mechanism for the acetylene. This change in mechanism may arise from the somewhat greater reactivity of olefins than acetylenes *via* the AdE2 mechanism, possibly combined with a lower sensitivity to steric effects for Ad3 addition to acetylenes relative to olefins. For both olefins and acetylenes the balance between AdE2 and Ad3 addition appears to be delicate, so that changes in reactant structure or reaction conditions can lead to a shift from one mechanism to the other as the predominant pathway for reaction.

Acknowledgments. This work was supported by National Science Foundation Grant GP 24562. We thank Mr. Raymond Carrillo for technical assistance with some of the experiments, and Professor Paul E. Peterson for helpful comments.

Registry No.—3, 10124-73-9; **5,** 42131-99-7; **7,** 42132-01-4; 2,2-dichlorohexane, 42131-89-5; 1-hexyne-*1-d*, 7299-48-1; 2-hexyne, 764-35-2; (*E*)-3-chloro-2-hexene, 4050-45-7; 1-phenylpropyne, 673-32-5.

References and Notes

(1) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **88**, 5555 (1966).
(2) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **90**, 2124 (1968).
(3) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **91**, 3865 (1969).
(4) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970).
(5) R. C. Fahey and M. W. Monahan, *J. Amer. Chem. Soc.*, **92**, 2816 (1970).
(6) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **93**, 2445 (1971).
(7) R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965).
(8) C. DuFraisse and J. E. Viel, *Bull. Soc. Chim. Fr.*, **37**, 877 (1925).
(9) E. B. Whipple, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, **82**, 3010 (1960).
(10) P. E. Peterson, R. J. Bopp, and M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970); R. J. Bopp, Ph.D. Thesis, St. Louis University, St. Louis, Mo., 1967.
(11) S. W. Tobey, *J. Org. Chem.*, **34**, 1281 (1969).
(12) K. Griesbaum and Z. Rehman, *J. Amer. Chem. Soc.*, **92**, 1417 (1970).
(13) D. S. Noyce, M. A. Matesich, M. D. Schiavelli, and P. E. Peterson, *J. Amer. Chem. Soc.*, **87**, 2295 (1965); D. S. Noyce and M. D. Schiavelli, *J. Org. Chem.*, **33**, 845 (1968).
(14) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Amer. Chem. Soc.*, **87**, 5163 (1965).

Acid-Catalyzed Hydrolysis of Monoalkyl Xanthates[1]

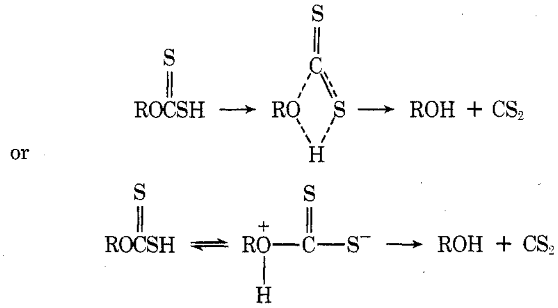
Clifford A. Bunton,* Patricia Ng, and Luis Sepulveda

Department of Chemistry, University of California, Santa Barbara, California 93106, and Faculty of Chemical Sciences, University of Chile, Santiago, Chile

Received October 5, 1973

The decomposition of *n*-butyl xanthate in water, pH <5, and in metanolic methanesulfonic acid gives *n*-butyl alcohol and CS_2 by spontaneous elimination from xanthic acid. Similar observations were made on ethyl xanthate in water. At pH <0 the rate decreases because of the formation of unreactive protonated xanthic acid, and acid dissociation constants for both protonation equilibria are calculated. The decomposition of *tert*-butyl xanthate occurs with alkyl-oxygen fission and isobutylene is a major product. The reaction is much faster than that of *n*-butyl xanthate, and the rate is proportional to the concentration of *tert*-butylxanthic acid up to 1 *M* HCl or $HClO_4$, but at higher hydrogen ion concentrations protonation of *tert*-butylxanthic acid increases the rate. The activation parameters for reaction of *n*-butyl- and *tert*-butylxanthic acid are, respectively, $\Delta H^* = 16.3$ and 18.1 kcal mol^{-1}, and $\Delta S^* = -8.4$ and 2 eu.

