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Acid Decomposition of Metal Xanthate Complexes and Their Stability Constants

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The formation of 1 : 1 complexes was confirmed by means of the kinetic method. The acid decomposition of xanthate was delayed by the addition of metal ions because of the decrease in the concentration of ethyl xanthic acid in an equilibrium. By using the rate equation, the stability constants were found to be $(1.0\pm0.2)\times10^4$, $(1.7\pm0.4)\times10$ and $(2.5\pm0.4)\times10^4$ for $Cd(EX)^+$, $Zn(EX)^+$, and $Pb(EX)^+$ respectively.

The behavior of xanthates in solutions has been the subject of numerous investigations because of the complexity of the system.[1-6] Alkali metal xanthates are especially known to be quite unstable in an acidic aqueous solution. This instability of xanthates presents a problem both in research and in the plant operation of mineral flotation with reference to the actual concentration of xanthates remaining in the pulp solution.

The acid decomposition of xanthates has been studied by several investigators. By using a UV spectrophotometer, Iwasaki and Cooke[1] were led to an important implication as to the mechanism of the acid decomposition in the low pH range, where the decomposition is extremely rapid. Majima[2] obtained the same results by using a UV spectrophotometer.

However, there have not yet been any reports that metal ions in the pulps of mineral flotation affect the acid decomposition of xanthate, which is also present in the solution. It should be emphasized that the plant operation of mineral flotation is not conducted in pure water but in

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1) I. Iwasaki and S. R. B. Cooke, a) *J. Am. Chem. Soc.*, **80**, 285 (1958); b) *J. Phys. Chem.*, **63**, 1321 (1959); c) *ibid.*, **68**, 2031 (1964).

2) H. Majima, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **13**, 183 (1961).

3) A. Pomianowski and J. Leja, *Can. J. Chem.*, **46**, 2219 (1963).

4) E. Klein, J. K. Bosarge and I. Norman, *J. Phys. Chem.*, **64**, 1666 (1960).

5) a) C. V. King and E. Dublon, *J. Am. Chem. Soc.*, **54**, 2177 (1932). b) A. Chatenever and C. V. King, *ibid.*, **71**, 3587 (1949). c) M. L. Schochet and C. V. King, *ibid.*, **77**, 4745 (1955).

6) M. A. Cook and J. C. Nixon, *J. Phys. Chem.*, **54**, 445 (1950).

solution, and that the products obtained from xanthate ions with metal ions probably affect the flotation behavior also.

The present paper will show that such metal ions as cadmium, lead, and zinc delay the acid decomposition of potassium ethyl xanthate (KEX) in the low pH range. The reaction can be quantitatively explained by the complex formation between metal ions and the ethyl xanthate ion (EX^-) prior to the rate-determining step.

Experimental

Materials. The KEX and metal perchlorates were prepared and recrystallized by the usual method. All the other chemicals were of a guaranteed grade and were used without further purification. The sodium acetate-acetic acid buffers were prepared by mixing a solution of sodium carbonate and acetic acid.

Procedure. The kinetic measurements were made in 0.2 M buffer solutions or in a concentrated perchloric acid solution. The ionic strength was adjusted to 1.0 with sodium perchlorate through all the measurements. The KEX was dissolved in a dilute sodium hydroxide solution (pH 10—11) to prevent the solution from any acid decomposition before measurements started; then the solution was pipetted into 100 m*l* measuring flasks in which metal ions, sodium perchlorate and sodium acetate-acetic acid buffers or perchloric acid had previously been placed, and the flasks were kept in a thermostat at the temperature of 25°C. The sample solution was then transferred quickly to a quartz absorption cell.

The decomposition of EX^- is easily influenced by the temperature of the solutions,[1-c)] so the cell chamber was kept at 25°C by means of a thermostating water jacket.

The decomposition rates were determined by following the absorbance at 301 mμ or 270 mμ employing a Shimadzu Model QR-50 spectrophotometer.

A Toa Model HM-5A pH meter was used for the pH measurements.

