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KINETICS OF THE OXIDATION OF ACRYLIC ACID BY Ce(IV) IN ACID PERCHLORATE SOLUTION

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Abstract—The kinetics of oxidation of acrylic acid by Ce(IV)-perchlorate in perchloric acid were studied by following the rate of dissappearance of Ce(IV). The reaction order was zero with respect of Ce(IV) and unity with the acrylic acid. The addition of [H$^+$] shows a proton catalysis and no salt effect is observed. Spectrophotometric studies do not reveal the formation of intermediate complex and thus a mechanism postulating the hydrolysis of the acid is suggested which undergoes first oxidation by the reactive species of Ce(IV). Thermodynamic parameters have also been calculated.

Cerium(IV) in various acidic media has been widely utilised for the oxidation of organic as well as inorganic compounds.[1,2a–d] In some cases the mechanistic approach has been based on the intermediate complex formation and in other cases the results have been interpretated by the formation of free radical, as the evidence for complex formation could not be obtained either kinetically or spectrophotometrically. The facts have also been interpretated by taking into account the anionic species present in the reaction which have been found responsible for deciding the cationic species of Ce(IV). The oxidation of some aliphatic acids such as formic acid,[3] lactic acid[4] and acetic acid[5] could only be attempted by using ceric perchlorate as an oxidant. Krishna and Tewari[6] examined the oxidation of mandelic acid, lactic and DL-malic acids by ceric ions at 25°, and also studied the rate dependence of the reaction on sulphuric acid concentration. The oxidation of glycollic acid by ceric sulphate has been studied by McAuley.[7] Sengupta *et al.*[8] have worked also on mandelic acid oxidation by ceric salts. These authors have studied the oxidation of mandelic acid by ceric perchlorate at 5° keeping the concentration of oxidant higher than the concentration of substrates and they could only determine the total order of the reaction indicating that the reaction was very rapid, and the usual isolation method could not be employed.

The mechanism suggested by the various authors is not found to be uniform revealing that wide varieties of mechanism are possible depending upon the nature of cationic species as well as the substrates and any inference made on analogy would be naive.

Materials and method. The stock solution of Ce(IV)-perchlorate was prepared by dissolving ceric ammonium nitrate A.R. (B.D.H.) in aqueous perchloric acid[9] (Riedel, 60%). The acid strength of the stock solution was determined as described in literature.[7] The stock solution of acrylic acid (E. Merck) was prepared by weighing and dissolving in distilled water. Other reagents were sodium perchlorate (Riedel, Grade), barium perchlorate (E. Merck, Germany), sodium hydroxide A.R. (B.D.H.), ferrous ammonium sulphate A.R. (B.D.H.) and ferroin indicator (E. Merck).

Rate measurement. The solns of reactants were kept in a thermostat bath to attain the thermal equilibrium. The required amount of the reactants were mixed together and aliquot (5.00 ml) was withdrawn from the mixture at different intervals of time and immediately quenched by adding a known volume of ferrous ammonium sulphate soln. The excess of ferrous was volumetrically titrated with a standard soln 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 constant (k_0) was measured by applying the zero order rate expression.

The following kinetic runs (Tables 1 and 2) are being reproduced to indicate that the order is zero with respect to oxidant.

Table 1. Temperature 40°C ± 0.1°C [Ceric perchlorate] = 1.25×10^{-3} N [Acrylic acid] = 2.50×10^{-2} M [Perchloric acid] = 1.00 N

Time (min)	ml of N/903.6 ceric sulphate required by 5 ml of the reaction mixture	Zero order constants ($k_0 \times 10^4$ mole sec^{-1})
00	4.52	—
10	4.86	5.67
20	5.16	5.33
40	5.82	5.42
55	6.28	5.33
70	6.76	5.33
80	7.10	5.37
95	7.58	5.37
115	8.28	5.35
130	8.66	5.30
∞	10.04	—

Av. value of $k_0 = 5.38 \times 10^{-4}$ mole sec^{-1}.

Av. deviation = ±1.26%.

Stoichiometry and products analysis. Number of reaction mixture containing excess of Ce(IV) perchlorate, to that of acrylic acid were kept in a thermostat at 30°. The estimation of unreacted Ce(IV) shows that ten equivalents of Ce(IV) are being used for one mole of acrylic acid Table (3).

The product formed was identified as formic acid. This was done by ascending type of paper chromatography using n-butanol saturated with ammonia as solvent sys-

Table 2. Temperature 50°C ± 0.1°C [Ceric perchlorate] = 4.00×10^{-3} N [Acrylic acid] = 2.50×10^{-2} M [Perchloric acid] = 1.00 N

Time (min)	ml. or N/292.2 ceric sulphate required by 5 ml of the reaction mixture	Zero order constants ($k_0 \times 10^4$ mole sec^{-1})
00	3.80	—
10	4.64	14.00
15	5.04	13.78
25	5.88	13.86
30	6.28	13.78
35	6.70	13.80
40	7.12	13.83
45	7.54	13.85
52	8.12	13.85
58	8.62	13.85
∞	9.74	—

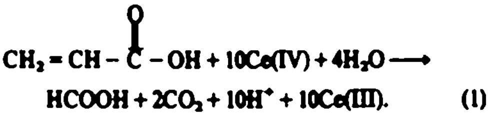
Av. value of $k_0 = 13.84 \times 10^{-4}$ mole sec^{-1}.

