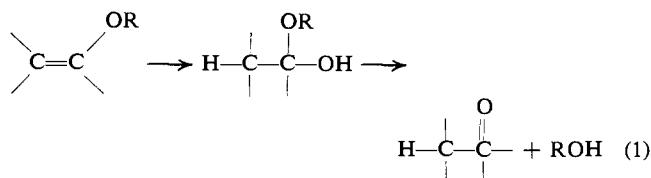# Vinyl Ether Hydrolysis. V. The Effect of β-Phenyl Substitution[1]

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Abstract: Introduction of a phenyl substituent at the β position of a vinyl ether, as in β-methoxy-*trans*-β-methylstyrene, could possibly shift the mechanism for hydrolysis from rate-determining proton transfer from catalyst to substrate to rapidly reversible protonation followed by rate-determining hydration of the ensuing alkoxy carbonium ion intermediate. The hydrolysis of this substrate, however, shows the solvent isotope effect $k_{H_3O^+}/k_{D_3O^+} = 3.0$ and is strongly catalyzed by undissociated acids in carboxylic acid buffer solutions; the Brønsted relation is obeyed with $\alpha = 0.70$. These data show that no mechanistic change has occurred and that hydration of the alkoxy carbonium ion intermediate remains more rapid than proton elimination. Consideration of the energetic changes produced by phenyl substitution suggests that all of the 3.0 kcal mol^{-1} increase in $\Delta G^{\ddagger}$ observed is the result of initial state (vinyl ether) stabilization and that the rate of hydration of the alkoxy carbonium ion intermediate is brought nearer to that for proton elimination by a factor of only approximately 5.
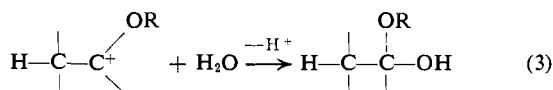
The hydrolysis of vinyl ethers occurs by a mechanism which requires hydration of the carbon–carbon double bond; the hemiacetal, or hemiketal, thus formed then reacts further to give alcohol and aldehyde, or ketone, as the ultimate reaction products (eq 1). In all examples of this process studied so

$$
\begin{array}{c}
\diagup\!\!\!\diagdown\!\!\!C\!=\!C\diagup\!\!\!^{OR}_{\diagdown} \longrightarrow H-\overset{|}{\underset{|}{C}}-\overset{OR}{\underset{|}{C}}-OH \longrightarrow \\[2mm]
H-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\parallel}{C}}- + ROH \quad (1)
\end{array}
$$

far,[1b,2-7] the proton transfer which initiates hydration (eq 2) has proved to be rate determining. In all of

$$
\diagup\!\!\!C\!=\!C\diagup^{OR} + HA \rightleftharpoons H-\overset{|}{\underset{|}{C}}-\overset{OR}{\underset{\diagdown}{C^+}} + A^- \quad (2)
$$
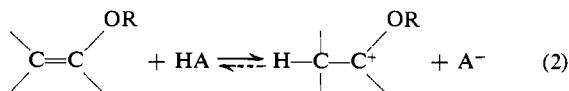
these cases, therefore, the alkoxy carbonium ion produced by proton transfer reacts more rapidly with water (eq 3) than it eliminates a proton to reverse the

$$
H-\overset{|}{\underset{|}{C}}-\overset{OR}{\underset{\diagdown}{C^+}} + H_2O \xrightarrow{-H^+} H-\overset{|}{\underset{|}{C}}-\overset{OR}{\underset{|}{C}}-OH \quad (3)
$$

reaction of eq 2.[8]

It is of interest to inquire into the margin by which this mechanism predominates over one in which proton transfer is rapid and reversible, and hydration, slow, *i.e.*, into the factor by which the alkoxy carbonium ion generated in vinyl ether hydrolysis undergoes hydration in preference to elimination. The corresponding margin in the case of the nonfunctionally substituted carbonium ions formed in the hydration of simple olefins is not large, at least in the case of tertiary carbonium ions, for the alcohol products of this reaction are known to undergo oxygen exchange only one to two orders of magnitude more rapidly than they dehydrate to regenerate the olefins.[9] In the hydration of enamines, moreover, reversible protonation on carbon is not uncommon,[10] which means that the amino-substituted carbonium ions generated in this reaction actually prefer elimination over hydration under some conditions. It would seem likely, therefore, that hydration is not preferred over elimination in vinyl ether hydrolysis by an overwhelming margin, and that a relatively minor substrate modification might serve to change the mechanism of this reaction.

