gives rise to **3g** (50%) together with some **4g**, phenanthrene, and unidentified products.

α-Phenylcinnamonitrile (1h) was prepared according to the prescription in "Organic Syntheses".[22]

9-Cyano-9,10-dihydrophenanthrene (3h) was obtained by irradiating a 2×10^{-3} M solution in a mixture of methanol and water (1:1), buffered at pH 3 for 16 h. The yield, after purification by column chromatography over Al_2O_3 with hexane-toluene (3:1) as the eluent, was 80%: mp 84-85 °C (lit.[20] 83-84 °C); UV λ_{max} (CH_3OH) 297 nm (log ϵ 3.53), 280 (4.16), 267 (4.34), and 259 (4.29). The NMR spectrum matched that reported.[22] Mass spectrum m/e (rel intensity) 205 (M^+, 100), 204 (60), 203 (45), 190 (M − 15, 40), 178 ($C_{14}H_{10}$, 45), and 165 (65).

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Effect of Sulfuric Acid Concentration on the Rates of Hydrolysis of Ethyl Benzoate, Ethyl Thiolbenzoate, and Ethyl Thionbenzoate

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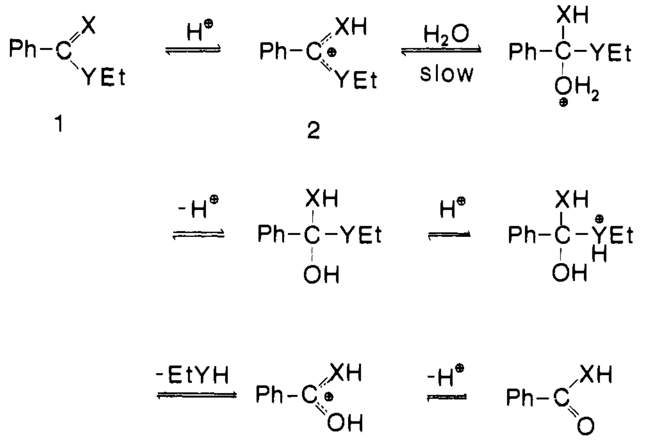
Abstract: The kinetics of the hydrolysis of ethyl benzoate, ethyl thiolbenzoate, and ethyl thionbenzoate has been studied in 30-99% sulfuric acid. Application of Yates-McClelland r and $f_{S^{\ddagger}}{}^*$ treatments to the data shows that ethyl thionbenzoate hydrolyzes by an $A_{Ac}2$ mechanism in all concentrations of acid, while ethyl thiolbenzoate hydrolyzes by an $A_{Ac}2$ mechanism in acid concentrations up to 60%, but by an $A_{Ac}1$ mechanism in more concentrated acid. The results show the greatly superior stability of the acylium ion as compared with the thioacylium ion.

The role of coenzyme A as a natural acylating agent[1] and the use of thiol esters for peptide synthesis[2] depend on the "energy-rich" nature of the S-acyl linkage.[3] In water, a reaction competitive of these acylations is acyl transfer to the solvent (hydrolysis). This reaction has received considerable attention recently, and persuasive evidence for a tetrahedral intermediate has been advanced.[4] However, there has been no study of the rate-acidity profile for these hydrolyses in varying concentrations of sulfuric acid. The power of this mechanistic probe has been amply demonstrated by Yates and his colleagues.[5-8] The rate-acidity profile of a typical ester hydrolyzing in a large excess of acid has the following features: the pseudo-first-order rate constant k_ψ reaches a maximum in 50-60% sulfuric acid, and then decreases to a minimum in 80% acid; over this range of concentrations the ester is hydrolyzing by an $A_{Ac}2$ mechanism (Scheme I, X = Y = O). In higher concentrations of acid k_ψ increases again, the ester now hydrolyzing by an $A_{Ac}1$ (Scheme II, X = Y = O) or an $A_{Al}1$ mechanism.

