column at 200 °C. The ratio of the remaining **6** and **21** was observed to be 2:1.

Registry No.—**1**, 69455-09-0; **3**, 69455-10-3; **19**, 55561-42-7; **20**, 14982-15-1; **21**, 834-25-3; phenyltropone a, 69455-11-4; 3-bromo-4-hydroxybenzaldehyde, 2973-78-6; benzyl chloride, 100-44-7; 3-bromo-4-benzyloxybenzaldehyde, 69455-12-5; 2-chlorotropone, 3839-48-3; ethanethiol, 75-08-1.

References and Notes

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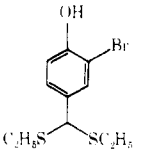
(16) The structure of the oily phenol obtained from **9** was fully characterized as follows: NMR ($CDCl_3$) δ 1.22 (t, J = 7.4 Hz, 6 H), 2.35 (q, J = 7.4 Hz, 4 H), 4.60 (s, 1 H), 5.40 (br s, 1 H), 6.70 (d, J = 8.4 Hz, 1 H), 7.07 (dd, J = 8.4, 2.4 Hz, 1 H), 7.34 (d, J = 2.4 Hz, 1 H); IR ($CHCl_3$) ν 2880, 1596, 1486 cm^{-1}. Anal. Calcd for $C_{11}H_{15}OS_2Br$: C, 43.00; H, 4.92. Found: C, 42.77; H, 4.89.



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General Acid-Catalyzed Decomposition of Alkyl Xanthates

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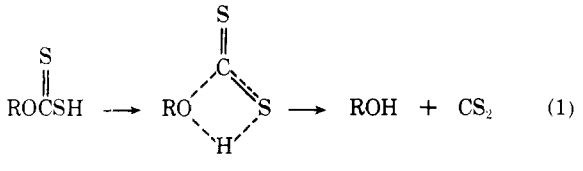
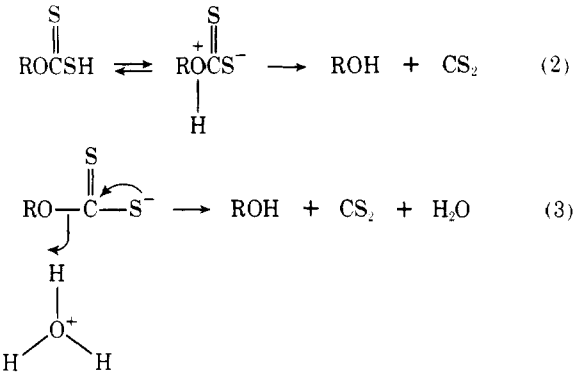
Xanthates of 2,2,2-trifluoroethanol, methoxyethanol, and ethanol have been prepared, and their decomposition in aqueous carboxylic acid buffers has been studied. pH–rate profiles reveal that the pK_a values for the ionization of the xanthic acids are 1.60 for ethyl, 1.30 for trifluoroethyl, and 1.45 for methoxyethyl. Brønsted α values for the general acid catalysis of the breakdown of xanthates are 0.96 for ethyl, 0.88 for methoxyethyl, and 0.79 for trifluoroethyl. These results are interpreted in terms of a concerted process for proton transfer and carbon–oxygen bond breaking. Positive deviations from linearity were observed at high values of mole fraction of the catalyzing acid in plots of k_{BT} vs. mole fraction of HA. These results have been discussed in terms of a general acid-catalyzed breakdown of xanthic acids and solvent-assisted breakdown of xanthate anion.

Monoalkyl xanthates have found important applications in the cellulose industry and in mineral flotation processes.[1] The breakdown of ethyl xanthate catalyzed by hydronium ion has been extensively studied.[2] At pH greater than 2 the first-order rate constant was proportional to the concentration of ethylxanthic acid. The acid-catalyzed hydrolysis of *n*-butyl xanthate and *tert*-butyl xanthate in solutions of hydrochloric acid and perchloric acid has also been studied, and similar dependence on the concentration of xanthic acid has been noted.[3] Further, the effect of cationic micelles, anionic micelles, and nonionic micelles on the hydrolysis of ethyl, *n*-butyl, and *n*-octyl xanthates has been investigated.[3] It was found that the decomposition of the xanthate to the alcohol and carbon disulfide was inhibited by cationic micelles of cetyltrimethylammonium bromide and catalyzed by anionic micelles of Triton X-100A at pH > 2. These results were explained in terms of micellar effects upon the protonation of the xanthate ion.

Previous workers have suggested a variety of mechanisms to account for xanthate decompositions in acid solution. These are summarized in eq 1–3.



