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Cellulose Xanthic Acid.[1] I. Studies of Model Systems

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ABSTRACT: Decomposition of simple alcohol xanthates in acidic solution has been studied using ultraviolet absorption spectrophotometry. In aqueous acidic solution, $\pi \rightarrow \pi^*$ transition absorptions of three separate xanthate species with a thiocarbonyl chromophore have been observed: the xanthate ion, λ_{max} 300 mμ, free xanthic acid, λ_{max} 285 mμ and protonated xanthic acid, λ_{max} 270 mμ. In addition, the formation of an orthocarbonate by transxanthation with the hydronium ion is suggested as an intermediate in the mechanism of decomposition. The rate of decomposition was related to the acidity and structure of the parent alcohol. Thus, for methyl, ethyl and *n*-hexyl xanthates, the rate passed through a maximum at a low pH and decreased smoothly as the acidity increased. For these compounds, decomposition was retarded by the formation of a protonated xanthic acid. It is suggested that protonation was by association between the xanthic acid oxygen and excess hydrogen ions. With *t*-butyl xanthate, the bulky *t*-butyl group prevented association and no stabilization was observed. A mechanism of decomposition consistent with these observations is given.

The decomposition of cellulose xanthate in acidic solution is the basis for the commercial production of rayon and cellophane. There have been many attempts to elucidate the mechanism of decomposition but none have been completely successful. In general, the approach has been to derive a mechanism from studies of model systems and to attempt to apply this to cellulose xanthate. However, failure to recognize that reactions other than decomposition occur in the acidic solutions and the experimental difficulties of studying the more complex system led to the conclusion that the results for cellulose xanthate were not consistent with the proposed mechanism.

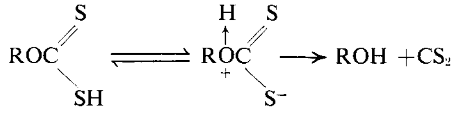
In this study, the model systems and cellulose have been considered separately. In part I, the decomposition of simple alcohol xanthates is reviewed and a more complete mechanism is suggested. In part II, cellulose xanthic acid is discussed and its behavior in acidic solution is shown to be completely consistent with that of the model xanthates.

Studies of Model Systems

The decomposition of xanthates in acidic solution has been the subject of a number of papers in recent years. The over-all reaction derived from these studies has been generally assumed to be formation of the xanthic acid followed by decomposition (eq 1).

$$\text{ROCSS}^- + \text{H}^+ \rightleftharpoons \text{ROCSSH} \longrightarrow \text{ROH} + \text{CS}_2 \quad (1)$$

Lewis[2] has suggested that the mechanism of decomposition involves protonation of the oxygen (eq 2).



(2)

However, there is no evidence for the existence of the ion pair.

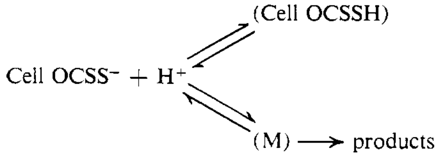
Chatenever and King,[3] Chicowski,[4] Cranedonc,[5] and Philipp and Fichte[6] have reported that in dilute acid the kinetics of the reaction are described by eq 3, where k_{exp}

$$k_{exp} = \frac{k[\text{H}^+]}{K_i + [\text{H}^+]} \quad (3)$$

is the rate loss of xanthic acid, k is the decomposition rate constant, and K_i is the dissociation constant.

It has been reported that k_{exp} passes through a maximum as the hydrogen ion concentration is increased, *i.e.*, in strongly acidic solution, decomposition is slower, and eq 3 is no longer valid.[7]

From work of Klein, *et al.*,[7] on the decomposition of ethyl xanthate, the idea was proposed of the more complicated mechanism (eq 4), where (M) is defined as an



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[1] Presented in part at the Second International Dissolving Pulps Conference of the Technical Association of the Pulp and Paper Industries, New Orleans, La., June 3–6, 1968.

[2] G. M. Lewis, Dissertation, New York University, 1947.

[3] C. V. King and A. Chatenever, *J. Amer. Chem. Soc.*, **71**, 3587 (1949).

[4] Z. Cichowski, *Polimery*, **11**, 326 (1966).

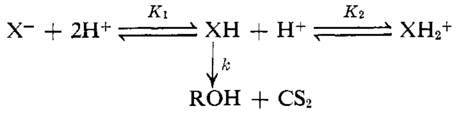
[5] A. C. Cranedonc, *Rec. Trav. Chim. Pays-Bas*, **70**, 431 (1951).

[6] B. Philipp and C. Fichte, *Faserforsch. Textiltech.*, **11**, 118, 172 (1960).

[7] E. Klein, J. K. Bosarge, and J. Norman, *J. Phys. Chem.*, **64**, 1666 (1960).

activated complex. M was identical with the ion pair postulated by Lewis. The kinetic expression derived from the mechanism involved the Hammett function and satisfactorily accounted for the maximum. Klein also offered an alternate mechanism based on earlier work by Ballard, *et al.*,[8] who postulated the formation of a protonated xanthic acid and an ion pair activated complex. However, both of these mechanisms are subject to objections, *viz.*, the existence of an ion pair.

