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Alkaline hexacyanoferrate(III) oxidation of substituted 4-oxo acids: a mechanistic study

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ABSTRACT: The kinetics of the oxidation of substituted 4-oxo-4-arylbutanoic acids by hexacyanoferrate(III) in aqueous alkaline medium were studied. The reactions are found to be first order in each of the reagents, the oxo acid, hydroxide ion and the hexacyanoferrate(III) ion. A mechanism involving the formation of enolate anion from the oxo compound and subsequent rate-determining electron transfer is proposed. Application of the Olson–Simonson rule substantiated the participation of negatively charged ions in the rate-determining step. The experimental rate constant is found to be composite, being the product of the equilibrium constant for the enolate anion formation and the rate constant of the oxidation step (Kk_2). The effect of addition of solvents such as methanol and DMSO is discussed and a quantitative relationship is derived between the ionic strength and the composite rate constant. The low activation energies and even the negative activation energy in the oxidation of 4-(3-nitrophey1)-4-oxobutanoic acid are explained. The ρ values are positive and decrease with temperature. Contrary to the expected electronic effect, the methyl group in the *ortho* position accelerates the reaction owing to steric factors. From the intersection of the lines in the Hammett and Arrhenius plots, the isokinetic relationship is discussed.

KEYWORDS: 4-oxo acids; oxidation; hexacyanoferrate(III); mechanism; kinetics

INTRODUCTION

Hexacyanoferrate(III) is a complex ion, capable of abstracting one electron from an electron-rich site in an organic molecule. The transfer of the electron occurs from the substrate to the metal ion by an outer-sphere mechanism.[1] It is capable of oxidizing under both acidic and alkaline conditions and has been utilized extensively in the oxidation of organic compunds.[2] The oxidation of organic compounds by hexacyanoferrate(III) in alkaline medium presents some special kinetic features. The rate constant decreases when the initial concentration of the oxidant[3–6] increases. Although the ionic strength of the medium has a great influence on the rate of oxidation,[7–9] no quantitative relationship has so far been established between them. The experimental energy of activation is low in all cases and no explanation has so far been offered. The Hammett reaction constant ρ for the oxidation of aromatic oxo compounds such as acetophenone has high positive values,[10] although oxidation reactions, in general, are expected to yield low negative values.

The present study on the oxidation of 4-oxo-4-arylbutanoic acids was undertaken to gain a clear mechanistic picture of the reaction and also to seek an explanation for the above-mentioned features of oxidation by hexacyanoferrate. The solubility in an aqueous alkaline medium due to the carboxyl group makes these oxo acids a system of choice.

EXPERIMENTAL

Preparation of 4-oxo-4-acids

4-Oxo-4-arylbutanoic acids were prepared by standard procedures found in the literature.[11–14] These involve mainly Friedel–Crafts reaction of benzene and its analogues with succinic anhydride in the presence of anhydrous aluminium chloride. Nitration of 4-oxo-4-arylbutanoic acids gave the 3-nitro compounds.[15] 4-Oxo-2,4-diphenylbutanoic was prepared from chalcone via the formation of the nitrile[16] and subsequent hydrolysis. All the oxo acids were crystallized twice from water and their purity was checked by their melting-points and UV, IR and NMR spectra.

Kinetic measurements

All the kinetic measurements were carried out using doubly distilled water with analytical-grade KCl,

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$K_3Fe(CN)_6$ and NaOH. In a typical run, 20 cm^3 of freshly prepared 0.05 M oxo acid in 0.1 M NaOH was pipetted into a reaction bottle that was painted black to avoid photochemical conversion of hexacyanoferrate(II) to hexacyanoferrate(III). A 25 cm^3 volume of water was added and the bottle was thermostated. The reaction was started by pipetting 5 cm^3 of thermostated 0.02 M hexacyanoferrate(III) solution. The reaction was followed by estimating the unreacted hexacyanoferrate(III) iodimetrically. Addition of 5 cm^3 at 10% $ZnSO_4$ solution ensured the completion of the reaction between iodide and hexacyanoferrate(III) ions. The pesudo-first-order rate constants were calculated by a graphical method and the values were reproducible to within 3%. The ionic strength of the medium was maintained using KCl.

Duplicate experiments were conducted in an atmosphere of nitrogen and without nitrogen. Since no difference was observed in the results, all the experiments reported in this paper were obtained without nitrogen. Freshly prepared solutions of oxo acids in sodium hydroxide were used to avoid any possible side-reactions.

