The Kinetics of the Acid-Catalyzed Hydrolysis of α-Acetoxystilbene[1]

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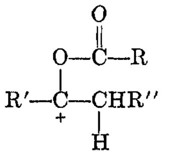
We have recently shown that enol esters are hydrolyzed in mineral acid by two alternative mechanisms.[3,4] One of these mechanisms is the normal ester hydrolysis process; the other mechanism is a process initiated by olefin protonation to give rise to a carbonium ion of type A as the first intermediate. In the absence of substantial carbonium ion stabilization by R′, the normal ester mechanism predominates in dilute mineral acid. This is the situation which is observed for vinyl acetate[4] and for *p*-nitro-α-acetoxystyrene.[3] Structures providing better carbonium ion stabilization allow olefin protonation to predominate even at low acidities, *e.g.*, *p*-methoxy-α-acetoxystyrene.



$$R'-\overset{\displaystyle O-\overset{\displaystyle O}{\overset{\|}{C}}-R}{\overset{|}{\underset{+}{C}}}-\underset{\displaystyle H}{\underset{|}{C}}HR''$$

A

In the present study we wish to examine briefly other factors which may influence the balance between these two mechanisms. It is well known that the rate of acid-catalyzed hydrolysis of esters is relatively insensitive to wide variation of the alcoholic moiety in terms of both steric and electronic effects. For example, Euranto[5] has reported that the rates for the hydrolysis of a diverse group of formate esters are within a factor of 3, for structural variation including methyl formate, chloromethyl formate, and *t*-butyl formate. Extremes of steric hindrance might be expected to result in some diminution of the rate of hydrolysis. In the present situation, it is to be noted that *trans*-α-acetoxystilbene (**1**) has the acetate group in a position which is severely crowded. Nevertheless, the depression of rate is relatively modest. In 50% mineral acid, **1** hydrolyzes 60 times more slowly than vinyl acetate; *cis*-α-acetoxystilbene (**2**) hydrolyzes only 10 times more slowly than vinyl acetate. This situation should be contrasted with the very sharp differences observed when structural changes are made in the carboxylate moiety (R).

On the other hand, rates of olefin protonation are relatively sensitive to structural variation at the carbon β to the potential carbonium ion center. For example, the hydration of styrene occurs 500 times more rapidly than proton attack upon *cis*-stilbene initiates isomerization.[6,7]

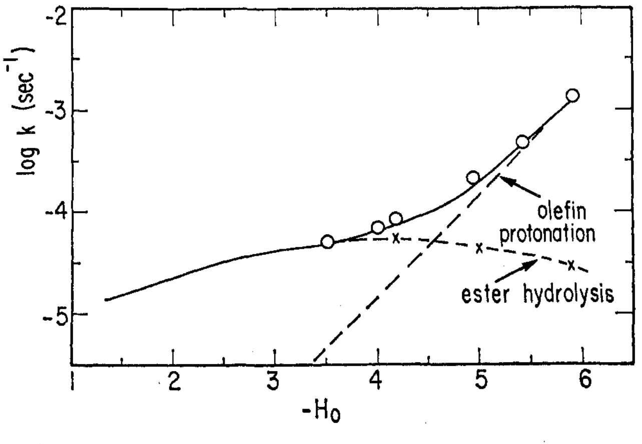


Figure 1.– Rate of hydrolysis of *trans*-α-acetoxystilbene: X---X, calculated rate of normal ester hydrolysis; ---, calculated rate of hydrolysis by olefin protonation; ——, calculated total rate of hydrolysis; ○ ○, observed rate of hydrolysis.

