

Oxidative Conversion of Lactic Acid by Chloramine-T in Sulfuric Acid Medium: a Kinetic and Mechanistic Study

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Abstract Lactic acid or LA ($C_3H_6O_3$) plays a major role in several biomedical processes and in organic syntheses. The stoichiometry of the LA-chloramine-T (CAT) reaction in sulfuric acid medium shows that two moles of CAT are consumed per mole of LA with carbon dioxide, acetic acid, and *p*-toluenesulfonamide (PTS) as main products. The oxidation of LA by CAT in acid solutions has been spectrophotometrically monitored at $\lambda_{max} = 255$ nm at 323 K. The reaction, studied under pseudo-first order conditions of $[LA]_0 \gg [CAT]_0$, follows a first-order dependence of the rate on $[CAT]$ and a fractional order on $[LA]$. Variations of the $[PTS]$, $[H^+]$, $[SO_4^{2-}]$, dielectric constant, and ionic strength of the reaction medium have no effect on the rate. Kinetic and activation parameters are evaluated based on the temperature effect on the rate. A mechanism consistent with the observed kinetics and activation data has been proposed leading to the derived rate law.

Keywords Lactic Acid, Chloramine-T, Oxidation, Reduction, Spectrophotometry, Stoichiometry, Mechanism, Rate Law, P-Toulenesulfonamide, Kinetics

1. Introduction

Lactic acid (LA) is a naturally occurring organic acid, which is a monomer of polylactic acid. The focus of the US market is on the production of lactic acid, due to its variety of applications such as in food processing[2], biomedical products[3], and textiles[4]. It also finds applications in the manufacture of bio-plastics, fibers, solvents, and oxygenated chemicals[1,5-7]. Furthermore, polymeric lactic acid ester, polylactide (PLA), has a number of biomedical applications in products such as sutures, stents, dialysis media and drug delivery devices[8].

Aromatic sulfonylhaloamines such as chloramine-T (CAT), chloramines-B (CAB), and bromamine-T (BAT) contain a polar N-halo bond, which is capable of forming a halonium (X^+) ion in solutions. This electrophilic species can function as an oxidizing and halogenating agent in solutions. Inorganic chloramines are the byproducts formed in drinking water due to chlorination[9]. Chloramines can be used as bleaching agents, disinfectants and oxidants. During the water disinfection, chloramines can improve the odor and flavor of water[10] by oxidizing the environmental sulfur and other contaminations[11]. Aromatic sulfonylhaloamines are widely used in chemistry[12-14] to study the oxidation reaction mechanisms for a variety of substrates. Other ox-

dants such as water-soluble (colloidal) manganese dioxide have been previously used to study the oxidation of lactic acid[15]. A literature search showed no reports on the mechanism of oxidation of LA by CAT in acid solutions. Hence, it was decided to spectrophotometrically investigate the kinetics and mechanism of oxidation of LA by CAT in sulfuric acid solutions.

2. Experimental

Lactic acid from Acros Co, USA was used as supplied (99.9% purity) to prepare the standard aqueous solutions and stored at 4°C until further use. Chloramine-T (Aldrich Chemical Co., USA), sodium thiosulfate (Spectrum Chemicals, USA), potassium iodide and iodate (both MCB reagents) were used. All chemicals were of accepted analytical grades of purity. Double distilled water was used in all solutions for the experiments.

Kinetic Measurements

Kinetic runs were performed under pseudo-first order conditions with a large excess of the substrate, LA, over the oxidant, CAT, at 50°C. For each run, requisite amounts of solutions of LA and sulfuric acid were mixed in a 50.0 mL volumetric flask. To this solution mixture, a measured amount of a standard concentrated CAT solution was added to give a desired overall concentration. Enough water was added to the flask to make-up the final volume to 50.0 mL. The reaction mixture was stirred for uniform concentrations and thermostatted in a water bath at 50°C for 10 min to allow

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thermal equilibration. Photocell (1.0 cm path-length) containing the above reaction mixture was placed in the thermostatted (50°C) chamber of the Shimadzu UV-Vis spectrophotometer (model 1601) connected to a computer and the course of reaction was monitored by measuring its absorbance at $\lambda_{\text{max}} = 255 \text{ nm}$ at varying time intervals. The pseudo-first-order rate constant, k' or k_{obs} , was obtained from the slope of the linear plot of $\ln(\text{absorbance})$ vs. time. Each run was performed in duplicate and the average of the two values was considered.

