grouped according to single cleavage (1–9), molecular reaction (10–14), and multiple cleavage (15–25). The binary pairs in 1–9 can, of course give rise to the more numerous products of 15–24; indeed, the simultaneous concentration of sufficient energy in two or more bonds which is required to give the third group seems inherently less probable than having the products arise from further fragmentation of the group 1 species. Although distinctions between decompositions from excited states, *e.g.*, singlet *vs.* triplet, etc., are not made here, these will certainly have to be established too.[34]

In their survey, Calvert and Pitts documented most of the homolytic and molecular processes and one polar example (17) of Table III.[5a] However, one can no longer neglect the heterolytic paths: the photodecarboxylations of phenylacetate ion[4] and the nitrophenylacetic acids[7] produce benzylic anions; the photohydrolyses of methoxybenzyl ester produce benzylic cations.[35] Since the thermal decomposition of phenylacetyl and other diacyl peroxides has been shown to proceed by both a polar as well as a radical route,[36] we believe that similar competitive processes should be found in the photolyses of these compounds. The ejection of an electron by photoionization, according to 9 in Table III, is known from mass spectroscopic and flash photolysis studies.[2] The detection of additional species, *e.g.*, B, in aqueous solutions of **1** indicates that 22 was observed.[2] In fact, the examination of new systems and the reexamination of old ones for both the solvated electron and coproducts should turn up examples in the group 21–25. To summarize, perhaps one-third to one-half of the entries in Table III remain hypothetical; of the recognized cleavage modes, a relatively small number has been characterized and understood even at the semiquantitative level of (or beyond) the present work.

In the light of Table III, the photocleavage mechanisms of **1** and **2** might appear to be very simple. The primary steps, at least, essentially involve only the carboxyl function. The α and β homolyses (1, 4) indicated in **3** predominate. It is difficult, however, to rationalize this preference by using thermochemical data relating to overall product stabilities. For if these were critical, then the molecular reactions leading to stable molecules (10–14) would normally be observed. We do know that the activation energy for α and β cleavage is $\sim$ 55 kcal/mol,[23] which makes these kinetically accessible. Beyond this, it would seem that further photolysis studies of **1** and **2** with narrower energy ranges,[5a] *e.g.*, in the n–π^* region (200–250 nm), in the π–π^* region (250–275 nm), with sensitizers (>275 nm), etc., may lead to fewer products and even greater understanding of the primary processes.

Acknowledgment. We are grateful to Professor L. I. Grossweiner and his associates for assistance with the flash photolysis measurements and to the Lake Michigan Basin Office of the Federal Water Pollution Control Administration for making their Micro Tek Chromatograph available to us.

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A Probable Diffusion-Limited Mechanism in the Hydrolysis of a Thiolester

Ronald J. Zygmunt and Ronald E. Barnett*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received June 2, 1971*

Abstract: The hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate is subject to general base catalysis. The Brønsted β is near zero for catalysis by eight carboxylate anions varying in pK_a from 2.1 to 4.3. No catalysis could be seen by trifluoroacetate ion, indicating the value of β must increase sharply for catalysts with pK_a's near zero. Similar behavior is observed for weakly basic amine catalysts. The results are interpreted in terms of a rate-determining, diffusion-limited deprotonation of a zwitterionic intermediate formed by the uncatalyzed addition of water to the thiolester.

Fedor and Bruice[1] found hydrolysis of ethyl trifluorothiolacetate proceeds by a general base catalyzed formation of an anionic intermediate and its uncatalyzed breakdown. Calculations based on assumptions as to the pK_a of the intermediate and the equilibrium constant for its formation from the thiolester indicated that the rate constants for the partitioning of the anionic intermediate to thiolester and products is within 10–100 of the diffusion limit.[2] Preliminary data on the more reactive thiolester ethyl *S*-trifluoroacetylmercaptoacetate indicated that breakdown of the anionic intermediate formed in the hydrolysis of this ester to give starting materials is diffusion limited.[2] The purpose of this paper is to present further evidence that the hydrolysis of this ester and its more water soluble methyl analog is diffusion limited.

Experimental Section

Materials. Commercially available carboxylic acids and amines were purified by distillation or recrystallization. Samples of 2,2′,2′′-tricyanotriethylamine and 2-hydroxy-2′,2′′-dicyanotriethyl-

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(1) L. R. Fedor and T. C. Bruice, *J. Amer. Chem. Soc.*, **86**, 5697 (1964); **87**, 4138 (1965).