Product analysis and stoichiometry

A 20 cm^3 volume of 1 M hexacyanoferrate(III) solution was mixed with 20 cm^3 of a 0.1 M solution of 4-oxo-4-arylbutanoic acid in sodium hydroxide and the reaction was allowed to go to completion in a thermostat at 40 °C for 3–4 h. The solution was then cooled and acidified. A precipitate was formed along with effervescence due to the evolution of carbon dioxide. The precipitate was extracted into diethyl ether, which on evaporation gave benzoic acid, identified by TLC and chemical analysis. It is well known that 4-oxo-acids on oxidation give α,β-unsaturated ketones,[17,18] but when the oxo acid is unsubstituted in the α- or β-position, α,β-unsaturated ketones are not isolated.[19] The possibility of phenyl vinyl ketone being formed in our experiments cannot be ruled out. Although it may be formed, it is highly susceptible to nucleophilic attack in alkaline medium.[20] To obtain a clear picture, the oxidation of 4-oxo-2,4-diphenylbutanoic acid was carried out. It was found that as soon as the oxo acid solution was mixed with the oxidant solution, a precipitate was formed that was identified as chalcone by its melting-point and IR spectrum.

The stoichiometry of the reaction (substrate:oxidant) was observed to be variable and ranged from 1:2 to 1:5. The ultimate products of oxidation of the oxo acid are benzoic acid and CO_2 and this oxidation requires 6 equiv. of the oxidant, whereas oxidative decarboxylation would require 2 equiv. The observed stoichiometry could therefore arise from the interplay of several such incomplete oxidations.

Polymerization test

When a few drops of methyl acrylate were added to the oxo acid solution in NaOH containing hexacyanoferrate(III), turbidity occurred, indicating polymerization. This indicates the formation of intermediate free radicals during oxidation.

RESULTS

The kinetics of oxidation of unsubstituted and substituted 4-oxo-4-arylbutanoic acids by hexacyanoferrate(III) in aqueous alkaline solution are found to be first order with respect to the substrate, oxidant and OH^- ions. At fixed [substrate] and [OH^-] which are always in excess over the [oxidant], the plots of log[oxidant] against time are linear for all the substrates for at least two half-lives of the oxidant. The pseudo-first-order rate constants calculated from the first-order plots are given in Table 1.

Although a decrease in the rate constant occurs with increase in the initial concentration of hexacyanoferrate(III) [Table 1(a)], the reaction shows no deviation in the first-order dependence on the oxidant at any concentration. Such a decrease in the rate constant has also been reported in the oxidation of other oxo compounds.[3–6]

Table 1. Pseudo-first order rate constants for the oxidation of 4-oxo-4-arylbutanoic acids: effect of variation of (a) [oxidant]$_0$, (b) [substrate] and (c) [OH^-][a]

(a) [Substrate] = 2×10^{-2} mol dm^{-3}; [OH^-] = 1.5×10^{-2} mol dm^{-3}; $I = 0.118$							
10^3 [oxidant]$_0$ (mol dm^{-3})	2.0	3.0	4.0	5.5	8.0	10.0	12.0
$10^3 k$ (s^{-1})	1.44	1.40	1.30	1.22	1.09	0.96	0.82
(b) [Oxidant] = 2×10^{-3} mol dm^{-3}; [OH^-] = 5.4×10^{-2} mol dm^{-3}; $I = 0.082$							
10^3 [substrate] (mol dm^{-3})	6.0	8.0	10.0	12.0	16.0		
$10^3 k$ (s^{-1})	1.14	1.50	1.90	2.20	3.00		
(c) [Oxidant] = 2×10^{-3} mol dm^{-3}; [substrate] = 1×10^{-2} mol dm^{-3}; $I = 0.108$							
10^2 [OH^-] (mol dm^{-3})	4.0	5.0	6.0	7.0	8.0		
$10^3 k$ (s^{-1})	1.51	1.92	2.38	2.64	3.01		

[a] [OH^-] refers to the concentration of free hydroxide ions left after neutralization of the carboxyl group in the substrate.