Recently, Yates and his colleagues[7,8] have shown how to obtain information about the transition state of the A-2 and A-1 reactions by combining a study of the change in the activity coefficient of the substrate along with the change in k_ψ with changing acid concentration. In the present paper we

Scheme I



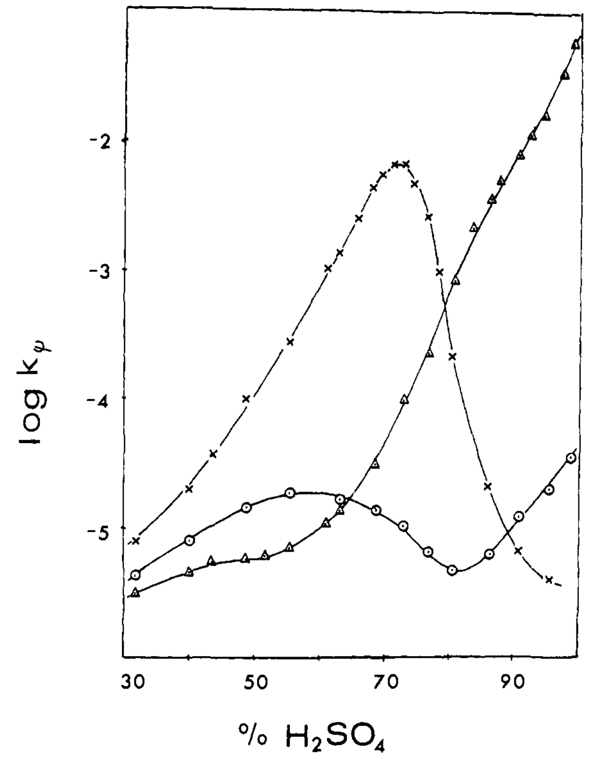


Figure 1. Rate-acidity profiles for hydrolysis of ethyl benzoate (○), ethyl thiolbenzoate (△), and ethyl thionbenzoate (×).

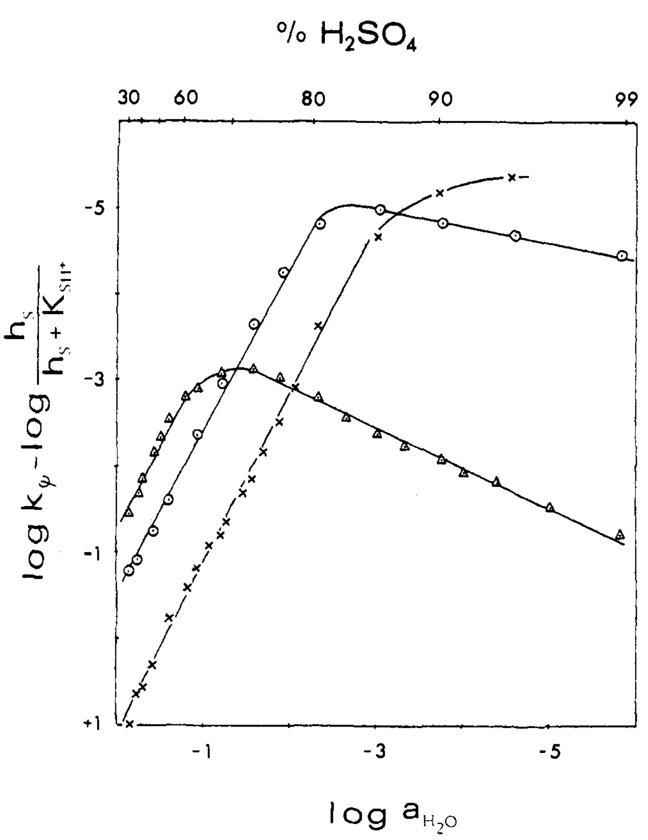
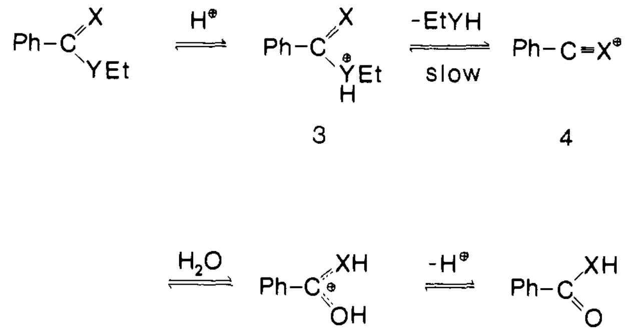


Figure 2. *r* plots for hydrolysis of ethyl benzoate (○), ethyl thiolbenzoate (△), and ethyl thionbenzoate (×).