In more recent work by Iwasaki and Cooke,[9] the xanthic acid was considered to be the unstable entity which was stabilized by protonation. The reaction mechanism these workers proposed was



$$X^- + 2H^+ \overset{K_1}{\rightleftharpoons} XH + H^+ \overset{K_2}{\rightleftharpoons} XH_2^+ \quad (5)$$
$$XH \xrightarrow{k} ROH + CS_2$$

The loss of xanthate derived for this mechanism was given by eq 6, where K_2 is the dissociation constant of

$$k_{\text{exp}} = \frac{k[\text{H}^+]}{[\text{H}^+] + K_1 + ([\text{H}^+]^2/K_2)} \quad (6)$$

the protonated xanthic acid. At low acidity, eq 6 is compatible with eq 3. The absorptions of the xanthic acid and protonated xanthic acid were not resolved although the composition of the decomposing mixture was calculated (with approximations) from eq 6.

An alternative mechanism of decomposition by a transxanthation with water has been proposed[10] (eq 7).

$$\text{ROCS}_2^- + \text{HOH} \rightleftharpoons \text{ROCS}_2\text{HOH}^- \longrightarrow \text{ROH} + \text{CS}_2 + \text{OH}^- \quad (7)$$

The rate expression for this mechanism also has the same general form as eq 6.

The work reported in this paper was directed toward characterization of the entities present in acidic solutions containing xanthates, and formulating a complete mechanism which was consistent with the data obtained from model xanthate acid decomposition studies.

Experimental Section

Equipment. A Cary Model 14 recording spectrophotometer equipped with constant-temperature cell housing and standard square quartz spectrophotometer cells with 10-mm light path were used for all experiments. The temperature of the sample compartment was maintained constant by circulation of liquid from a thermostated bath. Solutions were rapidly introduced into the sample cell through a hole in the lid using a long-needled syringe. All reagents and the syringe were conditioned to the experimental temperature before use.

Materials. Potassium methyl xanthate and potassium *n*-hexyl xanthate were prepared by reacting stoichiometric amounts of the alcohols, carbon disulfide and potassium hydroxide at 25°. The alkali was dissolved in a minimum amount of water before addition of the alcohol. After approximately 1 hr, crystals of the xanthates had formed. The reaction mixtures were filtered and the crystals washed with ether and dried *in vacuo*. No attempt was made to recover stoichiometric amounts of the xanthates or to recrystallize the product. Potassium *t*-butyl xanthate was prepared by reacting 0.5 mol of potassium metal with an excess of *t*-butyl alcohol (approximately 2 mol). Slightly more than 0.5 mol of CS_2 was added to react completely with the resulting alcoholate. The excess alcohol and CS_2 were removed by washing with hexane. The xanthates, dissolved in 1.5 *M* sodium hydroxide, had molar absorptivities at 300 mμ of about 17,000 and the ultraviolet absorption spectra indicated the absence of by-products. Potassium ethyl xanthate was commercially available and Baker grade, M352, was used without further purification.

Aqueous acidic solutions of pH 0.17–1.91 were prepared by mixing molar solutions of sodium hydrogen sulfate and sodium sulfate in different proportions or by adding sulfuric acid to molar sodium hydrogen sulfate. Standardized 16 *N* and 4 *N* sulfuric acid solutions were also used. The pH values of the aqueous solutions were measured using a Leeds and Northrup pH meter.

Methods. Approximately 10 mg of xanthate was dissolved in 10 ml of 1.5 *M* sodium hydroxide. A small volume of the xanthate solution, conveniently 50–70 μl, was placed in the spectrophotometer cell. Then 3 ml of an acidic solution was rapidly injected into the cell. The absorbance of the sample was repeatedly scanned to decreasing wavelength at 25 Å/sec after injection of the acid (Figure 1). The spectra of the decomposing sample at any time during decomposition could be extrapolated from the recorded absorbance.

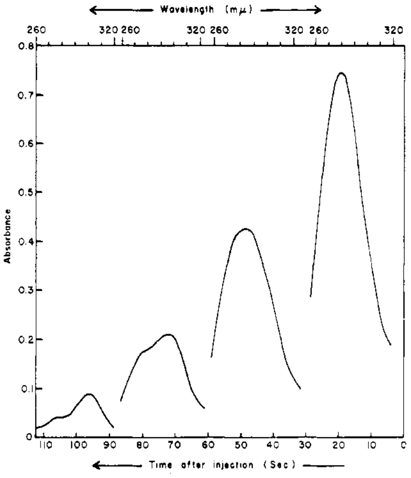


Figure 1. Consecutive scans of the absorbance of potassium *n*-hexyl xanthate at pH 1.23.

Alternatively, the absorbance at constant wavelength was followed and the kinetics of decomposition determined from the slopes of semilogarithmic plots of the absorbances as functions of time.

