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KINETICS OF OXIDATION OF UNSATURATED ACID BY THALLIUM(III) IN AQUEOUS ACETIC ACID AND MICELLAR MEDIUM

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ABSTRACT

The oxidation of α-crotonic acid by thallium (III) perchlorate proceeds by a mechanism approach involving direct two-electron transfer with lack of free radical intervention from substrate to the oxidant via an intermediate complex. The stoichiometry (1:1) of the reaction followed by its decomposition in a rate-determining step to product acetaldehyde. The orders in oxidant and acid were found to be unity, whereas solvent, micellar (CTAB) exhibited fraction-order kinetics. The activation parameters were also discussed.

Keywords: Crotonic Acid, Thallium (III), Perchlorate, Cetyltrimethylammonium Bromide (CTAB), Oxidation, Stoichiometry

1. INTRODUCTION

The chemistry of α-crotonic acid, an unsaturated acid containing a double bond, and carboxylic a functional group in non-aqueous solvent causes cleavage of >C=C bond. Owing to this properly, it received much attention in the recent past due to its applications in biochemistry Banerji (1972) solvolysis process, synthetic material chemistry and pharmaceuticals. α-crotonic acid behaves differently than other aliphatic, and aromatic carboxylic acids towards many oxidants. Oxidation of crotonic acid by chromine-T, Shrivastava & Neelam (2015) N-bromoisonicotinamide Prajapati et al. (2019) and N-chlorosaccharin Singh, & Dubey (2023) etc. have been reported. The micelles are of special significance because of their biological relevance, and are also important in enzyme Josh et al. (2006),

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Agnihotri & Tiwari (2021), Singh & Swami (2022) catalysed (CTAB) reactions as well as a solvent. Bhuvaneshwari & Elango (2006), Ramachandrappaet al. (1998) The thallium(III) perchlorate is used as oxidant for various organic transformations Hemkar et al. (2013) Tunable physical properties like redox potential, and acidity of transition metal makes it attraction from catalytic point of view. Most of the electron transfer reactions of Tl(III), and their mechanistic studies concentrated. The oxidation of crotonic acid by Tl^{+3} was undertaken to elaborate the mechanism of the reaction prone to form complex with Tl^{+3} in aqueous acetic acid, and micellar medium for the tittle reaction.

2. EXPERIMENTAL

Materials: All the solutions of the reagents were prepared in double distilled water. The micellar cationic cetyltrimethylammonium bromide (Sigma), and α-crotonic acid (S.D. fine) were used as such received without purification. The solution of sodium thiosulphate was freshly prepared every day, and standardized iodometrically. Thallium(III) perchlorate oxidant was prepared by reported method Shah et al. (2022) as follows. The sample of thallic oxide (B.D.H.) in calculated amount was dissolved in 70% perchloric acid (AREM), and the solution was heated to 110˚C for about 15 minutes with constant stirring, quickly filtered and cooled. The solution of Tl(III) perchlorate was standardized by iodometric method.

Kinetic measurements

The reaction between Tl^{+3}, and crotonic acid was studied under pseudo first-order conditions [crotonic acid] >> [Tl^{+3}] at constant temperature of ± 0.1˚K. The reaction was initiated by mixing previously thermostated solutions of substrate, and oxidant which also contained the required amount of $HClO_4$, CH_3COOH, and micellar cationic CTAB. The reaction was followed upto ca. 80% conversion by monitoring the concentration of remaining Tl^{+3} iodometrically. The pseudo first-order rate constants were determined from the plots of log [Tl^{+3}] against time, and the rate constants were reproducible to within ±3%.