Scheme II



apply these ideas to a study of the effect of changing concentration (30–99%) of sulfuric acid on the rates of hydrolysis of ethyl benzoate (**1**, X = O; Y = O), ethyl thiolbenzoate (**1**, X = O; Y = S), and ethyl thionbenzoate (**1**, X = S; Y = O).

Results and Discussion

The variation in k_ψ with acid concentration for the three esters is shown in Figure 1. Ethyl benzoate behaves as expected, hydrolyzing by an $A_{Ac}2$ mechanism in concentrations below 80%, and by an $A_{Ac}1$ mechanism in concentrations above 85%. The profile for ethyl thiolbenzoate shows a slower $A_{Ac}2$ reaction which is superseded in acid more concentrated than 60% by a fast A-1 reaction. The profile for ethyl thionbenzoate shows the maximum in 70% acid characteristic of an $A_{Ac}2$ mechanism, but no upturn in the most concentrated acid to indicate switchover to an $A_{Ac}1$ or $A_{Al}1$ mechanism. Thioamides show a similar profile.[9] The absence of an A-1 reaction for these compounds even at the highest acidities indicates that **4** (X = S) is a high energy intermediate because the sulfur atom forms 3π–2π bonds only with difficulty, so that an $A_{Ac}1$ mechanism is disfavored, and that the ethyl cation also is too unstable to permit the alternative $A_{Al}1$ mechanism.

These qualitative interpretations are supported by the Yates–McClelland *r* and $f_{S^{\ddagger}}{}^*$ treatments[6-8] of the experimental data.

***r* Treatment for A-2 Reactions.** For the A-2 hydrolysis of a substrate S by the mechanism

$$S + H^+ \overset{K_{SH^+}}{\rightleftharpoons} SH^+ \qquad (1)$$

$$SH^+ + pH_2O \xrightarrow[\text{slow}]{k_2} S^{\ddagger} \rightarrow \text{products} \qquad (2)$$

the Brønsted–Bjerrum rate equation leads to

$$\log k_\psi - \log \left(\frac{h_S}{h_S + K_{SH^+}}\right) = \log k_2 + p \log a_{H_2O} + \log (f_{SH^+}/f_{S^{\ddagger}}) \qquad (3)$$

where *a* is activity, *f* is activity coefficient, and $S^{\ddagger}$ is the transition state. The acidity functions appropriate to eq 1 are known: the protonation of ethyl thionbenzoate follows h_T, and has a pK_{SH^+} of −8.55;[10] the protonation of ethyl benzoate and ethyl thiolbenzoate follows $h_0{}^m$[6] with m = 0.74 for ethyl benzoate[11] and 0.72 for ethyl thiolbenzoate,[12] their pK_{SH^+} values being −5.94 and −5.49, respectively. If, as first assumed by Yates and McClelland,[6] $\log (f_{SH^+}/f_{S^{\ddagger}}) = 0$, the slope *r* of a plot of the left-hand side of eq 3 against $\log a_{H_2O}$ should equal *p*, the number of water molecules forming partial covalent bonds with SH^+ to give $S^{\ddagger}$.[13]

In Figure 2 is shown such a plot, using h_0,[14] h_T,[10] and a_{H_2O} values[15] from the literature. In the more dilute acid solutions the plots are straight lines having slopes *r* (ethyl benzoate, 1.94; ethyl thiolbenzoate, 2.11; ethyl thionbenzoate, 1.95) close to the values of ~2 found by Yates and McClelland[6] for $A_{Ac}2$ hydrolyses of a variety of acetate esters. These investigators concluded that the slow step of the reaction involved the concerted attack of two molecules of water upon the protonated ester. However, *r* for other hydrolyses can be unreasonably