One structural change which is known to have this effect is incorporation of the vinyl ether carbon–carbon double bond into an aromatic system. For example, when this bond is part of the aromatic ring of a phenol ether, reversible protonation occurs readily,[11] but hydrolysis is very difficult;[12] furan and its derivatives are also vinyl ethers in this sense, and their hy-

(1) (a) This research was supported by a grant (GP 23578) from the National Science Foundation; (b) part IV: A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, **94**, 2814 (1972).

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(8) It has been discovered very recently (V. P. Vitullo, personal communication; J. D. Cooper, V. P. Vitullo, and D. L. Whalen, *J. Amer. Chem. Soc.*, **93**, 6294 (1971)) that the cyclic vinyl ether, 2-methoxy-2,3,4,5,6,7-hexahydroxonin, affords the first exception to this general mechanism; in the hydrolysis of this substance, under some conditions, proton transfer (eq 2) is rapid and reversible and hydration (eq 3) is slow.

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drolysis also occurs through reversible protonation on carbon followed by slow hydration.[13]

These structural changes are, of course, rather drastic; they undoubtedly exceed the minimum required for a mechanistic change. In order to determine whether extending the conjugation of a vinyl ether without incorporation into an aromatic system would be sufficient, we have examined the hydration of β-phenyl-substituted vinyl ethers. The simplest substance of this type, β-methoxystyrene, proved to be too unreactive to permit one of the diagnostic experiments, a search for general acid catalysis, to be performed. Introduction of a methyl group on the α carbon of the double bond system, however, increased hydrolysis rates substantially, and the study was therefore performed with β-methoxy-β-methylstyrene.

Experimental Section

Materials. 1-Methoxystyrene was prepared by the addition of methanol to phenylacetylene in the presence of sodium methoxide[14] and also by the Wittig reaction between benzaldehyde and methoxymethyltriphenylphosphonium chloride.[15] The first method gave only the cis isomer in a stereospecific trans addition, as evidenced by the nmr spectrum of the product: J_{HH} (vinyl) = 7 Hz, whereas the Wittig reaction produced a mixture of cis and trans (J_{HH} = 13 Hz) β-methoxystyrenes.

Only a small amount (ca. 20%) of β-methoxy-β-methylstyrene was formed when methylphenylacetylene was treated with methanol and sodium methoxide, even under forcing conditions (100°, 35 hr). This substance was therefore prepared from the dimethyl ketal of phenylacetone in a reaction analogous to that found successful for the synthesis of β-ethoxy-β-methylstyrene.[16] The product here contained comparable amounts of the cis and trans isomers; these were partially separated by distillation. The nmr spectra of the two principal fractions showed that the lower boiling cut (37–43° (0.5 mm)) was an approximately 95:5 mixture and that the higher boiling cut (43–53° (0.5 mm)), a 50:50 mixture of cis and trans β-methoxy-β-methylstyrenes. The lower boiling isomer was identified as β-methoxy-trans-β-methylstyrene by the fact that it gave a methyl-group nmr signal at lower field than the other substance (τ 8.07 and 8.27 ppm, respectively); differences such as this have been found to be characteristic of 1-phenylpropene derivatives[17] and have proved useful in making structural assignments.[18] The present conclusion is also consistent with the fact that the lower boiling isomer predominated in the product of the incomplete reaction of methanol with methylphenylacetylene, which, by analogy with the stereospecific addition of methanol to phenylacetylene, should have occurred in a trans manner to give β-methoxy-trans-β-methylstyrene.

These vinyl ethers were purified for kinetic measurement by vapor phase chromatography. All other materials were the best available commercial grades.

Aqueous perchloric acid solutions were prepared from 70–72% HClO₄ and either deionized water, which had been further purified by distillation from alkaline permanganate, or deuterium oxide (Bio-Rad Labs) as received. Buffer solutions were made by partly neutralizing carboxylic acid solutions of known concentration with standard aqueous sodium hydroxide.