Av. deviation = +0.30%.

Table 3. Temperature 30°

[Ceric perchlorate] $\times 10^3$ N	[Acrylic acid] $\times 10^3$ M	[Ce(IV)]/[Acrylic acid]
1.00	1.00	9.89
1.67	1.00	10.12
2.00	1.00	10.22
Average value of equivalents =		10.08

tem and bromo-phenol blue as spot revealing reagent. The R_f value was found to be 0.50. The reaction could be written as shown below:



$$CH_2=CH-\overset{\overset{O}{\|}}{C}-OH + 10Ce(IV) + 4H_2O \longrightarrow HCOOH + 2CO_2 + 10H^+ + 10Ce(III). \quad (1)$$

RESULTS AND DISCUSSION

Unlike the order of reaction mentioned in the literature in the cases of oxidation of carboxylic acid by Ce(IV), the rate of disappearance of Ce(IV) follows a zero order rate expression in the oxidation of acrylic acid. The values of rate constants (k_0) at different concentrations of Ce(IV) are given in Table 4.

The rate dependence of the reaction on acrylic acid indicates first order. The rate of reaction increases on increasing the concentration of acrylic acid and have direct proportionality (see Table 5 and Fig. 1(a)).

Table 4. Effect of variation of Ceric perchlorate on the rate of reaction

Temperature 40°, [Acrylic acid] = 2.50×10^{-2} M & $[HClO_4]$ = 1.00 N

[Ceric perchlorate]	6.67	5.00	4.00	2.50	2.00	1.25	1.00
$k_0 \times 10^3$ mole sec^{-1}	0.44	0.48	0.48	0.51	0.53	0.53	0.54

Table 5. Effect of change of concentration of acrylic acid over the velocity constant. Temperature 40°, [Ceric perchlorate] = 4.00×10^{-3} N and [Perchloric acid] = 1.00 N

[Acrylic acid] M $\times 10^2$	10.00	5.00	3.33	2.50	2.00	1.67
$k_0 \times 10^3$ mole sec^{-1}	1.85	0.97	0.65	0.48	0.38	0.32

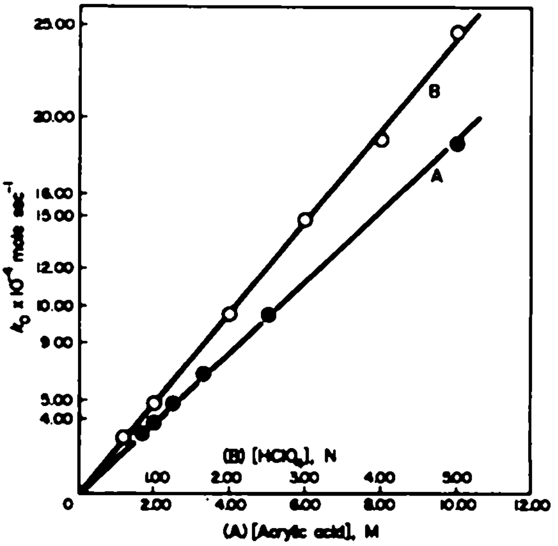


Fig. 1. (A)(●), plot of k_0 vs [Acrylic acid]; $[Ce(ClO_4)_4] = 4.00 \times 10^{-3}$ N, $[HClO_4]$ = 1.00 N; (B)(○), Plot of k_0 vs $[HClO_4]$; $[Ce(ClO_4)_4] = 4.00 \times 10^{-3}$ N, [Acrylic acid] = 2.50×10^{-2} M.

The rate of reaction increases with the increase of $[H^+]$ and the plot of k_0 vs $[HClO_4]$ is linear passing through the origin, characterising the proton catalysis (Fig. 1(b)). At constant perchlorate ion concentration, the addition of $[H^+]$ also shows a proton catalysis. The reaction does not show any salt effect on addition of $NaClO_4$ or $Ba(ClO_4)_2$.

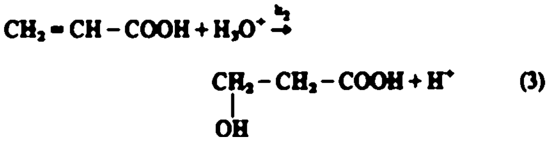
The spectrophotometric studies do not indicate any complex formation between the Ce(IV) and acrylic acid because neither any additional absorption maximum nor intensification of absorbance is obtained. Spectrophotometer employed was Perkin–Elmer Model-202.

