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Fundamental Studies on the Collection of Sulphide Minerals with Xanthic Acids. I
On the Dissociation and Decomposition of Xanthic Aicds*

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Synopsis

The dissociation constants of xanthic acids and the rates of decomposition of xanthic ions in acidified aqueous solutions were determined by spectrophotometric measurements. It was found that xanthic ion and xanthic acid are virtually in equilibrium, and that the dissociation constants of methyl-, ethyl, propyl-, butyl-, amyl-, iso-propyl-, and iso-butylxanthic acids are respectively 3.4×10^{-2}, 2.9×10^{-2}, 2.5×10^{-2}, 2.3×10^{-2}, 1.9×10^{-2}, 2.0×10^{-2}, and 1.4×10^{-2} at 25°C and the ionic strength of 0. The instability of xanthic ion in acidic range is due to the bimoleucular decomposition of xanthic ion and hydrogen ion. The rate constants of decomposition of methyl-, ethyl-, propyl-, amyl-, iso-propyl-, and iso-butylxanthic ions are respectively 233, 226, 214, 209, 211, 207, and 202 $\text{mole}^{-1}\text{min}^{-1}$ at 25°C and the ionic strength of 0. The dissociation constants of these xanthic acids and the rate constants of these xanthic ions decreased the increase in carbon numbers of these alkyl groups, and iso-isomer has smaller values of these constants than those of normal ones. Furthermore, it was shown that the peak of absorption spectrum of xanthic ion is at 301 mμ and that of xanthic acid at 270 mμ.

I. Introduction

It is very important, both in research and in plant operation, to be well aware of the actual concentration of xanthic ion present in the pulp solution of xanthate flotation. Nevertheless, few fundamental studies had been made on the dissociation and the decomposition of xanthate. The only one was made by Cook and Nixon(1). Several studies on the dissociation and the stability of xanthic acids have been reported in the past. Von Halban and his collaborators(2),(3) are the earleist investigators of this problem. The rates of decomposition of methyl- and ethylxanthic acids in organic solvents with regard to the temperature and the polarity of solvents were studied in detail by von Halban and Kirsch(2). Von Halban and Hecht(3) made an extensive study of the stability of xanthic acids in aqueous solutions. They attempted to follow the decomposition by analyzing

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

(2) H. von Halban und A. Kirsch, Z. physik. Chem., **32** (1913), 325.

(3) H. von Halban und W. Hecht, Z. Elektrochem., **24** (1918), 24.

xanthate with the aid of jodometry. King and Dublon(4) measured the decomposition rate from the increase in vapor pressure, due primarily to the formation of carbon disulfide, and analyzed the salt effects. Further they analyzed the experimental results of von Halban et al., and pointed out that the values of decomposition rate of methyl- and ethylxanthic acids, given by von Halban et al., correspond to those at the ionic strength of 0. King and his associates(5),(6) continued their studies from a thermodynamical point of view. Cook and Nixon(1) determined the decomposition constant of xanthic acid by measuring pH at different time intervals. But pH titration method adapted by them seems to be unreliable on account of considerably violent decomposition of xanthic acid at the pK point of dissociation. Mukai(7) measured the optical density at the wave length of 300 mμ and discussed the stability of amylxanthate in acidic solution. Recently Iwasaki and Cooke(8) made a kinetic study of the decomposition of xanthate using spectrophotmetric method, and evaluated the dissociation constant and the rate constant of instability. Hantzsch and Bucirius(9) measured the electric conductivity and determined the dissociation constant of ethylxanthic acid. Komagata(10) discussed the relation between the concentration and the degree of dissociation of xanthate from the conductivity measurements.

As King et al. had pointed out, suitable methods for measuring the decomposition rates accurately had not been found for a long time. Therefore, no systematic study has been reported so far.

In the present work the dissociation of xanthic acids and the decomposition of those xanthic ions in acidified aqueous solution were studied systematically by means of a spectrophotometric methods in ultraviolet range. The purpose of this work was to obtain the dissociation constants and the rate constants of decomposition of xanthates and to offer the fundamental data on the flotation collection of sulphide minerals with xanthic acids.

II. Experimental apparatus and procedure

The measurement of the decomposition rate was based upon light absorption at the wave length of 301 mμ, characteristic of xanthic ion. The absorption spectrum of alkali xanthate had been measured first by Hantzsch and Scharf(11), and thereafter by Delépine and Compin(12), Atsuki and Takada(13), Hagihara(14),

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(4) C.V. King and E. Dublon, J. Am. Chem. Soc., **54** (1939), 2177.
(5) A. Chatenever and C.V. King, J. Am. Chem. Soc., **77** (1955), 3587.
(6) M.L. Schocket and C.V. King, J. Am. Chem. Soc., **77** (1955), 4745.
(7) S. Mukai, Reports Res. Inst. Sci. Ind., Kyushu Univ., No. 17 (1955), 47.
(8) I. Iwasaki and S.R.B. Cooke, J. Am. Chem. Soc., **80** (1958), 285.
(9) A. Hantzsch und W. Bucirius, Ber., **59** (1920), 793.
(10) S. Komagata, Rept. 13th Special Commitee on Flotation, No. 2 (1943), 17.
(11) A. Hantzsch, Ber., **46** (1913), 3570.
(12) M. Delépine and L. Compin, Bull. soc. chim. France, **27** (1920), 469 ; C.A. 14, 3368.
(13) K. Atsuki and T. Takada, J. Chem. Soc. Japan, Ind. Chem. Sect., **43** (1940), 868.
(14) H. Hagihara, Bull. Kobayashi Inst. Phys. Research, Japan, **4** (1954), 30.

Mukai(7), Bushell and Malnarich(15),(16), Wada and his collaborators(17), and Iwasaki and Cooke(18). The light absorption peak at the wave length of 301 mμ of xanthate is very sharp, serving as a convenient basis for the colorimetric analysis of substance.

