

## Ruthenium(III) catalyzed oxidation of 1-phenylethanol and substituted 1-phenylethanols by phenyliodosoacetate

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**Abstract.** Ruthenium(III) catalysed oxidation of 1-phenylethanol and substituted 1-phenylethanols by phenyliodosoacetate (PIA) in acetic acid is studied and a probable mechanism suggested. The proposed mechanism involves the formation of a complex of Ru(III) and (PIA) which reacts with the substrate, S, in a slow step. Spectrophotometric evidence for this complex is presented. Studies on the effect of substituents suggest a transition state involving a  $\pi$ -complex.

**Keywords.** Oxidation; 1-phenylethanol; Ru(III) catalyst; phenyliodosoacetate.

### 1. Introduction

Organic substrates like diols, cyclanols and unsaturated systems are oxidized by phenyliodosoacetate (PIA) in the presence of Ru(III) (Radhakrishnamurti and Panda 1979; Pati and Dev 1982). In the present work oxidation of 1-phenylethanol and substituted 1-phenylethanols has been investigated using Ru(III) chloride as the catalyst.

Oxidants like permanganate, chlorine and peroxydisulphate oxidize Ru(III) to higher oxidation states (Cotton and Wilkinson 1972). Of these,  $\text{Ru}^{6+}$ ,  $\text{Ru}^{7+}$  and  $\text{Ru}^{8+}$  exist only in alkaline medium (Connick and Hurley 1952). A solution of  $\text{RuCl}_3$  in acetic acid shows an absorption maximum at 460 nm (figure 1a). A mixture of  $\text{RuCl}_3$  and excess of PIA shows an absorption maximum at 385 nm (figure 1b). PIA absorbs below 320 nm (figure 1c). The spectral pattern does not change on adding 1-phenylethanol to  $\text{RuCl}_3$  in acetic acid (figure 1a). On adding the substrate to the reaction mixture containing  $\text{RuCl}_3$  and PIA, the spectral pattern is similar to that of  $\text{RuCl}_3$ . This suggests that the catalyst is released from the complex during the course of the reaction. EPR studies reveal the same splitting pattern for both  $\text{RuCl}_3$  and for the mixture of  $\text{RuCl}_3$  and PIA, indicating that there is no change in the oxidation state of Ru(III).

### 2. Experimental

1-Phenylethanol (Fluka) and ruthenium(III) chloride [Johnson Matthey (London)] were used as such. Acetic acid (BDH, AR) was purified by the method due to Orton (Orton and Bradfield 1950), potassium permanganate being used instead of chromic acid. The fraction boiling between 117° and 118°C (freezing point = 16.4°C) has been

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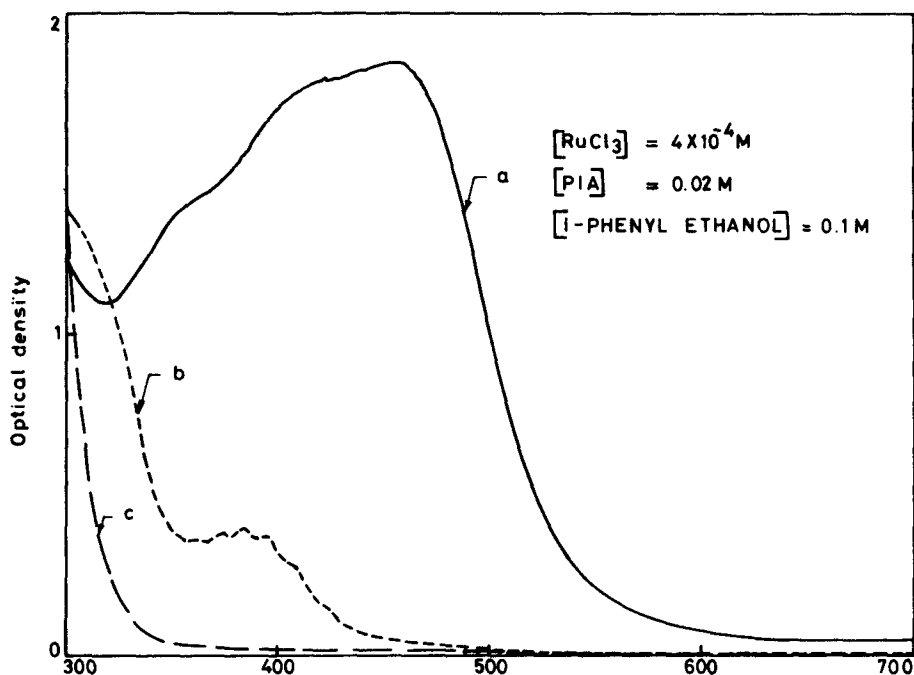


