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Structure and Reactivity of α, β-Unsaturated Ethers. IV.[1] The Effects of Ring Substituents on the Acid-Catalyzed Hydrolysis Rate of Phenyl Vinyl Ether

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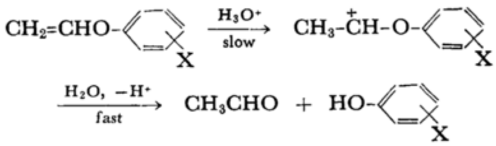
The rates of hydrolysis of various ring-substituted phenyl vinyl ethers, $CH_2=CHOC_6H_4X$, have been measured in 80 : 20 dioxane-water containing hydrochloric acid as catalyst. The ring substituents investigated include H, p-CH_3O, m-CH_3O, p-CH_3, m-CH_3, p-Cl and m-Cl. The reaction was first order with respect to both the acid and the ethers. It has been found that the effect of substituents on the hydrolysis rates obeys the Hammett $\rho\sigma$ relationship with the reaction constant $\rho=-2.21$ at 35°C. These results are compatible with the previous conclusion that the acid-catalyzed hydrolysis of alkenyl ethers involves the rate-determining protonation of the ethers at their β-carbon atom, to form intermediate oxycarbonium ions. It has been shown that the observed substituent effect can be rationalized from the π-electronic energy changes of the ethers on protonation, which have been calculated by an empirical molecular orbital method.

It is generally accepted that the acid-catalyzed hydrolysis of α, β-unsaturated ethers involves irreversible protonation of the β-carbon atom of the unsaturated bond.[2-6] In a previous paper (Part I) of this series,[7] we investigated the kinetic courses of hydrolysis of various alkenyl alkyl ethers, $R_1R_2C=CH(OR_3)$, and presented direct evidence that the protonation step is rate-determining. It was also shown that the relative reactivities of the various ethers may best be interpreted in terms of the conjugative stabilities of the intermediate carbonium ions that are formed on the transfer of a proton from a hydronium ion to the ethers.

In the present communication, we will report the rates of hydrolysis of several ring-substituted phenyl vinyl ethers in an acidic dioxane-water medium in the temperature range 25 to 45°C. From the outset, we may assume, in analogy to the hydrolysis mechanism of alkenyl alkyl ethers, that the reaction under question will proceed according to the scheme:



(1)

where the first protonation step is rate-determining. The rate data obtained have shown that the effects of substituents on the hydrolysis rates nicely fit the Hammett $\rho\sigma$ relationship with the reaction constant, ρ, ranging from -1.89 to -2.26, depending on the reaction temperature selected. That the observed substituent effects are compatible with the mechanism (1) appears to be justifiable from the linear correlation which has been found to hold between the Hammett σ constants and the β-carbon localization energies of the phenyl vinyl ether derivatives as calculated by an empirical molecular orbital method.

Experimental

Materials. Phenyl vinyl ether (PVE) and its p-CH_3O, m-CH_3O, p-CH_3, m-CH_3, p-Cl and m-Cl derivatives were prepared from ethylene dibromide and appropriate substituted phenols according to the method of McElvain and Fajardo-Pinzón.[8]

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[1] Part III: T. Okuyama, T. Fueno, J. Furukawa and K. Uyeo, *J. Polymer Sci.*, *A1*, in press.

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

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

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

[5] T. H. Fife, *J. Am. Chem. Soc.*, **87**, 1084 (1965).

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

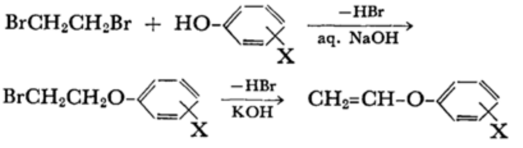
[7] T. Okuyama, T. Fueno, H. Nakatsuji and J. Furukawa, *J. Am. Chem. Soc.*, **89**, 5826 (1967).

[8] S. M. McElvain and B. Fajardo-Pinzón, *ibid.*, **67**, 650 (1945).