Kinetics. Rates were measured spectroscopically by taking advantage of the fact that, as hydrolysis proceeds, the strong absorption band of these vinyl ethers at 250–260 nm is replaced by much weaker phenyl and carbonyl group absorbances at 250–260 and 280–290 nm, respectively. Measurements were made for the most part at λ_{max} for the vinyl ether (258 nm for β-methoxystyrene and 253 nm for β-methoxy-β-methylstyrene); a few determinations were carried out at longer wavelengths (280–290 nm). The spec-

trometer (Cary 11) cell compartment was thermostated by water circulating from a constant-temperature bath operating at 25.0 ± 0.02°. Reaction mixtures were prepared by adding enough vinyl ether to give an absorbance reading of ca. 1.0 to acid or buffer solution contained in a 1-cm quartz cuvette, which had been allowed to come to thermal equilibrium with the spectrometer cell compartment. Absorbance was recorded continuously as a function of time for 3–4 half-lives, and infinite time readings were taken after 8–10 half-lives. First-order rate constants were evaluated as slopes of plots of ln $(A - A_\infty)$ vs. time; in the case of some of the slower reactions, infinity readings were not made and the data were treated by the method of Guggenheim[19] and/or Swinbourne.[20] In all cases, the data conformed to the first-order rate law exactly within the precision of the measurement over the entire course of the reaction.

Results

First-order rate constants for the hydrolysis of β-methoxy-trans-β-methylstyrene in dilute aqueous perchloric acid solutions are summarized in Table I. The

Table I. Rates of Hydrolysis of β-Methoxy-trans-β-methylstyrene in Aqueous Perchloric Acid at 25° [a]

10^2[acid]	$10^3 k_{obsd}$, sec^{-1}
	H₂O
0.201	3.17, 3.21
0.403	6.53, 6.51, 6.44
0.604	10.3, 9.82, 9.99
0.806	13.7, 13.9, 12.9
1.01	16.6, 16.9
1.21	19.7, 20.4, 19.8
1.41	23.5, 23.6, 24.2, 23.4
	k_{H^+} = 1.667 ± 0.006 M^{-1} sec^{-1}
	D₂O
0.515	2.72, 2.75, 2.79
1.03	5.69, 5.42, 5.52
1.55	8.66, 8.87, 8.73
2.06	11.5, 11.2
2.58	14.8, 14.4, 14.1
	k_{D^+} = 0.557 ± 0.004 M^{-1} sec^{-1}
	k_H/k_D = 2.994 ± 0.008

[a] Ionic strength maintained at 0.040 M through addition of NaCl.

reaction proved to be accurately first order in acid over a sevenfold variation in acid concentration in H₂O and over a fivefold variation in D₂O, and is thus second-order overall.

Specific rates of hydrolysis were also evaluated for buffer solutions of seven carboxylic acids over a five- to eightfold variation in buffer concentration at constant buffer ratio (Table II). In some of the stronger carboxylic acid solutions, hydronium ion concentrations did not remain constant as the buffer was diluted, and corrections for changes in the rate of hydrolysis catalyzed by hydronium ion therefore had to be made before catalysis by undissociated acid could be assessed. These corrections were made[4b] by calculating the hydronium ion concentration of each buffer solution, using concentration quotients evaluated from pK_a's and activity coefficients based on the Debye–Hückel formula with an ion size parameter of 4.5 Å. In all cases, adjusted rate constants proved to be linear functions of undissociated acid concentration, and carboxylic acid catalytic coefficients were therefore evaluated by least-squares analysis as slopes of plots of adjusted first-order rate constants vs. buffer acid concen-

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Table II. Rates of Hydrolysis of β-Methoxy-*trans*-β-methylstyrene in Aqueous Buffer Solutions at 25° [a]

10^2[HA], M	$10^3 k_{obsd}$, sec^{-1}
HA = CNCH$_2$CO$_2$H; [HA]/[NaA] = 1.00	
0.50	3.55, 3.55, 3.51, 3.57
1.00	4.78, 4.77, 4.94
1.50	6.00, 5.92, 5.95
2.00	6.85, 6.91, 6.55
2.50	7.50, 7.46, 7.69, 7.82

k_1 (sec^{-1}) = (6.44 ± 0.07) × 10^{-3} + (7.91 ± 0.53) × 10^{-2}[HA]
k_{H^+} = 1.61 M^{-1} sec^{-1}

