

CHEMISTRY

Physical Chemistry

OXIDATION OF ORGANIC COMPOUNDS BY PHENYLIODOSO ACETATE (PIA)

PART VII

KINETICS AND MECHANISM OF Ru(III) CATALYSED OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS IN ACID MEDIUM

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The kinetics and mechanism of Ru(III) catalysed oxidation of aliphatic primary and secondary alcohols by phenyliodoso acetate (PIA) in aqueous acetic acid medium is reported. The reaction is independent of initial concentration of oxidant and there is a fractional dependence with respect to substrate concentration in case of primary alcohols and the dependence is unity in secondary alcohols, which is a novel feature of the reaction. The rate of the reaction is not influenced by perchloric acid concentration in case of unsubstituted primary alcohols whereas substituted and secondary alcohols have direct fractional dependence on acidity. The rate of the reaction is influenced by the increase of acetic acid in case of primary alcohols while the rate is not influenced by changing the acetic acid composition in case of secondary alcohols. The dependence with respect to catalyst is unity in all the alcohols studied. From the Taft constants the ρ^* values are found to be -1.8 and -4.0 for primary and secondary alcohols respectively. The various thermodynamic parameters have been evaluated and a suitable mechanism consistent with the observed results is proposed.

Keywords: Phenyliodoso Acetate; Kinetics; Alcohols; Oxidation; Ruthenium

INTRODUCTION

PAUSACKER *et al.* (1953) have studied the oxidation of ethylene glycols by phenyliodoso acetate (PIA) and stated that the oxidation of primary and secondary alcohols by PIA is not facile. Vaidyanathan and Venkatasubramanian (1973) reported in the oxidation of α -hydroxy acids by PIA that the presence of carboxylic group activates the oxidation of alcoholic group. In continuation with our work (Pati & Mahapatro, 1978, 1979, *in press*; and Pati & Dev, 1979) on oxidation of organic molecules by PIA, in the present communication, we are reporting the results on oxidation of some alcohols in acetic acid medium in presence of perchloric acid, catalysed by Ru(III).

MATERIALS AND METHODS

All the alcohols used were of BDH(AR) grade and were redistilled before use. Analar grade acetic acid was purified by standard methods and solutions were

prepared in conductivity water. Ru(III) solution was prepared according to the standard procedure. Phenyliodoso acetate was obtained by the method due to Boeseken and Schneider (1931). The reaction kinetics have been followed iodometrically as reported earlier. The kinetic runs were carried in duplicate and the rate constants were reproducible within ± 3 per cent error.

RESULTS AND DISCUSSION

Kinetics of the oxidation of primary alcohols like methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, ethoxy ethyl alcohol, 2-chloro ethyl alcohol, methoxy ethyl alcohol, amyl alcohol and secondary alcohols like isopropyl alcohol, secondary butyl alcohol, benzhydrol and fluorene-9-ol was studied in aqueous acetic acid in presence of perchloric acid with phenyliodoso acetate catalysed by Ru(III) chloride.

Effect of Varying Oxidant Concentration on the Reaction Rate

The plots of PIA concentration vs. time are linear showing typical zero order rates for the oxidation of primary and secondary alcohols in presence of Ru (III) chloride in acid medium, the rate constants k_0 are computed from the initial percentages of reactions. The values of $k_0(-dc/dt)$ are fairly constant for different PIA concentrations.

Effect of Varying Substrate Concentration on the Reaction Rate

The computation of the order with respect to substrate concentration presents some interesting features. It is observed that with the increase in concentration of substrate there is enhancement in rate for all the alcohols. In the case of primary alcohols studied however, with the increase in concentration of substrate, the rate of the reaction increases and the plot of $\log k_0$ versus $\log [S]$ is found to be linear with a slope less than unity showing fractional dependence with respect to substrate. Further, in the case of secondary alcohols, it is observed that the reaction shows first order dependence on the substrate concentration, which is confirmed by the constancy in the k_1 first order constant values obtained as $k_1 = (k_0/[S])$.