TABLE 1. SOME PHYSICAL CONSTANTS AND THE ELEMENTAL ANALYSIS DATA OF PHENYL VINYL ETHERS[a]

Substituent	Elemental analysis, % C	Elemental analysis, % H	Boiling point °C/mmHg	Specific gravity[b] d_4^{25}	Refractive index[b] n_D^{25}
H	79.44	6.89	54/17	0.974	1.5209
	(79.97)	(6.71)	(54—55/17)[d]	(0.9770)[f]	(1.5224)[g]
p-CH_3O	71.81	6.73	91.0—91.5/12	1.048	1.5275
	(71.98)	(6.71)	—	—	—
m-CH_3O	72.10	6.93	96/13	1.051	1.5300
	(71.98)	(6.71)	—	—	—
p-CH_3	81.65	7.57	72.5/17	0.956	1.5169
	(80.56)	(7.51)	(75/18)[d]	(0.9587)[f]	(1.5168)[g]
m-CH_3	80.93	7.71	71/16	0.957	1.5180
	(80.56)	(7.51)	(74/20)[d]	—	(1.5183)[g]
p-Cl[c]	62.20	4.72	85.5—86.5/19	1.137	1.5398
	(62.15)	(4.56)	(83—86/10)[e]	(1.0039)[e]	(1.5404)[g]
m-Cl[c]	61.97	4.68	82.5—83.5/17	1.138	1.5390
	(62.15)	(4.56)	—	—	(1.5401)[g]

a) The figures in parentheses are either the calculated or literature values.
b) The literature values are all for 20°C.
c) Analysis of Cl: Calcd. 22.93. Obsd. *p*-Cl, 22.84; *m*-Cl, 22.86.
d) Ref. 10. e) Ref. 11. f) Ref. 12. g) Ref. 13.


(2)

Syntheses of the intermediate β-bromophenetole derivatives were carried out by heating a mixture of ethylene dibromide, sodium hydroxide and phenols in boiling water for 10 hr. The phenetoles were separated from the aqueous layer and distilled. Their boiling points were as follows: H, 90—94°C/5.5 mmHg; *p*-CH_3O, 125.5°C/6 mmHg; *m*-CH_3O, 93°C/2.5 mmHg; *p*-CH_3, 87°C/3 mmHg; *m*-CH_3, 94—99°C/2.5 mmHg; *p*-Cl, 102—105°C/3 mmHg; *m*-Cl, 110.5—112.5°C/3 mmHg.

The phenetole derivatives were then subjected to dehydrobromination by heating in the presence of an equal amount (in weight) of powdered potassium hydroxide in a copper flask at *ca.* 200°C. The resulting PVE derivatives were collected in a glass flask, distilled over calcium hydride and stocked in the dark under a nitrogen atmosphere.

Gas chromatography of the ethers prepared as above indicated that they were over 99.5% pure. The ethers were also checked for isomeric purity by both infrared and NMR spectroscopies. Some physical constants of these ethers are summarized in Table 1, together with their elemental analysis data.

Tetralin, which was used as an internal standard for gas chromatography, was of the best grade commercially available. Dioxane of guaranteed grade was further purified by a conventional method.

Kinetic Measurements. Hydrolysis was carried out in 80% aqueous dioxane containing 0.2 N hydrochloric acid at 25, 35 and 45°C, thermostatically maintained.

The initial concentrations of the reactant ethers were typically *ca.* 1.5×10^{-2} M. The courses of the hydrolysis reactions were pursued by gas chromatographic determinations of the ethers remaining in the reaction mixtures. Details of the procedures for the rate measurements were the same as those described previously.[7]

Product Identifications. Phenyl vinyl ethers are expected to give acetaldehyde and the corresponding phenols on hydrolysis. For the case of the nonsubstituted PVE, the formations of these products were confirmed by gas chromatography; their retention times were in perfect agreement with those of the authentic samples. The products were also identified by the routine procedures of qualitative analysis. Tollens' reagent[9a] and an aqueous ferric chloride solution[9b] were used to identify acetaldehyde and phenol, respectively; both reagents gave positive results.

