# Kinetics & Mechanism of Oxidation of Methylmalonic Acid & Its Diethyl Ester by Cerium (IV) Sulphate

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Oxidation of methylmalonic acid and its diethyl ester by Ce(IV) sulphate in sulphuric acid medium shows first order dependence each in [substrate] and Ce(IV). The reactive oxidant species have been shown to be $Ce(SO_4)_2$ and $Ce(SO_4)_3^{2-}$. The oxidation of acid is found to be faster than that of its ester. A tentative mechanism has been proposed.

Kinetics of oxidation of methylmalonic acid and its diethyl ester by Ce(IV) has been studied by Yadav and Bhagwat[1] in sulphuric acid, Ignaczak[2] and Tischler, and Morrow[3] in perchloric acid and Prasad and Tripathi[4] in sulphuric, acetic and phosphoric acids. Two different mechanisms have been proposed for this oxidation. The first mechanism involves rapid formation of a Ce(IV) complex (activated) followed by its slow decomposition. In the second mechanism, the oxidation proceeds without complex formation. In view of these divergent views it was considered of interest to undertake the title investigation with a view to throwing light on the mechanism of this oxidation reaction.

Ceric sulphate (E Merck), methylmalonic acid (John Baker), diethyl ester (Koch Light), sodium bisulphate (BDH) and sodium perchlorate (Riedel) and perchloric acid (70%, AR, BDH) were used as such. All other chemicals were Sarabhai-Merck reagents. Ceric sulphate solutions were prepared by dissolving known amount of ceric sulphate in 1 mol $dm^{-3}$ $H_2SO_4$. Doubly distilled water was used to prepare all solutions. The reaction was carried out in dark coloured bottles. All the experiments were carried out in acetic acid (25%, v/v) in presence of sulphuric acid.

The requisite amounts of reactant solutions were separately equilibrated at the desired temperature maintained with an accuracy of ± 0.02°C. Ceric sulphate solution of known concentration was preequilibrated at the desired temperature and was ra-

pidly added to the substrate (however, in case of the ester as the substrate, it was added in the last). Aliquots were withdrawn at regular time intervals and quenched in a known excess of ferrous ammonium sulphate. Excess of ferrous ions was then back titrated against standard Ce(IV) solution with ferroin as an indicator.

Stoichiometric investigation reveals that one mol of methylmalonic acid required eight mol of Ce(IV) whereas the corresponding diethyl ester required sixteen mol of Ce(IV). The final products of oxidation were characterized as formaldehyde and formic acid[5-7a]. The reaction mixture also gave positive spot test for glyoxalic acid[7b]. The induced reduction of mercuric chloride by the reaction mixture indicated participation of free radicals[8]. When the concentrations of methylmalonic acid and perchloric acid were in excess, the disappearance of ceric sulphate followed a first order rate law.

Varying initial [Ce(IV)] did not affect the rate constant confirming the order in [Ce(IV)] as one. The plot of log $k$ versus log [substrate] was linear with a unit slope, indicating the order in [substrate] also as one. There was no kinetic evidence for intermediate complex formation between substrate and oxidants. However, absorbances of two solutions (blank and reaction mixture) did change. This indicated that either the concentration of reversible complex is small or sulphato-cerate complex of ester of malonic acid decomposed rapidly. Further the oxidation of methylmalonic acid was faster as compared to the oxidation of diethyl ester of methylmalonic acid.

