Kinetics and Mechanism of the Oxidation of Xanthates with Iodine in Aqueous Solution

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The kinetics of the oxidation by iodine of ethyl xanthate to dixanthogen have been investigated in aqueous solution. The results can be simply interpreted in terms of a mechanism in which $EtOCS_2I$ is formed in an initial, very rapid reaction between iodine and xanthate. $EtOCS_2I$ then reacts at a measurable rate with a further mole of xanthate to give dixanthogen, with displacement of iodine. The mechanism may be summarized as in (i) and (ii) where the

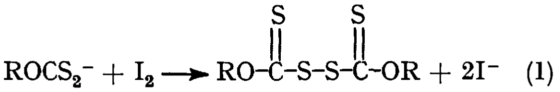
$$EtOCS_2^- + I_2(I_3^-) \overset{\text{fast}}{\rightleftharpoons} EtOCS_2I + I^-(2I^-) \qquad \text{(i)}$$

$$EtOCS_2I + EtOCS_2^- \xrightarrow{k} (EtOCS_2)_2 + I^- \qquad \text{(ii)}$$

equilibrium for reaction (i) lies far to the right, with an equilibrium constant $K \geq 10^7$ (for reaction with I_2). The second step has a rate constant k of 9.1×10^5 dm^3 mol^{-1} s^{-1} at 25 °C. An increase in iodide concentration results in a decrease in the reaction rate. Evidence is presented to suggest that this results from the formation of an adduct ($EtOCS_2I_2^-$, stability constant K_1 6.6 dm^3 mol^{-1}) between iodide and $EtOCS_2I$, rather than from the reversal of equilibrium (i). The reaction rate is also reduced in the presence of acid, and this can be quantitatively accounted for in terms of the formation of ethyl hydrogen xanthate.

THE importance of xanthates in mineral flotation and the cellulose industry has generated considerable interest in their chemical and physical properties.[1]

One of the major characteristics of xanthates is their susceptibility to oxidation, resulting in the formation of dixanthogens. In particular the oxidation of xanthates by iodine [equation (1)] is widely employed in the routine analysis of xanthates. No kinetic or mechanistic investigations of these reactions have, however, been reported.



$$ROCS_2^- + I_2 \longrightarrow RO\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}S\text{-}S\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}OR + 2I^- \qquad (1)$$

Earlier investigations [2,3] of the iodine oxidation of thiols to disulphides suggest that the initiating event in these reactions is the nucleophilic attack of the thiol (or thiolate ion) on iodine to form a sulphenyl iodide. The oxidation is then completed by an attack of thiol on sulphenyl iodide, displacing iodide and forming a disulphide (Scheme 1). An analogous mechanism has also been proposed for the oxidation of thiosulphate to tetrathionate.[4,5]

$$RS^- + I_2 \rightleftharpoons RSI + I^- \xrightarrow{RS^-} RSSR + I^-$$

SCHEME 1

In this paper we report the results of a kinetic study of the oxidation of ethyl xanthate by iodine in aqueous solutions of varying pH, and containing varying amounts of added iodide.

EXPERIMENTAL

Materials.—Ethyl potassium xanthate was prepared by the addition of carbon disulphide to a solution of potassium ethoxide in ethanol as previously described.[6] No impurities were visible in the n.m.r. spectrum of the product, and titration with iodine suggested a purity of >98%.

Stoicheiometry of the Reaction.—The stoicheiometry of the oxidation has been extensively investigated [1] and the reaction has been shown to proceed quantitatively according to equation (1).

Kinetic Measurements.—The reactions were followed spectrophotometrically by observing the decrease in absorbance at 355 nm with a Durrum–Gibson stopped-flow spectrophotometer. This wavelength corresponds to a maximum in the tri-iodide absorption spectrum. Both the xanthate ion and dixanthogen also absorb at this wavelength, but have extinction coefficients considerably lower than that of I_3^-. It was not possible under the present conditions (excess of xanthate ion) to study the reaction at wavelengths significantly shorter than 355 nm because of very strong absorption by xanthate and dixanthogen. The rate constants were reproducible to ±5% except at low iodide concentrations (<0.1M) where a scatter of *ca.* ±10% was observed. All reactions were followed over at least two and normally four half-lives. All kinetic measurements were carried out at 25 (±0.2) °C.