Experimental Results

Kinetic Data. The hydrolysis of phenyl vinyl ethers (PVE) was found to be first order with respect to both ether and acid. The first-order decay of the reactant ether, as is seen in Fig. 1, proved to hold uniformly down to over 80% conversions for all the PVE derivatives investigated.

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9) a) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York (1956), p. 112; b) *ibid.*, p. 162.

10) W. Reppe *et al.*, *Ann.*, **601**, 81 (1956).

11) M. Ban, H. Yamamoto and S. Otsuka, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **77**, 176 (1956).

12) M. F. Shostakovskii and M. S. Burmistrava, *J. Applied Chem. (USSR)*, **15**, 260 (1942); *Chem. Abstr.* **37**, 2336 (1943).

13) Y. L. Frolov and A. v. Kalabina, *Spectroskopiya, Metody Primenenie Akad. Nauk SSSR, Sibirsk. Old*, 171, 173 (1964); *Chem. Abstr.*, **62**, 5156 (1965).

The first-order rate constants, k_1, were exactly proportional to the concentration of hydrochloric acid, as may be seen in Fig. 2. These results preclude the possibility that the phenols which were produced on hydrolysis may partake in the kinetics to any appreciable extent as acid catalysts, whether as the Brönsted-type or as the general acid catalyst.

The second-order rate constants, defined as $k_2=k_1/[\mathrm{HCl}]$, were measured for the various PVE derivatives at varying temperatures. The results are given in Table 2, where it may be seen that electron-releasing substituents enhance the reactivity of PVE, while electron-attracting ones lower it.

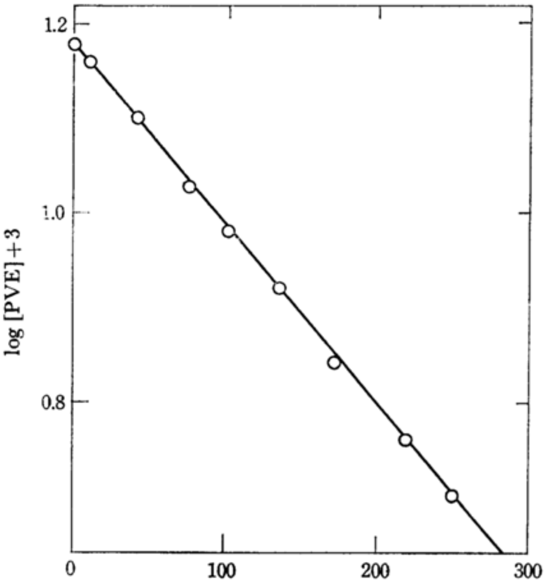

Fig. 1. First-order plots for the hydrolysis of phenyl vinyl ether.
The initial concentration, 1.53×10^{-2} M.
[HCl], 0.2 N. Temperature, 35°C.

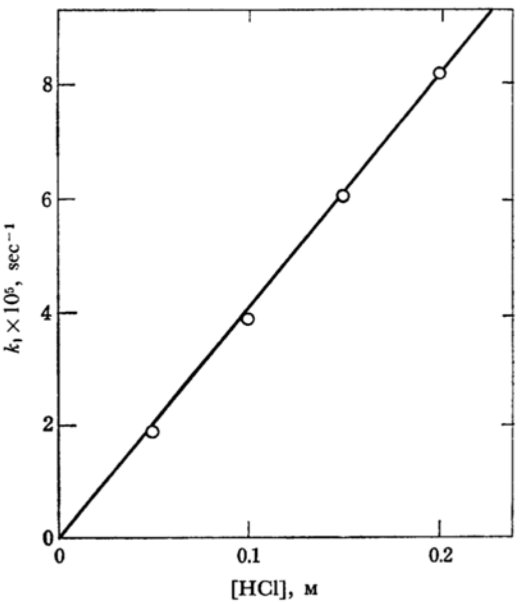

Fig. 2. Linear dependence of the first-order rate constant of the phenyl vinyl ether hydrolysis on the hydrochloric acid concentration.
Temperature, 35°C.