In the present work, Hitachi EPU-2 Photoelectric Spectrophotometer with 1 cm path-length quartz cuvette was used for optical density measurements. The calibaration of the wave length was carried out by using Toshiba SHL-100UV Ultra High-pressure Mercury Lamp. Decomposition of xanthate is easily influenced by the temperature of solution, so water at constant temperature was sent around the cell chamber of spectrophotometer to keep the temperature (25°C) constant during the optical density measurements. The experimental procedure for the decomposition rate consisted of mixing xanthate solution with a known quantity of hydrochloric acid, transferring the mixture to an absorption cell and measuring the optical density of the solution at suitable time intervals. In all the experiments mixing was achieved by mutual shaking in a 200 ml stoppered Ehrenmyer flask. Ninety-nine ml of solution contained known quantities of hydrochloric acid and potassium chloride was added to a flask and kept in thermostat at 25°C. One ml of xanthate solution was added to the flask agitating vigorously with a magnetic stirrer and agitation was continued for 15 seconds. The resulting solution was transferred to a quartz cuvette and the optical density was recorded at suitable time intervals. While performing experiments, special attention was paid to rapid and uniform mixing of xanthate with hydrochloric acid and potassium chloride, to keeping the constant temperature, and to accurate measuring of the optical density. The same composition solution without xanthate was used as a reference.

In all the experiments, the concentration of xanthate was kept at 2×10^{-4} mole/l and the pH values was adjusted at 2.00 and 2.20. When the experimental conditions were fixed as above, it is possible to keep the concentration variation in hydrogen ion within 2 per cent.

Potassium xanthates were prepared by recrystalizing samples from acetone solutions, synthesized according to the usual manner in the laboratory. Recrystalization was repeated 3 times by acetone-petroleum ether method. The cyrstals of pure xanthates were sucked dry and further dried over silica gel, and stored at a dark and cool place. Xanthate crystals, passed more than 3 days after recrystalized, were recrystalized. The xanthate solution was prepared each time the experiment was performed. Water was purified by using ion-exchange resin, and was redistilled, and then it was boiled for 10 minutes. Aqueous xanthate solution was stored in a stoppered amber-coloured bottle and was rejected when it expired more than 3 hours after preparation.

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(15) C.H.G. Bushell and M. Malnarich, Am. Inst. Mining Met. Engrs., Tech. Publ. No. **4235**B (in Mining Eng., 8) (1956), 734.

(16) C.H.G. Bushell, Trans. Can. Inst. Mining Met. **61** (1958), 65.

(17) M. Wada, H. Majima, T. Hashimoto, S. Koseki, Y. Suzuki, and N. Miyamoto, Bull. Res. Inst. Min. Dress. Met., Tohoku Univ., **13** (1957), 31.

(18) I. Iwasaki and S. R. B. Cooke, Mining Eng., **9** (1957), 1267.

III. Experimental results

The absorption spectra of the aqueous solution of potassium ethylxanthate are shown in Fig 1. The wave lengths of the absorption maxima were 226 mμ and 301 mμ. Besides, a very feeble absorption peak was observed at 380 mμ,. The molar extinction coefficients were 8,780 at 226 mμ, 17,460 at 301 mμ, and 52 at 380 mμ. Other potassium xanthates had the same absorption peaks as potassium ethylxanthate. The data on the absorption maxima are summarized in Table 2. The last column in the table shows the ratio of the molar extinction

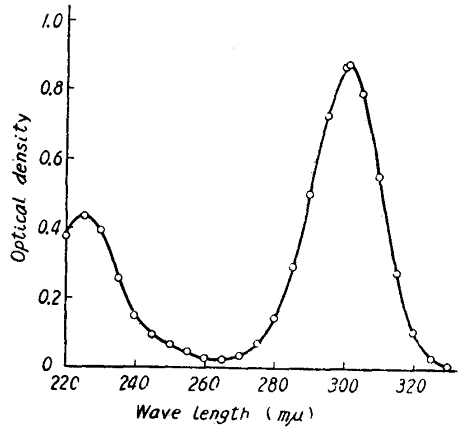

Fig. 1. Absorption spectra of potassium ethylxanthate.
$C_2H_5OCS_2K$: 5×10^{-1} mole/l, pH : 7

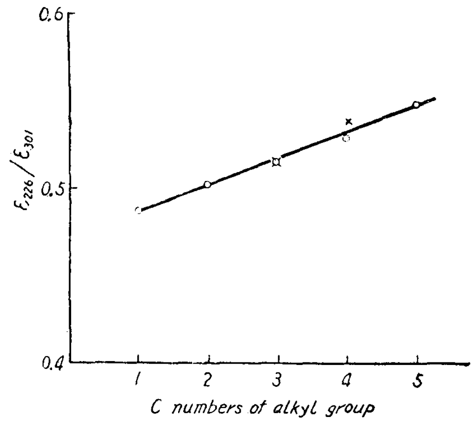

Fig. 2. Relationship between the carbon numbers of alkyl group and the ratio of molar extinction coefficients at 226 mμ and 301 mμ of xanthate.
o n-xanthate × iso-xanthate

Table 1. Calibration of the wave length of spectrophotometer.

Wave length of spectrum (mμ)	Reading of dial (mμ)	Deviation (mμ)
253.6	253.6	0
302.2	302.4	+ 0.2
334.1	334.2	+ 0.1
365.0	365.1	+ 0.1
404.7	405.0	+ 0.3
435.8	436.0	+ 0.2
546.1	546.2	+ 0.1

Table 2. Molar extinction coefficients of xanthates in aqueous solution.