Monoalkyl xanthates and their derivatives are important in the cellulose industry and in mineral flotation.[2] The acid-catalyzed hydrolyses of ethyl xanthate have been examined by several workers,[4,5] and at pH >2 the first-order rate constant was proportional to the concentration of ethylxanthic acid. It has been suggested that an ion-pair complex of a proton and an alkyl xanthate ion is the reactive species,[6] but such an ion pair seems to be an improbable reactive intermediate and alternative formulations of a unimolecular mechanism are



$$\mathrm{ROC(=S)SH} \rightleftharpoons \mathrm{RO^{+}(H)\!-\!C(=S)\!-\!S^{-}} \longrightarrow \mathrm{ROH} + \mathrm{CS_2}$$

I

Similar spontaneous unimolecular eliminations have been observed in decarboxylations[7] and hydrolysis of phosphate ester monoanions.[8] However, the evidence does not exclude the $A_{Ac}2$ mechanism of ether hydrolysis.[9]

The rate of hydrolysis of ethylxanthic acid reaches a maximum at *ca.* 0.5 *M* HCl and then decreases. This behavior was treated in terms of formation of a xanthic acid-hydronium ion association,[5] but Iwasaki and Cooke detected a new species spectrophotometrically when the acid concentration was >0.5 *M*, and they suggested that this was the unreactive protonated xanthic acid.[4b] However, similar rate maxima are very common in the acid hydrolysis of weakly basic substrates such as amides, and are explained, at least partially, in terms of decreasing water activity at acidities where the substrate is fully protonated.[10] Rate maxima are also observed in A2 hydrolyses of some weakly basic substrates, such as aryl phosphates[8] and phosphonates.[11] However, these reactions involve nucleophilic attack by water. In the hope of throwing more light on this problem, we used *n*-butyl and *tert*-butyl xanthate, because the ease of formation of the *tert*-butyl cation might introduce a new mechanism of hydrolysis,[12] with a change in the dependence of rate upon acidity. A few experiments were also made with ethyl xanthate.

Experimental Section

Materials. The potassium alkyl xanthates were prepared in the usual way by the reaction of CS_2 with the alkoxide ion in the alcohol or CS_2 as solvent.[13] They were purified by precipitation from the alcohol or acetone by addition of Et_2O followed by recrystallization.

Table I
Decomposition of *n*-Butyl Xanthate in Aqueous Acids[a]

[HCl], *M*	[HClO$_4$], *M*	$10^2 k_\psi$, sec^{-1} Obsd	$10^2 k_\psi$, sec^{-1} Calcd[c]
0.001		0.37	0.38
0.002		0.75	0.74
0.005		1.66	1.67
0.01		2.79	2.90
0.02		4.38	4.59
0.05		6.92	7.02
0.1		9.02	8.60
0.2		10.6	9.66
0.5		9.90	9.58
0.5		9.45[b]	9.58
	0.5	9.01[b]	8.95
1.0		9.05	8.63
1.0		8.70[b]	8.63
	1.00	7.71[b]	8.10
1.25		8.84[b]	8.52
	1.25	7.33[b]	7.65
1.5		8.42[b]	8.33
	1.5	6.13[b]	7.10
2.0		7.28	7.55
2.25		6.72[b]	7.05
	2.25	4.91[b]	5.10
2.5		6.48[b]	6.55
	2.5	4.39[b]	4.35
3.0		6.01[b]	5.55
	3.05	3.63[b]	3.01
4.0		3.93	3.55

[a] At 25.0°. [b] Stopped-flow measurements. [c] Calculated using $k = 0.11$ sec^{-1} and $K_a = 2.9 \times 10^{-2}$; and $K_a' = 14$ in HCl and 9 in HClO$_4$.

Table II
Reaction of *n*-Butyl Xanthate in Acidic Methanol[a]

10^3 [H$^+$], *M*	$10^2 k_\psi$, sec^{-1}
0.82	4.90[b]
0.96	4.85[c]
4.8	4.74
9.6	5.00[b]
19.0	5.08

[a] Followed at 301 nm at 25.0° in MeSO$_3$H–MeOH. [b] Mean of two values. [c] Mean of three values.

Methanesulfonic acid was purified by vacuum distillation, and freshly prepared solutions of it in dried MeOH were used.