Results and Discussion

Ultraviolet Absorption of the Xanthate Ion and Its Acidic Forms. The thiocarbonyl chromophore, C=S, has a characteristic absorbance due to π → π* transitions in the wavelength range 250–350 mμ. The wavelength of maximum absorbance is significantly influenced by the electronic environment of the chromophore. Thus trithiocarbonate ion, CS_3^{2-}, absorbs at 332–336 mμ,[11] and xanthate ion, $ROCS_2^-$, at 300–306 mμ.[12] The substituent, R, of the xanthate ion has little effect on the absorption characteristics. The ab-

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[8] D. G. H. Ballard, C. H. Bamford, K. L. Gray, and E. D Totman, cited by E. Klein, *et al.*,[7] as a private communication.

[9] I. Iwasaki and S. R. B. Cooke, *J. Phys. Chem.*, **68**, 2031 (1964).

[10] J. Dyer and L. H. Phifer, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract E30. See also A. Hantzsch and W. Bucerius, *Ber.*, **59**, 793 (1926).

[11] J. Dyer, *Tappi*, **49**, 447 (1966).

[12] V. von Halban, A. Mackert, and W. Z. Ott, *Z. Electrochem.*, **29**, 445 (1923).

sorbance of xanthate derviatives, $ROCS_2R^1$, where R^1 is a metal, alkyl group or hydrogen, is shifted to a lower wavelength due to a reduction of electron density, with the degree of the shift being related to the electronegativity of the R^1 group and the nature of the bond between R^1 and S. The maximum blue shift of the xanthate spectra occurs when R^1 is covalently bound to the S, *e.g.*, S-methyl ethyl xanthate at 280 mμ, and ethyl xanthic acid at 268 mμ in hexane.

Consistent with shifts usually observed in $\pi \rightarrow \pi^*$ transitions,[13] xanthic acids, ROC(=S)SH, should have an absorption maximum in water in the order of 20 mμ above 268 mμ if the solubility is related to partial ionization of the acid or some other association mechanism with the sulfur hydrogen end of the molecules. Absorption in water at a lower wavelength can only be accounted for by a reduction of the electron density in the solubilizing mechanism. This may be achieved by association with the oxygen or sulfur lone pair electrons.

The ultraviolet spectrum illustrated in Figure 2 was obtained when potassium ethyl xanthate was allowed to react with dilute sulfuric acid. The xanthate was decomposing at a relatively rapid rate and this spectrum was obtained by extrapolation to zero time. It has been reported that the absorbance is due to a mixture of the xanthate ion and xanthic acid (ROC(=S)SH). The absorbance of this xanthic acid has been characterized[7] and shown to have a maximum in water at 270 mμ. This is inconsistent with the proposed free acid structure and would suggest that the electron density of the thiocarbonyl chromophore has been reduced by association of the xanthic acid with a hydronium ion (protonated acid). The existence of three species, *i.e.*, the xanthate ion, xanthic acid, and protonated xanthic acid, in the acidic solution has been proposed[7,9] although the absorption of only two of the entities have been resolved.

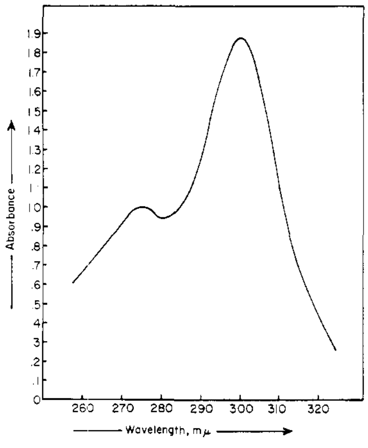

Figure 2. Absorbance of potassium ethyl xanthate at pH 1.23.

A sample of potassium *n*-hexyl xanthate was treated with a sulfuric acid buffer solution (pH 1.23) and the ultraviolet spectrum plotted at successive intervals, with the results given in Figure 3. Close visual observation of the reaction mixture indicated that very finely dispersed droplets were being produced immediately after the addition of the sulfuric acid solution, and that these were disappearing as the decomposition occurred. The spectral contribution of the xanthate ion and 270-mμ species measured in 1.5 *N* NaOH and 16 *N* H_2SO_4, respectively, were subtracted from the spectrum, leaving a spectral residue with a maximum absorbance at 285 mμ shown in Figure 4. The position of this absorption maximum is consistent with the predicted absorption of free xanthic acid, ROC(=S)SH in water solution.

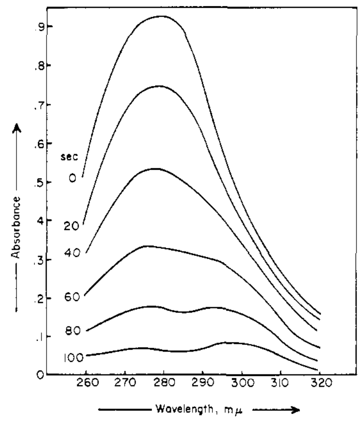

Figure 3. Absorbance of potassium *n*-hexyl xanthate at pH 1.23 at different times after adding acid.

