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Kinetics of Aquation of Tris(oxalato)chromate(III) and Tris(malonato)chromate(III) from Sulfuric Acid Solutions: A Solvent Extraction Study

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The kinetics of aquation of *tris*(oxalato)chromate(III) and *tris*(malonato)-chromate(III) anions have been studied by the solvent extraction technique. Trilaurylamine is used as an extractant. The extraction of these complex species is carried out using trilaurylamine in chloroform as extractant with appropriate concentrations of sulfuric acid in the aqueous phase. The observed first order rate constants are found to depend on the H^+ concentration. Rate constants are determined by using KINTOB software procedure. The activation parameters are calculated. The spectra of *tris*(oxalato)chromate(III) and *tris*(malonato)chromate(III) in aqueous phase are recorded as a function of standing time, in order to understand the formed product species. The product species are identified as mixture of species $[Cr(Ox)_2(H_2O)_2]^-$, $[Cr(Ox)(H_2O)_4]^+$ and $Cr(H_2O)_6^{3+}$ in the case of *tris*(oxalato)chromate(III) and $[Cr(mal)_2(H_2O)_2]^-$ and $Cr(H_2O)_6^{3+}$ in case of *tris*(malonato)chromate(III).

Key Words: Solvent extraction, Aquation, *Tris*(oxalato)chromate(III).

INTRODUCTION

The extraction of carboxylate complexes of group VIII metals by long chain amines has been reported[1]. Although the extraction of chromium in hexavalent state into various ion association system is studied by several workers[2-5], but not much is known about the liquid-liquid extraction of chromium(III) into tervalent state. The survey of literature on the extraction of chromium(III) into ion association systems indicates that most of the work is carried out by complexation with halides[6] and with a few amino carboxylic acids[7-10].

The studies on the extraction of *tris*(oxalato)chromate(III) and *tris*(malonato)-chromate(III) from mineral acid solutions are reported[11] and the mechanism of extraction of metal complex in terms of the competition between various anions and metal complex is discussed. In present communication, the solvent extraction technique is used for the study of the kinetics of aquation of *tris*(oxalato)chromate(III) and *tris*(malonato)chromate(III) using tertiary amine, trilaurylamine (TLA) in chloroform as extractant.

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In kinetics the rate of a reaction is monitored by measuring the chemical or physical property of either reactant or product formed as a function of time. The conventional approach is to follow the concentration of the reactant by titrimetric procedures. This method is tedious. The other alternative methods in common use are spectrophotometry (UV and visible region), conductometry and measurement of viscosity, pH and the NMR signal. In certain situations a product formed in the reaction transforms to another product with almost similar physical characteristics as of the former. This can be represented by a general equation of the type $A \rightarrow B \rightarrow C$ (where B and C represent products for a sequential reaction). Such situations arise when acid hydrolysis or base hydrolysis of transition metal complexes take place, for instance, the acid hydrolysis of *tris*(oxalato)chromate(III). In such situations, it is necessary to isolate the reactant/product from the reaction mixture to monitor the progress of the reaction employing separation methods such as precipitation, solvent extraction, ion exchange, *etc*.

In the present communication, the results related to acid hydrolysis of *tris*(oxalato)-chromate(III) and *tris*(malonato)chromate(III) are reported. The reaction is followed by extracting the reactant, {*tris*(oxalato)chromate(III)/*tris*(malonato)chromate(III)} from the reaction mixture as a function of time using a long chain alkylamine, trilaurylamine (TLA) in chloroform as extractant. The studies on the effect of various solvents including cyclohexane, carbon tetrachloride, heptane, chloroform and nitrobenzene on the extraction of the complex in sulfuric acid medium (0.05-1.50 M) reveal that maximum extraction occurs with chloroform as diluent. On the other hand, partial extraction is noticed with other diluents. Hence chloroform is chosen as the organic solvent for extraction. This method of isolation followed by estimation of the reactant using spectrophotometric method eliminates the influence of the product on the absorption measurements. This procedure adopted in these studies conforms that most of the rate law equations reported in chemical dynamics literature pertain to the monitoring of the reactant generally. In the same way, *cis*-*bis*-(oxalato)chromate(III) and *cis*-*bis*(malonato)chromate(III) are also prepared[12,13] and the similar procedure is followed to find the feasibility of separation of these species by solvent extraction technique. It is observed that the species cannot be extracted presumably due to the presence of water molecules in the coordinated sphere of chromium. The *cis*-*bis*(oxalato) and *cis*-*bis*(malonato)complexes of chromium(III) contains coordinated water molecules. The hydrophilic nature of these complexes is responsible for retaining in the aqueous phase.