Kinetics. The reaction was followed spectrophotometrically, usually at 25.0°, using a Gilford spectrophotometer for the slower reactions and a Durrum-Gibson stopped-flow spectrophotometer for the faster reactions, especially of *tert*-butyl xanthate. Under conditions in which the substrate is present as the xanthate ion the reaction was followed at 301 nm, but in acidic solution where the xanthic acid is present the reaction was followed at 270 nm. These wavelengths correspond to λ_{max} for xanthates and xanthic acids. Using the stopped-flow spectrophotometer we could observe the spectrum of *n*-butylxanthic acid formed by the rapid mixing of HCl and the potassium xanthate and observed λ_{max} 270 nm (ϵ 4520) in 0.05 *M* HCl in agreement with data for ethylxanthic acid in water and in CHCl$_3$.[14]

Ethyl and *n*-butyl xanthate are stable in neutral water, but *tert*-butyl xanthate slowly decomposes under these conditions and freshly made up solutions of it were always used.

The alkyl xanthate concentration was *ca.* 5×10^{-5} *M*, and the first-order rate constants, k_ψ, in reciprocal seconds, were calculated using the integrated first-order rate equation.

For experiments using the Gilford spectrophotometer a small amount of xanthate solution was added to the reaction solution using a square Teflon plunger. For reactions in the stopped-flow spectrophotometer, the xanthate in water was mixed with an equal volume of acid. Heat of dilution of the acid is apparently not causing a problem because rate measurements in both the Gilford and stopped-flow spectrophotometers agreed.

Products. The decomposition of *n*-alkyl xanthates in dilute aqueous acid gives the alcohol and CS$_2$.[4,5] The reaction of *n*-butyl xanthate in methanol containing methanesulfonic acid also gives CS$_2$ (as shown by its absorbance at 206 nm). For the reaction of *n*-butyl xanthate in aqueous 0.05 *M* HCl we identified *n*-butyl alcohol as the reaction product by glc (Carbowax 600 14 ft × 0.125 in. on Chromosorb W 60/80), and found no evidence for butene formation; however, the reaction of *tert*-butyl xanthate gave only a small peak for *tert*-butyl alcohol, and a large peak for isobutylene.

Results and Discussion

Variation of Rate Constant with pH. Our results with ethyl xanthate agree with earlier work,[4,5] and *n*-butyl xanthate behaves very similarly; and the rate–acidity profile fits the following scheme.

$$\mathrm{ROCS_2^-} + \mathrm{H^+} \underset{K_a}{\rightleftharpoons} \mathrm{ROCS_2H} \xrightarrow{k} \text{products}$$

Neglecting activity effects we obtain eq 1, which fits the data up to 0.5 *M* hydrochloric acid (Figure 1 and Table I).

$$k_\psi = k[\mathrm{H^+}]/(K_a + [\mathrm{H^+}]) \qquad (1)$$

The values for up to 0.5 *M* HCl (Table I) were calculated using $k = 0.11$ sec^{-1}, and $K_a = 2.9 \times 10^{-2}$ (measured spectrophotometrically).[15]

The relation between rate and pH is essentially the same for buffers and dilute HCl (Figure 1), with no evidence for general acid catalysis.

For methanesulfonic acid in methanol in the concentration range 1–20 × 10^{-3} *M* the first-order rate constant is independent of the acid concentration (Table II), suggesting that *n*-butylxanthic acid is much weaker in methanol than in water. The formation of CS$_2$ in this reaction confirms that the predominant mechanism of decomposition is a spontaneous elimination, because bimolecular attack would lead to ester exchange and would not be observed spectrophotometrically.

$$n\text{-BuO-S}_2\text{H} + \text{MeOH} \rightleftharpoons n\text{-BuOH} + \text{MeO-CS}_2\text{H}$$

tert-Butyl xanthate is much more reactive than the *n*-alkyl xanthates, although for dilute acid the rate–pH profiles are very similar (Figure 2). There are many examples