Figure 1. Absorption spectra of a.  $\text{RuCl}_3$  in acetic acid and a mixture of  $\text{RuCl}_3$  and 1-phenylethanol, b. a mixture of  $\text{RuCl}_3$  and excess of PIA, and c. PIA alone in acetic acid.

used. Phenyliodosoacetate (melting point =  $158^\circ\text{C}$ ) was prepared by the modified method of Boeseken (Boeseken and Schneider 1931). Solutions of ruthenium(III) chloride in acetic acid were standardised by the method of Horiuchi (Horiuchi and Ichiyo 1970). All the reactions have been carried out in glacial acetic acid at  $35 \pm 0.1^\circ\text{C}$ . The progress of the reaction was monitored by determining the concentration of unreacted PIA, iodometrically, at any instant as a function of time.

### 3. Results and discussion

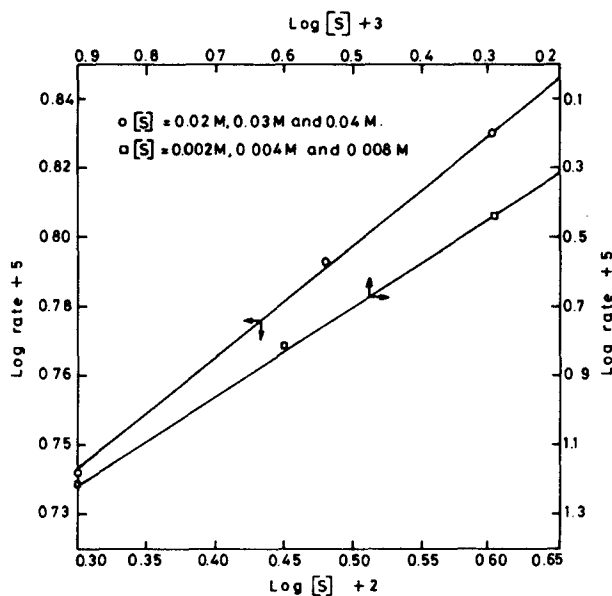
The product of the reaction is found to be acetophenone by TLC, GLC and from the melting point of the 2,4-dinitrophenylhydrazone ( $250^\circ\text{C}$ ). The reaction follows 1:1 stoichiometry under all conditions, i.e. whether PIA or alcohol is in excess. The amount of ketone formed corresponds to that of PIA consumed. The concentration of the ketone has been determined spectrophotometrically by measuring the absorbance at 500 nm of a wine-coloured quinonoid compound (Lappin and Clark 1951) obtained by the action of KOH on a solution of the 2,4-dinitrophenylhydrazone in alcohol. The phenylhydrazine is not affected by the alkali and it absorbs only at 255 nm and 350 nm. The reaction is found to be first order in PIA and first order in catalyst (table 1). The order in substrate is variable being fractional at low concentrations (figure 2) and zero (table 1) at high concentrations ( $> 0.1 \text{ M}$ ).

The rate of the reaction is not affected by introducing acetophenone in the reaction

**Table 1.** Effect of varying the concentrations of PIA, Ru(III) and substrate on the rate of the reaction.

[PIA] (M)	[S] (M)	[Ru(III)] × 10 <sup>6</sup>	<i>k'</i> × 10 <sup>3</sup> (min <sup>-1</sup> )	<i>k</i> <sub>1</sub> × 10 <sup>-3</sup> (M <sup>-1</sup> min <sup>-1</sup> )
0.006	0.10	2.0	4.88	
0.005	0.10	2.0	5.32	2.55 ± 0.10
0.004	0.10	2.0	5.28	
0.003	0.10	2.0	4.90	
0.010	0.10	2.0	5.30	
0.010	0.10	3.0	7.53	2.59 ± 0.06
0.010	0.10	4.0	10.40	
0.010	0.15	2.0	5.29	
0.010	0.25	2.0	5.06	2.55 ± 0.07
0.010	0.35	2.0	4.95	

Solvent: glacial acetic acid; temperature: 35°C; *k'* = pseudo first order rate constant; *k*<sub>1</sub> = second order rate constant.