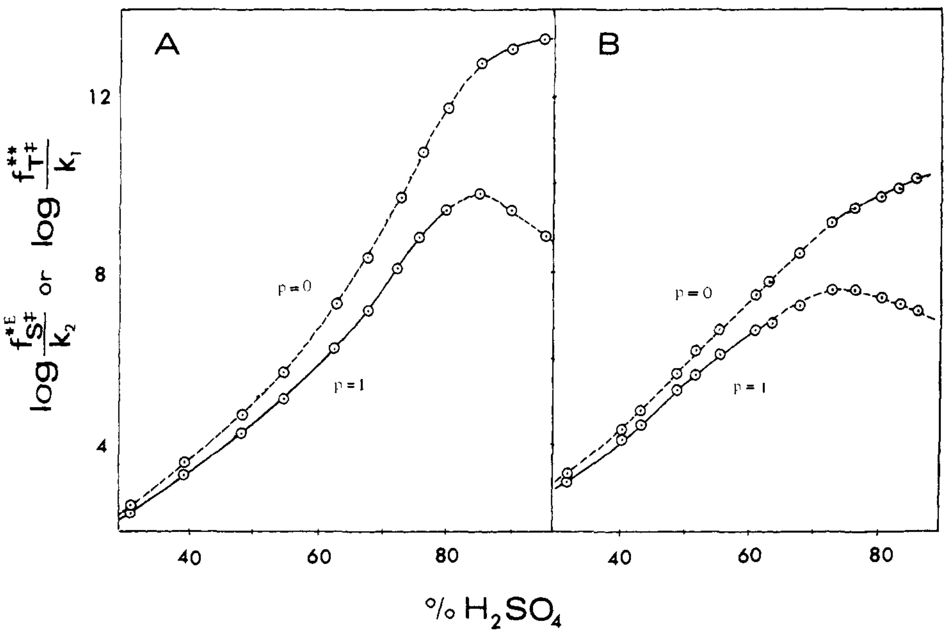
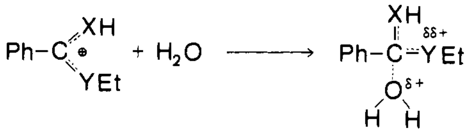


Figure 3. Plots of log ($f_{S^\ddagger}{}^{*E}/k_2$) (eq 6) and log ($f_{T^\ddagger}{}^{**}/k_1$) (eq 10) against acid concentration for the hydrolysis of (A) ethyl benzoate and (B) ethyl thiolbenzoate.

large,[9] and it should be regarded only as an empirical parameter characterizing different mechanisms. This is to be expected, because the assumption that log ($f_{SH^+}/f_{S^\ddagger}$) = 0 now seems unlikely.[8] If SH^+ and $S^\ddagger$ are represented as shown in reaction 4, $S^\ddagger$, which has the charge largely localized at the



(4)

SH^+ $S^\ddagger$

position marked δ^+, should be salted out in increasing acid concentration more strongly than SH^+. (The solvation requirements, and hence salting out, decrease in the order $H_3O^+ > ROH_2^+ > R_2OH^+ > RY{=}CR'{=}XH^+$.[8,16]) Consequently, log ($f_{SH^+}/f_{S^\ddagger}$) should become increasingly negative with rising acid concentration. If log ($f_{SH^+}/f_{S^\ddagger}$) = q log a_{H_2O}, then $r = p + q$, with plausibly $p = 1$.