Species of potassium xanthates	Molar extinction coefficient (ε_λ)			Ratio of ε_{226} to ε_{301} ($\varepsilon_{226}/\varepsilon_{301}$)
	λ=226 mμ	λ=301 mμ	λ=380 mμ	
Methyl-	8,250	16,950	51	0.487
Ethyl-	8,780	17,460	54	0.503
Propyl-	8,900	17,270	53	0.516
iso-Propyl-	8,430	16,400	48	0.514
Butyl-	10,140	19,170	60	0.529
iso-Butyl-	8,920	16,540	51	0.539
Amyl-	9,070	16,830	53	0.549

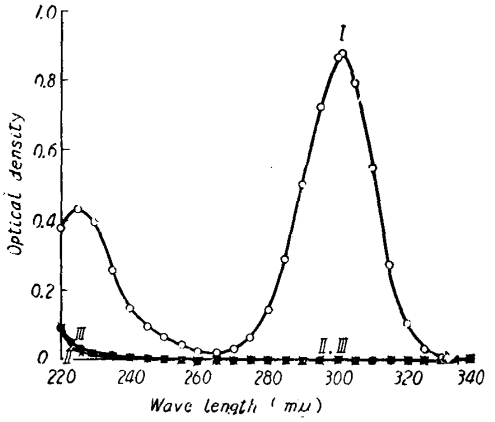

Fig. 3. Decomposition of potassium ethylxanthate in acidified aqueous solution.

I : $C_2H_5OCS_2K$ 5×10^{-5} mole/l, pH : 7

II : $C_2H_5OCS_2K$ 1×10^{-4} mole/l +HCl 0.5 mole/l, holding time : 20 min

III : After treated under the same conditions as II, adjusting at pH 6 with ammonia water.

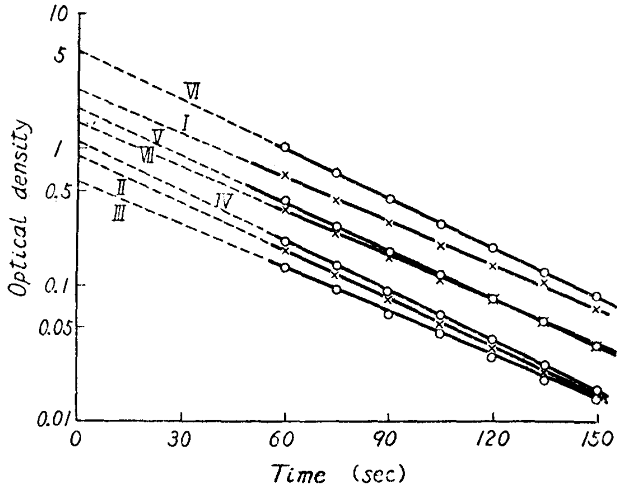

Fig. 4. Time variation of optical density of potassium ethylxanthate solution at pH 2.02. ($C_2H_5OCS_2K$ 3.92×10^{-4}mole/l)

Wave length : I 226 mμ, II 240 mμ, III 255 mμ, IV 270 mμ, V 285 mμ, VI 300 mμ, VII 315 mμ

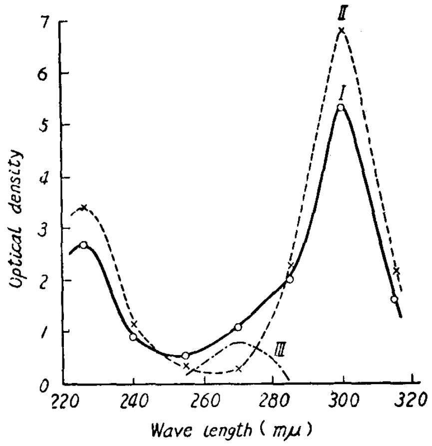

Fig. 5. Absorption spectra of ethylxanthate at pH 2.02 and at neutral. ($C_2H_5OCS_2K$ 3.92×10^{-4} mole/l)

I : pH 2.02, II neutral, III=I−II

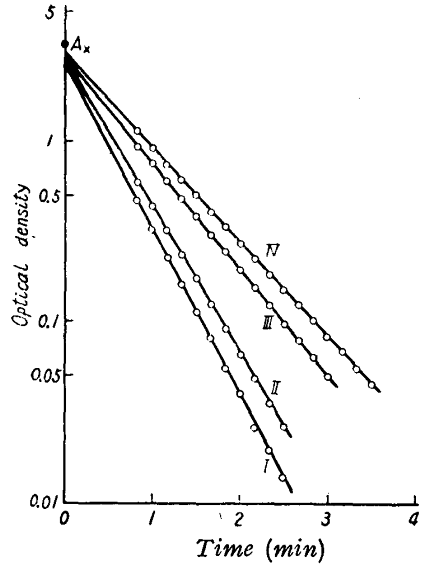

Fig. 6. Decomposition of methylxanthic ion with hydrogen ion.

I : pH 2.00, $\sqrt{u}=0.1$,

II : pH 2.00, $\sqrt{u}=0.25$,

III : pH 2.20, $\sqrt{u}=0.08$,

IV : pH 2.20, $\sqrt{u}=0.24$.

coefficients at the wave length of 226 mμ and 301 mμ. As seen in Table 2, the values of $\varepsilon_{226}/\varepsilon_{301}$ increased with an increase in the carbon number of alkyl groups of xanthate. It is shown in Fig. 2 that there is a straight-line relationship between the values of $\varepsilon_{226}/\varepsilon_{301}$ and the carbon number of alkyl groups. Curve II in Fig. 3. shows the absorption spectra of the solution, allowed to stand for 20 minutes after adjusting with 0.5 mole/l of hydrochloric acid and 1×10^{-4} mole/l of potassium ethylaxanthate. No absorption band was observed over the wave length range

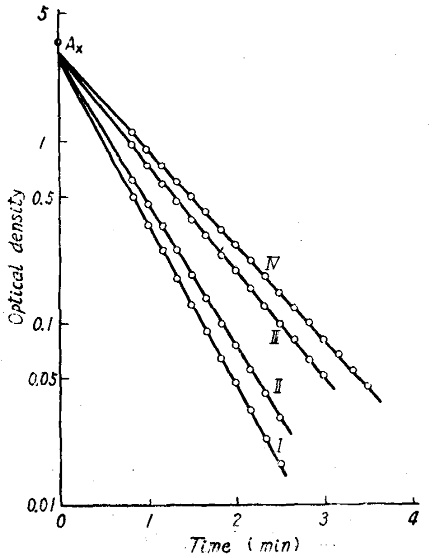

Fig. 7. Decomposition of ethylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

