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KINETICS AND MECHANISM OF Ru(III)-CATALYSED OXIDATION OF UNSATURATED ACIDS BY TRICHLOROISOCYANURIC ACID (TCCA) IN ACID MEDIUM

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Kinetics and mechanism of Ru(III) catalysed oxidation of some unsaturated acids like fumaric acid, maleic acid and acrylic acid by trichloroisocyanuric acid (TCCA) have been studied in aq. acetic-perchloric acid medium. The reaction exhibits unit dependence each in TCCA and Ru(III). Zero order dependence in fumaric acid and maleic acid and fractional dependence in case of acrylic acid have been observed. The reaction is independent of acidity. Addition of Cl^- has no effect on the reaction rate. Various Arrhenius parameters have been evaluated.

Key Words : Trichloroisocyanuric Acid (TCCA); Ru(III)-Catalyst; Oxidation Kinetics; Fumaric Acid; Maleic Acid; Acrylic Acid

INTRODUCTION

OXIDATION of unsaturated acids using various oxidants has received considerable attention. Oxidation of unsaturated acids by various oxidants like Ce(IV),[1] Mn(VII),[2,3,4] chlorate,[5] bromate[6] and PIA[7] has already been reported. Literature survey reveals that TCCA has not been utilised extensively in the oxidation of organic substrates. In continuation to our work on TCCA[8,9] with various organic substrates we now report our results on Ru(III)-catalysed oxidation of unsaturated acids by TCCA in order to throw light in the mechanistic pathways involved in the system in the present communication.

EXPERIMENTAL

All solid substrates were of AnalaR (BDH) grade and used after recrystallisation. Acrylic acid was of AnalaR (BDH) sample and used after redistillation. Trichloroisocyanuric acid (TCCA) was of AnalaR (Fluka) grade. $RuCl_3$ (Johnson Mathey Chemicals, London) solution was standardised by the method of Horiuchi *et al.*[10] Standard iodometric procedure[11] was adopted and the progress of the reaction was monitored by withdrawing 5.0ml of the reaction mixture at regular intervals of time and quenching into acidified potassium iodide solution. The liberated iodine was titrated against standard thiosulphate solution using starch as an indicator.

Kinetic Measurements

All reactions were followed iodometrically upto 70 per cent and rate constants were calculated from the linear plots of log titre versus time. Duplicate kinetic runs showed that the rates were reproducible to within ± 5 per cent error.

RESULTS

The kinetics of Ru(III)-catalysed oxidation of unsaturated acids by trichloroisocyanuric acid (TCCA) exhibits first order pattern upto 70 per cent. The rate constants were calculated from the linear plots of log titre versus time.

Effect of Change in [TCCA] on the Reaction Rate

The effect of TCCA on the reaction rate was studied by changing the initial [TCCA]. The plots of log titre versus time (Fig. 1), for individual runs were linear. The fair constancy in the rates in the range studied indicates a unit dependence of $[\mathrm{TCCA}]_0$ (Table I).

Effect of Change in [Substrate] on the Reaction Rate

The effect of change in $[S]$ on the reaction kinetics was determined by varying $[S]$ in the range studied. The k_{obs} for all $[S]$ was found to be almost constant (Table II). However, in case of acrylic acid there is slight increase in k_{obs} on increasing $[S]_0$.

Effect of Acidity

The reaction was carried out by changing the initial [H⁺] and the rate is unaffected by increasing [H⁺]. This means that the reaction rate is independent of acidity (Table III).

TABLE I

Effect of varying [TCCA] on the reaction rate

$[S] = 0.0005\mathrm{M}$, $[\mathrm{HClO_4}] = 0.01\mathrm{M}$, Solvent = 30 per cent HOAc (v/v),
$[\mathrm{Ru(III)}] = 6.12 \times 10^{-6}\mathrm{M}$, Temp. = 35 °C.

