

Study of Kinetics of Electron Transfer reactions between unsaturated Acids and Thallium (III) in Aqueous Acetic Acid and Micellar Medium

Jafar Jilane¹, K.N.Sharma²

¹Department of Chemistry, A. P. S. University, Rewa (M.P.) India.

²Department of Chemistry, Govt. Girls P.G. College, Rewa (M.P.) India.

Abstract

The oxidative degradation of acrylic acid, and cinnamic acid in aqueous acetic acid, and micellar medium by thallium (III) perchlorate resulted in the formation of the corresponding aliphatic/aromatic aldehydes. The cationic micellar cetyl trimethyl-ammonium bromide (CTAB) has been found to act both as catalysis, and solvent when used under CMC range show non-integral order of reaction. The reactions follow Michaelis-Menten types kinetics. A first-order rate is co-related with rate coefficient, and specific acidity function. A mechanism involving formation of intermediate with CTAB, and Tl^{+3} reacting species in the slow step has been proposed.

Keywords: Acrylic acid, Cinnamic acid, Thallium (III), Perchlorate, Cetyl Trimethyl ammonium bromide (CTAB), kinetics.

1. INTRODUCTION

The redox mechanism usually involve either atom or electron transfer, both producing the same effect which is carried out by some oxidants. One such an oxidant is thallium (III), in aqueous solution, its trivalent ion is strongly solvated.¹ The relatively high stability of Tl(I), and moderate high redox potential ($E^{\circ} = 125$ V) for Tl^{+3} / Tl^{+1} couple makes Tl(III) a good oxidizing agent in various medium. The oxidation process with Tl(III) may be completed two electron transfer in a single or in two steps through exhibiting intermediate path with Tl(III). Tl(III) has been employed as an oxidant for a number of transformations including alcohols,³ aldehyde,⁴ ketones,^{5,6} carboxylic acids,⁷ amino acids⁸ etc., and their reports available in surveyed literature. Further, more prototypical micellar cationic CTAB has emerged as the non-aqueous solvent of the choice vis-a-vis acetic acid used also as a catalysis. The micelle specificity functions on particular pH, range, concentration temperature. They can achieve self-segregation of their hydrophobic portions from the solvent, and electrostatic forces in the presence of surfactants, influence the rates of several redox reactions of organic compounds⁹ with variety of oxidizing agents.¹⁰⁻¹² The investigations is a modest attempt to include CTAB based junctional region of Gouy-Chapman stern layer of the micelles.¹³

The study of solutes solvent interactions in ternary mixtures is more complex than in pure solvents. In pure solvent the cybotactic region is the same as in the bulk solvent, but in ternary mixtures, the solute can interact to a different degree with the component of the mixture, and the difference in the liner actions is reflected in the composition of the micro sphere of the preferential solvation.¹⁴

One of the rarely untrapped research areas involves unsaturated acids containing $>C=C<$ and $-COOH$ (carboxylic) group with common skeleton of the molecule comprises $CH=CH-COOH$ in substrate makes them susceptible to undergo for oxidation reaction. Moreover, unsaturated acids (aliphatic / aromatic) have been kinetically well explored by oxidants - CTAB,¹⁵ NBIN,¹⁶ and NCSA¹⁷. However, the kinetics, and oxidation of acrylic acid, and cinnamic acid by Tl^{+3} reagent has not yet been probed. The aim of the present work includes a systematic study of the solvents on the oxidation of unsaturated acids by Tl(III) with an objective to get better mechanism of oxidation.

2. EXPERIMENTAL

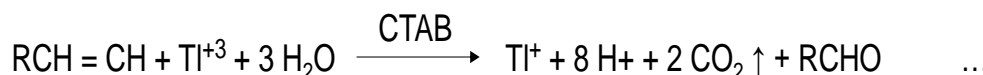
Materials : At the outset of these investigation, the synthetic operation was simplified by reducing the reaction time, and by employing unpurified CTAB (sigma), and distilled acetic acid (B.D.H.) at 118⁰C. The acrylic acid, and cinnamic acid were obtained from B.D.H., and were used as substrate without purification in calculated amount. In another experiment, we have used a simple, and high yielding methodology for the preparation of thallium(III) perchlorate solution. The experimental details are discussed in ref. ⁸.The requisite weighed sample of thallic oxide (B.D.H.) was dissolved in 70% perchloric acid (AREM), at 110⁰C, and standardized analytically. All other reagents used were of G. R. grade.