From the k_2 values listed in Table 2, the heats and entropies of activation, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, at 35°C were evaluated in a usual manner. The linearities of the plots of $\log(k_2/T)$ *vs.* $1/T$ were satisfactorily good for all the PVE derivatives studied here. The activation parameters obtained are included in Table 2.

Free Energy Correlations. In Fig. 3 the logarithms of the rate constants, k_2, listed in Table 2 have been plotted against Hammett's σ values. The plots are satisfactorily linear at every temperature studied.

TABLE 2. THE SECOND-ORDER RATE CONSTANTS AND THE ACTIVATION PARAMETERS OF THE ACID-CATALYZED HYDROLYSIS OF VARIOUS PHENYL VINYL ETHER DERIVATIVES

Substituent	Hammett's σ	$10^4 k_2$, l mol^{-1} sec^{-1}			$\Delta H^{\neq}_{308}$,[a] kcal mol^{-1}	$\Delta S^{\neq}_{308}$[b] e. u.	$\delta\Delta E$[c] $-\gamma^2/\beta$
		25°C	35°C	40°C			
p-CH$_3$O	−0.268	4.35	14.1	36.9	19.5	−8.3	0.0334
p-CH$_3$	−0.170	2.46	8.41	22.4	20.2	−7.0	0.0225
m-CH$_3$	−0.069	1.34	5.19	14.1	21.8	−2.8	0.0135
H	0	1.01	4.01	10.9	21.9	−3.0	0
m-CH$_3$O	0.115	0.85	3.44	9.03	21.8	−3.6	−0.0196
p-Cl	0.227	0.31	1.16	3.98	23.5	−0.3	−0.0450
m-Cl	0.373	—	0.52	2.06	26.1	6.6	−0.0483

a) The probable errors do not exceed 0.3 kcal mol^{-1}.

b) Accurate only to within ±1.0 e. u.

c) The relative stabilities of carbonium ions, $XC_6H_4O\overset{+}{C}HCH_3$, as calculated by the empirical molecular orbital theory. See the text.

TABLE 3. THE REACTION CONSTANTS, ρ, THE CORRELATION COEFFICIENTS, r, AND THE STANDARD DEVIATIONS, s, OF THE HAMMETT PLOTS

Temperature °C	$\sigma_{m\text{-}CH_3O}=0.115$			$\sigma_{m\text{-}CH_3O}=0.060$		
	ρ	r	s	ρ	r	s
25	−2.138	0.982	0.084	−2.261	0.997	0.035
35	−2.158	0.984	0.096	−2.209	0.996	0.059
45	−1.889	0.992	0.066	−1.925	0.999	0.020

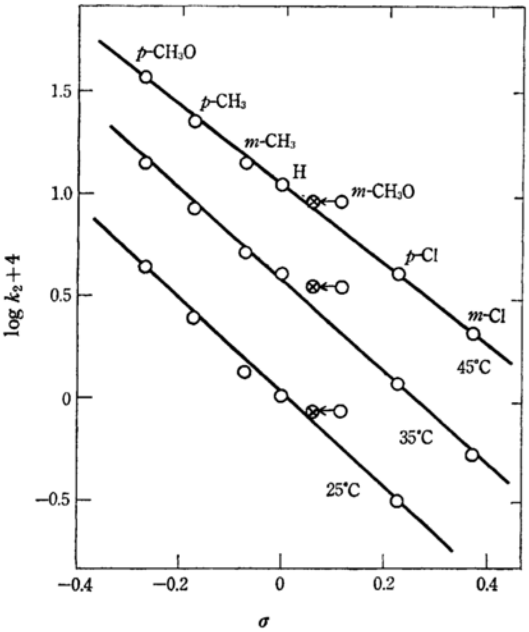

Fig. 3. The Hammett correlations of the acid-catalyzed hydrolysis rates of ring-substituted phenyl vinyl ethers.
The crossed circles are plots for the m-CH$_3$O group, for which a special value (0.060) has been adopted.