Reaction Stoichiometry

Reaction mixtures containing $[\text{CAT}]_0 \gg [\text{LA}]_0$ in 0.05 M H_2SO_4 were kept at 50°C with stirring for varying time intervals ranging from 1h to 48 h. At the end of each time period, the unreacted CAT remaining in the reaction mixture was titrated iodometrically against a standardized thiosulfate solution using 1% starch solution as an indicator near the endpoint. It showed that two moles of CAT were consumed per mole of LA resulting in the formation of acetic acid, carbon dioxide, sodium chloride, and *p*-toluenesulfonamide (PTS) as products.

Product Analysis

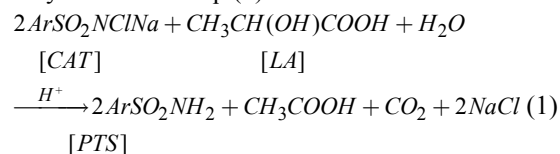
A reaction mixture with $[\text{CAT}]_0 \gg [\text{LA}]_0$ was stirred for 48 hrs at 50°C for product analysis. The pH of the reaction mixture was raised to 8-9 by the addition of 1.00 M NaOH solution before liquid-liquid extractions. These were performed thrice using dichloromethane-petroleum ether mixture (1:1 v/v). The organic layer was rotary evaporated to obtain PTS as a dry residue while the aqueous layer retained polar products, acetic acid, NaCl and unreacted CAT. The reduction product, PTS, was further recrystallized in diethyl ether and identified using a gas-chromatography mass spectrometer (GC/MS). The CAT reduction product, PTS, was analyzed on a Shimadzu GC/MS (model # 5050) under the following conditions: temp. = 80° – 250°C and pressure = 72 kPa. The mass spectrum showed a parent M^+ ion peak at 171 amu confirming PTS. The aqueous fraction consisting of acetic acid, NaCl and unreacted CAT was extracted with ethyl acetate (1:1 v/v) thrice. $^1\text{H-NMR}$ data revealed the identity of the main oxidation product, acetic acid. Another oxidation product, CO_2 , was detected by its conventional lime water test. The presence of chloride was detected by its AgNO_3 reaction precipitating AgCl in solution.

Test for free radicals

Under the inert atmosphere of nitrogen, a freshly prepared 10% solution of acrylamide or acrylonitrile monomer was added to the LA-CAT reaction mixtures in 0.05 M H_2SO_4 in flasks, which were kept overnight in dark to prevent photochemical effects. Suitable controls without LA, CAT, and the LA-CAT mixture were used under similar conditions for comparison. The reaction mixture was monitored for the *in situ* formation of free radicals. A lack of turbidity due to non-polymerization of the monomer indicated the absence of free radicals.

3. Results and Discussion

Reaction Stoichiometry. Preliminary results showed that two moles of CAT were consumed per mole of LA resulting in the formation of acetic acid and PTS as the main oxidation and reduction products, respectively. The 2:1 reaction stoichiometry is shown in eq. (1) below.



Kinetics

Effect of CAT on the reaction rate. Under the pseudo first-order conditions, $[\text{LA}]_0 \gg [\text{CAT}]_0$, at constant $[\text{H}_2\text{SO}_4]$ and temperature, the $[\text{CAT}]_0$ was varied from 0.2 – 2.0 mM. Plots of $\ln(\text{abs.})$ vs. time were linear indicating a first-order dependence of the rate on $[\text{CAT}]$ (Fig. 1). Pseudo-first-order rate constants (k') calculated from the slopes of $\ln(\text{abs.})$ -time plots are presented in Table 1. Rate constants remained constant with the increase in $[\text{CAT}]$, further confirming the first-order rate dependence on $[\text{CAT}]$.

Effect of LA on the reaction rate. Under constant $[\text{CAT}]_0$, $[\text{H}_2\text{SO}_4]$ and temperature, the $[\text{LA}]_0$ was varied from $5.00 \times 10^{-3} \text{ M}$ to $8.00 \times 10^{-2} \text{ M}$. An increase in the rate was observed with an increase in $[\text{LA}]$ (Table 1). A linear plot of $\ln[\text{LA}]$ vs. $\ln k'$ (Fig. 2) with a slope of 0.80 showed a fractional order dependence on $[\text{LA}]$.

