



KINETICS OF OXIDATION OF PROPAN-2-OL BY TRICHLOROISOCYANURIC ACID IN AQUEOUS ACETIC ACID MEDIUM

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ABSTRACT

The kinetics of oxidation of an aliphatic secondary alcohol namely, propan-2-ol by trichloroisocyanuric acid in aqueous acetic acid medium in the presence of added chloride ions have been investigated. The observed rate of oxidation shows a first order dependence on both; the [PAL] and [TCI] and a fractional order dependence on $[Cl^-]$. The main product of the oxidation is dimethyl ketone. The reaction is not complicated by any product oxidation or chlorination under the conditions of the reactions. Variation in strength of mineral acid has no significant effect on the rate of oxidation, although a very small negative dependence is indicated. The complex formed by the reaction of Cl^- and protonated $TCIH^+$ ($TCIH^+Cl^-$), has been postulated as the reactive oxidizing species. A suitable mechanism consistent with the experimental results has been proposed.

Key word : Kinetics, Oxidation, Propan-2-ol, Trichloroisocyanuric acid

INTRODUCTION

N-Halogeno compounds have been extensively employed as halogenating and oxidising agents for substrates^{1,2}. The widespread use of a variety of N-halo compounds arises from the fact that they are good source of positive halogen^{3,4}. The nature of active oxidizing species and mechanism depends on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. Although a lot of work has been reported on the oxidation of organic compounds by N-halo compounds⁵⁻⁸ it is to be noted that no systematic kinetic investigation on the oxidation of aliphatic secondary alcohols by trichloroisocyanuric acid has yet been reported in the literature. Here, the results of the kinetics of the oxidation of propan-2-ol (PAL) with trichloroisocyanuric Acid (TCI) in aqueous acetic acid medium in the presence of chloride ion, have been reported.

EXPERIMENTAL

Propan-2-ol (Analar) and trichloroisocyanuric acid (Aldrich, USA), were used as supplied. Doubly distilled water and purified acetic acid were used. Potassium chloride (Analar) was used

as source of chloride ions. Sulphuric acid (BDH/AR) was standardised using sodium hydroxide solution with phenolphthalein as an indicator.

Most of the reactions were carried out under pseudo-first order condition ($[PAL] \gg [TCI]$). The course of the reaction was followed by pipetting out 5 mL aliquote of the reaction mixture at various time intervals (as read by an accurate stop-watch) and analysing the TCI concentration iodometrically^{9,10}. The pseudo-first order rate constants computed from the plots of $\log(b-x)$ against time were reproducible within $\pm 3\%$.

RESULTS AND DISCUSSION

Reaction products— 0.05 M of propan-2-ol and 0.05 M trichloroisocyanuric acid were dissolved in 50% H_2O (v/v) containing 0.05 M NaCl. The reaction was allowed for completion and then the reaction mixture was poured into 25 mL of a saturated solution of 2 : 4 dinitrophenyl hydrazine in 2 M HCl with stirring. The solution was kept at low temperature and left overnight to ensure completion of the hydrazone formation. The product was identified as acetone by a 2, 4-DNP derivative.

Order of the reaction— The reaction orders were determined from the slopes of the double logarithmic plots by varying the concentrations of substrate [PAL] in turn, while keeping others constant. The plot of $\log k_1$ against $\log [PAL]$ is linear ($r = 0.997$) with a slope value of 0.9287 in the presence of mineral acid and the plot of $\log k$ against $\log [PAL]$ is also linear ($r = 0.9978$) with a slope value of 0.8528 in the absence of mineral acid. The linearity of the plots of $\log [TCI]$ versus time indicates that the order w.r.t. [TCI] is unity, which is also confirmed by the constant k_1 values at varying [TCI] (Table 1). These results indicate clearly that the reaction is first order with respect to each; [PAL] and [TCI].

Table 1. Rate constant for the oxidation of propan-2-ol by TCI in aqueous acetic acid medium at 30°C

$10^2 [PAL]$ mol dm ⁻³	$10^3 [TCI]$ mol dm ⁻³	$[H^+]$ mol dm ⁻³	$10^2 [KCl]$ mol dm ⁻³	$10^4 k^1$ s ⁻¹	$10^3 [k_2]$ dm ³ mol ⁻¹ s ⁻¹
1.0	1.0	0.1	1.0	3.05	30.5
2.0	1.0	0.1	1.0	5.50	27.5
3.0	1.0	0.1	1.0	9.12	30.4
4.0	1.0	0.1	1.0	11.1	27.6
1.0	1.0	—	1.0	3.51	35.1
2.0	1.0	—	1.0	6.52	32.6
3.0	1.0	—	1.0	9.50	31.6
4.0	1.0	—	1.0	11.6	29.1
2.0	1.0	0.005	1.0	6.45	32.25
2.0	1.0	0.01	1.0	6.02	30.1

Table 1 Continued,....

