In the *absence* of BHT, a chain reaction occurs, eq 18-20,

$$CO\cdot + COOOH \rightarrow COH + COOO\cdot \quad (18)$$

$$HOO\cdot + COOOH \rightarrow H_2O_2 + COOO\cdot \quad (19)$$

$$COOO\cdot \rightarrow CO\cdot + O_2 \quad (20)$$

leading to cumyl alcohol and acetophenone; additional expected products, as shown, are hydrogen peroxide[15] and oxygen (probably singlet[12,15]). Acetophenone is produced from β-scission of cumyloxyl radicals, eq 21.

$$CO\cdot \rightarrow PhCOCH_3 + CH_3\cdot \quad (21)$$

Ring vs. Side-Chain Ozonation. We obtain a partition between ring and side-chain ozonation of about 30/70 at temperatures from -78 to -40 °C. Literature data are not in complete accord on this ratio for cumene, but it is clear that side-chain ozonation is faster for this substrate than is attack on this ring.[14b,22]

It is tempting to propose that the CT complex is an intermediate in both ring and side-chain ozonation and that partition occurs following complexation, as shown in Figure 9. Bailey has previously suggested complexation prior to reaction for aromatic compounds.[14b,22]

Acknowledgment. This work was supported in part by grants from the National Science Foundation, the National Institutes of Health, HL-16029, and the National Foundation for Cancer Research. We thank Professor William Cherry and Dr. E. Mooberry for helpful suggestions.

Registry No. COOOH, 82951-48-2; BHT, 128-37-0; COO·, 7175-54-4; CH, 98-82-8; COH, 536-60-7; COOH, 80-15-9; H, 12385-13-6; isobutane, 75-28-5; propene, 115-07-1; 1,4-pentadiene, 591-93-5.

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Uncatalyzed and General Acid Catalyzed Decomposition of Alkyl Xanthates and Monothiocarbonates in Aqueous Solutions

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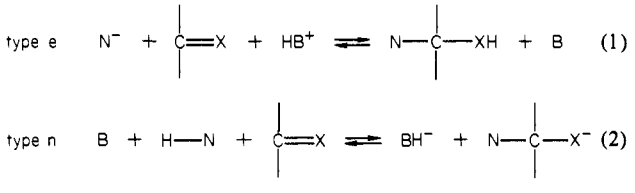
Abstract: The decomposition of potassium alkyl xanthates and alkyl monothiocarbonates follows the rate law $k_{obsd} = k_{H_3O^+}[H_3O^+] + k_{HA}[HA] + k_{H_2O}$ in aqueous buffer solutions. The Brønsted coefficient β_{lg} for the k_{H_2O} term is -1.1 for the monothiocarbonates and -1.3 for the xanthates. These results complement the value of -1.1 observed for the alkyl monocarbonates and have been interpreted as late transition states in the decomposition direction. The reactions are also subject to general acid catalysis with α values of 0.9 ± 0.2 and 0.8 ± 0.1 for ethyl and methoxyethyl xanthates; α values for the monothiocarbonates are 0.58 ± 0.05 and 0.57 ± 0.01 for the methyl and methoxyethyl compounds, respectively. Solvent kinetic isotope effects ($k_{D_3O^+}/k_{H_3O^+}$) for ethyl and methoxyethyl xanthates are 2.53 and 2.12, respectively; for ethyl, methyl, and methoxyethyl monothiocarbonate they are 1.95, 1.94, and 1.91, respectively. The high Brønsted value for ethyl xanthate and the resultant uncertainty in its numerical value coupled with the high inverse solvent isotope effect place this reaction on the borderline between a specific acid catalyzed mechanism and a concerted mechanism. The latter is favored because the value for $k_{H_3O^+}$ is larger than that predicted for the protonation of the alcohol oxygen of the xanthates and monothiocarbonates; further, the formation of such protonated species is estimated to be sufficiently unfavorable as to require a breakdown step faster than a molecular vibration to account for the observed rates. Acetic acid does not catalyze the $k_{H_3O^+}$ term for ethyl xanthate at very low pH; the small amount of catalysis at higher pH must therefore be true general acid catalysis and not a solvent effect. Brønsted β_{lg} values for the acid-catalyzed decompositions of the xanthates and monothiocarbonates are small. These results have been interpreted in terms of concerted general acid catalysis where little change in charge occurs on the leaving group oxygen in going from the starting material to the transition state.

Introduction

The behavior of the Brønsted coefficients for reactions in aqueous solution involving the addition-elimination reactions of nucleophiles with carbonyl groups has been used to differentiate between mechanisms for general acid catalysis designated as type e and type n.[1,2] The mechanisms are illustrated in eq 1 and 2.



Type e reactions are characterized by a decrease in α when the pK_a of the nucleophile is increased,[3] whereas type n reactions show an increase in α (measured for the reverse of eq 2) with increasing basicity of the nucleophile in a number of related systems.[4-12] The

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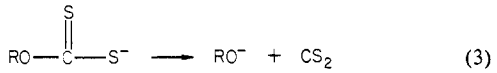
interpretation of these results in terms of three-dimensional free-energy diagrams has found utility not only in explaining such relationships between the Brønsted coefficients of catalysts and basicity of nucleophiles,[13] but also in rationalizing the differences in concerted vs. stepwise mechanisms.[14]

We report here the results of experiments on the uncatalyzed breakdown of alkyl xanthates (eq 3) and alkyl monothiocarbonates



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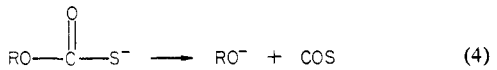
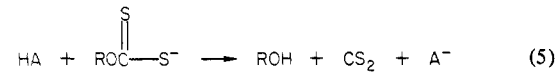


(4)

(eq 4) as well as general acid catalyzed breakdowns of these two systems (eq 5 and 6). In earlier work we reported experiments



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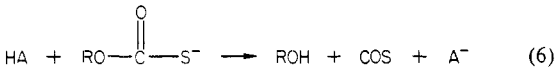

(6)

on the uncatalyzed decomposition of alkyl monocarbonates in aqueous solutions at high pH,[15] and others have discussed acid-catalyzed breakdown of these compounds as well as bicarbonates.[16] An earlier communication by us on the acid catalysis of xanthate breakdown was marred by the lack of corrections for the small drift in pH with buffer dilution.[17] We have repeated these experiments making the above corrections and under conditions where the percentage of the reactions proceeding via a buffer-catalyzed pathway has been increased. Further, we have now extended the study to include the uncatalyzed decomposition of both xanthates and monothiocarbonates as well as the general acid catalyzed decomposition of the latter.

These reactions constitute a series of unambiguous class n reactions, which complement earlier studies of the addition–elimination of nitrogen nucleophiles to carbon dioxide, carbonyl sulfide, and carbon disulfide.[8]

Experimental Section

A. Instrumentation and Materials. Infrared spectra were performed on a Perkin-Elmer Model 710A; absorbances are reported in cm^{-1}. NMR spectra were recorded using a Varian Model EM-360 60-MHz instrument; resonances are reported relative to 3-(trimethylsilyl)-1-propanesulfonic acid or to tetramethylsilane. Ultraviolet spectra were recorded on a Cary Model 118. Melting points are uncorrected. Measurements of pH were performed in a thermostated (25 °C) water bath with either a Beckman 1019 or Corning 130 meter and a Broadly-James 9008 combination electrode. Microanalyses are by Galbraith Laboratory, Knoxville, Tenn.

Chemicals for synthesis were reagent grade and were used without further purification. Buffer acids were generally used without further purification. D_2O and DCl were 99+ atom % D and were used within 1 month of purchase (Aldrich Chemical Co.). All solvents used were spectrophotometric grade. Water was distilled, deionized, then distilled through glass before use. Carbonyl sulfide for synthesis was generated by the action of aqueous sulfuric acid on ammonium thiocyanate solutions. Certified buffer solutions (Fisher, ±0.02 pH) were used to standardize the pH meter.

B. Buffer Solutions. Buffer solutions were prepared from the acidic or basic form of the buffer compound to which was added sufficient 1 N HCl or 1 N NaOH (Fisher standardized solution, 1.000 ± 0.002 N) to give the desired mole fraction of the acidic form. The ionic strength was maintained at 1.00 with KCl except as noted. Experimental pK_a determinations were made from pH measurements on the buffer solutions used in the kinetic experiments.

