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Structure and Reactivity of α,β-Unsaturated Ethers. X. The Acid-Catalyzed Hydrolysis of Ring-Substituted Styryl Ethyl Ethers

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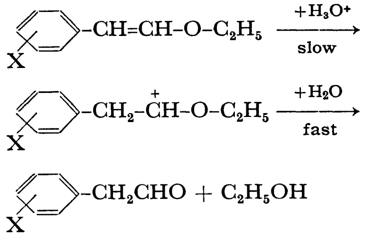
The acid-catalyzed hydrolysis of *cis*- and *trans*-styryl ethyl ethers (SEE) and several of their ring-substituted derivatives has been kinetically investigated in 80% aqueous dioxane. It has been found that these ethers are less reactive than vinyl ethyl ether by a factor of *ca.* 500 and that all the *cis* isomers studied are about twice as reactive as the corresponding *trans* isomers. The hydrolysis of the substituted ethers at 35°C has proved to obey the Hammett relation with the reaction constants $\rho = -1.07$ and -0.70 for the *cis* and the *trans* isomers, respectively. All these results appear to be interpretable at least qualitatively in terms of the reaction scheme involving the rate-determining protonation to the β-carbon atom.

It is generally accepted that the acid-catalyzed hydrolysis of α,β-unsaturated ethers involves irreversible protonation to the unsaturated bond. In a previous paper[1] of this series, the kinetic courses of hydrolysis of various alkenyl alkyl ethers were investigated and direct evidence that the protonation step is rate-determining was given. It was also shown that the effects of β-alkyl substitutions on the reactivity of vinyl ether can best be interpreted in terms of the conjugative stabilities of the intermediate carbonium ions which are formed on transfer of a proton from the hydronium ion to the ethers. Further, it was demonstrated both experimentally and theoretically that the electronic effect of α-alkoxyl groups is an important contribution to the rates of hydrolysis of ring-substituted phenyl vinyl ethers.[2]

In order to gain a deeper insight into the electronic factors of β-substituents influencing the vinyl ether hydrolysis, we have investigated the effect of ring substituents in the hydrolysis rates of *cis*- and *trans*-styryl ethyl ethers (SEE). The results were interpreted in terms of the reaction scheme involving the rate-determining protonation:



(1)

Experimental

Materials. Styryl ethyl ether (SEE) and its ring-substituted derivatives were prepared by the method of Dufraisse and Chaux[3,4] from diethyl acetals of appropriate substituted phenylacetaldehydes, which were obtained by the Grignard method[5] from benzyl bromides or chlorides. Methyl-, chloro-, and fluorobenzyl bromides were prepared by bromination of corresponding substituted toluenes.[6] *p*-Methoxybenzyl chloride was obtained by the solvolysis of *p*-anisyl alcohol. *p*- and *m*-fluorotoluenes were prepared from *p*- and *m*-toluidines, respectively, according to the procedure of Roe.[7]

The unsaturated ethers thus obtained were nearly equimolar mixtures of geometrical isomers, and their boiling points were as follows: H, 112—115°C/20 mmHg; *p*-CH_3O, 110—113°C/3 mmHg; *p*-CH_3, 87—89°C/5 mmHg; *m*-CH_3, 90—93°C/5 mmHg; *p*-F, 115—116°C/22 mmHg; *m*-F, 82—83°C/5 mmHg; *p*-Cl, 77—78°C/2 mmHg; *m*-Cl, 97—100°C/5 mmHg. Purities were checked by gas chromatography (>99%).

Dioxane, tetralin and carbon tetrachloride were obtained as described previously.[1]

Kinetic Measurements. Hydrolysis was carried

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[1] T. Okuyama, T. Fueno, H. Nakatsuji and J. Furukawa, *J. Amer. Chem. Soc.*, **89**, 5826 (1967).

[2] T. Fueno, I. Matsumura, T. Okuyama and J. Furukawa, This Bulletin, **41**, 818 (1968).

