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Kinetics of the Oxidation Via Enolization of Di-Ethylester of Ethyl Malonic Acid by Ceric Sulphate in Sulphuric Acid.

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The rate of bromination with respect to diethyl ester of ethyl malonic acid, bromine and hydrogen ion concentration is one, zero and one respectively, while the rate of oxidation is first order with respect to all the cerium (IV), diethyl ester of ethyl malonic acid and hydrogen ions. It was confirmed that the oxidation proceeds through enol form of ester, as the rate of bromination was found to be 1.35 times faster than the rate of oxidation. The energies for activation for bromination and oxidation were obtained to be 62.90 and 67.67 KJ mole^{-1}, respectively. A mechanism of oxidation involving enol forms of the ester has been proposed.

INTRODUCTION

Kinetics of oxidation of aliphatic ketones by cerium(IV) has been studied and the results interpreted in the terms of enol form in sulphuric acid[1,2] and nitric acid[3] while keto form in prechloric acid[4] medium. The oxidation of keto form of cyclo hexanone by cerium(IV)[5], enol form of aliphatic ketone by acid permangnate[6] and enol form malonic acid by Mn(II)[7] have also been reported. Oxidation of malonic acid and diethyl malonate by cerium(IV) have been studied[8–16], but no one has reported so far, whether the oxidation takes place *via.* enol form or keto form of the ester in view of this, the oxidation of diethyl ester of ethyl malonic acid by cerium (IV) in sulphuric acid was investigated to understand the mechanistic path of the oxidation.

EXPERIMENTAL

Ceric sulphate solution were prepared by dissolving known weight of ceric sulphate in 1M H_2SO_4. The reacting solutions were placed in stoppered bottles and than rapidly mixed at constant temperature, ester being last to be added. Aliquots were withdrawn at different time intervals and quenched in excess ferrous ammonium sulphate solution. The excess ferrous ion was then back titrated against standard cerium(IV) solution with ferroin used as indicator. The rate of enolisation of the ester have been obtained by measuring its rate of bromination[17]. The disappearence of bromine was measured by addition of potassium iodide containing sodium bicarbonate to the aliquots drawn at regular interval and titrating the iodine liberated with standardised solution of hypo[18]. Oxidation of ester by cerium(IV) in presence of bromine was carried out. Bromine was extracted with carbon tetrachloride before the ceric ions was titrated with ferrous ammonium sulphate solution. The rate of diappearance of $[(\text{cerium (IV)} + Br_2)]^3$ is measured by titration with liberated iodine and standard sodium thiosulphate.

RESULTS AND DISCUSSIONS

Stoichiometric investigation reveals that one mole of diethyl ester of ethyl malonic acid required fourteen moles of cerium(IV). The final products of oxidation were characterised as acetaldehyde, acetic acid and propionic acid[19–21]. The reaction mixture also gave positive test for ethyl substituted glyoxalic acid[22]. The induced reaction of mercuric chloride by the reaction mixture indicated participation of free radicals[23].

Plot of log titre value against time are linear indicating that the decay in Ce(IV) is of first order. The reaction was also first order with respect to ester concentration as the plots of K_1 versus [ester] was found to be linear.

In the acid medium bromine reacts with the diethyl ester of ethyl malonic acid to give bromine substituted products. This reaction occurs through enolisation of diethyl ester of ethyl malonic acid catalised by H^+. The zero order with respect to bromine suggests the rate determining step in the reaction is the enolisation process.

The rate of bromination is therefore, assumed to be equal to the rate of acid catalysed enolisation of diethyl ester of ethyl malonic acid. The reaction was found to be first order with respect to substrate as the plot of rate versus [ester] was linear. The reaction was studied at different temperature to evalute the activation parameters. The energy of activation for bromination reaction and for oxidation reaction is summarised in (Table 1). The rate is first order with respect to diethyl ester of ethyl malonic acid and first order with respect to hydrogen ion concentration (Table 2). The rate of enolisation is approximately 1.35 times faster than the rate of oxidation (Table 3). The oxidation seems to be proceed *via* enolic form of diethyl ester of ethyl malonic acid.

