

UV Light Induced Oxidation of Dicarboxylic acids: A Kinetic Approach

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Abstract- The kinetics of the photo-oxidation of dicarboxylic acids by chloramine-T (CAT) in an aqueous medium has been studied. The acids selected for the study are glutaric acid and adipic acid. It is found that reaction obeys first order kinetics with respect to the oxidant (CAT). The reaction shows zero order dependence with respect to substrates. The reaction is found to be catalysed by H⁺ ions. Different parameters like 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: Dicarboxylic acids, Photo-oxidation, Chloramine-T, Hydrochloric acid.

Introduction

Glutaric acid and adipic acid are the important dicarboxylic acids from the industrial perspective. Glutaric acid (HOOC (CH₂)₃COOH) is used in the production of polymers. It is useful in decreasing the polymer elasticity due to its odd number of carbon atoms. Adipic acid (HOOC (CH₂)₄COOH) is used as a monomer for production of nylon by polycondensation reaction as well as for production of polyurethane. The sodium salt of N-chloro p-toluene sulphonamide, (known as chloramine-T; p-CH₃C₆H₄SO₂NCINa.3H₂O), is widely studied and easy to handle oxidant¹⁻⁴.

The interesting feature of dicarboxylic acids to give up protons is well justified by the fact that the inductive effect of one carboxyl group is expected to enhance the acidity of the other. Literature surveys show that oxidation of dicarboxylic acids has been studied using various oxidising agents, e.g. pyridinium chlorochromate, chromium (VI), peroxodisulphate, ceric ions⁵⁻⁸. But the light induced oxidation of by chloramine-T has not got much attention. It was, therefore, thought to be of interest to study the kinetics of the photooxidation of dicarboxylic acid by chloramine-T. 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. Hans and Elzbieta Brand⁹ examined the huge impact of photochemistry and concluded that the photochemical reactions are the major source of free radicals.

Experimental

All the reagents used were of Analar grade. Requisite amount of the substrate was dissolved in water to prepare N/2 solution, 0.1N HCl (5ml) and N/50 chloramine-T (20ml) were added to it and the reaction vessel was then placed in front of the UV light source (200 W tungsten lamp).

The progress of the reaction was studied by withdrawing aliquots 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, HCl, product (p-toluene sulphonamide), KCl and light intensity,

Results and Discussion

The dependence of reaction rate of photochemical oxidation of selected dicarboxylic acids on the concentration of different reactants was determined by calculating the order with respect to each reactant separately. 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 catalysed by light.

The kinetics of the photo oxidation of dicarboxylic acids by chloramine-T was studied by carrying out reaction under the following conditions.

1. Effect of variation of substrate concentration

The reaction rate was not affected at all by increasing the substrate concentration (Table 1.1 & 1.2). Therefore the order with respect to substrate is zero.

Table 1.1 Effect of variation of Glutaric acid concentration

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

$[(\text{CH}_2)_3(\text{COOH})_2] \times 10^{-3}$ (mol dm ⁻³)	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
2.5	2.907	2.917
5.0	3.143	2.942
7.5	3.180	3.098
10.0	3.238	3.225

Table 1.2 Effect of variation of Adipic acid concentration

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

$[(\text{CH}_2)_4(\text{COOH})_2] \times 10^{-3}$ (mol dm ⁻³)	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
2.5	2.205	2.281
5.0	2.395	2.391
7.5	2.488	2.389
10.0	2.600	2.680

2. Effect of variation of oxidant concentration

From the results given in Table, 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 purpose, which results in retardation of the reaction rate (Table 2.1 & 2.2)

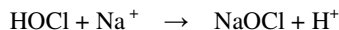


Table 2.1. Effect of variation of CAT concentration

$[(\text{CH}_2)_3(\text{COOH})_2] = 12.5 \times 10^{-2}$ mol dm⁻³, [HCl] = 1×10^{-3} mol dm⁻³, Temperature= 298 K

[CAT] $\times 10^{-3}$ (mol dm ⁻³)	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
2.5	2.272	2.047

3.7	2.073	2.047
5.0	1.275	1.279
6.25	1.206	1.279
7.50	1.148	1.128
10.0	0.979	0.995

Table 2.2 Effect of variation of CAT concentration

$[(\text{CH}_2)_4(\text{COOH})_2] = 12.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HCl}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, temperature 298 K

$[\text{CAT}] \times 10^{-3}$ (mol dm^{-3})	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
2.5	2.122	2.125
3.7	2.093	2.089
5.0	2.043	2.047
6.25	1.688	1.679
7.50	1.577	1.596
10.0	1.392	1.394

3. Effect of variation of HCl concentration

The increase of HCl concentration was found to decrease the reaction rate. (Table 3.1 & 3.2)