HA = ClCH$_2$CO$_2$H; [HA]/[NaA] = 1.00	
0.50	2.18, 2.16
1.00	2.94, 2.92
1.50	3.38, 3.43
2.00	3.76, 3.64, 3.69
2.50	4.19, 4.07
3.00	4.35, 4.30, 4.43
3.50	4.79, 4.61
4.00	4.83, 4.93, 5.03

k_1 (sec^{-1}) = (3.00 ± 0.04) × 10^{-3} + (5.14 ± 0.15) × 10^{-2}[HA]
k_{H^+} = 1.69 M^{-1} sec^{-1}

HA = CH$_3$OCH$_2$CO$_2$H; [HA]/[NaA] = 1.00	
0.50	0.622, 0.639
1.00	0.756, 0.752
2.00	0.936, 0.937
3.00	1.10, 1.12
4.00	1.24, 1.23

k_1 (sec^{-1}) = (3.36 ± 0.12) × 10^{-4} + (1.55 ± 0.05) × 10^{-2}[HA]
k_{H^+} = 1.66 M^{-1} sec^{-1}

HA = HCO$_2$H; [HA]/[NaA] = 1.00	
0.48	0.425
0.97	0.487, 0.473
1.94	0.561, 0.588
2.91	0.673, 0.675
3.87	0.757, 0.748

k_1 (sec^{-1}) = (4.15 ± 0.04) × 10^{-4} + (8.83 ± 0.19) × 10^{-3}[HA]
k_{H^+} = 1.64 M^{-1} sec^{-1}

HA = HOCH$_2$CO$_2$H; [HA]/[NaA] = 4.00	
1.50	1.26
2.63	1.45, 1.47
3.75	1.58, 1.60
5.63	1.83, 1.77, 1.81
7.13	1.96, 2.00

k_1 (sec^{-1}) = (1.32 ± 0.01) × 10^{-3} + (9.15 ± 0.27) × 10^{-3}[HA]
k_{H^+} = 1.65 M^{-1} sec^{-1}

HA = CH$_3$CO$_2$H; [HA]/[NaA] = 4.00	
3.12	0.218
6.24	0.284
9.36	0.346
12.5	0.397, 0.394, 0.417
15.0	0.451, 0.458, 0.454

k_1 (sec^{-1}) = (1.61 ± 0.03) × 10^{-4} + (1.96 × 0.03) × 10^{-3}[HA]
k_{H^+} = 1.64 M^{-1} sec^{-1}

HA = CH$_3$CH$_2$CO$_2$H; [HA]/[NaA] = 4.00	
3.18	0.191, 0.188
6.35	0.247. 0.263, 0.256
9.53	0.323, 0.326
12.7	0.382, 0.380, 0.382
15.2	0.416, 0.422

k_1 (sec^{-1}) = (1.35 ± 0.08) × 10^{-4} + (1.91 ± 0.07) × 10^{-3}[HA]
k_{H^+} = 1.76 M^{-1} sec^{-1}

k_{H^+} = (1.66 ± 0.02) M^{-1} sec^{-1} (average for all buffers)

[a] Ionic strength maintained at 0.040 M through addition of NaCl.

Table III. Summary of Catalytic Coefficients for the Hydrolysis of β-Methoxy-*trans*-β-methylstyrene at 25°

Catalyst	pK_a	k_{HA}, M^{-1} sec^{-1}	% dev from Brønsted relation[a]
H$_3$O$^+$	−1.74	1.67	−4000
CNCH$_2$CO$_2$H	2.47[b]	0.0791	−7
ClCH$_2$CO$_2$H	2.87[c]	0.0514	16
CH$_3$OCH$_2$CO$_2$H	3.57[d]	0.0155	9
HCO$_2$H	3.75[e]	0.00883	−21
HOCH$_2$CO$_2$H	3.83[f]	0.00915	−2
CH$_3$CO$_2$H	4.76[g]	0.00196	−5
CH$_3$CH$_2$CO$_2$H	4.88[h]	0.00191	11

