(viii) Independent experiments have established that IO_3^- has no effect on the reaction rate in alkaline medium. However in the presence of Os(VIII) the oxidation takes place quite smoothly. The reaction is first order in oxidant and first order in substrate at constant [Os(VIII)] and [alkali] (Table 4).

The reaction is first order in substrate at constant [alkali] and [Os(VIII)] which is also indicated by the plot of log k_1 vs log [S].

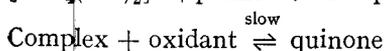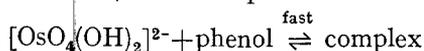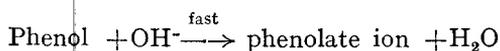(ix) The reaction has inverse first order dependence on [alkali].

(x) The effect of different substituents on the reaction kinetics has been studied. Log k_2 vs σ^+ plot was found to be linear (yielding ρ^+ value of $-3 \cdot 0$), indicating that the reaction proceeds through an oxonium ion.

We had earlier explained that the oxidation of phenol by IO_4^- is passing through an oxonium ion leading to a quinone. In the absence of Os(VIII) the same mechanism holds good in alkaline medium as well. But in the presence of Os(VIII) the oxidation by IO_4^- and IO_3^- takes place through the formation of a complex between substrate and Os(VIII).

It has been reported that in the alkaline medium[4] OsO_4 exists as the octahedral complexes (transforms) of the types $[OsO_4(OH)H_2O]^{1-}$ and $[OsO_4(OH)_2]^{2-}$. The experimental results indicate the existence of equilibrium (1) in alkaline medium.

$$[OsO_4(OH)H_2O]^{1-} + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} + H_2O \quad \ldots(1)$$
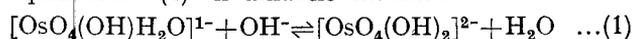
This is supported by an earlier work[5]. The reaction sequence in the presence of OsO_4 is as follows:

$$Phenol + OH^- \xrightarrow{fast} phenolate\ ion + H_2O$$

$$[OsO_4(OH)_2]^{2-} + phenol \underset{fast}{\rightleftharpoons} complex$$

$$Complex + oxidant \underset{slow}{\rightleftharpoons} quinone$$

This explains all the features observed in this oxidation process including the inverse dependence on alkali, as it appears that the phenol and not the phenolate anion is the active species involved in the complex formation. Prima facie it may appear that the possibility of neutral molecule of phenol may not be there as the concentration of alkali is quite high. There is always a reversible equilibrium in these systems and at any instant there is a definite concentration of the neutral molecules as well. This is also clear from the work of Bell and Ramsden[6] who have used $8M$ H_2SO_4 in bromination reactions of alkylamines. The concentration of alkylaniline is very low and still they postulate, in spite of high concentration of the acid a free amine as the reacting species. Hence a neutral molecule is postulated as the reactive species to explain the inverse dependence on alkali.

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Kinetics of Ag+-catalysed Oxidation of Succinic, Adipic, Pimelic, Suberic & Sebacic Acids by Ce4+

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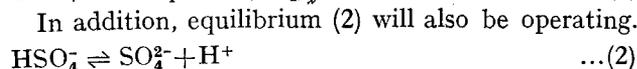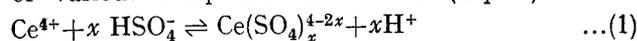Department of Chemistry, Berhampur University
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Kinetics of oxidation of saturated dicarboxylic acids by Ce4+ catalysed by Ag+ in H_2SO_4 medium is reported at different [acid], [substrate] and [Ag+]. The reaction rate shows first order dependence in [Ce4+] and [Ag+] but fractional dependence on [substrate] and [acid]. The uncatalysed reaction also has the same dependence on [substrate] and [acid]. Structural influences are analysed in the light of Taft's substituent parameters. A mechanism consistent with the results is postulated.

SATURATED aliphatic dicarboxylic acids appear to be inert towards oxidants under mild conditions. The acids above succinic acid appear to undergo oxidation by Ce4+ only at reflux temperature[1]. However, the presence of Ag+ in catalytic amounts has now been found to facilitate the oxidation by Ce4+ even under mild conditions. In this paper we report the kinetics of Ag+-catalysed oxidation of succinic, adipic, pimelic, suberic and sebacic acids by Ce4+ in sulphuric acid medium.

