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Kinetics of Os(VIII) & Ru(III) Catalysed Oxidations of Styrene & Stilbene by Acid Iodate

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Osmium (VIII) and Ru(III) catalysed oxidations of styrene and stilbene by iodate in aqueous acetic acid and perchloric acid media are zero order in iodate and first order each in both substrate and catalyst; Os(VIII) catalysed oxidations are insensitive towards any change in acidity whereas for Ru(III) catalysed oxidation, dependence on [H^+] is unity. Increase in the percentage of acetic acid in the solvent medium decreases the rate of reaction in the case of Os(VIII) catalysed reaction, whereas the rate is increased in the case of Ru(III) catalysed reaction.

In earlier papers from our laboratory kinetics and mechanism of uncatalysed and Ru(III), Os(VIII) and Rh(III) catalysed oxidations of styrene and stilbene by phenyl iodosoacetate[1], thallium(III)[2], bromate[3] and periodate[4] were reported. The title investigation is an extension of the earlier work.

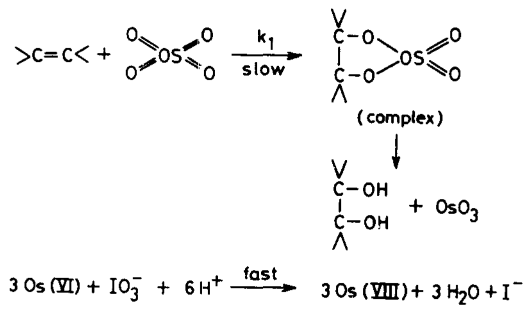
All the chemicals used were of pure quality. Osmium tetroxide was used after allowing proper correction for the alkali present in it. Ruthenium(III) solution was prepared from $RuCl_3$ and standardised by the method of Houriuchi *et al.*[5]. The oxidation reactions were carried out in aq. acetic acid (85%, v/v). The progress of the reaction was followed by estimating the unreacted iodate iodometrically at regular time intervals.

In the case of Os(VIII) catalysed iodate oxidation the overall stoichiometry is 1:4 (substrate:oxidant) leading to benzoic acid and a mixture of benzoic acid and formic acid in the case of stilbene and styrene respectively. However, under the present experimental conditions ([substrate] $\gg$ [oxidant]) the primary products are diols for both the compounds.

In Ru(III) catalysed iodate oxidation of stilbene and styrene the stoichiometry is 1:2 (substrate:oxidant) and the final products, benzaldehyde and benzaldehyde and formaldehyde respectively are obtained in 70% yields as revealed by gravimetric determination of 2, 4-diphenylhydrazones of these aldehydes.

Os(VIII) catalysed oxidation

The order in [oxidant] is found to be zero, and first order each in [substrate] and [Os(VIII)]. The reactions are independent of [H^+]. Increasing the percentage of acetic acid in the solvent medium decreases the rate of reaction. In other words decrease in dielectric constant of the medium decreases the rate of reaction. The reaction has been carried out at 50°, 60° and 70°C. The Arrhenius parameters computed at 60°C are: $E_a = 41.89$ kJmol^{-1}, $\Delta H\ddagger = 39.13$ kJmol^{-1}, $\log_{10}A = 2.03$, $\Delta S\ddagger = -315.4$ JK^{-1}mol^{-1} for styrene; and 47.9 kJmol^{-1}, 45.1 kJmol^{-1}, 13.0 and -194.7 JK^{-1}mol^{-1} for stilbene. The higher reactivity of stilbene over styrene is due to the presence of extra phenyl group.



Scheme 1

Mechanism

In the present investigation Os(VIII) functions as a catalyst mainly through the alternate redox process as a result of which IO_3^- is reduced. The zero order dependence in [oxidant] shows that the oxidant is not taking part in the rate-determining step or in a step prior to the rate-determining step. The first order dependence in [sustrate] and [catalyst] indicates that a complex is formed between substrate and Os(VIII) in the rate-determining step. This complex breaks down in a fast step to give Os(VI) which is finally converted into Os(VIII) in subsequent fast steps leading to zero order dependence in [iodate]. All these observations can be explained on the basis of the mechanism shown in Scheme 1.

Ru(III) catalysed oxidation

The reaction is zero order in [IO_3^-] as revealed by the linear plot of percentage of the reaction versus time. The k_0 values remain invariant over four-fold variation in [iodate]. The zero order rate constants increase linearly with the increase in [substrate] and [Ru(III)] indicating unit dependence in both the cases. This is also revealed by the linear plots with unit slopes of log k_0 versus log [S] and log k_0 versus log [Ru(III)] (Figs 1 and 2, respectively). The rate increases with increase in [H^+] and the dependence is unity. An increase in the proportion of acetic acid in the solvent