C. Synthesis and Characterization. 1. Xanthates. Xanthates of aliphatic alcohols were synthesized by the addition of carbon disulfide to the potassium alkoxide.[18] The alkoxides were prepared by heating the alcohol with an equimolar amount of partially powdered KOH, and the CS_2 was added either directly onto the crystalline salt with scratching of the surface or by addition to a well-stirred slurry of the alkoxide in diethyl ether. The crude solids were purified by dissolving in acetone, the red insoluble oils being removed by decantation.[19] The resulting pale yellow solution was vigorously stirred during addition of an equal volume of petroleum ether, and the pale yellow precipitate was collected by suction filtration, dried under vacuum, and stored in a desiccator in a freezer.

Potassium ethyl xanthate had a melting point of 190 °C dec; the NMR in D_2O consisted of a quartet at δ 4.56 and a triplet at δ 1.31 (J = 5 Hz); the ultraviolet spectrum in 1 N KCl gave λ_{max} 301 nm (ϵ 10^4), identical with previous determinations.[20] Potassium methoxyethyl xanthate gave mp 195 °C dec; NMR in D_2O showed a singlet at δ 3.43 and triplets at δ 3.60 and 4.52 (J = 4 Hz), and UV data were identical with those of the ethyl compound. Potassium trifluoroethyl xanthate was prepared in trifluoroethanol as a solvent. It could not be isolated because it rapidly decomposed in water at all pH's. Earlier we reported[17] isolation of this compound, but it is believed that reaction of the xanthate with MeOH had occurred and that the kinetics reported were actually for methyl xanthate.

2. Monothiocarbonates. Monothiocarbonates of aliphatic alcohols were prepared by the addition of carbonyl sulfide to the alkoxide.[21] The alkoxide was prepared by reaction of the alcohol with potassium in excess alcohol under nitrogen, and the carbonyl sulfide was bubbled above the vigorously stirred slurry with a pipet. The resulting white powders were collected by vacuum filtration, washed free of colored impurity with petroleum ether, and stored in a freezer as solutions in the parent alcohol. A synthesis of methyl monothiocarbonate using bottled carbonyl sulfide gas gave a material indistinguishable from that prepared in the above manner. Both preparations gave IR (KBr disk) with prominent absorbances at 1582 and 1100 cm^{-1}; UV (1 N KCl as solvent) λ_{max} 221 nm (ϵ 1 × 10^4). Murphy and Winter[21] report IR 1590 and 1045 cm^{-1} and UV λ_{max} 222 nm (log ϵ 4.004) for their preparation of the methyl compound. The NMR of this compound (D_2O) consisted of a singlet at δ 3.59; over the course of several days this peak decreased in size and a new singlet appeared at the resonance of methanol (δ 3.34). The synthesis of methoxyethyl monothiocarbonate yielded a white powder with strong absorbance in the infrared at 1600 and 1100 cm^{-1} (KBr disk), untraviolet absorbance at 221 nm (ϵ 10^4), and NMR (D_2O) consisting of a singlet at δ 3.39, a multiplet at δ 3.65, and a triplet (J = 4 Hz) at δ 4.15. This spectrum changed over the course of several days into that of the parent alcohol. The methoxyethyl monothiocarbonate was converted into dimethoxyethyl carbonate as follows. A solution of the monothiocarbonate in methoxyethanol was treated with excess methyl iodide. After 24 h the precipitated potassium iodide was filtered, and the filtrate was distilled at atmosphere pressure until all of the methoxyethanol had been removed. The residue was then distilled under reduced pressure yielding dimethoxyethyl carbonate, bp 130 °C (25 mm): NMR (CCl_4) δ 3.02 (3 H), 3.16 (2 H), 3.80 (2 H). Anal. Calcd for $C_7H_{14}O_5$: C, 47.18; H, 7.92. Found: C, 47.57; H, 7.97. The sulfur content was zero or a trace; IR (neat) 1750 cm^{-1}. Ethyl monothiocarbonate was prepared as the potassium salt in ethanol. The UV spectrum was comparable to that previously reported.[21] Synthesis of the monothiocarbonate from 2-butyn-1-ol was attempted; the product had a shoulder at 220 nm which disappeared when the compound was allowed to stand in aqueous base ($k_{obsd} \simeq 5 \times 10^{-4}$ s^{-1}). First-order kinetics were not observed; a nitrogen atmosphere helped but still did not produce clean kinetic runs.

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D. Kinetic Measurements. Pseudo-first-order rate constants for the breakdown of the xanthates and monothiocarbonates were determined using a Gilford Model 240 UV-vis spectrophotometer fitted with an automatic sample-handling system and a Honeywell or Fisher strip chart recorder. The sample compartment was thermostated at 25.0 ± 0.05 C by a constant-temperature unit consisting of a pump, refrigeration unit, and control unit designed by Jersey Technical Consultants in Piscataway, NJ. Reactions at temperatures other than 25 °C were performed using a Gilford thermoprogrammer, Model 2527. In a typical reaction, 2.5–3.0 mL of buffer solution was introduced into the four cuvettes of the sample compartment and thermally equilibrated for at least 10 min. Reactions were initiated by injection of 2–20 μL of a stock solution of xanthate in water or the monothiocarbonate in the parent alcohol. The chart recorder was then activated, and the cuvette holder then inverted five times and reinserted into the sample compartment, the complete procedure usually taking less than 20 s. Faster reactions ($t_{1/2}$ < 10 s) were monitored using a Tektronix Model 5103N storage oscilloscope and a rapid mixing system described earlier;[17] the mixing time was less than 0.1 s, and the temperature control was 25.0 ± 0.02 °C. All units were powered through a Sola constant-voltage transformer, and all were allowed at least 1 h to equilibrate before use. pH measurements on the reaction solutions were performed at the end of reaction on the solution in the cuvette.

The breakdown of xanthates was monitored at 301 nm; that of monothiocarbonates was observed at λ_{max} 221 nm except for carboxylic acid and carbonate buffer solutions, which were run at 230 nm to avoid background absorbance from the buffer species. [Pseudo-first-order rate constants were determined from hand-drawn plots of log $(A - A_\infty)$ against time on semilog graph paper and were calculated from the relation $k_{obsd} = 0.693/t_{1/2}$.] Except as otherwise noted, such plots were linear to four or more half-lives; this linearity was confirmed by performing regressions of typical data, which gave correlations of 0.998 or better. Individual rate constants were reproducible to within ±10%. All experiments involving buffer catalysis were performed using four or more buffer concentrations of 0.125–0.5 or 1.0 M B_T. Individual values of k were corrected for small changes in pH with changing $[B_T]$ by the equation

$$k_{corr} = k_{obsd} + ([H^+]_0 - [H^+])k_{H_3O^+} \quad (7)$$

where k_{corr} is the corrected rate constant, k_{obsd} is the observed pseudo-first-order rate constant, $[H^+]_0$ is calculated from the extrapolation of plots $[H^+]$ against $[B_T]$ to $[B_T] = 0$, $[H^+]$ is calculated from the measured pH of the reaction solutions, and $k_{H_3O^+}$ is the rate coefficient for catalysis of the decomposition by the proton. The value of $k_{H_3O^+}$ is determined by the slope of a plot of k_0 against $[H^+]$, where k_0 is the intercept at $[B_T] = 0$ of plots of k_{obsd} vs. $[B_T]$. The application of this correction requires two assumptions: first, that $[H^+]$ is linear with $[B_T]$. Such plots were found either to be linear or the variation in $[H^+]$ was too small to have any meaningful effect on the results. The second assumption involves the determination of $k_{H_3O^+}$. This value is obtained from k_0, which is itself calculated as the intercept of plots involving the uncorrected k_{obsd} and from independent measurements in HCl–KCl solutions. This procedure can be justified by the fact that $k_{H_3O^+}$ was determined from a plot utilizing all k_0's determined, and any small variation in $[H^+]$ with $[B_T]$ is compensated for by the much greater difference in $[H^+]$ between different experiments. The pH values used in calculating $k_{H_3O^+}$ were measured in the reaction cuvette at the same temperature as the reaction, the pH meter having been standardized against certified buffer solutions at the same temperature. The measured pH's of the solutions at a given temperature were than corrected for the change in temperature from 25 °C using published tables of pH and temperature for this 0.5 mol fraction $H_2PO_4^-$ buffer.[22]

Measurements of pD in D_2O solutions were calculated from pD = pH + 0.4, where pH is the apparent pH as measured by electrodes calibrated against standard H_2O buffers. Reactions run in DCl/D_2O solutions were performed at pD ~3.0, which is well above the pK_a of either xanthate or monothiocarbonate. The increase in pK_a from H_2O to D_2O should be no more than 0.26.[23] In addition, the pH was low enough so that $k_{H_3O^+}[H_3O^+] \gg k_{H_2O}$, thus allowing $k_0 \approx k_{H_3O^+}[H_3O^+]$ for the calculation of $k_{D_3O^+}$ or $k_{H_3O^+}$. The pH (pD) was measured at the end of each run, and the last portion of the absorbance vs. time curve was used for the calculation of k_{obsd}.

