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Research Article

Kinetic Approach to Photochemical Oxidation of Succinic Acid by Chloramine-T in Presence of UV-Light

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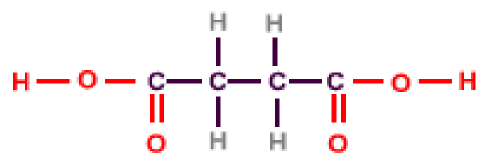
Abstract

The oxidation of succinic acid carried out under ultraviolet light source by using chloramine-T (CAT) as an oxidant. The reaction was done in aqueous acidic medium. The results obtained reveal that reaction follows first order kinetics with respect to oxidant while zero order kinetics is followed with respect to the substrate. H^+ ions were found to catalyse the reaction as an increase in reaction rate was observed with the increase in concentration of acid concentration. The effect of the variation of concentration of the reactants as well as the addition of product (p-toluene sulphonamide) and the effect of variation of intensity of light source on the reaction rate were studied. A suitable mechanism is proposed depending on the experimental findings.

Keywords: Photo-oxidation, Chloramine-T, Succinic acid, Hydrochloric acid.



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Introduction

Succinic acid is a dicarboxylic structure having formula $HOOC-(CH_2)_2COOH$. It was used externally for rheumatic aches and pains. The acid is combustible, corrosive and capable of causing burns. Eye contact may cause serious damage. The sodium salt of N-chloro p-toluene sulphonamide, (known as chloramine-T; p-$CH_3C_6H_4SO_2NClNa.3H_2O$), is widely studied and easy to handle oxidant [1-4]. Literature surveys show that oxidation of succinic acid has been studied using various oxidising agents, viz, chloride ion, chromium (VI), peroxidisulphate, ceric ions [5-8]. But the light induced oxidation of succinic acid by chloramine-T has not got much attention. It was, therefore, thought to be of interest to study the kinetics of the photooxidation of succinic acid by chloramine-T. The present study was carried out for optimisation of the reaction conditions and for finding out the reaction mechanism. The reaction was studied in the presence and absence of light. Better results were obtained in the former case.

Experimental

Materials and Methods

All the reagents used were of Analar grade. The reagent solutions of substrate, oxidant, HCl and p-toluene sulphonamide were prepared in doubly distilled water. Requisite amount of the substrate was mixed with HCl and chlormine-T was added to it. The reaction vessel was then placed under UV light source (Mercury vapour lamp). The progress of the reaction was studied by withdrawing 4 ml of the reaction mixture at a suitable time interval and adding a solution of KI to quench the reaction velocity. The unreacted chloramine-T reacts with KI and liberates I2 that was titrated against standard hypo solution using starch as an indicator. The kinetics of the reaction was studied by carrying out the reaction in the presence of light and by varying the concentration of oxidant (CAT), substrate (succinic acid), HCl, product (p-toluene sulphonamide), KCl and intensity of light source.

Results and Discussion

The kinetics of the photo oxidation of succinic acid by chloramine-T was studied by considering various parameters. In the presence and absence of the light, the reaction rate was found to be greater in the presence of light, which shows that the reaction is catalyzed by light.

Effect of variation of substrate concentration

The reaction rate was not affected much by increasing the substrate concentration (**Table 1**) the reaction shows zero order kinetics with respect to the substrate concentration.

Table 1 Effect of variation of succinic acid concentration

[Succinic Acid]$\times 10^{-3}$ (mol dm^{-3})	Average $k_1 \times 10^{-4}$ (s^{-1})	Graphical $k_1 \times 10^{-4}$(s^{-1})
2.5	1.733	1.653
5.0	1.710	1.741
7.5	1.712	1.649
10.0	1.732	1.798

[CAT] = 1×10^{-2} mol dm^{-3}, [HCl] = 1×10^{-1} mol dm^{-3}, temperature 298 K

Effect of variation of oxidant concentration

From the results given in **Table 2**, it is observed that the rate of the reaction decreases by increasing the concentration of chloramine-T. Since chloramine-T is itself photo reactive, hence as its concentration increases it starts its own reaction forming inactive sodium hypochlorite. Thus, it becomes less available for the oxidation of succinic acid, which results in retardation of the reaction rate (Table 2)

$$HOCl + Na^+ \rightarrow NaOCl + H^+$$

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

Table 2 Effect of variation of CAT concentration

[CAT]$\times 10^{-3}$ (mol dm^{-3})	Average $k_1 \times 10^{-4}$(s^{-1})	Graphical $k_1 \times 10^{-4}$(s^{-1})
2.5	3.21	3.37
3.7	2.56	2.55
5.0	2.31	2.35
6.25	2.04	204
7.50	0.73	0.66

