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Kinetics of Oxidation of α-Hydroxy Acids by Ceric Sulfate

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The mechanism of the oxidation of α-hydroxy acids by ceric sulfate in sulfuric acid medium has been re-examined in the temperature range 15—30 °C and the thermodynamic parameters have been calculated. The role of HSO_4^- ion as an active inhibitor has been discussed quantitatively.

Kinetics of the oxidation of α-hydroxy acids with ceric sulfate as oxidant has been the subject of several recent studies.[1-8] The mechanism of oxidation in presence of moderate sulfuric acid concentration, in general, involves a rapid formation of an activated complex between the hydroxy acid and the metal species which then decomposes slowly to yield organic radical and reduced metal ion. However, the present work on the oxidation of lactic, DL-malic, and mandelic acid by ceric sulfate was undertaken to re-examine the conflicting claims on the assumption of reactive species of cerium by different authors,[1,4,5] the effect of sulfuric acid on the reaction rate, particularly the role of HSO_4^- ion as an active inhibitor and to furnish further information on the little known temperature dependence of ceric oxidation.

Experimental

The materials used were of the highest purity available (AnalaR or E. Merck's Guaranteed Reagents).

A solution[9] of ceric sulfate in 1: 1 v/v sulfuric acid was diluted and standardized by titration against ferrous ammonium sulfate, *N*-phenylanthranilic acid being used as an indicator. The sulfuric acid contents were determined by the method reported by McAuley.[5] The solutions of organic acids were standardized by titration against sodium hydroxide. The progress of the reaction was followed as for the reaction between ceric ion and thallous ion.[10] The stoichiometry of the reaction was determined by allowing the reaction mixtures containing large excess of Ce(IV) to stand for several days in a thermostat-bath at 25 °C. The excess of Ce(IV) was then estimated by titration against ferrous ammonium sulfate. An average of five determinations in each case showed that one mol of mandelic, DL-malic, and lactic acid requires 2.0, 8.5, and 5.75 mol, respectively, of ceric ion.

Results

Our kinetic result on the oxidation of α-hydroxy acids by ceric sulfate, in presence of sulfuric acid of moderate concentration, are in agreement with that reported by Krishna and Tewari.[1] The concentration range 0.5—3.0 N of sulfuric acid is referred to as moderate concentration. The reaction is of simple kinetic order if the molar concentration of ceric sulfate is not greater than that of the hydroxy acid. The rate studies were made at temperatures 15—30 °C, in moderate sulfuric acid medium and found to be of first order with respect to each reactant. The second order rate constant, k_2, was derived from the plot of $\log [(a-x)/(b-x/y)]$ against time t, where a and b are the initial concentrations of the reactants, x is the amount of ceric sulfate consumed after time t and y is the moles of ceric sulfate required for complete oxidation of one mole of the hydroxy acid.

The reaction rate depends inversely on the square of concentration of sulfuric acid present. Sulfuric acid was varied in the concentration range 0.5—3.0N.

Table 1. Variation of reaction rate with temperature

$[Ce(SO_4)_2]=1\times10^{-2}$ M

[Hydroxy acid] $=1\times10^{-2}$ M

Hydroxy acid	$[H_2SO_4]$ M	Temperature °C	$k_2\times10^3$ $l\ mol^{-1}\ s^{-1}$
Lactic	0.6	20.0	3.23
		23.0	4.53
		25.0	5.69
		27.5	8.15
		30.0	10.89
	1.0	20.0	1.23
		25.0	2.39
		30.0	4.46
DL-Malic	1.0	20.0	6.80
		23.0	10.43
		25.0	12.93
		27.0	16.10
		30.0	23.50
Mandelic	2.0	15.0	32.75
		20.0	56.46
		25.0	96.26
		30.0	166.02

Table 2. Thermodynamic parameters for ceric oxidation at 25 °C

Hydroxy acid	$[H_2SO_4]$ M	Frequency factor $\times10^{-14}$ $l\ mol^{-1}\ s^{-1}$	Activation energy kcal mol^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta F^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ e.u.	Ref.
Lactic	0.6	0.62	21.8	21.21	20.52	2.0	
	1.0	1.19	22.7	22.11	21.43	2.3	
DL-Malic	1.0	1.03	21.6	21.00	20.98	0.1	
Mandelic	2.0	0.11	19.1	18.51	18.31	0.7	
	1.0	0.18	18.9	18.30	18.40	−0.3	6
Glycollic	1.0	0.36	23.2	22.61	22.18	1.4	5

Addition of nitric or hydrochloric acid in small amounts produces only insignificant retardation. However, hydrogen sulfate and sulfate ions produce a marked retardation. Addition of potassium chloride or nitrate produces negative salt effect while thorium nitrate increases the reaction rate.