(2) R. Barnett and W. P. Jencks, *J. Org. Chem.*, **34**, 2777 (1969).

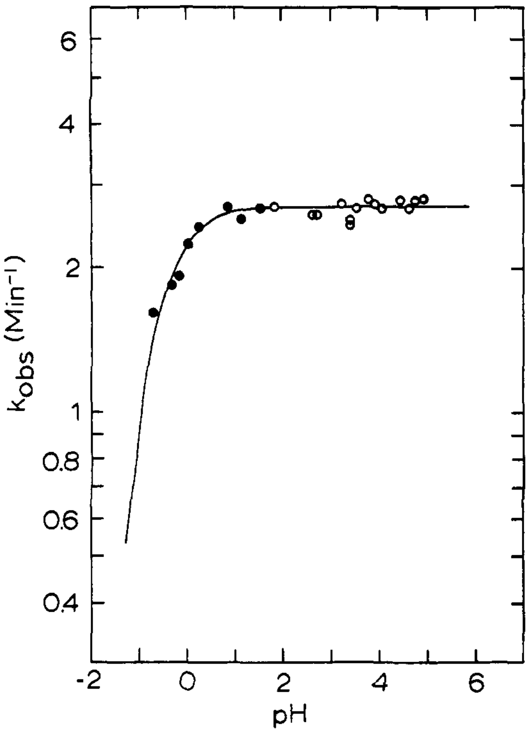
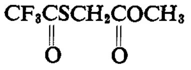


Figure 1. pH–rate profile for the hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate at 25° and ionic strength 3.0 *M* in HCl, ●; in buffers extrapolating to zero buffer concentration, ○.

amine hydrochloride were the gift of Sea-wha Oh. Ethyl trifluorothiolacetate was obtained commercially, and gave a λ_{max} at 244 nm with ϵ_{244} 4050. Methyl *S*-trifluoroacetylmercaptoacetate (**1**) was synthesized from trifluoroacetic anhydride and methyl mercaptoacetate at 0°. Excess trifluoroacetic anhydride and trifluoroacetic acid were distilled off at atmospheric pressure. Distillation



$$CF_3\underset{\underset{O}{\|}}{C}SCH_2\underset{\underset{O}{\|}}{C}OCH_3$$

1

at 75 mm yielded two fractions, bp 98–100 and 101–102°, respectively. Both fractions gave λ_{max} 241 nm. The higher boiling fraction, which had infrared absorption at 1709 and 1739 cm^{-1} (ϵ_{241} 4280), was used for kinetic studies.

Anal. Calcd for $C_5H_5F_3O_3S$: C, 29.71; H, 2.49. Found: C, 29.80; H, 2.55.

Kinetic Measurements. The reaction was initiated by addition of 10–15 μl of thiolester in acetonitrile to 3 ml of buffer, covering the cuvette with parafilm, and inverting several times. The reaction was followed spectrophotometrically at the λ_{max} of the thiolester using a Coleman 124 spectrophotometer with a chart recorder and a thermostated cuvette holder, except for chloroacetate and β-chloropropionate buffers, which, due to buffer absorption, were followed at 250 nm. The temperature was maintained at 25.00 ± 0.05° with a Haake FE circulating heater. The ionic strength was maintained at 3.0 *M* with lithium chloride. Measurements of pH were made with a Radiometer PHM 26 pH meter. An effort was made to follow thiolester hydrolysis by the neutral hydroxamate method.[3] An aliquot of the thiolester was added to a neutral hydroxylamine solution followed by the addition of the ferric chloride reagent. The initial brown color of the ferric hydroxamate complex almost completely faded within 2–3 min, making its spectrophotometric determination impossible.

To determine the products of hydrolysis the aqueous solution was extracted with ether 5 min after the addition of the thiolester. The ether extract was dried with magnesium sulfate and the ether removed *in vacuo*. The remaining oil was identified by ir and tlc as methyl mercaptoacetate (93%), demonstrating that the thiolester rather than the oxygen ester portion of **1** is being hydrolyzed.