[3] C. Dufraisse and R. Chaux, *Bull. Soc. Chim. France*, [4] **39**, 905 (1926).

[4] S. I. Miller, *J. Amer. Chem. Soc.*, **78**, 6091 (1965).

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

[6] S. S. Jenkins, *J. Amer. Chem. Soc.*, **55**, 2896 (1933).

[7] A. Roe, "Organic Reactions," Vol. **5**, p. 193 (1949).

out in 80% aqueous dioxane containing *ca.* 0.2N hydrochloric acid at a specified temperature between 25 and 45°C. Each SEE derivative was hydrolyzed as a mixture of *cis* and *trans* isomers, but the kinetic courses were followed for each isomer separately by simultaneous determination of the isomers by gas chromatography. A Shimadzu Model 4APT gas chromatograph with a 3-m column packed with Apiezon Grease L was operated at a column temperature of *ca.* 130°C with hydrogen as carrier gas. In all cases, the *trans* isomers had a greater retention time. The initial total concentration of the reactant ethers was typically *ca.* 0.15M. Tetralin or dichlorobenzene was used as internal standard. The internal standard method coupled with the half-height width evaluation of the peak areas was sufficient for the determination of the ethers. Other details of the procedures for the rate measurements were the same as those described previously.[1,2] Each rate constant was obtained as an average of three to five independent runs and accurate to within 5%.

Results

It is known that the acid-catalyzed hydrolysis of α,β-unsaturated ethers is first order in both ether and acid.[1,2] Although most of the kinetic courses investigated here were pursued with the mixture of geometrical isomers, the first-order decay was found to hold for each isomer separately over the range up to 80% conversion. Figure 1 shows an example.

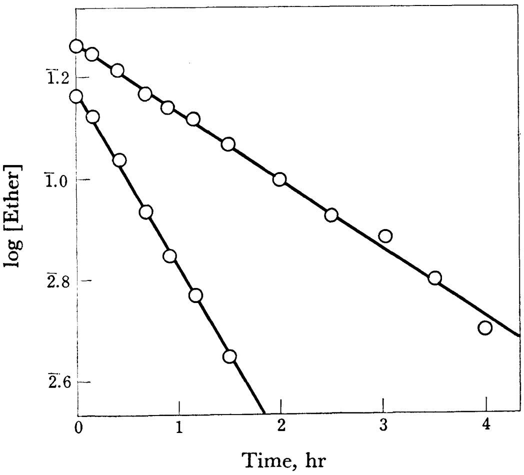

Fig. 1. First-order plots for the hydrolysis of *cis*- and *trans*-*p*-methylstyryl ethyl ethers.
[HCl], 0.189M. Temperature, 35°C.

The situation is in agreement with the previous observation that geometrical isomerization does not take place during the hydrolysis of alkenyl alkyl ethers.[1] This in turn endorses the conclusion that the hydrolysis involves the rate-determining protonation to an olefinic carbon atom. Formation of the products as expected from Eq. (1) was confirmed for the nonsubstituted compounds; the gas-chromatographic retention times of the products measured with the use of two different columns, polyethylene glycol and Apiezon Grease L, both exactly coincided with those of the authentic samples.

TABLE 1. SECOND-ORDER RATE CONSTANTS FOR THE ACID-CATALYZED HYDROLYSIS OF RING-SUBSTITUTED STYRYL ETHYL ETHERS AT 35°C

Substituent	10^4k_2, $M^{-1}sec^{-1}$	
	cis	*trans*
p-CH_3O	10.4_2	5.43
p-CH_3	11.8_4	4.72
m-CH_3	9.39	4.22
H	1.99[a]	1.14[a]
	7.33	3.85
	25.2[b]	13.8[b]
p-F	3.90	2.28
p-Cl	3.37	2.12
m-Cl	3.16	2.07

a) At 25°C.
b) At 45°C.