(1)



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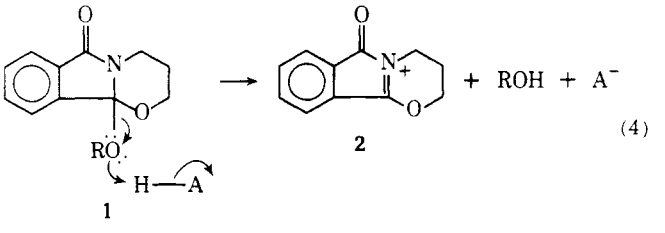
(3)

We wished to know whether carboxylic acid catalysts would lead to the breakdown of xanthates. Thus, we initiated the present structure–reactivity study for the purpose of determining whether general acid catalysis exists, and if so, whether the reactions are stepwise or concerted.[4–6]

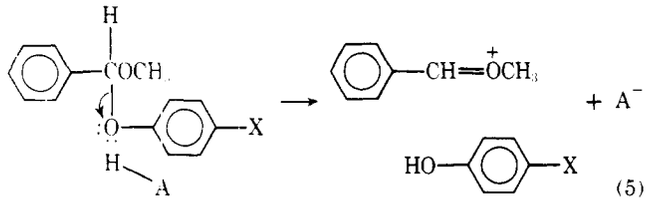


(4)

0022-3263/79/1944-1664$01.00/0

The breakdown of the tetrahedral addition compounds, **1**, from alcohols and a phthalimidium cation[2] has been studied by Gravitz and Jencks.[7] These workers determined from the dependence of Brønsted α values on alcohol acidity that the reaction involves concerted general acid catalysis.

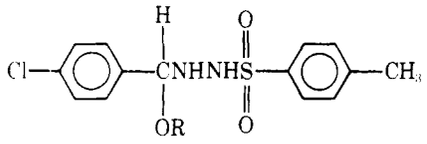
The general acid-catalyzed hydrolysis of benzaldehyde arylmethyl acetals **3** has also been found to proceed by general



(5)

3

acid catalysis of the leaving phenoxide concerted with carbon–oxygen bond breaking.[8a] A large number of other acetals, ketals, and orthoesters exhibit general acid-catalyzed breakdowns.[8b] Structure–reactivity studies have indicated that these reactions proceed by proton transfer concerted with carbon–oxygen bond breaking. Furthermore, the breakdown of carbinolamine ethers **4** in the presence of general acids was found to proceed by a concerted mechanism.[9]



4

In each of the above cases the starting material is a tetrahedral substance or intermediate and the product is trigonal. We wish to determine whether or not our trigonal potassium xanthate system would proceed to the linear carbon disulfide product via similar mechanisms.

Experimental Section

Ethyl xanthate was purchased from Eastman Organic Chemicals and was recrystallized from acetone–petroleum ether solutions before use. All other xanthates were prepared by adding carbon disulfide to a slurry of powdered potassium hydroxide in the alcohol. The thick cake which formed was dissolved in acetone, and the red insoluble oils were separated by decantation. The pale yellow acetone solution which resulted was precipitated with petroleum ether, and the pale yellow xanthate was collected and dried under vacuum.[10] Recrystallization was carried out using acetone–petroleum ether.

Propargyl alcohol and 2-chloroethanol preparations ignited shortly after the addition of carbon disulfide. Therefore, attempts to prepare these xanthates were abandoned. Trifluoroethyl xanthate had mp 193 °C dec and NMR δ 4.96 (quartet). Methoxyethyl xanthate had mp 195 °C and NMR δ 3.43 (singlet), 3.60 (triplet), and 4.52 (triplet). The UV spectra for these compounds were as follows: trifluoroethyl, λ_{max} 305 nm (ϵ 23 000); methoxyethyl, λ_{max} 308 nm (ϵ 16 700). Microanalyses were not obtained on these compounds because of the noticeable vapor of carbon disulfide which emanated from the solid compounds. However, the NMR analyses showed that there was less than 2% of impurities present.

Kinetics were run at a constant ionic strength of 1.0 maintained with potassium chloride.

Fast reactions were followed using a spring-loaded rapid-injection syringe with a cylindrical cuvette held in a thermostatted brass cuvette holder inserted into the cell compartment of a Gilford Model 240 spectrophotometer.[11,12] The mixing time was less than 0.1 s. The wavelength near the maximum absorption (300 nm) for the xanthates was monitored as a function of time using a Honeywell recorder or a storage oscilloscope. Pseudo-first-order rate constants were determined from semilogarithmic plots of absorbance change against time.

