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OXIDATION OF HYDROCARBONS : KINETICS AND MECHANISM OF Ru(III) CATALYSED OXIDATION OF TOLUENE AND SUBSTITUTED TOLUENES BY TRICHLOROISOCYANURIC ACID (TCCA)

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The kinetics of Ru(III) chloride catalysed oxidation of toluene, *o*-chloro toluene, *m*-chloro toluene, *p*-chloro toluene, *o*-nitro toluene, *m*-nitro toluene and *p*-nitro toluene by trichloroisocyanuric acid (TCCA) in aqueous acetic acid in presence of perchloric acid ($HClO_4$) have been studied. The reaction is zero order with respect to oxidant [TCCA]. The reaction is first order in substrate and first order in catalyst Ru(III). The reaction is found to be insensitive towards the change in the acid concentration. An increase in the percentage of acetic acid retards the rate. Effect of temperature has been studied and various thermodynamic parameters are evaluated.

Taking into the observed kinetic data a suitable mechanism and the rate law of the type, Rate = k_2k_1 substrate] [Ru(III)] is postulated.

Key Words : Trichloroisocyanuric Acid; Toluenes; Kinetics and Mechanism of Oxidation; Ru(III) Catalysed

INTRODUCTION

OXIDATION of toluene and substituted toluenes by Ce^{4+} has been studied.[1-3] Cullis *et al.* [4,5] reported the oxidation of toluene and its derivatives by MnO_4^-. Oxidation of toluenes by $Co(ClO_4)_3$ has been reported by Cooper[6,7] Cr^{6+} oxidation of toluenes has been studied by Ogata[8] and Radhakrishnamurti[9] Oxidation of toluenes by V^{5+} has been reported by Radhakrishnamurti.[10,11] Phenyliodoso acetate (PIA) oxidation of toluene and substituted toluenes has been reported by Pati.[12] In continuation to our work on catalysed oxidation of toluene and substituted toluenes by Potassium bromate by Pati[13] in this present communication we are reporting the Ru(III) catalysed oxidation of toluene and substituted toluenes by TCCA in aqueous acetic acid medium in presence of perchloric acid.

MATERIALS AND METHODS

All the reagents used were extra pure. Standard iodometric procedure was adopted for monitoring the progress of the reaction and also for estimating trichloroisocyanuric acid (TCCA).

Product Analysis

Under our experimental conditions the product of oxidation as found to be corresponding benzaldehydes (major) and benzoic acid (minor) as confirmed by TLC

and spot test. The spot test for benzaldehyde was done by treating the product with 5 per cent aqueous solution of phosphomolybdic acid and a drop of concentrated ammonia solution. A blue-green colour developed.

For benzoic acid, a red colour appeared after treatment of the sample with five drops of saturated benzene solution of rhodamine B and one drop of 1 per cent uranyl acetate solution.

Effect of varying [Oxidant] on the Reaction Rate

The dependence of the reactions on the oxidant concentration has been determined by studying the reaction at different initial oxidant concentrations and it was found to have zero order dependence on the oxidant concentration from the linearity of the plots of percentage of reaction versus time and constancy in the zero order rate constants (Table I).

TABLE I

Effect of varying [oxidant] on the reaction rate
[S] = 0.005M, [$HClO_4$] = 0.01M, [Ru(III)] = 1.538×10^{-5}M, HOAc = 50 per cent (v/v), Temp. = 35 °C.

Substrate	$10^4 \times$ [0]/M	$10^5 \times k_0$/M sec^{-1}
Toluene	2.62	87.4
	5.29	88.2
	9.63	89.1
	15.90	88.3
m-Chloro toluene	2.39	17.9
	4.19	17.5
	8.93	17.8
	14.58	17.9
p-Chloro toluene	2.27	1.4
	5.08	1.4
	10.20	1.4

Effect of Varying [Substrate] on the Reaction Rate

The effect of change in the substrate concentration on the kinetics has been determined by varying initial substrate concentration for a number of substrates. An increase in the substrate concentration increases the rate of the reaction (Table II). The plots of log k_0 versus log [*S*] are linear with unit slope (Fig. 1), confirming an unit dependence of the reaction kinetics on the substrate concentration.