The dependence of the rate with temperature for lactic, DL-malic and mandelic acid is shown in Table 1. The values of the activation energy were calculated from the slope of the straight line obtained by plotting log k_2 against $1/T$. The calculated thermodynamic parameters are given in Table 2.

Discussion

Ceric sulfate in aqueous sulfuric acid medium is known to exist[11–14] in variety of complex ions. The composition of these solutions, in general, is governed by the following equilibria:

$$\mathrm{Ce(SO_4)_2} \rightleftharpoons \mathrm{Ce(SO_4)^{2+}} + \mathrm{SO_4^{2-}}$$

$$\mathrm{Ce(SO_4)_2} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Ce(SO_4)_3^{2-}}$$

$$\mathrm{Ce(SO_4)_2} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{HCe(SO_4)_3^-} \rightleftharpoons \mathrm{Ce(SO_4)_3^{2-}} + \mathrm{H^+}$$

$$\mathrm{HCe(SO_4)_3^-} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{H_2Ce(SO_4)_4^{2-}} \rightleftharpoons \mathrm{Ce(SO_4)_4^{4-}} + 2\mathrm{H^+}$$

$Ce(SO_4)_2$, $HCe(SO_4)_3^-$, and $Ce(SO_4)^{2+}$ have been postulated as the reactive species by different authors[1,4,5] in the oxidation of α-hydroxy acids by ceric sulfate in a moderate sulfuric acid medium. From the equilibrium constants of Hardwick and Robertson,[14] for the formation of various ceric sulfate species, the concentration of various species at different $[HSO_4^-]$ and at constant acidity can be estimated. The results along with the observed dependence of the reaction rate on sulfuric acid concentration indicate $Ce(SO_4)_2$ and $Ce(SO_4)^{2+}$ are the possible reactive species. In the presence of moderate sulfuric acid, the experimental results could best be explained by assuming $Ce(SO_4)_2$ as the dominant reactive species as postulated by Krishna and Tewari.[1] At high acid concentration the reaction rate depends inversely on the square of concentration of sulfuric acid present. McAuley[5] has discussed the influence of $[HSO_4^-]$ on the reaction velocity over a smaller concentration range and found that the linear relationship deviates markedly at higher pH values. Possible existence of the reactive ions of the type $Ce(SO_4)^{2+}$ could not be ruled out[14] in a narrower concentration range.

In a solution containing a moderate amount of sulfuric acid and small amount of ceric sulfate, the concentration of HSO_4^- ion would be practically equal to the concentration of sulfuric acid taken. Sulfuric acid dissociates in the following stages

$$\text{(a)}\quad \mathrm{H_2SO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{HSO_4^-}$$

$$\text{(b)}\quad \mathrm{HSO_4^-} \overset{K}{\rightleftharpoons} \mathrm{H^+} + \mathrm{SO_4^{2-}}$$

In the first stage the dissociation is cent percent while in the second stage the dissociation is determined by the magnitude of K which is equal to 0.01 at zero ionic strength and 0.075 at an ionic strength of one unit.[15] At higher ionic strengths the equilibrium constant will be the same but the equilibrium quotient of the second stage, *i.e.* $(C_{H^+}C_{SO_4^{2-}}/C_{HSO_4^-})$ will be slightly greater. In any case the dissociation in the second stage will be limited and the concentration of HSO_4^- ion will be equal to the initial concentration of sulfuric acid taken. The active ceric complex species which reacts in the rate determining step is $Ce(SO_4)_2$ formed from the following reaction steps which occur rapidly in succession.

$$\text{(c)}\quad \mathrm{H_2Ce(SO_4)_4^{2-}} \rightleftharpoons \mathrm{HCe(SO_4)_3^-} + \mathrm{HSO_4^-}$$

$$\text{(d)}\quad \mathrm{HCe(SO_4)_3^-} \rightleftharpoons \mathrm{Ce(SO_4)_2} + \mathrm{HSO_4^-}$$

The scheme completely explains the inhibitory action of sulfuric acid and also the proportionality of the reaction rate to the ceric salt concentration. The assumption that most of the ceric salt in the presence of moderate concentration of sulfuric acid exists in the form $H_2Ce(SO_4)_4^{2-}$ in which hydrogen is tightly bound also explains why hydrogen ions from an external source, *i.e.* other than sulfuric acid, do not perceptibly affect the velocity of the reaction. This leads to the conclusion that HSO_4^- ion is the effective retarding agent. In the presence of a moderate sulfuric acid concentration the hydrogen ions added in small quantities, equilibrium (b) will shift very little from right to left and addition of hydrogen ion upto 0.1 M will be hardly perceptible. On the other hand, even a small quantity of SO_4^{2-} ion as will be available from K_2SO_4 up to 0.1 M due to the second dissociation of K_2SO_4 will produce a perceptible change in equilibrium from right to left with the consequent formation of HSO_4^- ions resulting in an appreciable inhibition of the reaction velocity. The observed lowering of reaction rate due to the addition of potassium sulfate could therefore be attributed partly to the increase in the ionic strength and partly to the dissociation in the following two stages.[16]