Buffers of the several general acids were prepared in 0.08–1.0 M total buffer concentration. The value of k_{B_T} was obtained as the slope of a plot of the observed rate constants against total buffer concentrations. Rate constants were determined from four or five runs at each of several different buffer ratios. Rate constants for the hydronium ion catalyzed reaction were determined from intercepts of the k_{obsd}–V total buffer concentration plots as well as at several values of the H^+ from 0.01 to 1 M.

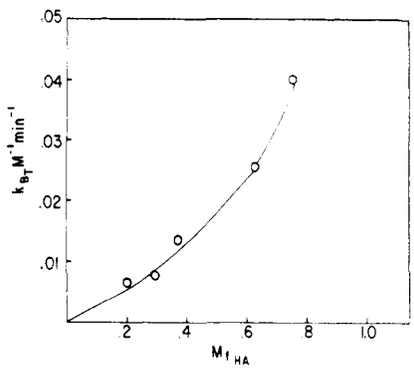


Figure 1. Effect of formic acid buffers on the decomposition of methoxyethyl xanthate in water at 25 °C.

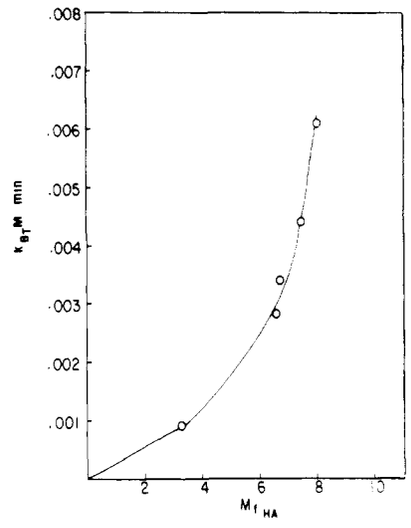


Figure 2. Effect of acetic acid buffers on the decomposition of ethyl xanthate in water at 25 °C.

Plots of k_{B_T} vs. M_f of the acidic form of the buffer intercepted at 0 for $M_f = 0$. Therefore, there was no catalysis observed for the basic forms of the buffers.

Values of k_{B_T} for the cyanoacetic acid buffers were corrected by dividing through by the fraction of xanthate in the ionized form. These corrected values of k_{B_T} were treated as described below.

Results

The values of k_{obsd} were plotted against B_T, where $B_T = [HA] + [A^-]$, for each of several different buffer ratios. These plots were found to be linear, and the intercepts of these plots at zero buffer concentration were plotted against the $[H_3O^+]$ values for the different buffers. No pH independent value for a water-catalyzed reaction was observed. Therefore, eq 6 was followed.

$$k_{obsd} = k_H[H_3O^+] + k_{B_T}[B_T] \quad (6)$$

Since for higher values of $[HA]/[A^-]$ the value of k_{B_T} increased, values of k_{B_T} were plotted against the mole fraction of the acidic form of the buffers (see Figures 1–4). Initially it was thought that these plots were linear, but when buffers of mole fractions of HA greater than 0.5 were studied considerable positive deviations from linearity were noted.

It was found that k_{B_T} behaved according to eq 7. Hence, plots of $k_{B_T}/M_{f_{HA}}$, where $M_{f_{HA}}$ is the mole fraction of the acidic form of the buffers, vs. $[H_3O^+]$ were straight lines with intercepts of k_1 and slopes of k_2' (see Figures 5–7). The values of

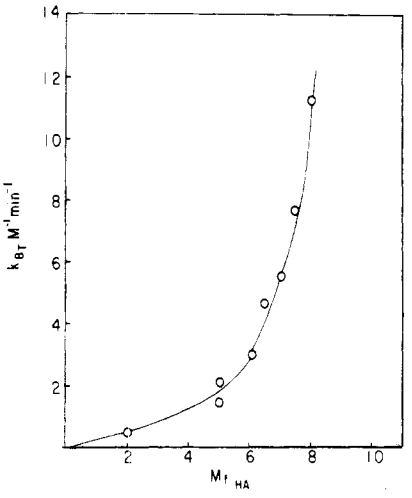


Figure 3. Effect of cyanoacetic acid buffers on the decomposition of trifluoroethyl xanthate in water at 25 °C.