From the kinetic point of view, the real problem in oxidation by Ce(IV) is the multiplicity of cerium species, probably each one with its own characteris-

Table 1—Effect of Varying $[H^+]$ on Rate Constant for Oxidation of Methylmalonic Acid and Its Diethyl Ester

[Substrate] = $1.0 \times 10^{-2}$ mol $dm^{-3}$; [Ce(IV)] = $4.0 \times 10^{-3}$ mol $dm^{-3}$; temp. 308 K; medium = 25% (v/v) aqu.acetic acid; and $\mu$ = 1.5 mol $dm^{-3}$

| $[H_2SO_4]$ mol $dm^{-3}$ | $[NaHSO_4]$ mol $dm^{-3}$ | $k_1 \times 10^4$ $(s^{-1})$* | $k_1 \times 10^5$ $(s^{-1})$† |
|---|---|---|---|
| 1.25 | 0.25 | 17.96 | 5.45 |
| 1.0 | 0.50 | 14.32 | 4.37 |
| 0.75 | 0.75 | 11.52 | 3.26 |
| 0.50 | 1.0 | 7.68 | 2.18 |
| 0.25 | 1.25 | 4.03 | 1.30 |

*for methylmalonic acid
§for diethyl ester of methylmalonic acid

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### Table 2—Effect of Varying [H$^+$] on Rate Constant of Ce(IV) Oxidation of Methylmalonic Acid and Its Diethyl Ester

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$; [Ce(IV)] = $4.0 \times 10^{-3}$ mol dm$^{-3}$; temp. = 308 K; medium = 25% (v/v)aq. acetic acid; and [H$_2$SO$_4$] = 0.1 mol dm$^{-3}$

| [HClO$_4$] mol dm$^{-3}$ | [NaClO$_4$] mol dm$^{-3}$ | $k_1 \times 10^3$ (s$^{-1}$)* | $k_1 \times 10^5$ (s$^{-1}$)§ |
|---|---|---|---|
| 1.15 | 0.25 | 6.17 | 8.70 |
| 0.90 | 0.50 | 4.99 | 7.41 |
| 0.65 | 0.75 | 3.74 | 5.56 |
| 0.40 | 1.0 | 2.69 | 3.95 |
| 0.15 | 1.25 | 1.30 | 2.11 |

*for methyl malonic acid
§for diethyl ester of methyl malonic acid

### Table 3—Concentration of Various Ce(IV) Species

[H$^+$] = 0.5 mol dm$^{-3}$

| Species | [Ce(IV)] in | |
|---|---|---|
| | [HSO$_4^-$] = 1.0 mol dm$^{-3}$ | [HSO$_4^-$] = 0.25 mol dm$^{-3}$ |
| Ce$^{+4}$ | $8.71 \times 10^{-9}$ | $5.19 \times 10^{-7}$ |
| Ce(SO$_4$)$^{+2}$ | $6.10 \times 10^{-5}$ | $9.08 \times 10^{-4}$ |
| Ce(SO$_4$)$_2$ | $2.43 \times 10^{-5}$ | $9.08 \times 10^{-2}$ |
| Ce(SO$_4$)$_3^{-2}$ | 0.97 | 0.91 |

### Table 4—Effect of Varying [Bisulphate] on Reaction Rate

[Substrate] = $1.0 \times 10^{-2}$ mol dm$^{-3}$; [Ce(IV)] = $4.0 \times 10^{-3}$ mol dm$^{-3}$; medium = 25% (v/v) aq. acetic acid; $\mu$ = 1.5 mol dm$^{-3}$ and [H$^+$] = 0.5 mol dm$^{-3}$

| [NaHSO$_4$] mol dm$^{-3}$ | [NaClO$_4$] mol dm$^{-3}$ | $k_1 \times 10^4$ (s$^{-1}$)* | $k_1 \times 10^5$ (s$^{-1}$)† |
|---|---|---|---|
| 1.0 | — | 10.23 | 2.53 |
| 0.75 | 0.25 | 13.44 | 2.76 |
| 0.50 | 0.50 | 16.31 | 3.02 |
| 0.25 | 0.75 | 25.03 | 3.65 |