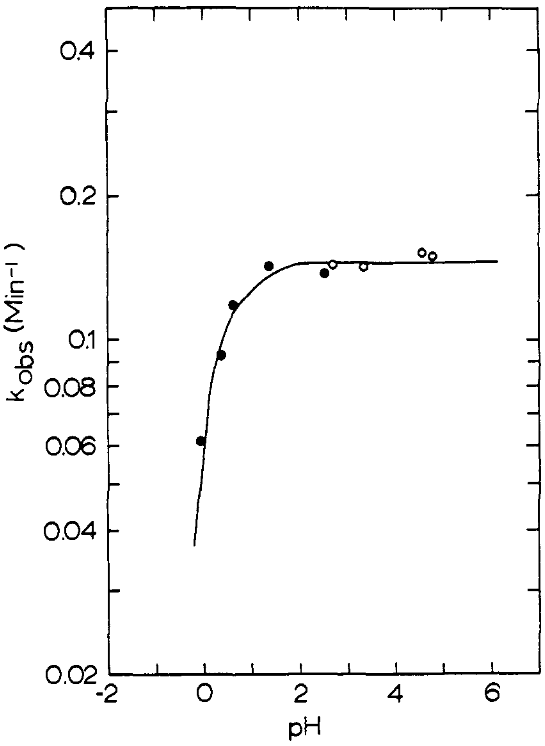


Figure 2. pH–rate profile for the hydrolysis of ethyl trifluorothiolacetate at 25° and ionic strength 3.0 *M* in HCl, ●; in buffers extrapolating to zero buffer concentration, ○.

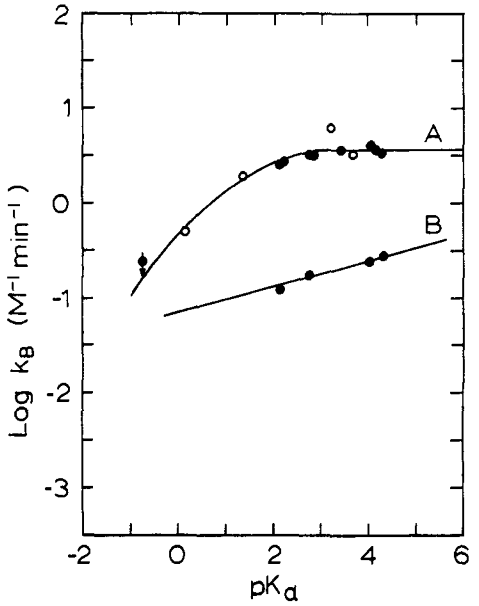


Figure 3. Brønsted plots for the general base catalyzed hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate (curve A) and ethyl trifluorothiolacetate (curve B) by carboxylate anions (●) and amines (○).

Results

The pH–rate profiles for the hydrolysis of **1** and ethyl trifluorothiolacetate (**2**) are shown in Figures 1 and 2. The rate constants for pH-independent hydrolysis of **1** and **2** are 2.7 and 0.145 min^{-1}, respectively, at ionic strength 3.0 *M*. Both thiolesters show a decrease in rate at low pH. The Brønsted plots for general base catalysis are shown in Figure 3 and the

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(3) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **86**, 4651 (1964).

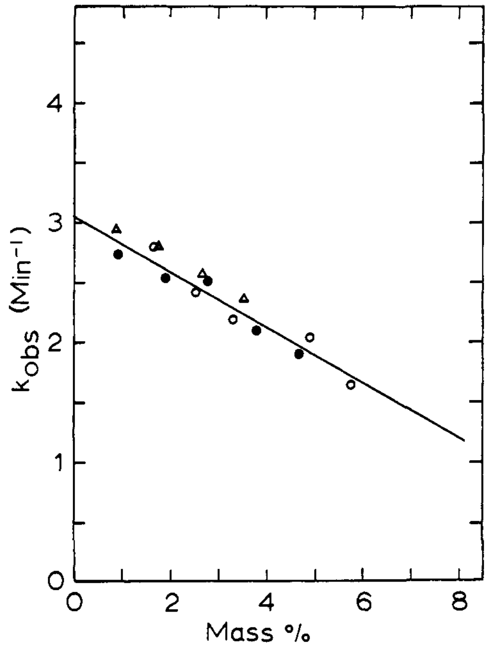

Figure 4. Solvent effects on the hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate by ethanol (●), butyl carbitol (○), and ethyl acetate (△) in 0.1 *M* acetate buffer, pH 4.0.