2.1 Kinetic measurements

The pseudo first-order conditions were attained by maintaining a large excess (X 15 or more) of unsaturated acid over Tl(III) perchlorate in a well equipped thermostat. The solvents were acetic acid, and CTAB unless specified otherwise. The reactions were followed at constant temperature (± 0.01 K) by monitoring the disappearance of [Tl⁺³] iodometrically at regular intervals of time. The pseudo first-order rate constant (k_{obs}) was evaluated from the linear plots of $\log [Tl^{+3}]_0 / [Tl^{+3}]_t$ against time for upto 80% reaction. The duplicate measurements of values were lie within $\pm 3\%$.

2.2 Stoichiometry

The stoichiometric studies for the Tl(III) mediated oxidation of acrylic acid, and cinnamic acid were determined with oxidant in excess. The unsaturated acids, and Tl(III) were mixed in suitable proportions, and were allowed to react with 2 days at 313, and 318K in acetic acid, and CTAB. The concentration of unreacted Tl(III) was periodically determined. The stoichiometry from the ratio between [unsaturated aid], and Tl(III) exhibited as 1:1 i.e., one mole of the unsaturated acids are reacted with one mole of Tl(III). Stoichiometry analysis showed that the following overall reaction :



where, $R = H-$, and C_6H_5- for corresponding acrylic acid, and cinnamic acid respectively.

2.3 Product analysis

The oxidation of unsaturated acids (acrylic, and cinnamic acids) lead to the formation of formaldehyde, and benzaldehyde respectively. After completion of the reaction under kinetic conditions, the reaction mixture was treated with NaHCO₃ followed by addition of ether, and at last with 2:4-dinitrophenyl hydrazine in HCl. The yield of the aldehydes 2:4-DNP derivative was about 78% range. The 2:4-DNP derivatives of formaldehyde, and benzaldehyde were identified by melting point analysis as 155⁰C, and 235⁰C, and this agreed well with literature values. They were also confirmed by spectroscopic, and chromatographic methods.

2.4 Test for free radicals

The oxidation reaction of acrylic acid and cinnamic acid, in an stream of nitrogen did not induce the polymerization of monomer acrylonitrile or BHT. It had no effect on the rate, ignoring one electron oxidation giving to free radicals is unlikely.

4. Results and Discussion

3.1 Order of reaction: The kinetics of oxidation of acrylic acid, and cinnamic acid by Tl(III) was investigated in acetic acid, and micellar (CTAB) medium at 313, and 318K in presence of perchloric acid. The reactions were of first-order with respect to Tl(III). The values of k_{obs} were independent of the initial concentration of Tl(III) perchlorate.

Reaction rates increase non linearly with rise in the concentrations of the unsaturated acid (Table 1), under pseudo first-order conditions. The double reciprocal plots of $1/k_{obs}$ vs. $1/[substrate]$ were found linear with a

positive intercept on ordinate axis (Fig.1) indicating the formation of intermediate compound, and thus order falls from 1 to 0. The second-order rate (k_2) was not found constant.