The dicarboxylic acids were of AR grade and were recrystallized before use. Kinetic measurements were carried out according to the method described earlier[2]. The rate constants have been computed by the usual tangential method and are reproducible within 3% error.

The reactions are first order in the oxidant as seen by linear plots of log $(a-x)$ vs time. The rate of the reaction increases with increasing [substrate] over the range studied. A plot of log k vs log [S] (where S = substrate) is linear and gives a slope of 0·5 showing fractional dependence on [substrate] (Table 1). The reaction rate decreases with increasing $[H_2SO_4]$ and the plot of log k vs log [H+] is linear with a slope of 0·5 indicating the fractional dependence on [acidity] (Table 1). The decrease in rate with increasing $[H_2SO_4]$ is due to the existence of various complexes in solution (Eq. 1)

$$Ce^{4+} + x\ HSO_4^- \rightleftharpoons Ce(SO_4)_x^{4-2x} + xH^+ \quad \ldots(1)$$

In addition, equilibrium (2) will also be operating.

$$HSO_4^- \rightleftharpoons SO_4^{2-} + H^+ \quad \ldots(2)$$

The sulphato cerate complex being less active, there is retardation as observed. It is reported[3]

TABLE 1 — EFFECT OF VARYING CONCENTRATIONS OF SUBSTRATE, ACIDITY AND Ag^+ AT 50°

[Ce⁴⁺] M	[Substrate] M	[H₂SO₄] M	[Ag⁺] M	$k \times 10^5$ min¹
		SUCCINIC ACID		
0·01	0·10	1·0	0·01	20·58
0·01	0·125	1·0	0·01	27·4
0·01	0·15	1·0	0·01	30·39
0·01	0·20	1·0	0·01	33·70
0·01	0·25	1·0	0·01	34·42
0·01	0·30	1·0	0·01	39·86
0·01	0·10	1·0	0·015	29·63
0·01	0·10	1·0	0·02	40·3
0·01	0·10	0·5	0·01	31·07
0·01	0·10	1·5	0·01	15·99
		ADIPIC ACID		
0·005	0·005	0·5	0·005	21·7
0·005	0·015	0·5	0·005	45·27
0·005	0·025	0·5	0·005	60·78
0·005	0·035	0·5	0·005	76·38
0·005	0·05	0·5	0·005	106·3
0·005	0·05	0·5	0·0075	148·75
0·005	0·05	0·5	0·01	196·66
0·005	0·05	1·0	0·005	76·78
0·005	0·05	1·5	0·005	59·21
		PIMELIC ACID		
0·005	0·005	0·5	0·005	32·5
0·005	0·005	0·5	0·0075	47·9
0·005	0·005	0·5	0·01	63·9
0·005	0·005	1·0	0·005	24·4
0·005	0·005	1·5	0·005	20·2
		SUBERIC ACID		
0·005	0·005	0·5	0·005	33·07
0·005	0·005	0·5	0·0075	49·07
0·005	0·005	0·5	0·01	63·99
0·005	0·005	1·0	0·005	23·58
0·005	0·005	1·5	0·005	19·2
		SEBACIC ACID		
0·005	0·001	0·5	0·005	12·97
0·005	0·001	0·5	0·0075	18·5
0·005	0·001	0·5	0·01	24·9
0·005	0·001	1·0	0·005	9·31
0·005	0·001	1·5	0·005	7·67

TABLE 2 — EFFECT OF VARYING [SUBSTRATE] AND [H⁺] ON THE RATE OF OXIDATION OF SUCCINIC ACID IN THE ABSENCE OF Ag^+

{[Ce⁴⁺] = 0·01M; temp. = 50°}

(Substrate) M	[H₂SO₄] M	$k \times 10^5$ min⁻¹
0·10	1·0	3·71
0·15	1·0	3·84
0·20	1·0	4·1
0·25	1·0	4·92
0·30	1·0	5·81
0·10	0·5	4·69
0·10	1·5	2·95

ceric ions in the $HClO_4$ medium. It is interesting to note here that the order with respect to [substrate] and [H⁺] does not change significantly even in the absence of Ag^+ (Table 2), as observed earlier by Levitt and Malinowski[4] on the uncatalysed peroxydisulphate oxidation of propan-2-ol.

