Indian Journal of Chemistry
Vol. 62, August 2023, pp. 803-807
DOI: 10.56042/ijc.v62i8.87

Kinetics and mechanism of oxidation of cinnamyl alcohol by N-chloro *p*-toluene sulphonamide (Chloramine-T) in acid perchlorate medium

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Received 25 March 2023; accepted 13 June 2023

The kinetics of oxidation of cinnamyl alcohol by N-chloro-*p*-toluene sulphonamide (Chloramine-T) in an aqueous acid medium has been studied. The reaction is first order with respect to the oxidant but exhibits rate independence of substrate concentration. Rate is retarded by hydrogen ion concentration due to protonation of Chloramine-T. The product toluene-*p*-sulphonamide does not affect the rate of reaction. The cinnamyl aldehyde has been observed to be the oxidation product spectrally.

Keywords: Kinetics, Mechanism, Oxidation, Cinnamyl Alcohol, Chloramine-T

Chloramine-T, a sodium salt[1-6] of N-Chloro *p*- toluene sulphonamide, is a well-established oxidant in acid and alkaline media. The reactions in acidic medium[7-12] are much faster than the reactions in alkaline media. So far as the speciation of Chloramine-T is concerned in acid as well as alkaline medium, much skill is required to understand the mechanistic aspect of its redox reactions. The kinetic analysis[13-22]of Chloramine-T is mostly based on the species which were suggested taking into account the various types of equilibria of Chloramine-T involved in acid medium. Chloramine-T has also been employed as a titrimetric reagent in volumetric analysis. Also, it is considered antiseptic and thus has attracted attention to understand this reagent's mechanistic aspect. With this view in mind, we have attempted to undertake the titled reaction to probe more about the oxidation of unsaturated alcohols which are not explored so far. We aimed to understand the pattern of reactivity of such alcohols so that a comparative analysis with the oxidation of saturated alcohols can be achieved.

Cinnamyl alcohol, Crotyl alcohol and Allyl alcohol are known unsaturated alcohols. In such alcohols, the primary or secondary alcoholic group are usually attacked by the oxidizing agent. The alcohol we have taken in this study is cinnamyl alcohol which has both unsaturation and primary alcoholic group. It will be interesting to know the role of oxidizing agent towards such alcohols whether the attack of oxidizing agent is *via* unsaturated carbon or through a primary alcoholic group.

Experimental Section

All the reagents employed in this study were of Analytical Reagent (AR) grade, and reagents were applied without any further treatment. However, cinnamyl alcohol was redistilled under high pressure. The chloramine-T solution was prepared by dissolving the requisite amount of its sodium salt and was standardized iodometrically. Doubly distilled water was employed throughout the study. The second distillation was from an alkaline permanganate solution in an all-glass apparatus.

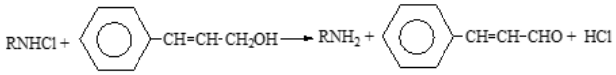
Kinetic Procedure

All reaction mixtures containing all other ingredients of the reaction mixture except Chloramine-T were taken in Erlenmeyer flasks painted black from the outside to check the decomposition of the oxidant at ambient temperature. The solution of Chloramine-T was taken in another flask. Both these flasks were suspended in a water bath controlled by a thermostat. When the bath temperature was attained by both these solutions, a known volume of Chloramine-T was withdrawn and then discharged into the reaction mixture. Stirring the reaction contents vigorously, an aliquot (5 cm^3 or 10 cm^3) was withdrawn periodically and discharged into an ice-cold potassium iodide solution(~10% KI). The

liberated iodine was titrated against the pre-standardized solution of thiosulphate to the colourless end-point. The results in triplicate were reproducible within ±5%.

Stoichiometry

The stoichiometry of the reaction was determined by allowing the reaction in an excess concentration of Chloramine-T than that of cinnamyl alcohol under similar conditions as were employed for kinetic analysis. Thus, after six-hour, it was ensured that the reaction is complete, and the excess Chloramine-T concentration was ensured by titrating the known volume of the reaction mixture. Similar titration was also carried out in the case of a stoichiometric mixture where the concentration of Chloramine-T was sufficiently large. These results indicate that a mole of alcohol requires a Chloramine-T, confirming the reaction's stoichiometry as represented by the equation below.



