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# Ultraviolet Light Induced Oxidation of Malonic Acid by Chloramine-T in an Aqueous Acidic Medium: A Kinetic Study

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***ABSTRACT***

*The kinetics of the photo-oxidation of malonic acid by chloramine-T in an aqueous medium has been studied. It is found that reaction obeys first order kinetics with respect to each of the substrate as well as oxidant. The reaction is found to be catalyzed by $H^+$ ions. Different parameters such as the effect of the variation of concentration of the reactants, product, and intensity of light on the reaction rate have been studied. A suitable mechanism has been proposed depending on the experimental findings.*

***Key words:*** *Photo-oxidation, Chloramine-T, Malonic acid, Hydrochloric acid.*

## 1. INTRODUCTION

Malonic acid is a dicarboxylic structure having formula $CH_2(COOH)_2$. It is frequently used as an enolate in Knoevenagel condensations. The sodium salt of N-chloro p-toluene sulfonamide, (known as chloramine-T [CAT]; p-$CH_3C_6H_4SO_2NClNa.3H_2O$), is widely studied and easy to handle oxidant [1-4].

Kinetics and mechanism of oxidation of malonic acid by chromium (VI) in aqueous perchlorate medium was studied by Rao *et al*. [5]. The oxidation of malonic acid by ceric ions has been investigated by Barkin *et al*. [6]. Kinetic study of the oxidation of malonic acid by the manganese (III) ions was reported by Treindl and Mrákavová [7]. In this way, the literature survey shows that oxidation of malonic acid has been studied using various oxidizing agents, e.g., chloride ion, chromium (VI), peroxidisulfate, and ceric ions [8-11]. However, the light induced oxidation of malonic acid by CAT has not get much attention. It was, therefore, thought to be of interest to study the kinetics of the photo-oxidation of malonic acid by CAT. The present study was carried out for optimization 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.

## 2. EXPERIMENTAL

All the reagents used were of Analar grade. The requisite amount of the substrate was dissolved in 15 ml water to prepare N/2 solution, 0.1 N HCl (5 ml), and N/50 chlormine-T (20 ml) were added to it and the reaction vessel was then placed in front of the light source (200 W tungsten 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 CAT reacts with KI and liberates $I_2$ 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 (malonic acid), HCl, product (p-toluene sulfonamide [PTS]), KCl, and light intensity.

## 3. RESULTS AND DISCUSSION

The kinetics of the photo-oxidation of malonic acid by CAT was studied by carrying out the reaction under the following conditions.

In the presence and absence of the light source, the reaction rate was found to be greater in the presence of light, which shows that the reaction is catalyzed by light.

### *3.1. Effect of Variation of Substrate Concentration*

The reaction rate was not affected at all by increasing the substrate concentration (Table 1).

### *3.2. 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

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the concentration of CAT. Since CAT 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 malonic acid, which results in retardation of the reaction rate (Table 2).

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

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

### *3.3. Effect of Variation of Product Concentration*

The addition of product (PTS) resulted in the fall of the reaction rate because of the shifting of equilibrium to the left (Table 3).

### *3.4. Effect of Variation of HCl Concentration*

The effect of HCl concentration was found to decrease the rate. It can be explained by the fact that a larger concentration of HCl converts malonate ions into malonic acid, which is difficult to ionize, hence rate falls (Table 4).

### *3.5. Effect of Variation of KCl Concentration*

The value of rate constant decreases by addition of KCl to CAT solution because of shifting of equilibrium to the left (Table 5).

### *3.6. 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).

**Table 1:** Effect of variation of malonic acid concentration.

| $[CH_2(COOH)_2]\times10^{-3}$ (mol $dm^{-3}$) | Average $k_1\times10^{-4}$ ($s^{-1}$) | Graphical $k_1\times10^{-4}$ ($s^{-1}$) |
|---|---|---|
| 2.5 | 4.036 | 3.96 |
| 5.0 | 4.176 | 3.94 |
| 7.5 | 4.174 | 4.39 |
| 10.0 | 4.207 | 4.22 |

**Table 2:** Effect of variation of CAT concentration.

| $CAT\times10^{-3}$ (mol $dm^{-3}$) | Average $k_1\times10^{-4}$ ($s^{-1}$) | Graphical $k_1\times10^{-4}$ ($s^{-1}$) |
|---|---|---|
| 2.5 | 2.122 | 2.125 |
| 3.7 | 2.043 | 2.047 |
| 5.0 | 1.688 | 1.679 |
| 6.25 | 1.577 | 1.596 |
| 7.50 | 1.392 | 1.394 |