Table 3.1 Effect HCl concentration variation

$[\text{CAT}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[(\text{CH}_2)_3(\text{COOH})_2] = 12.5 \times 10^{-2} \text{ mol dm}^{-3}$, temperature 296 K

$[\text{HCl}] \times 10^{-3}$ (mol dm^{-3})	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
0.2	4.668	4.599
0.4	4.223	4.423
0.6	3.710	3.590
0.8	3.116	3.313
1.0	2.525	2.503

Table 3.2 Effect HCl concentration variation

$[\text{CAT}] = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $[(\text{CH}_2)_4(\text{COOH})_2] = 12.5 \times 10^{-2} \text{ mol dm}^{-3}$, temperature 296 K

$[\text{HCl}] \times 10^{-3}$ (mol dm^{-3})	Average $k_1 \times 10^{-4} (\text{s}^{-1})$	Graphical $k_1 \times 10^{-4} (\text{s}^{-1})$
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0.2	5.395	5.345
0.4	4.293	4.294
0.6	3.709	3.710
0.8	3.212	3.310
1.0	2.688	2.559

4. Effect of variation of product concentration

The most probable reaction product is p-toluene sulphonamide, therefore, probability of its formation during the slow step has been tested by its addition. It was observed that the addition of product (p-toluene sulphonamide) resulted in the fall of the reaction rate because of the shifting of equilibrium to the left (Table 4.1 & 4.2). The decrease is the result of Mass-law effect according to which the addition of product causes the reversal of reaction.

Table 4.1. Effect of variation of p-toluene sulphonamide concentration

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₃(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

[PTS]×10 ⁻³ (mol dm ⁻³)	Average k ₁ ×10 ⁻⁴ (s ⁻¹)	Graphical k ₁ ×10 ⁻⁴ (s ⁻¹)
2.50	1.606	1.600
5.00	1.557	1.543
7.50	1.443	1.484
10.0	1.283	1.289
12.5	1.131	1.133

Table 4.2 Effect of variation of p-toluene sulphonamide concentration

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₄(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

[PTS]×10 ⁻³ (mol dm ⁻³)	Average k ₁ ×10 ⁻⁴ (s ⁻¹)	Graphical k ₁ ×10 ⁻⁴ (s ⁻¹)
2.50	1.962	1.859
5.00	1.823	1.893
7.50	1.637	1.731
10.0	1.497	1.500
12.5	1.396	1.337

5. 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 (Table 5.1 & 5.2)

Table 5.1 Effect of variation of KCl concentration

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₃(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

[KCl]×10 ⁻³ (mol dm ⁻³)	Average k ₁ ×10 ⁻⁴ (s ⁻¹)	Graphical k ₁ ×10 ⁻⁴ (s ⁻¹)
2.5	1.24	1.32
5.0	1.25	1.24
10.0	1.27	1.25
15.0	1.31	1.26

Table 5.2 Effect of variation of KCl concentration

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₄(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

[KCl]×10 ⁻³ (mol dm ⁻³)	Average k ₁ ×10 ⁻⁴ (s ⁻¹)	Graphical k ₁ ×10 ⁻⁴ (s ⁻¹)
2.5	1.643	1.628
5.0	1.623	1.598
10.0	1.605	1.580
15.0	1.598	1.499

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 6.1 & 6.2)

Table 6.1 Effect of intensity variation

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₃(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

Intensity of UV radiation (Watt)	Average k ₁ ×10 ⁻⁵ (s ⁻¹)	Graphical k ₁ ×10 ⁻⁵ (s ⁻¹)
40	1.815	1.821
60	2.099	2.074
80	2.342	2.334
100	2.670	2.678
120	2.904	2.923

Table 6.2 Effect of intensity variation

[CAT]= 1×10^{-2} mol dm⁻³, [(CH₂)₄(COOH)₂]= 12.5×10^{-2} mol dm⁻³, [HCl]= 1×10^{-3} mol dm⁻³, Temperature=298 K

Intensity of UV radiation (Watt)	Average $k_1 \times 10^{-5} (s^{-1})$	Graphical $k_1 \times 10^{-5} (s^{-1})$
40	2.220	2.220
60	3.212	2.230
80	3.708	3.711
100	4.309	4.299
120	5.714	5.720

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.⁹

Table 7 Kinetic & Activation Parameters

Activation parameters	Glutaric Acid	Adipic Acid
Energy of Activation (ΔE_a) KJ mol⁻¹	24.06	37.71
Frequency factor (log PZ)	4.52	6.193
Entropy of activation (ΔS^*) KJ mol⁻¹	-162.34	-130.33
Enthalpy of activation (ΔH^*) KJ mol⁻¹	21.41	35.06
Free energy of activation (ΔG^*) KJ mol⁻¹	73.04	76.51

Analysis of reaction products

The dicarboxylic acids Glutaric and Adipic acids when subjected to photo oxidation by chloramine-T in presence of UV light gave CO₂ and formic acid as the reaction products. The products of reaction were analysed qualitatively by various tests.¹⁰

Carbon di-oxide has been detected by usual lime water test and a method suggested by Feigl¹¹. 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 KIO₃. The test tube is closed at the mouth tightly and placed in boiling water for 1-2 minutes. After cooling, 8-10 drops of starch solution is added. The appearance of blue color confirms the presence of a carboxylic group.