…(1)

Results

Chloramine-T dependence

The concentration of Chloramine-T ranges from 1.0×10^{-3} to5.0×10^{-3} mol dm^{-3} at three different but fixed concentration of [CAL] = 1.0×10^{-2} mol dm^{-3}, 1.5×10^{-2} mol dm^{-3} and 2.0×10^{-2} mol dm^{-3}, respectively at 45, 40 and 35ºC. The concentration of other reaction ingredients was kept constant [$HClO_4$] = 0.1 mol dm^{-3}. The initial rate was calculated and a plot of the initial rate (k_i, mol dm^{-3} s^{-1} v/s [CAT]) was found to be a straight line passing through the origin confirming first-order dependence with respect to Chloramine-T.

The kinetics of this reaction was studied under pseudo-first-order conditions where Chloramine-T is at least 10 times the concentration of cinnamyl alcohol. Pseudo-first-order plots were obtained (Fig. 1) and rate constants are collected in Table 1.

Cinnamyl alcohol dependence

The concentration of cinnamyl alcohol varied from 1.0×10^{-3} to 1.5×10^{-2} mol dm^{-3} at three different but fixed concentration of [CAT] = 2.0×10^{-3} mol dm^{-3}, 4.0×10^{-3} mol dm^{-3} and 5.0×10^{-3} mol dm^{-3}, respectively at [$HClO_4$] = 0.1 mol dm^{-3} and 35ºC.

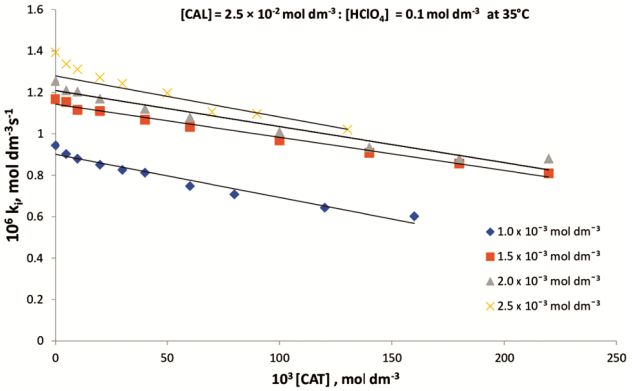


Fig. 1 — Pseudo first-order plots of chloramine-T

Initial rates (k_i, mol dm^{-3} s^{-1}) were calculated by the plain mirror method and were found to be independent of cinnamyl alcohol concentration. Chloramine-T appears to be involved in fast interaction with either of the reagents or an intermediate species of Chloramine-T. The rate was found to be independent of the initial concentration of alcohol.

Effect of Hydrogen ion

The concentration of hydrogen ions was varied by employing perchloric acid from 0.02 mol dm^{-3} to 0.2 mol dm^{-3} at a fixed concentration of other reaction components, [CAT]=2.0×10^{-3} mol dm^{-3}, [CAL] = 5.0×10^{-3} mol dm^{-3} and I = 0.5 mol dm^{-3}(ionic strength was adjusted by employing lithium perchlorate). This effect was studied at 30, 35, and 40ºC temperatures, respectively (Fig. 2). The rate of reaction decreases with increasing hydrogen ion concentration.

Effect of Ionic Strength

The effect of ionic strength was studied by employing lithium perchlorate from 0.2 to 1.0 mol dm^{-3} keeping a constant concentration of other reaction ingredients *viz*. [CAT] = 2.0×10^{-3} mol dm^{-3}, [CAL] = 5.0×10^{-3} mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3} at 35ºC.