Effect of Acidity

The effect of change in the concentration of perchloric acid on the reaction kinetics has been investigated. An increase in the concentration of $HClO_4$ has only a marginal effect on the reaction pointing to the absence of participation of acid in

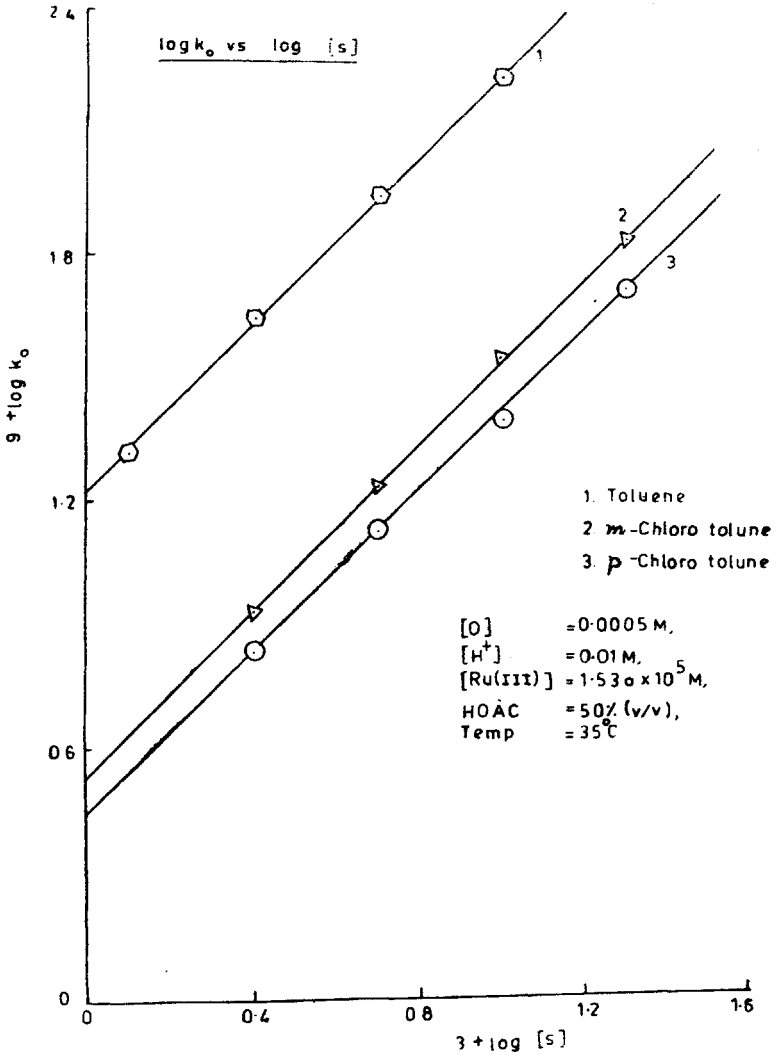


FIG 1

the rate determining step (Table III). The plots of log k_0 versus log [H^+] are linear with fractional slope (Fig. 2).

Effect of Catalyst on the Reaction Rate

The effect of change in the concentration of catalyst, Ru(III) chloride has been investigated. An increase in the concentration of Ru(III) chloride increases the rate of the reaction. The plots of log k_0 versus log [Ru^{3+}] are linear with unit slope confirming an unit dependence on Ru(III) (Table IV).