Results

A. Xanthates. Figure 1 is a plot of the pseudo-first-order rate constants k_{corr} for the decomposition of methoxyethyl xanthate in acetic acid/sodium acetate buffers (μ = 1.0 with KCl) vs. the total concentration of buffer species B_T. The slopes of the lines

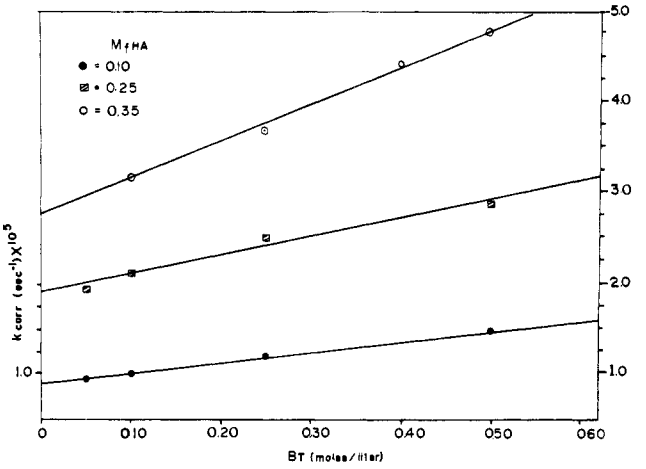

Figure 1. Data on the decomposition of methoxyethyl xanthate in acetic acid–acetate buffers.

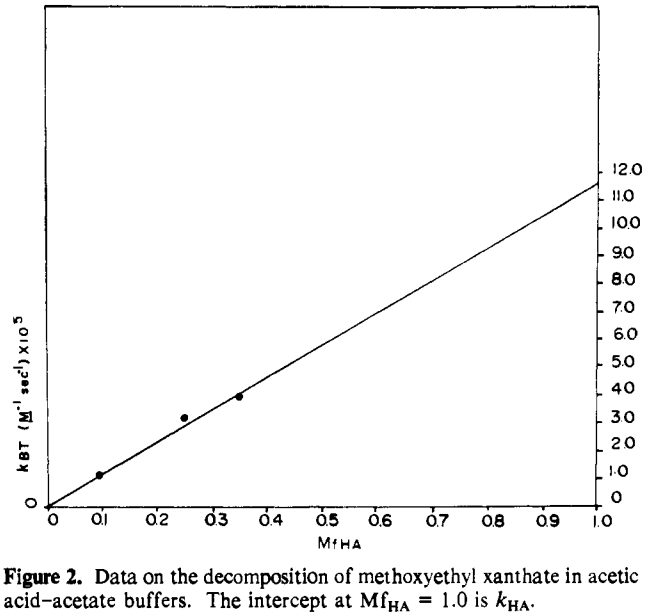

Figure 2. Data on the decomposition of methoxyethyl xanthate in acetic acid–acetate buffers. The intercept at $Mf_{HA} = 1.0$ is k_{HA}.

represent catalysis by the buffer k_{B_T}, and the intercept, k_0, includes the uncatalyzed breakdown and catalysis by the solvated proton ($k_{H_3O^+}[H_3O^+]$), giving the rate law:

$$k_{corr} = k_{HA}[HA] + k_{H_3O^+}[H_3O^+] + k_{H_2O} \quad (8)$$

In Figure 2 k_{B_T} for the various experiments is plotted vs. the mole fraction of the acidic form of the buffer: $Mf_{HA} \equiv [HA]/([HA] + [A])$. The intercept at $Mf_A = 1.0$ is k_A and that at $Mf_{HA} = 1.0$ is k_{HA}; in the systems examined there was no strong evidence for base catalysis. The high values for α make it impossible to obtain k_{B_T} values covering the entire range of mole fractions for the buffers. Consideration of the mechanisms would make conjugate base catalysis unlikely.

The pH–rate profiles of ethyl xanthate and methoxyethyl xanthate (Figures 3 and 4) show a break from a linear dependence of k_0 on $[H^+]$ to a rate that is independent of pH. This break occurs at pH 1.6 for ethyl xanthate and corresponds to the pK_a of the xanthic acid, in good agreement with previously reported values for this compound of 1.63[24] and 1.5.[25] The pK_a of methoxyethyl xanthate measured in this way (Figure 4) is 1.1. The rate constant for catalysis of the breakdown of ethyl xanthate by the proton is $k_{H_3O^+} = 2.85\ M^{-1}\ s^{-1}$, in fair agreement with previously reported values of 3.7 ± 0.08 for ethyl[24] and 3.8 for

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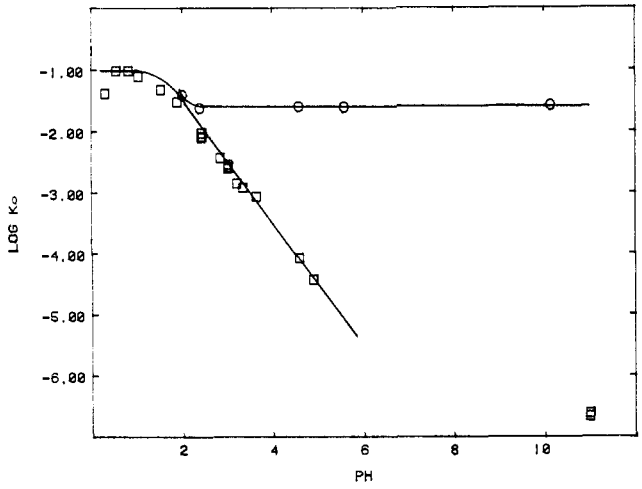


Figure 3. The pH–rate profile of ethyl xanthate (squares) and trifluoroethyl xanthate (circles) (see Table V, microfilm edition).

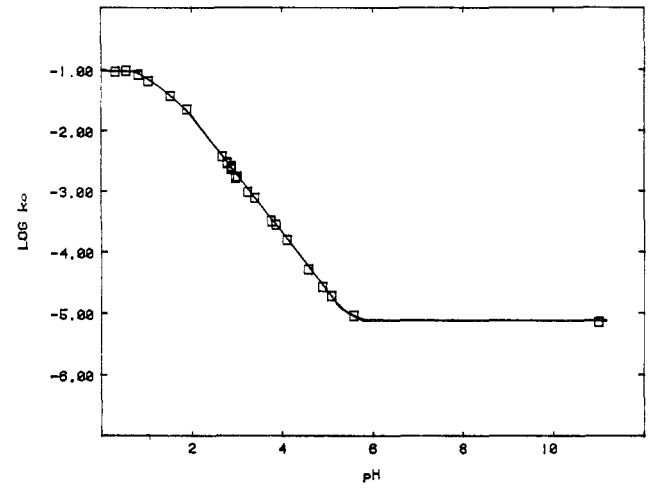


Figure 4. The pH–rate profile of methoxyethyl xanthate (see Table V, microfilm edition).

n-butyl xanthate. A calculation using the rate constants of Bunton, Ng, and Sepulveda[20] gives for this compound $k_{H_3O^+}$ = 2.4–3.6 M^{-1} s^{-1}. The value $k_{H_2O^+}$ for the methoxyethyl compound was measured as 1.72 M^{-1} s^{-1}. The values for k_{H_3O} (uncatalyzed reaction) were obtained by extrapolation from data at 80, 85, and 90 °C. The trifluoroethyl xanthate decomposition proceeded almost entirely via the uncatalyzed pathway k_{H_2O}.