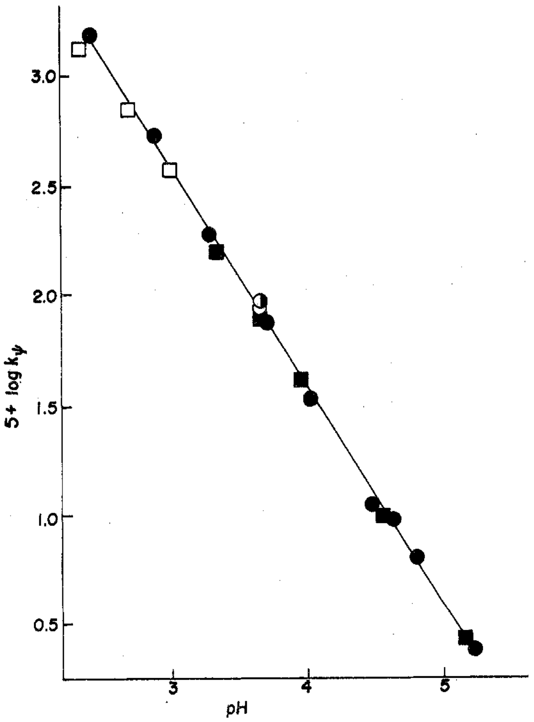


Figure 1. Variation of rate constant and absence of buffer catalysis for the hydrolysis of ethyl xanthate (circles) and *n*-butyl xanthate (squares) at 25.0°. The line is drawn with unit slope: ○, 0.1 *M* acetate; ●, 0.2 *M* acetate; ◑, 0.4 *M* acetate; □, dilute HCl; ■, acetate buffer.

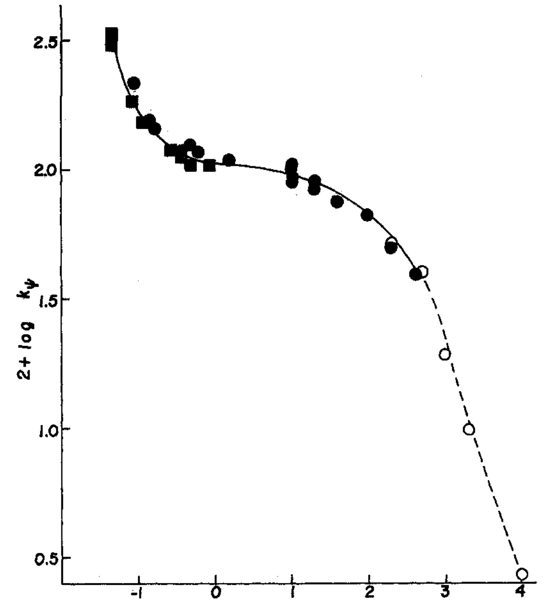


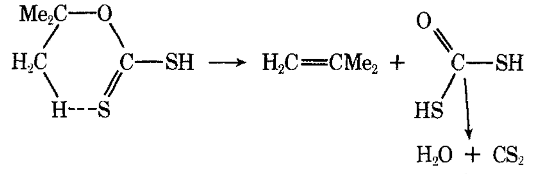
Figure 2. Variation of rate constant with acidity for the decomposition of *tert*-butyl xanthate at 25.0°. The broken line has unit slope. The data represented by solid points were obtained on a stopped-flow spectrophotometer, those represented by open points on a Gilford spectrophotometer: HCl, circles; $HClO_4$, squares.

of ester hydrolyses in which a *tert*-alkyl compound is much more reactive than the corresponding *n*- or *sec*-alkyl compound because of the ease of loss of *tert*-alkyl cations.[9,12] It is therefore tempting to suggest that *tert*-butyl xanthate reacts by an SN1 mechanism

$$t\text{-BuO-CS}_2^- \overset{H^+}{\rightleftharpoons} t\text{-BuO-CS}_2H \xrightarrow{\text{slow}} t\text{-Bu}^+ + OCS_2H^-$$

and the xanthate monoanion should be a reasonably good leaving group, especially in water.

The reaction of *tert*-butylxanthic acid in dilute acid gives largely isobutene, demonstrating alkyl oxygen fission in the decomposition. Xanthate esters pyrolyze to olefins, by a reaction which is probably a cyclic elimination,[16] although with some carbocation character in the transition state.[17] We could assume that the decomposition of *tert*-butylxanthic acid is similarly concerted with C–O bond breaking assisted by proton loss. Alternatively, we could

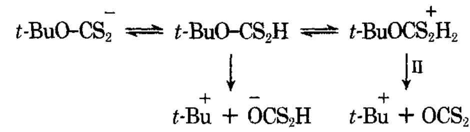


assume that an intimate ion pair is formed and then loses a proton either to the solvent or the counterion.[18] Sneen

$$Me_3C\text{-O-CS}_2H \rightleftharpoons [Me_3\overset{+}{C}\ \overset{-}{O}\text{-CS}_2H] \longrightarrow Me_2C{=}CH_2 + CS_2 + H_2O$$

and his coworkers have discussed these types of eliminations (*cf.* ref 19).