In all reactions, the total xanthate concentration was at least 10 times that of iodine (or tri-iodide). Initial iodine concentrations varied between 5×10^{-5} and 5×10^{-6}M. Under these conditions, there was a rapid decrease in absorbance (always too fast to measure) followed by a further, slower, first-order decrease in absorbance (D) as in equation (2). The initial rapid decrease in absorbance

$$-dD/dt = k_eD \qquad (2)$$

corresponded to between 80 and 95% of the initial absorbance due to I_2 and I_3^-, depending upon the iodide concentration (see later).

For a given concentration of iodide ion, and a fixed pH, the observed first-order rate constant, k_e, was given by equation (3), where Xa* represents the total xanthate

$$k_e = k_2[Xa^*] \qquad (3)$$

concentration (*i.e.* $[Xa^*] = [Xa^-] + [XaH]$, where Xa^- and XaH represent xanthate and xanthic acid, respectively). The magnitude of the first-order rate constant,

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[1] S. R. Rao, 'Xanthates and Related Compounds,' Marcel Dekker, New York, 1971.

[2] J. P. Danehy, B. T. Doherty, and C. P. Egan, *J. Org. Chem.*, 1971, **36**, 2525.

[3] H. Fraenkel-Conrat, *J. Biol. Chem.*, 1955, **217**, 373.

[4] A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1341.

[5] G. Dodd and R. O. Griffith, *Trans. Faraday Soc.*, 1949, **45**, 546.

[6] A. I. Vogel, 'Textbook of Practical Organic Chemistry,' Longman, London, 1970, p. 499.

k_e, was studied as a function of the total xanthate concentration, the iodide concentration, and the acid concentration.

(i) *Variation of xanthate concentration.* The reaction rates for solutions containing a variety of xanthate concentrations as well as either 0.1 or 0.4M-KI have been measured. The acid concentration was kept $<5 \times 10^{-4}$M, so that xanthate was present as the free anion (see later). The results are given in Table 1, and show k_e to be proportional to the xanthate concentration [equation (3)]. In anticipation of the later discussion, the xanthate ion concentration quoted equals the added xanthate concentration minus the initial iodine concentration.

TABLE 1

Effect of xanthate concentration [a] on the rate of oxidation of ethyl xanthate by iodine at 25 °C

	$\frac{10^5[X_a^-]}{\text{mol dm}^{-3}}$	$\frac{k_e}{\text{s}^{-1}}$	$\frac{10^{-5}k_2\,^b}{\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	
(i) [KI] = 0.1M	8.3	54.5	6.6	
	12.8	74.3	5.8	
	14.0	85.1	6.1	
	17.7	113	6.4	
	22.6	140	6.2	Average
(ii) [KI] = 0.4M	4.38	11.8	2.69	
	6.9	19.6	2.85	
	10.4	23.4	2.48	
	14.0	34.6	2.47	
	21.9	53.0	2.42	
	23.7	64.0	2.70	
	36.2	104	2.87	
	48.8	121	2.48	
			2.61	Average

[a] $[H^+] < 5 \times 10^{-4}$M, $[I_2] + [I_3^-] = 3 \times 10^{-6}$—$6 \times 10^{-6}$M
[b] $k_2 = k_e/[X_a^-]$.

(ii) *Variation of acid concentration.* The reactions were carried out in the presence of various amounts of hydrochloric acid. To avoid acid hydrolysis of ethyl xanthate,[7] the reactions were initiated by mixing solutions containing the iodine and acid with an acid-free xanthate solution. All solutions contained 0.1M-KI, and the ionic strength was maintained at 0.2M by the addition of $NaClO_4$. The results are given in Table 2.

TABLE 2

Effect of acid concentration [a] on the rate of oxidation of ethyl xanthate by iodine at 25 °C

$\frac{[\text{HCl}]}{\text{mol dm}^{-3}}$	$\frac{10^5[X^*_a]\,^b}{\text{mol dm}^{-3}}$	$\frac{k_e}{\text{s}^{-1}}$	$\frac{10^{-5}k_2\,^c}{\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}}$
0.000 5	14.0	85.1	6.08
0.005	14.0	74.7	5.34
0.01	14.0	60.2	4.30
0.02	14.0	50.6	3.61
0.04	14.0	32.6	2.33
0.06	14.0	26.7	1.91
0.08	14.0	20.7	1.48
0.10	14.0	18.2	1.30

[a] [KI] = 0.1M, ionic strength = 0.2M($NaClO_4$). [b] $[X_a^*] = [X_a^-] + [X_aH]$. [c] $k_2 = k_e/[X_a^*]$.