Data from general acid catalysis are collected in Table I. It can be seen from Figure 1 that the increase in k_{OBSD} with increasing $[B_T]$ is small relative to the background reaction catalyzed by the proton. In such situations it is important to verify that the observed rate increases with B_T are actually due to general acid/base catalysis and not due to some other effect. Some possibilities are the following.[26]

(1) **A Change in pH with Dilution of the Buffer.** The individual rate constants are corrected for small changes in pH with $[B_T]$ as explained in the Experimental Section.[8]

(2) **Salt Effects.** The ionic strength was maintained constant at 1.0 with KCl; changing the supporting electrolyte to sodium perchlorate had no effect on k_{B_T} for the decomposition of ethyl xanthate in 0.5 $M f_{HA}$ formate buffer.

(3) **Solvent Effects.** A series of reactions were done to study the decomposition of ethyl xanthate in a formate buffer system in the presence of various added solvents; the data were previously reported.[17] It was noted that the rate of the reaction is increased by the addition of a cosolvent, and the effect is greatest with those solvents which can hydrogen bond. Ethyl alcohol at 0.43 M caused a 6% increase in the rate. This might explain at least a part of the observed buffer catalysis, except for the fact that carboxylic acids with very similar structure give significantly different k_{HA} terms which are derived from linear plots of k_{corr} vs. $[B_T]$; such linearity would be coincidental were the buffer catalysis to be solely the result of a solvent effect.[26] In addition, these (log k_{HA}) values give linear plots against the pK_a of the catalytic acids, thus supporting the idea that they represent true general acid catalysis. Acetic acid at 0.41 M at pH 2.4, where only the $k_{H_3O^+}$ term should be important, caused less than 1% increase in the rate, whereas at pH 4.89 in acetate buffer a 39% increase in rate is observed.

(4) **Change in the pK_a of a Reactant with $[B_T]$.** All reactions involving the buffer catalysis were performed at pH's well away from the measured pK_a of the xanthic acid.

The Brønsted plots are presented in Figure 5. Averaged values of log (k_{HA}/p) are used; the variation in individual determinations of k_{HA} is insignificant on this plot. These data lead to α values of 0.90 ± 0.2 and 0.78 ± 0.1 for ethyl and methoxyethyl xanthate, when the point representing catalysis by proton is not included in the regression. If all points are included, the values of α are 0.64 ± 0.09 and 0.57 ± 0.06, respectively.

The kinetic solvent isotope effect on the breakdown of the ethyl compound as catalyzed by L_3O^+ was determined from reactions

Table I. General Acid Catalysis of the Decomposition of Alkyl Xanthates

HA	pH	k_{HA}	Δ,[a] %
Potassium Ethyl Xanthate			
H_3O^+		2.85	
cyanoacetic	2.84	5.2×10^{-3}	25
	3.34	3.9×10^{-3}	41
chloroacetic	3.00	7.3×10^{-3}	49
	3.22	5.1×10^{-3}	54
formic	3.64	1.2×10^{-4}	34
	4.58	2.7×10^{-4}	24
acetic	4.89	7.5×10^{-5}	39
Potassium Methoxyethyl Xanthate			
H_3O^+		1.72	
cyanoacetic	2.68	1.8×10^{-3}	
	2.85	3.6×10^{-3}	31
	3.40	6.8×10^{-3}	41
chloroacetic	3.01	6.5×10^{-3}	67
	3.24	8.9×10^{-3}	100
	3.76	1.1×10^{-2}	154
formic	3.86	5.9×10^{-4}	39
	4.10	4.9×10^{-4}	90
	4.57	5.9×10^{-4}	46
acetic	4.87	1.2×10^{-4}	68
	5.09	1.3×10^{-4}	47
	5.58	1.2×10^{-4}	58

[a] Δ = increase in rate over the background rate at the highest buffer concentration.

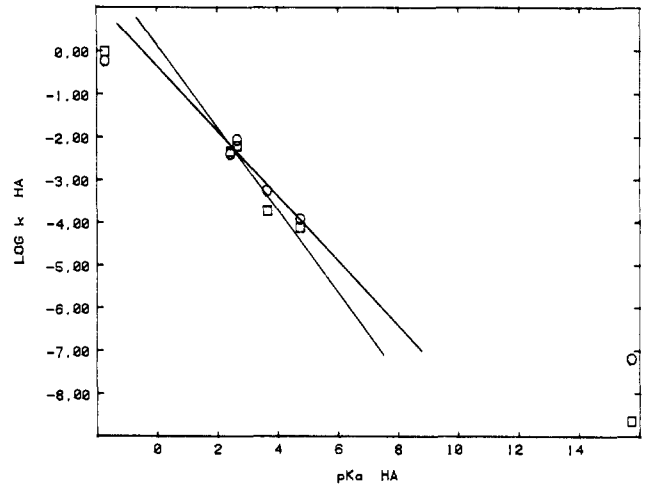


Figure 5. Brønsted plots for ethyl and methoxyethyl xanthates.

(26) Hand, E. S.; Jencks, W. P. *J. Am. Chem. Soc.* **1975**, *97*, 6221–6230.

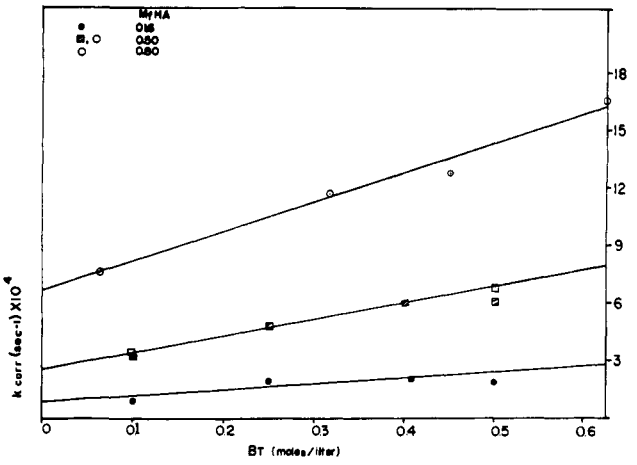


Figure 6. Data on the decomposition of methyl monothiocarbonate in phosphate buffers.

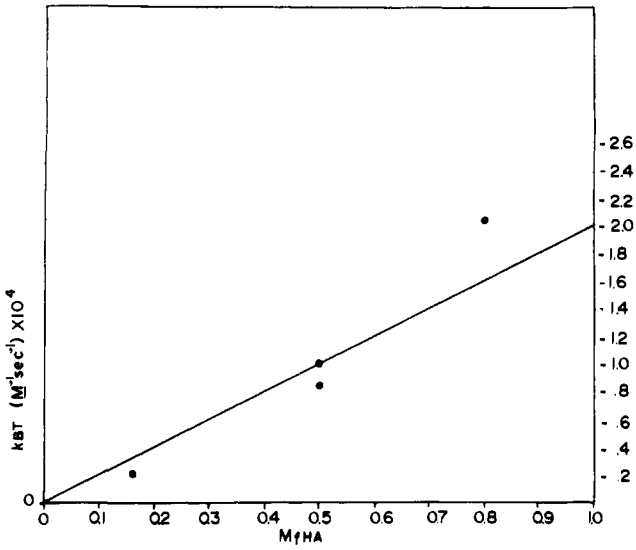


Figure 7. Data on the decomposition of methyl monothiocarbonate in phosphate buffers.

carried out in dilute (pH ≈ pD ≈ 3) solutions of HCl in H_2O and DCl in D_2O; the resulting values are $k_{D_3O^+}/k_{H_3O^+}$ = 2.53 and 2.14 for the ethyl and methoxyethyl compounds, respectively.