Reactions in Moderately Concentrated Acid. The rate maximum in the decomposition of ethylxanthic acid has been explained in terms of protonation of ethylxanthic acid to give an unreactive species.[4b] Alternative explanations are not particularly attractive; for example, there is no obvious reason why small changes in water activity should be important, or why hydronium or chloride ions of HCl should retard the reaction, because salt effects are small. Because it seemed probable that decomposition of *tert*-butylxanthic acid followed an SN1-E1 mechanism, we examined this reaction under conditions in which a protonated xanthic acid (II) should be present, because it should decompose with alkyl oxygen fission more readily than *tert*-butylxanthic acid.



$$\begin{array}{ccccc} t\text{-BuO-}\overset{-}{CS_2} & \rightleftharpoons & t\text{-BuO-CS}_2H & \rightleftharpoons & t\text{-BuOC}\overset{+}{S_2}H_2 \\ & & \downarrow & & \downarrow{\scriptstyle II} \\ & & t\text{-}\overset{+}{Bu} + \overset{-}{O}CS_2H & & t\text{-}\overset{+}{Bu} + OCS_2H_2 \end{array}$$

(In formulating these reactions we do not specify the position of the protons and we do not know whether isobutene is formed directly or from the *tert*-butyl cation because of the ease of interconversion of these species in strong acid.) The rate of decomposition of *tert*-butylxanthic acid increases sharply with acid concentrations greater than 0.5 *M* (Figure 2 and Table III), whereas that for *n*-butylxanthic acid decreases (Table I) as was found for ethylxanthic acid.[4,5] The most economical explanation for the different kinetic forms is that the decrease of the reaction rate of *n*-butylxanthic acid at hydrogen ion concentrations above 0.5 *M* is indeed due to protonation of the xanthic acid.

In this context we note that the rate decrease for *n*-butylxanthic acid at high acid concentrations is greater for perchloric than for hydrochloric acid (Table I) in accord with the greater protonating power of the former as shown by indicator measurements.[20]

For the decomposition of *tert*-butylxanthic acid at relatively high concentrations of perchloric or hydrochloric acid the situation is opposite to that observed with *n*-butylxanthic acid because the reaction rate in perchloric acid is faster than that in hydrochloric acid (Table III). This is in the expected direction in terms of protonating power of the acids,[20] and in addition it seems that perchloric acid is a more effective catalyst than hydrochloric acid for reactions in which carbocations are generated, probably because of favorable interactions between the carbocation and perchlorate ion.[21] However, the rates of decomposition of *tert*-butylxanthic acid are similar in media of the same protonating power as measured by $-H_0$.[20]

Quantitative Treatment of the Inhibition by Strong Acid. We assume that protonated *n*-butylxanthic acid cannot readily eliminate CS_2, and if protonation of the xanthic acid follows Hammett's acidity function[20] we obtain eq 2, where K_a' is the acid dissociation constant for

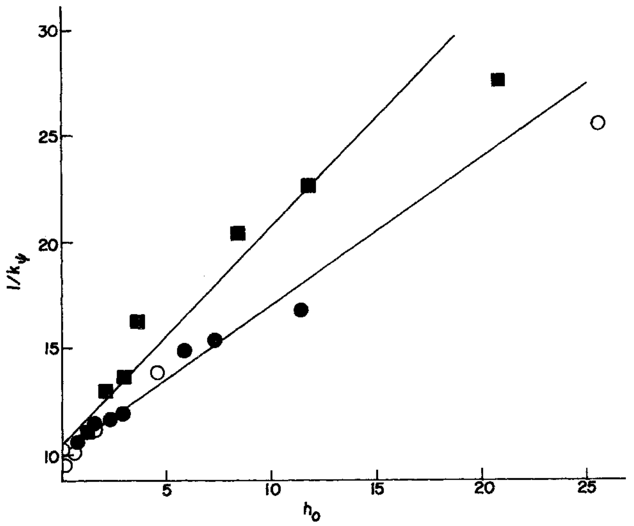


Figure 3. Relation between reaction rate and protonating power for hydrolysis of *n*-butyl xanthate in moderately concentrated acid. The points are calculated from the data in Table I and Figure 2: HCl, circles; $HClO_4$, squares. The solid points use data obtained on the stopped-flow spectrometer.