Results and Discussion

KEX is readily soluble in water. On dissolving, KEX is dissociated into K^+ and EX^-. Under some conditions, EX^- can be hydrolyzed. Hydrolysis will lead to the formation of xanthic acid:

$$\text{R-O-C(S)S}^- + \mathrm{H_2O} \rightleftarrows \text{R-O-C(S)SH} + \mathrm{HO^-} \qquad (\mathrm{R}=\mathrm{C_2H_5}) \quad (1)$$

Such a reaction involving ionic combination is known to be extremely rapid.[7)] Xanthic acids are very unstable compounds and decompose rapidly into carbon disulfide and alcohols:

$$\text{R-O-C(S)SH} \rightarrow \mathrm{CS_2} + \mathrm{ROH} \quad (2)$$

The hydrolysis of xanthate anios occurs much faster than does the decomposition of xanthic acid. Consequently, the rate of decomposition depends on the concentration of xanthic acid alone, and anything which affects the hydrolysis of the xanthate anion, such as the concentration of hydrogen ions and metal ions, affects the concentration of xanthic acid in equilibria.

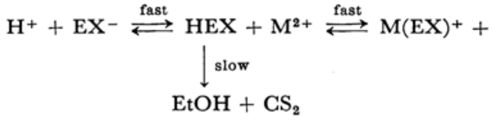
The decomposition rate equation was obtained by Iwasaki and Cooke[1)] spectrophotometrically as follows:

$$\begin{aligned} \mathrm{d}[\mathrm{EX^-}]_t/\mathrm{d}t &= -k_3[\mathrm{HEX}] \\ &= -k_3[\mathrm{EX^-}]_t/(1+K_a/[\mathrm{H^+}]) \equiv -k_{\mathrm{H}}[\mathrm{EX^-}]_t \end{aligned} \quad (3)$$

where $[\mathrm{EX^-}]_t$ means the total concentration of the ethyl xanthate species, $[\mathrm{EX^-}]_t=[\mathrm{HEX}]+[\mathrm{EX^-}]$, K_a is a dissociation constant of HEX, and k_3 express a monomolecular decomposition rate constant.

The formation of species other than EX^- and HEX results in a decrease of the concentration of HEX in equilibrium.

By assuming the formation of a stable and water-soluble metal xanthate complex ion, $\mathrm{M(EX)^+}$, in place of a insoluble metal xanthate, $\mathrm{M(EX)_2}$, in the presence of an excess of metal ions, the decomposition rate equation can be expressed as follows:



$$\begin{array}{c} \mathrm{H^+ + EX^-} \overset{\text{fast}}{\rightleftarrows} \mathrm{HEX + M^{2+}} \overset{\text{fast}}{\rightleftarrows} \mathrm{M(EX)^+ + H^+} \\ \big\downarrow \text{slow} \\ \mathrm{EtOH + CS_2} \end{array}$$

(4)

Since the absorbance at a given wavelength measures the total concentration of EX^-, HEX, and $\mathrm{M(EX)^+}$, the decomposition rate may be expressed as follows:

$$\begin{aligned} &\mathrm{d}[\mathrm{EX^-}]/\mathrm{d}t + \mathrm{d}[\mathrm{HEX}]/\mathrm{d}t + \mathrm{d}[\mathrm{M(EX)^+}]/\mathrm{d}t \\ &\quad = \mathrm{d}([\mathrm{EX^-}] + [\mathrm{HEX}] + [\mathrm{M(EX)^+}])/\mathrm{d}t \\ &\quad = -k_3[\mathrm{HEX}] \end{aligned} \quad (5)$$