Activation parameters were obtained by varying the temperature of a reaction of ethyl xanthate in 0.50 Mf_{HA} formate buffer from 25 to 80 °C; the results are as follows:

	$k_{H_3O^+}$	k_{HCO_2H}
E_{act} (kcal/mol)	17.8	20.0
$\Delta S^{\ddagger}$ (eu)	0.27	−1.5

B. Monothiocarbonates. The plot of k_{corr} vs. $[B_T]$ for the decomposition of methyl monothiocarbonate in phosphate buffers is shown in Figure 6; it is apparent that the term $k_{B_T}[B_T]$ is more easily separated from the "background" of $k_{H_3O^+}[H_3O^+]$ than in the xanthate case. From the representative plot of k_{B_T} vs. Mf_{HA} for these reactions (Figure 7) it is probable that only the acidic form of the buffer species is catalytically active. The value at high Mf_{HA} is less certain because it represents a smaller portion of the observed reaction. The data do not continue to acidities high enough to demonstrate the pK_a of the monothiocarbonic acids. Plots of log k_0 vs. pH are shown in Figures 8 and 9. The apparent leveling off at high pH is due to the uncatalyzed decomposition and yields a value of k_{H_2O} = 2.71 × 10^{-5} s^{-1} for methyl monothiocarbonate and k_{H_2O} = 1.1 × 10^{-4} s^{-1} for methoxyethyl monothiocarbonate from runs in bicarbonate buffer. The decomposition was examined in sodium hydroxide solutions in order to confirm the uncatalyzed rate constants yielding values of k_{obsd} = 3.06 × 10^{-5} and 2.5 × 10^{-4} s^{-1} (calculated from data at 60 and

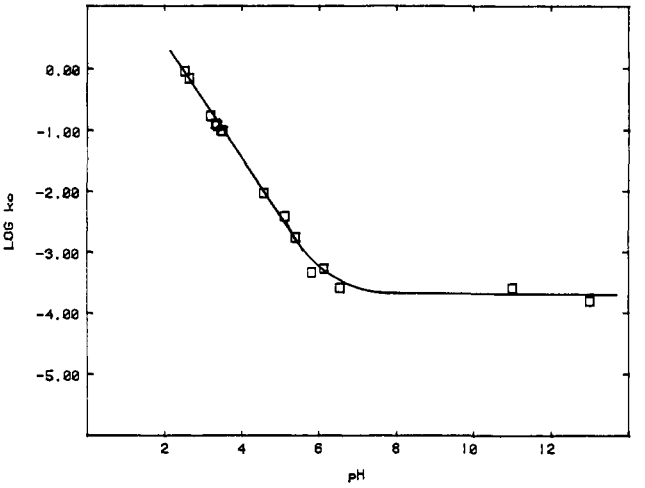


Figure 8. The pH–rate profile for methyl monothiocarbonate (see Table V, microfilm edition).

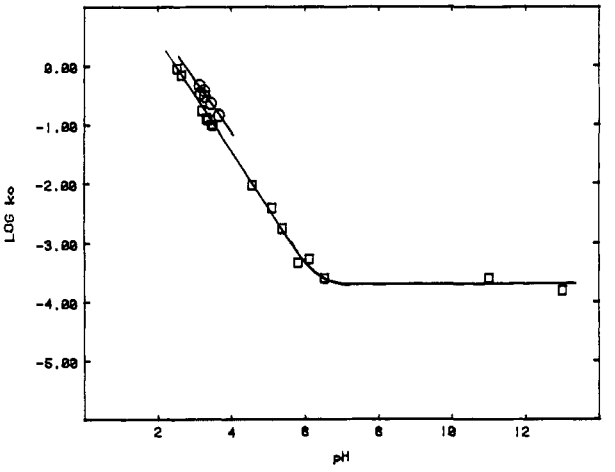


Figure 9. The pH–rate profile for ethyl and methoxyethyl monothiocarbonate (see Table V, microfilm edition).

Table II. General Acid Catalysis of the Decomposition of Alkyl Monothiocarbonates

HA	pH	k_{HA}	Δ, %
Potassium Methyl Monothiocarbonate			
H_3O^+		378	
formic	4.95	5.6 × 10^{-2}	57
acetic	5.09	5.8 × 10^{-2}	80
cacodylic	6.24	4.2 × 10^{-3}	190
dihydrogen phosphate	5.93	2.50 × 10^{-3}	298
	6.55	1.71 × 10^{-3}	250
	6.57	2.03 × 10^{-3}	260
	7.23	1.30 × 10^{-3}	160
Potassium Methoxyethyl Monothiocarbonate			
H_3O^+		280	
formic	4.58	1.12 × 10^{-1}	63
	5.12	9.60 × 10^{-2}	52
acetic	5.40	2.30 × 10^{-2}	50
	5.81	3.05 × 10^{-2}	161
	6.12	2.15 × 10^{-2}	100
cacodylic	6.46	8.00 × 10^{-3}	300
	6.88	7.60 × 10^{-3}	500
dihydrogen phosphate	6.53	1.90 × 10^{-3}	285
	5.78	1.53 × 10^{-3}	173
	6.30	1.79 × 10^{-3}	238
	6.75	1.14 × 10^{-3}	200
Potassium Ethyl Monothiocarbonate			
H_3O^+		590	

85 °C) for the methyl and methoxyethyl compounds, respectively. The value for methoxyethyl monothiocarbonate measured at pH 13 at 25 °C is 1.55 × 10^{-4} s^{-1}. The appropriate plots give $k_{H_3O^+}$

Table III. Brønsted Coefficients and Isotope Effects for Xanthates, Monothiocarbonates, Monocarbonates, and Bicarbonates

compound	α	$k_{D_3O^+}/k_{H_3O^+}$[d]	$\beta_{1g}(H_3O^+)$	$\beta_{1g}(H_2PO_4^-)$	β_{1g} uncatalyzed
$HOCO_2^-$	0.64[a]	1.79,[a] 1.61[b]			
$CH_3OCO_2^-$	0.66[b]	1.85[b]			
$CH_3CH_2OCO_2^-$	0.68[b]	1.53[b]	0.5[b]	−0.33[b]	−1.1[c]
$CH_3CH_2C(CH_3)HOCO_2^-$	0.72[b]	1.61[b]			
$CH_3CH_2OCOS^-$		1.95			
CH_3OCOS^-	0.58	1.94	0.27	0	−1.1
$CH_3OCH_2CH_2OCOS^-$	0.57	1.91			
$CH_3CH_2OCS_2^-$	0.9	2.53			
			0.22		−1.3
$CH_3OCH_2CH_2OCS_2^-$	0.8	2.12			

[a] Reference 40. [b] Reference 16. [c] Reference 15. [d] Individual rate runs are in Tables V and VI, available on microfiche.

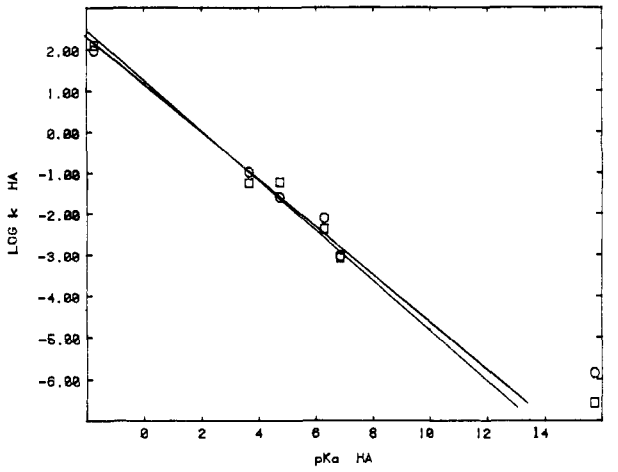


Figure 10. Brønsted plots for methyl and methoxyethyl monothiocarbonates.

= 590, 378, and 280 M^{-1} s^{-1} for the ethyl, methyl, and methoxyethyl compounds, respectively. The rate expression is then:

$$k_{obsd} = k_{H_3O^+}[H_3O^+] + k_{HA}[HA] + k_{H_2O} \quad (9)$$

The data for the general acid catalyzed reactions are collected in Table II, and the Brønsted coefficients are calculated as 0.58 ± 0.05 for methyl monothiocarbonate and 0.57 ± 0.01 for methoxyethyl monothiocarbonate, if the proton is not included in the regression. If it is, the α values are 0.57 ± 0.03 and 0.55 ± 0.01, respectively. These data are plotted in Figure 10. The solvent kinetic isotope effect on the decomposition of the methyl compound is $k_{D_3O^+}/k_{H_3O^+}$ = 1.95, 1.94, and 1.91 for ethyl, methyl, and methoxyethyl, respectively. The decomposition of methyl monothiocarbonate catalyzed by a phosphate buffer in D_2O solution yielded a value of k_{HA}/k_{DA} = 1.6 for this reaction. The measured activation parameters are (methyl monothiocarbonate reacting in a phosphate buffer, 5–85 °C):

	$k_{H_3O^+}$	k_{HA}
E_{act} (kcal/mol)	17.8	16.2
$\Delta S^{\ddagger}$ (eu)	2.2	−4.0