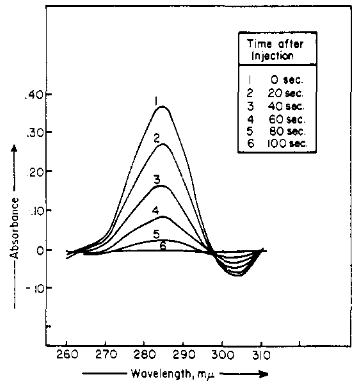

Figure 4. Residual absorbance of *n*-hexyl xanthate at pH 1.23 at different times after adding acid.

Direct evidence of the xanthic acid absorption characteristics was obtained when potassium *t*-butyl xanthate was treated with dilute acid (pH 1.91). In this case, the charge density at the protonation site and/or steric hindrance apparently prevented the formation of a protonated acid and only the spectra of xanthic acid (ROC(=S)SH) was obtained (Figure 5). For this compound, the ion had a maximum absorbance at 306 mμ and the free acid at 290 mμ. No absorbance due to protonated acid was observed.

Characterization of the Xanthates in Acidic Solution. A. The 285-mμ Species.[14] Free xanthic acid, which should have an absorption maximum above 268 mμ in water solution, will be produced by an ionic reaction

$$ROCS_2^- + H^+ \rightleftharpoons ROCS_2H \qquad (8)$$

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[13] J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

[14] The terms "285-mμ species" and "270-mμ species" are used to identify species absorbing in that region in aqueous solution. The exact wavelength of maximum absorbance depends on the nature of the alkyl group.

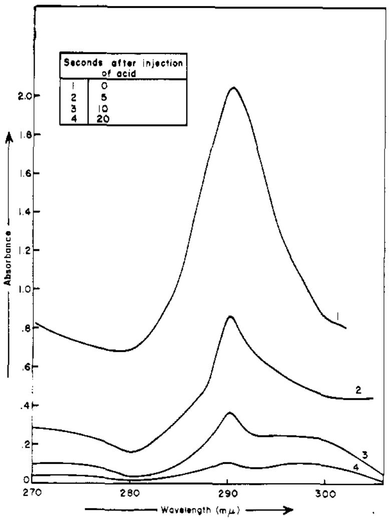


Figure 5. Absorbance of potassium *t*-butyl xanthate at pH 1.91 at different times after adding acid.

In most xanthate acid systems, the xanthic acid is then partially associated at a somewhat slower rate. A direct study of the xanthic acid was possible using *t*-butyl xanthate which does not form the protonated acid. Treating potassium *t*-butyl xanthate with acid (pH 1.91) and extrapolating the absorbance to zero time gave the spectrum shown in Figure 5. The absorption maximum at 290 mμ is apparently that of the xanthic acid in a hydrated (soluble) state. Using higher concentrations of xanthate (0.1 *M*), an oil separates which is soluble in hexane. The hexane solution had an absorption maximum at 274 mμ. Titration with sodium hydroxide showed the oil in the hexane solution to be free xanthic acid.

A small amount of the oil was smeared on the inside wall of the absorption cell and an absorbance maximum was again found at 274 mμ. This implies the absence of association in the hexane solution and that the solubility in water is due to association. The red shift in water solution is characteristic of the influence of polar solvents on $\pi \rightarrow \pi^*$ transitions. The oil or hexane solution of the oil was relatively stable suggesting that the hydration is a necessary step in over-all acid reactions of the xanthates (decomposition of the xanthate or protonation of the xanthic acid). The implication is that *t*-butyl xanthic acid is a slightly water soluble compound having an absorption maximum in water solutions at 290 mμ and in hexane solutions at 274 mμ.

Free xanthic acid is not normally observed during spectrophotometric studies of the acid decomposition of ethyl and methyl xanthates since it is relatively soluble and is rapidly converted into the associated acid form. Solubilization of the xanthic acid should be related to the length of the alkyl group. When *n*-hexyl xanthate was treated with dilute acid (pH 1.23), fine droplets of the free xanthic acid separated even at the low concentration of xanthates normally used for spectrophotometric studies (10^{-4} *M*). In the presence of 10% dioxane, the xanthic acid was soluble and only the absorbance of the associated acid at 269 mμ was observed (similar results were obtained using extremely dilute xanthate solutions). When the spectral contribution of the free xanthic acid was plotted against time (Figure 6), it was observed that the absorbance decreased relatively slowly (behavior related to solubility) until the droplets disappeared and then decreased at a rate similar to the other xanthate species (xanthate ion and protonated acid).