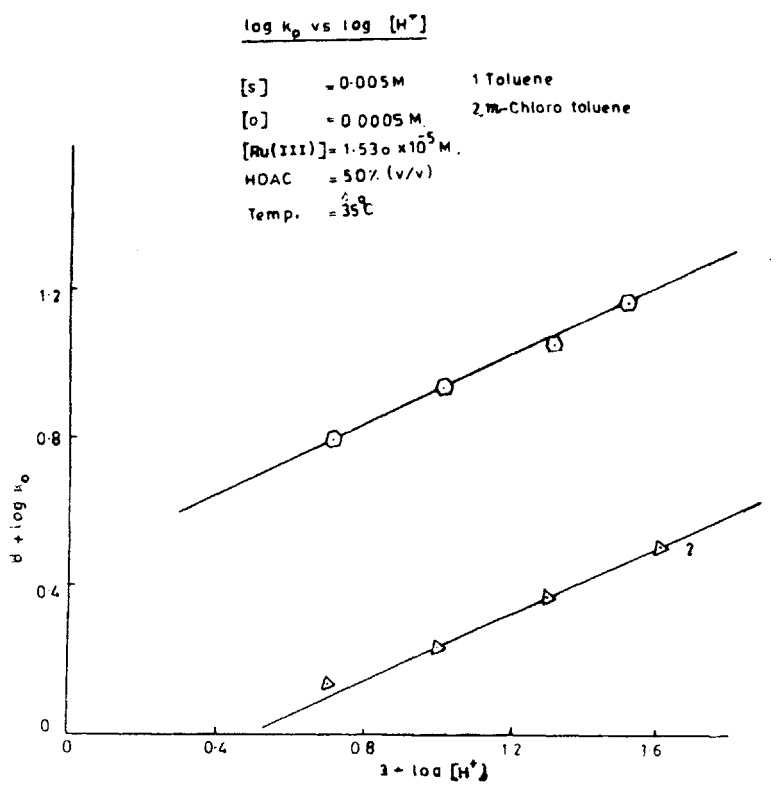


FIG 2

TABLE II

Effect of varying [substrate] on the reaction rate
[O] = 0.0005M, [$HClO_4$] = 0.01M, [Ru(III)] = 1.538 × 10^{-5}M,
HOAc = 50 per cent (v/v), Temp. = 35°C.

Substrate	10^3 × [S]/M	10^5 × k_0/M sec^{-1}	10^5 × k_1/sec^{-1} ($k_1 = k_0$/[S])
Toluene	1.25	21.1	168.8
	2.52	44.7	177.4
	5.00	88.2	176.4
	10.00	175.0	175.0
m-Chloro toluene	2.51	8.6	34.3
	5.05	17.5	34.7
	10.00	36.3	36.3
	20.00	70.8	35.4
p-Chloro toluene	2.50	0.7	2.8
	5.00	1.4	2.8
	10.00	2.6	2.6
	20.00	5.4	2.7

TABLE III

Effect of varying $[HClO_4]$ *on the reaction rate*
[S] = 0.005M, [O] = 0.0005M, [Ru(III)] = 1.538×10^{-6}M, HOAc = 50 per cent (v/v), Temp. = 35 °C.

Substrate	$10^2 \times [HClO_4]$/M	$10^7 \times k_0$/M sec^{-1}
Toluene	0.50	6.3
	1.00	8.8
	2.00	11.8
	4.00	15.4
m–Chloro toluene	0.50	1.4
	1.00	1.8
	2.00	2.4
	4.00	3.3

TABLE IV

Effect of varying catalyst [*Ru(III)*] *on the reaction rate*
[S] = 0.005M, [O] = 0.0005M, $[HClO_4]$ = 0.01M, HOAc = 50 per cent (v/v), Temp. = 35 °C.

Substrate	$10^6 \times$ [Ru(III)]/M	$10^7 \times k_0$/M sec^{-1}
Toluene	3.85	2.4
	7.69	4.7
	15.38	8.8
	30.76	17.2
m–Chloro toluene	7.69	0.9
	15.38	1.8
	30.76	3.5
	46.14	5.4

Effect of Varying Solvent Composition

The effect of varying solvent composition on the reaction kinetics has been studied by varying the amount of acetic acid in the reaction mixture. It has been observed that increasing proportion of acetic acid has retarding effect on the reaction rate (Table V).

Structure and Reactivity

The zero order rate constants for various toluenes are given in Table VI. The kinetic data reveals that the order of reactivity is toluene > *m*–chloro toluene > *p*–chloro toluene > *o*–chloro toluene > *m*–nitro toluene > *p*–nitro toluene > *o*–nitro toluene.

TABLE V

Effect of varying percentage of HOAc on the reaction rate

[S] = 0.005M, [O] = 0.0005M, [$HClO_4$] = 0.01M, [Ru(III)] = 1.538×10^{-5}M, Temp. = 35 °C.

Substrate	% of HOAc (v/v)	$10^7 \times k_0$/M sec^{-1}
Toluene	50	8.8
	60	7.5
	70	5.0
m-Chloro toluene	50	1.8
	60	1.6
	70	1.1

TABLE VI

The zero order rate constants for various substrates

[S] = 0.005M, [O] = 0.0005M, [$HClO_4$] = 0.01M, HOAc = 50 per cent (v/v), [Ru(III)] = 1.538×10^{-5}M, Temp. = 35 °C.