(iii) *Variation in iodide concentration.* The effect of iodide concentration on the reaction rate was studied, using iodide concentrations between 0.02 and 0.50M. No attempt was made to maintain constant ionic strength. However, it was found that the addition of 0.25 and 0.50M-$NaClO_4$ to the solutions containing 0.02M-KI had no measurable effect on the rate. Acid concentrations in all cases were $<5 \times 10^{-4}$M. It was noticeable that in solutions with low iodide concentrations, the initial absorbance observed on the oscilloscope was only *ca.* 5% of the initial absorbance due to I_2 and I_3^-, but that at higher KI concentrations (0.4—0.5M) it was *ca.* 20% of that due to I_2 and I_3^-. At KI concentrations below 0.02M it was not possible to determine rate constants accurately because the change in absorbance occurring during the reaction was too small. The results are given in Table 3.

TABLE 3

Effect of iodide concentration [a] on the rate of oxidation of ethyl xanthate by iodine at 25 °C

$\frac{[\text{KI}]}{\text{mol dm}^{-3}}$	$\frac{10^5[X_a^-]}{\text{mol dm}^{-3}}$	$\frac{k_e}{\text{s}^{-1}}$	$\frac{10^{-5}k_2\,^b}{\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}}$
0.02	8.7	62.2	7.15
0.06	9.5	62.6	6.59
0.10 [c]			6.2
0.16	9.5	42.8	4.51
0.20	9.5	37.2	3.92
0.24	9.5	34.5	3.63
0.32	9.5	27.4	2.88
0.32	21.5	59.8	2.78
0.40 [c]			2.61
0.50	9.5	20.5	2.16

[a] $[H^+] < 5 \times 10^{-4}$M. [b] $k_2 = k_e/[X_a^-]$. [c] Average value from Table 1.

DISCUSSION

The initial, rapid decrease in absorbance suggests that there is a fast initial reaction that either consumes most of the iodine, or converts the iodine into an intermediate having a significantly lower extinction coefficient at 355 nm than I_3^-. In the former case the slower subsequent reaction would correspond to the consumption of the remaining iodine and in the latter case to the conversion of the intermediate into the products (dixanthogen and I^-).

In the following discussion it is suggested that the results can most simply be explained in terms of a mechanism involving a rapid and quantitative conversion of iodine into an iodine xanthate (XaI) followed by attack by a further xanthate ion, liberating iodide with formation of dixanthogen (Xa_2), analogous to the mechanism earlier suggested for the oxidation of thiols [2,3] and thiosulphate.[4,5] In addition, we suggest that the observed iodide dependence of the reaction can be best explained in terms of an adduct (XaI_2^-), analogous to I_3^-, formed between XaI and I^-. The mechanism is summarized in Scheme 2.

$$Xa^- + I_2 \xrightarrow{K} XaI + I^- \qquad (4)$$

$$XaI + I^- \xrightleftharpoons{K_1} XaI_2^- \qquad (5)$$

$$XaI + Xa^- \xrightarrow{k} Xa_2 + I^- \qquad (6)$$

SCHEME 2

Equations (4) and (5) represent rapid equilibria, with the value of K in equation (4) being very large (see below), and equation (6) represents the rate-determining step of the reaction. In interpreting the results it is also necessary to consider the acid–base equilibria of the xanthate ion [8] [equation (7)] and the formation of I_3^-

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[7] C. A. Bunton, P. Ng, and L. Sepulveda, *J. Org. Chem.*, 1974, **39**, 1130.

[8] I. Iwaski and S. R. B. Cooke, *J. Phys. Chem.*, 1959, **63**, 1321.

[equation (8)]. Equations (4) and (8) could, of course, be combined and written in terms of an equilibrium between I_3^- and Xa^-.

$$XaH \overset{K_a}{\rightleftharpoons} Xa^- + H^+ \qquad (7)$$

$$I_2 + I^- \overset{K_{I_3^-}}{\rightleftharpoons} I_3^- \qquad (8)$$

It can readily be seen that the mechanism given above is in qualitative agreement with the results obtained, provided that the observed slower decrease in absorbance [equation (2)] can be identified with the conversion of XaI (and XaI_2^-) into products. Thus the rapid decrease in absorbance could be accounted for by the conversion of I_2 (and I_3^-) to XaI and XaI_2^-, and equations (6), (5), and (7), respectively, predict an increase in the rate with increasing xanthate concentration and a decrease in the rate with increasing concentration of iodide and acid. We have no spectral data for the intermediates XaI and XaI_2^- because of their short lifetimes and the above mentioned difficulty of following the reaction at wavelengths significantly below 350 nm. However, as both Xa^- and Xa_2 absorb at 355 nm, it would be surprising if XaI and XaI_2^- did not also absorb at 355 nm.