It is noticeable, however, that the m-CH$_3$O points uniformly deviate from linearity. Yet, these points become aligned with the others if we use the "special" σ value, 0.060, that Taft recommended for the m-CH$_3$O group in the free energy correlations of the reactions in nonaqueous and mixed solvents.[14] Such an improvement in the Hammett correlation by use of the value 0.060 for the m-CH$_3$O group has also been noted recently by Ceska and Grunwald for the ionization equilibria of anilines in acetic acid.[15]

The least squares treatments of the linearities of Fig. 3 have led to the reaction constants, ρ, which are given in Table 3. Also listed in Table 3 are the correlation coefficients, r, of the plots, and their standard deviations, s,[16] from the regression lines.

For the sake of comparison, the two σ values, 0.115 and 0.060, have been used for the m-CH$_3$O group. Although the number of points included in the correlations is only modest, the linearities may be regarded as sufficiently good, especially when the m-CH$_3$O group is allowed to have the value 0.060.

The Extrathermodynamic Relation. It is known that in a series of reactions a change of substituent tends to cause $\Delta H^{\neq}$ and $\Delta S^{\neq}$ to vary in the same direction. This extrathermodynamic relation[17] between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is often linear so as to permit the quantitative assessment of the relative importances of the two quantities governing the observed substituent effects.

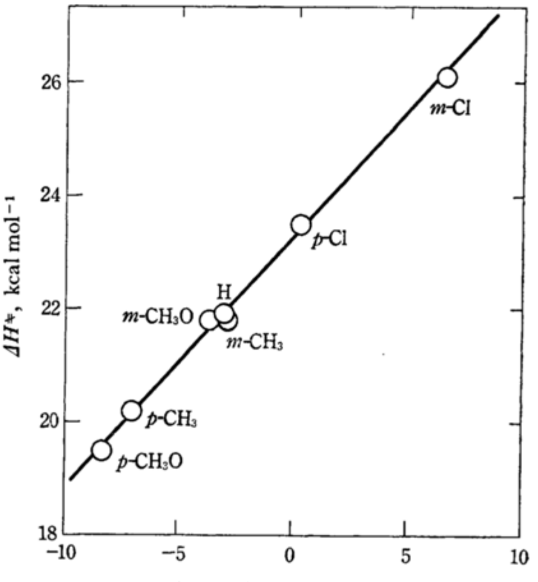

Fig. 4. Plots of $\Delta H^{\neq}$ *vs.* ΔS.

In our present series of reactions, such a linear, compensating relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is indeed discernible with fair precision, as may be seen in Fig. 4. The isokinetic temperature, defined as the slope of the linearity, has been found to be 465°K. Thus we may draw the conclusion

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[14] R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).
[15] G. W. Ceska and E. Grunwald, *J. Am. Chem. Soc.*, **89**, 1371 (1967).
[16] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).
[17] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York (1963), pp. 315—402.

that the observed substituent effects are primarily enthalpy-controlled.

Empirical Molecular Orbital Considerations

It is a widely accepted view that the sigma values of para substituents are more or less subject to a variation in magnitude, depending on the type of reaction being investigated. This nonlinearity of free energy correlations is believed to arise from the different extents of direct conjugation between substituents and reaction centers in the transition states of different reaction types.

We have previously reported that such a multiplicity of substituent constants, as represented by σ°, σ, σ^{+} and σ^{-}, can be interpreted on a unified ground in terms of the π-electron energy changes as calculated by the empirical molecular orbital method for the activation processes of relevant side-chain reactions of benzene derivatives.[18] In the following, we will apply an analogous treatment to the hydrolyses of ring-substituted PVE's and examine whether or not the general trends of the observed substituent effects may be justifiable.