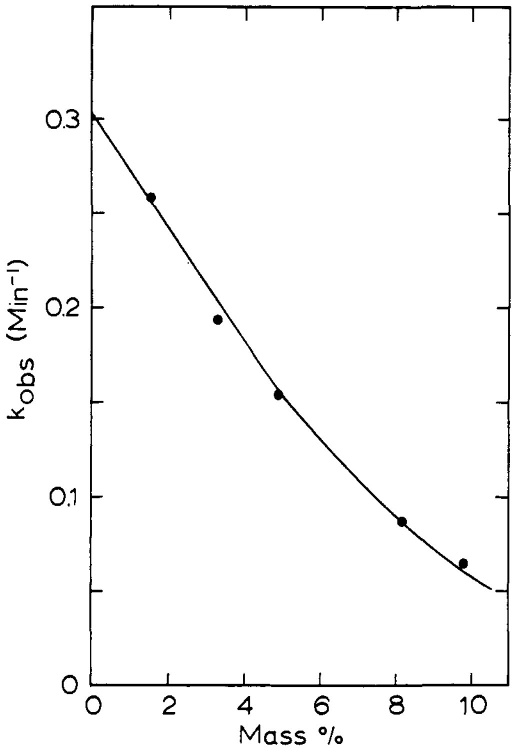

Figure 5. Solvent effects of butyl carbitol on the hydrolysis of ethyl trifluorothiolacetate in 1.0 *M* acetate buffer, pH 4.0.

data for the rate constants summarized in Tables I and II. Hydrolysis is inhibited both by organic solvents and by replacement of chloride by carboxylate ions (Figures 4–6). Formate-catalyzed hydrolysis of **1** is linear with buffer concentration up to 3 *M* formate after corrections are made for solvent and salt effects.[4]

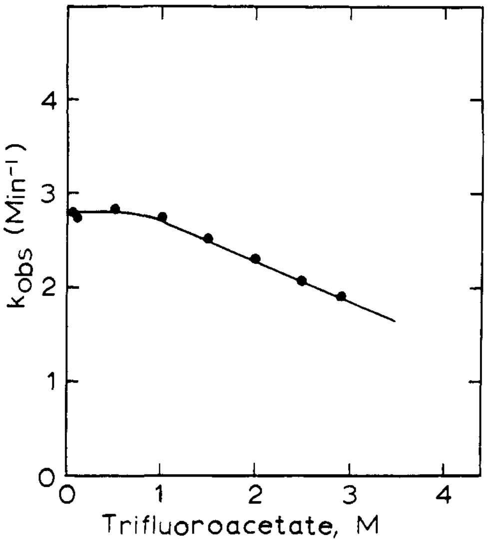

Figure 6. Effect of trifluoroacetate ion on the hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate in 0.1 *M* acetate buffer, pH 4.0.

The pK_a of trifluoroacetic acid at an ionic strength of 3 *M* was estimated from the salt effect of 3 *M* lithium chloride on the pK_a of the seven neutral carboxylic

Table I. Rate Constants for the Hydrolysis of Methyl *S*-Trifluoroacetylmercaptoacetate at 25° and Ionic Strength 3.0 *M*

Base	No. of runs	pK_a[a,b]	k_B,[c] M^{-1} min^{-1}
Trifluoroacetate[d]	9	−0.8[e]	0.25[f]
Sulfamate	22	0.1	0.5[g]
2,2′,2″-Tricyano-triethylamine	12	1.40	1.9[g]
Glycine	10	2.07	2.63
Chloroacetate	10	2.11	2.9[g]
Methoxyacetate	10	2.73	3.40
Formate	28	2.89	3.35
1,4-Diazabicyclo[2.2.2]octane hydrochloride	20	3.19	6.60
β-Chloropropionate	16	3.40	3.6[g]
2,2′-Dicyano-2″-hydroxytri-ethylamine	12	3.63	3.3[g]
Acetate	32	4.00	4.25
Propionate	10	4.17	3.91
Pivalate	10	4.30	3.58

[a] pK_a of the conjugate acid. [b] Determined from the pH of buffers of known composition, correcting for self-ionization at low pH. [c] Corrected for solvent effects. [d] Run in 0.1 *M* acetate buffer, pH 4.00. [e] See text for determination. [f] An upper limit obtained assuming a 5% increase in rate could be missed. [g] Approximate value.