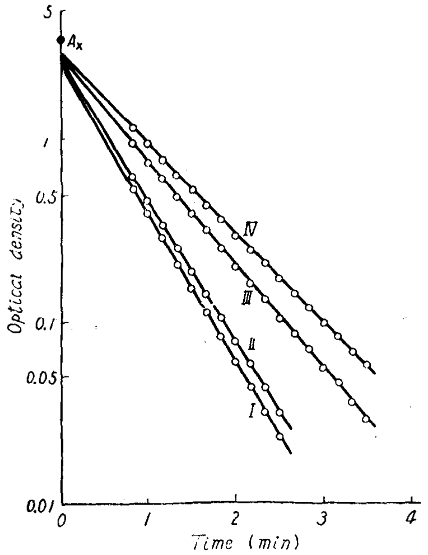

Fig. 8. Decomposition of propylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

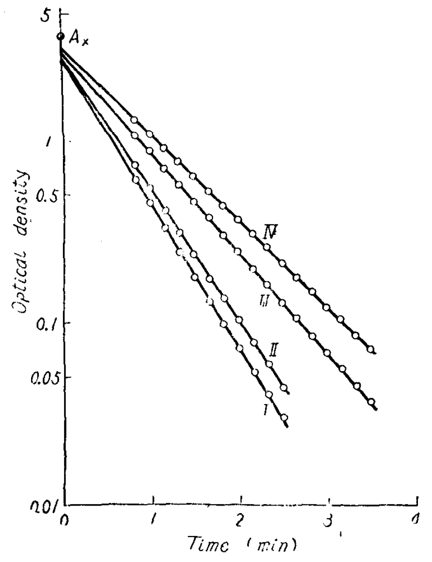

Fig. 9. Decomposition of butylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

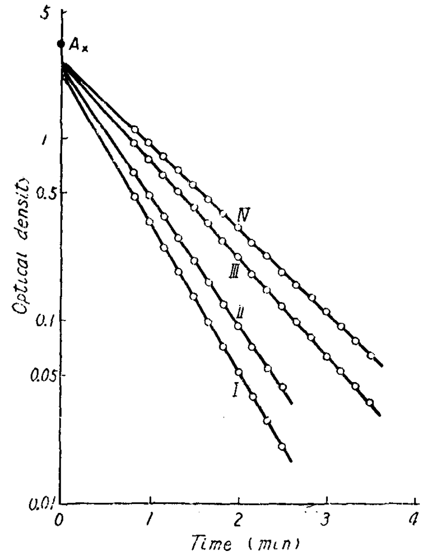

Fig. 10. Decomposition of amylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

of 220–340 mμ, but feeble absorption spectra were found in the wave length less than 220 mμ. Restoration of pH to 6 by the addition of ammonia water did not bring back the absorption peaks at 226 mμ and 301 mμ, indicating that the decomposition reaction was considerably rapid and no reverse reaction was

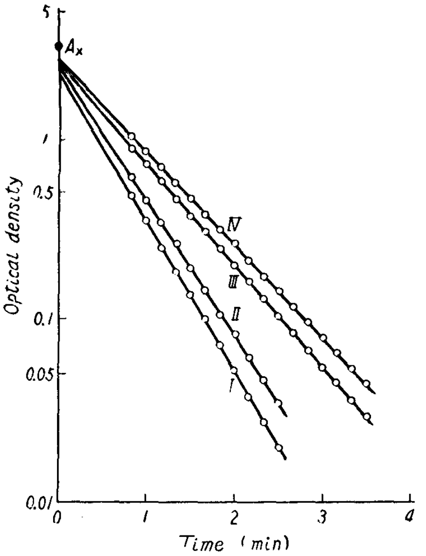

Fig. 11. Decomposition of iso-propylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

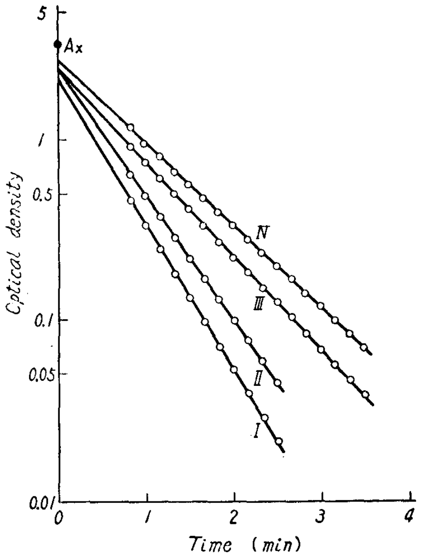

Fig. 12. Decomposition of iso-butylxanthic ion with hydrogen ion.
I : pH 2.00, $\sqrt{u}=0.1$,
II : pH 2.00, $\sqrt{u}=0.25$,
III : pH 2.20, $\sqrt{u}=0.08$,
IV : pH 2.20, $\sqrt{u}=0.24$.

possible after the decomposition was complete. But it was noticed that the decomposition reaction was halted when a sufficient amount of alkali was added to the acidified potassium xanthate solution, as pointed out by King and Dublon⁽⁴⁾, and Iwasaki and Cooke⁽⁵⁾.

The results of measurements obtained in this study are plotted in Figs. 4–10. As seen in these figures, when the logarithm of the optical density was plotted against time, straight lines were obtained, the slope of which was influenced with pH and ionic strength.