$f_{S^\ddagger}{}^*$ Treatment for A-2 Reactions. More recently, Yates and his colleagues[7,8] have introduced the relative activity coefficient of the transition state, $f_{S^\ddagger}{}^*$, as a criterion of reaction mechanism. We shall use the symbol $f_{S^\ddagger}{}^{*E}$, because of a slight difference in our treatment, discussed below. The Brønsted–Bjerrum analysis of the mechanism of eq 1 and 2 gives, besides eq 3,

$$\frac{f_{S^\ddagger}}{k_2} = \frac{a_{H^+}a_{H_2O}{}^p f_S}{k_\psi(1 + I)K_{SH^+}} \qquad (5)$$

Both $f_{S^\ddagger}$ and a_{H^+} refer to the activities of single ions, which are experimentally inaccessible, but may be replaced by *relative* values, $f_{S^\ddagger}{}^{*E}$ ($\equiv f_{S^\ddagger}/f_{TEA^+}$) and $a_{H^+}{}^*$ ($\equiv a_{H^+}/f_{TEA^+}$), referring activities to that of the tetraethylammonium ion (TEA^+) as a standard.[17] Equation 5 becomes

$$\log (f_{S^\ddagger}{}^{*E}/k_2) = -\log k_\psi(1 + I) - \log K_{SH^+} + \log f_S + \log a_{H^+}{}^* + p \log a_{H_2O} \qquad (6)$$

Except for p, all the terms on the right-hand side of this equation are experimentally determinable.[7] We have obtained the activity coefficients f_S of ethyl benzoate and ethyl thiolbenzoate in varying concentrations of sulfuric acid by the partition method of Yates et al.[7] and have arbitrarily set $p = 1$, as in eq 4.

The variation with acid concentration of log ($f_{S^\ddagger}{}^{*E}/k_2$) is shown in Figure 3. Also shown in this figure is the variation of log ($f_{S^\ddagger}{}^*/k_2$), $f_{S^\ddagger}{}^*$ being defined by Yates and his colleagues[7,8] by eq 6 with $p = 0$ and $f_{S^\ddagger}{}^* = f_{S^\ddagger}{}^{*E}$. (This has the advantage of avoiding the uncertainties inherent in p but, in our estimation, is a less physically reasonable parameter for reactions known on other grounds to involve one or more molecules of water entering into the transition state.) In either case, the changes in slope for ethyl benzoate when 85% acid concentration is reached, and for ethyl thiolbenzoate when 73% concentration is reached, point to a change in mechanism. Considering only the change in log ($f_{S^\ddagger}{}^{*E}/k_2$) in the more dilute acid region where the $A_{Ac}2$ mechanism prevails, the increase of ~3 logarithmic units on going from 30 to 60% acid is the same as the increase in $f_{ROH_2^+}$ for this change of acid concentration[8] and supports the formulation of $S^\ddagger$ as shown in eq 4 above, with $\delta^+ \gg \delta\delta^+$.

Rates and Activity Coefficients for the A-1 Reaction in Concentrated Acid. Above 85% acid, the slope r for ethyl benzoate becomes −0.19, in the range expected for an $A_{Ac}1$ mechanism.[6] However, the slope r for ethyl thiolbenzoate in acid above 75% becomes −0.46, which lies in the range expected for an $A_{Al}1$ mechanism for ordinary esters. In the present case, this possibility can be excluded: the $A_{Al}1$ mechanism would yield thiobenzoic acid as an intermediate, and the spectral changes show that this is not formed (cf. the discussion below for ethyl thionbenzoate in concentrated acid).

The $A_{Ac}1$ hydrolysis of the two esters must involve the less stable tautomeric O- or S-protonated ester TH^+ (**3**, X = O; Y = O or S), rather than the more abundant carbonyl-protonated ester SH^+ (**2**, X = O; Y = O or S):[18]

$$SH^+ \underset{\text{fast}}{\overset{K_{SH^+}}{\rightleftharpoons}} S + H^+ \underset{\text{fast}}{\overset{K_{TH^+}}{\rightleftharpoons}} TH^+ \qquad (7)$$

$$TH^+ \xrightarrow[\text{slow}]{k_1} T^\ddagger \rightarrow \text{products} \qquad (8)$$