Test for free radicals

No precipitate due to the polymerization of the added acrylonitrile / acryloamide (monomer) was observed, thus discorded the presence of any free radicals present in the reaction. Mahesh et al. (2004)

3. RESULTS AND DISCUSSION

Stoichiometry and Products analysis

The stoichiometric of the reaction was determined under kinetic conditions when crotonic acid concentration was taken sufficiently lower than that of Tl^{+3} in acetic acid, perchloric acid, and micellar medium. The excess of [Tl^{+3}] was estimated iodometrically, and the results indicated a reaction of a mole of crotonic acid for a mole of per Tl^{+3} as represented in equation .

$$CH_3CH = CH \cdot COOH + Tl^{+3} + 3H_2O \underset{Micellar}{\overset{CTAB}{\leftrightharpoons}} Tl^{+} + 8H^{+} + 2CO_2 \uparrow$$

$$+CH_3CHO \quad .... (1)$$

The reaction mixture containing excess of thallium(III) perchlorate was kept undisturbed upto 24 h, and the complete disappearance of the crotonic acid was confirmed chromatographically. The aldehyde product was isolated from the reaction mixture by forming its 2:4-DNP derivative characterized by its m.p.

determination (162°C). The reaction is of first-order with respect to Tl^{+3}. Michaelis-Menen type kinetics is observed with respect to the crotonic acid (Table 1), as verified by double reciprocal plot of k_{obs}^{-1} vs. [substrate]$^{-1}$ (Fig. 1).

Table 1

Table 1 Dependence of k_{obs} on [α-crotonic acid] at 35°C

[Tl(III)] = 4.0 ×10^{-3} (mol dm^{-3}) ; [$HClO_4$] = 0.15 (mol dm^{-3}) ;

[CTAB] = 0.80 ×10^{-3} (mol dm^{-3}) ; CH_3COOH:H_2O = 40 :60 %, (v/v)

[α-crotonic acid] ×10^{-2} (mol dm^{-3})	k_{obs} 10^4 s^{-1}	$100\ k_2 = \frac{k_{obsd}}{[\alpha - crotonic\ acid]}$ $\ell\ mol^{-1}s^{-1}$
0.50	1.66	3.32
1.00	2.97	2.97
1.66	3.70	2.22
2.00	4.15	2.07
2.50	4.64	1.85
3.33	5.36	1.60
4.00	5.05	1.26

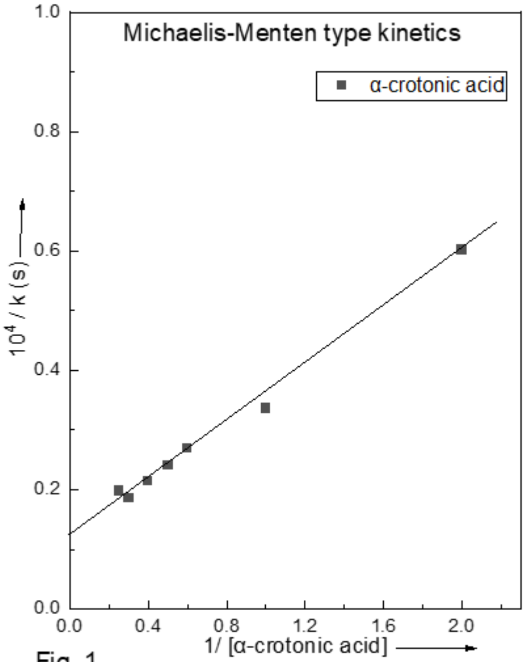

Fig. 1

Plot of k^{-1} vs. [α-crotonic acid]$^{-1}$

[Tl(III)] = 4.0 ×10^{-3} (mol dm^{-3}) ;

[$HClO_4$] = 0.15 (mol dm^{-3}) ;

[CTAB] = 0.80 ×10^{-3} (mol dm^{-3}) ;

Ac-OH: H_2O = 40 : 60 % (v/v) ;

Temp. = 35^0C

The reaction is catalysed by H^+ ions. The oxidation of α-crotonic acid was studied in binary organic solvents viz. acetic acid, and micellar (CTAB). CTAB attributed to capability of forming intermediate complex (Table 2), but the rate constant exhibited much variation in values with micellar solvent plot of log k_{obs} vs. log [CTAB] (Fig. 2). The data on the solvent effect showed an excellent correlation in terms of Swain's equation. Swain (1983) The successive addition of neutral salt, and ionic strength of the medium have no effect on rate.