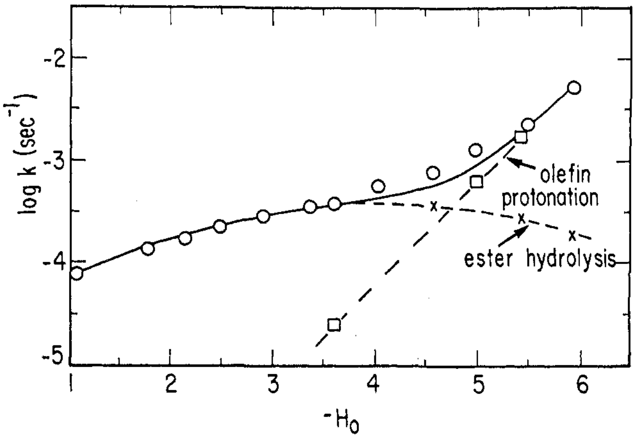


Figure 2.—Rate of hydrolysis of *cis*-α-acetoxystilbene: X---X, calculated rate of normal ester hydrolysis; □---□, calculated rate of hydrolysis by olefin protonation; ——, calculated total rate of hydrolysis; ○ ○, observed rate of hydrolysis.

It should thus be expected that α-acetoxystilbene should show a rate of hydrolysis by the normal ester mechanism similar to that observed for *p*-nitro-α-acetoxystyrene, and an olefin protonation rate substantially suppressed from that observed for α-acetoxystyrene. We have therefore measured the rates of acid-catalyzed hydrolysis for both stereoisomers of α-acetoxystilbene.

The two stereoisomers were prepared by the procedure of House and Trost.[8] The higher melting isomer mp 100–101.5° has been previously obtained by Nesmeyanov, *et al.*[9] That this is the *trans* stereoisomer **1** is supported by its spectral characteristics, with the vinyl proton signal in the nmr occurring at lower fields than in **2**.[10]

The results of the kinetic measurements are graphically displayed in Figures 1 and 2.

It is to be noted that, as the acidity of the medium is increased, the rate of hydrolysis effectively reaches a

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[1] Supported in part by a grant from the National Science Foundation, GP-6133X.

[2] National Institutes of Health Postdoctoral Fellow, 1965–1968 (GM-20266).

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plateau between 40 and 50% perchloric acid, and finally near 60% acid abruptly begins to increase again. We ascribe this complex profile to the interplay of the two mechanistic pathways available for hydrolysis of enol acetates. For the *cis* isomer **2**, below 59% perchloric acid, the predominant mode of hydrolysis is the normal ester pathway; above this acidity, the majority of the hydrolysis proceeds by way of olefin protonation.

For calculation of the predicted rate for hydrolysis by the normal ester mechanism, the following procedure was used. Yates and McClelland[11] have observed that many esters show a very similar rate–acidity profile in the middle range of sulfuric acid concentration, with eq 1 describing the behavior of the ester, with $m \cong 0.62$ and $r \cong 2$. Lane, Cheung, and Dorsey,[12]

$$\log k + mH_0 = r \log a_{H_2O} + \text{constant} \qquad (1)$$

in a particularly careful study of the behavior of ethyl acetate, show that $m = 0.645$ and $r = 2$. To calculate the expected rate for normal ester hydrolysis for *cis*-α-acetoxystilbene (**2**) we have used eq 2, with data for the activity of water from Robinson and Baker[13] with

$$\log (\text{rate}_{\text{ester}})_{cis} = -0.62H_0 + 2 \log a_{H_2O} - 4.65 \qquad (2)$$

the constant term (−4.65) chosen to give a predicted rate in agreement with experiment at the lower acidities ($H_0 \cong -1.5$). In the most concentrated acid solution a very small correction for protonation of the ester has been made assuming pK_{BH^+} of −7.00. For the predicted rate of reaction by way of olefin protonation, eq 3 was used[14] with the constant term (−8.22) chosen to match the observed rates in 63% sulfuric acid ($H_0 = -5.9$).

$$\log (\text{rate}_{\text{olef}})_{cis} = -H_0 - 8.22 \qquad (3)$$

Calculated rates for the *trans* isomer are obtained in a similar fashion, using eq 4 and 5, with the constant terms chosen as above.

$$\log (\text{rate}_{\text{ester}})_{trans} = -0.62H_0 + 2 \log a_{H_2O} - 5.51 \qquad (4)$$

$$\log (\text{rate}_{\text{olef}})_{trans} = -H_0 - 8.82 \qquad (5)$$

Finally it should be noted that the rates of olefin protonation for *cis*-stilbene[7] and for *cis*-α-acetoxystilbene are very similar.