Table 1: Effect of varying concentration of substrate on rate of oxidation

$10^3 \times [\text{Ti(III)}]$ (mol dm⁻³) = 2.50 (1), 4.0 (2); $[\text{HClO}_4]$ (mol dm⁻³) = 0.20 (1, 2);
 $10^3 \times [\text{CTAB}]$ (mol dm⁻³) = 1.0 (1), 1.25 (2); $\text{CH}_3\text{COOH}:\text{H}_2\text{O}$ %, (v/v) = 40 : 60 (1, 2);
 Temp. K = 313 (1), 318 (2)

[Substrate] $\times 10^2$ (mol dm ⁻³)	$10^4 k$ (s ⁻¹)	
	Acrylic acid (1)	Cinnamic acid (2)
1.00	1.40	0.96
1.25	1.65	-
1.50	-	1.33
2.00	2.01	1.62
2.50	2.22	1.91
3.33	2.82	2.37
4.00	3.05	2.49
5.00	3.25	2.81
6.25	3.35	2.93

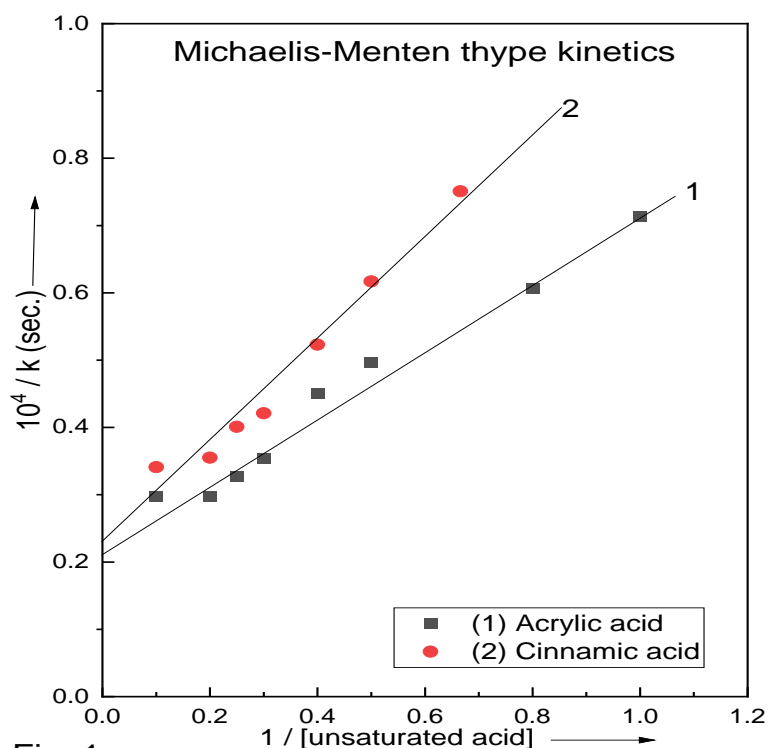


Fig. 1 Plot of $1/k_{\text{obs}}$ against $1/[\text{unsaturated acid}]$

$10^3 \times [\text{Ti(III)}]$ (mol dm⁻³) = 2.50 (1), 4.0 (2);
 $[\text{HClO}_4]$ (mol dm⁻³) = 0.20 (1, 2);
 $10^3 \times [\text{CTAB}]$ (mol dm⁻³) = 1.0 (1), 1.25 (2);
 $\text{CH}_3\text{COOH} : \text{H}_2\text{O}$ %, (v/v) = 40 : 60 (1, 2);
 Temp. K = 313 (1), 318 (2)

3.2 Effect of acidity: The reaction is catalysed by hydrogen ions, and exhibited first-order with respect to $[H^+]$. This rate is also evidenced in good co-relation with rate, and specific acidity function ($r^2 = 0.9983$). It has been proved by graphical means too.

3.3 Effect of solvent polarity on reaction rate : The oxidation of unsaturated acids have been probed in the binary mixture of acetic acid (20% to 40%) micellar (CTAB) mixture. The reaction rate decreased steadily with increase in the proportion of acetic acid in the solvent medium. Amis plot made between $\log k_{obs}$ against $D-1/2D+1$ with negative slope affects, the polar nature of transition state as compared to the reactant.

3.4 Effect of Micellar on reaction rate : The micellar shows non-integral order at its higher concentration due to tendency to dimerize in micellar non-polar solvent. The rate of reaction is initially catalysed by addendum of CTAB (Table 2), and attained limiting value at its definite optimum concentration, and catalyses the reaction showing existence of "Stern, and Gouy-Chapman layers" junctural region. The plots of $1/k_{obs}$ vs. $1/[micellar]$ (Fig. 2), provide evidence likewise Michaelis-Menten type kinetics.