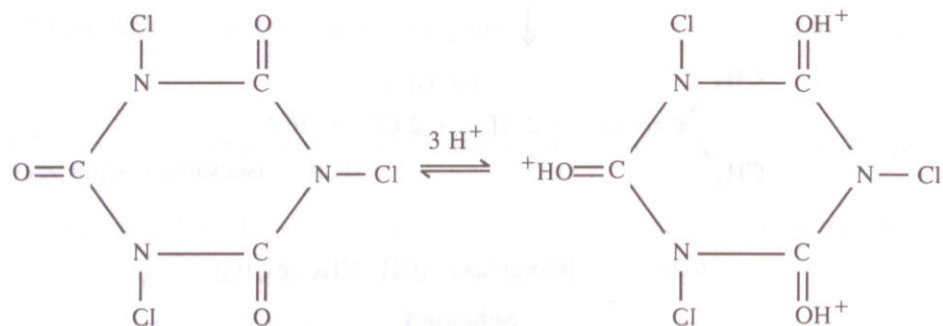
10^2 [PAL] mol dm ⁻³	10^3 [TCI] mol dm ⁻³	[H ⁺] mol dm ⁻³	10^2 [KCl] mol dm ⁻³	$10^4 k_1$ s ⁻¹	$10^3 [k_2]$ dm ³ mol ⁻¹ s ⁻¹
2.0	1.0	0.05	1.0	5.75	28.75
2.0	1.0	0.1	1.0	5.50	27.5
2.0	1.0	—	—	5.50	—
2.0	1.5	—	—	5.62	—
2.0	2.0	—	—	5.45	—
2.0	1.0	0.1	1.0	5.50	—
2.0	1.0	0.1	2.0	7.51	—
2.0	1.0	0.1	3.0	8.13	—
2.0	1.0	0.1	4.0	9.12	—
2.0	1.0	—	0.5	5.51	—
2.0	1.0	—	1.0	6.52	—
2.0	1.0	—	1.5	8.14	—
2.0	1.0	—	2.0	9.50	—

Effect of added KCl : The effect of addition of KCl on the rate of oxidation of propan-2-ol by TCI was studied by varying the concentration of KCl in both; in the presence and absence of mineral acid. In both cases, the order was found to be fractional.

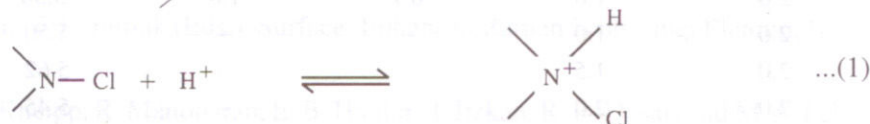
Effect of mineral acid : As the kinetics was observed in almost the same manner both; in the absence and in the presence of mineral acid, the effect of acid was studied by varying the concentration of H₂SO₄ added in the range 0.005 M to 0.1M. It was found that the rate was little affected by a change in [H⁺]. The order w.r.t [H⁺] can be taken as zero, although, actually a very small negative dependence has been observed.

Mechanism

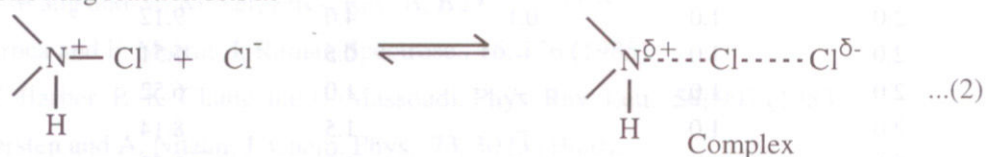
It is clear from the literature¹¹ that the probable reactive species of TCI in acid solution is TCIH⁺Cl⁻. The reaction is first order in [TCI] and [PAL] and fractional order in [Cl]. It is quite likely that under the conditions of solvent medium employed, the TCI exists in the following equilibrium.