Effect of *p*-toluene sulphonamide (RNH_2)

The effect of *p*-toluene sulphonamide, as one of the reaction products, was also studied by employing its concentration 0.02 – 0.06 mol dm^{-3} at a fixed concentration of other reaction ingredients *viz*. [CAT] = 2.0×10^{-3} mol dm^{-3}, [CAL] = 5.0×10^{-3} mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3} at 35 ºC. The rate remains unchanged with the variation of *p*-toluene sulphonamide, suggesting that no fast equilibrium

Table 1 — Initial rates, and pseudo-first-order rate constants in the reaction of Cinnamyl alcohol with Chloramine-T in acid perchlorate medium. $[HClO_4]$ = 0.1 mol dm^{-3}, Temp. = 35°C

10^3[CAT]mol dm^{-3}	10^3[CAL]mol dm^{-3}	10^6 (k_i) mol dm^{-3} s^{-1}	10^5 (k')s^{-1}
1.0	20.0	0.12	11.7
1.5	20.0	0.17	11.1
2.0	20.0	0.23	11.7
2.5	20.0	0.30	12.0
3.0	20.0	0.33	11.1
3.5	20.0	0.42	11.9
4.0	20.0	0.50	12.5
4.5	20.0	0.57	12.5
5.0	20.0	0.58	11.7
1.0	25.0	–	11.5
1.5	25.0	–	11.5
2.0	25.0	–	11.5
2.5	25.0	–	11.5
10^3[CAT]mol dm^{-3}	10^3[CAL]mol dm^{-3}	10^6 (k_i)mol dm^{-3} s^{-1}	10^5 (k')s^{-1}
1.0	10.0	–	11.5
1.0	15.0	–	11.5
1.0	20.0	–	11.5
1.0	25.0	–	11.5
1.0	30.0	–	11.5
2.0	0.8	0.23	11.5
2.0	1.0	0.23	11.5
2.0	1.5	0.23	11.5
2.0	2.0	0.23	11.5
2.0	3.0	0.23	11.5
2.0	4.0	0.23	11.5
2.0	5.0	0.23	11.5
2.0	6.0	0.23	11.5
2.0	7.0	0.23	11.5
2.0	10.0	0.23	11.5
2.0	15.0	0.23	11.5
2.0	20.0	0.23	11.5
10^3[CAT]mol dm^{-3}	10^3[CAL]mol dm^{-3}	10^6 (k_i)mol dm^{-3} s^{-1}	10^5 (k')s^{-1}
4.0	0.8	0.47	11.7
4.0	1.0	0.47	11.7
4.0	1.5	0.47	11.7
4.0	2.0	0.47	11.7
4.0	3.0	0.47	11.7
4.0	4.0	0.47	11.7
4.0	5.0	0.47	11.7
4.0	6.0	0.47	11.7
4.0	7.0	0.47	11.7
4.0	10.0	0.47	11.7
4.0	15.0	0.47	11.7
5.0	1.0	0.58	11.7
5.0	3.0	0.58	11.7
5.0	5.0	0.58	11.7
5.0	7.0	0.58	11.7
5.0	10.0	0.58	11.7
5.0	15.0	0.58	11.7

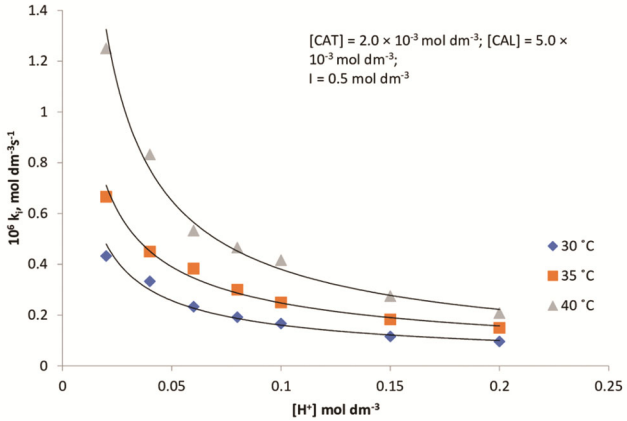


Fig. 2 — Variation of hydrogen-ion

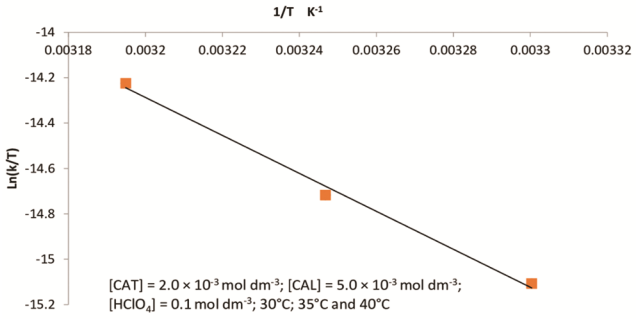


Fig. 3 — A plot of ln k/T *versus* 1/T K^{-1}.

involving *p*-toluene sulphonamide is preceded by the rate-determining step.