By using the dissociation constant of HEX, K_a, and the stability constant of the metal xanthate ion, K_1, Eq. (5) can be rewritten in terms of the total concentration of ethyl xanthate species:

$$\begin{aligned} \mathrm{d}[\mathrm{EX^-}]_t/\mathrm{d}t &= -k_3[\mathrm{HEX}] \\ &= -k_3[\mathrm{EX^-}]_t/(K_a/[\mathrm{H^+}]+1 \\ &\quad + K_1\cdot K_a\cdot[\mathrm{M^{2+}}]/[\mathrm{H^+}]) \equiv -k_{\mathrm{M}}[\mathrm{EX^-}]_t. \end{aligned} \quad (6)$$

or $-\mathrm{d}\ln[\mathrm{EX^-}]_t/\mathrm{d}t$

$$= k_3/(K_a/[\mathrm{H^+}] + 1 + K_1\cdot K_a\cdot[\mathrm{M^{2+}}]/[\mathrm{H^+}]) \equiv k_{\mathrm{M}}. \quad (7)$$

were $K_1=[\mathrm{M(EX)^+}]/[\mathrm{M^{2+}}][\mathrm{EX^-}]$

Upon integrating, we have:

$$\begin{aligned} &\log([\mathrm{EX^-}]_{t_1}/[\mathrm{EX^-}]_{t_2}) \\ &\quad = \log(\text{absorbance, } d_1)/(\text{absorbance, } d_2) \\ &\quad = k_{\mathrm{M}}(t_2-t_1)/2.303 \end{aligned} \quad (8)$$

Generally, the absorbance for ternary components is represented as follows:

$$d = \varepsilon_{\mathrm{EX^-}}[\mathrm{EX^-}] + \varepsilon_{\mathrm{HEX}}[\mathrm{HEX}] + \varepsilon_{\mathrm{M(EX)^+}}[\mathrm{M(EX)^+}] \quad (9)$$

where $\varepsilon_{\mathrm{EX^-}}$, $\varepsilon_{\mathrm{HEX}}$, and $\varepsilon_{\mathrm{M(EX)^+}}$ are the molar extinction coefficents of the ethyl xanthate ion, ethyl

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[7)] M. Eigen, *Discussions Faraday Soc.*, **17**, 194 (1954).

xanthic acid, and the complex ion respectively. The absorption of the metal ion is negligibly small at any given wavelength. In the $\mathrm{pH}>1+\mathrm{p}K_a$ range, in which the $\mathrm{p}K_a$ is that of HEX ($\mathrm{p}K_a=1.34$),[8] scarcely any undissociated xanthic acid remains in the solution; therefore, the second term in Eq. (9) is negligibly small and the equation may be written as follows:

$$d=\varepsilon_{\mathrm{EX}^-}[\mathrm{EX}^-]+\varepsilon_{\mathrm{M(EX)}^+}[\mathrm{M(EX)}^+]. \tag{10}$$

Ethyl xanthic acid is known[3] to have an absorption maximum at 270 mμ ($\varepsilon=10670$), and the spectrum recorded shows only a weak absorption at 301 mμ ($\varepsilon=117$). As has been shown in a previous paper,[9] almost all the spectra have an absorption near 300 mμ. Bearing the above facts in mind, the absorbance at 301 mμ may, therefore, be attributed to the total of all the xanthate species except HEX in the high pH range, and the constants for the apparent pseudo first-order rates, k_H and k_M, can easily be obtained from the slope of the logarithm of the absorbance against the time by using Eq. (8). The measurements were made under the conditions of $[\mathrm{EX}^-]_t \ll [\mathrm{M}^{2+}]_t$ and $[\mathrm{EX}^-]_t \ll [\mathrm{H}^+]_t$, for which $[\mathrm{H}^+]$ and $[\mathrm{M}^{2+}]$ were kept constant during the decomposition. When a sodium acetate - acetic acid buffer is used to adjust the pH values, $[\mathrm{M}^{2+}]$ is given approximately as follows, taking the formation of acetatometal complexes into consideration:

$$[\mathrm{M}^{2+}]=[\mathrm{M}^{2+}]_t/(1+K_{\mathrm{MOAc}}\cdot[\mathrm{OAc}^-]), \tag{11}$$

in which K_{MOAc} represents the stability constants of acetate complexes.[10,11]