IV. Discussion

The decomposition may take placed by either of the following mechanisms,

$$ROC\Big\langle\begin{matrix}S\\ SH\end{matrix} \xrightarrow{\quad\quad} CS_2+ROH \tag{1}$$

or

$$\left[ROC\Big\langle\begin{matrix}S\\ S\end{matrix}\right]^- + H^+ \longrightarrow CS_2 + ROH \tag{2}$$

With regard to the decomposition mechanism, von Halban and Hecht⁽³⁾ assumed that the reaction was a unimolecular decomposition of undissociated xanthic acid, although they recognized that this was kinetically identical with a bimolecular reaction between the hydrogen ion and xanthic ion. King and Dublon⁽⁴⁾ applied the kinetic equation of decomposition reaction of xanthic ion with hydrogen ion. Further, King et al.⁽⁵⁾ mentioned that a bimolecular decomposition was essential and unimolecular decomposition of undissociated xanthic acid did not seem plausible for two reasons. One is that since molecular xanthic acid is stable in aprotic solvents, there is no reason why it should decompose spontaneously in water and the rate-determining step must then be a bimolecular reaction with hydrogen ion. This could not be a rapid equilibrium reaction which keeps a very small concentration of undissociated xanthic acid. Against these opinions, Iwasaki and Cooke(8) assumed that the decomposition of potassium xanthate in an acidified aqueous solution would take place in accordance with

$$H^+ + X^- \rightleftarrows HX \longrightarrow ROH + CS_2 \qquad (3)$$

And they calculated the rate constant as a unimolecular decomposition of undissociated xanthic acid.

As we have seen in the above, there is so far no established theory for the decomposition mechanism of xanthate.

Another problem should be considered that the optical density of xanthate solution at the wave length of 301 mμ due to the optical density of xanthic ion or the combined absorption by xanthic ion and its acid. Bushell(16), and Iwasaki and Cooke(8) assumed that the optical denisty of xanthate at the wave length of 301 mμ due to the combined absorption by xanthic ion and xanthic acid. But there is no experimental proof on this assumption. In order to make this point clear, the author analyzed the data given by Iwasaki and Cooke(18). Iwasaki and Cooke measured the time variation of the optical density at the wave length of 301 mμ over the pH range of 4.71–0.01, and observed that the optical density of ethylxanthate solution at zero time became so low with lower pH solution, but they made no reference to that cause. Similar phenomena were observed in the present study. Taking this into consideration, the dissociation of xanthic acid would be restrained at lower pH and undissociated xanthic acid become rich. Since the reaction involving ionic combination are known to be extremely rapid(19), this assumption is probably reasonable. Consequently, it may be considered tentatively that the increase in the optical density at zero time due to the increase in the concentration of undissociated xanthic acid. When the total concentrations of xanthic acid and xanthic ion are constant, as the optical density at zero time decreases with the lowering in pH, it seems that the molar extinction coefficient for undissociated xanthic acid at the wave length of 301 mμ is smaller than that for xanthic ion.

Generally, the optical density for binary components system is represented as the sum of the products of molar extinction coefficent of each component as follows:

$$A = \varepsilon_{X^-} C_{X^-} + \varepsilon_{HX} C_{HX} \qquad (4)$$

where ε_{X^-} and C_{X^-} are respectively the molar extinction coefficient and the molar concentration of xanthic ion, and ε_{HX} and C_{HX} are those of xanthic acid.

The optical density, evalulated from the figure given by Iwasaki and Cooke,

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(19) M. Eigen, Discussion Faraday Soc., **17** (1954), 194.

at pH 4.71 was recognized at about 1.05 at zero time. The ratio of the concentrations of xanthic ion and undissociated xanthic acid was calculated to be 1,590 : 1, by using the dissociation constant for ethylxanthic acid given by King and Dublon(4) ($K_h=0.031$). In the case of using $K_h=0.020$, given by Iwasaki and Cooke, this ratio becomes 1,026 : 1. Since ε_{X^-} is larger than ε_{HX}, as we have seen in the above, it may be considered that the optical density at pH 4.71 is due almost all to the absorption of ethylxanthic ion. Therefore, substituting the relationship of $\varepsilon_{HX} C_{HX} \ll \varepsilon_{X^-} C_{X^-}$ in Eq. (4), this equation may be written as $A=\varepsilon_{X^-} C_{X^-}$. Hence, the molar extinction coefficient for ethylxanthic ion was calculated to be 16,900 by using the values of A and C_{X^-}, given by Iwasaki and Cooke.

Table 3. Examination of the data of Iwasaki and Cooke.

pH	Potassium ethyl-xanthate added (mole/l)	[H+] (mole/l)	[X-]/[HX]*	[X-] (mole/l)	Optical destity** (calculated)	Optical destiny*** (measured)
4.71	6.2×10^{-5}	1.95×10^{-5}	1,590	6.2×10^{-5}	1.05	1.05
2.70	1.25×10^{-4}	2.0×10^{-3}	15.5	1.17×10^{-4}	1.98	0.92
2.40	〃	$4.0\times$ 〃	7.75	$1.11\times$ 〃	1.88	0.90
2.06	〃	$8.7\times$ 〃	3.56	9.76×10^{-5}	1.65	0.80
1.70	〃	2.0×10^{-2}	1.55	$7.60\times$ 〃	1.28	0.60
1.40	〃	$4.0\times$ 〃	0.775	$5.46\times$ 〃	0.92	0.44
1.11	6.25×10^{-4}	$7.7\times$ 〃	0.403	1.80×10^{-4}	3.04	1.4
0.74	〃	1.8×10^{-1}	0.172	9.19×10^{-5}	1.55	0.78
9.42	〃	$3.8\times$ 〃	0.082	$4.73\times$ 〃	0.80	0.42
0.10	〃	$7.9\times$ 〃	0.040	$2.40\times$ 〃	0.41	0.22

* These values were calculated using the dissociation constant of $K_h=0.031$, given by King and Dublon.

** Molar extinction coefficient required for the calculation of the optical density was used the value of $\varepsilon_\lambda=16{,}900$, calculated from the optical destiny at pH 4.71.