Table 2: Effect of variation of cationic Micellar cetyltrimethylammonium bromide (CTAB) on the rate of reaction

$10^3 \times [Ti(III)]$ (mol dm^{-3}) = 2.50 (1), 4.0 (2) ;
 $10^2 \times [Substrate]$ (mol dm^{-3}) = 2.00 (1), 2.50 (2) ;
 $CH_3COOH:H_2O$ %, (v/v) = 40 : 60 (1, 2) ; Temp. K = 313 (1), 318 (2)

$[Substrate] \times 10^3$ (mol dm^{-3})	$10^4 k (s^{-1})$	
	Acrylic acid (1)	Cinnamic acid (2)
1.00	2.01	1.51
1.25	2.17	1.91
2.00	3.16	2.44
2.50	3.26	2.70
3.33	-	2.85
4.00	3.45	2.98
5.00	2.72	2.68

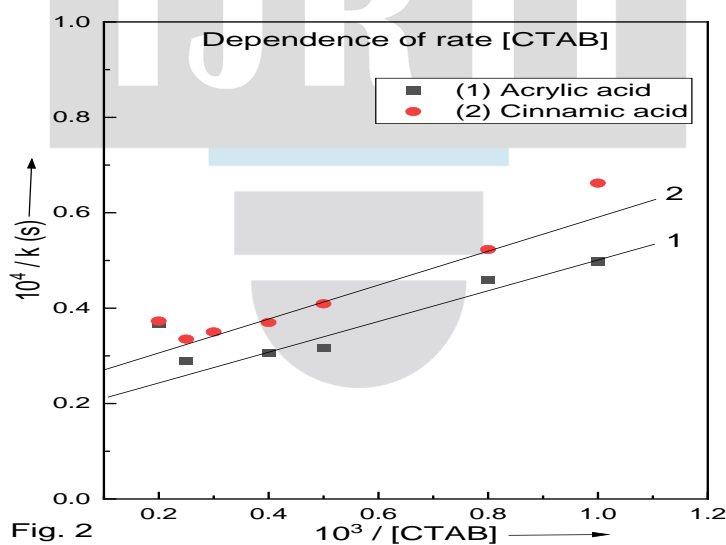


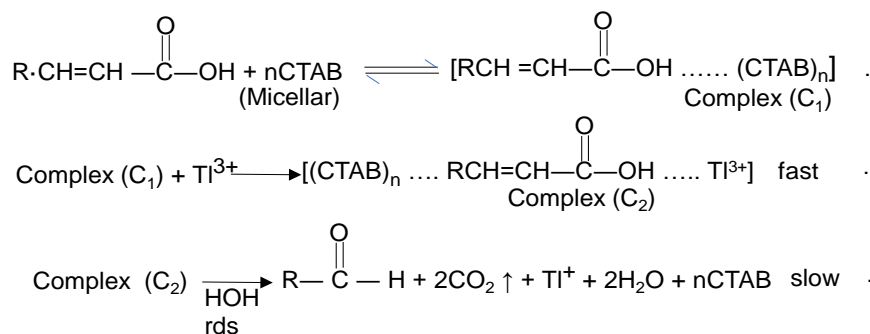
Fig. 2 Reciprocal plot of $1/k_{obs}$ vs. $1/[CTAB]$
 $10^3 \times [Ti(III)]$ (mol dm^{-3}) = 2.50 (1), 4.0 (2) ;
 $10^2 \times [Substrate]$ (mol dm^{-3}) = 2.00 (1), 2.50 (2) ;
 $CH_3COOH : H_2O$ %, (v/v) = 40 : 60 (1, 2) ;
 Temp. K = 313 (1), 318 (2)

The effect of ionic strength of salt on rate by varying five-times concentrations of NaCl at constant conditions remains almost unchanged. It indicates that interaction in rate-determining step is not of ion-ion type.¹⁸