Substrate	$10^5 \times k_0$/M sec^{-1}
Toluene	88.2
m-Chloro toluene	17.5
p-Chloro toluene	13.8
o-Chloro toluene	11.9
m-Nitro toluene	0.9
p-Nitro toluene	0.5
o-Nitro toluene	0.4

The oxidation of xylenes and methoxy toluenes are very fast. The observed fastness of the reaction in case of xylenes and methoxy toluenes, is due to the high electron releasing ability of $-CH_3$ and $-OCH_3$ group by the $+M$ effect. Similar observation has been made by Radhakrishnamurti and Mohapatro[14] in their work on oxidation of toluenes by $KMnO_4$.

The observed reactivity order is well in consonance with the structural effects as electron releasing groups accelerate the reaction and electron withdrawing groups retard the reaction.

ρ-σ^+ Relationship

It was thought worthwhile to correlate the rate constants with substituent constants. Plots of log k_0 versus σ^+ is linear with a ρ^+ value of -3.75 (Fig. 3), which indicates that electron releasing groups accelerate the reaction rate and electron withdrawing groups retard the process. Such kinetic observation was reported in the oxidation of toluenes by PIA by Pati and Dev,[12] in the oxidation of

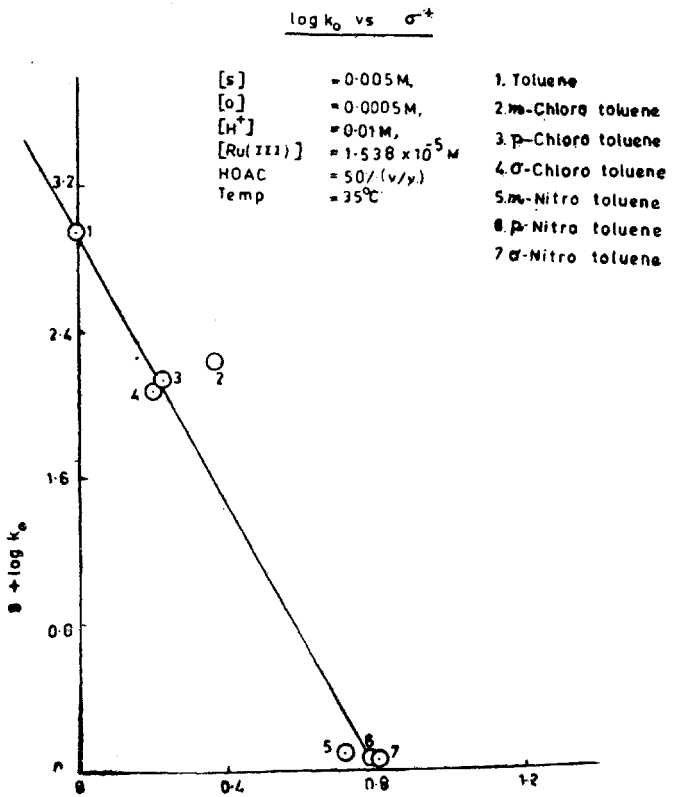


FIG 3

toluenes by pentavalent vanadium by Radhakrishnamurti and Pati.[10] This is quite in consonance with the reaction proceeding through an ionic path.

Effect of Temperature

In order to investigate the effect of temperature and to evaluate the various activation parameters the reaction has been carried out at various temperature (303 °K to 318 °K). Plots of log k_0 versus $1/T$ are found to be linear. The rate constants at different temerature are given in Table VII. The computed values of various activation parameters have been recorded in Table VIII. The lower $\log_{10}$ A values indicate that the rate is much lower than the calculated one from collision theory. This shows that at least one of the following factors is at work :—

(*i*) Endothermic formation of a complex prior to the reaction proper.

(*ii*) The necessity for the ionisation of either or both of the reactants.

(*iii*) Deactivation by solvent molecules.

(*iv*) Stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact and

(*v*) The existence of strong forces of repulsion.