EXPERIMENTAL

Trilaurylamine (TLA) supplied as a gift by General Mill Inc., Kankakee, Illinois, USA is used as such without any further purification.

Potassium *tris*(oxalato)chromate(III) was prepared by the method reported by Brauer[14]. The purity of the complex was checked by the following procedure. The complex is decomposed with hot sodium hydroxide solution and heated to boiling for a few minutes. Then it is oxidized with alkaline H_2O_2 to chromium(VI), which is estimated iodometrically. A known amount of complex is treated with hot NaOH for decomposing the complex. This solution is filtered to separate the precipitated chromium hydroxide. The filtrate containing the oxalate is acidified with H_2SO_4 and treated with standard permanganate solution. From analysis of this complex, {$K_3Cr(C_2O_4)_3.3H_2O$; calcd.: Cr = 10.67 %; oxalate = 54.17 %; found: Cr = 10.78 %; oxalate = 53.71 %} agreed well with reported values[15]. Other method is also followed to confirm the purity of the synthesized complex. The visible absorption spectrum of the synthesized metal complex shows maxima at 420 nm ($\varepsilon = 95.0\ M^{-1}\ cm^{-1}$) and 570 nm ($\varepsilon = 74.0\ M^{-1}\ cm^{-1}$) as against reported[15] maxima at 420 nm ($\varepsilon = 97.0\ M^{-1}\ cm^{-1}$) and 570 nm ($\varepsilon = 75.0\ M^{-1}\ cm^{-1}$).

Potassium *tris*(malonato)chromate(III) complex was also prepared by the method reported by Britton and Jarret[16] and its purity is confirmed by analysis. The complex is analyzed for chromium and malonate. The chromium present in the complex is estimated by iodometrically {after decomposition and oxidation of Cr(III) to Cr(VI)}. Malonate[17] is estimated by extensive oxidation with chromium(VI) by the following method. A known quantity of *tris*(malonato)chromate(III) complex and 10 mL of 1.0 M sodium hydroxide solution is taken and it is diluted to 50 mL and heated gently for a few minutes. The chromium hydroxide formed is filtered off and the contents are reduced to 10 mL by evaporation. To this 20 mL of concentrated sulphuric acid and 10 mL of 0.05 M potassium dichromate are added and heated on a steam bath for 2 h. The reaction mixtures are cooled to room temperature and 5 mL of concentrated phosphoric acid is added and the unreacted chromium(VI) is titrated with standard Fe^{2+}. From analysis of this complex, {$K_3Cr(C_3H_2O_4)_3.3H_2O$; calcd: Cr = 9.82 %; malonate = 57.83 %; found: Cr = 9.76 %; malonate = 57.64 %} agreed well with reported values. Other method is also followed to confirm the purity of the synthesized complex. The visible absorption spectrum of the synthesized metal complex shows maxima at 420 nm ($\varepsilon = 56.0\ M^{-1}\ cm^{-1}$) and 570 nm ($\varepsilon = 69.0\ M^{-1}\ cm^{-1}$) as against reported[13] maxima at 420 nm ($\varepsilon = 55.6\ M^{-1}\ cm^{-1}$) and 570 nm ($\varepsilon = 68.7\ M^{-1}\ cm^{-1}$).

All other reagents used are of anala'R grade or purified according to the standard methods. Triple distilled water is used to prepare all the experimental solutions.

Equipment: Absorption measurements are made on a Milton Roy spectronic 1201 UV visible spectrophotometer (USA). Shimadzu thermostat TB 85 is used for temperature control of the experimental solutions.

Procedure: Stock solutions of sulfuric acid (2.5 M), the metal complex (0.05 M) and triple distilled water are kept in separate stoppered containers. These containers are kept in a thermostat (maintained at the required temperature) for sufficient period to attain the temperature of the bath. Appropriate volumes of sulfuric acid and metal complex {*tris*(oxalato)chromate(III)/*tris*(malonato)chromate(III)} are mixed and diluted to a definite volume with triple distilled water and the appropriate temperature is maintained through out the reaction. A 10 mL aliquot of the reaction mixture is withdrawn at regular intervals of time and the unreacted metal complex is extracted with 10 mL of pre-equilibrated 0.025 M TLA in chloroform. The optical density of the metal complex present in the organic phase is then measured at 420 nm using trilaurylamine-chloroform as blank. This procedure is repeated at intervals of time. The decrease in absorbance with increase in standing time revealed that there is a decrease in extraction of the metal complex with time. The reaction was followed upto 85-90 % completion.

