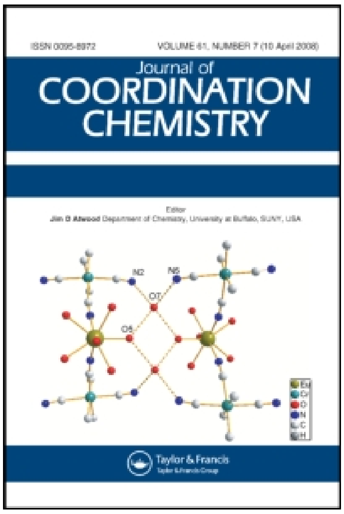

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Kinetics and mechanism of the aquation of a series of mixed-metal oxo-centered trinuclear cations, μ_3-oxo-triaqua-hexakis(carboxylato)bis-(chromium(III)(iron(III))$^+$, $[(RCOO)_6(H_2O)_3]^+$, (R=H, CH_3, CH_3CH_2 and $(CH_3)_2CH$) in perchloric acid media

Mark A. W. Lawrence[a]; Paul T. Maragh[a]; Tara P. Dasgupta[a]
[a] Department of Chemistry, University of the West Indies, Mona Campus, Kingston 7, Jamaica, West Indies

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Kinetics and mechanism of the aquation of a series of mixed-metal oxo-centered trinuclear cations, μ_3-oxo-triaqua-hexakis(carboxylato)bis-(chromium(III)(iron(III))$^+$, $[Cr_2^{III}Fe^{III}O(RCOO)_6(H_2O)_3]^+$, ($R = H$, CH_3, CH_3CH_2 and $(CH_3)_2CH$) in perchloric acid media

MARK A.W. LAWRENCE, PAUL T. MARAGH and TARA P. DASGUPTA*

Department of Chemistry, University of the West Indies, Mona Campus,
Kingston 7, Jamaica, West Indies

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The aquation of a series of $[Cr_2Fe(\mu_3\text{-}O)\mu_2\text{-}(RCO_2)_6(H_2O)_3]^+$ cations, where $R = H$, CH_3, CH_3CH_2, and $(CH_3)_2CH$ was investigated in aqueous perchloric acid, $0.01 \le [H^+] \le 0.17\,mol\,dm^{-3}$ and $25 \le \theta \le 35°C$. The mechanism is postulated as an equilibrium between the protons and the complex cation, where the oxygens of the carboxylate coordinated to the metal center are protonated, followed by Fe–O bond cleavage. This is followed by rapid decomposition to produce aqueous iron(III), a dinuclear chromium(III) species (which is further hydrolyzed), and carboxylate ions. First-order rate constants for the reactions at 25°C and $0.5\,mol\,dm^{-3}$ ionic strength ($NaClO_4$) and corresponding activation parameters are: $R = (CH_3)_2CH$; $k_1 = (7.18 \pm 0.07) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 52 \pm 2\,kJ\,mol^{-1}$, $\Delta S^‡ = -151 \pm 8\,J\,K^{-1}\,mol^{-1}$), $R = CH_3CH_2$; $k_1 = (13.67 \pm 0.02) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 57.8 \pm 0.6\,kJ\,mol^{-1}$, $\Delta S^‡ = -125 \pm 2\,J\,K^{-1}\,mol^{-1}$), $R = CH_3$; $k_1 = (17.6 \pm 0.3) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 30 \pm 5\,kJ\,mol^{-1}$, $\Delta S^‡ = -216 \pm 16\,J\,K^{-1}\,mol^{-1}$), $R = H$; $k_1 = (3.86 \pm 3.01) \times 10^{-2}\,s^{-1}$ ($\Delta H^‡ = 75 \pm 1\,kJ\,mol^{-1}$, $\Delta S^‡ = -22 \pm 5\,J\,K^{-1}\,mol^{-1}$). Spontaneous hydrolysis rate constants and activation parameters were also determined at 25°C and $0.5\,mol\,dm^{-3}$ ionic strength ($NaClO_4$): $R = (CH_3)_2CH$; $k_0 = (3.18 \pm 0.05) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 12.0 \pm 0.1\,kJ\,mol^{-1}$, $\Delta S^‡ = -291 \pm 1\,J\,K^{-1}\,mol^{-1}$), $R = CH_3CH_2$; $k_0 = (4.04 \pm 0.01) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 22.4 \pm 0.9\,kJ\,mol^{-1}$, $\Delta S^‡ = -254 \pm 3\,J\,K^{-1}\,mol^{-1}$), $R = CH_3$; $k_0 = (4.05 \pm 0.17) \times 10^{-5}\,s^{-1}$ ($\Delta H^‡ = 34.1 \pm 0.1\,kJ\,mol^{-1}$, $\Delta S^‡ = -214 \pm 1\,J\,K^{-1}\,mol^{-1}$), $R = H$; $k_0 = (3.4 \pm 0.2) \times 10^{-3}\,s^{-1}$ ($\Delta H^‡ = 25.3 \pm 0.4\,kJ\,mol^{-1}$, $\Delta S^‡ = -207 \pm 1\,J\,K^{-1}\,mol^{-1}$).