Effect of Acid

The effect of change of [perchloric acid] on the catalysed oxidation of different alcohols has been studied. It has been observed that the reaction is independent of acid concentration in the range studied i.e., from 0.005 M to 0.2 M for unsubstituted primary alcohols like ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol (Table I). However, the substituted alcohols i.e., ethoxy ethyl alcohol, methoxy ethyl alcohol and 2-chloro ethyl alcohol shows dependence with respect to acid. The increase in concentration of perchloric acid increases the rate in substituted alcohols and the plot of $\log k_0$ versus $\log [H^+]$ is linear with a slope less than unity showing fractional dependence on acidity. Such fractional dependence on acidity by the same type of alcohols can be attributed to the fact that in the case of unsubstituted primary alcohols, the protonation of the alcohol by the acid is difficult, whereas in case of substituted alcohols because of +M effect of $-OCH_3$, $-OC_2H_5$ and $-Cl$, the electronic

TABLE I

Effect of [HClO₄] on the Ru(III) catalysed oxidation of primary and secondary alcohols
 [PIA] = 0.005M; Acetic acid = 10% V/V; [S] = 0.005M; Temp. = 35 °C

Substrate	10 ⁷ [Ru(III)]M	10 ⁵ × k ₀ moles. lit ⁻¹ min ⁻¹ at [HClO ₄]					
		0.01M	0.02M	0.05M	0.1M	0.15M	0.2M
Ethyl alcohol	9.28	1.49	1.23	1.27	1.27	—	1.61
<i>n</i> -propyl alcohol	4.64	1.72	1.57	1.61	1.73	—	1.73
<i>n</i> -Butyl alcohol	4.64	1.32	—	1.24	1.25	—	1.31
Ethoxy ethyl alcohol	4.64	0.2	—	0.22	0.24	0.26	0.32
2-Chloroethyl alcohol	9.28	0.17	—	0.2	0.30	0.39	0.47
Methoxy ethyl alcohol	9.28	0.16	—	0.27	0.46	0.62	0.65
Isopropyl alcohol	9.28	0.42	—	0.57	0.83	1.01	1.44
sec-butyl alcohol	9.28	0.48	—	0.69	0.9	1.16	1.4
Benzhydrol	4.64	2.57	—	2.74	3.22	—	4.5

cloud on the oxygen of the —OH group makes the molecule facile for protonation. Hence, there is participation of both the protonated and unprotonated species in the reaction. The dependence on acidity in case of secondary alcohols is similar to that of substituted primary alcohols. It has been observed that increase in the concentration of acid increases the rate (Table I). The plot of log *k*₀ versus log [H⁺] is linear with a slope less than unity showing fractional dependence with respect to acid, indicating the participation of both protonated and unprotonated species in case of secondary alcohols.

Effect of Ru(III)

In the absence of Ru(III) the reaction is not facile. While the reaction is smooth, in presence of Ru(III). With the increase in concentration of Ru(III), there is proportionate enhancement in the rate (Table II) of the reaction in case of both the primary and secondary alcohols studied. The plots of log *k*₀ vs. log [Ru(III)] (Fig. 1) are linear with unit slope showing the participation of Ru(III) i.e., formation of similar type of complex with the substrate, in primary and secondary alcohols since Ru(III) in acid medium mostly exists as a hexaaqua Ru(III) i.e., [Ru(H₂O)₆]³⁺ which is the active species taking part in the reaction.

Effect of Solvent

In order to determine the effect of change of solvent composition on the rate of reaction, the reaction has been studied at different solvent compositions. It has been observed that in case of all primary alcohols, with the increase in percentage of acetic acid i.e., with the decreasing dielectric constant of the medium, the reaction is accelerated (Table III). The plots of log *k*₀ vs. 1/*D* are linear showing the control of dielectric nature of the medium over the reaction. But in case of secondary alcohols the rate of the reaction is not influenced by the change of solvent composition.

