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NOTES

Mechanism of Ru (III) Catalysis in Oxidation of Acrylic Acid by Ceric Sulphate

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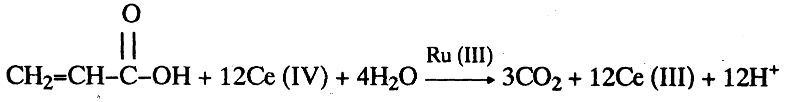
The kinetics of oxidation of acrylic acid by ceric sulphate in the presence of ruthenium (III) chloride as catalyst were studied by following the rate of disappearance of Ce (IV). The reaction order was zero with respect to Ce (IV) and unity with respect to both Ru (III) and acrylic acid. Negative effect of H^+ and inverse first order Cl^- was observed while negligible effect of ionic strength variation and bisulphate was observed, carbon dioxide was detected as end product.

The present paper deals with kinetics and mechanism of Ru (III) catalysed oxidation of acrylic acid by ceric sulphate in sulphuric acid.

The stock solution of Ce (IV) was prepared by dissolving ceric sulphate (A.R., B.D.H.) in aqueous sulphuric acid of known strength. The stock solution of acrylic acid (E.Merck) was prepared by weighing and dissolving in distilled water. Other reagents were sodium perchlorate (Riedel grade), ferrous ammonium sulphate (B.D.H.) and ferroin indicator (E.Merck) solution of ruthenium (III) chloride (Johnson and Matthey) was prepared by dissolving its 1 gm sample in HCl (0.1M).

The solutions of reactants were kept in a thermostatic bath to attain the thermal equilibrium. The required amount of reactants were mixed together and aliquot (5 ml) was withdrawn from the mixture at different intervals of time and immediately quenched by adding a known volume of ferrous ammonium sulphate solution. The excess of ferrous ions was volumetrically titrated with a standard solution of ceric sulphate using ferroin as an indicator. Kinetic runs were studied using excess of acrylic acid in the mixture and the value of zero order rate constants (K_o) was measured by applying the zero-order rate expression.

Stoichiometry of the reaction was obtained by equilibrating the number of reaction mixture containing excess of Ce (IV) sulphate to that of acrylic acid in presence of ruthenium (III) chloride in a thermostat at 30°C. The estimation of unreacted Ce (IV) showed that 12 equivalents of Ce (IV) were used for oxidation of one mole of acrylic acid and accordingly stoichiometric equation (1) was written as:



$$CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OH + 12Ce\,(IV) + 4H_2O \xrightarrow{Ru\,(III)} 3CO_2 + 12Ce\,(III) + 12H^+ \quad (1)$$

The results of various experimetnts are given in Table 1. The reaction follows zero-order kinetics in Ce (IV) as is evidenced by near constant values of k_0 (zero-order rate constant) at different initial concentrations of Ce (IV). The rate of the reaction increases linearly with concentration of acrylic acid, showing first-order in acrylic acid. The rate dependence of the reaction on Ru (III) indicates first-order. The zero-order rate constant decreases non-linearly with $[H^+]$ which shows negative effect of H^+. Inverse first-order in Cl^- is obvious from k_0 values at different concentration of KCl. Negligible effect of HSO_4^- and ionic strength (affected by addition of different amounts of sodium perchlorate) was observed.