Keywords: Trinuclear; Oxo-centered; Iron(III); Chromium(III); Acid hydrolysis; Mechanism

1. Introduction

Oxo-centered trinuclear complexes have attracted our attention because of their potentially rich chemistry. For several decades, their structural properties [1–3] as well as their electronic properties in the solid state [4–6] have been investigated. The substitution of the terminal water ligands, with strongly coordinating

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*Corresponding author. Email: tara.dasgupta@gmail.com

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organic molecules, have also been reported for some oxo-centered trinuclear complexes [7, 8] and the rates have been found to be significantly greater than similar monometallic species investigated, possibly the result of the *trans* effect of the central oxygen atom.

Trinuclear complexes have been previously employed as catalysts to various reactions and specifically the oxo-centered trinuclear complexes are studied extensively as classes of mixed-valence model compounds due to their relative simplicity, their potential further use in oxidation catalysis and their many interesting physical properties [9–11]. The ability to vary the redox capacity of the $[M_3O(RCO_2)_6L_3]^{+/0}$ core by alteration of R and L (where L is a terminal ligand) provides a means of tuning the electron density of the metal centers of these complexes, and could further develop the use of these systems as oxidation catalysts [9, 12]. Many acetate salts of M^{3+} were once thought to be simple salts, but as characterization technology improved most of these where found to be oxo-centered trinuclear species.

There are issues surrounding the use and study of these systems in an aqueous environment, and the instability of an iron containing oxo-centered trinuclear complex in perchloric acid media has been investigated by our research group [13]. From a review of the literature and our experience with these systems, the presence of a terminal ligand that can be ionized e.g., H_2O can make these systems complicated to handle mechanistically, as well as influence the stability of the oxo-centered trinuclear core in an aqueous environment. Our interest in these complexes results from a lack of detailed understanding as to how the carboxylate ligand influences the aqueous chemistry of these complexes. In this report, we present a detailed kinetic analysis and a mechanism for the acid and spontaneous hydrolysis of a series of $[Cr_2FeO(RCO_2)_6(H_2O)_3]^+$ cations in aqueous perchloric acid.

2. Experimental

2.1. *Preparation of complexes*

The complexes, $[Cr_2FeO(RCO_2)_6(H_2O)_3]NO_3$, prepared by a modified method of Revenco *et al.* [14]. $Cr(NO_3)_3 \cdot 9H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ in a 2 : 1 ratio, respectively, were dissolved and refluxed in the respective carboxylic acid for 2 h resulting (in some cases) in evolution of NO_2. The resulting mixture was concentrated and allowed to slowly crystallize (for up to 1 week). The dark red-violet microcrystalline to crystalline material was filtered by vacuum and washed with trichloromethane (chloroform) or dichloromethane, diethyl ether and air dried. Typical yield of the crude products $[Cr_2FeO(RCO_2)_6(H_2O)_3]NO_3$: $R = H$, 80%; $R = CH_3$, 70%; $R = CH_2CH_3$, 74%; $R = CH(CH_3)_2$, 70%.

Note: The final product, if it is not crystalline, can be recrystallized from a 9 : 2 mixture of the respective acid and water. The resulting dark red-violet crystals were then treated as described previously. Recrystallization can be eliminated if a small amount of water is added to the synthetic mixture.