We will be primarily concerned with the difference in the total π-electronic energies between reactants, XC_6H_4Y, and intermediates, XC_6H_4Y'. Here, X is a substituent, and Y and Y′ are the side-chain reaction centers in the initial and intermediate states, respectively, which are $-O-CH=CH_2$ and $-O-\overset{+}{C}H-CH_3$ in the present instance. In conformity with our previous treatments,[18] the energy difference under question may be expressed as

$$\begin{aligned} E(XC_6H_4Y') - E(XC_6H_4Y) &= [E(XC_6H_5) + E(Y') - DE'] \\ &\quad - [E(XC_6H_5) + E(Y) - DE] \\ &= [E(Y') - E(Y)] - (DE' - DE) \qquad (3) \end{aligned}$$

where E's are the π-electronic energies of the compounds or groups specified in the parentheses, and where DE and DE' are the delocalization energies of the two states due to the linkage of XC_6H_5 with Y and Y′ to form XC_6H_4Y and XC_6H_4Y', respectively. The delocalization energies can be computed from the following familiar expression that Dewar[19] derived by a perturbation technique:

$$DE = 2\left\{\sum_{i}^{\text{occ}} \sum_{j}^{\text{un}} - \sum_{i}^{\text{un}} \sum_{j}^{\text{occ}}\right\} \frac{c_{ir}^2\, c_{js}^2}{m_i - m_j}\left(-\frac{\gamma^2}{\beta}\right) \qquad (4)$$

The notations involved in Eq. (4) are the same as have been described previously.[18]

Since, in Eq. (4), the difference between E (Y′) and E (Y) is constant for a given reactive side chain, the difference between the delocalization energies, defined as

$$\Delta E = DE' - DE \qquad (5)$$

should be a quantity which may be regarded as a measure of the effects of substituents on the stabilities of the intermediate carbonium ions. Thus, it is to be expected that the greater the ΔE, the more stable is a carbonium ion, $XC_6H_4O\overset{+}{C}HCH_3$, and hence the greater is the reactivity of its parent PVE derivative, $XC_6H_4OCH=CH_2$.

Perturbation calculations of ΔE have been carried out for the various phenyl vinyl ethers. The molecular orbital functions and energies of monosubstituted benzenes as unperturbed systems were the same as those used previously.[18] The integral parameters adopted for the composite groups Y and Y′ were as follows:

For $-O-CH=CH_2$, the Coulomb integral parameters were $k_O=0.5$, $k_{C\alpha}=0.1$ and $k_{C\beta}=0$, and the resonance integral parameters were $h_{C-O}=0.5$ and $h_{C=C}=1$. For $-O-\overset{+}{C}HCH_3$, these parameters were $k_O=0.5$, $k_{C\alpha^+}=0.3$ and $h_{O-C}=0.5$. The value of $k_{C\alpha^+}=0.3$, which was most crucial to the calculated results, was simply a sum of $k_{C^+}=0.2$ that was adopted previously for a side chain $-\overset{+}{C}(CH_3)_2$ and $k_{C\alpha}=0.1$ that was assumed for the α-carbon of an ether in the initial state. Variations of the other parameters caused no material changes in the general trends of the calculated results.

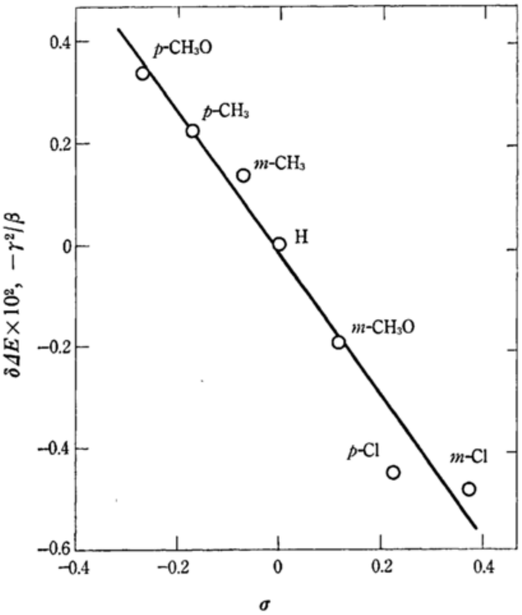

Fig. 5. Linear variation of the relative stabilities, $\delta\Delta E$, of the carbonium ions, $XC_6H_4O\overset{+}{C}HCH_3$, as calculated by the empirical molecular orbital theory, with the Hammett σ values of the substituents, X.