In Table 1 are summarized the second-order rate constants, $k_2=k_1/[HCl]$. In all the cases studied, *cis* isomers were *ca.* twice more reactive than the *trans* isomers, and their reactivities diminished with increasing electron-attracting ability of the ring substituents. From temperature dependence data, the heats and the entropies of activation, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were calculated for the unsubstituted SEE's: *cis*-SEE, $\Delta H^{\neq}=23.3$ kcal mol^{-1} and $\Delta S^{\neq}=2.7$ e.u.; *trans*-SEE, $\Delta H^{\neq}=21.4$ kcal mol^{-1} and $\Delta S^{\neq}=-4.9$ e.u.

Discussion

It has been reported[1] that the acid-catalyzed hydrolysis of vinyl ethyl ether in 80% aqueous dioxane at 25°C is $k_2=7.51\times10^{-2}M^{-1}\,sec^{-1}$. The reactivity of styryl ethyl ether toward proton is thus smaller than that of vinyl ethyl ether by a factor of *ca.* 500. This effect of the β-phenyl group in lowering the vinyl ether reactivity is far greater than that of a β-methyl group, which reduces the reactivity only by a factor of *ca.* 5.[1]

The effect of the β-phenyl group may be interpreted qualitatively from the greater stability of styryl ether in the ground state as compared with vinyl ether. Because of the excessive ground-state stability due to the conjugation between phenyl group and the olefinic bond, the π-electronic energy required for localizing an electron pair on the β-carbon ought to be greater for the styryl ether than for the vinyl ether. Simple calculations of the Hückel type readily confirm the above view. The difference in localization energy between the two ethers must reflect itself in the difference in the activation energies for their hydrolysis.[8]

All the *cis*-SEE's are more reactive than the corresponding *trans* isomers in the temperature region studied here. Nonetheless, the heat of activation for *cis*-SEE was found to be greater than that for *trans*-SEE. Hence, the relative reactivities of *cis*- and *trans*-SEE's are entropy-controlled at the ordinary temperature region. The isomerization equilibrium experiments showed that *cis*-SEE is thermochemically less stable than *trans*-SEE in the liquid phase, and it was deduced that the former isomer is in a non-planar conformation in contrast to the planar structure for the latter.[9] This structural irregularity may have some bearing with the unusual entropy effect found between the activation profiles of *cis*- and *trans*-SEE's. A similar trend was also found in the cationic polymerization of SEE.[10]

As has been stated above, the reactivity of SEE is enhanced by electron-donating substituents and is lowered by electron-attracting substituents. As is seen in Fig. 2, the effects of the ring substituents obey the Hammett $\rho\sigma$ relationship for the *cis* and *trans* isomer series separately, although a relatively large deviation from the line was found for the *cis*-*p*-methoxy derivative. The reaction constants, ρ, are -1.07 ($r=0.990$, excluding a point for the *p*-methoxy compound) and -0.70 ($r=0.991$) for the *cis* and *trans* series, respectively.

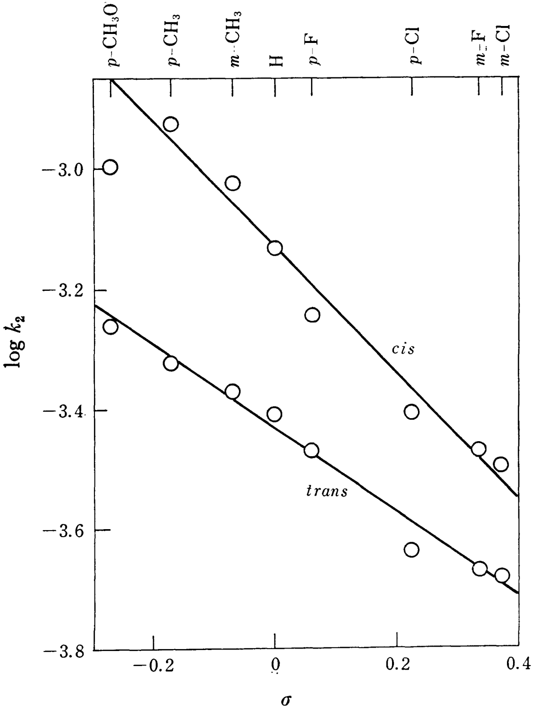

Fig. 2. The Hammett relationships of the hydrolysis rates of ring-substituted styryl ethyl ethers. Temperature, 35°C.