The effect of temperature on the rate of reaction and the values of activation parameters are given in Table 7.

The species of Ce(IV)–perchlorate in perchloric acid media depending on the concentration of acid and Ce(IV) is reported to be present[10] as $[Ce(H_2O)_8]^{4+}$, $[Ce(H_2O)_7OH]^{3+}$ besides $Ce-O-Ce^{6+}$ and $Ce_2O_3^{6+}$. Since the predominant species in consistance with out experimental conditions is hydrolysed monomeric species. We can write the equilibrium[11] in (2).

$$[Ce(OH)(H_2O)_7]^{3+} + H^+ \overset{K_1}{\rightleftharpoons} [Ce(H_2O)_8]^{4+} \quad (2)$$

The reactive species has been presumed to be $[Ce(H_2O)_8]^{4+}$ as envisaged in the oxidation of acetic acid by Ce(IV)–perchlorate.[5] The mechanism can be visualised as below:



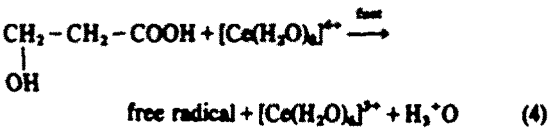
$$CH_2=CH-COOH + H_3O^+ \xrightarrow{k_2} \underset{\underset{OH}{|}}{CH_2}-CH_2-COOH + H^+ \quad (3)$$

Table 6. Effect of variation of concentration of salts on the rate of reaction. Temp. 40°, [Ceric perchlorate] = 4.00×10^{-3} N, [Acrylic acid] = 2.50×10^{-2} M & [$HClO_4$] = 1.00 N

[$NaClO_4$] × N	$k_o \times 10^3$ mole sec^{-1}	[$Ba(ClO_4)_2$] M × 10	$k_o \times 10^3$ mole sec^{-1}
0.00	0.48	0.00	0.48
0.10	0.48	1.00	0.49
0.25	0.48	2.00	0.48
0.50	0.49	3.00	0.48
0.75	0.50	4.00	0.50
1.00	0.55		
1.50	0.57		

Table 7. [Ceric perchlorate] = 4.00×10^{-3} N, [Acrylic acid] = 2.50×10^{-2} M, and [$HClO_4$] = 1.00 N

Temperature, °C	$k_o \times 10^3$ mole sec^{-1}
35	0.26
40	0.48
45	0.76
50	1.37
55	2.07
Energy of activation (ΔE)	= 20.75 kcal. mole^{-1}
Free energy of activation (ΔF‡)	= 21.43 kcal. mole^{-1}
Entropy of activation (ΔS‡)	= −2.17 e.u



$$\underset{\displaystyle OH}{\underset{|}{CH_2}} - CH_2 - COOH + [Ce(H_2O)_6]^{4+} \xrightarrow{\text{fast}} \text{free radical} + [Ce(H_2O)_6]^{3+} + H_3^+O \quad (4)$$

$$\text{Free radical} + [Ce(H_2O)_6]^{4+} \rightarrow \text{Product} + [Ce(H_2O)_6]^{3+}. \quad (5)$$

Equation (3) shows a proton catalysed hydration of the acrylic acid forming a hydroxy acid. The acid catalysed hydration of olefinic double bond[12] is a well known fact and the hydration will be more pronounced in the case of carboxylic acids. The equation in the above mechanistic step shows the oxidation of hydroxy acid by ceric perchlorate is a fast process. This has been experimentally confirmed that the oxidation of hydroxy acids, viz. mandelic, lactic and malic acid is an instantaneous process even at low temperature when the concentrations were identical to the experimental conditions employed in the oxidation of acrylic acid. The survey of literature reveals that the hydroxy acids are oxidised by Ce(IV)–sulphate[4,6–8] and by ceric perchlorate[4,8] but in these cases the concentration of oxidant was kept higher than the substrate and temperature was also kept comparably low. It has also been shown that Ce(IV)–perchlorate[4] oxidises much faster than the Ce(IV)–sulphate.

Equation (3) is a rate determining step and the formation of free radical takes place through C–H bond fission which undergo further fragmentation.[13]

In accordance with the mechanistic scheme the rate expression:

$$\frac{-d}{dt}[Ce(IV)]_T = k_o \quad (6)$$

because the rate is independent of the concentration of Ce(IV). Hence,

$$k_o = k_3[CH_2 = CH - \overset{\displaystyle O}{\overset{\|}{C}} - OH][H^+]. \quad (7)$$

According to expression (7) the rate will be independent of Ce(IV) and unity with respect to acrylic acid. This indicates the linearity of the plot k_o vs [$HClO_4$] as observed experimentally. It also negates the appreciable salt effect.

The entropy of activation has been found to be negative, characterising the formation of free radical[4] and the value of other thermodynamic parameters reported can be used for comparing the results of other reactions.

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