The formation of Formic acid as the reaction product 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. H₂SO₄, it evolves carbon di-oxide which burns with blue flame.

Finally the products were confirmed by paper chromatography¹² using a solvent system of methanol: water: HCl in the ratio of 9:1:1. The spray of H₂SO₄ was used as a locating reagent and the spots of the reported products have been identified using authentic samples as references.

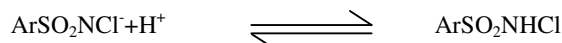
Reaction Mechanism

The mechanism of the reaction of CAT is as follows¹³⁻¹⁵.

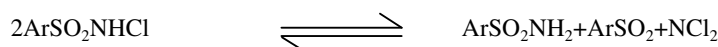
The oxidant chloramine-T is a strong electrolyte in aqueous solution which dissociates into the solution.



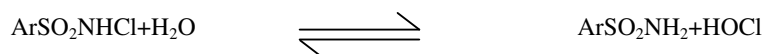
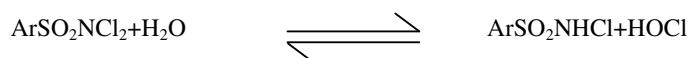
The anion of chloramine-T in acidic medium undergoes protonation to give free acid, ArSO₂NHCl (mono chloramine-T)



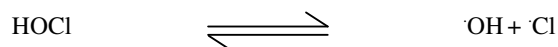
The free acid undergoes disproportionation, giving rise to p-toluene sulphonamide (ArSO₂NH₂) and dichloramine-T (ArSO₂NCl₂)



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



Finally HOCl dissociates as :



On the basis of experimental findings and results the overall reaction for the photo-oxidation of dicarboxylic acids by CAT is given as follows:



Conclusion:

The reaction rate and reaction mechanism for the photooxidation of dicarboxylic acids by CAT is described. The reaction rate was found to be higher in the presence of light source. The order of reaction with respect to oxidant (CAT) is one. The order with respect to substrate is zero. The reaction is found to be catalysed by H⁺ ions. The reaction rate increase with increase in the intensity of light radiation as the number of photons striking per unit area increase by increasing the intensity. Due to photochemical conditions, the reaction follows radical mechanism which has further been confirmed by using quenchers.

References

- [1]. Kitagawa H and Mukaiyama T (2002) Chemical and Pharmaceutical Bulletin **50** (9) 127.
- [2]. Prashanth PA, Mantelingu K, Anandamurthy AS, Anitha N, Rangaswamy and Rangappa KS (2001) J. Ind. Chem. Soc. **78** 241-245.
- [3]. Viroopakshappa J and Jagannadh V. (2004) Indian Journal of Chemistry-B **43** 374-377.
- [4]. Mythily CK, Rangappa KS and Made Gowda NM (1991) International Journal of Chemical Kinetics **23**(2) 127-136.
- [5]. Rao I, Mishra SK and Sharma PD (1992) Transition Metal Chemistry **17**(5) 449-454.
- [6]. Rangappa KS, Raghavendra MP, Mahadevappa DS and Gowda DC (1998) Carbohydrate research **306** 57-67.
- [7]. Vasudeva WC and Wasif S (1972) Journal of Inorganic and Nuclear Chemistry **34** 3153-3157.
- [8]. Barkin S, Bixon M, Noyes R. M. (1978) International Journal of Chemical Kinetics **10** 619-636.
- [9]. Brand Hans and Brand Elzbieta (2002) Goliath Buissness Knowledge on Demand.
- [10]. Gillion RD (1970) Introduction to Physical Organic Chemistry, Addison wesby, London.
- [11]. Agarwal OP (1996) Advanced Practical Organic Chemistry, Krishna prakashan, Meerut.
- [12]. Feigl F (1956) Spot test in Organic Analysis Elsevier Publishing Co. Amsterdam p. 331.
- [13]. Stock R and Rice CBF (1963) Chromatographic Methods, Chapman & Hall Ltd.
- [14]. Rangappa KS (2004) J. Ind. Chem. Soc. **81** 1025-1037.
- [15]. Mahadevappa DS and Naidu HMK (1974) Australian Journal of Chemistry **27**(6) 1203-1207.