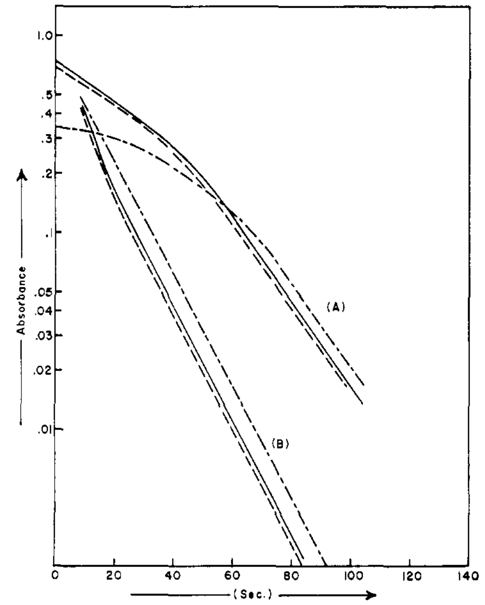


Figure 6. Absorbance of potassium *n*-hexyl xanthate at constant wavelengths at pH 1.23 (A) without dioxane and (B) with 10% added dioxane: - - - -, 300 mμ; - - -, 285 mμ; —, 270 mμ.

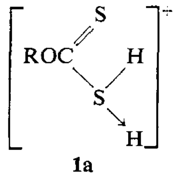
To characterize the insoluble material, the reaction mixture (*n*-hexyl xanthate and acid) was extracted with hexane. All of the xanthate present in the mixture at that time dissolved in the hexane layer. Since the xanthate ion and protonated acid should be insoluble, this indicated that the system was in equilibrium, a situation confirmed in a later section from studies of the decomposition kinetics. The hexane layer had an absorption maximum at 268 mμ and titration with NaOH indicated only the presence of the free xanthic acid. On evaporating the hexane from the sample and dissolving the residue in water, a characteristic xanthate ion spectrum was obtained. This reflected the ionization of the acid in the aqueous solution, since the concentration of the aqueous solution was about 10^{-4} *M*.

B. The 270-mμ Species.[14] In acidic solutions of xanthates, the initial reaction will be the rapid formation of xanthic acid (eq 9) which may then associate with hydronium ions to form a protonated acid (eq 10).

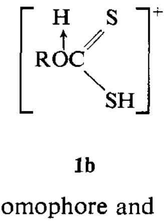
$$\mathrm{ROCS_2^- + H_3O^+ \rightleftharpoons ROCS_2H + H_2O} \quad (9)$$

$$\mathrm{ROCS_2H + H_3O^+ \rightleftharpoons [ROCS_2H_2]^+ + H_2O} \quad (10)$$

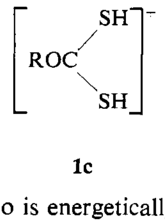
This may occur in at least three ways. Structure **1c** has no thiocarbonyl chromophore and also is energetically unfavorable. The formation of a protonated acid as in



1a



1b



1c

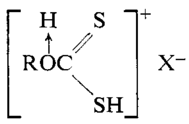
structure **1a** will be related to the acidity of the xanthic acid; the larger the ionization constant, the less tendency to protonate. The oxygen lone pair electrons are conjugated with the electrons of the thiocarbonyl chromophore; association with hydrogen ion as in **1b** would shift the absorbance to a lower wavelength. In both cases, **1a** and **1b**, protonation would stabilize the xanthic acid. Several experimental observations were made which indicated that the 270-mμ species was not a protonated acid of type **1a**.

1. Comparison of the ratio of the amount of the 270-mμ species to that of the xanthate ions when ethyl and *n*-hexyl xanthates were treated at the same acidity indicated higher concentrations of the ethyl xanthic acid species. If type **1a** were the form of the protonated acid, it is to be expected that there would be a larger amount of the *n*-hexyl derivative since it is the weaker acid (by analogy with carboxylic acids).

2. In strongly acidic solutions, *n*-hexyl xanthate has a faster decomposition rate than ethyl xanthate. Since the protonated acid has a stabilizing effect on the system, this again indicates a lower ratio of protonated hexyl xanthic acid to the hexyl xanthate ion.

3. There was no stabilization of *t*-butyl xanthate in strongly acidic solution. This implies the absence of protonation. In addition, no 270-mμ species was observed during the decomposition. Steric hindrance due to the bulky *t*-butyl group should prevent protonation of type **1b** but not of type **1a**.

Considering the above experimental observations and that oxygen is more nucleophilic than sulfur, it is proposed that the structure of the 270-mμ species is **2**.



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This oxonium-type compound will be insoluble in hexane but since it is in equilibrium with the undissociated acid, it will be completely removed from solution on extraction.

$$\mathrm{ROCS_2^-} \underset{\mathrm{OH^-}}{\overset{\mathrm{H_3O^+}}{\rightleftharpoons}} \mathrm{ROCS_2H} \underset{\mathrm{OH^-}}{\overset{\mathrm{H_3O^+}}{\rightleftharpoons}} [\mathrm{ROCS_2H_2}]^+ \quad (11)$$

A white insoluble precipitate formed on addition of a 10% solution of silico-12-tungstic acid, which can form oxonium-type compounds by association with ether oxygen,[15] to aqueous solutions of potassium methyl and ethyl xanthate. Potassium *t*-butyl xanthate did not give an insoluble precipitate. This behavior is related to the ability of the xanthates to form oxonium-type compounds and is in complete agreement with observations of the 270-mμ species.

Since the 270-mμ species has an absorption maximum which is very close to that of the insoluble xanthic acid, it might be suggested that the 270-mμ species is only the insoluble xanthic acid. Several arguments can be presented that it is not.