Temperature effect

The reaction was also studied at 30, 35, and 40ºC respectively keeping a fixed concentration of other reaction ingredients. Initial rates, energy, and entropy of activation were calculated from the Eyring plot (Fig. 3) to be 69.53±0.64 kJ mol^{-1} and -93.78±2.1 JK^{-1} mol^{-1}.

Test of free radicals

A test of free radicals was made by adding acrylonitrile to the reaction mixture; no white precipitate was obtained even after keeping the reaction mixture for more than two hours. This indicates that no free radicals are formed in the reaction.

Discussion

Organic haloamines are now well-established mild oxidants, and a prominent member of this class is N-chloro-p-toluene sulphonamide (Chloramine-T, CAT). The sodium salt of N-chloro-p-toluene sulphonamide is frequently available and is highly

soluble in water. This reagent has been employed extensively in synthesis and analytical chemistry as an oxidizing agent. Chloramine-T is a two-electron transfer reagent and the reduction product are *p*-toluene sulphonamide and Cl^-. The reactivity of chloramine-T is *p*H dependent[23-30]due to which the kinetics of chloramine-T reactions are complex in nature. The N-Cl bond is highly polar and is fairly strong electrophilicsince chlorine leaves as Cl^- in the reaction. Several equilibria governing various forms of Chloramine-T in an aqueous acid medium[31-34]are as follows:

$$RNCl^- + H^+ \rightleftharpoons RNHCl \quad \ldots(2)$$

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \quad \ldots(3)$$

$$RNHCl + H_2O \rightleftharpoons HOCl + RNH_2 \quad \ldots(4)$$

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \quad \ldots(5)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \quad \ldots(6)$$

where, R = $-CH_3C_6H_4SO$

The anionic form in the acid medium immediately converts to free acid form RNHCl in an aqueous acid medium. The disproportionation of RNHCl giving $RNCl_2$ species cannot be considered as this corresponds to the second order with respect to Chloramine-T, whereas the experimental order observed for the oxidant is one. Moreover, the rate of the reaction is not retarded by *p*-toluene sulphonamide (RNH_2); such an observation further negates the reactivity of dichloramine-T ($RNCl_2$). Similarly, the hydrolytic product of Chloramine-T, be HOCl, is ruled out as the reactive form of the oxidant. OCl^- species in an acid medium is ruled out as it demands catalysis by hydroxide ions.

The species [$RNHCl^+$....Cl^-] is only possible in high chloride ion concentration to give chlorine species as the reactive species. Thus, considering RNHCl to be the reactive form of Chloramine-T in the oxidation of cinnamyl alcohol in an acid medium, all the equilibria governing other species are insignificant so far, which the reaction mechanism demands.

One surprising observation (repeatedly tested under varied experimental conditions) is the rate being independent of the substrate concentration. Since the oxidation product of alcohol is 2,4-dinitrophenyl hydrazine derivative, its spectral analysis suggests that the alcohol is oxidized to cinnamaldehyde. Some impurity at the trace level is suspected to be responsible for this behaviour.

Moreover, hydrogen ion dependence cannot be correlated to alcohol; in all probability, can be correlated to Chloramine-T species. This rate is independent of the concentration of the substrate, first order with respect to the oxidant and inverse dependence of hydrogen ion concentration; the following mechanism accounting for all experimental observations can be envisaged as follows.