The kinetics of the hydrolysis of *tris*(oxalato)chromate(III) is studied by varying the parameters such as concentration of sulfuric acid (0.50-1.50 M), temperature (30, 35 and 40 ºC) and the metal complex (0.004-0.007 M). In the case of *tris*(malonato)-chromate(III) the concentration of sulfuric acid is varied in the range 0.10-0.30 M, keeping other parameters same as those in the case of *tris*(oxalato)chromate(III). The first order rate constants are evaluated by using KINTOB[18,19] software procedures. Each experiment is carried out three times with same conditions for the estimation of rate constants for reproducibility of the data. The rate constants obtained are with an accuracy of ± 5 %.

RESULTS AND DISCUSSION

Effect of pre-equilibration of trilaurylamine with mineral acids: A known quantity of the metal complex is extracted into 0.025 M solution of free base amine in chloroform which is pre-equilibrated with different mineral acid solutions (0.10 M). An increase in percentage extraction on pre-equilibration of the amine with acid solutions is noticed in the case of all mineral acids excepting perchloric acid (Table-1). Hence it is clear that the extraction with $HClO_4$ is poor and hence it is not suitable for studies. It is further observed that the quantitative extraction of metal complex is possible with amine solution pre-equilibrated with 0.10 M H_2SO_4 and H_3PO_4. The present study is carried out in the sulfuric acid medium. Further, the order of preference for anions for the extractant is thus $ClO^{4-} > NO^{3-} > Cl^{-} > SO_4^{2-} \approx PO_4^{3-}$ which is similar to that with anion exchange resin[20]. Hence tertiary and quaternary ammonium compounds are called as liquid anion exchangers.

The kinetics of the hydrolysis is studied varying the sulfuric acid concentration, metal complex and temperature. It is observed that the rate constants increased by increasing the concentration of sulfuric acid and also with increase in temperature (Tables 2 and 3). The concentration of the substrate (metal complex) does not have any effect on the rate constant; showing there by, that the order with respect to substrate is unity. The reaction is found to be completed after a period of 2 h at 2.5 M sulfuric acid in the case of *tris*(oxalato)chromate(III) ion. In case of *tris*(malonato)-chromate(III) ion the reaction is completed after a period of 1 h at 1.0 M sulfuric acid. The ionic strength could not be maintained due to the limitation arising from the preferential extraction of the anion of the salt (ClO_4^-, NO_3^-) used for the purpose by the extractant[20].

TABLE-1
PERCENTAGE EXTRACTION OF THE METAL COMPLEXES BY TRILAURYLAMINE IN CHLOROFORM AFTER PRE EQUILIBRATION WITH MINERAL ACIDS
$[Cr(Ox)_3^{3-}] = 0.005$ M, $[Cr(mal)_3^{3-}] = 0.005$ M, [TLA] = 0.025 M

Pre equilibrated acid (0.1 M)	Percentage extraction in the case of *tris*(oxalato)chromate(III)	Percentage extraction in the case of *tris*(malonato)chromate(III)
Free base amine	35.2	18.7
$HClO_4$	28.9	5.8
HNO_3	41.3	9.7
HCl	78.4	30.7
H_2SO_4	99.8	99.7
H_3PO_4	99.9	99.8

TABLE-2
VARIATION OF RATE CONSTANTS WITH SULFURIC ACID AND *TRIS*(OXALATO)CHROMATE(III)

$Cr(Ox)_3^{3-}$ M	H_2SO_4 M	$k_{obs} \times 10^4$ sec^{-1}		
		30 ± 0.1 ºC	35 ± 0.1 ºC	40 ± 0.1 ºC
0.005	0.50	0.14	0.38	0.83
0.005	0.75	0.32	0.91	1.53
0.005	1.00	0.51	1.43	2.34
0.005	1.25	0.67	1.99	3.27
0.005	1.50	0.85	2.55	4.09
0.004	1.00	0.49	1.41	2.31
0.006	1.00	0.52	1.43	2.37
0.007	1.00	0.51	1.40	2.33