[Succinic Acid] = 12.5×10^{-2} mol dm^{-3}, [HCl] = 1×10^{-3}mol dm^{-3}, temperature 298 K

Effect of variation of p-toluene sulphonamide concentration

The most probable reaction product is p-toluene sulphonamide therefore, probability of its formation during the slowest step has been tested by its addition and it is observed that the addition of p-toluene sulphonamide resulted in the fall of the reaction rate because of the shifting of equilibrium to the left (**Table 3**). The decrease is the result of mass-law effect according to which the addition of product causes the reversal of reaction.

Table 3 Effect of variation of p-toluene sulphonamide concentration

[PTS]×10^{-3} (mol dm^{-3})	**Average $k_1 \times 10^{-4}$(s^{-1})**	**Graphical $k_1 \times 10^{-4}$(s^{-1})**
2.50	2.31	2.35
5.00	2.04	2.10
7.50	1.19	1.20
10.0	1.19	1.19
12.5	0.52	0.51

[CAT] = 1×10^{-2} mol dm^{-3}, [Succinic Acid] = 12.5×10^{-2} mol dm^{-3}, [HCl] = 1×10^{-3}mol dm^{-3}, Temperature 298 K

Effect of variation of HCl concentration

The increase in HCl concentration was found to decrease the rate. It can be explained by the fact that a larger concentration of HCl will convert HOCl into water and Cl2 and hence the rate falls (**Table 4)**.

$$HCl + HOCl \rightarrow H_2O + Cl_2$$

Table 4 Effect HCl concentration variation

[HCl]×10^{-3} (mol dm^{-3})	**Average $k_1 \times 10^{-4}$(s^{-1})**	**Graphical $k_1 \times 10^{-4}$(s^{-1})**
0.2	1.96	1.85
0.4	1.82	1.89
0.6	1.63	1.73
0.8	1.49	1.50
1.0	1.39	1.33

[CAT] = 1×10^{-3}mol dm^{-3}, [Succinic Acid] = 12.5×10^{-2}mol dm^{-3}, Temperature 298 K

Effect of variation of KCl concentration

The value of rate constant decreases by addition of KCl to chloramine -T solution because of shifting of equilibrium to the left in the following equation due to the common ion effect (**Table 5**)

$$ArSO_2NClNa + HCl \rightarrow ArSO_2NHCl + NaCl$$

Effect of light intensity

An increase in light intensity increases the reaction rate because as the light increases, the photon flux increases, therefore a greater number of substrate molecules are excited per unit time. Hence, the reaction rate increases(**Table 6**).

Kinetics and activation parameters

The values of enthalpy of activation ,entropy of activation and free energy of activation give an idea about the progress of reaction (**Table 7**) It has been observed that if (Δ H*) is positive, (Δ S*)is negative and (Δ G*)is positive then the reaction is non spontaneous [9].

Table 5 Effect of variation of KCl concentration

$[KCl]\times10^{-3}$ (mol dm^{-3})	Average $k_1\times10^{-4}(s^{-1})$	Graphical $k_1\times10^{-4}(s^{-1})$
2.5	3.53	3.53
5.0	2.44	2.48
7.5	1.99	2.04
10.0	1.38	1.43

[CAT] = 1×10^{-2} mol dm^{-3}, [Succinic Acid] = 12.5×10^{-2} mol dm^{-3}, [HCl] = 1×10^{-3}mol dm^{-3}, Temperature 298 K

Table 6 Effect of intensity variation

Intensity of UV radiation (Watt)	Average $k_1\times10^{-5}(s^{-1})$	Graphical $k_1\times10^{-5}(s^{-1})$
40	0.81	0.76
60	1.15	1.02
80	1.81	1.79
100	2.17	2.04
120	2.60	2.55

[CAT] = 1×10^{-2} mol dm^{-3}, [Succinic Acid] = 12.5×10^{-2} mol dm^{-3}, [HCl] = 1×10^{-3}mol dm^{-3}, Temperature 298 K

