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Decarboxylation of succinic acid by permanganate ion

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Abstract

This study of oxidative decarboxylation of Succinic acid by permanganate ion in moderately concentrated acidic medium has been found to be two-stage i.e. slow first stage followed by relatively faster second stage. The log (a-x) versus t curve displays an inflection. In both the stages the reaction follows first order behavior with respect to each, substrate and the oxidant. The cause of autocatalysis has been attributed to Mn(II) ions, which was further substantiated by the initial addition of MnSO₄. The oxidation reactions are acid catalysed and therefore, various hypotheses for the mechanism of acid catalysis were tested. Thus, the role of water molecule as proton abstracting agent is established. On addition of flouride ions a known complexing agent, there is a decrease in the reaction rate. The stoichiometry for the succinic acid reaction is $(\text{CH}_2\text{COOH})_2 + 2 \text{MnO}_4 + 6\text{H}^+ \rightarrow 5 \text{HCOOH} + 10 \text{H}_2\text{O} + 5 \text{CO}_2 + 2 \text{Mn}^{2+}$. The effect of variation of ionic strength has also been studied. Thermodynamic parameters have been computed by studying the reaction at different temperatures. On the basis of the various observations and product characterization a most plausible mechanism has been envisaged.

Keywords: Decarboxylation and succinic acid

Introduction

Autocatalytic oxidative decarboxylation of various organic substrates by permanganate ion has been studied considerably ^[1, 8] but information available on the autocatalytic oxidation of succinic acid in moderately concentrated acid medium by permanganate is scanty. Therefore, the present study is undertaken.

Experimental

All chemicals used were of BDH or AnalaR. Potassium permanganate solution was prepared in doubly distilled water as given by Vogel ^[9]. The progress of the reaction was monitored by iodometric estimations of the reaction mixture at various time intervals.

Results and Discussion

This has been observed that in the oxidative decarboxylation of Succinic acid, plots of log (a-x) versus time exhibits two stages, initial slow stage followed by relatively faster

Table-1: Variation of substrate concentration
 $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 2.0 \text{ mol dm}^{-3}$, Temp. = 303 K

S. No	Concentration Mol dm ⁻³	$k_1 \times 10^5$ Succinic acid	$k_1 \times 10^5$ Succinic acid
1.	0.10	1.51	4.01
2.	0.20	3.33	5.16
3.	0.30	3.78	6.82
4.	0.50	4.75	12.45
5.	0.60	6.36	16.09

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Table 2: Correlation of rate with H₂SO₄ concentration
[KMnO₄] = 1.0 × 10⁻³ mol dm⁻³, [H₂SO₄] = 2.0 mol dm⁻³, Temp. = 303 K

Correlation Parameter	Slope Values Succinic acid	
	Stage-1	Stage-2
(A) Zucker-Hammet ^[13] Plots		
1. HO vs log k	0.88	1.03
2. log [acid] vs log k	2.48	2.94
(B) Bunnet Plots		
log k - log [acid] vs log a H ₂ O	1.94	1.42
(C). Bunnet-Olsen ^[15] Plot (LFER)		
log k + H ₀ vs H ₀ + log [acid]	0.70	0.64

Step. The [Fig-1] depicts the slow initial reaction followed by a relatively faster reaction. Linearity of both the stages indicates unit order with respect to permanganate in both the stages. The variation of initial concentration of permanganate has practically no effect on the reaction velocity and the values- of pseudo first order constants k₁ (for first stage) and k'₁ (for second stage) are found to be fairly constant. The order with respect to permanganate is thus confirmed to be one. With the increase in the concentration of substrates the pseudo first order rate constants k₁ and k'₁ are found to be increased. Plot of log k₁, and (log k'₁) versus log [Succinic acid] give straight lines with slopes equal to 1.17 and 1.13 for the first and second stage respectively. This confirms the order of reaction with

respect to succinic acid as one in both the stages. Plots-of 1/k₁ (and log k'₁) versus 1/[substrate] give straight lines passing almost through the origin. This confirms again the,, order with respect to substrate as one and there is no kinetic evidence, for intermediate complex formation between substrate and 'permanganate'¹⁰. To serve the effect of acid concentration on the action, the reactions were studied at different concentrations of sulphuric acid. In order) avoid complications from precipitation of MnO₂ reactions were carried out in strongly acidic medium. The MnO₄⁻ ion gets protonated on accordance with the equilibrium MnO₄⁻ + H⁺ ⇌ HMnO₄ Supported by the spectral studies suggesting that the HMnO₄ is one of the active oxidising species^[4(b), 11]. The rate of oxidation that is strictly propotional to the

Table 3: Effect of addition of MnSO₄
[KMnO₄] = 1.0×10³ mol dm³, [H₂SO₄] = 2.0 mol dm³, Temp. = 303 K

S. No	Concentration Mol dm ⁻¹	*Succinic acid k ₁ ×10 ⁵
1.	0.0	1.23
2.	1.0	1.86
3.	1.5	2.76
4.	2.0	3.01
5.	3.0	3.67
6.	4.0	4.35
7.	5.0	6.03

*only stage-1

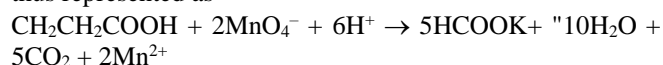
Concentration of the substrate indicates that HMnO₄ oxidizes substrate directly^[12]. The two Zucker-Hammet^[13] plots were found linear. This indicates that the reactions are acid catalyzed. However, none of the plots produce ideal slope values of unity (Table 2). In view of these departures from the ideal slope values the Bunnett^[14] and Bunnett-Olsen's hypothesis^[15] were tested. The slope values indicate that the water molecule should act as a proton abstracting agent in the rate determining step^[14-a]. The value of -H₀ and log a_{H₂O} corresponding to a given acid concentration have been taken from Paul and Long^[16] and Bunnet^[14-b] respectively.