Table III
Decomposition of *tert*-Butyl Xanthate in Aqueous Acid[a]

[H$^+$], *M*	HCl	HClO$_4$
0.05	0.85	
0.10	0.98	
0.50	1.08	1.03
1.00	1.12	1.14
1.25	1.23	1.20
1.50	1.17	1.19
2.25	1.44	1.53
2.50	1.56	1.82
3.00	2.16	
3.05		3.03
3.05		3.44

[a] Values of k_ψ at 25.0°, in reciprocal seconds.

Table IV
Kinetic Salt Effects on the Decomposition of *n*-Butyl Xanthate[a]

[NaClO$_4$], *M*	0.001 *M* HCl	0.1 *M* HCl
	3.69	90.2
0.05	3.16	
0.08	2.70	
0.10	2.49	75.5
0.20	2.51	75.5

[a] Values of $10^3\ k_\psi$ at 25.0°, in reciprocal seconds.

protonated *n*-butylxanthic acid and k is the first-order rate constant for decomposition of *n*-butylxanthic acid.[22]

$$\frac{1}{k_\psi} = \frac{1}{k} + \frac{h_0}{kK_a'} \qquad (2)$$

Equation 2 is followed reasonably well except that plots of k/k_ψ against h_0 curve at high acid concentrations (Figure 3). From these plots we calculate k = 0.1 sec^{-1} and K_a' = 14 for reaction in HCl and 9 in HClO$_4$. (The results for ethylxanthic acid[5] can be fitted to $K_a' \cong 10$, although they are too few to test the treatment.) The difference between the values of K_a' in the two acids is not at all unreasonable because there is no reason why the protonation of an alkylxanthic acid should exactly follow h_0, and there could be kinetic salt effects of the acids. These values are slightly larger than that of 7.68 calculated at 20° using "hydrogen ion activity."[4] The value of k = 0.1 sec^{-1} agrees with the value of 0.11 sec^{-1} obtained from results at higher pH (Table I).

Kinetic Salt Effects. Kinetic salt effects are small. The decomposition of *n*-butyl xanthate is retarded by added sodium perchlorate (Table IV), and the retardation at pH 3 can be explained at least in part by increased acid dissociation of *n*-butylxanthic acid; this explanation is consistent with the smaller salt effect at pH 1. At pH 3 the decomposition of *tert*-butyl xanthate is inhibited by sodium chloride, although for sodium perchlorate we observed a rate minimum (Table V). These observations are consistent with the assumption that here the net effect is that of increased acid dissociation of *tert*-butylxanthic acid, and stabilization of a cationoid transition state, especially by perchlorate ion.[21] Transition-state stabilization would become relatively more important with decreasing pH.

Activation Parameters. Values of entropies of activation are useful mechanistic criteria for acid-catalyzed hydrolysis, and generally activation entropies are zero or positive for A1 hydrolyses of weakly basic substrates and 20–30 eu more negative for A2 hydrolyses.[23]

Table V
Kinetic Salt Effects upon the Decomposition of *tert*-Butyl Xanthate[a]

[NaCl], *M*	[NaClO$_4$], *M*	0.001 *M* HCl	0.1 *M* HCl
		1.94	9.8
	0.10	1.90	9.44
	0.20	1.60	10.1
0.20		1.89	
	0.40	1.57	8.90
0.40		1.40	
	0.60	1.65	
	0.80	1.79	
0.80		1.52	
	0.98	2.09	
0.98		1.45	

[a] Values of 10 k_ψ, at 25.0°, in reciprocal seconds.

Table VI
Temperature Effects[a]

	Alkyl group	
Temp, °C	*n*-Bu	*t*-Bu
9.4		3.19
14.7	0.13	
14.7	3.14[b]	
16.7		42.6[b]
20.0	0.22	
20.0	5.62[b]	
25.0	0.37	21.3
25.0	9.02[b]	98.5[b]
29.3	0.59	
29.3	12.9[b]	
31.9		210[b]

[a] Values of $10^2\ k_\psi$, in reciprocal seconds, in 10^{-3} *M* HCl unless specified. [b] In 0.1 *M* HCl.