In the homologous series of the dicarboxylic acids studied the reactivity order is: sebacic > suberic > pimelic > adipic > succinic, indicating that the reactivity increases with increase in chain length. A plot of Taft substituent constants against log k is linear with ρ being equal to -6.2. As the carboxyl groups are separated farther, the deactivation due to other carboxyl group decreases and since this is a reaction requiring electron accession at the reaction site, it is favoured with increase in distance separating the carboxyl groups. The negative ρ is in conformity with the requirement of electron accession. But the high numerical value seems to indicate that the reaction might involve a two-electron transfer resulting in the formation of a carbonium ion and Ce^{2+} species which immediately reacts with Ce^{4+} forming the stable Ce^{3+}. Such instances of Ce^{2+} formation transiently are known[5].

With the observed first order dependence on [Ag⁺], fractional order on [substrate] and inverse fractional order on [H⁺], a probable rate law can be given.

As the Ce^{4+} is partly hydrolysed, the total Ce^{4+} represented by $[Ce^{4+}]_T$ is the sum of the hydrolysed form $[Ce(OH)^{3+}]$ and unhydrolysed form $[Ce^{4+}]$ (Eq. 3).

$$[Ce^{4+}]_T = [Ce^{4+}] + [Ce(OH)^{3+}] = [Ce^{4+}] + \frac{k_1[Ce^{4+}]}{[H^+]} \quad ...(3)$$

Similarly total $(Ag^+)_T$ is the sum of uncomplexed [Ag⁺] and complexed $[Ag^+]^C$ (Eqs. 4 and 5).

$$[Ag^+]_T = [Ag^+] + [Ag^+]^C = [Ag^+] + K_2[Ag^+][S] \quad ...(4)$$

or

$$[Ag^+] = \frac{[Ag^+]_T}{1 + K_2[S]} \quad ...(5)$$

Since the rate of disappearance is dependent on [Ag⁺], [S] and total [Ce⁴⁺], it can be written as given in Eq. (6)

$$-\frac{d[Ce^{4+}]_T}{dt} = k_{obs}[Ag^+][S][Ce^{4+}] \quad ...(6)$$

that if the [sulphate ion] is constant and if [H₂SO₄] is increased above the [sulphate], there will be increase in rate due to the equilibrium (1) being shifted to the left and the equilibrium (2) is negligibly affected. But if Na₂SO₄ (0·1M) is added at constant [H₂SO₄] a retardation in rate is observed ($k = 69·4 \times 10^{-5}$ min⁻¹ and $106·7 \times 10^{-5}$ min⁻¹ for adipic acid in the presence and absence of Na₂SO₄ respectively), The retardation may be due to the equilibrium (2) being pushed towards left which subsequently pushes equilibrium (1) to the right leading to the formation of inactive sulphato cerate complex.

Increasing [Ag⁺] increases the rate and plot of log k vs log [Ag⁺] is linear with unit slope establishing the order as unity with respect to [Ag⁺]. The complexation of Ag^+ with the carboxyl group presumably decreases the activation energy which may be responsible for the observed enhanced rates in the presence of Ag^+. Further there is dramatic catalysis by Ag^+ in $HClO_4$ medium as compared to H_2SO_4. This might be due to a higher redox potential of

Substituting the values of $[Ag^+]$ and $[Ce^{4+}]_T$, we get

$$-\frac{d[Ce^{4+}]_T}{dt} = \frac{k_{obs}[Ag^+][S][Ce^{4+}]}{1+K_2[S]}\left\{1+\frac{K_1}{[H^+]}\right\}$$

$$= k_{obs}\frac{[Ag^+]_T[S][Ce^{4+}]}{1+K_2[S]} + \frac{k_{obs}K_1[Ag^+]_T[S][Ce^{4+}]}{\{1+K_2[S]\}[H^+]} \quad ...(7)$$

At constant $[Ag^+]_T[S][Ce^{4+}]$, the rate expression is reduced to:

$$-\frac{d[Ce^{4+}]_T}{dt} = K'+K''\frac{1}{[H^+]} \quad ...(8)$$

The reason for the inverse half order on $[H^+]$ is due to the operation of the two terms in expression (7). Such reasoning for explaining fractional order dependence on $[H^+]$ has been advanced in chromic acid oxidation of organic substrates[6]. Further at constant [acid] the rate expression takes the form (9).

$$-\frac{d[Ce^{4+}]_T}{dt} = \frac{k_{obs}[Ag^+]_T[S][Ce^{4+}]}{1+K_2[S]} \quad ...(9)$$

This explains the first order with respect to Ag^+ and fractional order with respect to substrate. Such reasoning to explain the fractional order dependence on [substrate] has been invoked earlier by Saiprakash and Sethuram[7] while studying the oxidation of isopropyl alcohol by Ce^{4+}. Thus it is possible to postulate that Ag^+ complexes with the substrate to give a colourless adduct in a fast step which subsequently gets oxidized by Ce^{4+} leading to products. The product in each case is the corresponding monoketo dicarboxylic acid.