Table II. Rate Constants for the Hydrolysis of Ethyl Trifluorothiolacetate at 25° and Ionic Strength 3.0 *M*

Base	No. of runs	pK_a[a,b]	k_B,[c] M^{-1} min^{-1}
Chloroacetate	10	2.11	0.1[d]
Methoxyacetate	10	2.73	0.174
Acetate	10	4.00	0.249
Propionate	10	4.17	0.280

[a] pK_a of the conjugate acid. [b] Determined from the pH of buffers of known composition. [c] Corrected for solvent effects. [d] Approximate value.

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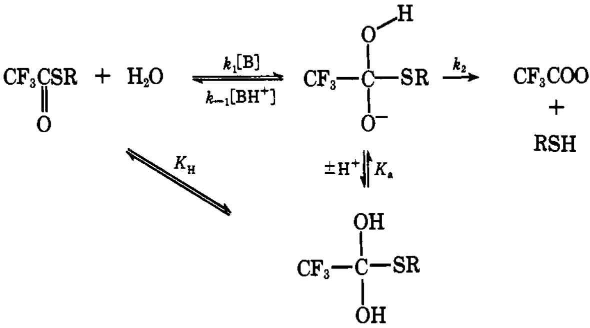
(4) Corrections for the solvent effect of formic acid were made using the data of Figure 4 as a model. Similarly, corrections for the salt effect of formate ion were made using the catalytically inactive trifluoroacetate ion as a model (Figure 6).

acids[5] in Table I and the pK_a of trifluoroacetic acid of -0.04 determined at zero ionic strength.[6] The ΔpK_a for the seven carboxylic acids is -0.75 ± 0.10, giving an estimated pK_a for trifluoroacetic acid of -0.8 ± 0.1.

Hydroxylamine catalyzes a rapid disappearance of **1** but is probably acting nucleophilically since aliquots taken immediately after addition of **1** to hydroxylamine buffers give a dark brown complex with ferric chloride absorbing at 540 nm, characteristic of a ferric hydroxamate. If the aliquot is taken several minutes after addition of the thiolester, no brown coloration is produced, indicating that trifluoroacetyl hydroxamic acid hydrolyzes rapidly.