It might appear that the observed decrease in rate with increasing iodide concentration could be explained in terms of the reversal of equation (4), but it will be shown below that this would lead to an incorrect iodide dependence, and a higher than first-order dependence of the rate on xanthate concentration.

If in the presence of excess of xanthate all the iodine is converted to XaI and XaI_2^- [equations (4) and (5)], then the mechanism represented in Scheme 2 leads to the rate law given in equation (9). In equation (9),

$$-\frac{d[I_2^*]}{dt} = k\left\{\frac{1}{1 + K_1[I^-]}\right\}\left\{\frac{1}{1 + [H^+]/K_a}\right\}[Xa^*][I_2^*] \qquad (9)$$

[Xa*] represents the total xanthate concentration ($[Xa^-] + [XaH]$) as defined above, and $[I_2^*]$ the total iodine concentration ($[I_2^*] = [XaI] + [XaI_2^-]$). The equilibrium constants K_1 and K_a are defined by equations (10) and (11). Equation (9) may be identified with the

$$K_1 = [XaI_2^-]/[XaI][I^-] \qquad (10)$$

$$K_a = [H^+][Xa^-]/[XaH] \qquad (11)$$

experimentally observed equations (2) and (3) with k_2 given by equation (12), if the absorbance D results from XaI and XaI_2^-.

$$k_2 = k\left\{\frac{1}{1 + K_1[I^-]}\right\}\left\{\frac{1}{1 + [H^+]/K_a}\right\} \qquad (12)$$

The results in Table 1 are clearly consistent with equation (12), as at constant iodide concentration and low acid concentration ($[H^+] \ll K_a$), k_2 should be independent of xanthate concentration as observed. The results in Table 2 correspond to a series of reactions with constant iodide concentration (0.1M) and varying acid concentration. Under these conditions, equation (12) reduces to (13), where $k' = k/(1 + 0.1\ K_1)$. Thus a

$$k_2 = k'/(1 + [H^+]/K_a) \qquad (13)$$

plot of $1/k_2$ against $[H^+]$ should give a straight line of slope $1/k'K_a$ and intercept $1/k'$. Such a plot, using the data in Table 2, is shown in Figure 1. From the slope and intercept of this plot values of $k' = 6.13 \times 10^5$ dm^3 mol^{-1} s^{-1} and $K_a = 0.026$ mol dm^{-3} were found. This latter value represents the acid dissociation constant of ethyl hydrogen xanthate at an ionic strength of 0.2M, corresponding to a value at zero ionic strength of K_a^T 0.015. Earlier reported values[8] of K_a (ethyl hydrogen xanthate) vary between 0.02 and 0.03 (ionic strength variable). The agreement is probably satisfactory as, because of the rapid decomposition of xanthates in solutions where they are appreciably protonated,[7] earlier values have come from an analysis of the pH dependence of the rate of acid-catalysed decomposition of ethyl xanthate.

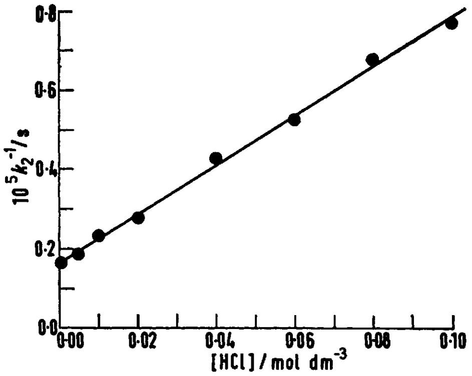

FIGURE 1 Effect of acid concentration on the rate of oxidation of ethyl xanthate by iodine at 25 °C