Decomposition in the Presence of an Excess of Cadmium Ions. The absorption spectra of the aqueous solutions of KEX in the presence and in the absence of an excess of cadmium(II) ions were given in a previous paper.[9] The change in the absorption spectra during the acid decomposition in the presence of an excess of cadmium(II) ions is shown in Fig. 1. As can be seen in Fig. 1, an isosbestic point was observed at 216 mμ. There was also a new band at 206 mμ which appeared when recording was done seprately in the higher-frequence region of the spectra. Carbon disulfide is known to absorb at this wavelength. This indicates that

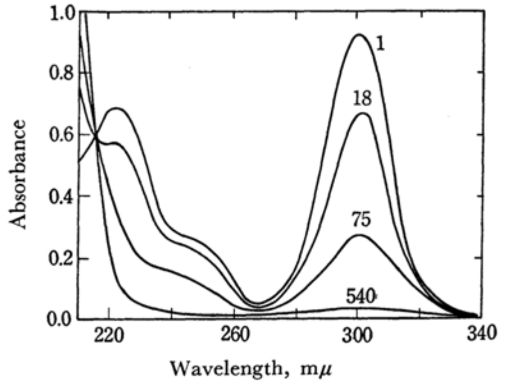

Fig. 1. Absorption spectra of KEX solution (4.32×10^{-5} M), decomposing in the presence of $\mathrm{CdSO_4}$ (3.40×10^{-4} M) at pH 0.7. Figures on the curves indicate the standing time of sample solutions in minutes.

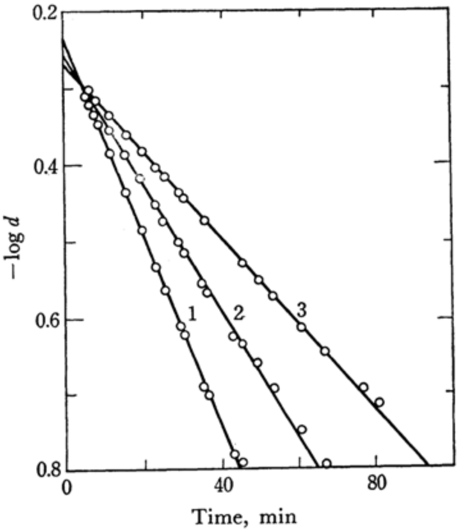

Fig. 2. First order rate plots of an acid decomposition of KEX solution (4.12×10^{-5} M) in the presence of 1) 1.43×10^{-4} M, 2) 2.85×10^{-4} M and 3) 4.75×10^{-4} M of $\mathrm{CdSO_4}$ at pH 3.1.

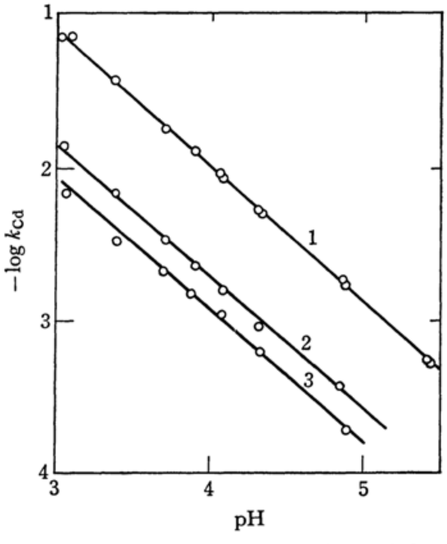

Fig. 3. Relation of pH with $\log k_\mathrm{H}$ and $\log k_{\mathrm{Cd}}$ in the presence of 0.2 M acetate buffer and 1) 0, 2) 4.8×10^{-4} M, and 3) 9.5×10^{-4} M of Cd(II) ion.*

* Cd(II) ion concentration was kept constant taking the formation of $\mathrm{Cd(OAc)^+}$ ion at various pH ranges in consideration.

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[8] B. Toernell, *Svensk Paperstidn,* **69**, 658 (1966); *Chem. Abstr.,* **66**, 37303 g.