Effect of H_2SO_4 on the reaction rate. The concentration of sulfuric acid was varied from $1.00 \times 10^{-2} \text{ M}$ to $2.50 \times 10^{-1} \text{ M}$ while keeping all the other conditions in the reaction constant. The rate constant remained approximately the same (Table 1) indicating a zero effect of $[\text{H}_2\text{SO}_4]$ or $[\text{H}^+]$ on the rate (Fig. 1).

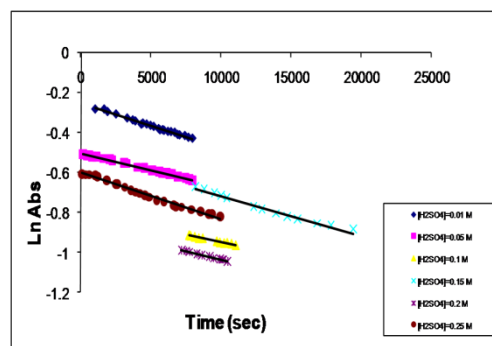


Figure 1. First-order plots with nearly constant slopes for different $[\text{H}_2\text{SO}_4]$. $1.00 \times 10^{-2} \text{ M}$ to $2.50 \times 10^{-1} \text{ M}$

Effect of Na_2SO_4 on the reaction rate. Varying the ionic strength using Na_2SO_4 in the range 0.100 M – 1.50 M at constant conditions, the reaction rate had negligible effect (Table 1). As a result, a constant ionic strength was not maintained in the reaction mixtures of other runs.

Effect of reduction product, PTS, on the reaction rate. The effect of the externally added reduction product, PTS, on the rate at other constant conditions was studied in the range, $1.00 \times 10^{-4} \text{ M}$ to $7.50 \times 10^{-3} \text{ M}$ PTS. Results presented in Table 1 show an insignificant effect of $[\text{PTS}]$ on the reaction rate.

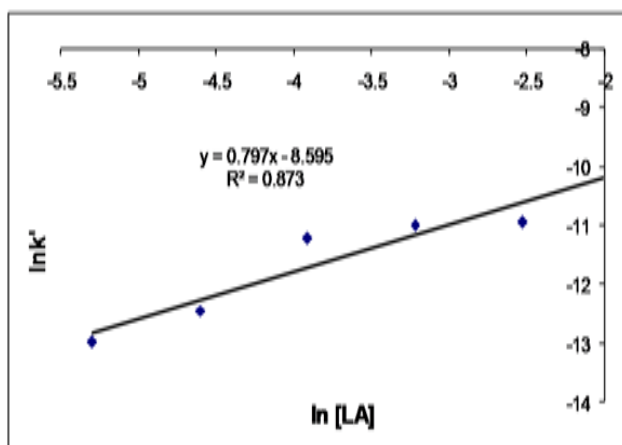
Table 1. Effects of chloramine-T (CAT), Lactic acid (LA), and H₂SO₄ on the Reaction Rate at 323 K

[CAT] ₀ (10 ⁻³ M)	[LA] ₀ (10 ⁻² M)	[H ₂ SO ₄] (10 ⁻¹ M)	k' (10 ⁻⁵ s ⁻¹)	
0.200	1.00	1.00	2.10	
1.00	1.00	1.00	1.67	
1.50	1.00	1.00	1.00	
2.00	1.00	1.00	1.13	
10.00	1.00	1.00	1.82	
1.00	0.50	0.50	0.23	
1.00	1.00	1.00	0.39	
1.00	2.00	2.00	1.35	
1.00	4.00	4.00	1.67	
1.00	8.00	8.00	1.77	
1.00	1.00	1.00	2.25	
1.00	1.00	1.00	1.67	
1.00	1.00	1.00	1.98	
1.00	1.00	1.00	1.71	
1.00	1.00	1.00	2.29	
1.00	1.00	1.00	1.67	
1.00	1.00	1.00	1.67	(1.19) ^a
1.00	1.00	1.00	1.67	(1.15) ^a
1.00	1.00	1.00	1.67	(1.75) ^b
1.00	1.00	1.00	1.67	(1.50) ^b
1.00	1.00	1.00	1.67	(1.69) ^b
1.00	1.00	1.00	1.67	(2.12) ^c
1.00	1.00	1.00	1.67	(2.46) ^c
1.00	1.00	1.00	1.67	(2.23) ^c

a: Values in parentheses refer to ionic strength variation: [Na₂SO₄] = 0.100 M - 1.50 M.b: Values in parentheses refer to variation of [PTS] = 1.00 x 10⁻⁴M - 7.50 x 10⁻³M

c: Values in parentheses refer to variation of MeOH content in the solvent medium: 5%, 15% and 25%

