KINETICS OF OXIDATIVE DECARBOXYLATION
OF L-SERINE BY POTASSIUM PERMANGANATE

By

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The acid catalysed oxidation kinetics of L-serine by potassium permanganate has been studied. The reaction has been found to obey first order in both, the L-serine and potassium permanganate. Various hypotheses for the mechanism of acid catalysis have been tested. The energy and the entropy of activation have been calculated as 13.5 and 14.6 kcal mole^{-1} and -23.4 and -22.6 e.u. for two-stages of the reaction, respectively. A mechanism is proposed, which is in agreement with the experimental data.

Potassium permanganate has been found to be a good oxidizing agent and the kinetics of oxidation of various organic compounds have been studied by previous workers [1—4]. However, a careful survey of the literature reveals that oxidative decarboxylation of amino acids by potassium permanganate has received little attention [5—9]. The present paper deals with the kinetic studies of the oxidative decarboxylation of L-serine by potassium permanganate in sulphuric acid medium.

Experimental

L-serine, potassium permanganate and other chemicals used were 'BDH'/'S. M.' products. Doubly distilled water was used to prepare all the solutions. The reaction vessels were coated with black paint to exclude any photochemical effect.

Solutions of sulphuric acid were standardized against previously standardized sodium hydroxide solution. Potassium permanganate solution was prepared by the method of Vogel [10].

The requisite amounts of L-serine and sulphuric acid were taken in the reaction flask and kept in a thermostat at the desired temperature within the range of ± 0.1 °C. The flask of potassium permanganate was also kept in the thermostat. Requisite volume of permanganate was then rapidly mixed and the kinetics of the reaction was followed by estimating unreacted permanganate iodometrically.

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Results and discussion

Dependence on oxidant concentration — The reaction was studied at different concentrations of the substrate, oxidant and sulphuric acid. It was observed that at constant concentration of L-serine and sulphuric acid, the value of pseudo-first order rate constant is not affected by the change in concentration of permanganate, hence, the order of the reaction with respect to permanganate is one. The value of pseudo-first order rate constants k_1 for various concentrations of permanganate are given in Table I.

Dependence on L-serine concentration — The plot of rate constant against concentration of L-serine gives a straight line passing through the origin, thus showing that the order of reaction with respect to L-serine is one and also that, there is apparently no kinetic evidence for the intermediate complex formation between L-serine and permanganate [11], and if at all any complex is formed, its formation constant should be extremely small [12]. The results are summarised below in Table II.

Dependence on acid concentration — Increase in sulphuric acid concentration also increases the rate of oxidation of L-serine. $HMnO_4$ is considered to as the active oxidizing species in this case, based on the fact that the rate of oxidation is directly proportional to the substrate concentration indicating that $HMnO_4$ oxidizes the substrate directly [13].

Further in an attempt to correlate the rate of oxidation with acid concentration, various hypotheses for the mechanism of acid catalysis were tested. In this case,

Table I

Variation of rate with concentration of permanganate

[L—Serine] $= 1.0 \times 10^{-2}$ M   [Sulphuric Acid] $= 2.0$ M
Temperature $= 30$ °C

$[KMnO_4] \times 10^4$ M	$k_1 \times 10^2$ min^{-1}	$k_1' \times 10^3$ min^{-1}
4.0	1.21	3.54
6.0	1.26	3.49
8.0	1.32	3.07
10.0	1.28	2.92

Table II

Variation of rate with concentration of L-serine

[Sulphuric Acid] $= 2.0$ M $[KMnO_4] = 1.0 \times 10^{-3}$ M
Temperature $= 30$ °C

[L—Serine] $\times 10^3$ M	$k_1 \times 10^3$ min^{-1}	$k_1' \times 10^3$ min^{-1}
5.0	6.31	1.57
10.0	12.79	2.92
15.0	22.47	4.27
20.0	28.78	6.22
25.0	34.12	7.68

Table III

Variation of rate with concentration of sulphuric acid

[L-Serine] $= 1.0 \times 10^{-2}$ M [KMnO$_4$] $= 1.0 \times 10^{-3}$ M
Temperature $= 30$ °C

[Sulphuric Acid] M	$k_1 \times 10^3$ min^{-1}	$k_1' \times 10^3$ min^{-1}
2.0	12.79	2.92
2.5	17.06	4.30
3.0	22.47	5.76
3.5	26.32	8.08
4.0	32.91	10.71

either of the two Zucker—Hammett plots [14], are linear, indicating that the reaction is acid catalysed, but however, no straight line of these plots produces the ideal slope of unity. In view of these departure from ideal slope values from unity, applicability of Bunnett's hypothesis [15] and Bunnett—Olsen l.f.e.r. [16] were tested. The values of — H_0 and log a_{H_2O}, corresponding to given acid concentrations have been taken from *Paul* and *Long* [17] and Bunnett [18], respectively.