[a] Brønsted relation: log (k_{HA}/p) = 0.451 ± 0.093 ± (0.702 ± 0.026) log($q/K_{HA}/p$). [b] F. S. Feates and D. J. G. Ives, *J. Chem. Soc.*, 2798 (1956); D. J. G. Ives and P.D. Marsden, *ibid.*, 649 (1965). [c] E. J. G. Ives and J. H. Pryor, *ibid.*, 2104 (1955). [d] E. J. King, *J. Amer. Chem. Soc.*, **82**, 3575 (1960). [e] H. S. Harned and N. D. Embree, *ibid.*, **56**, 1042 (1934). [f] L. F. Nims, *ibid.*, **58**, 987 (1936). [g] H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 652 (1933). [h] D. H. Everett, D. A. Landsman, and B. R. W. Pinsent, *Proc. Roy. Soc.*, *Ser. A*, **215**, 403 (1952).

The catalytic coefficients are summarized in Table III and are displayed in the form of a Brønsted plot in Figure 1. In constructing this plot, statistical factors of $p = 3$ and $q = 1$ were used for the hydronium ion and $p = 1$ and $q = 2$ for all of the carboxylic acids.
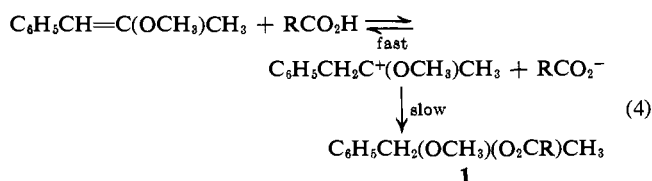
Discussion

Reaction Mechanism. The data of Table I show that the hydrolysis of β-methoxy-*trans*-β-methylstyrene catalyzed by the hydronium ion is three times faster in H$_2$O than in D$_2$O. An isotope effect of this magnitude in this direction is compatible only with a reaction mechanism in which proton transfer from catalyst to substrate is rate determining. Thus, the hydrolysis of this vinyl ether in dilute solutions of strong acids occurs by the normal mechanism in which proton transfer (eq 2) is slow and hydration of the intermediate carbonium ion (eq 3) fast.

Dilute solutions of strong acid, however, are the media in which the other reaction mechanism, rapid and reversible proton transfer followed by slow hydration, is least likely to occur. This may be seen by considering the factors which govern the rates of the two reactions by which the carbonium ion intermediate in this reaction is consumed, for it is the relative velocity of these two reactions which determines which of the mechanisms will operate: if hydration of the carbonium ion is more rapid than proton loss, proton transfer will be rate determining; if, on the other hand, proton loss is the more rapid reaction, then proton transfer will be rapid and reversible and hydration, rate determining. In dilute aqueous solution, the rate of carbonium ion hydration will be independent of added solutes, but the rate of proton loss can be influenced by the addition of bases. For any given substrate, therefore, proton transfer will be most likely to be rapid and reversible in the presence of the strongest base compatible with the requirement for acid catalysis, *i.e.*, in buffer solutions of the weakest acid which gives measurable rates of reaction.

It is highly significant, therefore, that the hydrolysis of β-methoxy-*trans*-β-methylstyrene remains strongly general acid catalyzed down to the weakest acid used in this study (Table II). If proton transfer were rap-

tration. Hydronium ion catalytic coefficients were calculated from the intercepts of these plots; the average of the values for the seven series of buffers, 1.66 ± 0.02 M^{-1} sec^{-1}, agreed exactly with that measured directly in perchloric acid solution, 1.67 ± 0.01 M^{-1} sec^{-1}.

idly reversible, the concentration of the carbonium ion intermediate, and therefore the reaction velocity, would depend only on pH and not on the concentration of any undissociated acid solute which happened to be present; the reaction thus would be subject to specific hydrogen ion catalysis as opposed to the general acid catalysis demanded by (and observed for) the rate-determining proton transfer mechanism.