Anal. Calcd for $Cr_2FeC_6H_{12}O_{19}N$ (calculated as $[Cr_2FeO(HCO_2)_6(H_2O)_3]0.5NO_3 \cdot 0.5HCO_2 \cdot 2H_2O$)%: C, 13.23; H, 2.80; N, 1.19. Found: C, 13.42; H, 2.77; N, 1.12. $Cr_2FeC_{12}H_{24}O_{19}N$ (calculated as $[Cr_2FeO(CH_3CO_2)_6(H_2O)_3]0.85NO_3 \cdot 0.15CH_3CO_2$)%:

C, 22.86; H, 3.82; N, 1.84. Found: C, 22.83; H, 3.92; N, 1.84. $Cr_2FeC_{18}H_{36}O_{19}N$ ($[Cr_2FeO(CH_3CH_2CO_2)_6(H_2O)_3]NO_3$)%: C, 29.56; H, 4.93; N, 1.92. Found: C, 29.85; H, 4.76; N, 2.10. $Cr_2FeC_{24}H_{48}O_{19}N$ ($[Cr_2FeO(CH_3)_2CHCO_2)_6(H_2O)_3]NO_3$)%: C, 35.36; H, 5.94; N, 1.72. Found: C, 35.49; H, 6.08; N, 1.54.

Selected IR data (cm^{-1}): 3430 (br, s) $\nu(H_2O)$, 1590 (*vs.*) ν_{asym}(COO–Cr), 1527 (s) ν_{asym}(COO–Fe), 1469 and 1438 (m–s) ν_{sym}(COO), 1385 and 1308 (m) $\nu_{symbend}(CH_3)$, 1090 and 1037 (m–w) $\nu_{rock}(CH_3)$, 646 (br, m) ν_{bend}(COO), 432 (w) $\nu_{asym}(Cr_2FeO)$; (intensity: br-broad, s-strong, m-medium, w-weak).

2.2. *Materials*

Deionized water was obtained by passing glass-distilled water (Fistreem Cyclon) through a Labconco Water Processor. All reagents were purchased from commercial sources and used without purification.

2.3. *Kinetic measurements*

For slow reactions ($R \neq H$) a 2.4–2.6 mmol L^{-1} stock solution of the complex as well as a 1.0 mol L^{-1} stock solution of perchloric acid were prepared for each temperature run. The respective volumes of the stock acid, and then electrolyte ($NaClO_4$ for $I_{tot} = 0.50\,mol\,L^{-1}$) were added to the flask. This mixture along with the amount of stock complex required for the reaction were equilibrated at the reaction temperature; following which complex was added to the flask. The reaction was then monitored at 373 nm for 2.5 h.

The hydrolysis reaction of the complex $[Cr_2FeO(HCO_2)_6(H_2O)_3]NO_3$ is fast and hence the reactions were followed on the SF-61 DX2 Hi-Tech Stopped flow. A 1.2 mmol L^{-1} ($I = 0.50\,mol\,L^{-1}$, $NaClO_4$) solution of the complex was prepared after the respective concentration of perchloric acid solutions with supporting electrolyte ($NaClO_4$, $I_{tot} = 0.50\,mol\,L^{-1}$) were prepared. The complex solution and the required concentration of perchloric acid were taken in the storage syringe of the stopped flow and equilibrated for 2 min and reactions were then monitored for 5–10 s (depending on the reaction temperature) at 373 nm.

All kinetic experiments were performed under pseudo-first-order conditions with perchloric acid in at least 10-fold excess. The rate constants were calculated from non-linear regression analysis on the absorbance–time data using the initial rates method[†] and were reproducible to within ±5%. The software used to calculate the rate constants were the Hewlett Packard 8453A diode array or STATGRAPHICS XV[‡] packages.

[†] The initial rates were calculated using the expression: $Abs = a + bt + ct^2$ where; b = rate constant. The experimental and predicted absorbance–time traces are compared.

[‡] STAGRAPHICS Centurion XV, StatPoint Inc., Warrenton, Virginia 20186, USA.

