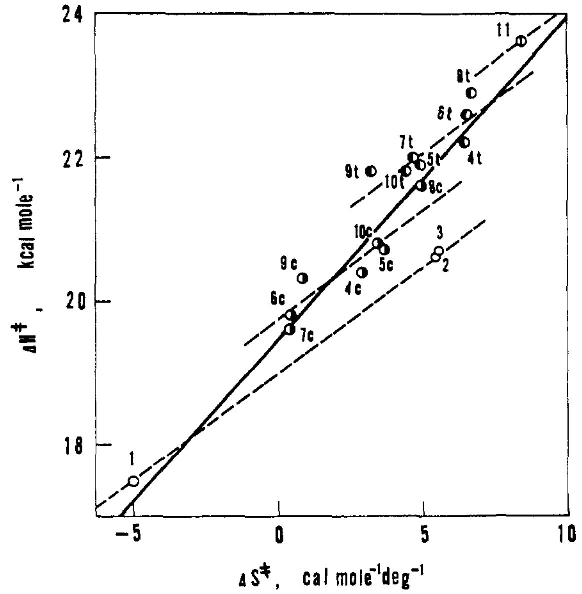


Figure 3. Plots of $\Delta H^{\neq}$ against $\Delta S^{\neq}$ for the hydrolysis of alkenyl ethers: ○, β-unsubstituted; ◑, *cis*-β-monosubstituted; ◐, *trans*-β-monosubstituted; and ⦶, β,β-disubstituted ethers. Numbers correspond to the ethers given in Table III.

B. Effect of Geometrical Configuration on the Rates. In all the cases where the geometrical isomerism occurs, the *cis* isomers are more reactive than the *trans* isomers. The difference in reactivity seems to be larger for compounds bearing bulkier β substituents. Since it is probable that the energy difference of the transition states for a given pair of geometrical isomers is small,[25] the difference in reactivity between the isomers may be largely due to the difference in the stabilities of the reactant isomers. Thus, it may be suggested that the *trans* isomers are more stable than the *cis* isomers. The differences in heat of activation, $\Delta H^{\neq}$, between *cis* and *trans* isomers are 1–3 kcal/mole, as is seen in Table III. Hence, the *trans* isomers will be thermochemically more stable than the corresponding *cis* isomers by this quantity, provided the carbonium ion intermediates formed from the respective isomers are the same in over-all heat content. This inference of the greater thermochemical stabilities of *trans*-alkenyl ethers was substantiated by our separate experiments on their *cis–trans* isomerization equilibria.[26,27]

Thus, the relative reactivities of the various ethers are explainable in terms of the stability of the intermediate carbonium ions relative to the parent ethers. The mechanism of the acid-catalyzed hydrolysis of α,β-unsaturated ethers may, therefore, be most conveniently depicted by the scheme which involves the rate-determining carbonium ion formation (eq 2), immediately followed by a rapid attack of water to form aldehydes and alcohols (eq 3), even though the assumed carbonium ion may be somewhat far from the true intermediate structure.

C. Activation Parameters. Inspection of the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ given in Table III shows that the relative reactivities of ethers are governed mostly by the enthalpy term and that the activation entropies take on small positive values except for ethyl vinyl ether (**1**). As is seen in Figure 3, the $\Delta H^{\neq}$ values of alkenyl ethers are roughly in a linear correlation with $\Delta S^{\neq}$ values, the isokinetic temperature being *ca.* 450°K. Clearly, all the ethers studied in the present work are hydrolyzed through the same mechanism and their relative reactivities governed predominantly by the enthalpy term.

Nonetheless, a closer examination of the $\Delta H^{\neq}$-$\Delta S^{\neq}$ plots in Figure 3 seems to show that the points fall on a group of parallel straight lines which are drawn according to the types of β substitutions, *i.e.*, lines for β-unsubstituted, *trans*- and *cis*-β-monosubstituted, and β,β-disubstituted ethers. Similar, but far more clearly separated, parallel four lines were obtained with the ΔH and the ΔS values observed for the π-complex formation of the alkenyl ethers with silver ion.[28] This latter

---

[25] If the transition state possesses a sufficiently high degree of carbonium ion character, the difference under question may well be insignificant.

[26] T. Okuyama, T. Fueno, and J. Furukawa, to be published.

[27] In the case of β-phenylvinyl ethyl ether, the *trans* isomer was found to be less stable than the *cis* isomer and, hence, the more amenable to the acid-catalyzed hydrolysis.[26]

[28] T. Fueno, T. Okuyama, O. Kajimoto, and J. Furukawa, preprint of the IUPAC International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, Oct 1966, p 158.

ΔH-ΔS relation was interpreted in terms of the steric effects in the silver ion complexes. From the above comparison, it may be concluded that in the protonation process of alkenyl ethers the steric contribution, if any, of alkyl groups is far less important than that observed in the silver ion complexation.