Experimental Section[15]

α-Acetoxystilbenes.—The procedure of House and Trost[8] was followed. Ten grams of desoxybenzoin was dissolved in 150 ml of carbon tetrachloride and 51 g of acetic anhydride was added with stirring. After the dropwise addition of 0.5 ml of 70% perchloric acid, stirring was continued for 2.5 hr. The reaction mixture was washed thoroughly with aqueous sodium bicarbonate solution, the carbon tetrachloride layer was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The crude residue contained approximately 60% *trans*-α-acetoxystilbene, 10% *cis*-α-acetoxystilbene, and 30% deoxybenzoin as determined from the nmr spectrum.

The crude reaction mixture was dissolved in a minimum amount of diethyl ether and pentane was added to 500 ml. Upon cooling, 4.7 g of *trans*-α-acetoxystilbene was collected as pale yellow crystals.[16] Recrystallization from pentane gave colorless needles: mp 100.0–101.5° (lit. 100.5–101.0°); uv max 287 mμ (ε 27,400, ethanol); ir (CCl_4) 1764 cm^{-1}; nmr (CCl_4) δ 7.14–7.50 (m, 10 H), 6.55 (s, 1 H), 2.26 (s, 3 H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.65; H, 5.98.

The mother liquors from the crystallization of the *trans* isomer were concentrated, and the *cis* isomer was separated from desoxybenzoin and remaining *trans* isomer by glpc on a 5 ft × 0.25 in. 20% SE-30 column. ***cis*-α-Acetoxystilbene** was obtained as a viscous oil: uv max 262 mμ (ε 12,000); ir (CCl_4) 1764 cm^{-1}; nmr (CCl_4) δ 7.03–7.95 (broad multiplet, 10 H), 6.33 (s, 1 H), 2.14 (s, 3 H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.68; H, 6.04.

Kinetic Runs.—An aliquot (10–50 μl) of a stock solution of the substrate in ethanol was mixed with 3 ml of the appropriate acid solution in a stoppered cuvette. The kinetics were followed on a Gilford Model 2000 spectrophotometer with a thermostated cell compartment (25°). The rate constant obtained showed no dependence on the concentration of ethanol (0.3–1.6 vol %). For *cis*-α-acetoxystilbene reactions were followed at 280 mμ and showed good first-order behavior to greater than 85% reaction. For *trans*-α-acetoxystilbene the kinetics were followed at 288 mμ. All reactions of the *trans* compound showed excellent first-order behavior to greater than 95% reaction. Infinity spectra were recorded on a Cary Model 14 spectrophotometer, and were identical with those obtained for an authentic sample of desoxybenzoin in the same acid media. The rate constants were obtained from the slopes of the plots of log ($A_\infty - A_t$) *vs.* time.

Registry No.—*trans*-α-Acetoxystilbene, 13892-81-4; *cis*-α-acetoxystilbene, 24647-07-2.

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[12] C. A. Lane, M. F. Cheung, and G. F. Dorsey, *ibid.*, **90**, 6492 (1968).

[13] R. A. Robinson and O. J. Baker, *Trans. Proc. Roy. Soc. N. Z.*, **76**, 250 (1946).

[14] In the previous study, ref 3, it was observed that the slope of the plot for log *k vs.* $-H_0$ was close to unity for the carbonium ion pathway.

[15] Analyses are by the Microanalytical Laboratory of the Department of Chemistry, University of California.

[16] No attempt was made to maximize the yield.

Preparation of Maleoyl Fluoride. Nuclear Magnetic Resonance Spectra of Maleoyl Fluoride, Fumaryl Fluoride, and Fumaryl Chloride Fluoride

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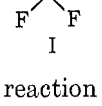
The preparation of maleoyl fluoride from maleic anhydride and sulfur tetrafluoride has been reported by Hasek, *et al.*[1] We have repeated their reaction conditions (13 hr at 150°) and observe that the products are fumaryl fluoride, unreacted anhydride, and a compound we believe to be 4,4-difluoroisocrotonolactone (I). Under the above conditions it is likely that maleoyl fluoride will be isomerized to fumaryl fluoride.



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We have used lower reaction temperatures and find that if the mixture is heated to about 75° for 5 hr maleoyl fluoride is one of the products. The amount produced varies from run to run but usually is in the range

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