TABLE II

Effect of $[Ru(III)]$ on the oxidation of primary and secondary alcohols by PIA
 $[PIA] = 0.0005M$, Acetic acid = 10% V/V; $[S] = 0.005M$; $[HClO_4] = 0.01M$; Temp. = 35 °C

Substrate	$10^6 k_o$ moles. lit ⁻¹ min ⁻¹ at $10^7 \times [Ru(III)]M$			
	4.64	9.28	13.93	18.57
Ethyl alcohol	0.63	1.49	2.0	2.82
<i>n</i> -propyl alcohol	1.72	3.21	4.4	6.4
<i>n</i> -butyl alcohol	1.32	2.61	3.7	5.17
Methyl alcohol	0.15	0.31	0.44	0.60
Ethoxy ethyl alcohol	0.2	0.37	0.44	0.81
2-Chloro ethyl alcohol	0.08	0.17	0.21	0.27
Methoxy ethyl alcohol	0.08	0.16	0.2	0.3
Isopropyl alcohol	0.18	0.42	0.57	0.73
Sec-butyl alcohol	0.25	0.48	0.7	0.98
Benzhydrol	2.57	4.0	7.51	9.57

PIA vs alcohols

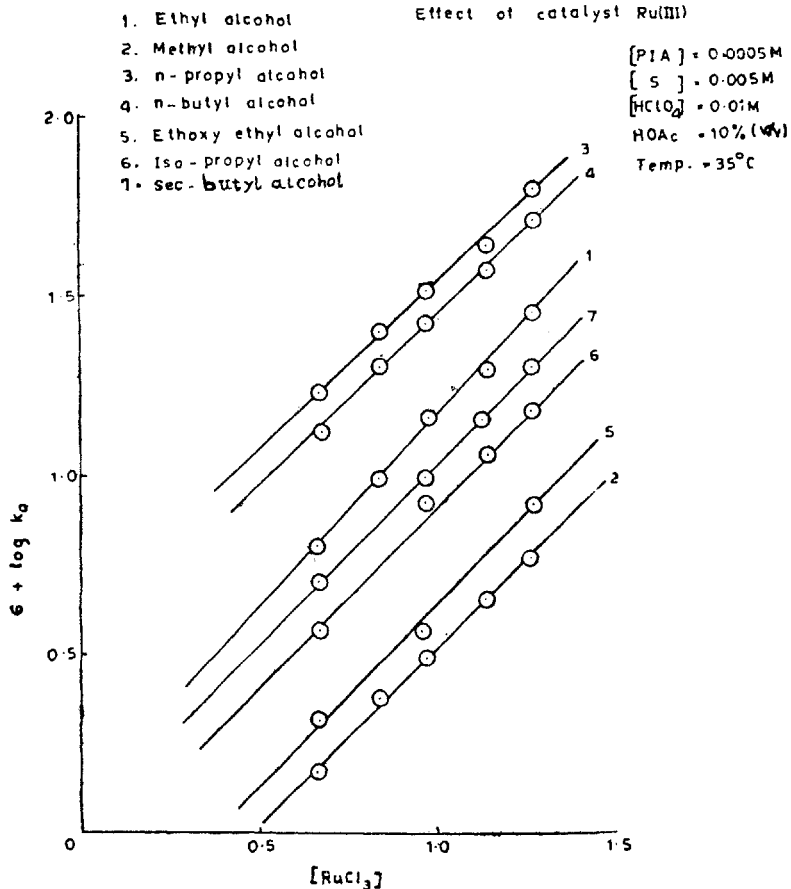
Effect of catalyst $Ru(III)$ 

FIG. 1.

TABLE III

Effect of solvent composition on Ru(III) catalysed oxidation of primary alcohols
 [PIA] = 0.0005M; [S] = 0.005M; [HClO₄] ; 0.01M; Temp. = 35 °C.

Substrate	10 ⁵ × k ₀ moles lit ⁻¹ min ⁻¹ at		
	10% aq.	20% aq.	30% aq.
	HOAc	HOAc	HOAc
Ethyl alcohol**	1.49	2.05	3.08
<i>n</i> -propyl alcohol*	1.72	2.20	3.2
<i>n</i> -butyl alcohol*	1.32	1.71	1.98
Methyl alcohol**	0.31	0.41	0.68
Ethoxy ethyl alcohol*	0.20	0.25	0.34
2-Chloro ethyl alcohol**	0.17	0.20	0.28
Methoxy ethyl alcohol**	0.16	0.19	0.32

*Ru(III) = 4.64 × 10⁻⁷M**Ru(III) = 9.28 × 10⁻⁷M.