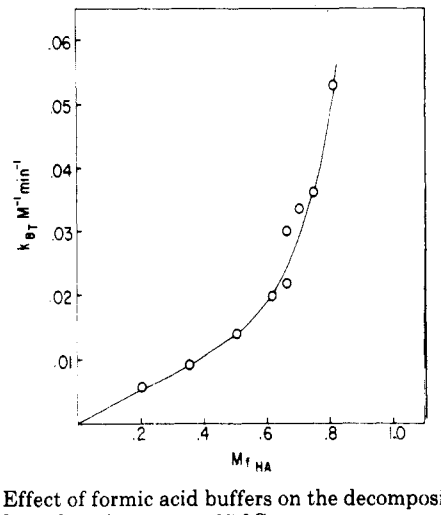


Figure 4. Effect of formic acid buffers on the decomposition of trifluoroethyl xanthate in water at 25 °C.

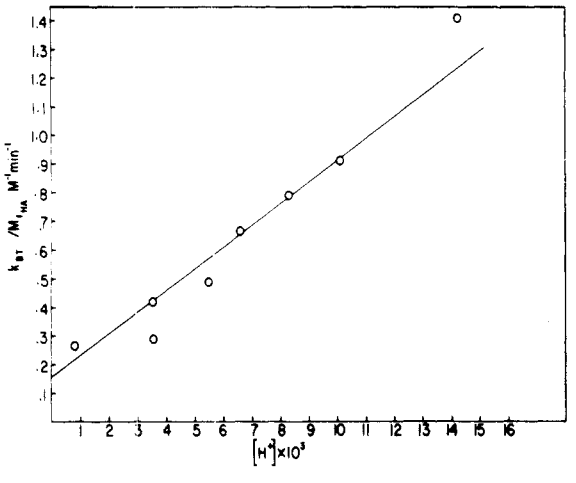


Figure 5. Plot of $k_{B_T}/M_{f_{HA}}$ vs. [H$^+$] for trifluoroethyl xanthate in cyanoacetic acid buffers at 25 °C.

k_1 and k_2' are listed in Table I for each of the three xanthates studied.

$$k_{B_T}[B_T] = k_1[HA] + k_2'[HA][H_3O^+] \quad (7)$$

pH–rate profiles for the three xanthates studied were obtained as shown in Figures 8–10. The breaks in the curve occur

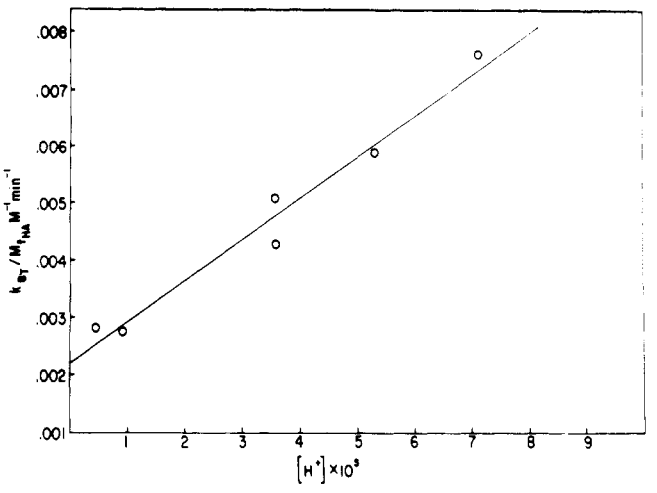


Figure 6. Plot of $k_{B_T}/M_{f_{HA}}$ vs. [H$^+$] for ethyl xanthate in acetic acid buffers at 25 °C.

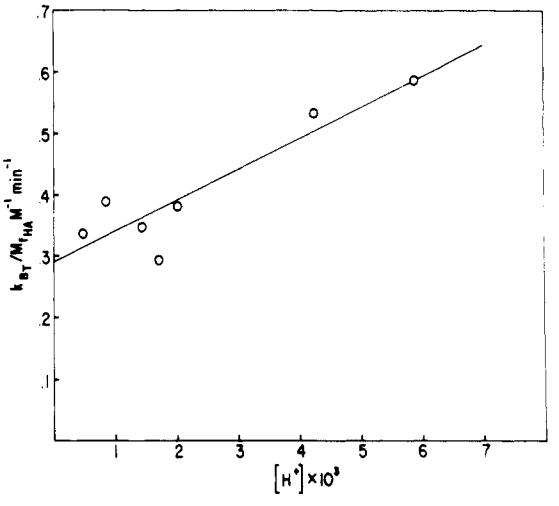


Figure 7. Plot of $k_{B_T}/M_{f_{HA}}$ vs. [H$^+$] for ethyl xanthate in chloroacetic acid buffers at 25 °C.