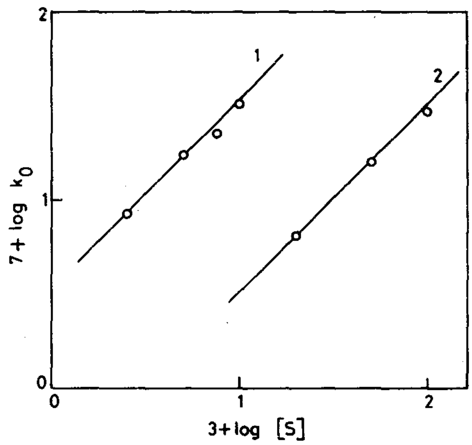


Fig. 1—Plots of log k_0 versus log[S] (1) stilbene, (2) styrene $[IO_3^-] = 0.0005$ mol dm^{-3}, $[HClO_4] = 0.04$ mol dm^{-3}, [Ru(III)] $= 1.54 \times 10^{-5}$ mol dm^{-3}, solvent = HOAc (85%, v/v) and temp. = 60°C)

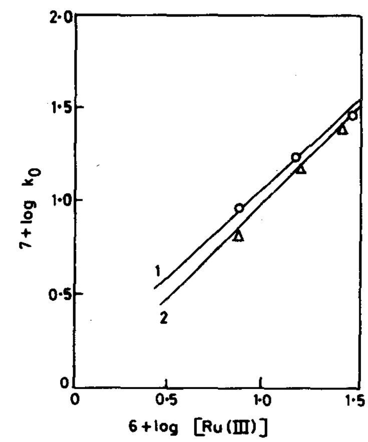


Fig. 2—Plots of log k_0 versus log[Ru(III)] (1) stilbene (2) styrene ([stilbene] = 0.005 mol dm^{-3}, [styrene] = 0.05 mol dm^{-3}, $[IO_3^-] = 0.0005$ mol dm^{-3}, $[HClO_4] = 0.04$ mol dm^{-3}, solvent = HOAc (85%, v/v) and temp. = 60°C)

medium accelerates the rate of oxidation indicating an ion-dipole type of reaction. The Arrhenius activation parameters computed at 60°C are: E_a, $\Delta H\ddagger$, $\log_{10}A$ and $\Delta S\ddagger$, for styrene are 89.45 kJmol^{-1}, 86.6 kJmol^{-1}, 7.74, -106.1 JK^{-1}mol^{-1} and for stilbene 95.8 kJmol^{-1}, 93.0 kJmol^{-1}, 9.76, -68.8 JK^{-1}mol^{-1} respectively.

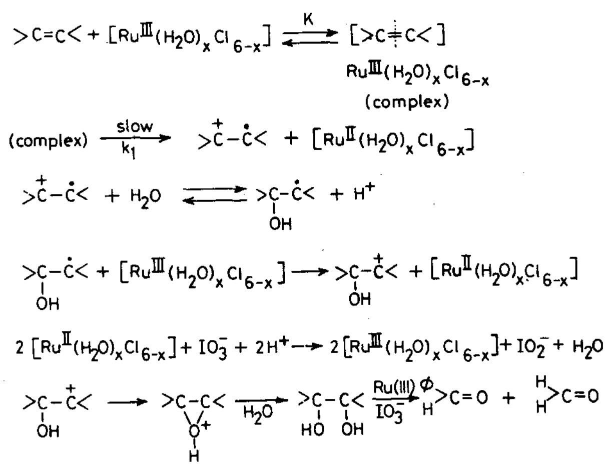
Mechanism

According to the spectral data of Connick and Fine[6], the following species of Ru(III) are present in aqueous solution of $RuCl_3'$, $[Ru(Cl)_5H_2O]^{2-}$, $[Ru(Cl)_4(H_2O)_2]^{1-}$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]$, $[RuCl_3(H_2O)_5]^{2+}$ and $[Ru(H_2O)_6]^{3+}$.

Of these species only $[Ru(H_2O)_6]^{3+}$ is predominant and probably it is the active species[7]. However, the formation of π-complexes between the olefin and the chloro complex species, cannot be ruled out, since such π-complex formation is facilitated by the minimisation of charge on Ru(III). Again the concentration of these chloro complex ions is controlled by water activity which bears an inverse relation with activity of hydrogen ions. Increase in reaction rate with increase in $[H^+]$ is thus attributed to a decrease in water activity and hence increase in the concentration of the chloro complex ions. Keeping in view the above results, the mechanism shown in Scheme 2 can be proposed for Ru(III) catalysed oxidation of styrene and stilbene.

It appears that IO_2^- formed as such participates further and IO_3^- is finally reduced to I^-.

Due to the oxidative decomposition of diols, the ultimate products of oxidation are benzaldehyde in the case of stilbene and both benzaldehyde and formaldehyde in the case of styrene. Such oxidative cleavage of C=C bond in the case of unsaturated compounds has been observed by Lee and Spitzer[8].



Scheme 2

References

1 Panda H P, Ph.D. Thesis, Berhampur University.
2 Radhakrishnamurti P S & Panda H P, *Int J chem Kinet*, **15** (1983) 587.
3 Radhakrishnamurti P S & Panda J K, *React Kinet Catal Lett*, **18** (1981) 357.
4 Radhakrishnamurti P S & Misra S A, *Int J chem Kinet*, **14** (1982) 631.
5 Houriuchi, Yoshizo, Ichijyo & Osamu, *Chem Abstr*, **72** (1970) 50624.
6 Connick D A & Fine F A, *J Am chem Soc*, **82** (1960) 4187.
7 Connick D A & Fine F A, *J Am chem Soc*, **83** (1961) 3414.
8 Lee D G & Spitzer U A, *J org Chem*, **41** (1976) 3644.