**Figure 2.** Plots of log rate versus log [S] for low concentrations of the substrate.

mixture. An equilibrium step involving the formation of acetophenone is therefore unlikely.

If the oxidation of alcohols goes through an electron-deficient transition state, one would expect electron releasing substituents to facilitate oxidation. Various substituted 1-phenylethanols have been employed to investigate the effect of the substituents (figure 3, table 2). The slope ( $\rho$ ) of the Hammett's plot using  $\sigma$  values is  $-0.4$ . The substituent effect though small indicates that the substrate is involved in the rate

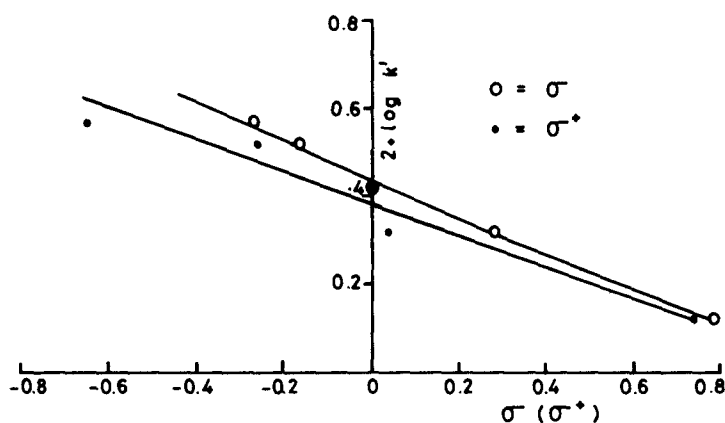


Figure 3. Variation of  $\log k'$  versus  $\sigma$  ( $\sigma^+$ ).

Table 2. Pseudo-first order rate constants for the oxidation of a few *p*-substituted 1-phenylethanol and their corresponding substituent constants. [Substrate] = 0.1 M; [PIA] = 0.01 M; [catalyst] =  $1.0 \times 10^{-5}$  M; solvent = 100%; acetic acid temperature = 35°C.

Substituted 1-phenylethanol	$2 + \log k'$	$\sigma^+$	$\sigma$
1-(4-Nitrophenyl)ethanol	0.120	0.74	0.78
1-(4-Chlorophenyl)ethanol	0.320	0.04	0.28
1-Phenylethanol	0.415	0	0
1-(4-Methylphenyl)ethanol	0.519	-0.26	-0.17
1-(4-Methoxyphenyl)ethanol	0.571	-0.65	-0.27

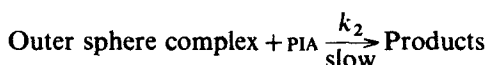
$\sigma^+$  values from Swain C G and Lupton E C 1968 *J. Am. Chem. Soc.* **90** 4328.  
 $\sigma$  values from Hammett L P 1940 *Physical organic chemistry*, 2nd ed. (New York: McGraw-Hill) p. 356.

determining step. However due to the small value of  $\rho$  it cannot be used unequivocally for mechanistic discrimination.

### 3.1 Mechanism and rate law

The absence of polymerization of acrylamide added to the reaction mixture indicates that the reaction is not proceeding by a free radical pathway. For Ru(III) catalyzed oxidation, three types of mechanisms could be proposed.