Table VII
Activation Parameters[a]

	Alkyl group	
[HCl], *M*	*n*-Bu	*t*-Bu
10^{-3}	17.7 (3.5)	19.8 (18)
0.1	16.3 (−8.4)	18.1 (2)

[a] Values of ΔH^* are in kilocalories per mole; the values of ΔS^* in entropy units are in parentheses.

The rate constants for decomposition of *n*- and *tert*-butyl xanthates at various temperatures are given in Table VI. For reactions in 10^{-3} *M* HCl where the xanthate ion is the predominant species the entropies of activation (Table VII) are calculated from the second-order rate constants, but in 0.1 *M* HCl the xanthic acid is the predominant species and the entropies are then calculated from the observed first-order rate constants. (To this extent the two sets of data are not directly comparable.) Although the mechanistic test based on entropies of activation is generally applied to acid-catalyzed hydrolyses, the values which we observe are reasonable for reactions which involve spontaneous heterolysis.[23] The values of ΔS^* are more positive for reactions of *tert*-butyl xanthate, which is understandable because the transition state for decomposition of *n*-butylxanthic acid could have a structure close to that of the dipolar species (I), and should therefore be more strongly hydrated than the transition state for decomposition of *tert*-butylxanthic acid, which should be similar to a carbocation–anion pair. The enthalpies of activation are slightly larger for *tert*-butyl than for *n*-butyl xanthate, as expected if decomposition of the latter involves loss of a carbocation. The values of ΔS^* are more positive for reaction in 10^{-3} *M* than in 0.1 *M* HCl for both esters, and this difference should be related to the entropy of protonation of the alkyl xanthate ions, and therefore be relatively independent of the nature of the alkyl group.

Registry No.—*n*-Butyl xanthate, 110-50-9; *tert*-butyl xanthate, 21807-44-3.

References and Notes

(1) Support of this work by the National Science Foundation and the University of Chile-University of California Cooperative Program supported by the Ford Foundation is gratefully acknowledged.
(2) For a general discussion of xanthate chemistry and the industrial applications of these compounds, see ref 3.
(3) S. R. Rao, "Xanthates and Related Compounds," Marcel Dekker, New York, N. Y., 1971.
(4) (a) I. Iwasaki and S. R. B. Cooke, *J. Amer. Chem. Soc.*, **80**, 285 (1958); *J. Phys. Chem.*, **63**, 1321 (1959); (b) *ibid.*, **68**, 2031 (1964).
(5) E. Klein, J. K. Bosarge, and I. Norman, *J. Phys. Chem.*, **64**, 1666 (1960).
(6) G. M. Lewis, cited in ref 5.
(7) D. S. Kemp and K. Paul, *J. Amer. Chem. Soc.* **92**, 2553 (1970); A. Thomson, *J. Chem. Soc. B*, 1198 (1970).
(8) C. A. Bunton, *Accounts Chem. Res.*, **3**, 247 (1970).
(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIV.
(10) C. J. O'Connor, *Quart. Rev., Chem. Soc.*, **24**, 553 (1970); R. B. Homer and C. D. Johnson, "The Chemistry of Amides," J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 187.
(11) P. Haake and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966); P. Haake, R. D. Cooke, and G. Hurst, *ibid.*, **89**, 2650 (1967).
(12) Reference 9, Chapter VII.
(13) A. I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1956.
(14) I. Iwasaki and S. R. B. Cooke, *J. Phys. Chem.*, **64**, 1666 (1960); A. Pomianowski and J. Leja, *Can. J. Chem.*, **41**, 2219 (1963).
(15) The values of K_a range from 0.02 to 0.03 and $k = 0.072\ \mathrm{sec}^{-1}$ for the hydrolysis of ethyl xanthate.[4,5]
(16) C. M. De Puy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).
(17) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature (London)*, **190**, 715 (1961).
(18) M. Cocivera and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 1702 (1963).
(19) R. A. Sneen, *Accounts Chem. Res.*, **6**, 46 (1973).
(20) R. H. Boyd in "Solvent Solute Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter III.
(21) C. A. Bunton, J. Crabtree, and L. Robinson, *J. Amer. Chem. Soc.*, **90**, 1258 (1968); C. A. Bunton and S. K. Huang, *ibid.*, **95**, 2701 (1973); C. A. Bunton, T. W. Del Pesco, A. M. Dunlop, and K.-U. Yang, *J. Org. Chem.*, **36**, 887 (1971).
(22) This treatment differs from that of Iwasaki and Cooke[4] in that we assume that protonation of the xanthic acid follows Hammett's acidity function, h_0, rather than "hydrogen ion activity."
(23) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