Table 2. Effect of varying the ionic strength in the oxidation of 4-oxo-4-phenylbutanoic acids by hexacyanoferrate(III) at 313 K

[Substrate] = 1.0×10^{-2} mol dm^{-3}; [OH$^-$] = 1.0×10^{-2} mol dm^{-3}; [oxidant] = 2.0×10^{-3} mol dm^{-3}									
I	0.038	0.050	0.060	0.074	0.098	0.134	0.158	0.188	0.218
10^4k (s^{-1})	1.84	2.42	2.54	3.58	4.32	5.12	5.53	6.89	8.21

Further, the reaction is found to be specifically hydroxide catalysed since other bases such as acetate ions fail to bring about the reaction.

Effect of ionic strength

An increase in ionic strength results in an increase in the rate constant (Table 2) and a plot of log k_{obs} against $I^{1/2}$ (Fig. 1) gives a limiting slope of 5.0.

Effect of solvents

A decrease in the relative permittivity (ε_r) of the medium, effected by adding methanol, decreases the rate of oxidation considerably. However, on addition of dimethyl sulfoxide the rate of oxidation decreases by up to 40%, then increases (Table 3).

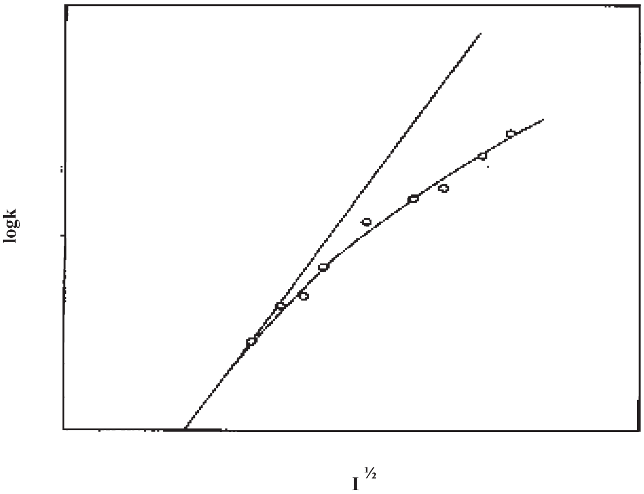


Figure 1. Effect of varying ionic strength

Table 3. Effect of addition of methanol and dimethyl sulfoxide on the oxidation of 4-oxo-4-phenylbutanoic acids by hexacyanoferrate(III) at 308 K

[Substrate] = 1.0×10^{-2} mol dm^{-3}; [OH$^-$] = 2.0×10^{-2} mol dm^{-3}; [oxidant] = 2×10^{-3} mol dm^{-3}					
Methanol (%, *v*/*v*)	0	5	10	15	20
10^4k (s^{-1})	3.42	2.8	1.46	1.26	0.78
DMSO (%, *v*/*v*)	10	20	40	50	60
10^4k (s^{-1})	5.29	3.06	1.90	2.28	3.0

Effect of adding hexacyanoferrate(II)

The addition of hexacyanoferrate(II) decreases the rate of reaction (Table 4). The dependence of the rate on hexacyanoferrate(II) is in the inverse order.

Substituent effects and evaluation of Arrhenius parameters

The oxidations of different phenyl-substituted oxo acids ($ArCOCH_2CH_2CO_2H$, where Ar = 4-methoxy, 4-ethoxy, 4-methyl, 3,4-dimethyl, 2,4-dimethyl, 2,4,4-trimethyl, 4-chloro, 4-bromo and 3-nitro substituted phenyl) were studied. The study was also extended to 4-oxo-4-(1-naphthyl)- and 4-oxo-4-(2-naphthyl)butanoic acids. In all these cases, the reaction orders are the same, namely first order with respect to oxidant, substrate and hydroxide. Electron-withdrawing substituents in the phenyl ring enhance the rate of oxidation and electron-releasing substituents decrease it. The Hammett plots (Fig. 2) are linear with good correlation coefficients at four different