General acid catalysis is compatible with rapidly reversible proton transfer if the mechanism is one in which capture of the carbonium ion intermediate by the conjugate base of the general acid (eq 4) competes

$$C_6H_5CH=C(OCH_3)CH_3 + RCO_2H \underset{fast}{\rightleftharpoons}$$

$$C_6H_5CH_2C^+(OCH_3)CH_3 + RCO_2^-$$

$$\downarrow slow \qquad\qquad (4)$$

$$C_6H_5CH_2(OCH_3)(O_2CR)CH_3$$

1

with hydration. Such a reaction scheme, however, can be ruled out in the present case because the substances formed in the carboxylic acid buffers used here would be acylals (**1**) ,and acylals of this type are known[21] to hydrolyze in acid solution through carbonium ion intermediates which are identical with those generated by hydrolysis of the corresponding vinyl ethers; thus acylal formation would not provide a new route to alcohol and ketone products and would therefore contribute nothing to the rate at which these substances are formed. If, of course, these acylals were not highly reactive species but rather fairly stable intermediates which reverted to vinyl ether and/or gave ketone product only slowly, then their formation would add to the rate of disappearance of vinyl ether and thus affect the rate constants as measured here. That this is in fact not the case is shown by the results of several experiments in which the reaction was followed both at λ_{max} for the vinyl ether (253 nm) and also at a wavelength where the ketone product absorbs strongly (280–286 nm). The two methods gave identical rate constants, both in dilute perchloric acid and in formic acid buffer solutions; demonstrating that the ketone product is formed at the same rate as the vinyl ether is consumed; thus, no intermediate species builds up during the course of this reaction.

Energetics. The results obtained in this study show, therefore, that the hydrolysis of β-methoxy-*trans*-β-methylstyrene occurs by the same rate-determining proton transfer mechanism established for other vinyl ethers, including 2-ethoxypropene,[4b] and that extending conjugation of the vinyl ether functional group into a β-phenyl substituent does not alter the reaction mechanism. Some insight into why this structural change does not lower the free energy of the proton transfer transition state below that of the hydration reaction may be gained by considering the effect of β-phenyl substitution in some detail.

The rate of hydrolysis of β-methoxy-*trans*-β-methylstyrene, with hydronium ion as the catalyst, is slower by a factor of 350 than that of 2-ethoxypropene;[4b] since ethyl vinyl ethers are generally twice as reactive as their methyl counterparts[4b,22] the effect of phenyl

(21) P. Salomaa, *Acta Chem. Scand.*, 11, 132, 239 (1957); 19, 1263 (1965).

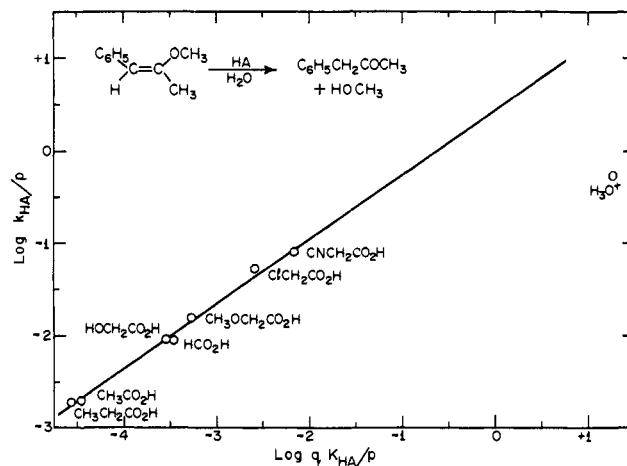(22) D. S. Sagatys, Ph.D. Thesis, Illinois Institute of Technology, Chicago, Ill., 1970.

Figure 1. Brønsted relation for the hydrolysis of β-methoxy-*trans*-β-methylstyrene.

substitution alone may be estimated as a factor of 175, which, at 25°, is equivalent to 3.0 kcal mol^{-1} in $\Delta G^{\pm}$.

This increase in free energy of activation may be attributed to two principal factors: (1) a decrease in the free energy of the initial state brought about by conjugation of the vinyl ether group into the phenyl substituent, and (2) an increase in the free energy of the proton transfer transition state produced by polar interaction between the positive charge being generated on the substrate and the electronegative phenyl group. The second of these effects may be estimated from the result of phenyl substitution on the rate of hydrolysis of acetone diethyl ketal, which occurs through rate-determining formation of an alkoxy carbonium ion analogous to that generated in the present reaction. In 50% aqueous dioxane, phenylacetone ketal is hydrolyzed nine times slower than the ketal of acetone,[23] which gives a difference in $\Delta G^{\pm}$ of 1.3 kcal mol^{-1}. The effect is likely to be somewhat less in the more polar, wholly aqueous medium used here, and 1.0 kcal mol^{-1} may be taken as a reasonable value. This leaves 2.0 kcal mol^{-1} as the contribution to $\Delta G^{\pm}$ from the other factor, stabilization of the initial state.