Structure Reactivity Relationship

The order of reactivity of the alcohols can be given as *n*-propyl alcohol ≥ amyl alcohol > *n*-butyl alcohol > ethyl alcohol > methyl alcohol all of which are independent of acid concentration, whereas the substituted alcohols which exhibit direct fractional dependence on acidity shows the order of reactivity as ethoxy ethyl alcohol > 2-chloro ethyl alcohol > methoxy ethyl alcohol as seen from Table IV. The plot of log k₀ versus σ* (Fig. 2) is linear with a slope of -1.8. Such negative e* value indicates the operation of usual hydride ion transfer.

TABLE IV

Structure reactivity of catalysed oxidation of alcohols by PIA

[PIA] = 0.005M; [Ru(III)] = 9.28 × 10⁻⁷; Acetic acid = 10% V/V; [S] = 0.005M;
 [HClO₄] 0.01M; Temp. = 35 °C

Substrate	σ*	10 ⁵ k ₀ moles lit ⁻¹ min ⁻¹	10 ² k ₁ min ⁻¹ (k ₀ /[S])
<i>n</i> -propyl alcohol	-0.1	3.21	
Amyl alcohol	-0.13	3.18	
<i>n</i> -butyl alcohol	-0.115	2.61	
Ethyl alcohol	0.0	1.49	
Methyl alcohol	+0.49	0.31	
Ethoxy ethyl alcohol	+0.40	0.37	
2-Chloro ethyl alcohol	+1.05	0.17	
Methoxy ethyl alcohol	+0.52	0.16	
Benzhydrol	-0.23	0.6	8.0
Fluorene-9-ol	—	0.55	1.09
Sec-butyl alcohol	-0.10	0.48	0.96
Iso-propyl alcohol	0.0	0.42	0.84

*Values are taken from Taft, R. W. (1956) *Steric effect in Organic Chemistry* (Ed. M. S. Newman), p. 556. Wiley, New York, 1956.

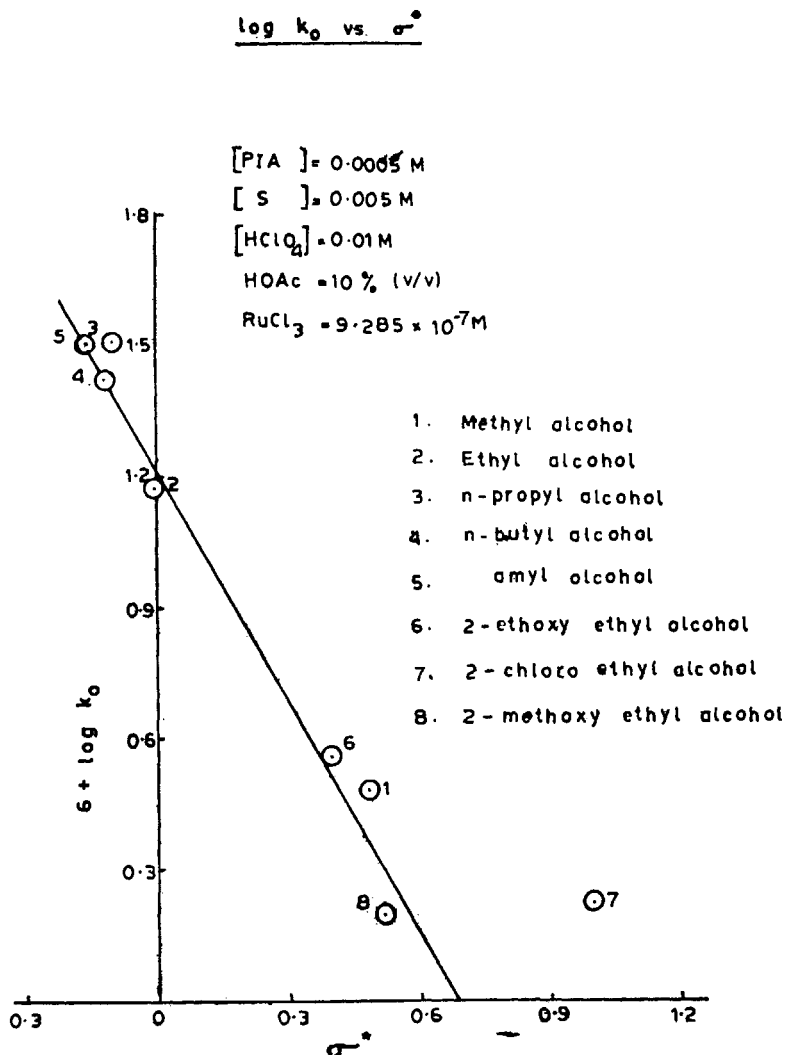


FIG. 2.