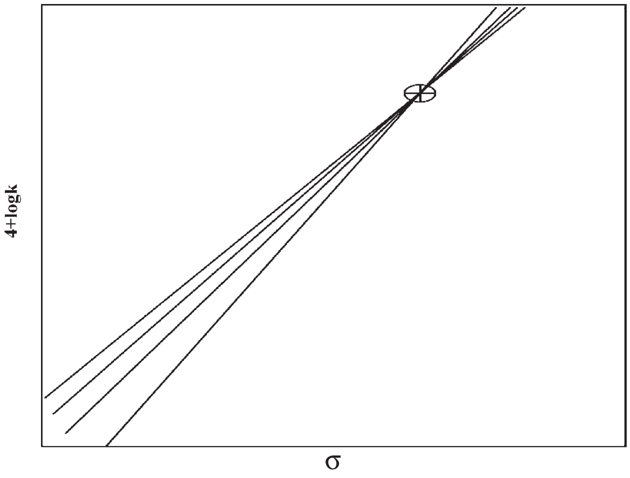


Figure 2. Hammett plots

Table 4. Effect of hexacyanoferrate(II) on the oxidation 4-oxo-4-phenylbutanoic acids by alkaline hexacyanoferrate(III) at 308 K

[Substrate] = 1.0×10^{-2} mol dm^{-3}; [OH$^-$] = 2.0×10^{-2} mol dm^{-3}; [oxidant] = 2.0×10^{-3} mol dm^{-3}; $I = 0.042$				
10^3 [Fe(CN)$_6$$^{4-}$]	0	1.0	2.0	3.0
10^4k (s^{-1})	6.2	4.78	4.5	3.97

Table 5. Substituent effect and activation parameters in the oxidation of $ArCO(CH_2)_2CO_2H$ by alkaline hexacyanoferrate(III)

[Substrate] = 1.0×10^{-2} mol dm^{-3}; [OH$^-$] = 2.0×10^{-2} mol dm^{-3}; [oxidant] = 2×10^{-3} mol dm^{-3}; $I = 0.042$

		10^4k (s^{-1})				E_a (kJ mol^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J mol^{-1} K^{-1})	$\Delta G^\ddagger$ (kJ mol^{-1})
Ar	σ	299 K	308 K	313 K	318 K				
Phenyl	0	2.56	3.42	4.20	5.06	29.0	26.5	−155.8	74.5
2-Naphthyl	0.17	5.56	6.00	6.92	7.32	21.7	19.1	−174.9	73.0
4-Bromophenyl	+0.23	6.68	8.04	8.90	10.8	19.8	17.2	−178.5	72.2
1-Naphthyl	+0.40	11.2	13.8	14.92	15.4	13.9	11.3	−193.2	70.8
3-Nitrophenyl	+0.71	36.14	35.16	34.76	32.48	−4.2	−6.7	−244.0	68.4
4-Chlorophenyl	+0.23	6.66	8.06	8.96	11.0	20.7	18.1	−175.7	72.2
4-Ethoxyphenyl	−0.25	1.10	1.80	2.24	2.52	36.0	33.4	−138.6	76.1
4-Methoxyphenyl	−0.27	1.08	1.70	2.20	2.28	33.2	30.6	−148.1	76.2
4-Methylphenyl	−0.17	1.46	2.18	2.24	3.02	29.3	26.7	−158.3	75.5
2,4-Dimethylphenyl	—	1.98	2.88	3.84	4.44	35.2	32.6	−137.3	74.9
3,4-Dimethylphenyl	−0.24	1.18	1.86	2.56	2.88	39.2	36.6	−127.9	76.0
2,4,6-Trimethylphenyl	—	7.76	10.10	10.70	12.6	20.0	17.4	−175.6	71.5
Reaction constant (ρ)		1.57	1.36	1.25	1.19				

temperatures: 299 K, 308 K, 313 K and 318 K (compounds with substituents in the 2- or 2,6-position of the benzene ring are not included for obvious reasons). The reaction constants (ρ) are positive and decrease with increasing temperature.

The Arrhenius relationship is observed in all cases but with poorer correlation coefficients than those of the Hammett plots. The reactions are characterized by low values of activation energy and large negative values of entropy of activation. Table 5 gives the values of the rate constants at four temperatures and also the Arrhenius parameters.

It is interesting to note that the experimentally obtained energy of activation is negative for the oxidation of 4-oxo-4-(3-nitrophenyl)butanoic acid.

DISCUSSION

Mechanism

Based on the above results and in analogy with the alkaline hexacyanoferrate(III) oxidation of other oxo compounds, the mechanism shown in Scheme 1 may be proposed, where K (k_1/k_{-1}) is the equilibrium constant for enolate anion (A^{2-}) formation.