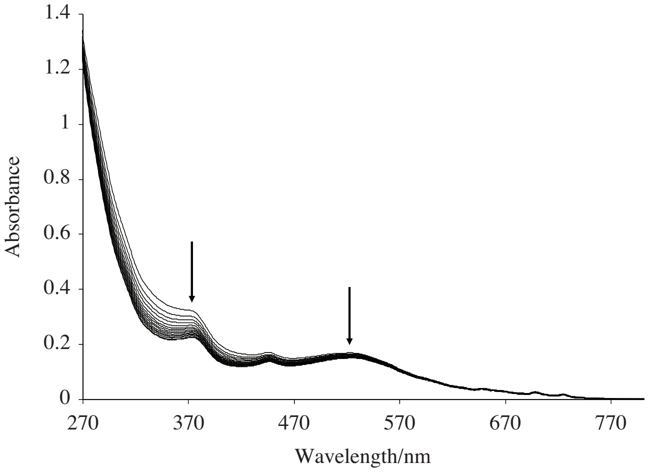


Figure 1. Typical repetitive scan spectra of the acid hydrolysis reaction.

3. Results and discussion

3.1. *Spectral observations*

The reaction results in fading of the red-violet color to a pale violet, which is persistent even at elevated temperatures. A repetitive scan of the electronic spectra of the acid catalyzed reaction(s) (figure 1) shows a gradual reduction of absorbance with time over the region 300–600 nm, and a relative retention of the band at 525 nm. The greatest decrease in absorbance occurs in the shoulder between 340 and 380 nm. No isosbestic point was observed, suggesting a complex reaction.

3.2. *Acid hydrolysis*

Acid hydrolyses of the complex cations were studied in dilute perchloric acid within the ranges $0.01 \le [H^+] \le 0.17\,\mathrm{mol\,dm^{-3}}$ and $25 \le \theta \le 35^\circ\mathrm{C}$ by recording the decrease in absorbance at 373 nm using conventional spectrophotometric methods.

The violet color that develops as the reaction progresses is postulated to be due to a dinuclear chromium(III) species, spectrally very similar to numerous reported acetate-/oxo-/hydroxo-bridged dinuclear complexes of chromium(III) having two characteristic bands at *ca* 400–430 and 520–580 nm [15–20]. In order to confirm the nature of this violet intermediate, we sought to synthesize the suspected compound. The dinuclear chromium(III) complexes containing acetate as bridging as well as peripheral ligands are generally very difficult to synthesize from Cr(III) salts because of their strong tendency to form the oxo-centered trinuclear species. To overcome this problem, we first prepared the dinuclear Cr(II) acetate [21], which was subjected to aerial oxidation [18], while the electronic spectrum of the species was monitored with time. The oxidation resulted in a species with similar spectral characteristics to the intermediate observed in the hydrolysis reaction(s). This species slowly decomposes to hexaaqua Cr(III) resembling the reaction of the kinetic intermediate in the hydrolysis.

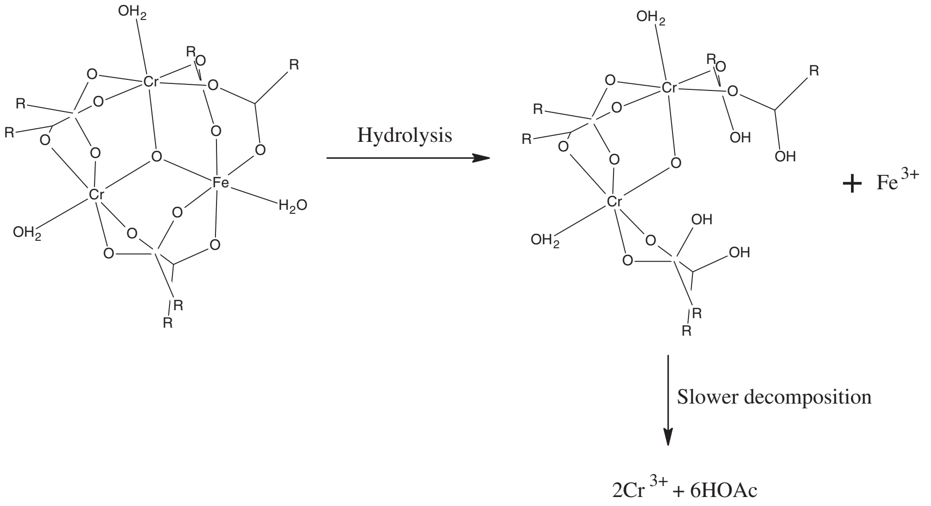


Figure 2. Proposed coordination mode of the reactant and intermediate of the hydrolysis reaction.