The reactions were' studied at 303, 308, 313 and 323 K to evaluate various kinetic and activation parameters. It has been observed that reactions follow the Arrhenius relationship. With the increase in the ionic strength by adding sodium sulfate there is an increase in the rate constant. Thus, positive salt effect indicates that there should be a participation neutral molecules or a neutral molecule and an ion^[11] in the rds.

Stoichiometry and product analysis

In order to determine the stoichiometry of. Oxidative decarboxylation of the succinic acid by permanganate ion in acid medium, known amount of substrates were allowed to react with of permanganate in 1:10 and 1:50 molar ratio

with excess of sulphuric acid. After incubation of 48 hours the excess permanganate was determined iodometrically. The observations indicate that one: mole, of substrate consumes two moles of permanganate, the stoichiometry is thus represented as

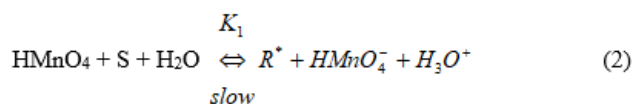


The formic acid and carbon dioxide have been found to be the oxidation products. The identification of carbon dioxide and formic acid was done by the method given in Fiegl^[17]. The formation of formic acid was further confirmed by thin layer, chromatography technique. The spot for test solution and for standard formic acid has the same R_f, value. Similar products have been obtained by Kansal, N. Singh and H. Singh^[18] in case of oxidation of succinic acid by Ce(IV) in acidic medium.

Mechanism

On the basis of experimental results and various findings the following reaction mechanism has been suggested for the first stage. The presence of free radicals as intermediates have been confirmed by the induced reduction of mercuric chloride^[19]. The first step envisaged is the protonation of MnO₄ to HMnO₄. It is followed by the slow second stage in which the substrate, HMnO₄ and water reacts and producing

a free radical and HMnO₄ species. The free radical thus formed will be attacked by HMnO₄ to give products.



Mechanism for autocatalysis

As mentioned earlier that the oxidative decarboxylation of succinic acid by, acid permanganate displays and inflection in the curve, Fig. 1. This is most probably due to the autocatalytic role of Mn(II) ions, since MnO₄⁻ undergoes reduction to the Mn(II) stage indicated by the fact that the final solutions are colourless. The Mn(II) thus formed gets oxidized by permanganate into Mn(III): In order to assess the validity of this view a few experiments were carried out with initially added Mn(II) (Table 3), the reaction rate increases with the increase in the Mn(II) concentration, whereas Mg(II) at comparable concentrations has no noticeable effect (table not given here). These observations suggest that here-in this case of oxidation of succinic acid' by permanganate Mn(II) probably has an autocatalytic role as in the case of oxalic-acid permanganate^[20] and hydrogen Peroxide-permanganate reactions^[21]. Catalysis by Mn(II) ions in the case of oxidation by permanganate is well known²². The addition of Mn(II) accelerate the rate of oxidative decarboxylation of succinic acid and even removes the second stage can be understood in the light of following chemical equation:



Additional experiments are needed though to determine the true nature of the inflection, which may arise due to the involvement of intermediates. These intermediates can lead to cyclic reactions that may result in autocatalysis. The possibility of MnO₂ formation is nil as the acid concentration is high enough and, naturbidity was seen even after keeping reaction solution for longer duration. Further to, ensure the presence and activity of Mn(III) as an intermediate oxidizing species, the effect of addition of flouride ions was tested. A sharp decrease in the reaction rate is observed. Flouride ions are well known to complex with Mn(III). Such complexation causes reduction in concentration of Mn(III)^[23]. However, even the substantial addition of flouride ions do not suppress the reaction Completely indicates unequivocally that Mn(VII) is the main oxidant and not the other intermediate manganese species. For the autocatalysis the first step is the oxidation of Mn(II) to Mn(III) by MnO₄⁻. The Mn(III) thus formed form a complex with the carboxylate anion in the step 2. There will be redox decomposition of this complex in the subsequent steps and giving rise to free radical. These steps are in accordance with the mechanism suggested by N. Ganapathisubramaniam in his studies on oxalate-permanganate autocatalytic reaction^[20, 21].

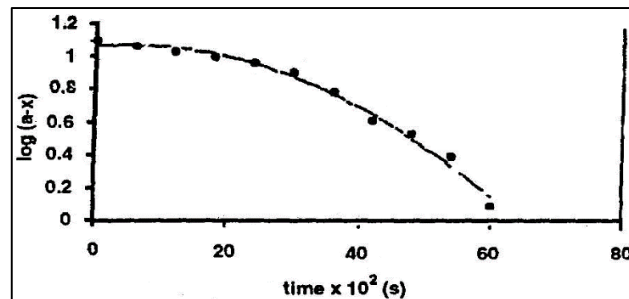
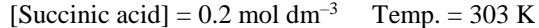
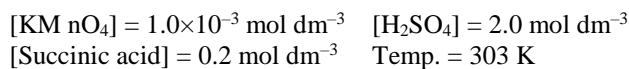
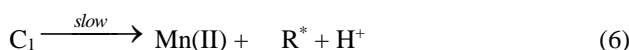
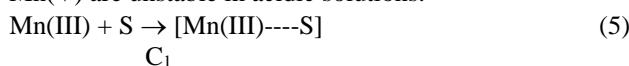


Fig. 1: Log (a-x) versus time in seconds



This free radical will give carbon dioxide and free radical. The other possible Mn intermediates like Mn(VI) and Mn(V) are unstable in acidic solutions.



The free radical Fr formed in the step 6 will be further oxidized as in the equation 3 to give rise the final products.

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