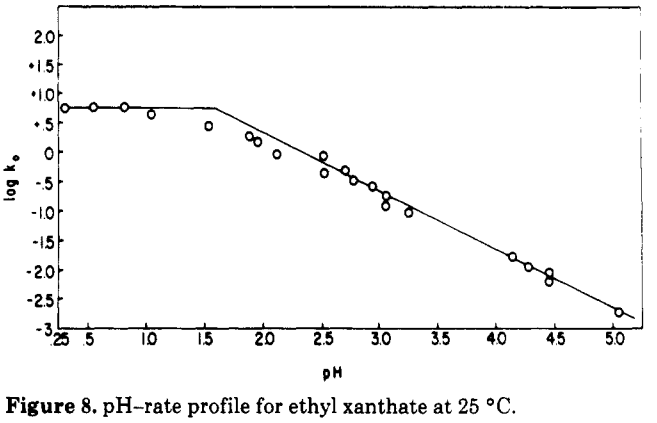


Figure 8. pH–rate profile for ethyl xanthate at 25 °C.

between 1.30 and 1.60 and demonstrate that the electronic effect of the substituents on the xanthic acid ionization is minimal. The pK_a for (methoxyethyl)xanthic acid was found to be 1.45, and the pK_a for (trifluoroethyl)xanthic acid was found to be 1.30. The pK_a for ethylxanthic acid was found to be 1.60 at 25 °C, which is in good agreement with the previously determined value of 1.70 at 23.5 °C.

Solvent effects for four polar organic solvents were studied. The rates of breakdown of xanthates were accelerated most by dimethylformamide and to a lesser extent by acetonitrile,

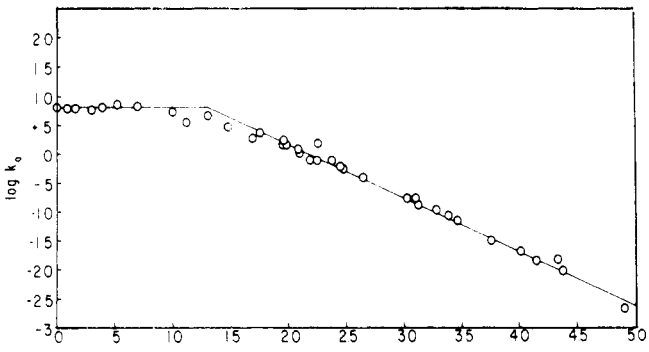


Figure 9. pH–rate profile for trifluoroethyl xanthate at 25 °C.

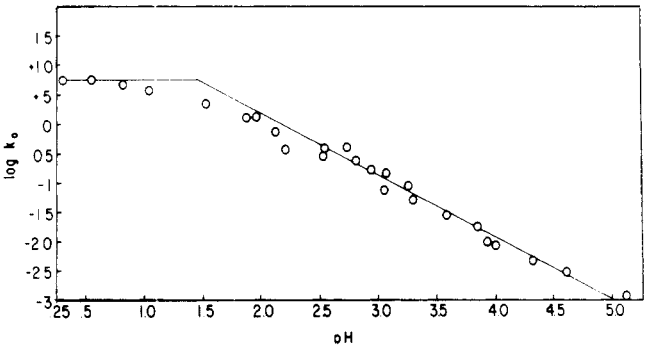


Figure 10. pH–rate profile for methoxyethyl xanthate at 25 °C.

Scheme I

$$X^- + HA \xrightarrow{k_1} ROH + CS_2$$

$$\uparrow\downarrow H^+$$

$$XH + HA \xrightarrow{k_2} ROH + HA + CS_2$$

ethanol, and acetamide. These results are summarized in Table II.

Discussion

The dependence of the k_{B_T} values on the mole fraction of the acidic form of the buffer on the hydrogen ion concentrations can be interpreted in terms of a mechanism which is shown in Scheme I, where X is xanthate and XH is xanthic acid. The k_{B_T} term should follow eq 8.

$$k_{B_T}[B_T][X^-] = k_1[HA][X^-] + k_2[HA][HX] \quad (8)$$

Since

$$K_{XH} = [H^+][X^-]/[HX] \quad (9)$$

then

$$k_{B_T}[B_T][X^-] = k_1[HA][X^-] + k_2[HA][X^-][H^+]/K_{XH} \quad (10)$$

and

$$k_{B_T}[B_T][X^-]/[HA] = k_1[X^-] + k_2/K_{XH}[X^-][H^+] \quad (11)$$

Thus, plots of $k_{B_T}/M_{f_{HA}}$ vs. $[H^+]$ are linear with k_1 as the intercept and $k_2' = k_2/K_{XH}$ as the slope. Calculated values for k_2 are given in Table III.