Effect of dielectric constant. The effect of dielectric constant (D) of the solvent medium was determined using the MeOH-water solvent system. An increase in the MeOH content (5 – 25% v/v) showed no significant change in the reaction rate (Table 1).

**Figure 2.** Ln-ln plot for the determination of the LA order

Effect of temperature. Kinetic runs were performed at various temperatures (303 – 328 K) while keeping the other experimental conditions the same. An Arrhenius plot of ln k' vs. 1/T (Fig. 3) and an Eyring plot of ln (k'/T) vs. 1/T (Fig. 4) were used to calculate the activation parameters, namely, energy of activation (E_a), entropy of activation (ΔS[‡]), enthalpy of activation (ΔH[‡]), and free energy of activation (ΔG[‡]). These results are summarized in Table 2.

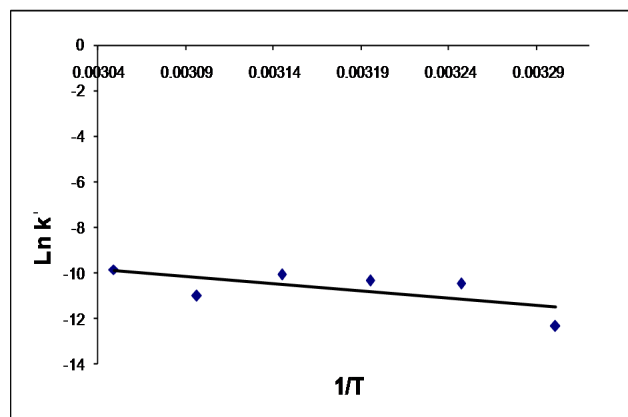
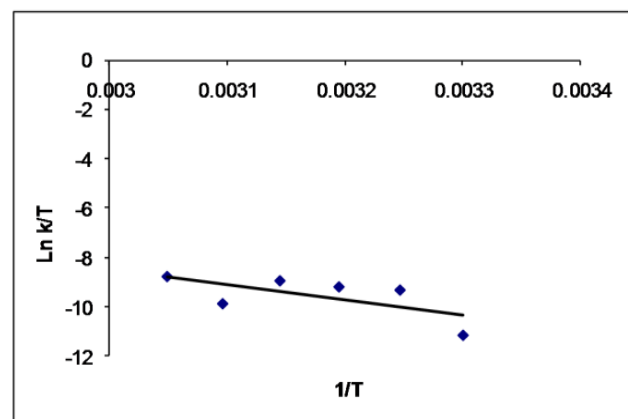
**Figure 3.** Arrhenius plot of ln k' vs. 1/T**Figure 4.** Eyring plot of ln (k'/T) vs. 1/T

Table 2. Rate constants (k') at different temperatures and activation parameters for the lactic acid oxidation by CAT in acid solutions

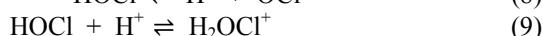
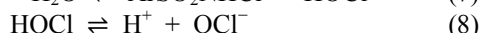
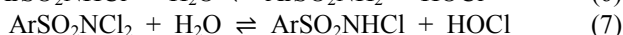
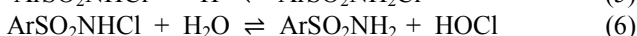
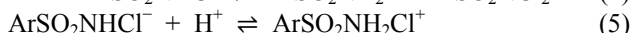
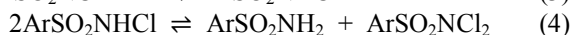
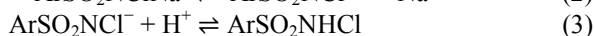
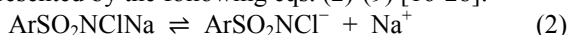
Temperature Or Activation parameter	$k' (10^{-5} \text{ s}^{-1})$
303 K	0.43
308 K	2.79
313 K	3.22
318 K	4.21
323 K	1.66
328 K	5.18
$E_a (\text{kJ mol}^{-1})$	53.7
$\Delta H^\ddagger (\text{kJ mol}^{-1})$	51.1
$\Delta S^\ddagger (\text{JK}^{-1} \text{ mol}^{-1})$	-280
$\Delta G^\ddagger (\text{kJ mol}^{-1})$	142 ^a