Substrate	10 × [TCCA]M	$10^4 \times k_1$ sec^{-1}
Fumaric acid	2.0	2.80
	4.32	2.44
	11.0	2.10
	20.0	1.28
Maleic aicd	2.5	3.07
	5.2	2.32
	10.7	1.56
	20.9	1.36
Acrylic acid	2.5	4.60
	4.6	2.75
	10.7	1.95
	17.5	0.99

TABLE I(A)

Effect of varying [TCCA] on the reaction rate in the absence of $NaClO_4$

[*S*] = 0.0005M, [$HClO_4$] = 0.01M, Solvent = 30 per cent HOAc (v/v),
[Ru(III)] = 6.12 × 10^{-6}M, Temp. = 35 °C.

Substrate	10^4 × [TCCA]M	10^4 × k_1 sec^{-1}
Maleic acid	2.5	3.07
	5.2	2.32
	10.7	1.56
	20.9	1.36

Effect of varying [TCCA] on the reaction rate in the presence of $NaClO_4$

[*S*] = 0.0005M, [$HClO_4$] = 0.01M, Solvent = 30 per cent HOAc (v/v),
[Ru(III)] = 6.12 × 10^{-6}M, [$NaClO_4$] = 0.05M, Temp. = 35 °C.

Substrate	10^4 × [TCCA]M	10^4 × k_1 sec^{-1}
Maleic acid	3.08	2.04
	5.38	1.70
	10.50	1.40

TABLE II

Effect of varying [substrate] on the reaction rate

[TCCA] = 0.0005M, [$HClO_4$] = 0.01M, Solvent = 30 per cent HOAc (v/v),
[Ru(III)] = 6.12 × 10^{-6}M, Temp. = 35 °C.

Substrate	10^4 × [*S*] M	10^4 × k_1 sec^{-1}
Fumaric acid	5.0	2.44
	50.0	2.50
	100.0	2.52
	200.0	2.52
	400.0	2.45
Maleic acid	5.0	2.32
	50.0	2.63
	100.0	2.51
	400.0	2.08
Acrylic acid	5.0	2.75
	20.0	3.37
	50.0	4.51
	100.0	5.38

Effect of Change in [Ru(III)]

The effect of Ru(III)-catalyst was studied at different [Ru(III)]. Increase in [Ru(III)] increases the reaction rate (Table IV). The plots of log k_{obs} *vs.* log [Ru(III)] are linear with unit slopes (Fig. 2) confirming the unit dependence of [Ru(III)] on the reaction rate.

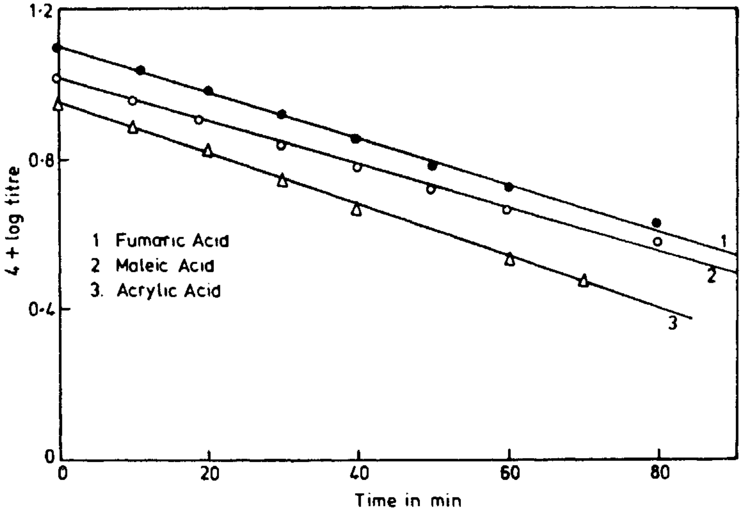


Fig. 1 log titre *vs* Time.