$$\text{(e)}\quad \mathrm{K_2SO_4} \longrightarrow \mathrm{K^+} + \mathrm{KSO_4^-}$$

$$\text{(f)}\quad \mathrm{KSO_4^-} \rightleftharpoons \mathrm{K^+} + \mathrm{SO_4^{2-}}$$

The dissociation constant for the second stage is 0.151. Addition of K_2SO_4 to a solution of sulfuric acid will produce more of HSO_4^- ion due to the reaction

$$\mathrm{SO_4^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HSO_4^-}$$

causing the observed retardation in the reaction velocity. Another reason for retardation in velocity could be that only a small part of KSO_4^- formed gives rise to SO_4^{2-} ions and the rest remains undissociated and very likely forms a complex with $Ce(SO_4)_2$ according to the following reaction

$$\text{(g)}\quad \mathrm{Ce(SO_4)_2} + 2\mathrm{KSO_4^-} \rightleftharpoons \mathrm{K_2Ce(SO_4)_4^{2-}}$$

thus reducing the active species. A similar reasoning could be given for the inhibitory action of $(NH_4)_2SO_4$.

The main inhibitory role of HSO_4^- ion can be examined quantitatively on the following consideration. In a solution containing sulfuric acid the increment in HSO_4^- will be equal to the concentration of $KHSO_4$ added. Since the velocity constant is inversely proportional to the square of the concentration of sulfuric acid, we may write

$$k_2 \propto \frac{1}{[\mathrm{H_2SO_4}]^2}$$

or

$$k_2 \propto \frac{1}{[HSO_4^-]^2} = \frac{b}{[HSO_4^-]^2} \qquad (1)$$

where b is the proportionality constant. Differentiating with respect to $[HSO_4^-]$ and rearranging, we obtain

$$-[HSO_4^-]^3 \frac{dk_2}{d[HSO_4^-]} = 2b = \text{constant} \qquad (2)$$

Since the amount of $KHSO_4$ added is small in comparison to the total concentration of H_2SO_4 already present, we can make the approximations

$$d[HSO_4^-] \approx \Delta[HSO_4^-] = \Delta[KHSO_4]$$

$$dk_2 \approx \Delta k_2$$

therefore,

$$-[HSO_4^-]^3 \frac{\Delta k_2}{\Delta[HSO_4^-]} = \text{constant}$$

or

$$-[H_2SO_4]^3 \frac{\Delta k_2}{\Delta[KHSO_4]} = \text{constant} \qquad (3)$$

where $[H_2SO_4]^3$ is the cube of the average concentration of H_2SO_4 initially taken, plus the concentration of $KHSO_4$ added, *i.e.* the average of the concentration of HSO_4^- ion between which Δk_2 is measured. The validity of Eq. 3 is shown in Table 3. The data both for mandelic and DL-malic acid have been taken from the oxidation studies reported by Krishna and Tewari.[1]

TABLE 3. INHIBITORY EFFECT OF HSO_4^- ION[a]

Hydroxy acid	$[H_2SO_4]$ M	$[KHSO_4]$ M	Δk_2	$-[H_2SO_4]^3 \cdot \Delta k_2/\Delta[KHSO_4]$
Mandelic	1.01	0.02	−0.245	12.61
	1.02	0.04	−0.426	11.30
	1.04	0.08	−0.920	12.93
	1.05	0.10	−1.091	12.63
DL-Malic	0.400	0.05	−0.379	0.486
	0.425	0.10	−0.588	0.456
	0.450	0.15	−0.800	0.486

a) Data taken from Ref. 1.

We see from Table 3 that the values in the last column are practically constant. This justifies the assumption that the main inhibitory ion is HSO_4^-.

The small negative salt effect observed by the addition of potassium chloride or nitrate follows no mathematical regularity and is hard to visualize in the presence of high ionic strength. The observed increase in the reaction velocity due to the addition of thorium nitrate may be due to some kind of complex formation between thorium and any one of the reactants.

A comparison of the values of different thermodynamic parameters (Table 2) for the oxidation of different hydroxy acids by ceric sulfate in presence of moderate sulfuric acid medium suggests a common mechanism,[17] *viz.*, a rapid formation of an activated complex between Ce(IV) and organic acid and subsequent slow decomposition into organic radical.

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