The secondary alcohols studied reveals the order of reactivity as benzhydrol > secondary butyl alcohol > iso-propyl alcohol > fluorene-9-ol, as seen from Table IV. Usually fluorene-9-ol is more reactive compared to benzhydrol. But in the present system, fluorene-9-ol is less reactive than the benzhydrol which may be due to the fact that the —OH group in case of fluorene-9-ol is attached to a —CH group which is a part of the ring. As fluorene-9-ol is a bulky molecule, it may not be possible for the Ru(III) to accommodate it in its sphere of ligands which causes the retardation in the rate of oxidation of fluorene-9-ol. The plot of $\log k_1$ vs σ^* (Fig. 3) is linear with a slope —4.0. Such negative e^* value is in consonance with the hydride ion abstraction.

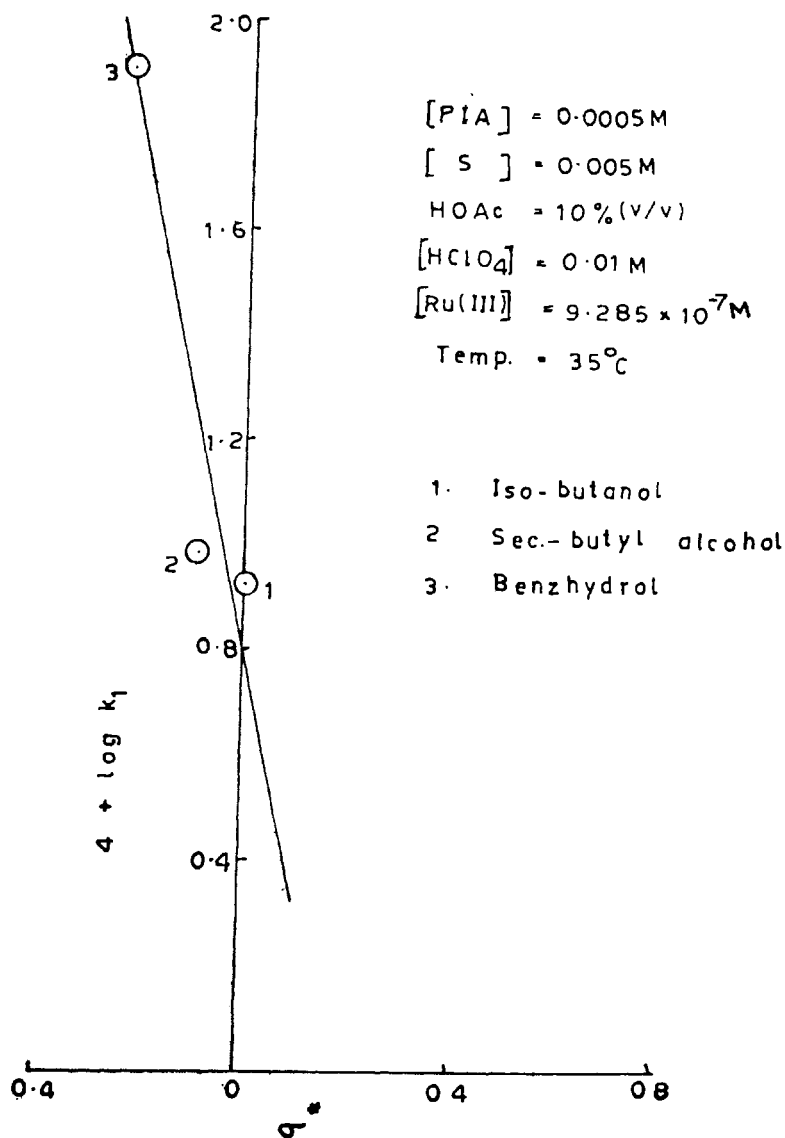
log k_1 vs σ^- 

FIG. 3.