Discussion

A. Uncatalyzed Decomposition. Calculation for β_{1g} for the uncatalyzed decomposition of the xanthates gives a value of −1.3. For the monothiocarbonates the value is −1.1 for β_{1g}. These values can be compared with the value of −1.1 for β_{1g} for the alkyl monocarbonates.[10] The conclusions reached in the latter study can be applied here. Thus, there appears to be a late transition state in the decomposition direction. The role of water must be that of hydrogen bonding. Water is almost certainly not acting as a general acid catalyst in these systems; the calculated k_{HA} value for water (k_{H2O}/55.5 M) would lie more than 2.3 log units above the Brønsted line. Further, proton transfer from water would not change from thermodynamically unfavorable to thermodynamically favorable as the reaction moves from the starting material to the transition state; i.e., general acid catalysis by water would represent a violation of the libido rule.[27] This situation is in contrast to systems like the general acid catalysis of *p*-nitrophenyl carbamate where the leaving group is an amine anion and water therefore is sufficiently acidic to serve as a general acid catalyst.[8]

Values of β_{1g} in this range for similar systems have been observed by others: alkyl and aryl carbamate anions lose alkoxide to generate phenyl isocyanate with β_{1g} = −1.15;[28] mixed alkyl, aryl malonic ester anions lose aryl oxide to generate ketene derivatives with β_{1g} = −1.29;[29] and substituted aryl sulfate anions lose aryl oxide to generater sulfur trioxide with β_{1g} = −1.2.[30]

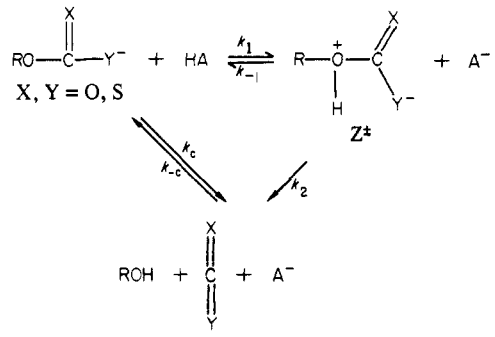
B. General Acid Catalysis. There appears to be general acid catalysis in both the xanthate and monothiocarbonate systems. Bunton and co-workers[20] failed to observe such catalysis by acetate buffer in the ethyl xanthate case; this may have been due to the fact that their most concentrated buffer was 0.4 M and that acetic acid is such a weak catalyst, giving a relatively small increase in k_{obsd} over the $k_{H_3O^+}$ background. It is clear that ethyl xanthate lies on the borderline for the observation of general acid catalysis. The fact that a 39% increase in rate is observed in the acetate buffer region when acetic acid is added but not in the region dominated by hydronium ion catalysis makes it almost certain that general acid catalysis occurs in the ethyl xanthate case as well as in the other systems studied.

The question arises as to whether the point for catalysis by the proton should be included in the regression to generate α. We have chosen to discuss those values which do not incorporate $k_{H_3O^+}$, because deviations from a Brønsted line from H_3O^+ are common, especially when a series of neutral and/or anionic catalysts are used. The errors which occur in α overlap as the leaving alcohol is changed; this is not an uncommon observation[5,6,9,11] for compounds where the pK_a's of the leaving group lie close together. In most of these other systems the entire series of compounds spans a larger change in pK_a's so that the decrease in α with decreasing pK_a of the leaving group can be clearly demonstrated for the series. The importance of the uncatalyzed breakdown in compounds where the pK_a of the leaving alcohol is low (i.e., trifluoroethyl xanthate) makes such a long series impossible to obtain in this case. Heavy reliance is thus placed on interpreting the solvent isotope effects reported in Table III.

The solvent kinetic isotope effects are consistent with proton transfer occurring in the transition state. Ewing, Lockshon, and Jencks[8] have explained data obtained for the decomposition of aryl carbamates in terms of a late transition state with hydrogen bonding between the catalytic acid and the protonated amine leaving group. The observed normal isotope effect for catalysis by bicarbonate (k_{HA}/k_{DA} = 1.4) is consistent with such hydrogen bonding. The small inverse isotope effect for catalysis by the proton ($k_{D_3O^+}/k_{H_3O^+}$ = 1.4) "suggests that the large inverse isotope effects that are expected for equilibrium proton transfer are partly compensated for by a normal isotope effect from formation of the

(27) Jencks, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 4731–4732.
(28) Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 808–812; **1973**, 1244–1247.
(29) Pratt, R. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1970**, *92*, 5956–5964. Holmquist, B.; Bruice, T. C. *Ibid.* **1969**, *91*, 2993–3002, 3003–3009.
(30) Fendler, E. J.; Fendler, J. H. *J. Org. Chem.* **1968**, *33*, 3852–3859.

Scheme I



hydrogen-bond transition state.".[8]

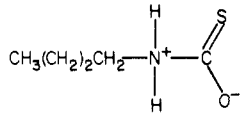
Consideration of the isotope effects calculated and compared with experimental values for complete and partial protonation on oxygen in a review article by Showen,[31] strongly support the role of hydronium ion as a general acid catalyst in the systems reported in this work. Thus simple acetal hydrolyses exhibit isotope effects of $k_{D_3O^+}/k_{H_3O^+} \simeq 3$ and do not exhibit buffer catalysis. In the series of hydrolyses of benzaldehyde methyl-substituted phenyl acetals studied by Capon and Nimmo,[5] α varies from 0.49 to 0.96 as the substituent on the phenoxide leaving group is changed from *m*-NO_2 to *p*-MeO; the corresponding change in $k_{D_3P^+}/k_{H_3O^+}$ is 0.92 to 1.61. However, benzaldehyde dimethyl acetal shows no general acid catalysis and has $k_{D_3O^+}/k_{H_3O^+} = 3.0$.[5] The general acid catalyzed decomposition of Meisenheimer complexes studied by Bernasconi and Gandler have values ranging from 0.65 to 0.35 as the leaving group changes from ethyl alcohol to propargyl alcohol and the corresponding $k_{D_3O^+}/k_{H_3O^+}$ values range from 2.04 for ethyl alcohol to 1.22 for propargyl alcohol.[6] However, 2-ethoxytetrahydropyran shows $k_{D_3O^+}/k_{H_3O^+}$ of 2.82 and 2-(*p*-methoxyphenoxy)tetrahydropyran has $k_{D_3O^+}/k_{H_3O^+}$ of 2.48 with no general acid catalysis although changing the substituent to more electron-withdrawing substituents in a series of four more substituted phenoxy compounds lowered the value of the inverse effect, and buffer catalysis was demonstrated.[5] The isotope effects reported in this study for ethyl xanthates are in the borderline region.

Stepwise protonation of the alcohol oxygen followed by decomposition of the resultant zwitterionic intermediate ($Z^{\pm}$, Scheme I) can be excluded on other grounds. In the case of the stepwise process one can consider first the possibility that the proton transfer step is rate determining. The equilibrium constant

$$K_1 = k_1/k_{-1} \qquad (10)$$

is the reciprocal of the K_a for $Z^{\pm}$ when HA represents the proton.

For the conjugate acid of *N*-(*n*-butyl)monothiocarbamate, the



pK_a has been estimated to lie 11.9 log units below that for *N*-(*n*-butyl)ammonium ion.[8] This estimate was based on the rate of exchange of protons on the nitrogen measured by NMR together with a 10^9 s^{-1} rate for the deprotonation reaction.[32,33] If one can assume a similar effect of substitution of the $-C(=O)S^-$ group on oxygen, one can estimate the pK_a of the $Z^{\pm}$ intermediate formed from methyl monothiocarbonate as −13.9 (where the pK_a of protonated methanol is −2[34]). Since the value of k_{-1} is in the range of 10^{10} because k_{-1} represents a thermodynamically favorable proton transfer,[32,33] then $k_1/k_{-1} = 1/K_a$ and k_1 is thus 5×10^{-4} s^{-1}. The value for $k_{H_3O^+}$ (which would be equal to k_1 if this mechanism were followed) is almost six orders of magnitude larger, thus ruling out rate-determining formation of $Z^{\pm}$. The effect of $-C(=S)S^-$ on the acidity of the alcohol oxygen should be as great or greater (the NMR chemical shifts for the methylene groups next to this oxygen support this view). Thus it is clear that this argument also excludes k_1 as the rate-determining step for the xanthates. The second step (k_2) cannot be determining since its calculation using $10^{-13.9}$ for the k_1/k_{-1} equilibrium gives a value for k_1 of 10^{16}–10^{17} which is larger than a molecular vibration.[35]

This reasoning is dependent on the assumptions involved in calculating the pK_a for $Z^{\pm}$. Bunton and De Wolfe[36] estimated the pK_a's of protonated ortho esters via the $\sigma^*\rho^*$ treatment, assuming that the value ρ^* for their system equalled that for the protonation of aliphatic amines. There are several difficulties in extending this to the present case, the greatest being the poor reliability of σ^* values determined for charged groups;[37] the analogy to the carbamate systems seems to be the best choice. The errors in pK_a for $Z^{\pm}$ are probably not large enough to affect the conclusions from this line of reasoning.