1. The 285-mμ species disappears initially faster than the 270-mμ species.

2. *n*-Hexyl xanthic acid should be less soluble than ethyl or methyl xanthic acid yet there is more 270-mμ species for a given H^+ concentration in the case of ethyl or methyl xanthate.

3. The solubility of xanthic acid should depend on salt concentration; for a given H^+ concentration, there are identical amounts of the 270-mμ species regardless of the salt concentration.

4. The nature of the relation between H^+ concentration and experimental decomposition rate suggests that a protonated acid is present (see following section).

5. There is about a 4-mμ difference between $\lambda_{\max}$ for the insoluble xanthic acid and the observed 270-mμ species.

6. No 270-mμ species is observed for the *t*-butyl xanthate–acid system.

7. The amounts of the 270-mμ species observed are direct functions of the concentrations of the xanthate used. If it were the insoluble xanthic acid, this would not be true.

Acid Decomposition of Xanthates. The decomposition of xanthates in acidic solution is second order; however, using dilute xanthate solutions (10^{-4} *M*) and buffered acid solutions, the system becomes pseudo first order.

When potassium ethyl xanthate was allowed to react with dilute acids, the ultraviolet spectra of the solution were the sum of the absorbance of several species, two of which were identified as the xanthate ion ($\lambda_{\max}$ 301 mμ) and the protonated xanthic acid ($\lambda_{\max}$ 270). The experimental decomposition rate, $k_{\exp}$, of the xanthate was determined by following the absorbances at constant wavelength as a function of time.

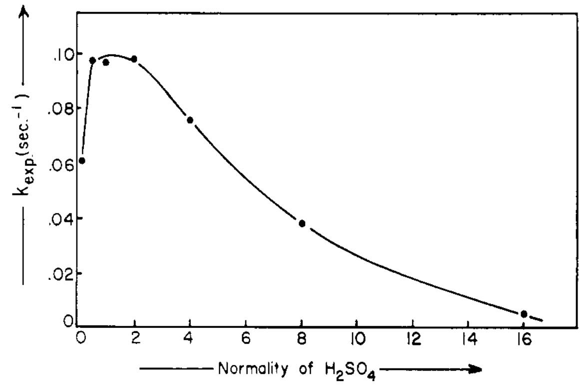

Figure 7. Decomposition of potassium ethyl xanthate at 24.5°; influence of acid strength on the experimental decomposition rate $k_{\exp}$.

The influence of acidity on $k_{\exp}$ is given in Figure 7. The rate passes through a maximum at a low pH and continues to decrease smoothly as the acidity increases. Similar results were obtained with methyl and *n*-hexyl xanthate. The ratio of the absorbance at 270 mμ to that at 300 mμ increased with increasing acid concentration (Figure 8), suggesting an increased concentration of the protonated acid. This observation, together with the observation that the decomposition rate was decreasing, led to the conclusion that the protonated acid was a relatively stable form of the xanthate and that the decomposition does not occur through this species.

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[15] W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. 1, Elsevier Publishing Co., New York, N. Y., 1950, p 184.

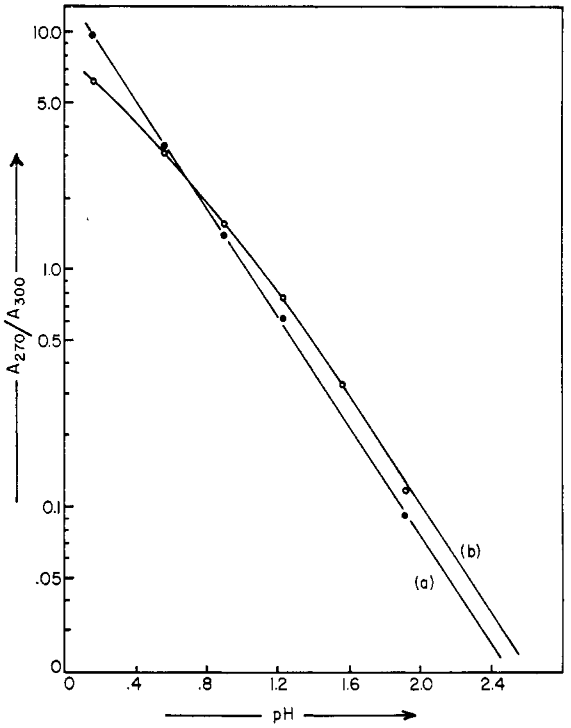


Figure 8. Decomposition of (a) potassium ethyl xanthate and (b) *n*-hexyl xanthate at 24.5°; influence of pH on the absorbance ratio A_{270}/A_{300}.

Since the reaction to form protonated xanthic acid is relatively slow as compared to the ionic reaction to form the xanthic acid, then immediately after the addition of acid the concentration of the xanthic acid could be very high. If xanthic acid were the decomposing species, the over-all decomposition should proceed at a very rapid rate while this species is present at a high concentration. There was, however, no evidence of an initial rapid decomposition. This was further confirmed when the experimental decomposition rates for potassium *n*-hexyl xanthate in acidic solution (pH 1.23), with and without added 10% dioxane, were compared. The rates were similar even though there was a large difference in the amounts of insoluble xanthic acid present (Figure 6).