[9] M. Nanjo and T. Yamasaki, This Bulletin, **42**, 968 (1969).

the isosbestic point arises from the formation of carbon disulfide and from the decomposition of ethyl xanthate species, and that no other side reactions covered in Eq. (4) occur.

There was no reverse reaction after the decomposition was completed under the conditions employed. Examinations were made at pH 3—5. The first-order plots are given in Fig. 2, the slope may be seen to have been influenced by the pH and by the concentration of cadmium(II) ions. The values of k_H and k_{Cd} were determined from Fig. 2, and the logarithms of k_H and k_{Cd} were plotted against pH (Fig. 3). As can be seen from Fig 3, the slope of the line of k_H was determined to be -0.92, and that of $\log k_3/K_a$, to be 1.69. The slope of k_M was also given as -0.92 at various concentrations of cadmium(II) ions.

These relations demonstrate that our initial assumption of the decomposition mechanism (Eq. (4)) is essentially reasonable; K_1 was also determined to be 1.0×10^4 by using Eq. (12), which was derived from Eqs. (3) and (6) under the condition of $\mathrm{p}K_a<\mathrm{pH}$:

$$(k_H/k_M)-1=[M^{2+}]\cdot K_1, \tag{12}$$

and $[M^{2+}]$ is calculated by Eq. (11).

In a 0.2M acetate buffer solution, $CdOAc^+$ is the predominant species formed by the reaction of cadmium(II) and acetate ions,[10] $(K_{CdOAc^+}=10)$.[11]

Decomposition in the Presence of an Excess of Zinc(II) Ions. The absorption spectra of the zinc(II) complex was given in a previous paper.[9] The isosbestic point was found at 216 mμ by the acid decomposition, and nearly the same plots were obtained as those shown in Fig. 3; this indicates a complex formation between zinc(II) and EX^-. The slope of k_{Zn} was determined to be -0.99 (Fig. 4). The zinc(II) ion is less effective in decreasing the decomposition rate than the cadmium(II) ion, which shows that $Zn(EX)^+$ is a less stable ion than that of cadmium.

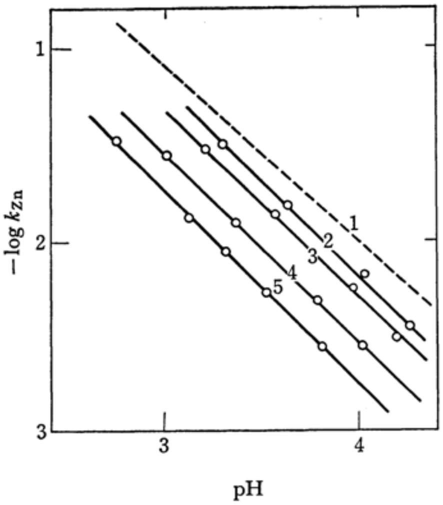

Fig. 4. Relation of pH with $\log k_{Zn}$ in the presence of 0.2 M of acetate buffer and 1) 0, 2) 3.21×10^{-2} M, 3) 6.42×10^{-2} M, 4) 1.61×10^{-1} M and 5) 3.21×10^{-1} M of $Zn(ClO_4)_2$.

Decomposition in the Presence of an Excess of Lead(II) ions. The absorption spectra of the lead(II) complex has also been presented in a previous paper[9]; they differed markedly from those of cadmium and zinc. Therefore, kinetic measurements were conducted in highly concentrated solutions of lead(II) ion and perchloric acid in order to avoid the precipitation of $Pb(EX)_2$ and to get the proper conditions for carring out the examinations. In the very low pH range, the formation of HEX should be taken into consideration, so the absorption bands at 270 mμ and 301 mμ were used separately to plot the first-order lines. The resulting values k_{Pb} were the same. This indicates that the absorption spectra are due to the complex ion, which is a very stable ions. The relation between $\log k_{Pb}$ and $\log[Pb^{2+}]_t$ is shown in Fig. 5. The relation between $\log k_{Pb}$ and $\log [H^+]_{add}$ is also represented in Fig. 6, which is derived from Fig. 5. From Figs. 5 and 6, the slopes were determined to be -1.2 and -0.8—-1.0 respectively. These values indicate that, under the present experimental conditions, the