We have no explanation for the fact that Bunton, Ng, and Sepulveda failed to observe acetate buffer catalysis of the breakdown of ethyl and *n*-butyl xanthates.[3] It is possible since the most concentrated buffer they used was 0.4 M that such catalysis went undetected.

Table I. Rate Constants for the General Acid-Catalyzed Decomposition of Xanthates

catalyst	k_1, M^{-1} min^{-1}	log k_1	k'_2, M^{-1} min^{-1}
potassium trifluoroethyl xanthate[a]			
H_3O^+	130 ± 8	2.11	
$CNCH_2COOH$	0.08 ± 0.09	−1.10	86 ± 8
$ClCH_2COOH$	0.24 ± 0.06	−0.620	70 ± 20
HCOOH	0.021 ± 0.005	−1.678	57 ± 7
CH_3COOH	0.0031 ± 0.0004	−2.509	68 ± 13
potassium methoxyethyl xanthate[b]			
H_3O^+	145 ± 4	2.16	
$CNCH_2COOH$	0.3 ± 0.2	−0.52	42 ± 8
$ClCH_2COOH$	0.28 ± 0.07	−0.55	40 ± 14
HCOOH	0.024 ± 0.005	−1.62	36 ± 9
CH_3COOH	0.0047 ± 0.0005	−2.33	17 ± 10
potassium ethyl xanthate[c]			
H_3O^+	194 ± 3	2.288	
$CNCH_2COOH$	0.4 ± 0.3	−0.40	67 ± 15
$ClCH_2COOH$	0.29 ± 0.05	−0.54	50 ± 10
HCOOH	0.013 ± 0.007	−1.89	80 ± 11
CH_3COOH	0.0022 ± 0.0003	−2.66	72 ± 6

[a] Registry no., 60564-16-1. [b] Registry no., 65944-33-4. [c] Registry no., 140-89-6.

Table II. Solvent Effects on the Buffer-Catalyzed Decomposition of Potassium Ethyl Xanthate in Water at Ionic Strength 1 (KCl) at 25.0 °C

added solvent	[solvent], M	1:1 buffer of HCOOH/HCOO⁻, M	k, min^{-1}	k_{B_T}, M^{-1} min^{-1}
none	0	1.00	0.0506	0.0125
	0	0.70	0.0476	
	0	0.50	0.0449	
	0	0.25	0.0412	
ethanol	1.71	1.00	0.0700	0.0206
	1.28	0.70	0.0527	
	0.85	0.50	0.0488	
	0.43	0.25	0.0436	
DMF	1.28	1.00	0.0766	0.0307
	0.96	0.70	0.0635	
	0.64	0.50	0.0557	
	0.32	0.25	0.0495	
acetamide	1.71	1.00	0.0525	0.0152
	1.28	0.70	0.0475	
	0.85	0.50	0.0444	
	0.43	0.25	0.0414	
acetonitrile	0.96	1.00	0.0545	0.0127
	0.96	0.70	0.0508	
	0.96	0.50	0.0485	
	0.96	0.25	0.0450	
acetonitrile	1.89	1.00	0.0564	0.0142
	1.42	0.70	0.0502	
	0.95	0.50	0.0475	
	0.47	0.25	0.0447	

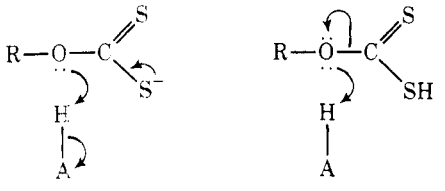
The difficulty with the mechanism outlined in Scheme I is apparent when one considers the details of the implied transition states (see Scheme II). The data indicate that general acid catalysis of the breakdown of xanthic acid predominates at higher acidic buffer ratios. However, inspection of the transition states depicted in Scheme II shows that the driving force for the decomposition should be diminished by protonation of the sulfur. In fact, there does not seem to be any adequate explanation for the observed catalysis of the breakdown of xanthic acid.

Table III. Rate Constants for the General Acid-Catalyzed Decomposition of Xanthic Acids

catalyst	k_2, M^{-1} min^{-1}
(trifluoroethyl)xanthic acid[a]	
$CNCH_2COOH$	4.32
$ClCH_2COOH$	3.51
HCOOH	2.86
CH_3COOH	3.41
(methoxyethyl)xanthic acid[b]	
$CNCH_2COOH$	1.49
$ClCH_2COOH$	1.42
HCOOH	1.27
CH_3COOH	0.60
ethylxanthic acid[c]	
$CNCH_2COOH$	1.68
$ClCH_2COOH$	1.25
HCOOH	2.01
CH_3COOH	1.80

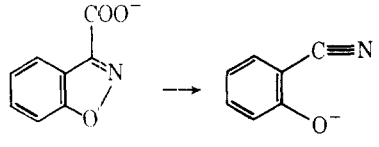
[a] Registry no., 24658-33-1. [b] Registry no., 69461-73-0. [c] Registry no., 151-01-9.