*** These values were given the rough values obtained from the figure of Iwasaki and Cooke.

Table 3 demonstrates the calculated values of the optical density due to ethylxanthic ion, using $\varepsilon_{X^-}=16{,}900$ and $K_h=0.031$. As is obvious in this table, the optical density at zero time, sought graphically, is smaller than the calculated value, assuming that the optical density is controlled with the concentration of ethylxanthic ion only. Such deviations in the optical density were observed when the dissociation constant of 0.020, given by Iwasaki and Cooke, was used. It should be noticed that the calculated optical density is greater than the observed one. But, since there is no case where the observed optical density is greater than that of calculated, it would be recognized that the optical density at the wave length of 301 mμ is principally due to xanthic ion.

To make sure of this point, the time variation of the optical density over the wave length range of 226–315 mμ was measured for the solution of pH 2.02 containing 3.92×10^{-4} mole/l of potassium ethylxanthate which was supposed to exisit in a considerably high concentration of undissociated xanthic acid. Experimental results is illustrated in Fig. 4. The absorption curve at zero time, deduced from Fig. 4, is shown in Fig. 5. As reference, the theoretical absorption curve for neutral solution containing the same quantity of xanthate is given on the same figure. As is obvious in this figure, when pH of the solution was adjusted at 2.02, the optical density at the wave length of 226 mμ and 301 mμ decreased, while the optical density at 270 mμ increased in comparison with that of neutral solution. Curve III in Fig. 5 shows the difference between the optical densities for Curve I and for Curve II. It may be considered that ionic form of ethylxanthate expresses a resonanace effect, while undissociated xanthic acid losses that effect. It is common that the absorption peak shifts to the short wave length when a resonanace is lost. Therefore, it may be regarded as appropriate that the lowering of the optical density at the wave length of 301 mμ corresponds to the decrease of ethylxanthic ion concentration, while the growing of the absorption maxima at the wave length of 270 mμ corresponds to undissociated acid form. A similar conception could be applied to the lowering of the absorption peak at the wave length of 226 mμ. But no experimental proof has been given to this problem. The foot of the absorption band of 270 mμ would diminish near the wave length of 285 mμ, so it seems probable that the influence on the optical density at 301 mμ by undissociated xanthic acid may be neglected*. Thus thes optical density at the wave length of 301 mμ may indeed be regarded to be due to xnathic ion.

Thus Figs. 3–9 demonstrate directly the decomposition reactions of xanthic ions. But as we have seen in Fig. 3, the absorption peak for the decomposition products of xanthate solution did not appear near the wave length of 270 mμ. To keep the equilibrium condition of dissociation between undissociated xanthic acid and xanthic ion, the concentration of molecular xanthic acid was controlled by the concentration decrease of xanthic ion, even though molecular xanthic acid was stable in water as had been pointed out by Chatenever and King(5). Accordingly, it may be possible to observe pseudo-unimolecular decomposition instead of a bimolecular decomposition between xanthic ion and hydrogen ion in the case of much high concentration of hydrogen ion against xanthic ion. Considering the experimental results given by von Halban and Hecht(3) and discussions stated by Chatenever and King(5), the decomposition mechanism of alkali xanthate would be appear as plausible as the bimolecular decomposition between xanthic ion with hydrogen ion.

In the present study, since the acid concentration was much high compared with the added quantity of xanthate, the general rate equation for bimolecular system, Eq. (5), might be expressed by the relation of Eq. (6), that is, the general rate equation is given as follows:

$$dx / dt = k (a-x)(b-x) \tag{5}$$

where a and b are the initial molar concentration of xanthic ion and hydrogen ion respectively, $a-x$ and $b-x$ are values at the time t (in minutes), and the value of k is the rate constant. When $b \gg a$, Eq. (5) may be expressed by the relation

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* Recently Klein and others(20) reported that the 270 mμ band is indeed due to the undissociated acid form, and the molar extinction coefficients at 270 mμ is 10,670 in water, and at 302 mμ about 117 in water considered from the data in isoöctane.

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

$$dx / dt = k'(a-x) \tag{6}$$

In the equation, k' is the value represented by $kb=k'$.

As we see clearly in Figs. 3–9, there are linear relationships between log A and t. Since the reaction of dissociation equilibrium for xanthic acid progress very fast, the optical density at zero time will lower because of the decrease in xanthic ion conctneration corresponding to xnathic acid newly formed in solution, that is, the optical density at zero time is smaller than the ideal optical density of xanthic ion of equal quantity with xanthate added. The optical density at zero time is influenced by the pH value and the ionic strength of solution.

Since the optical density at zero time, A_0, stands for the absorption due to xanthic ion being in the equilibrium condition of dissociation, it may be possible to evaluated the xanthic ion concentration from the values of A_0 and the molar extinction coefficent for xanthic ion. The values of A_0 were determined by using the method of least squares. The dissociation constant of xanthic acid

Table 4. The dissociation constants of xanthic acids and the rate constants of decomposition of those ions.
(Initial concentration of potassium xanthate 2×10^{-4}mole/l, 25°C)