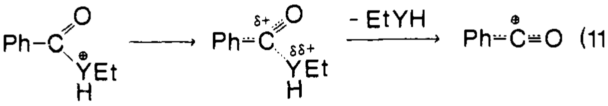
The Brønsted–Bjerrum analysis for a reaction proceeding by this mechanism gives

$$k_\psi(1 + I) = k_1 a_{H^+}{}^* f_S/K_{TH^+} f_{T^\ddagger}{}^* \qquad (9)$$

It is convenient to introduce the parameter $f_{T^{\ddagger}}^{**}$ ($\equiv f_{T^{\ddagger}}^{*} \cdot K_{TH^+}/K_{SH^+}$), so that eq 9 becomes

$$\log (f_{T^{\ddagger}}^{**}/k_1) = -\log k_{\psi}(1 + I) - \log K_{SH^+} + \log f_S + \log a_{H^+}^{*} \quad (10)$$

The right-hand side of this equation is identical with that of eq 6 with $p = 0$. The upper curves in the more concentrated acid regions of Figure 3 show that $f_{T^{\ddagger}}^{**}$ increases relatively slowly with acid concentration. This is in agreement with the formulation of $T^{\ddagger}$ in eq 11 ($\delta^+ \gg \delta\delta^+$), if $T^{\ddagger}$ is close to the high-energy delocalized acylium ion **5** in structure, and hence less salted out with increasing sulfuric acid concentration.[16]



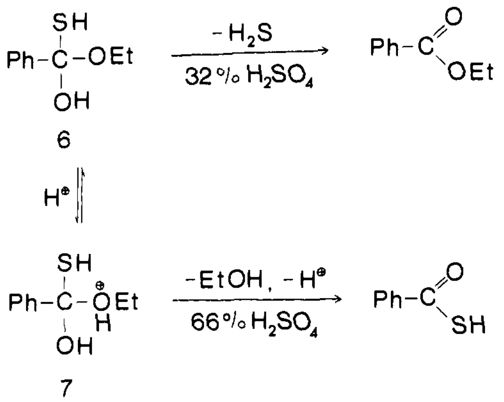
(11)

TH⁺ T‡ 5

"Real" Transition-State Activity Coefficients. According to these views, the change in activity coefficient of the transition state for the A-2 reaction with changing acid concentration is given by the solid lines on the left-hand side of Figures 3A and 3B, and that of the transition state for the A-1 reaction by the solid lines on the right-hand side of these figures. Extrapolation of the curve for the A-2 reaction to zero acid concentration (to the extent that it is possible) gives $-\log k_2$ as intercept, and extrapolation of the curve for the A-1 reaction gives $\log (K_{TH^+}/K_{SH^+}k_1)$ as intercept.

Partitioning of the Tetrahedral Intermediate from Ethyl Thionbenzoate among Various Products. The rapid hydrolysis of ethyl thionbenzoate prevented the f_S determinations necessary for the application of eq 6. However, the hydrolysis of this ester was of interest because of the dependence of the breakdown path of the tetrahedral intermediate **6** on the acidity of the medium. This is shown in Scheme III. In 32% sulfuric acid, spectral changes indicated that ethyl benzoate (and/or benzoic acid, which has an almost identical spectrum in this concentration of acid) and hydrogen sulfide were formed exclusively. However, as the acidity increased, thiobenzoic acid (and presumably ethanol) gradually became the preferred initial hydrolysis products. In 66% acid, spectral changes for the first 60 min indicated the formation of thiobenzoic acid (λ_{max} 260 nm), which subsequently was hydrolyzed to benzoic acid (λ_{max} 236 nm). This is shown in Figure 4. A possible explanation for the change in product distribution with acidity is the rapid protonation of the tetrahedral intermediate **6** to give **7**, from which elimination of ethanol would be easier than elimination of hydrogen sulfide (cf. ref 4 and 19).