Effect of Temperature

The reaction has been observed at three different temperatures i.e. 30°, 35° and 40 °C. The plots of $\log k_0$ vs. $1/T$ are linear. The different thermodynamic parameters have been calculated and given in Table V.

TABLE V

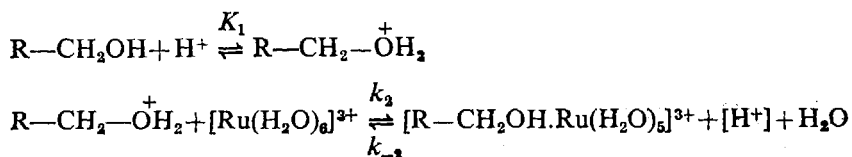
Arrhenius parameters for the Ru(III) catalysed oxidation of primary and secondary alcohols by phenyliodoso acetate (PIA)

[PIA] = 0.0005M; [HClO₄] = 0.01M; [S] = 0.005M; [Ru(III)] = 9.28 × 10⁻⁷M;
Acetic acid = 10% V/V

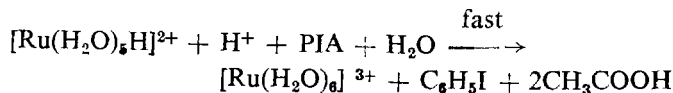
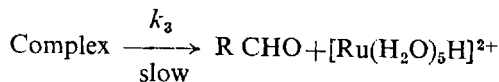
Substrate	ΔE_a^\ddagger K. J. mol ⁻¹	ΔH^\ddagger K. J. mol ⁻¹	ΔS^\ddagger K. J. mol ⁻¹
Ethyl alcohol	36.94	34.4	-257.3
<i>n</i> -propyl alcohol	58.53	55.96	-181.0
<i>n</i> -butyl alcohol	62.38	60.84	-166.9
2-methoxy ethyl alcohol	34.56	32.02	-283.5
2-ethoxy ethyl alcohol	55.46	52.92	-208.9
2-chloro ethyl alcohol	73.97	71.43	-154.8
Isopropyl alcohol	47.54	44.99	-233.5
Sec. butyl alcohol	54.33	51.79	-210.2

Mechanism and Rate Law

The reaction exhibited zero order dependence with respect to [PIA] and first order dependence with respect to [Ru(III)]. The dependence with respect to substrate is fractional in primary alcohols and unity in case of secondary alcohols. The dependence on acidity differs i.e., in case of unsubstituted primary alcohols it is independent of acid concentration whereas in case of substituted and secondary alcohols, there is direct fractional dependence on acidity. Such deviation in the acid concentration may be analysed in the light of protonation of alcohols. Hence the mechanism can be envisaged on the contribution of acid. The participation of both protonated and unprotonated alcohols which forms the complexes with [Ru(III)] leads to fractional dependence on acidity. Hence, the alcohol forms an intermediate complex with Ru(III) which breaks in a rate determining step with a hydride ion transfer from alcohols to Ru(III) leading to a carbonyl compound and [Ru(III) H]²⁺ through an outersphere mechanism. Such abstraction of hydride ion from the α -carbon of alcohol by transition metal in acid medium has been earlier invoked by Charman (1967). This [Ru(III) H]²⁺ reacts in a fast step in acid medium with PIA and finally being reconverted to [Ru(III)]³⁺. Thus the transfer of hydride ion leads to an outersphere mechanism without any valency change in [Ru(III)]³⁺ species in the rate determining step which breaks down in a fast step with PIA in acid medium, which explains the unit dependence on [Ru(III)] and independence of [PIA]. The detail steps of the mechanism can be given as :



Complex (C)



$$[\text{C}]\{k_3 + k_{-2}[\text{H}^+]\} = k_2[\text{SH}^+][\text{Ru}(\text{III})]$$

$$\text{Complex} = \frac{k_2[\text{SH}^+][\text{Ru}(\text{III})]}{k_3 + k_{-2}[\text{H}^+]}$$

$$[\text{Ru}(\text{III})]_{\text{Total}} = [\text{Ru}(\text{III})] + \text{Complex}$$

$$\begin{aligned} [\text{Ru}(\text{III})]_{\text{Total}} &= [\text{Ru}(\text{III})] + \frac{k_2[\text{SH}^+][\text{Ru}(\text{III})]}{k_3 + k_{-2}[\text{H}^+]} \\ &= \frac{[\text{Ru}(\text{III})]\{k_3 + k_{-2}[\text{H}^+] + k_2[\text{SH}^+]\}}{k_3 + k_{-2}[\text{H}^+]} \end{aligned}$$