The Mechanism of the Reaction of Aqueous Benzyldimethylsulfonium Chloride and Formaldehyde with Sodium Hydroxide

Masao Yoshimine and Melvin J. Hatch

Contribution from the Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640. Received May 25, 1967

Abstract: The mechanism of the reaction of aqueous benzyldimethylsulfonium chloride, formaldehyde, and sodium hydroxide is (1) a rapid and reversible formation of dimethylsulfonium benzylide, (2) a rate-determining nucleophilic attack of the ylide on formaldehyde to form a betaine intermediate, and (3) a rapid intramolecular displacement of methyl sulfide by the oxyanion to yield styrene oxide. The tentatively identified by-products of the reaction appear to be derived from the OH^- displacement reaction on the sulfonium ion, the rearrangement of ylides, and the attack of methyl sulfide and methanol on styrene oxide.

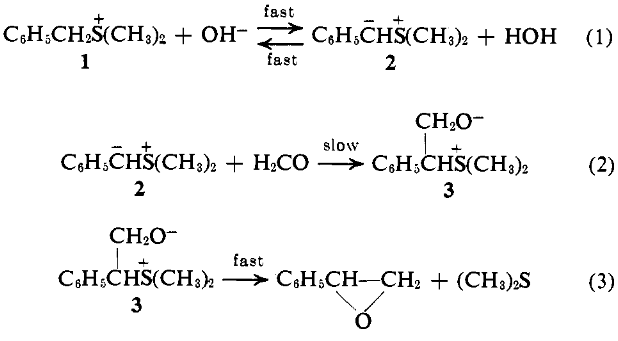
The general utility of the reaction of sulfonium ylides with aldehydes and ketones to yield the corresponding oxiranes has been reported recently.[1-3] The reactions ranged from a stabilized isolable dimethylsulfonium fluorenylide with activated benzaldehydes[4] to the thermally unstable dimethylsulfonium methylide with several ketones and aldehydes.[2] It should be noted that all the reactions were carried out in nonaqueous solvents at low temperatures (25 to −70°).

Hatch[5] has reported a method for selectively trapping the reactive ylide with various aldehydes and ketones in an aqueous alkaline system and removing the oxiranes as formed by an immiscible organic extractant. The reaction of benzyldimethylsulfonium chloride (**1**) with formaldehyde in aqueous sodium hydroxide gave styrene oxide in an 84% yield. The present paper describes a study of the mechanism of this reaction.

The nucleophilic attack of the ylide carbanion on the carbonyl carbon has been generally suggested for the reaction of sulfonium ylides with aldehydes and ketones in nonaqueous systems.[2-4] Sivaramakrishnan and Radhakrishnamurti[6] have proposed recently a carbene mechanism for the reaction of trimethylsulfonium iodide, benzaldehyde, and potassium *t*-butoxide in 90% DMSO.

The proposed mechanism illustrated in Chart I accounts for the products of the reaction (in an aqueous system). This is the mechanism the authors of this paper suggest.

Chart I



$$C_6H_5CH_2\overset{+}{S}(CH_3)_2 + OH^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2 + HOH \quad (1)$$
$$\textbf{1} \qquad\qquad\qquad\qquad \textbf{2}$$

$$C_6H_5\overset{-}{C}H\overset{+}{S}(CH_3)_2 + H_2CO \xrightarrow{\text{slow}} C_6H_5\overset{CH_2O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2 \quad (2)$$
$$\textbf{2} \qquad\qquad\qquad\qquad \textbf{3}$$

$$C_6H_5\overset{CH_2O^-}{\overset{|}{C}}H\overset{+}{S}(CH_3)_2 \xrightarrow{\text{fast}} C_6H_5\underset{\diagdown\; O \;\diagup}{CH{-}CH_2} + (CH_3)_2S \quad (3)$$
$$\textbf{3}$$

The initial step is a rapid and reversible formation of the ylide **2**. The second step is a slow nucleophilic attack of the ylide **2** on the formaldehyde to yield a betaine intermediate **3**. The third step is a fast decomposition of the betaine intermediate **3** *via* an intramolecular displacement of methyl sulfide by the oxyanion to yield styrene oxide.

To elucidate the nature of the first step in the proposed mechanism, the reaction was run short of completion in 38.3% D_2O to yield 18% styrene oxide. The proton nmr analysis of the styrene oxide product indicated approximately 36% deuteration in the α position which was essentially statistical distribution of the deuterium. The proton nmr analysis of the isolated benzyldimethylsulfonium perchlorate indicated approximately 35% deuteration in the benzylic protons and approximately 32% deuteration in the methyl protons. The extent of deuteration of benzylic protons of the benzyldimethylsulfonium perchlorate and of the α position of styrene oxide can be considered essentially the same within the accuracy of the nmr analyses. These results indicate that first step in the proposed mechanism is a rapid and reversible formation of dimethylsulfonium benzylide (**2**).

---

(1) A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Am. Chem. Soc.*, **86**, 918 (1964).

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

(3) V. Franzen and H. E. Driessen, *Tetrahedron Letters*, 661 (1962).

(4) A. W. Johnson and R. B. LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

(5) M. J. Hatch presented this work at the 22nd Annual Southwest Regional Meeting of the American Chemical Society, Albuquerque, N. M., Nov 1966.

(6) R. Sivaramakrishnan and P. S. Radhakrishnamurti, *Current Sci.* (India), **34**, 404 (1965).