Scheme II



A further difficulty with the general acid-catalyzed breakdown mechanism of xanthic acid to explain the data is provided by the fact that ethyl- and *n*-butylxanthic acids form an unreactive protonated species at extremely low pH.[3a] If a fully protonated xanthic acid does not decompose, it is hard to see why general acid catalysis of the breakdown of xanthic acids would be viable.

An alternative explanation for the positive deviations at high $M_{f_{HA}}$ values observed in Figures 1–4 is that the observed results may be due to a solvent effect. Remarkably large solvent effects have been observed in the decarboxylation of 3-carboxybenzisoxazoles.[13] Furthermore, 1 M dioxane enhanced the rate of decarboxylation of *N*-aryl carbamates by 16%.[14] One difficulty in making the analogy with the present system is that the most effective solvent catalysis of 3-carboxybenzisoxazoles was observed in polar aprotic solvents. When an ortho hydroxyl was introduced in the substrate, no solvent catalysis was observed. Thus, the lack of an opportunity for hydrogen bonding was implicated in the catalytic effect. Since our acidic catalysts should clearly be able to undergo hydrogen bonding with the substrate, the benzisoxazole results would predict that such catalysis should not be particularly important.



(12)

In fact, the data in Table II indicate a larger solvent effect for dimethylformamide. Solvent effects for acetamide and ethanol, which are capable of hydrogen bonding interactions with the xanthate, are smaller. The magnitude of these smaller effects does not seem sufficient to explain the large positive deviations in the mole fraction plots.

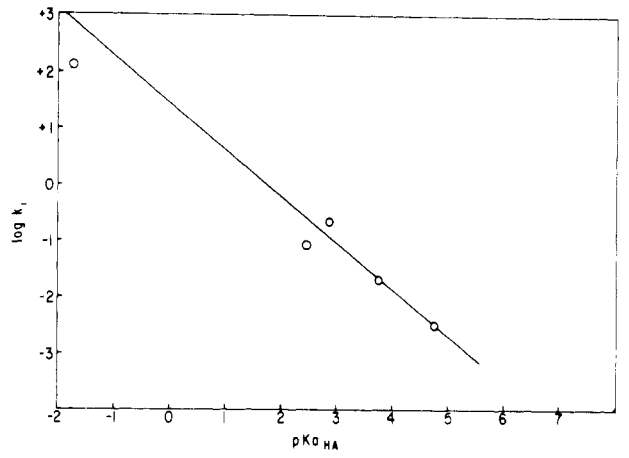
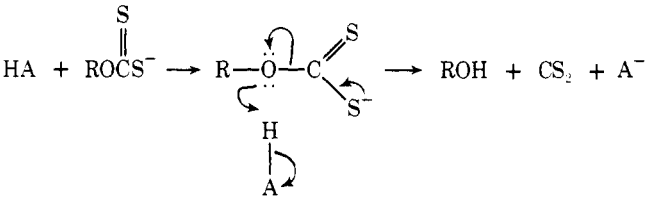


Figure 11. Brønsted plot for the general acid-catalyzed breakdown of trifluoroethylxanthate at 25 °C.

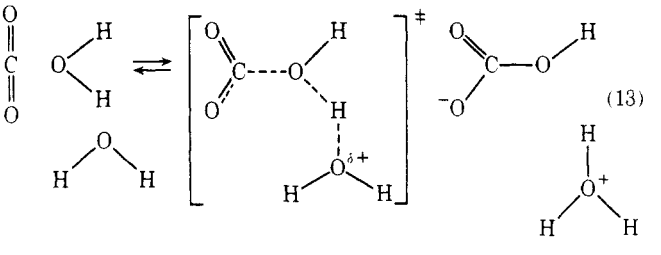
Scheme III



A referee has suggested that the deviations in the k_{B_T} vs. M_f of HA plots may be caused by a specific salt effect. Several runs were made at higher concentrations of KCl for formic acid and acetic acid buffers, and the values obtained for k_{B_T} fit right on the plots of k_{B_T} vs. $M_{f_{HA}}$ at an ionic strength of 1.0 maintained with potassium chloride. In addition, one series of runs was made with the ionic strength maintained with sodium perchlorate. The values obtained for k_{B_T} were identical within the limits of experimental error (0.0103 ± 0.001 M^{-1} min^{-1} for the potassium chloride plot vs. 0.0101 ± 0.0007 M^{-1} min^{-1} for the sodium perchlorate plot). Therefore, we do not believe that the deviations in k_{B_T} at high $M_{f_{HA}}$ values are caused by salt effects.