We therefore believe that the mechanisms for these reactions must be concerted transfer of a proton to the alcohol oxygen as the carbon–oxygen bond is broken (the k_c/k_{-c} pathway in Scheme I). This mechanism is the same as that proposed by Pocker, Davison, and Deits for the general acid catalyzed decomposition of alkyl monocarbonates.[16]

General acid catalysis for the breakdown of alkyl monothiocarbonates requires that the reverse reaction, the attack of water or alcohols on crabonyl sulfide, be general base catalyzed. Sharma has observed such catalysis for the addition of water to carbonyl sulfide.[38] Calculation using the second-order rate constants for three general bases, i.e., the monoanion of formaldehyde hydrate, arsenite, and monohydrogen phosphate, yields a β value of approximately 0.5 for this reaction.[39] This number is approximate because of uncertainty in values for monohydrogen phosphate and the formaldehyde hydrate monoanion.[40] The rate constant for the former compound was reported as an upper limit, and the rate constant for the latter compound may have errors resulting from the Cannizzaro reaction although Sharma's experiments were designed to minimize these.[38] With these approximations in mind, it is apparent that this β value is in the range of those expected for this reaction based on the predicted α value for the general acid catalyzed breakdown of $HOC(=O)S^-$ of $\simeq 0.55$ (β for the k_{-c} step = $1 - \alpha$ for the k_c step, and the pK_a of water is very close to the pK_a of methanol).

C. Equilibria for Hydroxide Reactions. Sharma's work also yielded a value of 14 M^{-1} s^{-1} for the reaction of hydroxide ion with carbonyl sulfide.[38] At pH 11 or 13 this suggests that rapid capture of carbonyl sulfide by hydroxide follows the slow uncatalyzed breakdown of the alkyl monothiocarbonates; i.e., the rate being observed in our work is truly the rate of reaction 4.

From the value of −1.1 for β_{1g} for reaction 4, one can predict a value of 4.85×10^{-5} for the uncatalyzed breakdown of $HOCOS^-$ into carbonyl sulfide and hydroxide ion (k_{-a} of eq 11).

$$HO^- + COS \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} HOCOS^- \qquad (11)$$

Combining this estimate with the value of $k_a = 14$ M^{-a} s^{-1} from Sharma's work yields a value of the equilibrium constant expected for eq 11 of 2.9×10^5 M^{-1}. Similarly, one can calculate the rate

(31) Schowen, R. L. "Progress in Physical Organic Chemistry"; Streitwieser, A., Taft, R. W., Eds.; Wiley-Interscience: New York, 1972; Vol. 9, pp 275–332.
(32) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1–19.
(33) See also footnote 30 in ref 8.
(34) Bender, M. L. "Mechanisms of Homogeneous Catalysis from Protons to Proteins"; Wiley: New York, 1971; p 40.
(35) An early example of the method applied to the reaction of benzaldehyde with semicarbazide is given by Jencks (ref 3, pp 190–192).
(36) Bunton, C. A.; De Wolfe, R. H. *J. Org. Chem.* **1965**, *30*, 1371–1375.
(37) Chapman, N. B., Shorter, J., Eds. "Advances in Linear Free Energy Relationships"; Plenum Press: New York, 1972; pp 71–117.
(38) Sharma, M. M. *Trans. Faraday Soc.* **1965**, *61*, 681–688.
(39) The pK_a of formaldehyde hydrate was the statistically corrected value of 13.57. See ref 7 and Bell, R. P.; Onwood, D. P. *Trans. Faraday Soc.* **1962**, *58*, 1557–1561.
(40) Pocker, Y., and Bjorkquist, D. W. (*J. Am. Chem. Soc.* **1977**, *99*, 6537–6543) also observed dibasic phosphate catalysis.

Table IV. Relative Rate Data on Systems of the Type $ROCXY^- \rightarrow ROH + X{=}C{=}Y$

compound	$RNHCO_2^-$ [a]		$RNHCOS^-$ [a]	$RNHCS_2^-$ [a]
$k_{H_3O^+}$ rel [b]	$\sim 10^5$		$10^{2.5}$	1
compound	HCO_3^- [c]	$H_3COCO_2^-$ [d]	$CH_3CH_2OCOS^-$	$H_3CCH_2OCS_2^-$
$k_{H_3O^+}$ rel [b]	$10^{4.2}$	$10^{4.2}$	$10^{2.4}$	1
compound			$H_3COCH_2CH_2OCSO^-$	$H_3COCH_2CH_2OCS_2^-$
$k_{H_3O^+}$ rel [b]			$10^{2.3}$	1
compound			H_3COCSO^-	$H_3CCH_2OCS_2^-$
$k_{H_3CCO_2H}$ rel [b]			$10^{1.8}$	1
compound		$CH_3CH_2OCO_2^-$	CH_3OCOS^-	$CH_3CH_2OCS_2^-$
k_{uncat} rel [b]		$10^{3.6}$	$10^{2.08}$	1

[a] Reference 8. [b] k_{rel} is defined as k for the compound presented divided by that for the S,S analogue. [c] Reference 40. [d] Reference 16.

constant for the uncatalyzed breakdown of $HOCS_2^-$ (k_{-a} of eq 12) as 6.67×10^{-1} s^{-1}. Combination of this value with the

$$HO^- + CS_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} HOCS_2^- \qquad (12)$$

measured value of $k_a = 1.1 \times 10^{-2}$ M^{-1} s^{-1} [41] yields an estimated equilibrium constant of 1.6×10^4 M^{-1} for eq 12.

These numbers may be compared with the carbon dioxide, hydroxide, bicarbonate equilibria (eq 13) for which direct measurements of k_a and k_{-a} are available.[15,42] Caution should be exercised in making comparisons with the K_{eq} estimates for eq 11 and 12 with eq 13 because the expected[15] deviations of OH^- from Brønsted relationships for k_{-a} were not considered. If the point for hydroxide as a leaving group in the reverse of eq 11 and 12 deviates by 1 log unit from the Brønsted plot (as it does in the reverse of reaction 13[15]), then the equilibrium constants for reactions 11 and 12 would be larger than the above estimates by one order of magnitude each.

$$HO^- + CO_2 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} HOCO_2^- \qquad (13)$$

In going from xanthate to monothiocarbonate, there is (a) an increase in the rate of reaction and (b) a probable decrease in α. The ratio of rate constant for decomposition of xanthates and monothiocarbonates is compared with that of other series in Table IV. Because of the different selectivity (α) of the two classes of compounds, k_{rel} decreases as the acidity of the catalyst decreases. A hypothetical acid catalyst of $pK_a = -3.4$ would be expected to show equal k_{HA}'s with ethyl xanthate and methyl monothiocarbonate. This decrease in α and faster decomposition upon substitution of oxygen for sulfur as well as decrease in β_{1g} for the acid-catalyzed reaction upon going from monocarbonate to monothiocarbonate to xanthate (see Table III) was also found in the carbamate system[8] and can be explained by considering the greater stability of both reactants and products relative to the transition state in the xanthates. In going from monothiocarbonate to xanthate, the transition state (for a given degree of proton transfer) becomes less stable relative to starting material or products; hence a greater amount of proton transfer (higher α) is needed to avoid high-energy intermediates. In other words, the transition state "adjusts istelf" to the less stable transition state by using more catalysis.[1,43]

In both the xanthates and monothiocarbonate studied, increasing the electron-withdrawing properties of the alcohol (decreasing its basicity) leads to a decrease in the value of α. This decrease can be quantified by the cross correlation $p_{xy'} \equiv \partial\alpha/\partial pK_{1g}$,[13b] which calculation yields estimated values of $p_{xy'} = 0.10$ for the xanthates and $p_{xy'} \approx 0.01$ for the monothiocarbonates. These numbers must be considered to be estimates, as there are only two leaving groups for each system and the changes in α lie within experimental error. According to the derivation, $p_{xy'} \equiv \partial\alpha/\partial pK_a = \beta_{1g}/\partial pK_{HA}$; the calculated change in for β_{1g} with changing pK_a of the catalyst for the monothiocarbonate leads to $p_{xy'} = 0.01$. The other parameters can be estimated as $p_x \equiv \partial\alpha/\partial pK_{HA} \approx 0$ for both systems (the Brønsted plots are linear), and $p_{x'} \equiv \partial\beta_{1g}/-\partial pK_{1g}$ cannot be determined.