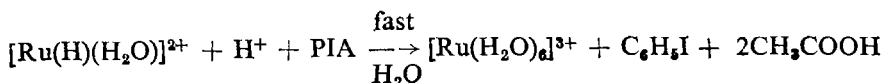
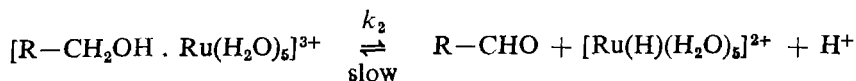
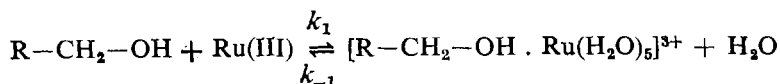
$$[\text{Ru}(\text{III})] = \frac{[\text{Ru}(\text{III})]_{\text{Total}}\{k_3 + k_{-2}[\text{H}^+]\}}{k_3 + k_{-2}[\text{H}^+] + k_2[\text{SH}^+]}$$

$$\begin{aligned} \text{rate} &= \frac{k_3 k_2 [\text{SH}^+][\text{Ru}(\text{III})]}{k_3 + k_{-2}[\text{H}^+] + k_2[\text{SH}^+]} \\ &= \frac{k_3 k_2 k_1 [\text{S}][\text{H}^+][\text{Ru}(\text{III})]_{\text{Total}}}{k_3 + k_{-2}[\text{H}^+] + K_1 k_2 [\text{S}][\text{H}^+]} \\ &= \frac{k_3 k_2 K_1 [\text{S}][\text{H}^+][\text{Ru}(\text{III})]_{\text{Total}}}{k_3 + [\text{H}^+]\{k_{-2} + K_1 k_2 [\text{S}]\}} \end{aligned}$$

As the order with respect to substrate is unity in case of secondary alcohols in the concentration range studied the $[\text{S}]$ in the denominator can be neglected. Thus the rate expression for secondary alcohols can be postulated as:

$$-d[\text{PIA}]/dt = \frac{k_3 k_2 K_1 [\text{S}][\text{H}^+][\text{Ru}(\text{III})]_{\text{Total}}}{k_3 + k_{-2}[\text{H}^+]}$$

This equation explains all the observed facts i.e. fractional dependence on acidity, unit dependence on $[\text{Ru}(\text{III})]$ and $[\text{substrate}]$ and independence of $[\text{PIA}]$. The different steps of the reaction in case of unsubstituted primary alcohols were:



Thus the rate expression can be derived as:

$$\begin{aligned}
 (k_{-1} + k_2) (\text{Complex}) &= k_1[\text{R-CH}_2\text{OH}] [\text{Ru(III)}] \\
 (\text{Complex}) &= \frac{k_1[\text{R-CH}_2\text{OH}][\text{Ru(III)}]}{(k_{-1} + k_2)} \\
 [\text{Ru(III)}]_{\text{Total}} &= [\text{Ru(III)}] + \frac{k_1[\text{R-CH}_2\text{OH}][\text{Ru(III)}]}{(k_{-1} + k_2)} \\
 &= \frac{[\text{Ru(III)}]\{k_{-1} + k_2 + k_1[\text{R-CH}_2\text{OH}]\}}{k_{-1} + k_2} \\
 \text{Ru(III)} &= \frac{[\text{Ru(III)}]_{\text{Total}}(k_{-1} + k_2)}{k_{-1} + k_2 + k_1[\text{R-CH}_2\text{OH}]} \\
 \text{rate} &= k_2(\text{Complex}) \\
 &= \frac{k_2 k_1 [\text{R-CH}_2\text{OH}][\text{Ru(III)}]_{\text{Total}}}{k_{-1} + k_2 + k_1[\text{R-CH}_2\text{OH}]}
 \end{aligned}$$

This rate expression explains the observed facts of unit dependence on [Ru(III)], fractional dependence on [substrate] and independence on [acid] and [PIA].

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