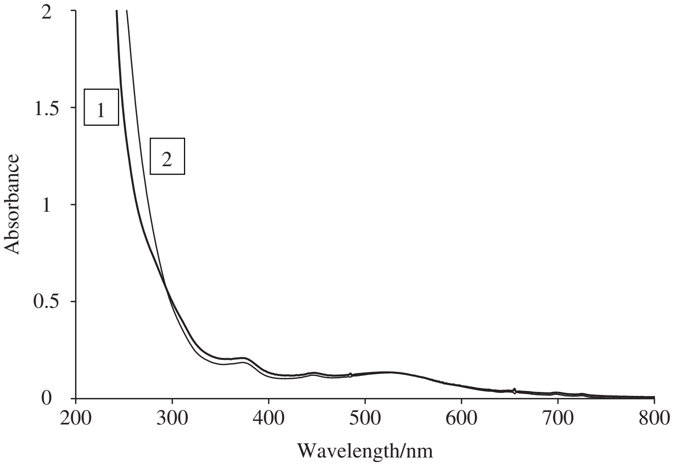


Figure 3. Comparison of synthetic mixture and final reaction mixture ($R = (CH_3)_2CH$) for the hydrolysis reaction (1 – reaction mixture, 2 – synthetic mixture, respectively).

This information suggests that the iron(III) center is hydrolyzed by mineral acid, destroying the trinuclear core of the complex. The result is a dinuclear chromium(III) complex containing possibly an oxo and carboxylate bridge since chromium(III) is relatively inert to substitution. The resulting dinuclear chromium complex is slowly hydrolyzed in the acidic environment to give free ions and ligand in solution (figure 2). The final product was confirmed to be free chromium(III), iron(III) and the carboxylate ions in aqueous solution, based on a comparison of electronic spectrum of the resulting reaction mixture with a synthetic mixture containing the metal ions and the ligand in a similar ratio to that of the reaction mixture (figure 3).

Table 1. Pseudo-first-order rate constants as a function of acid concentration at 298, 303, and 308 K for the acid hydrolysis of 0.485 mmol $\mathbf{L}^{-1}$ $[Cr_2FeO((CH_3)_2CHCO_2)_6(H_2O)_3]NO_3$ with $HClO_4$, $I = 0.50\,\mathrm{mol}\,\mathbf{L}^{-1}$ ($NaClO_4$).

	298 K	303 K	308 K
$[H^+]$ (mol L^{-1})	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})
0.01	3.59	4.12	4.73
0.02	3.91	4.52	5.33
0.03	4.12	4.92	5.94
0.05	4.55	5.52	6.81
0.07	4.92	6.23	7.82
0.09	5.15	6.63	8.47
0.1	5.38	6.85	8.72
0.12	5.48	7.13	9.28
0.15	5.60	7.46	9.78
0.17	–	7.66	10.01

Table 2. Pseudo-first-order rate constants as a function of acid concentration at 298, 303, and 308 K for the acid hydrolysis of 0.512 mmol L^{-1} $[Cr_2FeO(CH_3CH_2CO_2)_6(H_2O)_3]NO_3$ with $HClO_4$, $I = 0.50\,\mathrm{mol}\,L^{-1}$.

	298 K	303 K	308 K
$[H^+]$ (mol L^{-1})	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})
0.01	4.67	5.44	6.12
0.02	5.79	6.85	8.02
0.03	6.37	7.67	8.96
0.05	7.06	8.53	9.97
0.07	7.86	9.48	11.17
0.09	8.54	10.41	12.49
0.1	8.63	11.20	13.11
0.12	9.06	11.62	14.16
0.15	9.71	12.25	15.46
0.17	10.15	13.29	16.22

The electronic spectrum of the intermediate(s) interferes with that of the starting material, which makes a direct calculation of the first-order rates from the absorbance–time data difficult. The rates were calculated using the initial rate method (Au/s) and then converted to rate (mol $L^{-1}\,s^{-1}$) by dividing by the molar extinction coefficient [22, 23] at the wavelength being monitored. These were then converted to first-order rate constants (s^{-1}) dividing by the concentration of the complex. The initial rate method had to be adopted since the electronic spectra of the intermediates interfere with the spectrum of the trinuclear complex being monitored. The interference by the intermediate is much more obvious by the fact that both consecutive rate calculation and regular first-order rate evaluation gave inconsistent and spurious results. Applying initial rate calculations to the absorbance–time data give a trend, in the rate constants, that was consistent to what was observed with the reaction. These values are shown in tables 1–4.