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[18] T. Fueno, T. Okuyama and J. Furukawa, This Bulletin, **39**, 569 (1966).

[19] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

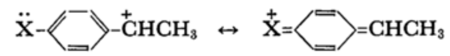
The delocalization energy differences, ΔE, obtained for the various PVE's were as follows: 0.0552 (p-CH_3O), 0.0443 (p-CH_3), 0.0353 (m-CH_3), 0.0218 (H), 0.0022 (m-CH_3O), -0.0232 (p-Cl) and -0.0265 (m-Cl) in units of $-\gamma^2/\beta$. Denote by $\delta\Delta E$ each value of ΔE relative to that (0.0218) obtained for the unsubstituted PVE. The $\delta\Delta E$ may then be regarded as a measure of the relative stabilities of the carbonium ions, $XC_6H_4O\overset{+}{C}HCH_3$, taking the unsubstituted ion as the standard. These values of $\delta\Delta E$ have been found to be proportional to the Hammett σ values of the substituents, as may be seen in Fig. 5. These results of calculation rationalize the observation that the effects of substituents on the rates of the acid-catalyzed hydrolysis of phenyl vinyl ethers obey the Hammett correlation, in which the original Hammett σ values have been used for substituents.

Discussion

The observed Hammett correlations, coupled with molecular orbital considerations, allow us to postulate that the Hammett σ value of the ring substituents is an adequate measure of the relative stabilities of the various intermediate carbonium ions, $XC_6H_4O\overset{+}{C}HCH_3$. The intervention of an oxygen atom between the benzene ring and the charged center suppresses direct conjugation between them, which otherwise would have permitted the correlation of $\log k_2$ with Brown's σ^+ values,[20] as in the case of the acid-catalyzed hydration of styrene derivatives.[21]

Perhaps the following are the best pictorial representations of the origin of the different effects of para $-$R substituents on the stabilities of the carbonium ions formed from styrene and phenyl vinyl ether:

For ions formed from styrene derivatives,



For ions formed from phenyl vinyl ether derivatives,

In the latter ions, the strong electron demand of the electron-deficient carbon is saturated by the migration toward it of the lone pair electrons of the neighboring oxygen, leaving no valency available to permit direct conjugation between the substituent and the side chain group.

Nonetheless, the oxygen atom certainly transmits the mesomeric effect of substituents onto the reaction center, even though only slightly. Otherwise, $\log k_2$ would have been better correlated with Taft's normal substituent constants, σ°.[14] Conjugation between the ring and the extracyclic vinyl linkage through the oxygen atom in phenyl vinyl ethers is also evidenced by the observed effect of ring substituents on the NMR chemical shifts of the β-protons of the ethers.[22] In our specific series of reactions, then, the stabilizations of the initial states and the intermediate cations due to such conjugations must have been of proper amount to just cancel each other, leading, as a net result, to the substituent effects which have been observed to conform to the Hammett σ constants.

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20) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

21) W. M. Schubert, B. Lamm and J. R. Reeffe, *ibid.*, **86**, 4727 (1964), have reported that the acid-catalyzed hydration of styrene derivatives involves the rate-determining protonation of the vinyl linkage, the effects of ring substituents thus conforming to the σ^+ values.

22) O. Kajimoto and T. Fueno, Abstracts of the papers presented at the Symposium on the Hammett Relationship, October 1967, Kyoto, p. 51.