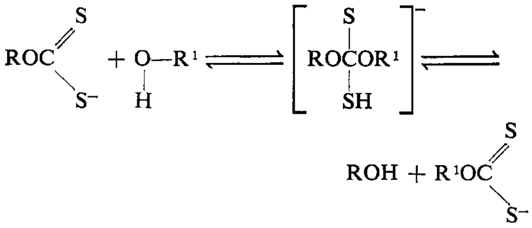
It was apparent from these observations that neither the free xanthic acid nor the protonated xanthic acid were decomposing directly. Since these are in equilibrium with the xanthate ion which also does not decompose directly, it must be assumed that the decomposition involves a fourth unstable species.

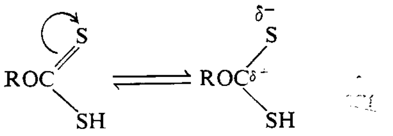
Decomposition of Xanthic Acids by Transxanthation with Water. In the presence of water, xanthates are unstable. It has been suggested that decomposition proceeds by transxanthation with water (eq 12). The reaction is analogous to the redistribution of xanthate groups in alcohols (eq 13).

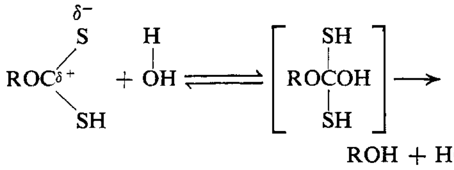
$$\mathrm{ROCS_2^- + HOH \rightleftharpoons HOCS_2^- + ROH} \quad (12)$$

$$\mathrm{ROCS_2^- + R^1OH \rightleftharpoons R^1OCS_2^- + ROH} \quad (13)$$

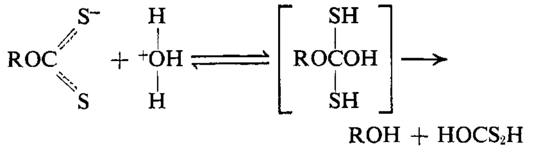
The mechanism of transxanthation is a bimolecular nucleophilic substitution (SN2). The rate of exchange is influenced by the acidity of the alcohol R^1OH. When R^1 is replaced by H, the product of exchange is very unstable. As a result, the reaction is displaced to the right and decomposition of the xanthate is accelerated. The rate-determining step is related to the relative acidities of both the xanthate and the alcohol. The xanthic acids may decompose by a similar mechanism.


(14)

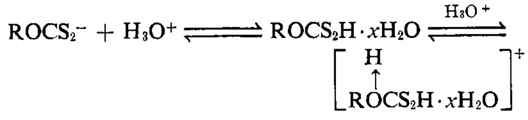

(15)


(16)

Alternatively, the hydronium ion may react directly with the xanthate ion to form the transxanthation intermediate (eq 17).


(17)

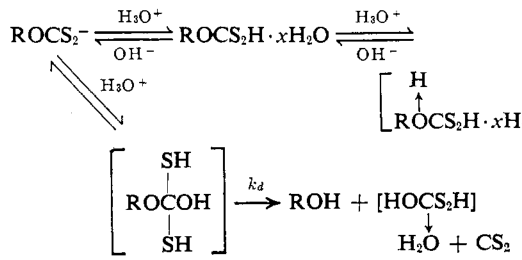
The initial existence of the xanthic acid at high concentration was influenced by its rate of formation and loss to establish the equilibrium (eq 18). It had no effect on the experimental decomposition rate indicating that the decomposition was not through this species. Therefore, eq 17 was considered the most probable mechanism of decomposition. Dithiocarbonic acid, the product of the exchange, would decompose irreversibly into carbon disulfide and water (eq 19).


(18)

$$\mathrm{ROCS_2^- + H_3O^+ \rightleftharpoons ROCS_2H\cdot xH_2O \overset{H_3O^+}{\rightleftharpoons} \left[\overset{H}{\overset{\uparrow}{ROCS_2H}}\cdot xH_2O\right]^+} \quad (18)$$

$$\mathrm{HOCS_2H \longrightarrow H_2O + CS_2} \quad (19)$$

In acidic solution, the thiocarbonyl chromophore is absent and the intermediate would not absorb in the wavelength region of interest (270–320 mμ).


(20)

Suggested Mechanism for the Decomposition of Xanthates in Acidic Solution. The decomposition reaction of xanthates in acidic solution is described on combining eq 17, 18 and 19.