TABLE 1
EFFECT OF [REACTANTS] ON REACTION RATE

A [Ce (IV) × 10^3 M]	0.83	1.00	1.67	2.00	2.5	4.00
$K_{obs} \times 10^5$ Ml^{-1} min^{-1}	0.98	1.07	1.13	1.08	1.12	1.02
A [Acrylic acid] = 5.00×10^{-2} M, [Ru (III)] = 4.95×10^{-7} M $[H_2SO_4]$ = 1.18 M, Temp. = 35°C						
B [Acrylic acid] × 10^2 M	1.66	2.50	3.34	5.00	10.00	20.00
$k_{obs} \times 10^5$ $M l^{-1}$ min^{-1}	0.83	1.50	1.76	2.53	4.89	9.86
B [Ce (IV)] = 2.00×10^{-3} M, [Ru (III)] = 4.95×10^{-7} M $[H_2SO_4]$ = 1.18 M and Temp. = 35°C						
C [Ru (III)] × 10^7 M	0.80	1.24	1.65	2.00	2.50	3.60
$k_{obs} \times 10^5$ Ml^{-1} min^{-1}	1.06	1.62	2.22	2.60	3.32	4.66
C [Ce(IV)] = 2.00×10^{-3} M, [Acrylic acid] = 5.00×10^{-2} M $[H_2SO_4]$ = 1.18 M and Temp. = 35°C						
D $[H_2SO_4]$M	0.75	1.00	3.00	6.50	7.50	
$k_{obs} \times 10^5$ $Ml^{-1}min^{-1}$	2.15	1.88	1.70	1.40	1.20	
D [Ce (IV)] = 2.00×10^{-3} M, [Acrylic acid] = 5.00×10^{-2} M [Ru (III)] = 4.95×10^{-7} M and Temp. = 35°C						
E [KCl] × 10^2 M	5.00	10.00	20.00	30.00	40.00	
$k_{obs} \times 10^4$ Ml^{-1} min^{-1}	1.18	0.58	0.30	0.19	0.16	
E [Ce (IV)] = 2.0×10^{-3} M, [Acrylic acid] = 5.00×10^{-2} M, $[H_2SO_4]$ = 1.18 M Temp. = 35°C and [Ru (III)] = 4.95×10^{-7} M						

Inverse first-order in chloride indicates that following equilibrium exists in right direction and $[RuCl_5H_2O]^{2-}$ is the reactive species of ruthenium (III) chloride.

$$[RuCl_6]^{3-} + H_2O \rightleftharpoons [RuCl_5H_2O]^{2-} + Cl^-$$

Zero-order dependence on Ce (IV) indicates that Ce (IV) is involved in the fast steps. Although several oxidative species of Ce (IV) have been suggested in

H_2SO_4, viz. $Ce(SO_4)_2$, $Ce(SO_4)^{2+}$, $Ce(SO_4)_3^{2-}$ $Ce(OH)_2^{2+}$by various workers[1-4] but species is one which can explain the observed kinetic data. Since in the present case zero-order in Ce (IV) is observed, it matters insignificant if either of above is assumed to be reactive species. Hence for simplicity Ce (IV) will be used for ceric sulphate species as species, in which Ce (IV) will exist, would not effect the mechanistic steps.

Now on the basis of the experimental results following scheme for the oxidation of acrylic acid is described:

$$[RuCl_6]^{3-} + H_2O \longrightarrow [RuCl_5H_2O]^{2-} + Cl^- \qquad \text{(i)}$$

$$[RuCl_5{\cdot}H_2O]^{2-} + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X\,(\text{complex}) + H^+ \qquad \text{(ii)}$$

$$(X) + H_2O \xrightarrow[\text{slow}]{k} [RuCl_5H]^{3-} + \text{Intermediate product } (Y) \qquad \text{(iii)}$$

$$Y + Ce\,(IV) \xrightarrow{\text{fast}} \text{Products} \qquad \text{(iv)}$$

$$[RuCl_5{\cdot}H_2O]^{2-} + 2Ce\,(IV) + H_2O \xrightarrow{\text{fast}} [RuCl_5H_2O]^{2-} + H^+ + 2Ce\,(III) \qquad \text{(v)}$$

Now from the above mechanism at steady state condition of the complex (X), the final rate law can be written as:

$$\frac{-d[Ce(IV)]}{dt} = \frac{k_1kk_2[S][Ru\,(III)]}{(k_{-2}[H^+] + k)[Cl^-]} \qquad (2)$$

The rate law clearly explains that the reaction rate follows zero-order kinetics in Ce (IV) and first-order in acrylic acid and Ru (III). It also explains negative effect of H^+ ions and inverse first-order in Cl^-. Negligible effect of ionic strength is also explained by step (iii) involving a dipole.

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