$[CH_2(COOH)_2]=12.5\times10^{-2}$ mol $dm^{-3}$, [HCl]= $1\times10^{-3}$ mol $dm^{-3}$, temperature 295 K. CAT=Chloramine-T

**Table 3:** Effect of variation of PTS concentration.

| $[PTS]\times10^{-3}$ (mol $dm^{-3}$) | Average $k_1\times10^{-4}$ ($s^{-1}$) | Graphical $k_1\times10^{-4}$ ($s^{-1}$) |
|---|---|---|
| 2.50 | 5.385 | 5.380 |
| 5.00 | 4.864 | 4.864 |
| 7.50 | 3.211 | 3.200 |
| 10.0 | 2.409 | 2.379 |
| 12.5 | 2.149 | 2.119 |

[CAT]= $1\times10^{-2}$ mol $dm^{-3}$, $[CH_2(COOH)_2]=$ $12.5\times10^{-2}$ mol $dm^{-3}$, [HCl]= $1\times10^{-3}$ mol $dm^{-3}$, temperature 296 K. PTS=P-toluene sulfonamide

**Table 4:** Effect HCl concentration variation.

| $[HCl]\times10^{-3}$ (mol $dm^{-3}$) | Average $k_1\times10^{-4}$ ($s^{-1}$) | Graphical $k_1\times10^{-4}$ ($s^{-1}$) |
|---|---|---|
| 0.2 | 1.30 | 1.27 |
| 0.4 | 1.22 | 1.27 |
| 0.6 | 1.19 | 1.27 |
| 0.8 | 0.98 | 0.95 |
| 1.0 | 0.89 | 0.93 |

[CAT]= $1\times10^{-3}$ mol $dm^{-3}$, $[CH_2(COOH)_2]=$ $12.5\times10^{-2}$ mol $dm^{-3}$, temperature 296 K

**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 | 2.68 | 2.68 |
| 5.0 | 2.48 | 2.55 |
| 10.0 | 1.94 | 1.91 |
| 15.0 | 1.93 | 1.91 |
| 20.0 | 1.77 | 1.79 |
| 25.0 | 1.37 | 1.22 |

[CAT]= $1\times10^{-2}$ mol $dm^{-3}$, $[CH_2(COOH)_2]=$ $12.5\times10^{-2}$ mol $dm^{-3}$, [HCl]= $1\times10^{-3}$ mol $dm^{-3}$, temperature 296 K

**Table 6:** Effect of intensity variation.

| Intensity of UV radiation (W) | Average $k_1\times10^{-5}$ ($s^{-1}$) | Graphical $k_1\times10^{-5}$ ($s^{-1}$) |
|---|---|---|
| 40 | 1.319 | 1.310 |
| 60 | 1.820 | 1.838 |
| 80 | 2.205 | 2.199 |
| 100 | 2.688 | 2.689 |
| 120 | 3.003 | 3.169 |

[CAT]= $1\times10^{-2}$ mol $dm^{-3}$, $[CH_2(COOH)_2]=$ $12.5\times10^{-2}$ mol $dm^{-3}$, [HCl]= $1\times10^{-3}$ mol $dm^{-3}$, temperature 292 K. UV=Ultrviolet

### *3.7. 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 ΔH* is positive, ΔS* is negative, and ΔG* is positive then the reaction is non-spontaneous [12].

### *3.8. Analysis of Reaction Products*

The products of the reaction were analyzed qualitatively by various tests [13]. For this, a known volume of the substrate was taken in a conical flask with an excess of CAT, keeping other factors constant. The reaction solution was kept in ultraviolet light for 30 min, and the unreacted CAT was estimated iodometrically.

Carbon di-oxide has been detected by usual lime water test and a method suggested by Feigl [14]. The carboxylic acid group has been detected by the sodium bicarbonate test as well as by iodate-iodide test; a little amount of reaction mixture is mixed with 5-6 drops of $KIO_3$. The test tube is closed at the mouth tightly and placed in boiling water for 1-2 min. After cooling, 8-10 drops of starch solution is added. The appearance of blue confirms the presence of a carboxylic group.