To derive a rate expression, reactions 21–24 were considered. The change in total concentration of all the

$$\mathrm{ROCS_2^- + H_3O^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ROCS_2H \cdot \mathit{x}H_2O} \qquad (21)$$

$$\mathrm{ROCS_2H \cdot \mathit{x}H_2O + H_3O^+ \underset{k_4}{\overset{k_3}{\rightleftharpoons}}} \left[\mathrm{R}\overset{\overset{\mathrm{H}}{\uparrow}}{\mathrm{O}}\mathrm{CS_2H \cdot \mathit{x}H_2O}\right]^+ \qquad (22)$$

$$\mathrm{ROCS_2^- + H_3O^+ \underset{k_6}{\overset{k_5}{\rightleftharpoons}} ROCS_2H_2OH} \qquad (23)$$

$$\mathrm{ROCS_2H_2OH \xrightarrow{k_d} ROH + HOCS_2H} \qquad (24)$$

$$K_1 = \frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]}{[\mathrm{ROCS_2H \cdot \mathit{x}H_2O}]} \times$$

$$[\mathrm{ROCS_2H \cdot \mathit{x}H_2O}] = \frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]}{K_1} \qquad (25)$$

$$K_2 = \frac{[\mathrm{ROCS_2H \cdot \mathit{x}H_2O}][\mathrm{H_3O^+}]}{\left[\mathrm{R}\overset{\overset{\mathrm{H}}{\uparrow}}{\mathrm{O}}\mathrm{CS_2H \cdot \mathit{x}H_2O}\right]^+} \times$$

$$\left[\mathrm{R}\overset{\overset{\mathrm{H}}{\uparrow}}{\mathrm{O}}\mathrm{CS_2H \cdot \mathit{x}H_2O}\right]^+ = \frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]^2}{K_1K_2} \qquad (26)$$

$$K_3 = \frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]}{[\mathrm{ROCS_2H_2OH}]} \times$$

$$[\mathrm{ROCS_2H_2OH}] = \frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]}{K_3} \qquad (27)$$

xanthate species, since these are in equilibrium, will be given by eq 28. Using equilibria 21, 22, and 23 and the

$$\frac{\mathrm{d}\left\{[\mathrm{ROCS_2^-}] + [\mathrm{ROCS_2H \cdot \mathit{x}H_2O}] + \left[\mathrm{R}\overset{\overset{\mathrm{H}}{\uparrow}}{\mathrm{O}}\mathrm{CS_2H \cdot \mathit{x}H_2O}\right]^+ + [\mathrm{ROCS_2H_2OH}]\right\}}{\mathrm{d}t} = -k_d[\mathrm{ROCS_2H_2OH}] \qquad (28)$$

dissociation constants K_1, K_2, and K_3, the concentrations of the various xanthate species may be expressed in terms of the xanthate ion concentration. On substituting in eq 28, the final rate equation becomes

$$\frac{\mathrm{d}[\mathrm{ROCS_2^-}]\left\{1 + \dfrac{[\mathrm{H_3O^+}]}{K_1} + \dfrac{[\mathrm{H_3O^+}]^2}{K_1K_2} + \dfrac{[\mathrm{H_3O^+}]}{K_3}\right\}}{\mathrm{d}t} = -k_d\frac{[\mathrm{ROCS_2^-}][\mathrm{H_3O^+}]}{K_3} \qquad (29)$$

$$\frac{\mathrm{d}[\mathrm{ROCS_2^-}]}{[\mathrm{ROCS_2^-}]} = \frac{-k_d[\mathrm{H_3O^+}]}{K_3} \times \left[\frac{1}{1 + \dfrac{[\mathrm{H_3O^+}]}{K_1} + \dfrac{[\mathrm{H_3O^+}]^2}{K_1K_2} + \dfrac{[\mathrm{H_3O^+}]}{K_3}}\right]\mathrm{d}t \qquad (30)$$

On integration, the experimental rate constant k_{exp} is given by eq 31, which accounts for a maximum for k_{exp}

$$k_{\mathrm{exp}} = \frac{-k_d}{\dfrac{K_3}{[\mathrm{H_3O^+}]} + \dfrac{K_3}{K_1} + \dfrac{K_3[\mathrm{H_3O^+}]}{K_1K_2} + 1} \qquad (31)$$

at low pH (Figure 7) and has the same general form as the equation of Klein, Bosarge, and Norman[7] and of Iwasaki and Cooke.[9]

Conclusions

1. A reaction mechanism for the decomposition of xanthates in acidic solution has been given.
2. Xanthic acid is formed rapidly by an ionic reaction. The free acid is mostly insoluble in water and separates as a yellow oil. A slight water solubility is probably due to hydration.
3. At high acidity, protonated xanthic acid, formed by an addition reaction, retards the decomposition. The protonated acid has an oxonium-type structure and is water soluble. In aqueous acidic solution, the protonated acid predominates. It does not form with *t*-butyl xanthate owing to steric hindrance, and, for this compound, the decomposition is not retarded in strongly acidic solution.
4. The mechanism of decomposition is by a transxanthation with water, with the formation of an orthocarbonate as a transition complex.
5. The xanthate ion, xanthic acid, protonated xanthic acid and orthocarbonate are in pseudoequilibrium.
6. The unstable material is the product of transxanthation with water which decomposes rapidly into water and $\mathrm{CS_2}$ displacing the transxanthation reaction toward complete decomposition.

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