The values in Table I for k_1 were plotted on a Brønsted plot. Without inclusion of the points for H_3O^+ catalysis the Brønsted α values were 0.96 for ethyl, 0.88 for methoxyethyl, and 0.79 for trifluorethyl (see Figures 11–13). Such values suggest that proton transfer has occurred to a large extent in the transition state for xanthate decomposition. The lack of an effect due to the leaving group ability of RO^- suggests that the charge on the alcohol oxygen has not changed much from the starting material to the transition state. This means that proton transfer is compensating for the buildup of negative charge associated with carbon–oxygen bond breaking. This is illustrated in Scheme III.

One of the mechanisms postulated by Pocker and Bjorquist for the dehydration of bicarbonate by hydronium ion to carbon dioxide (eq 13) involves the transfer of a proton from the



(13)

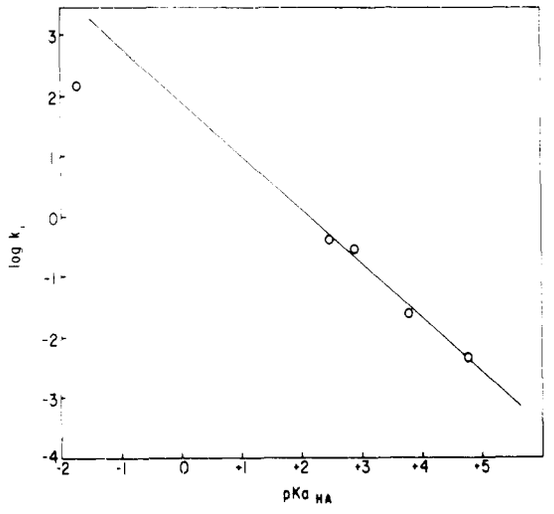


Figure 12. Brønsted plot for the general acid-catalyzed breakdown of methoxyethylxanthate at 25 °C.

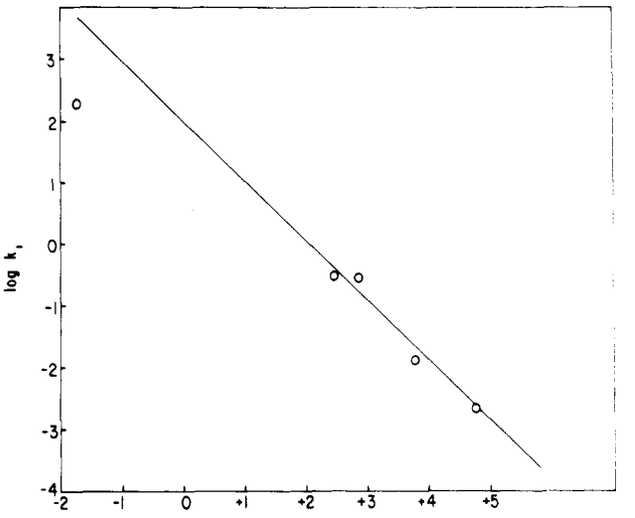


Figure 13. Brønsted plot for the general acid-catalyzed breakdown of ethyl xanthate at 25 °C.

catalyst to the bicarbonate concerted with the breaking of the carbon–oxygen bond.[15]

The mechanism for this trigonal to linear system in reverse is identical with the mechanism we are supporting for the breakdown of xanthates. The carbon dioxide mechanism was supported by isotope studies, although these results did not unequivocally rule out alternative proposals. It is of interest to learn that dihydrogen phosphate also catalyzes this dehydration.[15,16] The Brønsted α value of 0.7 was calculated for general acid catalysis of bicarbonate decarboxylation.[16] The reasonableness of this value was supported by a calculated α of 0.6 for the phosphate and hydronium ion catalyzed decarboxylation of *N*-carboxyimidazolidone.[17] The catalysis of bicarbonate dehydration by hypobromous acid appears to involve a concerted bromination–dehydration reaction. It has been suggested that a concerted mechanism for the dehydration of bicarbonate catalyzed by carbonic anhydrase is possible.[16,18] Thus, it appears that general acid catalysis coupled with C–O bond breaking may be widespread in these trigonal systems.

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Registry No.—carbon disulfide, 75-15-0; trifluoroethanol, 75-89-8; methoxyethanol, 109-86-4.

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