TABLE VII

Effect of varying temperature on the reaction rate
[S] = 0.005M, [O] = 0.0005M, [$HClO_4$] = 0.01M, [Ru(III)] = 1.538×10^{-6}M, HOAc = 50 per cent (v/v)

Substrate	Temperature °K	$10^7 \times k_0$/M sec^{-1}
Toluene	303	5.8
	308	8.8
	313	11.4
	318	15.2
m-Chloro toluene	303	1.4
	308	1.8
	313	2.3
	318	2.6

TABLE VIII

Thermodynamic parameters at 35 °C

Substrate	E_a k J mol^{-1}	$\Delta H^{\neq}$ k J mol^{-1}	$\log_{10}$ A	ΔS J K^{-1} mol^{-1}
Toluene	43.36	40.79	2.59	−217.47
m-Chloro toluene	38.30	35.74	1.04	−233.73

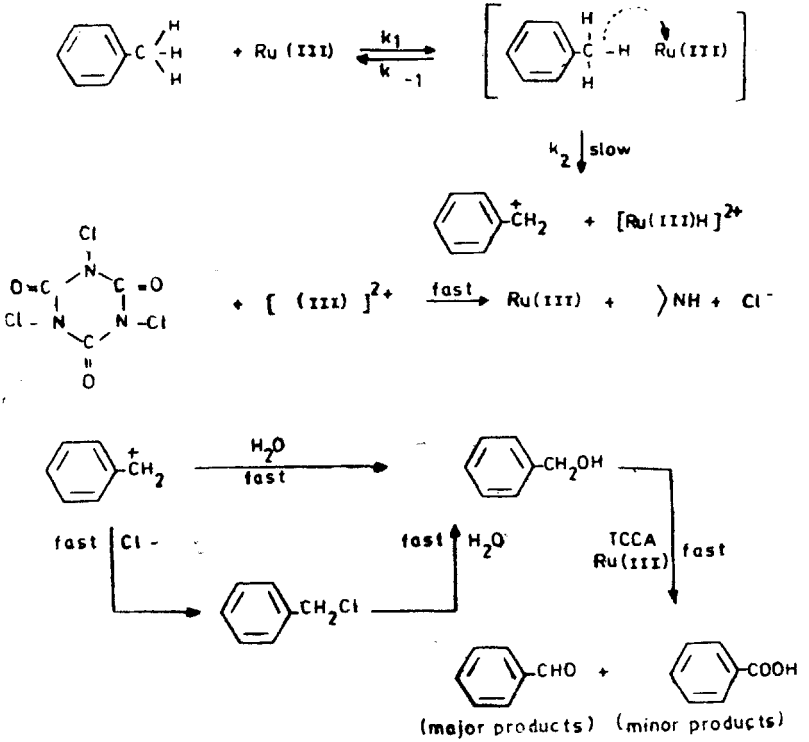
Mechanism and Rate Law

The observed zero order dependence of TCCA, a first order dependence on Ru(III) and first order dependence on substrates clearly show that the rate limiting step of the reaction involves the interaction between Ru(III) and aromatic moiety. Extensive study on the oxidation of these hydrocarbons by various workers reveals that the C–H bond cleavage is the rate limiting step which is well substantiated by kinetic isotope effects. The ρ^+ value of −3.75 points to an ionic mechanism involving two electron transfer. Thus, the negative ρ^+ value indicates the hydride ion transfer from the methyl group of the toluene to Ru(III) moiety forming $[Ru(H_2O)_5H]^{2+}$ without any change in the valency of Ru(III). Such hydride transfer from the organic substrates to the transitional metals has also been invoked in the oxidation of alcohol by $RuCl_3$ by Charman.[15]

The reactivity order is well in consonance with the structural effects in electron releasing group accelerates and electron withdrawing group retards the rate of the reaction. The attack of Ru(III) species on the aromatic moiety is therefore electrophilic.

Taking this into account the mechanism can be explained through outersphere mechanism without change in the valency of Ru(III). The intermediate $[Ru(III)H]^{2+}$ finally gets oxidised by TCCA is a fast step leading to zero order dependence in

TCCA. The detailed steps involved in the mechanism can be pictured as in Scheme–I.



Scheme I

Raw Law

$$\text{Rate} = -\frac{d[\text{TCCA}]}{dt} = \frac{k_2 k_1 [\text{Toluene}] [\text{Ru(III)}]_T}{(1 + k_2 k_1)}$$

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