

## Mechanistic studies of oxidation of substituted oxo acids by IFC in the presence of 1,10-phenanthroline

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The catalytic activity of 1,10-phenanthroline (phen) in imidazolium fluorochromate (IFC) oxidation of 4-oxo-4-phenylbutanoic acid (4-oxo acids) has been studied in 50% acetic acid-50% water medium. The reaction is first order each in imidazolium fluorochromate, oxo acid and hydrogen ion concentration. The rate of the reaction has been conducted at five different temperatures. Thermodynamic parameters have been calculated. A good correlation is found to exist between  $\log k_{1(308\text{ K})}$  and Hammett constant ( $\sigma$ ). For substituted oxoacids, the electron withdrawing substituents retard the reaction rate, while the electron releasing substituents enhance the rate of the reaction. The order of reactivities with substituents is  $p\text{-CH}_3\text{O} > p\text{-CH}_3 > p\text{-C}_6\text{H}_5 > \text{H} > p\text{-Cl} > p\text{-Br} > m\text{-NO}_2$  is due to the presence of +I and -I effect. The Exner plot  $k_{2(313\text{ K})}$  versus  $k_{2(318\text{ K})}$  is linear and isokinetic temperature is obtained. This supports that all the reactions under this investigation follow a common mechanism. The constant  $\Delta G$  values are obtained for all the substituted compounds. It also indicates that the substituted compounds are oxidized by same mechanism. Benzoic acid has been identified as the corresponding product of oxidation. Based on the kinetics results, a suitable mechanism has been proposed.

Keywords: Imidazolium fluorochromate, oxoacids, kinetics, oxidation.

### Introduction

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds<sup>1</sup>. Chromium especially, Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups<sup>2,3</sup>. Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry<sup>4</sup>. Imidazolium fluorochromate (IFC) is also one such reagent<sup>5</sup>. IFC has the following advantages over already reported Cr(VI) reagents: (i) quite stable at room temperature, (ii) not photosensitive, (iii) less hygroscopic and hence a suitable reagent for the oxidation of acid sensitive and ring strained alcohols. IFC as readily soluble in acetic acid. In oxo acids, two carbon atoms separate the carbonyl and the carboxyl groups and so they behave both as oxo compounds and as acids without the direct influence of the other group. Among the various organic compounds employed in these studies, a oxo acid is an attractive substrate in terms of its enolization. In the strong acid medium, the substrate undergoes enolization. Enol as

a reactive species of the substrate has been reported in the literature<sup>6</sup>. However, the kinetics of oxidation of oxo acids by imidazolium fluorochromate has not yet been reported. Hence, in the present investigation, the oxidation of oxo acids by imidazolium fluorochromate in aqueous acetic medium and the corresponding mechanism are reported.

### Experimental

#### Materials and methods:

The 4-oxo-4-phenylbutanoic acid, 4-oxo-4-biphenylbutanoic acid, 4-oxo-4-(4'-bromophenyl)butanoic acid and 4-oxo-4-(3'-nitrophenyl)butanoic acid were prepared by Friedel-Craft's acylation of the substituted benzene with succinic anhydride<sup>7-9</sup>. The remaining 4-oxo-4-(4'-methoxyphenyl)butanoic acid, 4-oxo-4-(4'-methylphenyl)butanoic acid, 4-oxo-4-(4'-chlorophenyl)butanoic acid, were obtained from Sigma-Aldrich Chemical Co. Imidazolium fluorochromate was prepared by reported method<sup>5</sup>, and its melting point (126–128°C) was checked. Acetic acid was purified<sup>10</sup> by standard method and the fraction distilling at 118°C was collected and its pu-

rity was checked by an iodometric method. All other chemicals used were of AnalaR grade. The solutions were prepared in double distilled water.

*Kinetic measurements:*

The kinetic studies were carried out under pseudo-first order conditions in 50% (v/v) aqueous acetic acid with the concentration of the 4-oxo acids in large excess compared to that of the oxidant. All reactant solutions were placed in a thermostated water bath for one hour to attain a temperature of 35°C. Appropriate quantities of the reagent solutions were mixed in a 250 cm<sup>3</sup> conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 430 nm for up to 80% of the reaction by using Systronics UV-Vis spectrophotometer. The reactions were followed determining the concentration of the unreacted IFC, at known intervals of time. The pseudo-first order rate constants  $k_1$  computed from the lin-

ear plots of log absorbance versus time by the least squares method were reproducible within  $\pm 3\%$ .