$[S]$ = 5.0×10^{-4}M
[TCCA[= 5.0×10^{-4}M
[Ru(III)] = 6.12×10^{-6}M
$[H^+]$ = 1.0×10^{-2}M
HOAc = 30 per cent (v/v)
Temp. = 35 °C.

TABLE III

Effect of varying [$HClO_4$] on the reaction rate

[S] = 0.0005M, [TCCA] = 0.0005M, Solvent = 30 per cent HOAC (v/v),
[Rv(III)] = 6.12×10^{-6}M, Temp. = 35°C.

Substrate	$10^2 \times [HClO_4]$M	$10^4 \times k_t$ sec^{-1}
Fumaric acid	0.25	2.44
	0.5	2.59
	1.0	2.44
	5.0	2.52
	10.0	2.52
Maleic acid	0.2	2.23
	0.5	2.33
	1.0	2.32
	5.0	1.57
Acrylic acid	0.2	2.48
	1.0	2.75
	5.0	2.90
	10.0	2.95

Role of Solvent

In order to find out the role of solvent composition on the reaction rate, the reaction was carried out at various solvent (HOAC-H_2O) compositions. The k_{obs}

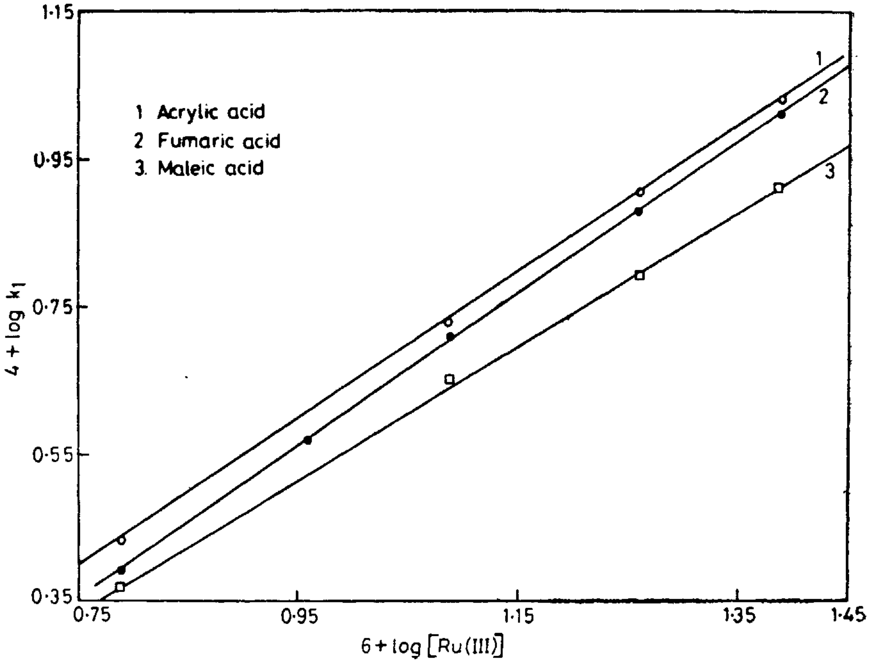


Fig. 2 log k_1 *vs* log [Ru(III)].

[S] = 5.0×10^{-4}M
[O] = 5.0×10^{-4}M
[H+] = 1.0×10^{-2}M
HOAC = 30 per cent (v/v)
Temp. = 35 °C

TABLE IV

Effect of varying [Ru(III)] on the reaction rate

[*S*] = 0.0005M, [TCCA] = 0.0005M, Solvent = 30 per cent HOAc (v/v), [HClO$_4$] = 0.01M, Temp. = 35°C.

Substrate	$10^6 \times$ [Ru(III)]M	$10^4 \times k_1$ sec^{-1}
Fumaric acid	6.12	2.44
	9.18	3.72
	12.24	5.23
	18.36	7.57
	24.48	10.39
Maleic acid	6.12	2.32
	12.24	4.32
	18.36	6.19
	24.48	8.08
Acrylic acid	6.12	2.75
	12.24	5.11
	18.36	7.96
	24.48	10.47

(Table V) indicates that the reaction rate is not sensitive to the change in dielectric constant of the medium.