TABLE 1

EFFECT OF TEMPERATURE ON RATE OF BROMINATION AND OF OXIDATION ON DIETHYL ESTER OF ETHYL MALONIC ACID $[Br_2] = 4 \times 10^{-3}$ mole dm^{-3} OR $[Ce(IV)] = 4 \times 10^{-3}$ mole dm^{-3}, $[H^+] = 1.0$ mole dm^{-3}, [DIETHYL ESTER OF ETHYL MALONIC ACID] $= 2 \times 10^{-2}$ mole dm^{-3} AND MEDIUM = 25% (V/V) AQUEOUS ACETIC ACID.

Ester	(δE) KJ. mole^{-1} oxidation	(δE) KJ. mole^{-1} Bromination
Diethyl Ester of Ethyl Malonic Acid	67.65 ± 0.43	62.60 ± 0.41

TABLE 2

EFFECT OF VARIATION OF RATE OF BROMINATION WITH H^+ CONCENTRATION $[Br_2] = 4 \times 10^{-3}$ mole dm^{-3}, [DIETHYL ESTER OF ETHYL MALONIC ACID] $= 2 \times 10^{-2}$ mole dm^{-3} TEMP = 303 K, MEDIUM = 25% (V/V) AQUEOUS ACETIC ACID AND $\mu = 1.0$ mole dm^{-3}

H_2SO_4 mole dm^{-3}	$(NaHSO_4)$ mole dm^{-3}	$K^o \times 10^7$ mole dm^{-3} Sec^{-1}
1.0	—	3.1085
0.70	0.20	2.7378
0.55	0.55	1.9771
0.30	0.80	1.0856

TABLE 3

EFFECT OF RATE OF BROMINATION AND OF OXIDATION ON DIETHYL ESTER OF ETHYL MALONIC ACID. $[Br_2] = 4 \times 10^{-3}$ mol dm^{-3} OR $[Ce(IV)] = 4 \times 10^{-3}$ mol dm^{-3}, [DIETHYL ESTER OF ETHYL MALONIC ACID] $= 1 \times 10^{-2}$ mol dm^{-3}, MEDIUM = 25% (V/V) aq. ACETIC ACID, $[H^+] = 1.0$ mol dm^{-3} AND TEMP. 303 K.

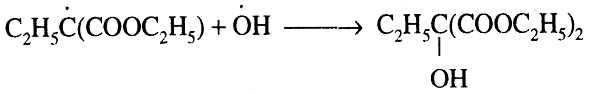
Ester	Rate of Oxidation mole dm^{-3} sec^{-1}	Rate of Bromination mole dm^{-3} sec^{-1}	$\frac{\text{K-Bromination}}{\text{K-Oxidation}}$
Diethyl Ester of Ethyl Malonic Acid	1.25×10^{-7}	1.52×10^{-7}	1.33

The enolic form of ester is involved in the oxidation by ceric salts, then presence of bromine in the reaction mixture should inhibit the oxidation by Ce(IV) by combining with the enol present. The rate of which the ceric ions was reduced in presence of ester and bromine. $r_0[Ce(IV)]$ was measured along with the combined rate for the disappearance of ceric ion and bromine, $r_0[Ce(IV) + (Br_2)]$ in a manner described earlier[1,2]. The rate of bromination $r_0[(Br_2)]$ of ester and the rate of oxidation of ester by ceric ions was measured in separate experiments under identical conditions.

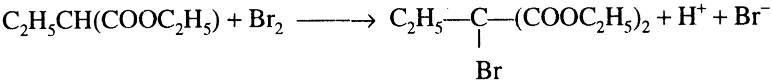
Solutions of ceric sulphate in sulphuric acid and reduced in the presence of bromine. Oxygen is evolved as a result of the reaction. Probably water is attacked by ceric ions under the influence of bromine. The rate of this reaction was also measured both by following the reduction of ceric ions and by observing the disappearence of ceric ions and bromine together. The rates of reaction were found to be identical confirming that the action of bromine was catalytic. The data on the influence of bromine has been summerised in Table 4. These values indicates that in the reaction system, the following steps take place:

$$Ce^{4+} + H_2O \xrightarrow{\text{Bromine}} Ce^{3+} + \dot{O}H + H^+ \qquad (i)$$

$$C_2H_5CH(COOC_2H_5)_2 + \dot{O}H \longrightarrow C_2H_5\dot{C}(COOC_2H_5)_2 + H_2O \qquad (ii)$$



$$C_2H_5\dot{C}(COOC_2H_5) + \dot{O}H \longrightarrow C_2H_5C(OH)(COOC_2H_5)_2 \quad \text{(iii)}$$



$$C_2H_5CH(COOC_2H_5) + Br_2 \longrightarrow C_2H_5—C(Br)—(COOC_2H_5)_2 + H^+ + Br^-$$