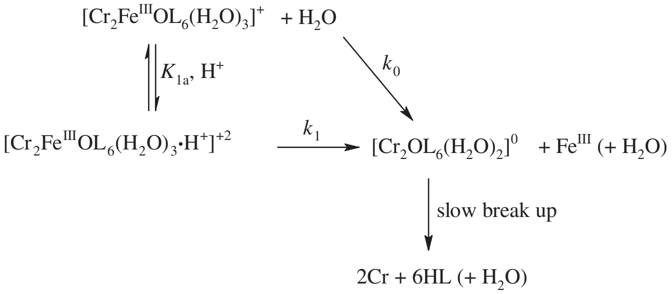
A plot of observed rate constant (k_{obs}) as a function of acid concentration gave a plot trending to saturation. On the basis of the results obtained a mechanism is proposed

Table 3. Pseudo-first-order rate constants as a function of acid concentration at 298, 303, and 308 K for the acid hydrolysis of 0.509 mmol L^{-1} $[Cr_2FeO(CH_3CO_2)_6(H_2O)_3]NO_3$ with $HClO_4$, $I = 0.50$ mol L^{-1} ($NaClO_4$).

$[H^+]$ (mol L^{-1})	298 K	303 K	308 K
	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})	$10^5\ k_{obs}$ (s^{-1})
0.01	5.12	6.41	7.81
0.02	5.93	7.44	9.10
0.03	6.55	8.51	10.45
0.05	7.56	9.86	11.80
0.07	8.64	10.86	13.24
0.09	9.91	12.48	14.17
0.1	10.28	13.08	15.51
0.12	10.78	13.47	15.89
0.15	11.13	14.64	17.23
0.17	11.70	14.94	17.65

Table 4. Pseudo-first-order rate constants as a function of acid concentration at 298, 302.6, and 307.2 K for the acid hydrolysis of 0.514 mmol L^{-1} $[Cr_2FeO(HCO_2)_6(H_2O)_3]NO_3$ with $HClO_4$, $I = 0.50$ mol L^{-1} ($NaClO_4$).

$[H^+]$ (mol L^{-1})	298 K	302.6 K	307.2 K
	$10^3\ k_{obs}$ (s^{-1})	$10^3\ k_{obs}$ (s^{-1})	$10^3\ k_{obs}$ (s^{-1})
0.01	3.90	4.69	5.57
0.02	4.31	5.38	6.46
0.03	5.04	6.13	7.24
0.05	5.97	6.98	8.69
0.07	6.39	8.24	10.1
0.09	7.37	9.54	11.7
0.1	7.94	9.85	12.2
0.12	8.60	10.9	13.6



Scheme 1. Mechanism of acid hydrolysis of the Cr_2Fe oxo-centered complexes.

(scheme 1), and the rate equation derived from the mechanism is depicted in equation (1).

$$\text{Rate} = \frac{k_0 + k_1 K_{1a}[H^+]}{1 + K_{1a}[H^+]}[\text{complex}]. \qquad (1)$$

Table 5. Specific rate constants and thermodynamic parameters for the acid hydrolysis reaction of $[Cr_2FeO(RCO_2)_6(H_2O)_3]^+$.