*Stoichiometry and product analysis:*

Reaction mixture containing an excess of oxidant over 4-oxo acid were kept at room temperature with perchloric acid in the presence of 1,10-phenanthroline for 24 h. Estimation of the unreacted oxidant showed that one mole of 4-oxo acid consumed one mole of the oxidant. The benzoic acid is formed as the main product under kinetic condition and it was confirmed by TLC, IR, GC-MS spectra.

**Results and discussion**

Oxidation of oxo acids by imidazolium fluorochromate has been conducted in 50% acetic acid and 50% water (v/v) medium at 308 K under pseudo-first order conditions and the observed results were discussed below.

The reaction was first order with respect to the oxidant

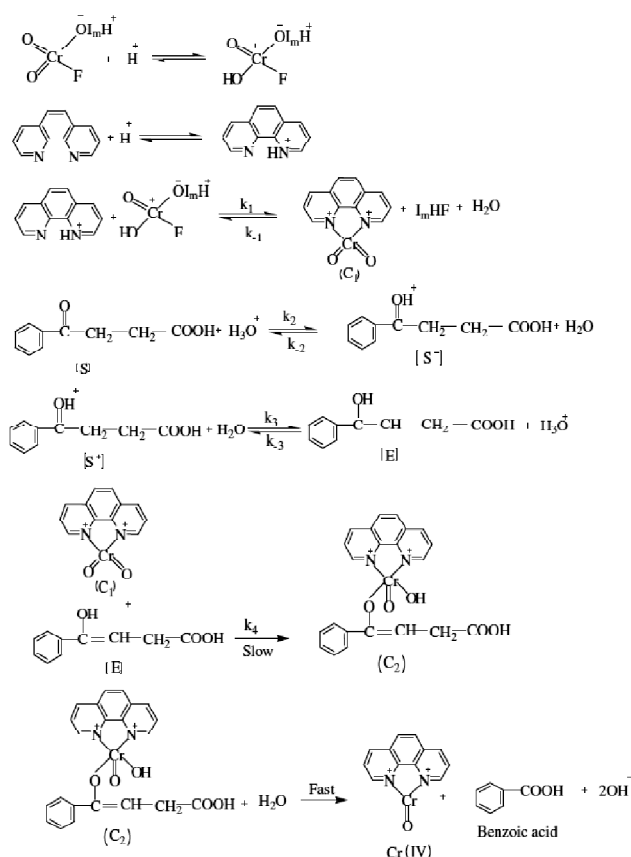
**Table 1.** Rate data for oxidation of 4-oxo acid by imidazolium fluorochromate at 308 K

[Oxidant] 10 <sup>3</sup> (mol dm <sup>-3</sup> )	[Substrate] 10 <sup>2</sup> (mol dm <sup>-3</sup> )	[HClO <sub>4</sub> ] 10 <sup>1</sup> (mol dm <sup>-3</sup> )	%CH <sub>3</sub> COOH-%H <sub>2</sub> O (% v/v)	[phen] 10 <sup>2</sup> (mol dm <sup>-3</sup> )	$k_{\text{obs}}$ 10 <sup>4</sup> (s <sup>-1</sup> )
1.0	2.0	2.0	50-50	2.0	3.89
1.5	2.0	2.0	50-50	2.0	3.88
2.0	2.0	2.0	50-50	2.0	3.87
2.5	2.0	2.0	50-50	2.0	3.86
3.0	2.0	2.0	50-50	2.0	3.86
1.0	1.0	2.0	50-50	2.0	2.04
1.0	1.5	2.0	50-50	2.0	2.99
1.0	2.0	2.0	50-50	2.0	3.89
1.0	2.5	2.0	50-50	2.0	5.24
1.0	3.0	2.0	50-50	2.0	5.89
1.0	2.0	1.0	50-50	2.0	3.89
1.0	2.0	1.5	50-50	2.0	4.99
1.0	2.0	2.0	50-50	2.0	5.78
1.0	2.0	2.5	50-50	2.0	7.07
1.0	2.0	3.0	50-50	2.0	7.64
1.0	2.0	2.0	50-50	2.0	3.89
1.0	2.0	2.0	55-45	2.0	4.64
1.0	2.0	2.0	60-40	2.0	5.88
1.0	2.0	2.0	65-35	2.0	8.31
1.0	2.0	2.0	70-30	2.0	13.80
1.0	2.0	2.0	50-50	1.0	1.81
1.0	2.0	2.0	50-50	1.5	2.63
1.0	2.0	2.0	50-50	2.0	3.89
1.0	2.0	2.0	50-50	2.5	5.12
1.0	2.0	2.0	50-50	3.0	6.02