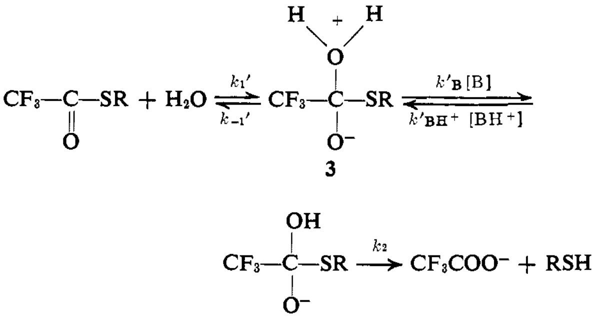
Discussion

Both the hydrolyses of **1** and **2** show a decrease in rate at low pH. For **2** ^{18}O exchange is seen with the solvent below pH 2 but not above pH 2,[7] indicating that the decrease in rate is not an effect on the activity coefficient of water due to increasing hydronium ion concentration, but represents a change in rate-determining step, with breakdown of an anionic intermediate being rate determining below pH 2 and its formation above pH 2. The decrease in rate for **1** at low pH also probably represents a change in rate-determining step since the analogous compound ethyl *S*-trifluoroacetylmercaptoacetate shows the decrease in rate in both 1.0 *M* potassium chloride and 3.0 *M* lithium chloride,[2] making it unlikely that the decrease is due to an effect on the activity coefficient of water. The step which is rate determining at low pH for **1** cannot be the attack of hydroxide ion since the rate constant would have to be 2×10^{13} M^{-1} sec^{-1}, much faster than any known reaction in aqueous solution, and so this step must also represent breakdown of an anionic intermediate. For both thiolesters, formation of the intermediate is general base catalyzed. A mechanism consistent with the data for both thiolesters is shown in eq 1. Taking $K_a = 10^{-9}$ and $K_H \leqslant 0.1$,[2] estimates of k_{-1} and k_2 can be obtained. For thiolester **1** with hydronium ion as the general acid, $k_{-1} \geqslant 4.6 \times 10^8$ M^{-1} sec^{-1} and $k_2 \geqslant 2.2 \times 10^9$ sec^{-1}. The corresponding values for **2** are 2.4×10^7 M^{-1} sec^{-1} and 1.7×10^7 sec^{-1}. For compound **1** the estimated rate constants for the partitioning of the intermediate approach those for diffusion-limited processes,[8] and so the mechanism shown in eq 2 has been suggested,[2] where k'_B is rate determining above pH 1 and k_2 below pH 1. Such a mechanism would require that the Brønsted β for general base catalysis be near zero for catalysts with pK_a's greater than the pK_a of **3** and unity for very weakly basic catalysts. The Brønsted plots for general base catalyzed hydrolysis of **1** and **2** are shown in Figure 3. For **1**, $\beta \approx 0$ for eight carboxylate anions. Amine catalysts behave similarly. Since amines are generally much better nucleophiles than oxygen anions of the same pK_a[9] and since the amines show no elevated catalytic activity, the catalysis observed is almost certainly general base rather than nucleophilic catalysis. No catalysis could be seen by trifluoroacetate ion, and so β must increase rapidly for catalysts with pK_a's near -0.5. Since the transition from $\beta = 0$ to $\beta = 1$ should occur near the pK_a of the substrate being deprotonated,[8] the pK_a of **3** should be near -0.5 for the mechanism of eq 2 to be possible. Since **3** is a protonated alcohol, a pK_a of -0.5 is reasonable. Taking the pK_a of **3** to be -0.5 and the rate constant for protonation of a strong base by hydronium ion to be 5×10^{10} M^{-1} sec^{-1},[7] the estimated values of k'_{H_2O} and $k'_{H_3O^+}$ are 3.8×10^{10} sec^{-1} and 1.2×10^{10} M^{-1} sec^{-1}, respectively. This requires that $k_{-1}' > 3.8 \times 10^{10}$ sec^{-1} and $k_2 = 5.8 \times 10^{10}$ sec^{-1}. A limit for k_{-1}' can also be obtained from the data for formate catalysis. Saturation of buffer catalysis should be seen as $k'_B[B]$ becomes larger than k_{-1}', but no curvature is seen in the formate catalyzed reaction up to 3 *M* formate. Taking the rate constant for formate-catalyzed proton abstraction to be 3×10^9 M^{-1} sec^{-1}[8] and assuming a 20% decrease in rate could be missed owing to masking by solvent and salt effects, then $k_{-1}' \geqslant 4.5 \times 10^{10}$ sec^{-1}. Are such large rate constants reasonable? A reaction similar to the breakdown of **4** to carboxylate and thiol is the hydroxide ion catalyzed decomposition of hemithioacetals.[10] If the pK_a of the departing thiol is less than 8, the rate-limiting step is the diffusion-controlled encounter of hydroxide ion and the hemithioacetal, and so the rate of thiol anion expulsion from the hemithioacetal anion **5**



$$CF_3\underset{\underset{O}{\|}}{C}SR + H_2O \underset{k_{-1}[BH^+]}{\overset{k_1[B]}{\rightleftharpoons}} CF_3-\underset{O^-}{\overset{O-H}{C}}-SR \xrightarrow{k_2} CF_3COO^- + RSH \qquad (1)$$

$$\xrightarrow{K_H} \quad \pm H^+ \updownarrow K_a \quad CF_3-\underset{OH}{\overset{OH}{C}}-SR$$

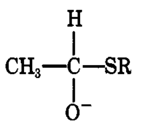


$$CF_3-\underset{\underset{O}{\|}}{C}-SR + H_2O \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} CF_3-\underset{O^-}{\overset{H\overset{+}{O}H}{C}}-SR \underset{k'_{BH^+}[BH^+]}{\overset{k'_B[B]}{\rightleftharpoons}}$$

3

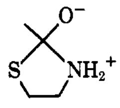
$$CF_3-\underset{O^-}{\overset{OH}{C}}-SR \xrightarrow{k_2} CF_3COO^- + RSH \qquad (2)$$

4



$$CH_3-\underset{O^-}{\overset{H}{C}}-SR$$

5



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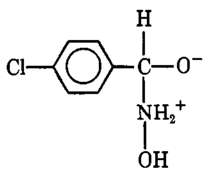

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must be greater than 10^{10} sec^{-1}. The predicted value for k_{-1}' is also reasonable. The rate constants for the elimination of amine ($\mathrm{p}K_\mathrm{a} \approx 9$) from **6** and of hydroxylamine ($\mathrm{p}K_\mathrm{a} \approx 6$) from **7** are 7×10^8 [11] and about 10^9 sec^{-1},[12] respectively. Expulsion of very weakly basic water ($\mathrm{p}K_\mathrm{a} = -1.74$) should occur even more readily.