a, ΔG^\ddagger value at 323 K*Reaction Conditions: $[\text{CAT}]_0 = 1.00 \times 10^{-3} \text{ M}$; $[\text{LA}]_0 = 4.00 \times 10^{-2} \text{ M}$; $[\text{H}_2\text{SO}_4] = 0.100 \text{ M}$.

Detection of free radicals. The negative polymerization test with monomers for the detection of free radicals generated *in situ* in the reaction mixture showed the absence of free radicals.

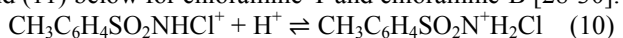
Reaction mechanism. The observed stoichiometry of 2 mol CAT: 1 mol LA for the reaction in acid solutions, resulting in the formation of acetic acid and PTS as major products, is represented by eq. (1).

In aqueous solutions, CAT and its derivatives such as chloramine-B (CAB) and bromamine-T act as electrolytes. Some of the important equilibria exhibited by CAT and CAB are represented by the following eqs. (2)-(9) [16-28]:



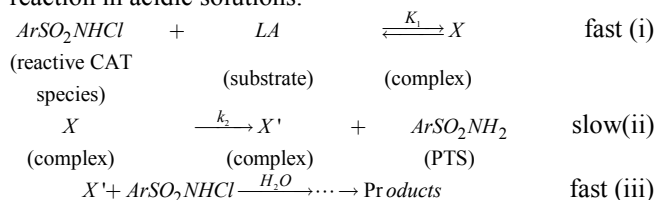
where Ar = *p*-Me-C₆H₄ for CAT and Ar = C₆H₅ for CAB.

The free acid of CAT (ArSO₂NHCl), dichloramine-T (ArSO₂NCl₂), HOCl, and H₂OCl⁺ are the probable oxidizing species in acid medium. As Eq. (6) indicates a slow hydrolysis, if HOCl were the primary oxidizing species, a first-order retardation of the rate by the added ArSO₂NH₂ or PTS would be expected, which is contrary to the observed results of the LA-CAT reaction. Relative concentrations of the CAT species, which are pH dependent, present in acidified solutions of haloamines of comparable molarities proved ArSO₂NHCl to be the oxidizing species in acid solutions[30]. If dichloramine-T were involved, the reaction rate would have shown a second-order dependence on it (eq. (4)), which is different from the determined first-order. Also, the PTS would have a negative effect, which was not shown by the observed results. Other probable CAT species could be eliminated on similar grounds. Further protonation of monohaloamines is possible below pH 2 as shown in eqs. (10) and (11) below for chloramine-T and chloramine-B [28-30].



In the present study, the [H₂SO₄] has no effect on rate. These results suggest that the free acid species, ArSO₂NHCl, is the most likely active oxidizing species involved in the mechanism of LA oxidation.

The experimental rate law involves a first-order dependence of the rate on [CAT]₀, a fractional-order on [LA], and a zero-order each on [H₂SO₄] and [PTS]. Free radicals were not formed in the reaction mixtures. Furthermore, the rate was not affected by the ionic strength and dielectric constant of the reaction medium. On the basis of the above discussion, a simple mechanism (Scheme 1) has been proposed for the reaction in acidic solutions.

**Scheme 1.** Mechanistic steps for the LA oxidation by CAT in acid medium

Molecular structures of complexes X and X', and other intermediate species formed are shown in Scheme 2. This scheme shows a detailed interpretation of electronic mechanism for the oxidation of LA by ArSO₂NHCl, which is the acidic reactive oxidizing species of CAT. In the fast pre-equilibrium (step (i)), there is an electrophilic attack of the chlorinium ion of the oxidant on the hydroxyl group of LA to form a chloroxy lactic acid intermediate (X) and ArSO₂NH⁻ ion. The latter anion on abstraction of an α -proton from complex X forms the reduction product, PTS. In the rate-determining process (slow step (ii)), deprotonation of complex X and intramolecular rearrangements occur forming the next intermediate (complex X') which leads to pyruvic acid. The reaction of pyruvic acid with a second mole of the reactive oxidant species, ArSO₂NHCl, leads to a chloroderivative (complex X''), which in a series of fast steps yields the oxidation end product, CH₃COOH. Scheme 2 is consistent with the reported mechanisms for similar redox reactions[13-17].