Steady-state equation:

$$d/dt(\mathrm{RA}) = k_2[\mathrm{A}^{2-}][\mathrm{F}] - k_{-2}[\mathrm{RA}][\mathrm{F}^1] - k_3[\mathrm{RA}] = 0 \tag{1}$$

where RA = radical anion

$$[\mathrm{RA}](k_{-2}[\mathrm{F}^1] + k_3) = k_2[\mathrm{A}^{2-}][\mathrm{F}]$$

$$[\mathrm{RA}] = \frac{k_2[\mathrm{A}^{2-}][\mathrm{F}]}{k_{-2}[\mathrm{F}^1] + k_3} \tag{2}$$

$$[k_1] = \frac{[\mathrm{A}^{2-}][\mathrm{H_2O}]}{[\mathrm{HA}^-][\mathrm{OH}^-]} \text{ or } [\mathrm{A}^{2-}] = \frac{k_1[\mathrm{HA}^-][\mathrm{OH}^-]}{[\mathrm{H_2O}]} \tag{3}$$

$$[\mathrm{RA}] = \frac{k_1k_2[\mathrm{HA}^-][\mathrm{OH}^-][\mathrm{F}]}{(k_2[\mathrm{F}^1] + k_3)[\mathrm{H_2O}]} \tag{4}$$

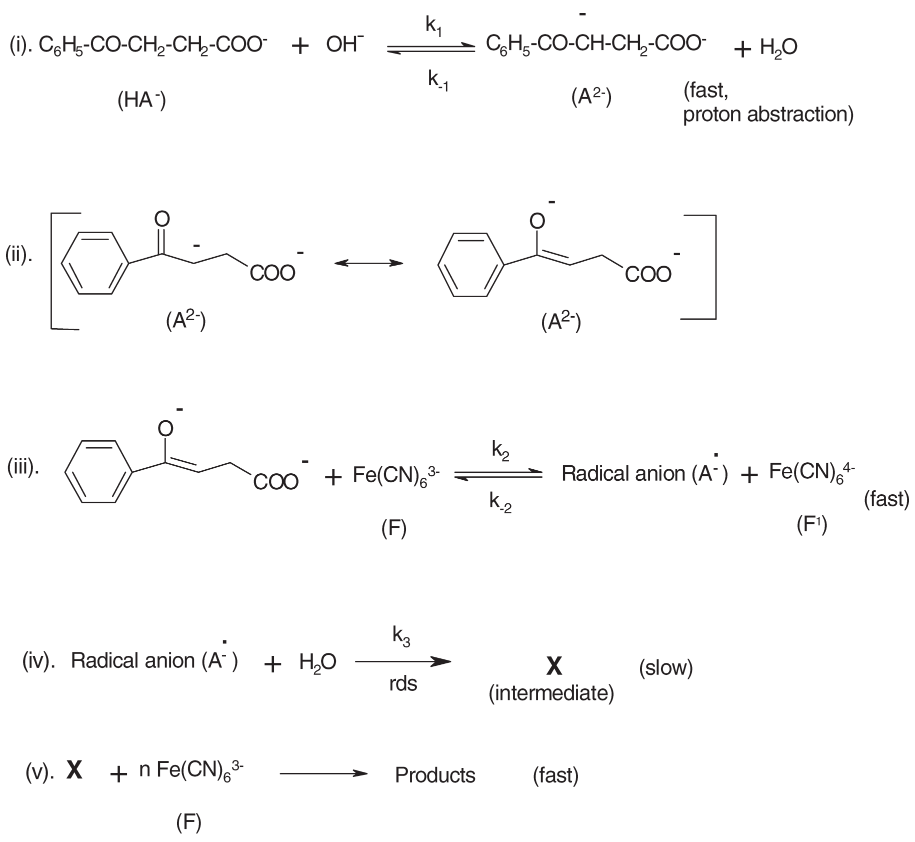
$$\text{rate} = \mathrm{k_3}[\mathrm{RA}][\mathrm{H_2O}] \text{ (assuming slow step)}$$

$$\text{rate} = \frac{k_1k_2k_3[\mathrm{HA}^-][\mathrm{OH}^-][\mathrm{F}]}{k_{-2}[\mathrm{F}^1] + k_3} \tag{5}$$

$$\text{rate} = \frac{k_1k_2k_3[\mathrm{HA}^-][\mathrm{F}][\mathrm{OH}^-]}{k_{-2}[\mathrm{F}^1]} \tag{6}$$

Equation (5) shows a negative fractional order in ferrate(II) and Eqn (6) supports a negative fractional order. This explains the observed first-order dependence on the oxidant, substrate and OH$^-$. The experimental rate constant when divided by the concentrations of the oxo acid and OH$^-$ gives a value of k_2K which is the product of the rate constant for the electron transfer step and of the equilibrium constant for the proton abstraction. The formation of enolate anion is a prerequisite for the oxidation,[21] as benzaldehyde, which cannot enolize, is not oxidized by alkaline hexacyanoferrate(III).