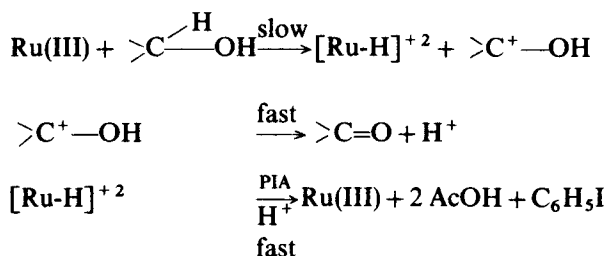
#### Scheme 1



Here the substrate is represented by *S*. This mechanism cannot be valid since  $\text{RuCl}_3$  does not form a complex with 1-phenylethanol (figure 1a). Another mechanism

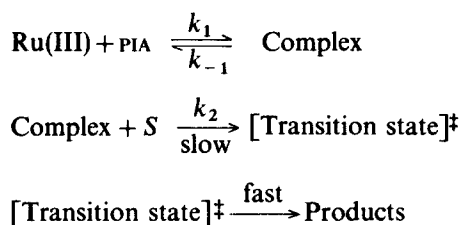
(scheme 2) proposed by Singh (Singh *et al* 1977) to explain the first order in the substrate and zero order in PIA is not applicable for the reaction under consideration since the order with respect to PIA is found to be unity. Moreover IR studies do not show any stretching frequency due to Ru-H at  $2020\text{ cm}^{-1}$  (Hallman *et al* 1968).

## Scheme 2



Scheme 3 accounts for all the experimental observations satisfactorily.

## Scheme 3



The rate expression for the above scheme is given as,

$$\text{Rate} = \frac{k_1 k_2 [\text{S}] [\text{Ru(III)}] [\text{PIA}]}{k_{-1} + k_2 [\text{S}]} \quad (1)$$

Equation (1) can be rearranged to give (2).

$$\frac{1}{\text{Rate}} = \frac{k_{-1}}{k_1 k_2 [\text{S}] [\text{Ru(III)}] [\text{PIA}]} + \frac{1}{k_1 [\text{Ru(III)}] [\text{PIA}]} \quad (2)$$

A plot of  $1/\text{rate}$  versus  $1/[\text{S}]$  for low concentrations (0.02 to 0.08 M) of the substrate at constant concentrations of Ru(III) and PIA is linear (figure 4). From the intercept  $k_1$  is found to be  $2.9 \times 10^3$ . From the slope and the intercept the value of  $k_{-1}/k_2 = 0.014$ . This value is sufficiently small to justify the assumption that  $k_{-1}/k_2 \ll [\text{S}]$  for high concentrations of the substrate (0.1 to 0.35 M) where the order in substrate is found to be zero. Under these conditions the rate expression (1) reduces to

$$\text{Rate} = k_1 [\text{Ru(III)}] [\text{PIA}].$$

However  $[\text{S}]$  being comparable to  $k_{-1}/k_2$  at low concentrations of substrate, a fractional order dependence in the substrate is observed. Evaluation of  $k_2$  is possible if  $k_1/k_{-1}$  is known. Attempts to arrive at this value from spectral measurements were unsuccessful since the absorbance due to Ru(III) is still considerable in the region where a mixture of Ru(III) and PIA absorbs. The postulated mechanism (scheme 3) given

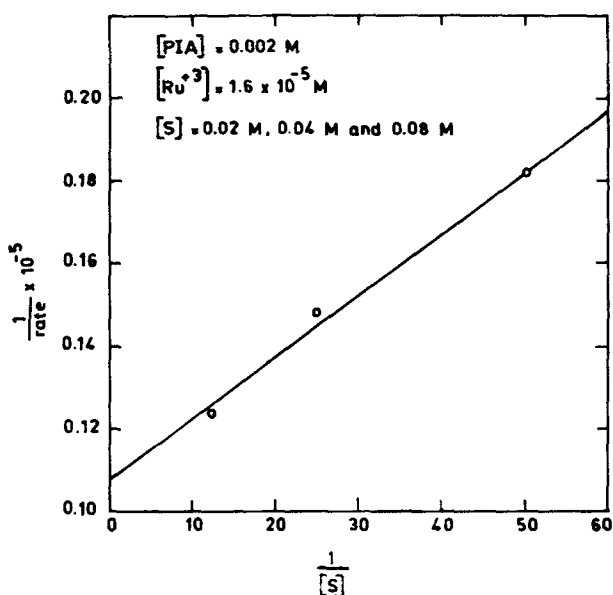


Figure 4. A plot of  $1/\text{rate}$  versus  $1/[S]$ .

above accounts for all the experimental observations in Ru(III)-catalyzed oxidation of 1-phenylethanol.

### Acknowledgements

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