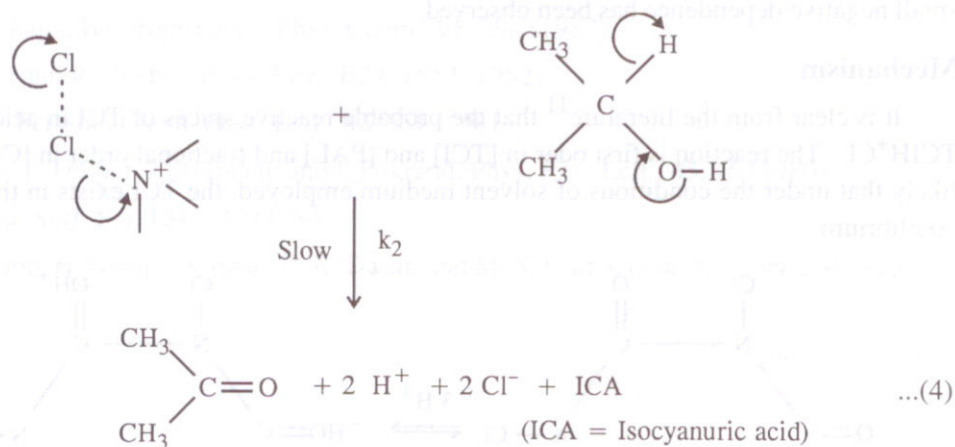
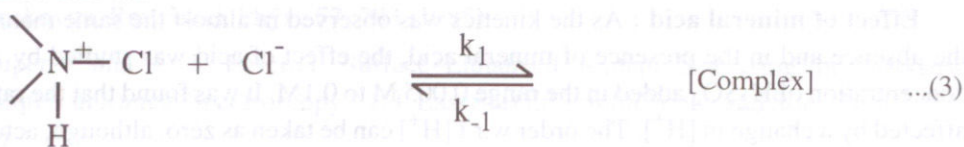
The outcome of such a protonation is to weaken the N-Cl bond due to an inductive transfer of the positive charge. Although TCI has three such potentially reactive centres, it may be represented as N-chlororeagent, N-Cl . The protonated form TCIH^+ may be represented as



Based on the earlier kinetic work using TCI,¹¹⁻¹⁴ one can reasonably suggest that the most likely oxidizing species is TCIH^+ under acidic condition. However, in the presence of added Cl^- , the following reaction sets in -



The complex thus generated is probably the effective oxidising agent in a bimolecular pathway. If, the slow reactions can be traced as an interaction between this complex formed and the alcohol molecule, the following mechanism can be proposed for the oxidation, for which the rate law can be derived.



$$\text{Rate} = k_2 [\text{Complex}] [\text{CH}_3\text{-CHOH-CH}_3] \quad \dots(5)$$

Scheme 1

The concentration of the complex in the above rate expression may be calculated assuming that all the TCI is reacting as TCIH^+ . Rate expression for [Complex] can be obtained as.

$$[\text{Complex}] = k [\text{TCIH}^+]_{\text{eq}} [\text{Cl}^-]_{\text{eq}} \quad \dots(6)$$

$$[\text{TCIH}^+]_{\text{eq}} = [\text{TCIH}^+]_{\text{total}} - [\text{Complex}] \quad \dots(7)$$

$$\text{Therefore } [\text{Complex}] = k [\text{TCIH}^+]_{\text{total}} - [\text{Complex}] [\text{Cl}^-]_{\text{eq}} \quad \dots(8)$$

$$[\text{Complex}] \{1 + k [\text{Cl}^-]_{\text{eq}}\} = k [\text{TCIH}^+]_{\text{total}} - [\text{Cl}^-]_{\text{eq}} \quad \dots(9)$$

$$\text{or } [\text{Complex}] = k [\text{TCIH}^+]_{\text{total}} - [\text{Cl}^-]_{\text{eq}} / \{1 + k [\text{Cl}^-]_{\text{eq}}\} \quad \dots(10)$$

$$\text{Assuming } [\text{Cl}^-]_{\text{eq}} = [\text{Cl}^-] - [\text{Complex}] \approx [\text{Cl}^-] \quad \dots(11)$$

$$[\text{Complex}] = \frac{k [\text{TCIH}^+]_{\text{total}} - [\text{Cl}^-]}{1 + k [\text{Cl}^-]} \quad \dots(12)$$

$$\text{Rate} = k_2 [\text{CH}_3 - \text{CHOH} - \text{CH}_3] [\text{Complex}] \quad \dots(13)$$

$$= \frac{k_2 [\text{CH}_3 - \text{CHOH} - \text{CH}_3] k [\text{TCIH}^+]_{\text{total}} - [\text{Cl}^-]}{1 + k [\text{Cl}^-]} \quad \dots(14)$$

The proposed mechanism is consistent with all the experimental data obtained in the present study.

Thus, it may be concluded that the reaction between TCI and the alcohol proceeds by a rapid equilibrium formation of a complex between TCI and Cl^- , which then reacts in a slow step with alcohol with the abstraction of the secondary hydrogen atom as a hydride ion.

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