Effect of [Cl^-]

In order to investigate the role of added chloride ion to the system, the reaction was carried out at different [Cl^-] and the relative rates (Table VI) show that the reaction rate is not affected by the change in [Cl^-]. This may be due to the reason that HOCl is more active as an oxidant than molecular chlorine for these olefinic systems.

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 (308 °K to 323 °K). Plots of log k_0 *vs* $1/T$ are found to be linear. The rate

TABLE V

Effect of varying percentage of acetic on the reaction rate

[S] = 0.0005M, [TCCA] = 0.0005 M, [Ru(III)] = 6.12×10^{-6}M, [$HClO_4$] = 0.01M, Temp. = 35°C.

Substrate	$10^4 \times k_1$ sec^{-1}			
	20%	30%	40%	50%
Fumaric acid	2.65	2.44	2.68	2.23
Maleic acid	2.55	2.32	2.25	2.09
Acrylic acid	2.45	2.75	2.56	2.40

TABLE VI

Effect of varying [*KCl*] *on the reaction rate*

[S] = 0.0005M, [TCCA] = 0.0005M, [Ru(III)] = 6.12×10^{-6}M, [$HClO_4$] = 0.01M, Solvent = 30 per cent HOAc (v/v) Temp. = 35 °C.

Substrate	$10^3 \times$ [KCl]M	$10^4 \times k_1$ sec^{-1}
Fumaric acid	0.0	2.44
	0.5	2.50
	2.5	2.55
	5.0	2.55
	10.0	2.60
Maleic acid	0.0	2.32
	0.5	2.33
	10.0	2.39
	50.0	2.59
	100.0	2.85
Acrylic acid	0.0	2.75
	5.0	3.26
	10.0	3.20
	50.0	3.29
	100.0	3.12

constants at different temperature are given in Table VII. The computed values of various activation parameters have been recorded in Table VII. The plots of $\log_{10}A$ *vs* $1\sqrt{E}$ as well as $\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ area lso linear. 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 :

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

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

(3) Deactivation by solvent molecules.

(4) Stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact.

(5) The existence of strong forces of repulsion.

TABLE VII

Effect of varying temperature on the reaction rate

$[S]$ = 0.0005M, [O] = 0.0005M, [Ru(III)] = 6.12×10^{-6}M, $[HClO_4]$ = 0(01M, Solvent = 30 per cent HOAc (v/v)

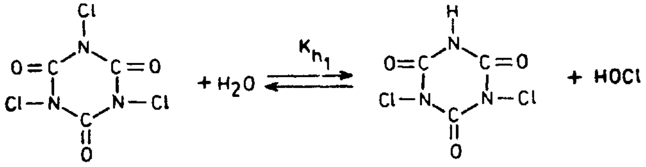
Substrate	$10^4 \times k_1$ sec^{-1}			
	35 °C	40 °C	45 °C	50 °C
Fumaric acid	2.44	3.14	5.26	7.57
Maleic acid	2.33	2.79	3.10	4.38
Acrylic acid	2.75	3.57	4.60	6.77

Arrhenius activation parameters

Substrate	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$-\Delta S^{\neq}$ Jk^{-1} mol^{-1}	$\log_{10} A$
Furmaric acid	60.5	56.6	130.5	6.4
Maleic acid	35.6	33.1	207.6	2.4
Acrylic acid	45.2	42.6	175.3	4.1

DISCUSSION

The order with respect to TCCA in the Ru(III)-catalysed oxidation of unsaturated acids is unity. However, an increase in $[TCCA]_0$ results in a slight decrease in k_{obs} values, but the plots of log titre *vs.* time were perfectly linear. Such an observation has been reported in the case of permanganate oxidation of unsaturated acids.[2,3] The rates observed on changing of initial substrate concentration $[S]$ indicate that the order with respect to $[S]$ in case of fumaric acid and maleic acid is zero. But in the case of acrylic acid an increase in rate with an increase in $[S]$ has been observed and this is attributed to fractional dependence of the substrate. The observed zero order dependence in substrate and the unit dependence in Ru(III) -catalyst establishes the formation of a rigid complex between the substrate and the catalyst. The formation of such a rigid complex is well supported by the observed high negative entropy values. The complex once formed reacts with the oxidizing species in a rate determining step to give products.