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Kinetics & Mechanism of Oxidation of D-Xylose & L-Arabinose by Cu(II) in the Presence of Ammonium Hydroxide

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The oxidation of D-xylose and L-arabinose by Cu(II) in the presence of ammonium hydroxide shows that the reaction rate is independent of [Cu(II)] and first order both with respect to [reducing sugar] and [OH⁻]. The reaction has an induction period. A general mechanism involving the intermediate enediol anion has been proposed for the oxidation of these reducing sugars. The results suggest that the rates of oxidation of these reducing sugars are their corresponding rates of enolization. Formic acid and 1,2,3-trihydroxybutyric acid have been identified as the oxidation products.

SINGH et al.[1] studied the kinetics of oxidation of D-glucose, D-galactose and D-fructose by Cu(II) in the alkaline medium in the presence of complexing agents and reported that the reaction is zero order with respect to [Cu(II)] and first order with respect to [reducing sugars] and [OH⁻]. They also observed that the reaction has an induction period and shows autocatalysis due to Cu_2O produced in the system. These results were confirmed by Marshall and Waters[2] and by Singh et al.[3].

Since Cu(II) oxidation of D-xylose and L-arabinose in the presence of ammonia as complexing agent has not been studied, prompted us to undertake the title investigation. The system becomes homogeneous due to formation of soluble Cu(I)-ammonia complex[4], $[Cu(NH_3)_2^+]$.

All the reagents used were AR grade samples. The standard solutions of the reducing sugars, D-xylose (E. Merck) and L-arabinose (K.L. Laboratories, England) were always prepared fresh. The rate of oxidation was followed by estimating the Cu(I) produced at different intervals of time against standard solution of potassium dichromate. The kinetic measurements for the rate of oxidation of D-xylose and L-arabinose by ammoniacal Cu(II) at varying [reactants].

The oxidation of these reducing sugars started after a slight induction period (Fig. 1, curve B). The order of the reaction with respect to [Cu(II)] was determined by keeping the concentration of other reactants in large excess. Table 1 shows that there is a gradual decrease in k_s values with increasing [Cu(II)], probably due to decrease in pH of the system, which was confirmed by performing the same study in a buffer of NH_4Cl and NH_4OH (pH
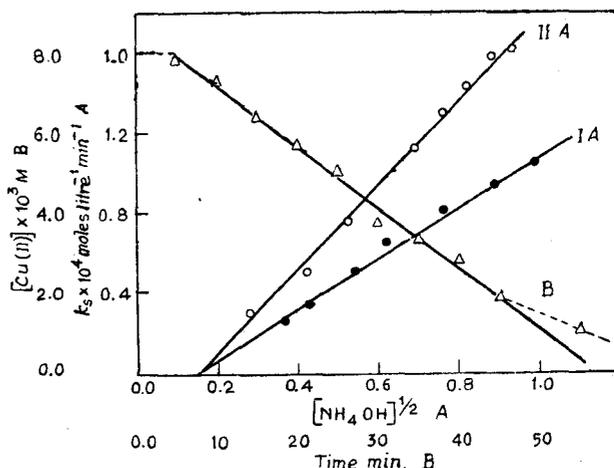

Fig. 1 — (A) Plots of k_s values versus $[NH_4OH]^{1/2}$ for D-xylose and L-arabinose at 40° (I) [L-arabinose] = 6·0 × $10^{-2}M$; $[CuSO_4.5H_2O]$ = 3·0 × $10^{-3}M$; (II) [D-xylose] = 5·40 × $10^{-2}M$; $[CuSO_4.5H_2O]$ = 5·0 × $10^{-3}M$. (B) A plot of [Cu(II)] against time at 40° {[D-xylose] = 4·0 × $10^{-2}M$; $[NH_4OH]$ = 15·0 × $10^{-1}N$; $[CuSO_4.5H_2O]$ = 8·0 × $10^{-3}M$; [KCl] = 4·68 × $10^{-1}M$}