The values of Bunnett parameters ω, ω^* and Φ were found to be —5.71, 0.87 and 0.88 for first stage and —5.00, 2.56 and 0.63 for second stage, respectively.

Activation Parameters — The reaction was studied at different temperatures to evaluate activation parameters. The results are summarised in Table IV.

Primary salt effect was not observed, but a linear plot of log k_1 against ionic strength was obtained at higher concentration of added neutral salts. This indicates that the reaction involves both the neutral molecules or a neutral species and an ion in the rate determining step.

Stoichiometry of the reaction was also studied. It was observed that two equivalents of permanganate was consumed by five equivalents of L-serine. Formation of ammonium ions and carbon dioxide was confirmed by usual tests. Glycolaldehyde was detected as the reaction product. The induced reduction of mercuric chloride by the reaction mixture indicates the presence of free radicals as intermediates [19].

The information gained from the experimental data leads to the following probable mechanism, which explains the observed results very well.
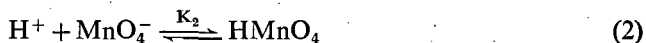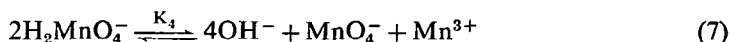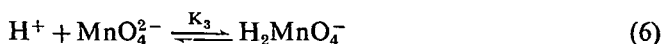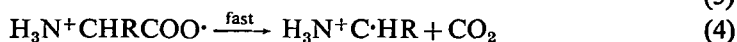
$$H_3N^+CHRCOO^- + H^+ \underset{K_1}{\rightleftharpoons} H_3N^+CHRCOOH \qquad (1)$$

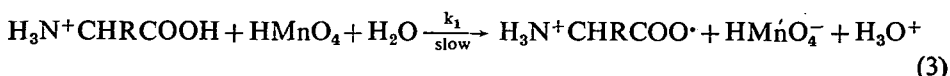$$H^+ + MnO_4^- \underset{K_2}{\rightleftharpoons} HMnO_4 \qquad (2)$$

Table IV

Activation Parameters

[L-Serine] $= 1.0 \times 10^{-2}$ M [KMnO$_4$] $= 1.0 \times 10^{-3}$ M
[Sulphuric Acid] $= 2.0$ M

Stage	Temp. Coeff.	$\Delta E^{\neq}$ Kcal/mole	$\Delta S^{\neq}$ cal. mole^{-1} K^{-1}	pZ liters mole^{-1} min^{-1}
First	2.05	13.5	—23.4	7.534×10^7
Second	2.07	14.6	—22.6	1.083×10^8

$$H_3N^+CHRCOOH + HMnO_4 + H_2O \xrightarrow[\text{slow}]{k_1} H_3N^+CHRCOO^\cdot + HMnO_4^- + H_3O^+ \tag{3}$$

$$H_3N^+CHRCOO^\cdot \xrightarrow{\text{fast}} H_3N^+C^\cdot HR + CO_2 \tag{4}$$

$$H_3N^+C^\cdot HR + HMnO_4^- + H_2O \xrightarrow{\text{fast}} H_2N^+ = CHR + HMnO_4^{2-} + H_3O^+ \tag{[(5)}$$

$$H^+ + MnO_4^{2-} \underset{K_3}{\rightleftharpoons} H_2MnO_4^- \tag{6}$$

$$2H_2MnO_4^- \underset{K_4}{\rightleftharpoons} 4OH^- + MnO_4^- + Mn^{3+} \tag{7}$$

$$H_2N^+ = CHR + H_2O \xrightarrow{\text{fast}} RCHO + H^+ + NH_3 \tag{8}$$

where $R = —CH_2OH$ for L-serine.

Rate expression for this mechanism has been developed as

$$-\frac{d[MnO_4^-]}{dt} = \frac{k_1 K_1 K_2 \,[\text{L-serine}]\,[H^+]^2[MnO_4^-][H_2O]}{1 + K_2[H^+]} . \tag{9}$$

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КИНЕТИКА ОКИСЛИТЕЛЬНОЙ ДЕКАРБОКСИЛИЗАЦИИ L-СЕРИНА ПЕРМАНГАНАТОМ КАЛИЯ

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Изучено катализированное кислотой окисление L-серина перманганатом калия. Реакция происходит по первому порядку, как относительно L-серина, так и перманганата калия. Предложен механизм реакции, который находится в хорошем соответствии с полученными экспериментальными данными.