(TCCA) (DCCA)

Scheme 1

$$\mathrm{Ru(III)} + S \overset{K_2}{\rightleftharpoons} \mathrm{C_1}$$

$$\mathrm{C_1} + \mathrm{HOCl} \overset{K_3}{\rightleftharpoons} \mathrm{C_2}$$

$$\mathrm{C_2} \overset{k_4}{\rightarrow} \text{Product}$$

$$\text{Rate} = k_4\,\mathrm{C_2}$$

$$\mathrm{C_2} = \frac{K_3\,\mathrm{C_1}\,[\mathrm{HOCl}]}{[1 + K_3\mathrm{C_1}\,[\mathrm{HOCl}]}$$

$$\mathrm{C_1} = \frac{K_2\,[\mathrm{Ru(III)}]\,[S]}{(1 + K_2\,[S]\,)}$$

$$\mathrm{C_2} = \frac{\dfrac{K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}]}{(1 + K_2\,[S]\,)}}{1 + \dfrac{K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}]}{(\,1 + K_2\,[S]\,)}}$$

$$= \frac{K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}]}{(1 + K_2\,[S]\,) + K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}}$$

$$\text{Rate} = \frac{k_4R_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}]}{(1 + K_2\,[S]\,) + K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{HOCl}]} \qquad \text{...(1)}$$

$$[\mathrm{HOCl}] = \frac{K_{h_1}\,[\mathrm{TCCA}]_T}{(\mathrm{DCCA} + K_{h_1})}$$

Substituting for [HOCl] in eqn. 1, the rate becomes,

$$= \frac{\dfrac{k_4K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,K_{h_1}\,[\mathrm{TCCA}]_T}{(\mathrm{DCCA} + K_{h_1})}}{1 + K_2\,[S] + \dfrac{K_3K_2\,[\mathrm{Ru(III)}]\,[S]\,K_{h_1}\,[\mathrm{TCCA}]_T}{(\mathrm{DCCA} + K_{h_1})}}$$

$$= \frac{k_4\,K_3\,K_2\,[\mathrm{Ru(III)}]\,[S]\,K_{h_1}\,[\mathrm{TCCA}]_T}{(\mathrm{DCCA} + K_{h_1})\,(1 + K_2[S]) + K_3K_2\,[\mathrm{Ru(III)}]\,[S][\mathrm{TCCA}]_T\,K_{h_1}} \qquad \text{...(2)}$$

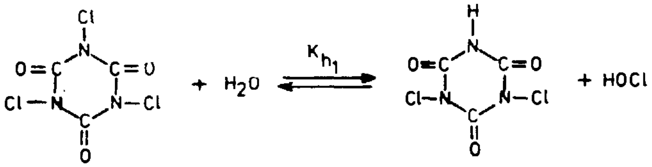
Assuming DCCA term in the denominator to be negligible, eqn. (2) becomes,

$$= \frac{K_{h_1} k_4 K_3 K_2 \,[\mathrm{Ru(III)}]\,[S]\,[\mathrm{TCCA}]_T}{K_{h_1}(\,1 + K_2\,[S]\,) + K_{h_1} K_3 K_2\,[\mathrm{Ru(III)}[\,[S]\,[\mathrm{TCCA}]_T}$$

The above rate law explains all the kinetic orders observed.