*for methyl malonic acid
†for diethyl ester of methylmalonic acid

tic rate constant. Using the values the equilibrium constants $K_1$, $K_2$ and $K_3$ for the formation of various ceric sulphate complexes[9] and the experimental data (dependence of reaction rate on H$^+$ ions—see Tables 1 and 2) concentration of various Ce(IV) sulphate species[10] have been calculated and are given in Table 3. The dependence of rate on [bisulphate] (cf. Table 4) rules out the possibility of Ce$^{4+}$ and Ce(SO$_4$)$^{2+}$ as the reactive species. The only species left in the present case are Ce(SO$_4$)$_2$ and Ce(SO$_4$)$_3^{2-}$. Assuming both of them to be reactive in this oxidation a mechanism consistent with the kinetic data has been proposed (see Scheme 1). This mechanism confirms the mechanism proposed by earlier worker[11,12].
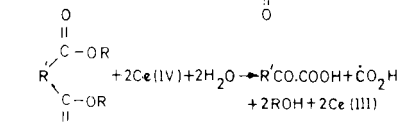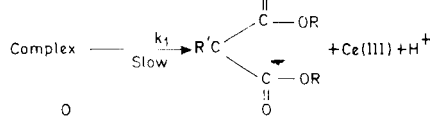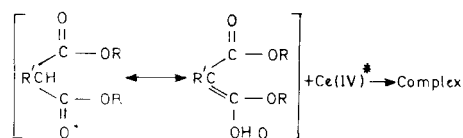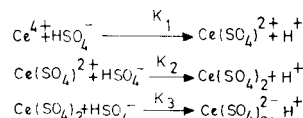


Scheme 1

In Scheme 1 R=H or C$_2$H$_5$, R'= –CH$_3$, Ce(IV)*= Ce(SO$_4$)$_2$ and Ce(SO$_4$)$_3^{2-}$

The rate law, in accord with Scheme 1 is given by Eq. (1)

$$\frac{k_1}{[\text{substrate}]} = \frac{k'[\text{H}^+]}{K_3[\text{HSO}_4^-]} + k'' \qquad \ldots (1)$$

where $k'$ and $k''$ are the rate constants for the oxidation of substrate (methylmalonic acid and its diethyl ester) by Ce(SO$_4$)$_2$ and Ce(SO$_4$)$_3^{2-}$ respectively. At constant [H$^+$] Eq. (1) reduces to Eq. (2)

$$\frac{k_1}{[\text{substrate}]} = \frac{a}{[\text{HSO}_4^-]} + b \qquad \ldots (2)$$

where $a = k'[\text{H}^+]/K_3$ and $b = k''$. $k'$ and $k''$ have been evaluated from the values of $a$ and $b$ determined by least squares method from the data of Table 4 and their values are given in Table 5.

### Table 5—Values of Rate Constants ($k'$ and $k''$) and the Parameters $a$ and $b$ (see Eq. 2)

[HSO$_4^-$] = 0.25 mol dm$^{-3}$ and 1.0 mol dm$^{-3}$; [H$^+$] = 0.5 mol dm$^{-3}$ and temp. = 308 K

| Parameters | Methylmalonic acid | Diethyl ester |
|---|---|---|
| $a$ (s$^{-1}$) | $3.99 \times 10^{-2}$ | $0.35 \times 10^{-3}$ |
| $k'$ (mol dm$^{-3}$ s$^{-1}$) | $159.6 \times 10^{-2}$ | $14.0 \times 10^{-3}$ |
| $b$ (dm$^{-3}$ mol$^{-1}$ s$^{-1}$) | $7.44 \times 10^{-2}$ | $2.25 \times 10^{-3}$ |
| $k''$ (mol dm$^{-3}$ s$^{-1}$) | $7.44 \times 10^{-2}$ | $2.25 \times 10^{-3}$ |

The reaction was studied at different temperatures to evaluate the activation parameters. The energies of activation for the oxidation of methylmalonic acid and the corresponding diethyl ester were evaluated as 56.7 and 70.3 kJ $mol^{-1}$ respectively.

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