The product toluene-p-sulphonamide does not affect the rate. RNHCl is reported to be protonated[35,36].

$$RNHCl + H^+ \overset{K}{\rightleftharpoons} RNH_2^+ Cl \quad \ldots(7)$$

$$M + CAL \overset{K'}{\rightleftharpoons} [M.CAL] \quad \ldots(8)$$

Complex

$$\text{Complex} + RNHCl \longrightarrow \text{Products} \quad \ldots(9)$$

Such a mechanism leads to the rate law (10)

$$-\frac{d[CAT]}{dt} = \frac{kK'[CAL][CAT][M]}{(1+K[H^+])(1+K'[CAL]} \quad \ldots(10)$$

Since *K′* is significantly high, the inequality *K′[CAL]*>> 1 is valid. If this is the situation, the rate law (10) is reduced to equation (11) as,

$$-\frac{d[CAT]}{dt} = \frac{k[CAT][M]}{(1+K[H^+])} \quad \ldots(11)$$

The rate equation (11) accounts for the rate dependence of Chloramine-T and hydrogen ion concentration at constant impurity concentration. Such a proposition of the reaction mechanism appears to be logical.

Equation (11) can be written as equation (12)

$$-\frac{d[CAT]/dt}{[CAT]} = k_1 = \frac{k[M]}{1+K[H^+]} \quad \ldots(12)$$

The double reciprocal of equation (12) yields equation (13) as,

$$\frac{1}{k_1} = \frac{1}{k[M]} + \frac{K[H^+]}{k[M]} \quad \ldots(13)$$

A plot of $1/k_1$ *versus* [H^+] was made from equation (13) that yielded a straight line with non-zero intercept (Fig. 4) at constant concentration of impurity.

The ratio of slope and intercept yielded K to be 25, 34.72 and 42.5 $dm^3\ mol^{-1}$ at 30, 35 and 40°C respectively. The enthalpy and entropy of activation

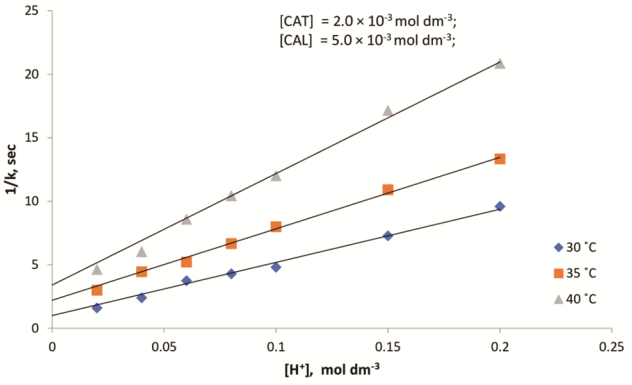
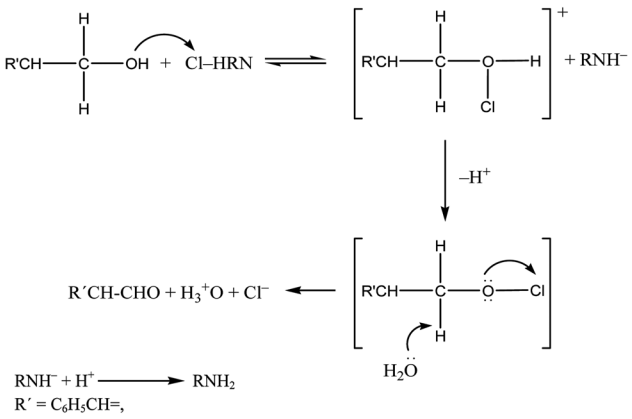


Fig. 4 — A plot of 1/k *versus* [H^+]



Scheme 1 — Reaction Events

for the equilibrium step were calculated to be 69.53±0.64 kJ mol^{-1} and −93.78±2.1 J K^{-1} mol^{-1} respectively. So far, the transfer of an electron[37] from the substrate (alcohol) to the oxidant (RNHCl) is concerned; the following Scheme 1 accounts for the reaction events.

$RNH^- + H^+ \longrightarrow RNH_2$

$R' = C_6H_5CH=$,

The proton abstraction from this species in the presence of the solvent is promoted by the π-electron cloud in the alcohol to form the conjugated oxidation product, such as cinnamyl aldehyde. The probability of participation of free radicals is ruled out.

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