Table 7 Kinetics & Activation Parameters

Activation parameters	Calculated values	Graphical values
Energy of Activation (ΔE_a)	47.54 KJ mol^{-1}	46.38 KJ mol^{-1}
Frequency factor (log PZ)	8.314	8.113
Entropy of activation (Δ S*)	-89.72 KJ mol^{-1}	-93.57 KJ mol^{-1}
Enthalpy of activation (Δ H*)	44.89 KJ mol^{-1}	43.74 KJ mol^{-1}
Free energy of activation (ΔG*)	73.42 KJ mol^{-1}	73.49 KJ mol^{-1}

Analysis of reaction products

The products of the reaction were analysed qualitatively by standard tests [10]. Carbon di-oxide has been detected by usual lime water test and a method suggested by Feigl [11]. The carboxylic acid group has been detected by the sodium bicarbonate test.

The formation of Formic acid has been confirmed by following tests:

1. The sample solution decolourises acidic potassium permanganate solution.
2. The solution develops red color with ferric chloride.
3. On warming with conc. H_2SO_4, it evolves carbon di-oxide which burns with blue flame.

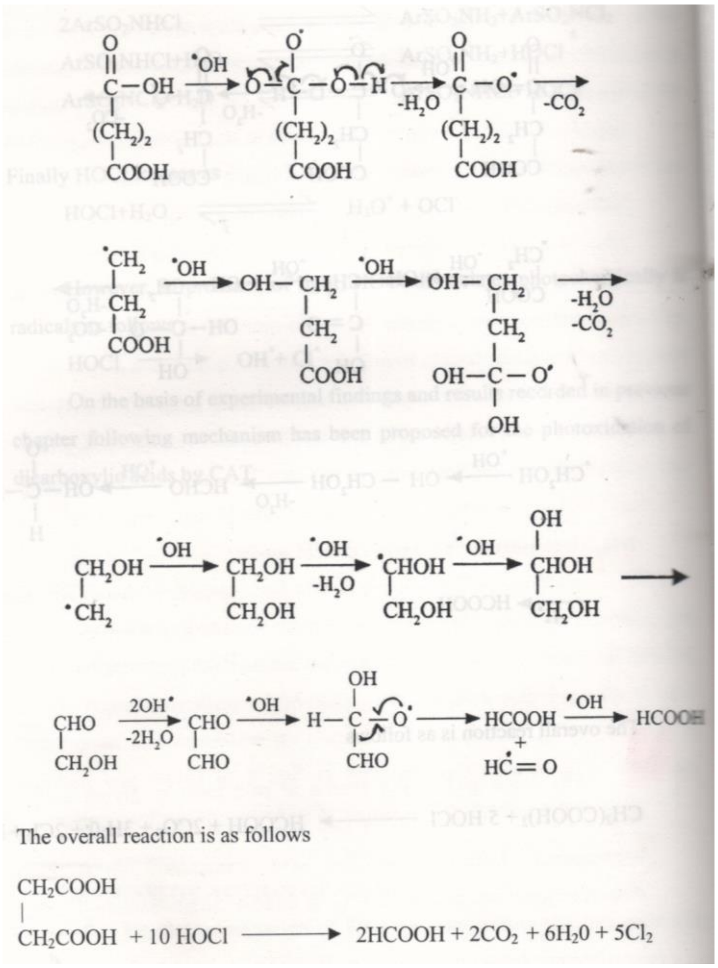
Finally the products are confirmed by co-TLC with authentic sample [12].

Reaction Mechanism

The mechanism of reaction of chloramines-T in acidic medium is already reported in literature [13-17]. On acid hydrolysis, it gives hypochlorous acid (HOCl), which behaves as the main oxidizing species. In presence of light, HOCl dissociates into free radicals as,

$$HOCl \rightarrow OH + Cl$$

The stepwise reaction mechanism for photochemical oxidation of succinic acid by chloramines-T under UV-light can be represented as follows:



Conclusion

1. The reaction rate for the photooxidation of succinic acid by CAT is found to be increased in the presence of UV- light.
2. The order of reaction with respect to oxidant is one.
3. The reaction shows zero order kinetics with respect to substrate.
4. The reaction is catalyzed by acid.
5. The reaction is non spontaneous as is indicated by the values of Δ H*, Δ S* and Δ G*.

The products of photochemical oxidation of succinic acid by CAT are found to be formic acid, CO_2 and Cl_2.

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