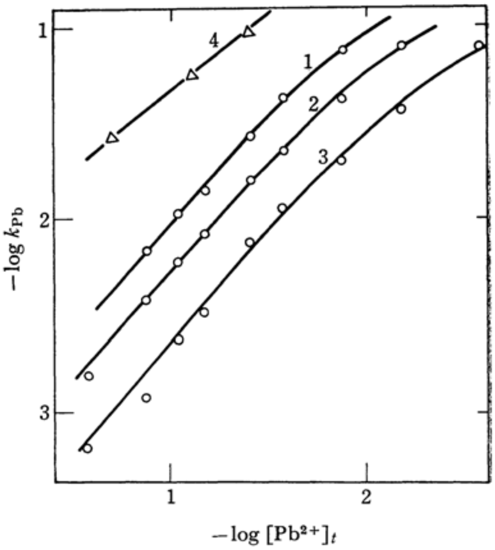

Fig. 5. Relation of $\log[Pb^{2+}]_t$ with $\log k_{Pb}$ in the presence of 1) 5.24×10^{-1} M, 2) 3.00×10^{-1} M and 3) 1.20×10^{-1} M of $HClO_4$.
Curve 4) shows the relation of $\log[Cd^{2+}]_t$ with k_{Cd} in the presence of 3.00×10^{-1} M of $HClO_4$ for the comparison with the curve 2).

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[10] N. Tanaka and K. Kato, This Bulletin, **33**, 417, 1412 (1960).

[11] I. Szilard, Dissertation, ETH, Zürich.

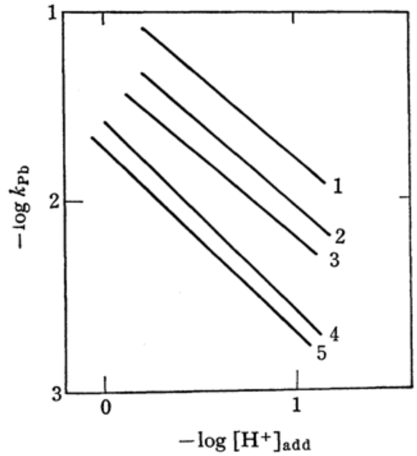

Fig. 6. Relation of $\log [H^+]_{add}$ with $\log k_{Pb}$ in the presence of 1) 1.34×10^{-2} M, 2) 2.68×10^{-2} M, 3) 4.02×10^{-2} M, 4) 6.70×10^{-2} M and 5) 9.38×10^{-2} M of $Pb(ClO_4)_2$.

formation of the complex is the predominant reaction and that the third term of the denominator of Eq. (6), $[M^{2+}]\cdot K_1\cdot K_a/[H^+]$, is larger than the other terms.

In the case of cadmium(II) and zinc(II), the relations between $\log k_M$ and $\log [M^{2+}]$ are not of the first order. They show that the curves are the same as those in Fig. 5 when there is a low concentration of lead(II) ions.

By using Eq. (7), K_1 was calculated from Fig. 5 to be 2.5×10^4; this indicates that the ethylxanthogenatolead(II) complex is more stable than the cadmium(II) complex.

These results are summarized in Table 1. The K_1 values calculated by the kinetic method are in good agreement with those by the spectroscopic method.[9]

TABLE 1. STABILITY CONSTANTS OF 1:1 COMPLEXES 25°C, $\mu=1(NaClO_4)$

Metal ion	K_1
Pb(II)	$(2.5\pm0.4)\times10^4$
Cd(II)	$(1.0\pm0.2)\times10^4$
Zn(II)	$(1.7\pm0.4)\times10$

The kinetic method is especially useful when the equilibrium method cannot be applied because of the formation of such hydroxides as $Pb(OH)_2$ and $Zn(OH)_2$ in a neutral pH range. Thus, the formation of 1 : 1 complexes is established.

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