TABLE-3
VARIATION OF RATE CONSTANTS WITH SULFURIC ACID AND *TRIS*(MALONATO)CHROMATE(III)

$Cr(mal)_3^{3-}$ M	H_2SO_4 M	$k_{obs} \times 10^4$ sec^{-1}		
		30 ± 0.1 ºC	35 ± 0.1 ºC	40 ± 0.1 ºC
0.005	0.10	0.90	1.51	2.51
0.005	0.15	1.12	1.88	3.07
0.005	0.20	1.28	2.26	3.88
0.005	0.25	1.46	2.50	4.66
0.005	0.30	1.71	2.88	5.37
0.004	0.20	1.26	2.29	3.88
0.006	0.20	1.29	2.23	3.90
0.007	0.20	1.25	2.27	3.86

In order to understand the product species formed in the course of reaction, the spectra of the reaction mixture in aqueous medium is recorded as a function of time (Figs. 1 and 2). It is evident that there is no shift in the wavelength of absorption maximum, but there is a significant decrease in the absorbance. An inspection of the spectra, reveals that at no stage the spectra exactly resembles that of either *bis* or monocarboxylic acid complexes of chromium(III) in terms of wavelength maximum or the peak ratio. This suggests that the product species appears to be a mixture of hydrolysis species of carboxylate complexes of chromium(III) namely, $[Cr(Ox)_2(H_2O)_2]^-$, $[Cr(Ox)(H_2O)_4]^+$ and $Cr(H_2O)_6^{3+}$ in the case of *tris*(oxalato)chromate(III). The analogous product species are also envisaged in the case of hydrolysis of *tris*(malonato)chromate(III). The final product formed in the aqueous phase is a mixture of three species namely *bis*-carboxylate complex, monocarboxylate complex and hexaaquochromium(III) ion. Since it is a complex mixture species containing one anion {*bis*-(carboxylate)complex} and two cations{mono(carboxylate)complex and $Cr(H_2O)_6^{3+}$}, the attempts to find out the proportion of each product species could not succeed by ion exchange method under the experimental conditions (since the acid concentration in the experimental solution is > 0.10 M and so perhaps, the product species cannot compete with the H^+ or anion to replace on the resin bed).

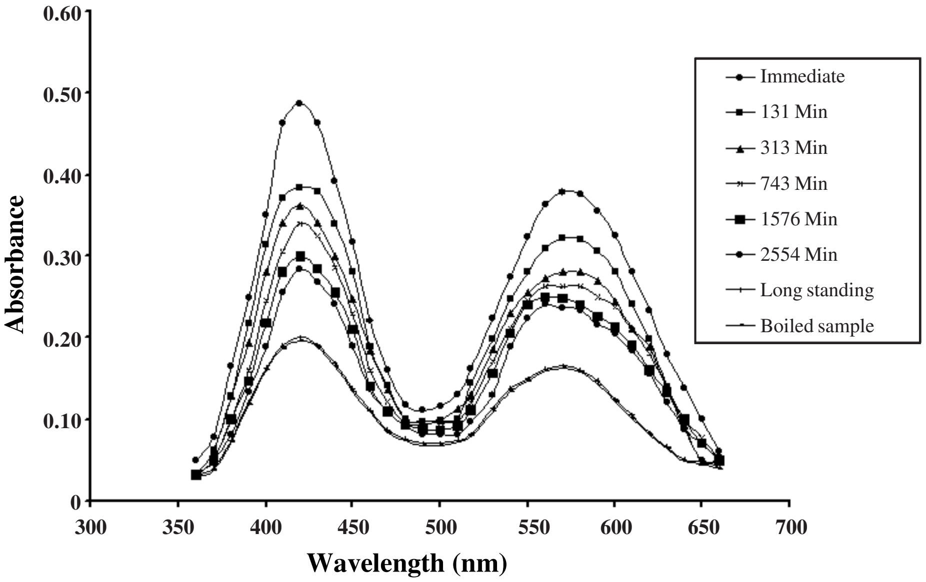

Fig. 1. Spectral changes of *tris*(oxalato)chromate(III) in sulfuric acid medium as a function of time. $[Cr(Ox)_3^{3-}] = 5.00 \times 10^{-3}$ M, $[H_2SO_4] = 1.0$ M

The spectral characteristics of the various oxalato complexes of chromium(III) and malonato complexes of chromium(III) are given in Table-4. The spectral parameters pertaining to the diverse products formed in these studies are also incorporated in the Table-4. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ obtained are 71.84 and -75.46 kJ mol^{-1}, respectively with *tris*(oxalato)chromate(III) and that with *tris*(malonato)chromate(III) are 86.12 and -91.72 kJ mol^{-1}.