Scheme III



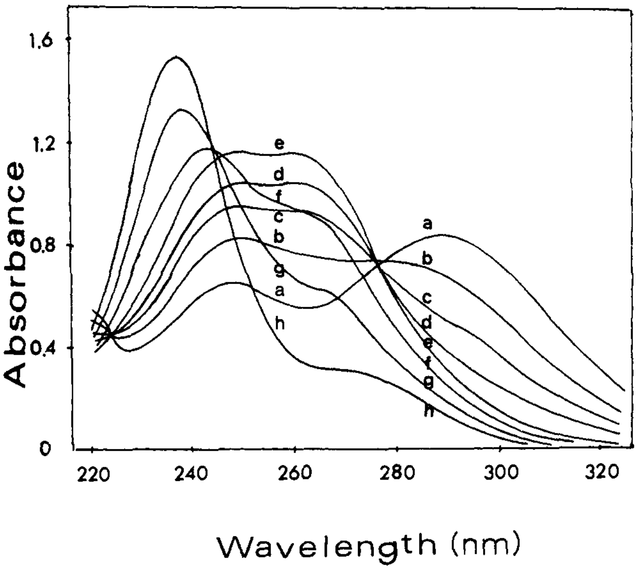


Figure 4. Spectral changes of ethyl thionbenzoate in 66% sulfuric acid: (a) $t = 0$, (b) $t = 2$ min, (c) $t = 5$ min, (d) $t = 10$ min, (e) $t = 1$ h, (f) $t = 8$ h, (g) $t = 16$ h, (h) $t = 24$ h.

Experimental Section

Materials. Ethyl benzoate, a commercial product, was redistilled before use. Ethyl thionbenzoate was prepared by reaction of ethyl benzimidate with hydrogen sulfide gas.[20] Ethyl thiolbenzoate was prepared by reaction of benzoyl chloride with ethanethiol.[20] Sulfuric acid solutions were made up and standardized by procedures described previously.[10,11]

Determination of Protonation Constants. The hydrolysis of ethyl *p*-nitrothiolbenzoate in all concentrations of sulfuric acid at 10.0 ± 0.1 °C was slow, and hence the ionization ratio I could be determined by the conventional spectrophotometric procedure.[21] (Spectral shifts due to the medium effect were small and could be ignored.) The ionization of the compound was found to follow h_0^m with $m = 0.74$, identical with that found previously for ethyl benzoate.[11]

Ethyl thiolbenzoate hydrolyzed very rapidly in concentrated acid. Extinction coefficients of the compound were therefore calculated by following the absorbance change due to hydrolysis and extrapolating to the time of preparation of the solution. These extrapolations became unreliable in very concentrated acid solutions, making it difficult to obtain the extinction coefficient ϵ_{SH^+} of the conjugate acid which was required for obtaining $I(=(\epsilon - \epsilon_S)/(\epsilon_{SH^+} - \epsilon))$ at all acidities. Consequently, a value of ϵ_{SH^+} was chosen by trial and error so that the plot of $\log I$ against $\log h_0$ would be linear. Confidence in this procedure came from the fact that m was found to be close to the value of 0.74 found for the more stable nitro compound.

Kinetic Measurements. Acid solutions of known concentration, placed in 1-cm UV cells with Teflon stoppers, were allowed to equilibrate in the thermostated (25.0 ± 0.1 °C) cell block of a UNICAM SP.800 spectrophotometer. Methanolic stock solutions of the esters were injected into the acid solutions using a Hamilton syringe. The cells were vigorously shaken for 4-5 s and placed back in the cell block, and the change in absorbance was followed for at least 1 to 2 half-lives. A least-squares computer program was used to calculate the pseudo-first-order rate constants. Triplicate runs agreed to within 4%.

Acknowledgment. We are very grateful to Dr. Graeme Welch for preliminary experimentation which revealed the main outlines of the problem and to the National Research Council of Canada for financial support.

Supplementary Material Available: Tables I (pseudo-first-order rate constants in different acid concentrations), II (ionization ratios), III (activity coefficients f_S), and IV (transition-state activity coefficient ratios $f_{S^{\ddagger}}^{*E}/k_2$ and $f_{S^{\ddagger}}^{*}/k_2$) (5 pages). Ordering information is given on any current masthead page.

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(18) The treatment which follows differs from that of Yates et al., because the esters which they were studying hydrolyzed in concentrated acid by an $A_{Al}1$, not by an $A_{Ac}1$ mechanism. The $A_{Al}1$ mechanism may proceed through the same protonated substrate SH^+ as the $A_{Ac}2$ mechanism, and hence it is not necessary to consider the equilibrium between SH^+ and TH^+, as we have in eq 7 et seq.