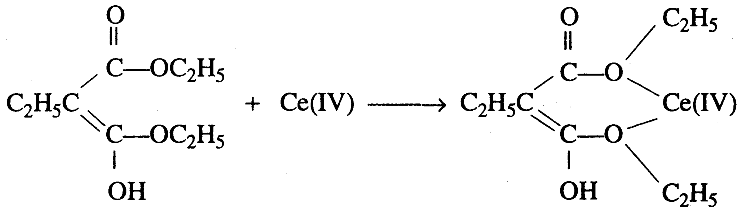
$$Br^- + Ce^{4+} \longrightarrow Ce^{3+} + \tfrac{1}{2}Br_2 \quad \text{(iv)}$$

TABLE 4

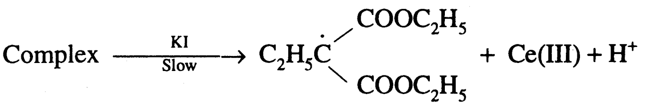
EFFECT OF BROMINE ON OXIDATION OF DIETHYL ESTER OF ETHYL MALONIC ACID (ESTER); [H_2SO_4] = 1.0 mol dm^{-3}, [Br_2] = 4 × 10^{-3} mol dm^{-3} (a.c.d), TEMP. 303 K; [DIETHYL ESTER OF ETHYL MALONICACID] = 1 × 10^{-2} mol dm^{-3} (b,c,d), Ce(IV) = 4 × 10^{-3} mol dm^{-3} (a,b,d) AND MEDIUM = 25% (V/V) aq. ACETIC ACID.

Reaction System	r_0[Ce(IV) × 10^7] mol dm^{-3} sec^{-1}	r_0[Ce(IV) + Br_2] × 10^7 mol dm^{-3} sec^{-1}	r_0[Br_2] × 10^7 mol dm^{-3} sec^{-1}
(a) [Ce(IV)] + [(Br_2)] + [H_2O]	0.85	0.88	—
(b) [Ce(IV)] + [Ester]	1.22	—	—
(c) [Br_2] + [Ester]	—	—	1.67
(d) [Ce(IV)] + [Br_2] + [Ester]	1.31	2.15	—

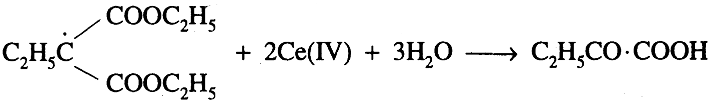
The oxidation of hydroxy ester is assumed to be slow reaction. Thus bromine appears inhibit the oxidation of ester by ceric sulphate. In sulphuric acid by the normal mechanism and the participation of the enol in this is thereby confirmed.



Diethyl Ester of Ethyl Malonic Acid (Enol Form)



$$\text{Complex} \xrightarrow[\text{Slow}]{\text{KI}} C_2H_5\dot{C}(COOC_2H_5)_2 + Ce(III) + H^+$$



$$C_2H_5\dot{C}(COOC_2H_5)_2 + 2Ce(IV) + 3H_2O \longrightarrow C_2H_5CO\cdot COOH$$

$$+ \dot{C}O_2H + 2C_2H_5OH + 2Ce(III) + 2H^+$$

$$2C_2H_5OH + 4Ce(IV) \longrightarrow 2CH_3CHO + 4Ce(III) + 4H^+$$

$$2CH_3CHO + 4Ce(IV) + 2H_2O \longrightarrow 2CH_3COOH + 4Ce(III) + 4H^+$$

$$\dot{C}O_2H + Ce(IV) \longrightarrow CO_2 + Ce(III) + H^+$$

$$C_2H_5CO\cdot COOH + 2Ce(IV) + H_2O \rightarrow C_2H_5COOH + 2Ce(III) + 2H^+ + CO_2$$

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