In Case of Scheme 2

Assuming the involvement of Ru(V)[7,12] as an active species a separate scheme has been derived where Ru(V) complexes with the substrate. The complex breaks in a fast step to give the product. Radhakrishnamurti *et al.*[6] have observed similar results in case of Ru(III)-catalysed oxidation of unsaturated acids by bromate.



Scheme 2

(TCCA) (DCCA)

$$\mathrm{Ru(III)} + \mathrm{HOCl} \overset{K'_2}{\rightleftharpoons} \mathrm{Ru(V)}$$

$$\mathrm{Ru(V)} + S \overset{K'_3}{\rightleftharpoons} \mathrm{Complex}$$

$$\mathrm{Complex} \overset{k'_4}{\longrightarrow} \mathrm{Product}$$

$$\begin{aligned}
\mathrm{Rate} &= k'_4\,[\mathrm{Complex}] \\
&= k'_4\,K'_3\,[\mathrm{Ru(V)}\,[S] \\
&= k'_4\,K'_3\,K'_2\,[\mathrm{Ru\ (III)}]\,[\mathrm{HOCl}]\,[S]
\end{aligned}$$

$$\begin{aligned}
[\mathrm{Ru(III)}]_T &= [\mathrm{Ru(III)}] + \mathrm{Complex} \\
&= [\mathrm{Ru(III)}] + K'_3\,[\mathrm{Ru(V)}]\,[S] \\
&= [\mathrm{Ru(III)}] + K'_3\,K'_2\,[\mathrm{Ru(III)}]\,[\mathrm{HOCl}]\,[S] \\
&= [\mathrm{Ru(III)}]\,(1 + K'_3\,K'_2\,[\mathrm{HOCl}]\,[S])
\end{aligned}$$

$$[\mathrm{Ru(III)}] = \frac{[\mathrm{Ru(III)}]_T}{(\,1 + K'_3\,K'_2\,[\mathrm{HOCl}]\,[S]\,)}$$

$$\mathrm{Rate} = \frac{k'_4\,K'_3\,K'_2\,[\mathrm{Ru(III)}]_T\,[\mathrm{HOCl}]\,[S]}{(\,1 + K'_3 K'_2\,[\mathrm{HOCl}]\,[S])} \qquad \ldots(3)$$

$$\text{But, } [\mathrm{HOCl}] = \frac{K_{h_1}\,[\mathrm{TCCA}]_T}{([\mathrm{DCCA}] + K_{h_1})}$$

Substituting for [HOCl] in the eqn. (3) the rate becomes,

$$= \frac{\dfrac{k'_4\, K'_3\, K'_2\, [\mathrm{Ru(III)}]_T\, [S]\, K_{h_1}\, [\mathrm{TCCA}]_T}{(\,[\mathrm{DCCA}] + K_{h_1}\,)}}{1 + \dfrac{K'_3\, K'_2\, [\mathrm{S}]\, K_{h_1}\, [\mathrm{TCCA}]_T}{(\,[\mathrm{DCCA}] + K_{h_1}\,)}}$$

$$= \frac{k'_4\, K'_3\, K'_2\, K_{h_1}\, [\mathrm{Ru(III)}]_T\, [S]\, [\mathrm{TCCA}]_T}{(\,[\mathrm{DCCA}] + K_{h_1}\,) + K'_3\, K'_2\, [S]\, K_{h_1}\, [\mathrm{TCCA}]_T} \qquad \ldots(4)$$

Assuming [DCCA] term in the denominator to be negligible, eqn. (4), becomes,

$$= \frac{k'_4\, K'_3\, K'_2\, K_{h_1}\, [\mathrm{Ru(III)}]_T\, [\mathrm{TCCA}]_T\, [S]}{(K_{h_1} + K'_3\, K'_2\, K_{h_1}\, [\mathrm{TCCA}]_T\, [S])}$$

The above rate law explains all the kinetic orders obrerved.

In all the casses the final product is formic acid.

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