Mechanism of oxidation

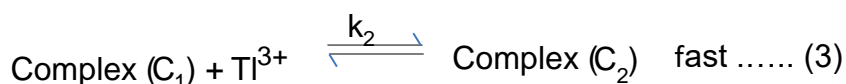
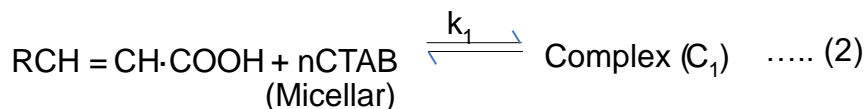
The following mechanism is proposed for the oxidation of unsaturated acids by Tl(III) perchlorate. The reacting species profile of the oxidant in aqueous acetic acid, and perchloric acid medium assumed, exists as $Tl(OH)^{2+}$, and $Tl(OH)_2$ hydrolysed form. Tl(III) is capable of forming complexes with organic anions as C-Tl bond.

Absence of any effect of acrylonitrile on the reaction discounts the possibility of a one electron oxidation leading to the formation of free radicals.



Rate law

The rate expression may be expediated as :



The final rate equation may be obtained in terms of disappearance of [Tl(III)] under the steady state hypothesis as :

$$k_{obs} = \frac{k K_1 K_2 [S][H^+][CTAB]}{k_H + [H^+] + K_1 K_2 [S][H^+][CTAB]} \quad \dots \dots (5)$$

This equation may lead Michaelis-Menten type kinetics (plot of k_{obs}^{-1} vs. $[S]^{-1}$), when equation (5) is brought in form of equation (6).

$$[CTAB] \times \frac{1}{k_{obs}} = \frac{1}{[S]} \left\{ \frac{K_H}{k K_1 K_2 [S][H^+]} + \frac{1}{k K_1 K_2} \right\} + \frac{1}{k} \quad \dots \dots (6)$$

Under the condition, when $k_H \gg K_1 K_2 [S][H^+] + [H^+]$.

The equation (5) follows first-order with respect to oxidant Tl(III), and $[H^+]$, and when $[K_H + H^+] \ll K_1 K_2 [S] [H^+]$ the equation (5) reduces to

$$k_{obs} = k \dots \dots \dots (7)$$

Structure and Reactivity

The observed order of reactivity is, acrylic acid > cinnamic acid. The Tl^{+3} attacks at $>C=C<$ for complex formation causes rupture of bond to produce aldehyde. The presence of C_6H_5- in cinnamic acid, hence occurrence of steric hinderance may cause slow rate of oxidation. The structure, and reactivity are further supported by thermodynamic parameters (Table 3). The values of activation energy (E_a) is lowest for fastest reaction, and vice-versa indicating that reaction is enthalpy controlled. The values of Gibbs free energy almost indicate that a common mechanism is operating in all studied solvent systems. The C_6H_5 group increases the ΔS^\ddagger value. The entropy of activation is negative for all unsaturated acids. The loss of ΔS^\ddagger leads the polar nature of transition state, and reduced the rotational degree of freedom of the intermediate complex.

Table 3. Thermodynamic parameters for the reaction between unsaturated acids and Tl(III) perchlorate

Substrate	E_a (kJ/mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (JK ⁻¹ mol ⁻¹)
Acrylic acid	63.17	61.48	84.45	88.94
Cinnamic acid	65.24	62.87	91.02	87.82

Conclusion

The hydrolysed form of reacting species of Tl(III) perchlorate oxidant forms intermediate complex with unsaturated acid in pre-equilibrium state. The rupture of C-C bond yield the corresponding products aldehydes are identified by forming their 2:4-DNP derivatives. The order of reactivity acrylic acid > cinnamic acid was discussed, and supported by kinetics, and thermodynamic parameters. The non-integral order kinetics was observed each with respect to substrate and micellar CTAB.

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Conflict of Interest

The authors declare conflict of no interest whatsoever.

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