This, of course, is not the amount by which the free energy of the initial state is actually lowered, but rather only a contribution to $\Delta G^{\pm}$: some stabilization by phenyl of the type present in the initial state will still be felt at the transition state because the carbon–carbon double bond will not yet be completely destroyed; some conjugation of phenyl and vinyl ether groups will therefore still remain. The fraction of the initial state effect remaining at the transition state may be estimated as $^1/_3$ on the basis of the fact that the Brønsted exponent for the reaction is $^2/_3$ ($\alpha = 0.64$ for 2-ethoxypropene[4b] and 0.70 for β-methoxy-*trans*-β-methylstyrene); this implies that this transition state lies two-thirds of the way along the reaction coordinate between initial state and carbonium ion.[24] It follows, then, that conjugation of phenyl and vinyl ether groups lowers the free energy of the initial state by 3 kcal mol^{-1} and that of the transition state by 1 kcal mol^{-1}. The

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

(24) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 235; A. J. Kresge, *J. Amer. Chem. Soc.*, 92, 3210 (1970).

first of these values is in good agreement with the 2–4 kcal mol^{-1} estimated as the extra stabilization of styrene resulting from conjugation of the double bond with the benzene ring.[25]

Thus, the net effect of β-phenyl substitution on the proton transfer step of this reaction is to lower the free energy of the initial state by 3 kcal mol^{-1} and leave that of the transition state unchanged. The effect on the hydration step is more difficult to assess, but, since the phenyl group is likely to exert only an electrostatic effect here, it may be approximated as the same as that produced on the proton transfer step by the second of the two factors discussed above, i.e., an increase in transition state free energy of ca. 1 kcal mol^{-1}. Thus, the overall effect of phenyl group substitution is to reduce the gap between the free energies of the transition states of the proton transfer step and the hydration reaction by a relatively small amount, only ca. 1 kcal mol^{-1}, which is equal to a rate factor of only 5 at 25°. In retrospect, it may be seen that the principal reason for the small difference produced by β-phenyl substitution is the lateness of the proton transfer transition state. If this had occurred at an earlier position along the reaction coordinate, more conjugative stabilization and less electrostatic destabilization would have been realized; both of these changes would, of course, serve to reduce the difference between the energies of this and the subsequent transition state.

Brønsted Relation. The carboxylic acid catalytic coefficients determined here for the hydrolysis of β-methoxy-*trans*-β-methylstyrene obey the Brønsted

relation[26] with acceptable precision (Figure 1) and give a Brønsted exponent, $\alpha = 0.70 \pm 0.03$, which is consistent with the values observed in other vinyl ether hydrolysis reactions;[4b] in fact, the value obtained here is identical with that determined for ethyl vinyl ether which also shows the same reactivity as the present substrate: $k_{H^+} = 1.75$ and $1.67 \ M^{-1} \ sec^{-1}$, respectively.

It is of interest that the minor deviations from exact compliance with the Brønsted relation shown by the carboxylic acid catalysts in the present case are, on the whole, quite similar to the deviations detected previously for other vinyl ether hydrolysis reactions.[4b] It may be seen in Figure 1 and Table III that the point for cyanoacetic acid lies below the Brønsted correlation line and that those for chloro- and methoxyacetic acid lie above, just as observed before. Formic acid, however, is here a significantly poorer catalyst than expected on the basis of the correlation, whereas, in the previously examined vinyl ether hydrolysis reactions, it generally conformed to the Brønsted relation very well.

The hydronium ion catalytic coefficient, here as before, shows a very strong negative deviation from the carboxylic acid correlation line. On the assumption that this is the result of an unrealistically large acidity constant for this acid (55.5 M),[27] the point may be fitted to the line and a new value of K_a determined. This gives p$K_a = 0.5$, which is not inconsistent with the values (0.7 to -0.2) obtained before.[4b]

(25) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 102.

(26) J. N. Brønsted and K. J. Pedersen, *Z. Phys. Chem.*, 108, 185 (1924).

(27) R. P. Bell, *Trans. Faraday Soc.*, 39, 253 (1943).