as evidenced by a good linearity in the plot  $\log [\text{IFC}]$  versus time ( $r = 0.99$ ). The rate of oxidation increased progressively on increasing the concentration of 4-oxo acid. The plot of  $\log k_1$  versus  $\log [4\text{-oxo acid}]$  gave the slope of 1.0 ( $r = 0.99$ ), shows that the oxidation reaction was first order with respect to 4-oxo acid. The rate of the reaction increases with the increasing the  $[\text{H}^+]$ . A plot of  $\log k_1$  versus  $\log [\text{H}^+]$  gave a straight line with a slope of 1.0 ( $r = 0.99$ ), it indicates first order with respect to hydrogen ion concentration. The rate of the reaction increases with decreasing the dielectric constant of the medium suggesting the ion-dipole interaction between the reactants. Rate of reaction increased with increase the concentration of 1,10-phenanthroline. The added  $\text{Mn}^{2+}$  ion decreases the rate of the reaction. It indicates the involvement of two electron processes in the reaction<sup>11</sup>. The rate constants were measured at five different temperatures and the activation parameters were calculated from a plot of  $\ln k_2/T$  versus  $1/T$  ( $r = 0.99$ ) of the Eyring's equation<sup>12</sup> and it was found to be linear<sup>13</sup>. The Cr(VI)-phen complex is believed to be the probable electrophile in the catalyzed oxidation.

#### Mechanism and rate law:

The mechanism of reaction for the oxidation of oxo acid by IFC in an acid medium is shown in Scheme 1. The reaction is first order each with respect to the oxo acid, IFC and  $\text{H}^+$  ion. The linear increase in the reaction rate with the increase in  $[\text{H}^+]$  ion is attributed to formation of protonated IFC i.e.  $\text{IFCH}^+$  and to the enolisation of the oxo acid. The formation of  $\text{IFCH}^+$  ion and the enolisation of the oxo acid is facilitated at lower dielectric constant of the medium. The rate of enolisation is found to be greater than the rate of oxidation. The course of oxidation does not involve any free radical intermediate. It is believed that the catalytic activity of complexing agent such as 1,10-phenanthroline depends on their ability to stabilize intermediate chromium valence states<sup>14</sup>. 1,10-Phenanthroline readily form complex ( $\text{C}_1$ ) with Cr(VI). In the next step, the complex reacts with the substrate to form a ternary complex ( $\text{C}_2$ ). These complex undergoes redox decomposition by two electron transfer within the cyclic transition state in a rate-determining step involving simultaneous rupture of C-C and C-H bonds to give a benzoic acid and the Cr(IV)-phen complexes. Considering all these facts and findings, a suitable mechanism has been proposed for the oxidation (Scheme 1).



**Scheme 1.** Mechanism of oxidation of 4-oxo acid by IFC in the presence of 1,10-phenanthroline.

$$\text{The rate law for this mechanism is } \frac{-d[\text{IFC}]}{dt} = k_4[\text{E}][\text{IFC}][\text{H}^+]$$

#### Effect of substituents:

The kinetics was carried out with a *meta* and few *para* substituted oxo acid at 308, 313, 318, 323 and 328 K. The observed rate constant increases with temperature for all of the compounds. The activation parameters for the oxidation of oxo acids by IFC have been evaluated. A plot of  $\log k_{1(308\text{K})}$  of the substituted oxo acid with reaction constant  $\sigma$  gave a good straight line with low value  $-0.82$  ( $r = 0.99$ ). The value indicates the sensitivity of a reaction to the effects of electronic perturbation. It also provides the information about the nature of the transition state involved during the reaction. A reaction involving development of positive charge in the transition state is aided by electron releasing substituents and

the  $\sigma$  value negative. The presence of electron releasing substituents in the phenyl ring activates the reaction rate while the electron withdrawing substituents retards in the reaction rate. The order of the reactivity of oxo acids is  $p\text{-OCH}_3 > p\text{-CH}_3 > p\text{-C}_6\text{H}_5 > \text{H} > p\text{-Cl} > p\text{-Br} > m\text{-NO}_2$  is due to the presence of +I with  $-\sigma$  values and  $-I$  effect with  $+\sigma$  values. The plot of  $\log k_1(313\text{ K})$  versus  $\log k_1(308\text{ K})$  gave a straight line with  $r = 0.99$  such a good correlation indicates that all the substituents follow a common mechanism. The entropy of activation is negative for all the oxo acids ranging from  $-211.07$  to  $-252.52\text{ JK}^{-1}\text{ mol}^{-1}$ .  $\Delta S^\ddagger$  values are negative indicating extensive solvation of transition state over the reactants. Free energy of activation  $\Delta G^\ddagger$  values is nearly constant which indicates that all the substituted oxo acids are oxidized by the same mechanism. The minimum  $E_a$  and  $\Delta H^\ddagger$  values support the proposed mechanism.