From the above mechanism, the experimental results can be explained.



Where n = 1 for 1:2 stoichiometry and n = 4 for 1:5 stoichiometry of HA^-:F

Scheme 1

Decrease of rate constant with increasing $[\text{oxidant}]_0$

The reason for the decrease in rate constant with increasing $[\text{hexacyanoferrate(III)}]_0$ may be found by considering the sequence of reaction steps. In the rate equation obtained from the proposed mechanism, it is assumed that $k_{-1}[H_2O]$ is much greater than k_2 [F]. At higher concentrations of hexacyanoferrate(III), k_2[F] may reach a value comparable to $k_1[H_2O]$ and may no longer be ignored.

From equation (5),

$$k_{\text{obs}} = \frac{k_1 k_2 k_3 [\text{HA}^-][\text{OH}^-][\text{F}]}{k_{-2}[\text{F}^1] + k_3}$$

and

$$\frac{1}{k_{\text{obs}}} = \frac{k_1 k_2 k_3 [\text{HA}^-][\text{OH}^-][\text{F}]}{k_{-2}[\text{F}^1] + k_3}$$

Therefore, a plot of $1/k_{\text{obs}}$ versus [F] must give a straight line from the slope of which k_1 can be calculated by following the method suggested by Maskill.[22] The k_1 values obtained were 2.73, 9.1×10^{-4} and $2.7 \times 10^{-4}\,\text{mol}^{-1}\,\text{dm}^3\,\text{min}^{-1}$. From earlier investigations on the oxidation of oxo compounds,[3,5,6] k_1 was calculated in this way for ethyl methyl ketone, formadehyde and pyruvic acid. The value thus obtained for ethyl methyl ketone agrees well with that found in the literature.[23,24] The k_1 values obtained for the oxidation of 4-oxo acids are given in Table 6.

The Hammett plot drawn with these k_1 values gives a ρ value of 0.69, which is comparable to the value of 0.88 reported for the alkaline hydrolysis of esters of these oxo acids.[24]

Effect of ionic strength

The large increase in the rate constants with increasing ionic strength of the medium clearly points to a reaction

Table 6. Values of the rate constants for proton abstraction from $XC_6H_4COCH_2CH_2\ CO_2^-$ by OH^- ions at 308 K

X	4-OCH$_3$	H	4-Cl	3-NO$_2$
$k_1\ \text{mol}^{-1}\,\text{dm}^{-3}\,\text{s}^{-1}$	0.0255	0.0328	0.0592	0.115

between similarly charged ions. The observed rate constant is the product of the equilibrium constant of the proton transfer equilibrium and the rate constant of the oxidation step (Kk_2). The Bjerrum–Brønsted equation relates k_2 to ionic strength as

$$\log k_2 = \text{constant} - 2QZ_\text{A}\ Z_\text{B}\ I^{0.5}$$

Consideration of the charges of enolate and hexacyanoferrate(III) ions results in the equation

$$\log k_2 = \text{constant} - 12QI^{0.5}$$

The equilibrium constant K and I are related as

$$\log K = \text{constant} + \log f_{\text{H2A}} - \log f_{\text{HA}^-} - \log f_{\text{OH}^-}$$

According to the Debye-Hückel limiting law:

$$\log f_i = -QZ_i^2 I^{0.5}$$

Therefore, $\log K = \text{constant} - 2QI^{0.5}$. Combining the equations for k_2 and K,

$$\log k_2 K = \text{constant} + 10I^{0.5}$$

At 40 °C, Q has a value of 0.52, so $\log k_2 K = \text{constant} + 5.2\ I^{0.5}$.

The limiting slope obtained from Fig. 1 is 5.0, which is in agreement with the above equation. The deviation from linearity at higher ionic strengths is due to failure of the Bjerrum–Brønsted equation and the Debye-Hückel limiting law.