Rate law derivation

From the slow step in Scheme 1,

$$\text{rate} = -d[\text{CAT}]/dt = k_2[\text{X}] \quad (12)$$

If [CAT]_{tot} represents the total effective concentration of the oxidant, CAT, then

$$[\text{CAT}]_{\text{tot}} = [\text{ArSO}_2\text{NHCl}] + [\text{X}] \quad (13)$$

By making an appropriate substitution from equilibrium step (i) of Scheme 1 into eq. (13) and solving for [X], one obtains,

$$\begin{aligned} [\text{CAT}]_{\text{tot}} &= [\text{X}]/(K_1[\text{LA}]) + [\text{X}] \text{ or } [\text{CAT}]_{\text{tot}} \\ &= [\text{X}] \{ (1 + K_1[\text{LA}]) / (K_1[\text{LA}]) \} \\ \text{Or } [\text{X}] &= K_1 [\text{CAT}]_{\text{tot}} [\text{LA}] / (1 + K_1[\text{LA}]) \end{aligned} \quad (14)$$

Substitution for [X] from eq. (14) into eq. (12), one gets the rate law [eq. (15)] given below.

$$\text{Rate} = K_1 k_2 [\text{CAT}]_{\text{tot}} [\text{LA}] / (1 + K_1[\text{LA}]) \quad (15)$$

Since rate = k_{obs} [CAT]_{tot}, eq. (15) can be transformed into eq. (16) as follows:

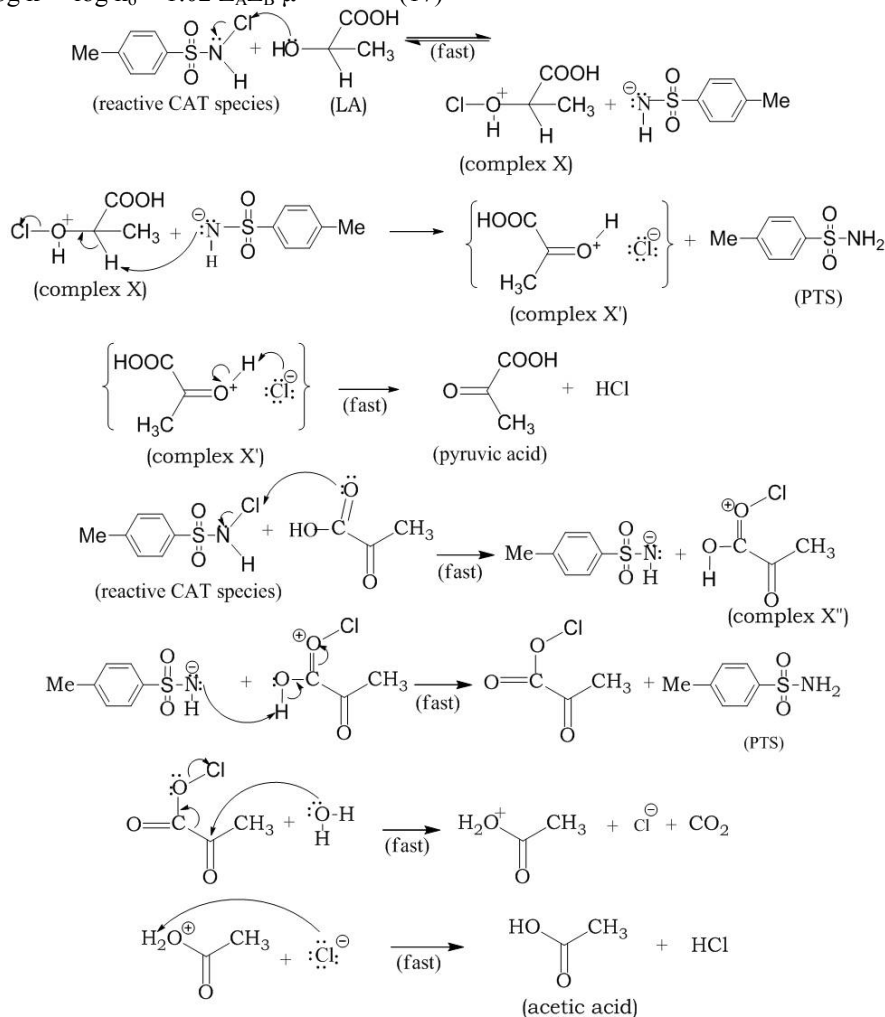
$$k' \text{ or } k_{\text{obs}} = K_1 k_2 [\text{LA}] / (1 + K_1[\text{LA}]) \text{ or } 1/k_{\text{obs}}$$