Table 2

Table 2 Dependence of k_{obsd} on micellar [CTAB] at 35°C

[α-crotonic acid] = 1.0×10^{-2} (mol dm^{-3}) ; [Tl(III)] = 4.0×10^{-3} (mol dm^{-3}) ; [$HClO_4$] = 0.15 (mol dm^{-3}) ; AcOH:H_2O = 40 : 60 %, (v/v)

$10^3 \times$ [CTAB] (mol dm^{-3})	k_{obs} 10^4 s^{-1}	$k_2 = \frac{k_{obsd}}{[CTAB]}$ $\ell\ mol^{-1}s^{-1}$
0.50	2.25	0.45
0.80	2.97	0.37
1.66	3.81	0.22
2.00	4.15	0.20
3.33	4.62	0.13
4.00	4.57	0.11
5.00	4.41	0.08

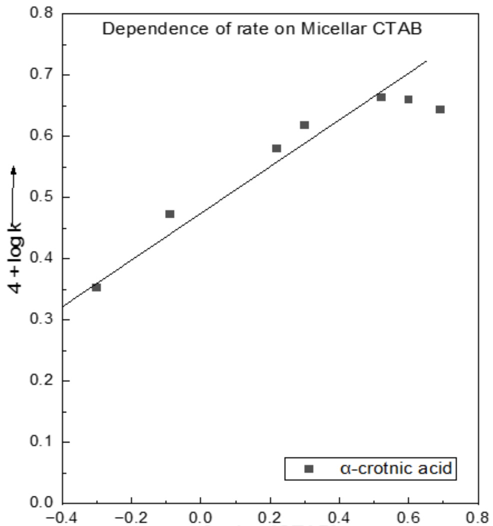

Fig. 2

Plot of log k vs. log [CTAB]

[α-crotonic acid] = 1.0×10^{-2} (mol dm^{-3}) ;
[Tl(III)] = 4.0×10^{-3} (mol dm^{-3}) ;
[$HClO_4$] = 0.15 (mol dm^{-3}) ;
Ac-OH : H_2O = 40 : 60 %, (v/v);
Temp. = 35^0C

4. RECTION MECHANISM

Since a one electron oxidation giving rise to free radicals is unlikely. The reaction proceeds with the rapid formation of complex between substrate, micelles and Tl^{+3}. The subsequent rate-determining decomposition of complex to yield acetaldehyde confirming the cleavage of the C-C bond in slow step. This leads to the postulation of following þath ways of mechanism, and rate law.

$$Tl^{3+} + H_2O \overset{k_H}{\rightleftharpoons} TlOH^{2+} + H^{+} \quad \ldots\ldots\ldots (2)$$

$$\underset{\text{(micellar)}}{CH_3 - CH \cdot COOH + nCTAB} \overset{k_1}{\rightleftharpoons} \text{Complex (X)} \quad \ldots\ldots (3)$$

$$\text{Complex (X)} + Tl^{3+} \overset{k_2}{\rightleftharpoons} \text{Complex (Y)} \quad \ldots\ldots (4)$$

$$\text{Complex (Y)} \xrightarrow[\text{slow rds}]{k} \text{Products} \quad \ldots\ldots (5)$$

Execution of stead-state approach, the rate is expedited as :

$$k_{obs} = \frac{k\, K_1 K_2 [S]\,[H^+]\,[CTAB]}{k_H + [H^+] + K_1 K_2\,[S]\,[H^+]\,[CTAB]} \quad \text{........ (6)}$$

The rate expression explains all observed kinetic facts under different conditions.

The moderate values of $\Delta E^{\#}$ = 57.87 kJ mol^{-1}, $\Delta H^{\#}$ = 54.72 kJ mol^{-1}, $\Delta G^{\#}$ = 84.24 kJ mol^{-1}, and $\Delta S^{\#}$ = -95.01 JK^{-1} mol^{-1} were favourable for electron transfer processes. The negative value of $\Delta S^{\#}$, can be ascribed to the nature of electron pairing and unpairing processes and to the loss of degree of freedom formerly available to reactant upon the formation of transition state. Lene et al. (2005)

5. CONCLUSION

The reaction followed Michaelis-Menten type kinetics both respect to α-crotonic acid. The order with respect to oxidant Tl^{+3} is unity. Micelles cationic CTAB acts both as catalyst and solvent. The stoichiometric ratio was found 1:1. The derived rate law based on proposed mechanism explains all the kinetic facts.

CONFLICT OF INTERESTS

None.

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