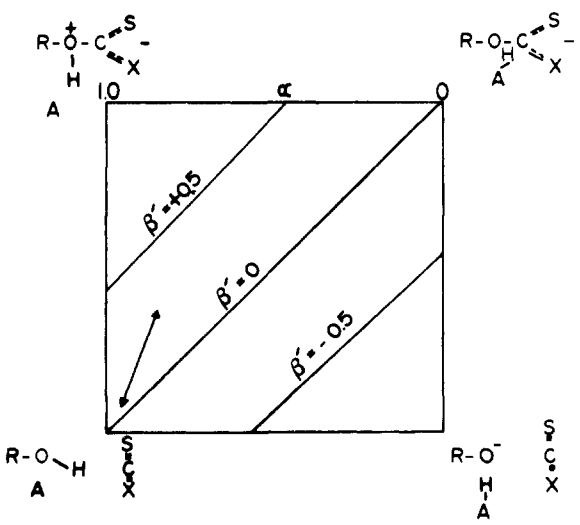


Figure 11. Three-dimensional energy diagram for the decomposition of xanthates (X = S) and monothiocarbonates (X = O). Formal charges on the acid are omitted (after ref 8, with modification). The double-headed arrow indicates the transition state for the xanthate reaction.

The small value of β_{1g} for acid-catalyzed decomposition of the xanthates is in accord with the observations of Ewing, Lockshon, and Jencks,[8] who observed a substantial decrease in β_{1g} upon substitution of sulfur for oxygen in the carbamate system, calculating $\beta_{1g} = 0.71$, 0.36, and 0 for the carbamate, monothiocarbamate, and dithiocarbamate, respectively. There are some data available on the proton- and phosphate-catalyzed decomposition of the alkyl monocarbonates. The change in α appears to be that expected for an unambiguous class n reaction; that is, as one goes from methane to ethanol to *sec*-butyl alcohol the α value (for H_3O^+ and $H_2PO_4^-$) changes from 0.66 to 0.68 to 0.72. The order of reactivity also changes from ethyl > methyl for H_3O^+ catalysis to methyl > ethyl for $H_2PO_4^-$ catalysis.

Figure 11 is the three-dimensional diagram for the systems under study. As before, the horizontal axis represents proton transfer and may be defined by the experimental value of α. The vertical axis represents the degree of bond formation or cleavage between the alcohol oxygen and the electrophile. The charge on the alcohol oxygen is the resultant of these two processes, and is measured by β_{1g}. If as seems likely (see Table III) $\beta_{1g} \approx 0.2$ for the xanthates, then the transition state for the decomposition of these species catalyzed by H_3O^+ may be placed slightly above diagonal $\beta' = 0$ towards the lower left corner of the diagram ($\alpha > 0.5$). The decrease in α with decreasing basicity of the leaving group ($p_{xy'} > 0$) and the constant value of α with respect to catalyst pK_a ($p_x \approx 0$) is consistent with the reaction coordinate rotated from the vertical, as indicated by the double-headed arrow. A coordinate lying on the diagonal line defined by $\beta' = 0$ would require $p_x > 0$, $p_y < 0$, and $p_{xy'} = 0$. A similar transition state (slightly above the line defined by $\beta' = 0$ and more toward the center of the diagram) is possible for the monothiocarbonates.

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Introduction of an electron-withdrawing substituent in the alcohol destabilizes the protonated zwitterionic species in the upper left corner of the diagram. This causes the transition state to "slide" downhill and to the right, that is to a transition state involving less proton transfer, and an expected lower value of α is seen.

Acknowledgment. We are grateful to the Rutgers Research Council and the Charles and Johanna Busch Memorial Fund, administered by Rutgers, for partial support of this work. The UV spectrophotometer was purchased from a grant awarded by the Research Corporation.

Registry No. $CH_3CH_2OCOS^-$·K, 35832-93-0; CH_3OCOS^-·K, 34520-64-4; $CH_3OCH_2CH_2OCOS^-$·K, 85319-49-9; $CH_3CH_2OCS_2^-$·K, 140-89-6; $CH_3OCH_2CH_2OCS_2^-$, 65944-33-4; cyanoacetic acid, 372-09-8; chloroacetic acid, 79-11-8; formic acid, 64-18-6; acetic acid, 64-19-7; cacodylic acid, 75-60-5; dihydrogen phosphate, 14066-20-7.

Supplementary Material Available: Tables V (pH and k_0 values for alkyl xanthates and monothiocarbamates) and VI (rate constants for D_3O^+ catalysis for xanthates and monothiocarbamates) (4 pages). Ordering information is given on any current masthead page.

Electroorganic Reactions on Organic Electrodes. 1. Asymmetric Reduction of Prochiral Activated Olefins on a Poly-L-valine-Coated Graphite†

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Received July 20, 1982

Abstract: The electrochemical asymmetric reduction of citraconic acid (**1**) and 4-methylcoumarin (**3**) was carried out at a poly-L-valine-coated graphite cathode. Maximum optical yields of methylsuccinic acid (**2**) and 3,4-dihydro-4-methylcoumarin (**4**) were 25 and 43%, respectively, in a phosphate-buffered solution (pH 6).

Some methods for electrochemical asymmetric reduction of prochiral ketones, imines, and olefins had been reported: As summarized by Tilborg and Smit,[1] the use of chiral solvents, chiral supporting electrolytes, chiral electrode surface-active materials, and chiral chemically modified electrodes could result in asymmetric induction. Although the use of chiral solvents[2] and supporting electrolytes[3] gave 6 and 20% optical yields, respectively, in each best case in the reduction of acetophenone, these methods inherently need large amounts of optically acitive materials as asymmetry-inducing reagents. In contrast to these, the other two methods should be characterized by the efficient use of extremely small amounts of the inducing reagents A pioneer work in the field of electrochemical asymmetric synthesis was made by Gourley et al.[4] using optically active alkaloids. They obtained a 17% optical yield in the reduction of 4-methylcoumarin (**3**) in the presence of sparteine (5 mM). Afterward, Miller and his co-workers[5,6] reported surprisingly high optical yields, close to 50%, in the reduction of 2-acetylpyridine in the presence of strychinine (0.5 mM). They also prepared chemically modified electrodes with optically active amino acids and attempted asymmetric induction in both reduction and oxidation.[7-9] The highest optical yield (14.5%)[7,10] seemed to be obtained in the reduction of 4-acetylpyridine on a graphite cathode modified with (*S*)-(−)-phenylalanine methyl ester.

Asymmetric reduction using chiral chemically modified electrodes should be an excellent method, since very small amounts of inducing reagents can act efficiently. However, there may be a disadvantage in this method due to low coverage of chiral species on electrode surface. This point may be able to improved by using polymer-coated electrodes[11-13] including a polypeptide.[14] Miller et al.[11b] reported an interesting electrolysis using a polymer-coated electrode. The electrocatalyzed reduction of *meso*-1,2-dibromo-1,2-diphenylethane at a poly-*p*-nitrostyrene-coated platinum cathode gave *trans*-stilbene in high yields, and the turnover number for catalyst sites was estimated to be 10^4.

In this work, as a part of a larger program for highly selective electrosyntheses of organic compounds using electrodes modified with organic materials, we first examined the asymmetric reduction of activated olefins on an optically active polymer-coated electrode. A number of works dealing with the asymmetric reduction of ketones[1-3,5-8,13,15] and imines[15k,16] had been reported, while only

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