Olson–Simonson rule[26]

In a reaction between ions of similar charge, the concentration of oppositely charged ions influences the rate constant more than the ionic strength of the medium. The application of this rule was attempted in the present oxidation studies, by keeping the concentration of potassium ions constant while varying the ionic strength (Table 7).

Table 7. Application of Olson–Simonson rule

$[\text{Substrate}]_0 = 1.0 \times 10^{-2}$ mol dm^{-3}; $[\text{OH}^-] = 2.0 \times 10^{-2}$ mol dm^{-3}; $[\text{oxidant}]_0 = 3.0 \times 10^{-3}$ mol dm^{-3}; $T = 313$ K

Added salt	[Salt] (mol dm^{-3})	[K$^+$] (mol dm^{-3})	I	$10^4\ k_\text{obs}$
None	—	0.027	0.038	2.76
KCl	0.012	0.0	0.050	3.60
K_2SO_4	0.006	0.041	0.056	3.64
KCl	0.06	0.089	0.098	6.50
K_2SO_4	0.03	0.089	0.121	6.20
KCl	0.18	0.209	0.218	12.3
K_2SO_4	0.09	0.209	0.308	12.0

It can be seen that if the potassium ion concentration is kept constant, the rate constants remain unaltered in spite of the change in ionic strength. The application of the Olson–Simonson rule underscores the participation of negatively charged ions in the rate-determining step.

Arrhenius parameters

In Equation (3), K/[H_2O] can be equated to K_a/K_w, where K_a is the ionization constant of the CH_2 adjacent to the oxo group. Being the ionization constant of a weak acid, K_a does not vary much with temperature,[27,28] whereas the ionic product of water, K_w, increases with temperature in the temperature range studied.[29] Since the equilibrium constant for the proton transfer is related to K_a/K_w, its value decreases with temperature. The observed rate constant in the oxidation of 4-oxo acids by alkaline hexacyanoferrate(III) is the product of this equilibrium constant and the rate constant of the oxidation step. The former decreases and the latter increases with temperature and the net result is that observed rate constants vary by only a small amount with temperature. This is reflected in the low values of the ‘activation energy’, which is in fact the sum of the enthalpy change for the proton transfer equilibrium (which is negative) and the activation energy of the electron abstraction step. The reason for the decrease in the observed rate constant with temperature in the oxidation of 4-oxo-4-(3-nitrophenyl)-butanoic acid is presumably due to the fact that the enthalpy change for the proton transfer is greater in magnitude than the activation energy of the oxidation step.

Attempts made to determine the equilibrium constant for enolate anion formation have not been successful. The classical method[30] of treating the oxo compound with bromine and titrating the excess bromine met with failure, as the oxo acid was completely oxidized by bromine in a very fast step. The e.m.f. method is unreliable in alkaline media.[31] Insufficient data are available for the determination of the equilibrium constant by the use of the Marcus equation.[32]

The entropy of activation is negative in all the cases. This is due to the increased electrostriction when similar charges come together in the activated state. In aqueous solution in a reaction between ions of charge z_A and z_B, the entropy of activation has been shown[33] to be approximately equal to $-41z_\text{A}z_\text{B}$ J K^{-1} mol^{-1}. Therefore, in the present studies, the entropy of activation for the oxidation step, involving enolate anion of charge 2− and hexacyanoferrate(III) of charge 3−, should be about −246 J K^{-1} mol^{-1}. It is seen that the observed entropies of activation are greater than this value, presumably owing to the positive entropy change in the proton transfer equilibrium.

Structure–reactivity correlations

Oxidation reactions usually have a low negative ρ value. In the present studies, the overall rate constant is the product of an equilibrium constant and a rate constant. The equilibrium leading to the formation of electron-rich enolate anion would necessarily have a positive ρ and the subsequent oxidation would have a low negative ρ. The net effect would therefore lead to a positive ρ for the overall reaction. The application of the modified Hammett equation, which incorporates the inductive and resonance parameters[34] of *para*-substituted compounds, shows that the inductive effect is 52.4% and the resonance effect is 47.6%.

Ortho effect

It is seen that whereas a methyl substituent in the *para* position of the phenyl ring is generally rate retarding, its introduction in the *ortho* position increases the rate considerably. Methyl groups in the two *ortho* positions increase the rate almost to that of the 4-chloro compound. Hence the reaction is subjected to steric acceleration by the *ortho* substituents.