R	pH	$\sqrt{u}$	A_0 (λ= 301mμ)	Molar extinction coefficient ε_{x^-}(λ= 301 mμ)	Initial conc. of X^- ($\times10^{-4}$ mole/l)	Initial conc. of HX ($\times10^{-4}$ mole/l)	Initial conc. of H^+ ($\times10^{-4}$ mole/l)	Dissociation constant of xanthic acid, K_h	Rate constant of xanthic ion, k (mole^{-1} min^{-1})
Methyl-	2.00	0.1	2.694	16,950	1.589	0.411	1.00	3.87×10^{-2}	212
	〃	〃	2.756	〃	1.625	0.375	〃	4.34× 〃	213
	〃	0.25	2.838	〃	1.674	0.326	〃	5.13× 〃	188
	2.20	0.08	2.900	〃	1.711	0.289	0.63	3.72× 〃	215
	〃	0.24	3.003	〃	1.771	0.229	〃	4.89× 〃	190
Ethyl-	2,00	0.1	2.715	17.458	1.555	0.445	1.00	3.50×10^{-2}	204
	〃	〃	2.729	〃	1.563	0.437	〃	3.58× 〃	204
	〃	0.25	2.849	〃	1.632	0.368	〃	4.44× 〃	182
	2.20	0.08	2.930	〃	1.678	0.322	0.63	3.29× 〃	216
	〃	0.24	3.059	〃	1.752	0.248	〃	4.46× 〃	192
Propyl-	2.00	0.1	2.613	17,266	1.513	0.487	1.00	3.11×10^{-2}	188
	〃	0.25	2.739	〃	1.586	0.414	〃	3.84× 〃	177
	2.20	0.08	2.839	〃	1.644	0.356	0.63	2.91× 〃	208
	〃	0.24	2.960	〃	1.714	0.286	〃	3.78× 〃	180
Butyl-	2.00	0.1	2.781	19,170	1.451	0.549	1.00	2.64×10^{-2}	183
	〃	0.25	2.929	〃	1.528	0.472	〃	3.23× 〃	169
	2.20	0.08	3.103	〃	1.619	0.381	0.63	2.67× 〃	204
	〃	0.24	3.248	〃	1.694	0.306	〃	3.48× 〃	175
Amyl-	2.00	0.1	2.287	16,832	1.359	0.641	1.00	2.12×10^{-2}	189
	〃	0.25	2.471	〃	1.468	0.532	〃	2.76× 〃	163
	2.20	0.08	2.620	〃	1.557	0.443	0.63	2.21× 〃	195
	〃	0.24	2.686	〃	1.596	0.404	〃	2.49× 〃	168
iso-Propyl-	2.00	0.1	2.352	16,404	1.434	0.566	1.00	2.53×10^{-2}	191
	〃	0.25	2.527	〃	1.540	0.460	〃	3.35× 〃	171
	2.20	0.08	2.571	〃	1.567	0.433	0.63	2.28× 〃	203
	〃	0.24	2.763	〃	1.685	0.315	〃	3.36× 〃	187
iso-Butyl-	2.00	0.1	2.109	16,536	1.290	0.710	1.00	1.82×10^{-2}	185
	〃	0.25	2.401	〃	1.452	0.548	〃	2.65× 〃	160
	2.20	0.08	2.435	〃	1.473	0.527	0.63	1.76× 〃	191
	〃	0.24	2.674	〃	1.617	0.383	〃	2.66× 〃	166

is given as follows:

$$K_h = \frac{[H^+][X^-]}{[HX]} \tag{7}$$

where K_h is the dissociation constant, $[H^+]$, $[X^-]$, and $[HX]$ are respectively the concentrations of hydrogen ion, xanthic ion and undissociated xanthic acid.

The rate constant of decomposition can be calculated from the data of time vairation in the optical density at the wave length of 301 mμ. In the case of much high concentration of hydrogen ion, compared with xanthic ion concentration employed in measurements, the following relation can be used to evaluated the rate constant, k:

$$k = 2.303\,a\,/\,[H^+] \tag{8}$$

In the present study, the value of slope, a, of the linear plots was calculated from the points obtained over the time range of 50–150 seconds with the aid of the method of least squares.

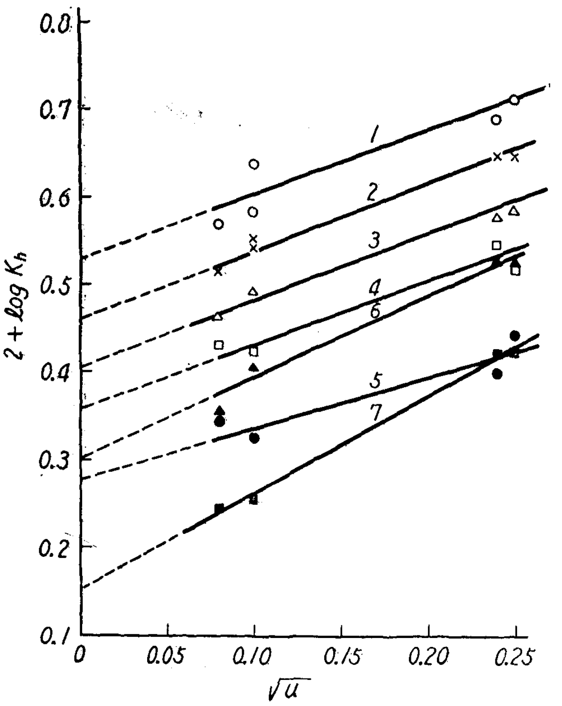

Fig. 13. Variation in dissociation constants of xanthic acids with ionic strength.
Species of xanthic acids:
1 (○) methyl-, 2 (×) ethyl-,
3 (△) propyl-, 4 (□) butyl-,
5 (▲) amyl-, 6 (●) iso-propyl-,
7 (■) iso-butyl-.

The dissociation constants and the rate constants of decomposition of methyl-, ethyl-, propyl-, butyl-, amyl-, iso-propyl-, and iso-butylxanthic acids and those ions are tabulated in Table 4.

In Figs. 13 and 14, the logarithmic values of K_h and k are plotted against the corresponding square root value of the ionic strength. As is seen from these figures, the straight line relationships were obtained. The logarithm of K_h decreased with the increase in the square root value of the ionic strength. As pointed out previously by King and Dublon⁽⁴⁾, the reaction velocity or dissociation constant of dilute solution of strong electrolyte are related closely to the ionic strength, which may be deduced easily by the Debye-Hückel's theorem.