Acid Chloride Chemistry. I. Phosgenation of Carboxylic Acids, a Catalyst Screening Study[1]

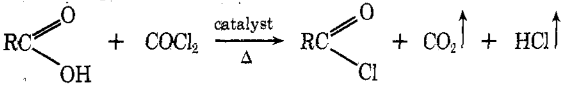
Charles F. Hauser* and Louis F. Theiling

Union Carbide Corporation, Chemicals and Plastics, P.O. Box 8361, South Charleston, West Virginia 25303

Received February 8, 1973

Imidazoles and several related structures with a $-\ddot{X}-Y{=}Z-$ system have been found to be excellent catalysts for phosgenation of lauric acid to lauroyl chloride. In contrast to carboxamide catalysts, imidazole can be recycled from batch to batch without appreciable loss of catalytic activity.

Over the past several decades the catalyzed phosgenation of carboxylic acids has become a prime preparative method (eq 1). Tertiary amines,[2] and more recently carboxamides,[3] have been used as catalysts for this phosgenation reaction. Both catalyst types, however, have restrictions which limit their large-scale application. Catalysis by tertiary amines[2] usually requires a reaction temperature in excess of 120°. Yields are variable, depending upon amine and type of carboxylic acid. Catalysis by carboxamides[3] normally provides high yields at reaction temperatures below 100°. Once the substrate acid has been consumed, however, the carboxamide-derived catalyst decomposes to nonactive tar. The tar can foul equipment[4] and has no catalytic value upon recycle to subsequent reactions.



$$\mathrm{RC(=O)OH} + \mathrm{COCl_2} \xrightarrow[\Delta]{\text{catalyst}} \mathrm{RC(=O)Cl} + \mathrm{CO_2}\uparrow + \mathrm{HCl}\uparrow \quad (1)$$

An ideal phosgenation catalyst should provide acid chlorides in high yield from an assortment of carboxylic acids at moderate reaction temperature and short residence time. Moreover, it should maintain its activity upon recycle with reaction residues from one batch reaction to another. We have found a number of catalysts which fit this description.

Results and Discussion

A large number of compounds have been tested as catalysts for the phosgenation of lauric acid to lauroyl chloride. The results of a number of these experiments are recorded in Table I. The catalysts in group A are five-membered heterocyclic compounds containing nitrogen, oxygen, or sulfur atoms adjacent to a carbon-nitrogen double bond. Most of these materials are excellent phosgenation catalysts, providing yields of lauroyl chloride in excess of 90% at reaction temperatures of less than 100°. Group B catalysts are six-membered heterocyclic compounds containing nitrogen, oxygen, or sulfur atoms adjacent to carbon-nitrogen unsaturation. Of those selected, the six-membered heterocyclics were less effective catalysts than the five-membered species. Group C is composed of compounds containing carbon-nitrogen unsaturation. The effectiveness of these materials for conversion of lauric acid to lauroyl chloride varies from excellent to essentially nil. This effectiveness is seen with the series of Schiff bases, isobutylidene-*n*-butylamine, *N*-benzylidenemethylamine, and *N*-benzylideneaniline, wherein the yield of lauroyl chloride varies inversely with aromatic substitution on the carbon-nitrogen double bond. Group D consists of isocyanates and compounds of carbon-carbon unsaturation. *n*-Butyl isocyanate provided an excellent yield of lauroyl chloride, whereas the aromatic specie did not. Carbon-carbon unsaturation provided poor conversion to lauroyl chloride, except for the enamine, 1-dimethylamino-2-methylpropene.

Carbon-nitrogen unsaturation, and in one case nitrogen-nitrogen unsaturation, is present in each compound in Table I which showed high catalytic activity. Usually, this unsaturation is adjacent to an atom possessing an available pair of electrons, the combination of which form the structure $-\ddot{X}-Y{=}Z-$. This XYZ structure is apparently responsible for the observed catalytic activity. Using