Isokinetic relationship (IKR)

The Hammett constant (ρ) decreases with increase in temperature, from 1.57 at 299 K to 1.19 at 318 K. The Hammett lines intersect at a point corresponding to a σ_{iso} value of 0.60 and a k_{iso} value of $3.090 \times 10^{-3}\ \text{s}^{-1}$ (Fig. 2). An oxo acid with a substituent having this σ value will be oxidized by alkaline hexacyanoferrate(III) with the same velocity at all temperatures. Such an insensitivity of the reaction rate to temperature is a pointer to the existence of an isokinetic phenomenon. Introduction of a nitro group in the phenyl ring which has a higher σ value results in a decrease in the rate constant with temperature.

A reaction series which exhibits a common point of intersection in the Hammett plot is expected to have a common point of intersection in the Arrhenius plot also.[35] The Arrhenius plots are shown in Fig. 3.

As the common point of intersection is not easily visible, the problem is tackled by the statistical method developed by Exner and Beranek.[36] In this method, the standard deviation S_{00} of the free regression lines (without the constraint of a common point of intersection) and the standard deviation S_0 of the new constrained lines are compared. In the present studies, these two values are approximately equal and so the isokinetic hypothesis cannot be rejected. From the plots of $\Delta H^\ddagger$ against $\Delta S^\ddagger$ and ρ against $1/T$, the T_{iso} value was found to be 385 K. It is interesting that although the rate constant is composite—k_2K, involving two reaction steps—an anti-compensation effect is not observed.

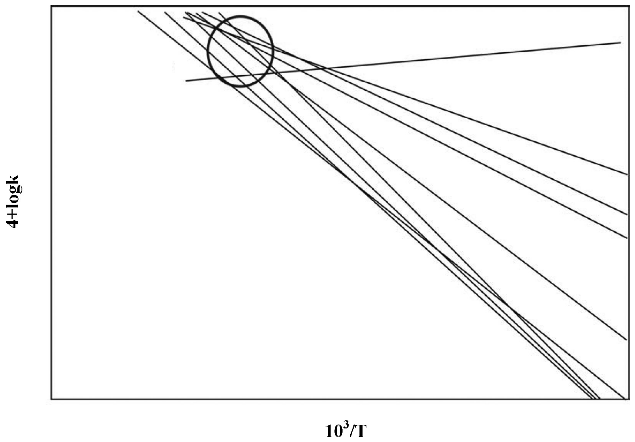
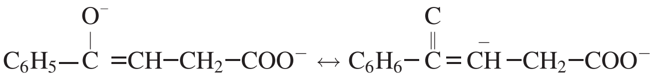


Figure 3. Arrhenius plots

Details of electron abstraction

The electron loss from the enolate dianion can occur either from the oxygen atom of the enolate function or from the carbon–carbon double bond. Both processes will lead to the formation of a mesomeric radical:



$$\mathrm{C_6H_5{-}\overset{O^-}{\overset{|}{C}}{=}CH{-}CH_2{-}COO^-} \leftrightarrow \mathrm{C_6H_6{-}\overset{C}{\overset{\|}{C}}{=}\overset{-}{C}H{-}CH_2{-}COO^-}$$

Generally, one-electron-abstracting agents do not readily attack the olefinic bonds.[21] The loss of electron from the carboxylate moiety of the molecule is less probable, as the substituent effects would have been negligible. In the oxidation of phenylacetic acid by Co(III), an electron is proposed to be removed from the phenyl ring rather than the carboxyl group, resulting in the aromatic radical cation and a highly negative ρ^+ is obtained.[37] The second electron removal occurs in a fast step with decarboxylation occurring at the same time, in accordance with the Kochi mechanism.[38]

This explains the formation of CO_2 in the oxidation of 4-oxo acids. Owing to the high reactivity of acrylophenone in alkaline solution, only benzoic acid is obtained in the oxidation of 4-oxo-4-phenylbutanoic acid, whereas chalcone is formed in the oxidation of 4-oxo-2,4-diphenylbutanoic acid.

CONCLUSION

From the Hammett and Arrhenius plots associated with the isokinetic relationship, it is noted that the ρ values are positive and decrease with increase in temperature. A methyl group in the *ortho* position accelerates the reaction owing to steric factors, contrary to the expected electronic effect. The structure–activity correlations are made on the basis of the results obtained and suggest a mesomeric radical-mediated mechanism.

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