The values of dissociation constants of various xanthic acids and the rate constants of those ions at 25°C and the ionic strength of 0 were determined by extrapolating of the straight lines shown in Figs. 13 and 14, and the results are demonstrated in Table 5. With regard to the dissociation constant of methylxanthic acid, von Halban and Hecht⁽³⁾ reported a value of 0.034 at 25°C

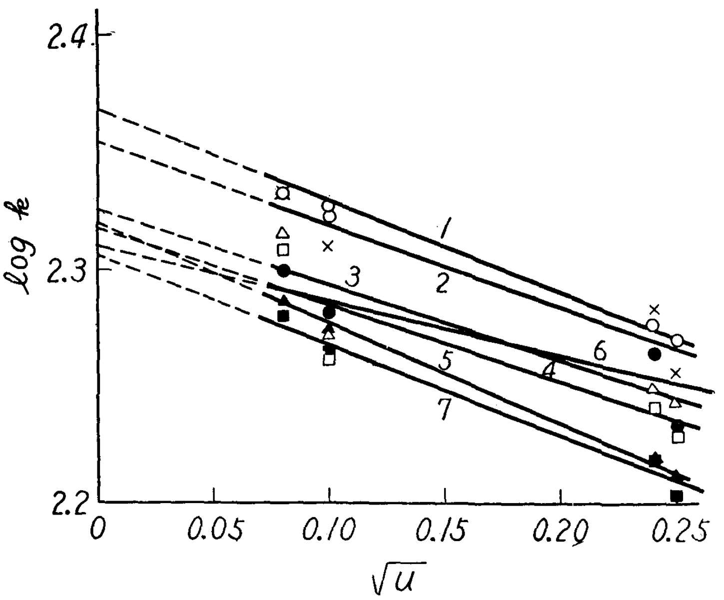

Fig. 14. Variation in decomposition rates of xanthic ions with ionic sterngth.
Species of xanthic ions :
1 (○) methyl-, 2 (×) ethyl-, 3 (△) propyl-, 4 (□) butyl-,
5 (▲) amyl-, 6 (●) iso-propyl-, 7 (■) iso-butyl-.

Table 5. The dissociation constants of xanthic acid and the rate constants of those ions at 25°C and the ionic strength of 0.

Species of xanthic acid	Dissociation constant K_{ho}	Rate constant k_0 (mole^{-1}min^{-1})
Methyl-	3.4×10^{-2}	233
Ethyl-	$2.9\times$ 〃	226
Propyl-	$2.5\times$ 〃	214
Butyl-	$2.3\times$ 〃	209
Amyl-	$1.9\times$ 〃	211
iso-Propyl-	$2.0\times$ 〃	207
iso-Butyl-	$1.4\times$ 〃	202

and the ionic strength of 0. King and Dublon(4) reported 0.035 under the same conditions. The present value, 0.034, checks very well with the previously reported values. With regard to ethylxanthic acid, von Halban and Hecht(3) reported a value of 0.030, King and Dublon(4), 0.031, Hantzsch and Bucirius(9), 0.028, Iwasaki and Cooke(8), 0.020, and Cook and Nixon(1), 0.007. The present value, 0.029, checks well the first three of previously reported values. Since the dissociation constants of xanthic acids other than methyl- and ethylxanthic acids have not yet been given, this is the first report of the dissociation constants for various xanthic acids.

With regard to the rate constant of decomposition of ethylxanthic ion, King and Dublon(4) reported a value of 270 mole^{-1}min^{-1} at 25°C, von Halban and Hecht(3) 16.0 mole^{-1}min^{-1} at 0°C, and Iwasaki and Cooke(8) 4.3±0.21 min^{-1} at 23.5°C as a unimolecular decomposition of undissociated xanthic acid. The present value, 226 mole^{-1}min^{-1} at 25°C bear a close parallel to the value given by King and Dublon. As we see in Table 5, the dissociation constants of xanthic acids decrease with the increase in carbon number of those alkyl groups, and iso-isomer has small values of these constants than those of normal ones. In other words, the pKa values of the dissociation decrease with the increase in carbon number. The similar tendensy is observed in the relation between the decomposition rates and carbon numbers. It may be recognized that the dissociation and decomposition are subject to the influence of the structure of alkyl group.

Summary

In a present work, a kinetic study of the decomposition of xanthates in acidified aqueous solutions was carried out systematically with the photoelectric spectrophotometer, and dissociation constants of xanthic acids and the rate constants of decomposition of xanthic ions were determined.

The main results outlined in this paper are as follows :

(1) The absorption bands for xanthic ion are observed at the wave length of 226 mμ and 301 mμ, and the values of the ratio of the molar extinction coefficients at 226 mμ and 301 mμ, $\varepsilon_{226}/\varepsilon_{301}$, increase with the increase in carbon number of alkyl groups of xanthates, and iso-isomer has greater values of the ratio than those of normal ones.

(2) The ionic form of xanthate has a absorption maxima at 226 mμ and 301 mμ, and the undissociated acid form has at 270 mμ in water.

(3) The dissociation constants were determined by using the data of the molar extinction coeifficent and the optical density at zero time for the wave length of 301 mμ. The dissociation constants of methyl-, ethyl-, propyl-, butyl-, amyl-, iso-propyl-, and iso-butylxanthic acids are respectively 3.4×10^{-2}, 2.9×10^{-2}, 2.5×10^{-2}, 2.3×10^{-2}, 1.9×10^{-2} 2.0×10^{-2}, and 1.4×10^{-2} at 25°C and the ionic strength of 0.

(4) These values of dissociation constant decrease with the increase in carbon number of alkyl group of xanthic acids, and iso-isomer has smaller values of these constants than those of normal ones.

(5) The time variation in the optical density at the wave length of 301 mμ represents the decomposition rate of xanthic ion directly. The rate constants of decomposition were evaluated as the reaction followed the bimolucular reaction between xanthic ion with hydrogen ion. The rate constants of methyl-, ethyl-, propyl-, butyl-, amyl-, is-propyl-, and iso-butylxanthic ions are respectively 233, 226, 214, 209, 211, 207, and 202 mole^{-1}min^{-1} at 25°C and the ionic strength of 0.

(6) These rate constants decrease with the increase in carbon number of alkyl groups of xanthic ions, and iso-isomer has smaller values of these constants than those of normal ones.

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