In summary, the data supporting the mechanism of eq 2 are (1) the estimated rate constants for the partitioning of **4**, based on assumptions as to the pK_a of the intermediate and the equilibrium constant for its formation, are near the diffusion limit; (2) the rate constants for the breakdown of analogous intermediates in other reactions are correspondingly large; (3) the Brønsted $\beta \approx 0$ is consistent with a diffusion-limited deprotonation of **3**; and (4) the change in slope of the Brønsted plot near $\mathrm{p}K_\mathrm{a} = -0.5$, which should correspond to the pK_a of **3** for a diffusion-limited mechanism, is reasonable in terms of the structure of **3**.

The Brønsted plot for ethyl trifluorothiolacetate, which has a much poorer leaving group, has a small ($\beta \approx 0.2$) but nonzero slope, implying that for this ester the concerted mechanism (eq 1) rather than the diffusion-limited mechanism holds. This is analogous to the behavior of the hydroxide catalyzed decomposition of hemithioacetals[10,13] in which it was observed that, when the pK_a of the departing thiol is less than 8, the diffusion-limited mechanism prevails, while for less acidic thiols it does not.

Since the original suggestion by Moffat and Hunt[14] that equilibration of the various ionic forms of a tetrahedral intermediate may not always be fast compared to making and breaking of bonds to carbon, diffusion-limited mechanisms have been implicated in thiolester hydrolysis, thiolester aminolysis,[11,15,16] amide hydrolysis,[17] and hemithioacetal decomposition.[10] It seems possible that such mechanisms will be found to be a relatively common phenomena.

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Stereospecific Introduction of Double Bonds *via* Thermolysis of β-Lactones[1]

Waldemar Adam,* Jaime Baeza,[2] and Ju-Chao Liu

Contribution from the Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931.

Received July 9, 1971

Abstract: The direct cyclization of β-hydroxy acids with benzenesulfonyl chloride in pyridine at 0–5° has been shown to be a general reaction affording tri- and tetrasubstituted β-lactones in high yield. The β-lactones are decarboxylated at moderate temperatures (140–160°) into the corresponding olefins with retention of the initial geometry and without double bond isomerization. At elevated temperatures (45–55°) benzenesulfonyl chloride in pyridine promotes the dehydrocarbonation of β-hydroxy acids directly to the desired olefins. This novel dehydrocarbonation of β-hydroxy acids, which are now readily prepared by the condensation of α-metalated carboxylate salts with ketones and aldehydes, constitutes a convenient alternative to the Wittig olefin synthesis.

A number of synthetic methods have become available in recent years for the stereospecific and stereoselective introduction of double bonds in carbon skeletons.[3] Of particular interest is the work of Corey and coworkers for the novel preparations of tri- and tetrasubstituted olefins.[4] β-Lactones are known to decompose at moderate temperatures into olefins and carbon dioxide essentially quantitatively.[5] This thermal lability imparts to this oxetanone ring system the unique property of serving as a convenient olefin carrier in which the carbon dioxide moiety acts as a vise for fixing double bonds.

It is surprising that this synthetic approach has not been utilized more extensively.[6] Presumably the reason for this is the fact that no convenient methods are available for the synthesis of β-lactones. Besides the classical approach which consists of internal nucleophilic displacement of halide ion from β-halocarboxylate salts,[7] some alternative methods working with variable degrees of success are deaminative cyclization of β-amino acids,[8] the cycloaddition of ketones to ketenes,[9] the

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(1) The general aspect of this work (J. C. Liu) was presented at Metrochem 71, Regional Meeting of the American Chemical Society, New York–New Jersey, Puerto Rico Sections, April 29 to May 2, 1971, San Juan, Puerto Rico. The stereochemical study (J. Baeza) was presented at the 23rd International Congress of Pure and Applied Chemistry (IUPAC), July 25–30, 1971, Boston, Mass.

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