The formation of formic acid as another reaction product has been confirmed by following tests:

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

Finally, the products were confirmed by paper chromatography [15] using a solvent system of methanol:water:HCl in the ratio of 9:1:1. The spray of $H_2SO_4$ was used as a locating reagent, and the spots of the reported products have been identified using authentic samples as references.

### *3.9. Reaction Mechanism*

The mechanism of the reaction of CAT in acidic medium, as already reported in literature [16-20], is as follows:

**Table 7:** Activation parameters.

| Activation parameters | Calculated values | Graphical values |
|---|---|---|
| Energy of activation ($\Delta E_a$) | 47.54 KJ $mol^{-1}$ | 46.38 KJ $mol^{-1}$ |
| Frequency factor (log PZ) | 8.314 | 8.113 |
| Entropy of activation (ΔS*) | −89.72 KJ $mol^{-1}$ | −93.57 KJ $mol^{-1}$ |
| Enthalpy of activation (ΔH*) | 44.89 KJ $mol^{-1}$ | 43.74 KJ $mol^{-1}$ |
| Free energy of activation (ΔG*) | 73.42 KJ $mol^{-1}$ | 73.49 KJ $mol^{-1}$ |

The oxidant CAT is a strong electrolyte in an aqueous solution which dissociates into the solution.

$$ArSO_2NClNa \rightleftharpoons ArSO_2NCl^- + Na^+ \quad \text{(fast)}$$

The anion of CAT in acidic medium undergoes protonation to give free acid, $ArSO_2NHCl$ (mono CAT).

$$ArSO_2NCl^- + H^- \rightleftharpoons ArSO_2NHCl$$

The free acid undergoes disproportionation, giving rise to PTS ($ArSO_2NH_2$) and dichloramine-T ($ArSO_2NCl_2$).

$$2ArSO_2NHCl \rightleftharpoons ArSO_2NH_2 + ArSO_2 + NCl_2$$

The dichloramine-T and the free acid on hydrolysis give hypochlorous acid (HOCl).

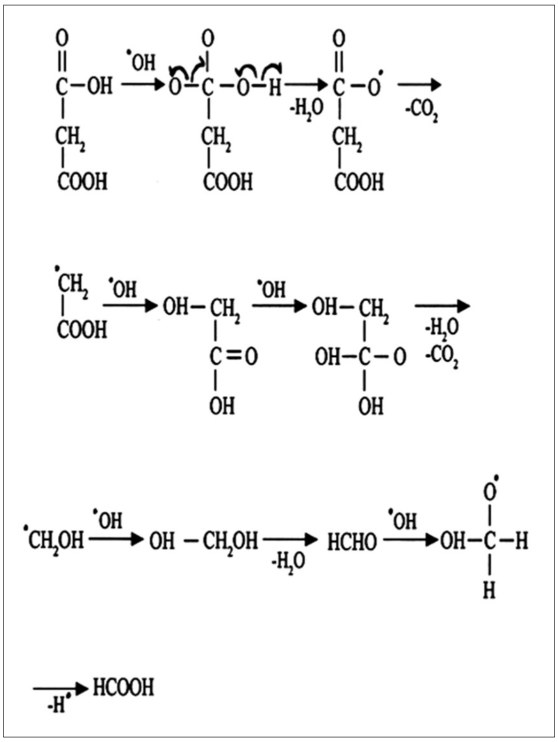
$$ArSO_2NCl_2 + H_2O \rightleftharpoons ArSO_2NHCl + HOCl$$

$$ArSO_2NHCl + H_2O \rightleftharpoons ArSO_2NH_2 + HOCl$$

Finally, HOCI dissociates as:

$$HOCl \rightleftharpoons {}^{\cdot}OH + {}^{\cdot}Cl$$

On the basis of experimental findings and results following mechanism (Scheme 1) has been proposed for the photo-oxidation of malonic acid by CAT.



**Scheme 1:** Reaction mechanism of the p hemical oxidation of malonic acid by chloramine-T under ultraviolet light source.

## 4. CONCLUSION

The reaction rate and reaction mechanism for the photo-oxidation of malonic acid by CAT are described. The reaction was found to be greater in the presence of light source. The order of reaction with respect to oxidant (CAT) is one.

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***Bibliographical Sketch**

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