Temperature (K)	R	$10^5\ k_0$ (s^{-1})	$10^5\ k_1$ (s^{-1})	K_{1a} (mol dm^{-3})
298	$(CH_3)_2CH$	3.18 ± 0.05	7.18 ± 0.07	10.96 ± 0.01
	CH_3CH_2	4.04 ± 0.01	13.67 ± 0.02	9.56 ± 0.03
	CH_3	4.05 ± 0.17	17.63 ± 0.31	7.77 ± 0.01
	H	344 ± 20	386 ± 301	1.43 ± 0.01
303	$(CH_3)_2CH$	3.50 ± 0.05	10.57 ± 0.08	8.63 ± 0.01
	CH_3CH_2	4.82 ± 0.02	20.58 ± 0.04	6.38 ± 0.01
	CH_3	5.17 ± 0.17	23.09 ± 0.31	7.32 ± 0.04
	H	410 ± 15	610 ± 377	1.13 ± 0.04
308	$(CH_3)_2CH$	3.84 ± 0.07	14.61 ± 0.01	8.18 ± 0.01
	CH_3CH_2	5.60 ± 0.02	30.15 ± 0.06	4.44 ± 0.02
	CH_3	6.55 ± 0.20	26.95 ± 0.37	7.15 ± 0.02
	H	482 ± 11	980 ± 449	0.87 ± 0.47
Pathway	R	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta G^{\ddagger}_{298K}$ (kJ mol^{-1})
k_0	$(CH_3)_2CH$	12.0 ± 0.1	-291 ± 1	98.7 ± 0.9
k_1		51.7 ± 2.3	-151 ± 8	96.7 ± 6.7
k_0	CH_3CH_2	22.4 ± 0.9	-254 ± 3	98.1 ± 4.1
k_1		57.8 ± 0.6	-125 ± 2	95.0 ± 1.8
k_0	CH_3	34.1 ± 0.1	-214 ± 1	97.9 ± 0.5
k_1		29.9 ± 4.8	-216 ± 16	94.3 ± 16.7
k_0	H	25.3 ± 0.4	-207 ± 1	87.0 ± 1.4
k_1		74.6 ± 1.5	-22 ± 5	81.2 ± 18.5
	R	ΔH^{θ} (kJ mol^{-1})	ΔS^{θ} (J K^{-1} mol^{-1})	ΔG^{θ}_{298K} (kJ mol^{-1})
K_{1a}	$(CH_3)_2CH$	-22.4 ± 7.9	-55 ± 26	-6.0 ± 3.5
	CH_3CH_2	-58.5 ± 1.3	-178 ± 4	-5.4 ± 0.2
	CH_3	-6.4 ± 1.5	-4 ± 5	-5.2 ± 6.6
	H	-40.8 ± 1.9	-134 ± 6	-0.9 ± 0.1

Under pseudo-first-order conditions, the expression can be modified to give equation (2).

$$k_{\mathrm{obs}} = \frac{k_0 + k_1 K_{1a}[H^+]}{1 + K_{1a}[H^+]}. \tag{2}$$

From equation (2), values of k_0, k_1, and K_{1a} were derived from non-linear regression analysis using the STAGRAPHICS XV package and these along with the activation parameters are shown in table 5. A comparison of the observed rates and the rates predicted by the mechanism is shown in figure 4.

The acidity of the water molecule coordinated to the metal center of the trinuclear complexes changes with the nature of the carboxylate groups wrapping around the metal center. Wilkinson [24], for example, attempted to determine the pK_a of the Ru oxo-centered trinuclear acetate complex. In acidic media, all trinulcear complexes are fully protonated as suggested by the mechanism. A good fit to experimental data was obtained suggesting that the proposed mechanism is appropriate. Owing to the fact that the electronic spectrum of the complex does not change dramatically with a proton addition/dissociation, or other subtle modifications, there might be the possibility of a very complicated mechanism. It is very difficult to follow any such complicated possibility using UV-Vis spectroscopy. However, based on what was observed in the

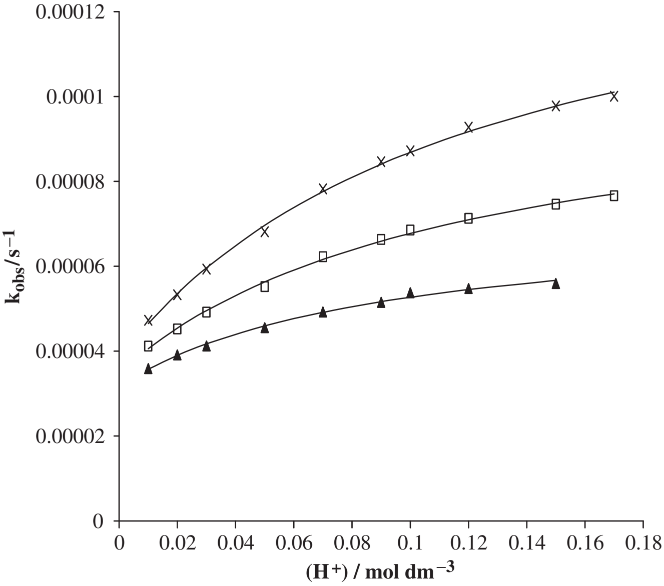


Figure 4. A comparison of the observed and predicted pseudo-first-order rate constants as a function of perchloric acid concentration for the acid hydrolysis of $[Cr_2FeO((CH_3)_2CHCO_2)_6(H_2O)_3]NO_3$ (▲: 298 K; □: 303 K; ×: 308 K).