In solutions of low acid concentration ($[H^+] \ll K_a$), equation (12) reduces to (14). Values of k, the second-

$$k_2 = k/(1 + K_1[I^-]) \qquad (14)$$

order rate constant for reaction between XaI and Xa^-, and the equilibrium constant K_1, may be determined as above from a plot of $1/k_2$ against $[I^-]$. Such a plot, using the results in Table 3, is shown in Figure 2. From this plot, values of $k = 9.1 \times 10^5$ dm^3 mol^{-1} s^{-1} and $K_1 = 6.6$ dm^3 mol^{-1} were obtained. The stability constant K_1 for formation of XaI_2^- from XaI is considerably lower than that for the formation of I_3^- from I_2 ($K_{I_3^-}$ 710 dm^3 mol^{-1}),[9] but is nevertheless quite significant. It may be noted that an analogous compound (HOI_2^-) is thought to occur as an intermediate in the alkaline hydrolysis of I_2.[10]

It can be seen that the mechanism proposed, including the proviso that equilibrium (4) must lie far to

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[8] J. Awtrey and D. Connick, *J. Amer. Chem. Soc.*, 1951, **73**, 1842.

[10] C. S. G. Phillips and R. J. P. Williams, 'Inorganic Chemistry,' Oxford, University Press, Oxford, **1965**, ch. 12.

the right even under conditions of high [I$^-$] and low [Xa$^-$], is in qualitative and quantitative agreement with the results. However, a plausible alternative within the same general mechanistic scheme is that, under the conditions studied, reaction (4) is reversible to a considerable extent and that the slower rates and higher initial absorbances observed in solutions of high iodide concentration may result from a smaller fraction of the available iodine ($I_2 + I_3^-$) being converted to XaI. This is shown in Scheme 3 where the pre-equilibrium has been written in terms of Xa$^-$ and I_3^- (under the present conditions where [I$^-$] $\geq$ 0.02M, [I_3^-] $\gg$ [I_2]). This leads, in the absence of added acid, to the rate law shown in equation (16), where [I_2*] (= [I_3^-] + [XaI]) again represents the total iodine concentration. This rate law, however, is not consistent with the results obtained, since k_2 as defined by equations (2) and (3) would then be given by equation (17). This equation predicts that $1/k_2$ should be linearly related to $[I^-]^2$ rather than [I$^-$], and furthermore that k_2 should increase with increasing [Xa$^-$]. The results in Table 1 show that even at [I$^-$] 0.4M where a significant rate reduction is observed, k_2 is independent of xanthate concentration.

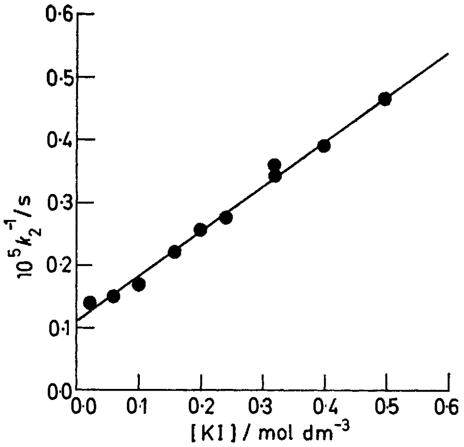

FIGURE 2 Effect of iodide concentration on the rate of oxidation of ethyl xanthate by iodine at 25 °C

$$\text{Xa}^- - \text{I}_3^- \underset{}{\overset{K_2}{\rightleftharpoons}} \text{XaI} + 2\text{I}^- \qquad (15)$$

$$\text{XaI} + \text{Xa}^- \xrightarrow{k} \text{Xa}_2 + \text{I}^-$$

SCHEME 3

$$\frac{-\text{d}[\text{I}_2^*]}{\text{d}t} = \frac{kK_2[\text{Xa}^-]^2[\text{I}_2^*]}{K_2[\text{Xa}^-] + [\text{I}^-]^2} \qquad (16)$$

$$k_2 = kK_2[\text{Xa}^-]/(K_2[\text{Xa}^-] + [\text{I}^-]^2) \qquad (17)$$

We were unable to determine the equilibrium constant K for reaction (4), but it is possible to set a lower limit to its value. Assuming that under the most extreme conditions ([I$^-$] 0.4M, [Xa$^-$] 4 × 10^{-5}M), at least 90% of I_3^- was converted to XaI, the value of K_2 in equation (15) must be at least 2 × 10^4 mol dm^{-3}. This then corresponds (using $K_{I_3^-}$ 710) to a value of $K \geq 10^7$.

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