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Vinyl Ether Hydrolysis. 9. Isotope Effects on Proton Transfer from the Hydronium Ion[1]

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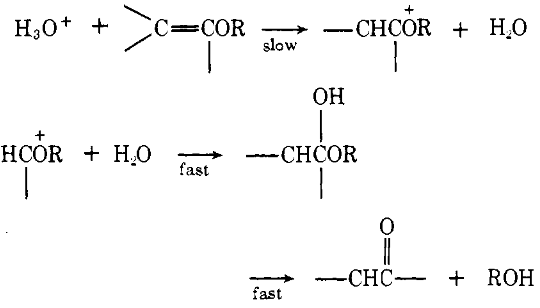
Abstract: Rates of vinyl ether hydrolysis catalyzed by the hydronium ion are reported for 14 substrates in H_2O solution and for 20 substrates in D_2O solution. These results, together with data already in the literature, provide kinetic isotope effects for rate-determining carbon protonation of 32 vinyl ethers. When fitted to expressions provided by Marcus rate theory, these data give an intrinsic barrier for this reaction of $\Delta G_0^\ddagger \simeq 5$ kcal/mol, a work term of $w^r \simeq 10$ kcal/mol, and a maximum isotope effect of $k_{H_3O^+}/k_{D_3O^+} \simeq 3.7$. These results suggest that the carbon protonation of certain enolate anions is an encounter plus desolvation-controlled reaction.

A number of systems are now known in which primary hydrogen isotope effects vary systematically with the free energy of reaction, showing a maximum near $\Delta G° = 0$ and dropping off toward unity as $\Delta G°$ becomes strongly positive or strongly negative.[2] This behavior was predicted a number of years ago on the basis of considerations dealing with transition-state symmetry,[3] but that view has recently been disputed and the phenomenon has been attributed to proton tunneling.[4] A somewhat different approach is provided by Marcus rate theory,[5] which also predicts an isotope effect maximum near $\Delta G° = 0$ but does not attempt to explain the phenomenon on a molecular level; the theory does, however, furnish an analytical expression relating k_H/k_D to $\Delta G°$, which is a connection not easily made from the other two points of view.

In some systems, $\Delta G°$ is not available, and it is useful therefore to have another quantity to which k_H/k_D can be related. In this paper we show how Marcus theory also leads to a relationship between k_H/k_D and $\Delta G^\ddagger$, the free energy of activation, and we then use this relationship to correlate values of k_H/k_D for the hydronium ion catalyzed hydrolysis of vinyl ethers. This is a reaction whose first and rate-determining step is proton transfer from the hydronium ion to the substrate, eq 1; since the cationic intermediate thus formed reacts very rapidly with water to give a hemiacetal or hemiketal, which itself decomposes quickly to alcohol and aldehyde or ketone products (eq 2), equilibrium constants for the reaction step to which $k_h.k_D$ refers cannot be measured and $\Delta G°$ cannot be determined.



(1)

(2)

The reaction mechanism of eq 1 and 2 is based upon a variety of evidence,[6] chief among which is the occurrence of sizable kinetic isotope effects; the isotope effects reported here therefore serve to reinforce this mechanistic assignment.

Experimental Section[7]

Materials. Ethyl, phenyl, and α-naphthyl isopropenyl ethers were prepared by decarboxylation of β-ethoxy-, β-phenoxy-, and β-(α-naphthoxy)crotonic acids, respectively.[8] All other substrates (with the exception of methyl and ethyl vinyl ethers which were obtained commercially) were synthesized from the corresponding acetals or ketals by eliminating 1 equiv of alcohol; this was accomplished either in the liquid phase through the catalytic action of *p*-toluenesulfonic acid,[9] or in the vapor phase by passage through a hot gas chromatography column.[10] The propenyl ethers were also prepared by isomerizing the corresponding allyl ethers in Me_2SO solution with potassium *tert*-butoxide as the catalyst. *cis*- and *trans*-propenyl ethers were separated by gas chromatography and were distinguished by their vinyl hydrogen NMR coupling constants.