That an electron-donating ring substituent enhances the rate of the acid-catalyzed reaction of SEE has by no means been intuitively obvious. In fact, Winterfeldt[11] observed that the *p*-$N(CH_3)_2$ group lowers the rate of the acid-catalyzed methanolysis of styryl ether and interpreted this rate lowering in terms of the "opposing" electron donation of the *p*-$N(CH_3)_2$ group. His observation thus conflicts with our present results on hydrolysis and, therefore, his interpretation is greatly dubious. It appears that, in the acidic medium where his measurement was carried out, the $N(CH_3)_2$ group was actually in the form of $N^+(CH_3)_2H$, which retarded the methanolysis rate.[12]

The ρ values (-1.07 and -0.70) for the SEE hydrolysis are somewhat small as compared with those for the usual electrophilic addition reactions to styryl compounds. For instance, the acid-catalyzed hydration of styrenes[13] and the chlorination of cinnamic acids[14] were reported to have the values of -3.42 and -4.01, respectively. These reactions occur with an electrophilic attack on the *beta* carbon atom with respect to the phenyl group.[15] In contrast to these reactions, the hydrolysis of styryl ether occurs with an *alpha*-attack of hydronium ion, as is shown in Eq. (1). The lower sensitivity of the present reaction to the ring substituents is undoubtedly due to the fact that the primary reaction center is the *alpha*-position. This is easily understandable considering that, in the intermediate carbonium ions, the cationic center is insulated out of the π-conjugation involving the phenyl group which carries a substituent.

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[8] The activation papameters for vinyl ethyl ether are $\Delta H^{\neq}=17.5$ kcal mol^{-1} and $\Delta S^{\neq}=-4.9$ e.u.

[9] T. Okuyama, T. Fueno and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969); Part IX of this series.

[10] T. Okuyama, N. Asami and T. Fueno, This Bulletin, in press.

[11] E. Winterfeldt, *Chem. Ber.*, **96**, 3346 (1963).

[12] The ammonium groups are electron-attracting in nature, as may be judged from their σ-values [D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958)]. Besides, part of the catalyst acid must have been consumed for the ammonium ion formation. These would have combined to act as a drawback of the electronic effect of the *p*-$N(CH_3)_2$ group which would otherwise have enhanced the rate of protonation to the olefinic carbon atom.

[13] W. H. Schubert, B. Lamm and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4272 (1964).

[14] H. P. Rothbaum, I. Ting and P. W. Robertson, *J. Chem. Soc.*, **1948**, 980.

[15] It is expedient to regard SEE as a derivative of styrene when chemical characteristics are to be compared between the two compounds. Thus, when we refer to those carbon atoms at the positions α and β with respect to the phenyl group, we make use of the word *alpha* and *beta* in order to avoid confusion with the α- and β-carbon atoms of an α,β-unsaturated ether. This expedience will be used whenever we discuss the properties of SEE in comparison with those of styrene.

Electrophilic reactions of styryl compounds involving the rate-determining *alpha*-attack do not seem to be very familiar at present. The only example that has been reported in connection with the substituent effects is the acid-catalyzed geometrical isomerization of substituted *cis*-stilbenes,16) where the ρ value was noted to be -0.96 or -3.30, depending on whether the primary reaction center is the *alpha*- or the *beta*-carbon with respect to the phenyl group that carries the substituents to be examined. The present studies provide another example of the electrophilic *alpha*-attack reactions of styryl compounds which should have a ρ value relatively small in magnitude.

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16) D. S. Noyce, D. R. Hatter and F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 4633 (1968).