Kinetics and Mechanism of Osmium(VIII) Catalyzed Oxidation of Propane-1,3-diol by *N*-Chloro-*p*-toluene Sulfonamide (Chloramine T) in Aqueous Alkaline Medium

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Divya Gupta, Indu Sharma and P. D. Sharma*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India

Osmium(VIII) catalyzed oxidation of propane-1,3-diol by chloramine T in alkaline medium subscribes to hydride ion abstraction from the α-carbon of the diol.

The kinetics and mechanism of osmium(VIII) catalyzed oxidation of propane-1,3-diol (Diol) by *N*-chloro-*p*-toluene sulfonamide (chloramine T, CAT) in aqueous alkaline medium have been studied. The stoichiometry of the reaction corresponds to the reaction as represented by eqn. (1)

$$\mathrm{RNHCl + CH_2OHCH_2CH_2OH \longrightarrow RNH_2 + CH(O)CH_2CH_2OH + HCl} \quad (1)$$

The product 3-hydroxypropan-1-al was identified and confirmed spectrally and by the determination of the mp of its hydrazone derivative.

The kinetics of the reaction were monitored by estimating the chloramine T iodometrically[5] without any interference from the propanediol or its oxidation product. The kinetics results in triplicate were reproducible to within ±4%.

The kinetic orders with respect to the oxidant and catalyst are both one. Toluene-*p*-sulfonamide ($\mathrm{RNH_2}$), one of the reaction products, does not affect the rate of the reaction. This rules out reactivity of RNHCl and $\mathrm{RNCl_2}$ species in view of the following equilibria [eqns. (2) and (3)].[7]

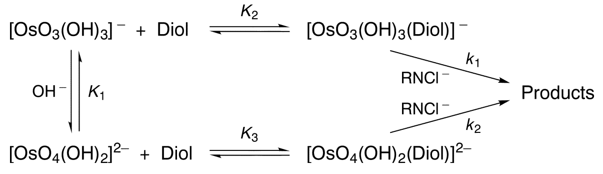
$$\mathrm{2\,RNHCl \rightleftharpoons RNCL_2 + RHN_2} \quad (2)$$

$$\mathrm{RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl} \quad (3)$$

Moreover, the reaction is first order with respect to chloramine T which further rules out $\mathrm{RNCl_2}$ as the reactive form. Generally chloride ion catalysis has been observed in the reactions of chloramine T when RNHCl is considered to be the reactive form. Since no catalysis by chloride ion has been found in this reaction, it also eliminates RNHCl as a reactive form of chloramine T. Since the medium is alkaline, $\mathrm{RNCl^-}$ is taken to be the predominantly reactive form of CAT. This view is also strengthened by the fact that the reaction is unaffected by chloride ion concentration. In fact, this effect of $\mathrm{Cl^-}$ in CAT reactions is taken as a diagnostic for the confirmation of $\mathrm{RNCl^-}$ species as the reactive form.

$\mathrm{[OsO_4(OH)_2]^{2-}}$ is considered to be the predominant osmium(VIII) species in a brown–red solution of osmium tetraoxide in concentrated alkaline medium.[10] This species is converted to $\mathrm{[OsO_3(OH)_3]^-}$ upon dilution of the solution.[11] Since the rate decreases with increasing hydroxide ion concentration, all other species governed by equilibria involving $\mathrm{[OsO_3(OH)_3]^-}$ with $\mathrm{OH^-}$ must be less reactive.

Thus, a reaction mechanism accounting for these reaction events is envisaged as shown in Scheme A.



Scheme A

The loss of chloramine T leads to the rate law (7) or (8)

$$-\frac{\mathrm{d[CAT]}}{\mathrm{d}t}=\frac{(k_1K_2+k_2K_1K_3[\mathrm{OH^-}])[\mathrm{CAT}][\mathrm{Diol}][\mathrm{Os^{(VIII)}}]}{1+K_1[\mathrm{OH^-}]+K_2[\mathrm{Diol}]+K_1K_3[\mathrm{Diol}][\mathrm{OH^-}]} \quad (7)$$

or

$$k=\frac{(k_1K_2+k_2K_1K_3[\mathrm{OH^-}][\mathrm{Diol}]}{1+K_1[\mathrm{OH^-}]+K_2[\mathrm{Diol}]+K_1K_3[\mathrm{Diol}][\mathrm{OH^-}]} \quad (8)$$

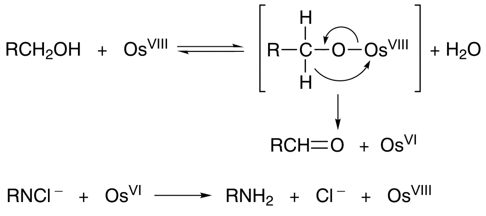
where k is the observed second order rate constant and [Diol] is the free equilibrium concentration of diol.

If the rate dependence on hydroxide ion concentration is any guide, it is logical to negate the contribution of path (k_2) as compared to path (k_1) particularly in view of the rate not attaining a limiting value at higher hydroxide ion concentration. This reduces the rate law (8) to (9).

$$k=\frac{k_1K_2[\mathrm{Diol}]}{1+K_1[\mathrm{OH^-}]+K_2[\mathrm{Diol}]+K_1K_3[\mathrm{OH^-}][\mathrm{Diol}]} \quad (9)$$

Graphical analysis at a variety of hydroxide ion and diol concentrations helped in evaluation of all the kinetic parameters. The value of K_1 ($41.2 \pm 4.0\ \mathrm{dm^3\,mol^{-1}}$) derived from these plots is in agreement with the reported[12] value under almost identical experimental conditions.

It appears in all probability that the act of electron transfer from the diol to the oxidant is *via* the catalyst where the osmium(VIII) species abstracts hydride ion from the α-carbon of the substrate (Scheme B).



Scheme B R = $\mathrm{CH_2CH_2OH}$, $\mathrm{Os^{VIII}} = \mathrm{[OsO_4(OH)_2]^{2-}}$ or $\mathrm{[OsO_3(OH)_3]^-}$

Techniques used: UV–VIS, iodometry, NMR

Tables: 1 Figs: 2 (kinetics plots) Schemes: 1 Refs: 15

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*To receive any correspondence.