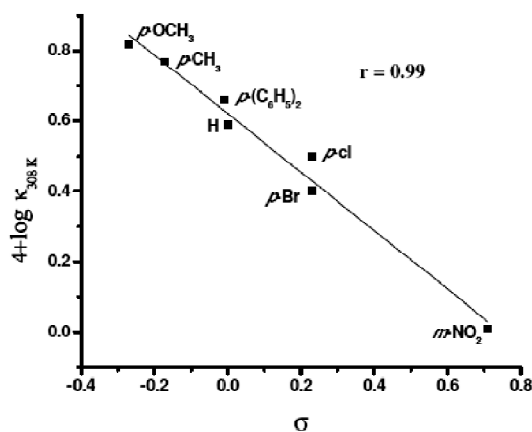


Fig. 1. Hammett's plot.

A plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  gave a straight line with a correlation coefficient 0.99. As  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  do not vary linearly, no isokinetic relationship is observed. This indicates absence of enthalpy and entropy compensation effect. The validity of the isokinetic relation can be tested graphically by plotting by Exner plots. Exner<sup>15,16</sup> criticized the validity of such a linear correlation between  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  as these quantities depend on each other when measurement at two temperatures are made, the experimental data can be treated by the following equation.

$$\log k_2(T_1) = a + b \log k_2(T_2)$$

$$\text{where } T_2 > T_1$$

A good correlation ( $r = 0.99$ ) is obtained when  $\log k_2(318\text{ K})$  is plotted against  $\log k_1(313\text{ K})$  shows that reaction under investigation follow common mechanism.

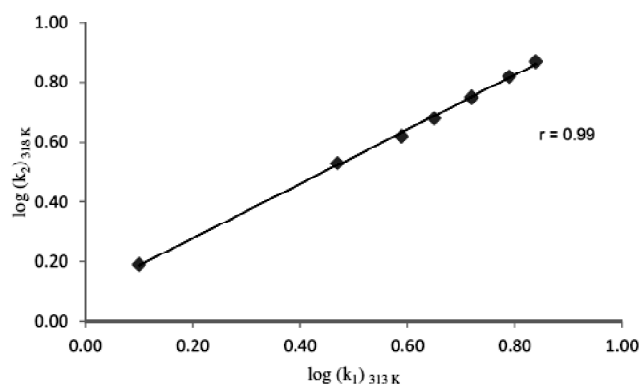


Fig. 2. Exner Plot of  $\log k_1(313\text{ K})$  versus  $\log k_2(318\text{ K})$  for the oxidation of substituted oxo acids by IFC.

Table 2. Thermodynamic parameters for the oxidation of *para-meta* substituted 4-oxo acids by IFC

[IFC] =  $1.0 \times 10^{-3}\text{ mol dm}^{-3}$ , [oxo] =  $2.0 \times 10^{-1}\text{ mol dm}^{-3}$ , [1,10-phen] =  $2.0 \times 10^{-2}\text{ mol dm}^{-3}$ , Solvent = 50% AcOH-50% H<sub>2</sub>O (v/v), [HClO<sub>4</sub>] =  $2.0 \times 10^{-1}\text{ mol dm}^{-3}$

Sl. No.	Substituents	$k_1 \times 10^4\text{ s}^{-1}$					$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> ) at 308 K	$E_a$ (kJ mol <sup>-1</sup> ) at 308 K	$r$	$\sigma$
		308 K	313 K	318 K	323 K	328 K						
1.	<i>p</i> -Methoxy	6.60	6.88	7.41	7.81	8.12	6.48	252.52	84.25	9.04	0.99	-0.27
2.	<i>p</i> -Methyl	5.88	6.22	6.62	7.14	7.41	7.31	250.76	84.53	9.87	0.99	-0.17
3.	<i>p</i> -Biphenyl	4.57	5.24	5.62	6.16	6.76	12.80	234.92	85.15	15.36	0.99	-0.01
4.	Parent	3.89	4.46	4.78	5.24	5.88	14.13	231.19	85.31	16.69	0.99	0.0
5.	<i>p</i> -Chloro	3.16	3.89	4.16	4.89	5.24	17.79	221.65	86.04	20.35	0.98	+0.23
6.	<i>p</i> -Bromo	2.51	2.95	3.38	3.80	4.36	20.28	215.75	86.87	22.84	0.99	+0.23
7.	<i>m</i> -Nitro	1.02	1.25	1.54	1.90	2.39	24.42	211.07	87.41	24.98	0.99	+0.71

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