hydrolysis of the trinuclear iron acetate species [13] we postulate that the carboxylate bridge is protonated and then a M–O bond is cleaved. At the point of protonation, the dominant factor is the ligand substitution/exchange rate of the iron(III) center compared to the chromium(III) center. The water exchange rate [25] for $Fe(H_2O)_6^{3+}$ and $Cr(H_2O)_6^{3+}$ is 1.6×10^2 and $2.8 \times 10^{-6}\,s^{-1}$, respectively, and as such the iron center is hydrolyzed much faster than the chromium center.

The rates of acid catalyzed hydrolysis have some implications. From the results (table 5) it is clear that there is a strong dependence of the spontaneous decomposition and the rates of acid catalyzed hydrolysis on the magnitude of K_{1a}, which is in turn related to the pK_a of the parent carboxylic acid. It has been suggested [7] that as the pK_a of the carboxylate ligand increases, there should be a corresponding increase in the bond length of the coordinated water molecule and the pK_a of the complex resulting from the enhanced sigma effect. An enhanced sigma effect would suggest enhanced electronic interaction between the metal center(s) and the ligand. Since the nature of the reactions is the same (i.e., acid assisted hydrolysis), one would expect that as the pK_a of the carboxylate increases, the enhanced interaction between the ligand and metal should retard the rate of hydrolysis. This general trend is depicted in table 5. There appears to be a linear correlation between the log of the rate (spontaneous or acid catalyzed) and the $\log K_{1a}$ of the intermediate cationic species. For these Cr_2FeO^{7+} complexes, the influence of the intermediate cation can be described by empirical equations (3) and (4).

$$\log k_1 = -1.86 \log K_{1a} - 2.115, \tag{3}$$

$$\log k_0 = -2.37 \log K_{1a} - 2.119. \tag{4}$$

We were, however, limited in the range of acid due to the solubility of organic acids of p$K_a \sim 4$, which reduces the precision of our correlation attempts. Clearly the rate of spontaneous hydrolysis prevents substantial analysis of the aqueous chemistry of complexes, such as when $R = ClCH_2$ (due to the low pK_a of the parent acid), even though it is easy to synthesize the complex.

The free energy of activation $\Delta G^\ddagger$ for the respective stages of the hydrolysis are comparable to the values obtained for the $[Fe_3O(CH_3CO_2)_6(H_2O)_3]^+$ complex cation [13], which suggests that the center of reaction is at the Fe(III) and also that the reactions follow a similar mechanism. The negative activation entropies for both proton assisted (k_1) and spontaneous (k_0) pathways support the associative or solvent-assisted mechanism for the hydrolysis. The intimate mechanistic details are difficult to establish; however, the similar values for Gibbs free energy of activation for both pathways definitely indicate that the mechanistic pathways for both processes are similar in nature.

As mentioned earlier, the prediction of intimate mechanism and as such the elementary steps involved for each step is indeed very difficult. Our experiment clearly indicates that the product of the reaction contains both Cr(III) dimer species and hexaaqua Fe(III), which would require the cleavage of at least five Fe–O bonds assisted by both proton and water molecules. This could generate five elementary steps involving five intermediates. We think that the first steps involving protonated species in the k_1 pathway and solvated species in the k_0 pathway are rate determining followed by continuous arrays of fast steps leading to formation of hexaaquairon(III). Since both paths require high negative entropy of activation one would envisage that the bond-making process involving formation of Fe(III) intermediates with higher coordination number is rate determining.

4. Conclusion

The results suggest that the rate-determining step is the hydrolysis of the protonated species generated in the equilibrium step between the complex cations and the proton. The rate is sensitive to the equilibrium constant of the intermediate species, which can be correlated with the pK_a of the parent carboxylic acid. As the pK_a of the parent acid increases the rate of the spontaneous and acid catalyzed hydrolysis decreases. It can also be concluded that the species follow a similar mechanism based on the similarity in the values of $\Delta G^\ddagger$ for the respective stages of the reaction. Both reaction pathways lead to a dinuclear chromium(III) species, which is hydrolyzed at a much slower rate.

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