$$= (1/K_1k_2[LA] + 1/k_2) \quad (16)$$

The derived rate law (eq. (15)) is in good agreement with the experimental kinetic results such as a first-order dependence of the rate on [CAT], a fractional-order on [LA], and a zero-order each on [H₂SO₄] and [PTS]. To test the validity of the above rate equation (15), a double reciprocal plot of $1/[LA]$ vs. $1/[k_{\text{obs}}]$, based on eq. (16), when all other conditions were kept constant, was found to be linear ($r^2 = 0.973$). From the slope and intercept values of 2164.5 and 8392, respectively, the formation constant (k_1) and the decomposition constant (k_2) calculated for the standard run (at 323 K, [CAT] = 1.00×10^{-3} M, [LA] = 4.00×10^{-2} M, and [H₂SO₄] = 5.00×10^{-3} M) were found to be 3.88 M^{-1} and $1.19 \times 10^{-4} \text{ s}^{-1}$, respectively. These values are supportive of the mechanism in Scheme 2.

The reaction mechanism and the derived rate law are also supported by the following facts: (i) the increasing concentration of the reduction product of the oxidant, PTS, does not influence the rate showing that it is not involved in any pre-equilibrium in the mechanism; (ii) Bronsted and Bjerrum[31] have described the primary salt effect on the reaction rate through the following relation:

$$\log k' = \log k_0 + 1.02 Z_A Z_B \mu^{1/2} \quad (17)$$



Scheme 2. Detailed electronic mechanism of LA oxidation by CAT in acid medium

where μ is the ionic strength of the medium, A and B are the reacting ions, Z_A and Z_B are charges on the respective species, k' and k_0 are rate constants in the presence and absence of the added electrolyte, respectively.

According to eq. (17), a plot of $\log k'$ vs. $\mu^{1/2}$ should be linear with a slope of $1.02 Z_A Z_B$ and intercept of $\log k_0$. As the slope of the line depends on $Z_A Z_B$, the reaction rate may increase, decrease or remain unaffected with the ionic strength variation in the reaction medium. In the present study, the variation of ionic strength of the medium does not affect the rate, which signifies that at least one of the reactant species is a neutral molecule as shown in slow step (ii) of Scheme 1. Hence, the observed zero ionic strength effect is consistent with the Bronsted-Bjerrum concept[31] for the proposed mechanism; and (iii) the fairly positive values of free energy and enthalpy of activation indicate that the transition state is highly solvated. Furthermore, the observed negative value of ΔS^\ddagger indicates that as a fraction of collisions becomes more stringent, the decomposition of the rigid activated complex involves a slow process. This is suggestive of the fact that the LA-CAT reaction is relatively more controlled by entropy than enthalpy.

4. Conclusions

The LA-CAT reaction has been investigated in acid solutions. The reaction stoichiometry involving the LA oxidation to acetic acid by CAT has been found to be 1:2 (eq. (1)). Kinetic results show that the redox reaction has the following experimental rate law: $\text{rate} = k' [\text{LA}]^{0.80} [\text{CAT}] [\text{H}^+]^0 [\text{PTS}]^0$. The ionic strength and $[\text{SO}_4^{2-}]$ of the reaction medium have no effect on the rate. The activation parameters, E_a , ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger , have been determined to understand whether the reaction is controlled by entropy or enthalpy. The negative ΔS^\ddagger ($-280 \text{ JK}^{-1}\text{mol}^{-1}$) indicates the rigid transition state formation and the entropy controlled reaction. A suitable mechanism consistent with the experimental observations has been proposed and a rate law has been derived.

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