Based on the results obtained, the mechanism of the reaction can be represented as:

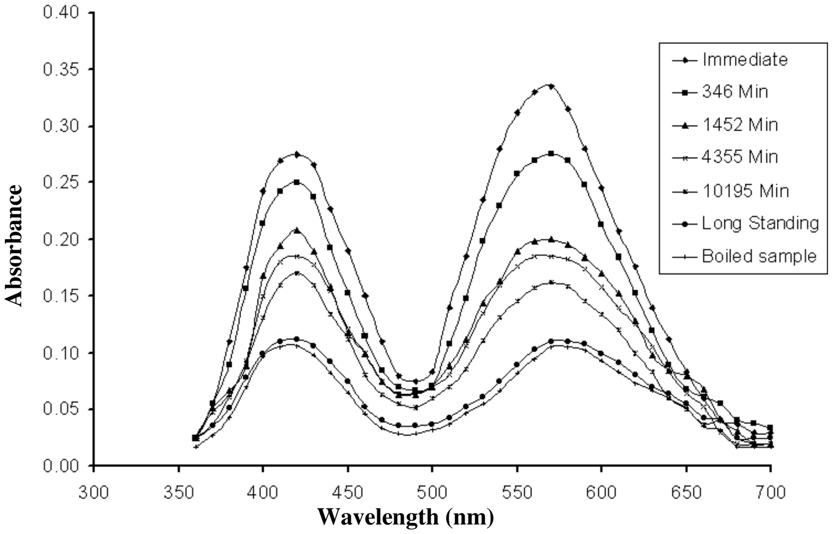

Fig. 2. Spectral changes of *tris*(malonato)chromate(III) in sulfuric acid medium as a function of time. $[Cr(mal)_3^{3-}] = 5.00 \times 10^{-3}$ M, $[H_2SO_4] = 0.25$ M

TABLE-4
SPECTRAL CHARACTERISTICS OF THE VARIOUS OXALATO AND MALONATO COMPLEXES OF CHROMIUM(III)

Species	λ_1 (nm)	λ_2 (nm)	ε_1 M^{-1} cm^{-1}	ε_2 M^{-1} cm^{-1}	Ratio $\varepsilon_1/\varepsilon_2$	Reference
$Cr(Ox)(H_2O)_4^+$	416	560	40.50	35.50	1.140	[21]
$Cr(Ox)_2(H_2O)_2^-$	415	560	66.00	50.80	1.299	[22]
$Cr(Ox)_3^{3-}$	420	570	97.00	75.00	1.293	[15]
$Cr(mal)(H_2O)_4^+$	415	559	26.10	31.40	0.831	[23]
$Cr(mal)_2(H_2O)_2^-$	417	566	41.40	49.90	0.829	[13]
$Cr(mal)_3^{3-}$	420	570	55.60	68.70	0.809	[13]
Product species with *tris*(oxalato)chromate(III)	420	570	40.00	33.30	1.201	Present study
Product species with *tris*(malonato)chromate(III)	420	570	22.40	21.60	1.037	Present study
$Cr(H_2O)_6^{3+}$	410	560	14.12	15.49	0.911	[24]

With *tris*(oxalato)chromate(III):

$$Cr(Ox)_3^{3-} + H_3O^+ \xrightleftharpoons{K} [Cr(Ox)_2(HOx)(H_2O)]^{2-}$$

$$[Cr(Ox)_2(HOx)(H_2O)]^{2-} + H_2O \xrightarrow{k} [Cr(Ox)_2(H_2O)_2]^- + HOx^-$$

Rate = $Kk[S][H_3O^+]$ (S represents substrate).

With tris(malonato)chromate(III):

$$Cr(mal)_3^{3-} + H_3O^+ \xrightleftharpoons{K} [Cr(mal)_2(Hmal)(H_2O)]^{2-}$$

$$[Cr(mal)_2(Hmal)(H_2O)]^{2-} + H_2O \xrightarrow{k} [Cr(mal)_2(H_2O)_2]^- + Hmal^-$$

Rate = $Kk[S][H_3O^+]$ (S represents substrate).

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