Research Article

Kinetics and Mechanism of Electron Transfer Reactions: Osmium(VIII) catalyzed oxidation of phenylphosphinic acid (PhP) by N-chloro-p-toluene sulfonamide (Chloramine-T) in alkaline medium

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Abstract

The kinetics of osmium(VIII) catalyzed oxidation of phenylphosphinic acid (PhP) by N-chloro-p-toluene sulfonamide (CAT) was studied by monitoring the latter iodometrically. A plausible reaction mechanism has been suggested conforming to the rate law.

Keywords: Kinetics, Mechanism, Osmium(VIII), Chloramine-T, Oxidation, Phenylphosphinic acid.

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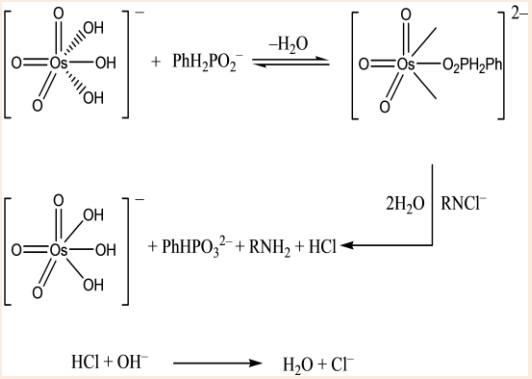


Introduction

The kinetic study of oxidation of phenylphosphinic acid with N-chloro-p-toluene sulfonamide (heretofore written as CAT) in the light of little known chemistry of the substrate in alkaline medium has been studied. The oxidation of phenylphosphinic acid (henceforth written as PhP) by oxidants such as V(V) [1, 2], Cr(VI) [3] and FeL_3^{3+} [4] (where L-bipyridyl or 1,10-phenanthroline) are reported. Oxidation of the acid by permanganate [5] ascribes participation of tautomeric equilibrium involving active and inactive forms of phenylphosphinic acid [4]. Since reactions of phenylphosphinic acid in alkaline medium are slow, probably it appears to be the reason of much less kinetics studies of oxidation of phenylphosphinic acid.

Further, despite extensive studies of alkaline chemistry of chloramine-T [6-18] still much more is required to know about speciation of this oxidant. Osmium(VIII) is usually employed as a catalyst in the reactions of chloramine-T in alkaline medium. The lack of speciation of both catalyst and CAT species respectively requires a detailed analytical approach for reasonable mechanistic proposals.

Such observations prompted us to undertake a detailed kinetic study of the title reaction with the following aims: The foremost requirement is to define and establish more precisely the species of chloramine-T under experimental conditions.

Secondly, does chloramine-T exhibit any intermediate complex formation with the substrate! Thirdly whether or not Osmium(VIII) as a catalyst in such a system acts in a catalyst redox cycle or in an otherwise manner.

Experimental

Materials and method

Solutions of chloramine-T were prepared by dissolving sodium salt of N-Chloro-p-toluene sulfonamide (E. Merck) in twice distilled water. The solutions were stored in brown glass bottles to eliminate decomposition due to diffused photo light. Chloramine-T solutions were standardized iodometrically [18,19]. Osmium tetraoxide (Johnson Matthey) was dissolved in 0.5 mol dm^{-3} NaOH and analyzed iodometrically. Such solutions of Osmium(VIII) are quite stable if concentration of hydroxide ion is kept $\geq$ 0.3 mol dm^{-3} and the solutions are kept at refrigerated temperature (~ 5°C). Other chemicals being either AnalaR or G. R. grade were employed as received.

Twice distilled water was employed throughout the kinetic study, the second distillation was from alkaline permanganate solution in an all glass apparatus. Corning glass vessels painted black from the outside were employed for reaction mixtures ensuring kinetics of the reaction to be free from the effect of diffused photolight.
Spectrophotometric studies for solutions of Os(VIII) showed a broad maximum in the spectral range of 320-360 nm. However, no change in spectrum was observed for $[OH^-]$ > 0.1 mol dm^{-3} and also for the mixture of Osmium(VIII) and chloramine-T.

Kinetic procedure

All the ingredients of the reaction mixture except chloramine-T were taken in flasks which were suspended in a water-bath thermostated at ±0.1°C unless specified otherwise. The reactions were initiated by adding requisite amount of chloramine-T solution into reaction mixtures. Nevertheless, order of addition is without any effect on the kinetics of the reaction. The progress of the reaction was monitored by estimating remaining CAT iodometrically at different time intervals. The iodine liberated by Osmium(VIII) was accounted for in subsequent calculations of concentrations of chloramine-T.

A slow reaction between iodine and phenylphosphinic acid for acid concentrations ~1.0 mol dm^{-3} was reported [20] but no such reaction was observed between phenylphosphinic acid or its oxidation product and iodine under experimental conditions for assaying chloramine-T. Initial rates (k_i, mol dm^{-3} s^{-1}) were computed employing plane-mirror method [21]. Pseudo first order rate constants (k', s^{-1}) were also evaluated for reactions where pseudo first order conditions ([PhP]>>10[CAT]) were maintained. Reactions in tripplicate were reproducible to within ±5%.

Stoichiometry

The stoichiometry of the reaction was determined by taking excess [CAT] over [PhP] in reaction mixtures which were allowed to occur in a thermostated water-bath for ca. 8h. The excess of chloramine-T was determined iodometrically. Such stoichiometric results correspond to a reaction as represented by eqn(1)

$$RNCl^- + C_6H_5H_2PO_2^- \xrightarrow{H_2O} RNH_2 + C_6H_5HPO_3^{2-} + HCl \qquad (1)$$

The stoichiometry of the reaction of CAT and phenylphosphinic acid was similar to that was observed for the reaction of hypophosphorous acid with CAT [22] under almost identical experimental conditions.

Results and Discussions

Chloramine-T dependence

The concentration of Chloramine-T was varied under pseudo first order conditions from 1.0×10^{-3} to 5.0×10^{-3} mol dm^{-3} at fixed concentrations of other reaction components viz. [PhP] = 5.0×10^{-2} mol dm^{-3}, [Os(VIII)] = 5.0×10^{-5} mol dm^{-3}

and [OH^-] = 0.10 mol dm^{-3} at 45°C. Pseudo first order plots were made (Figure 1) and the first order rate constants (k´, s^{-1}) evaluated from such plots were found to be independent of gross analytical concentrations of Chloramine-T conforming first order with respect to chloramine-T (Table 1).

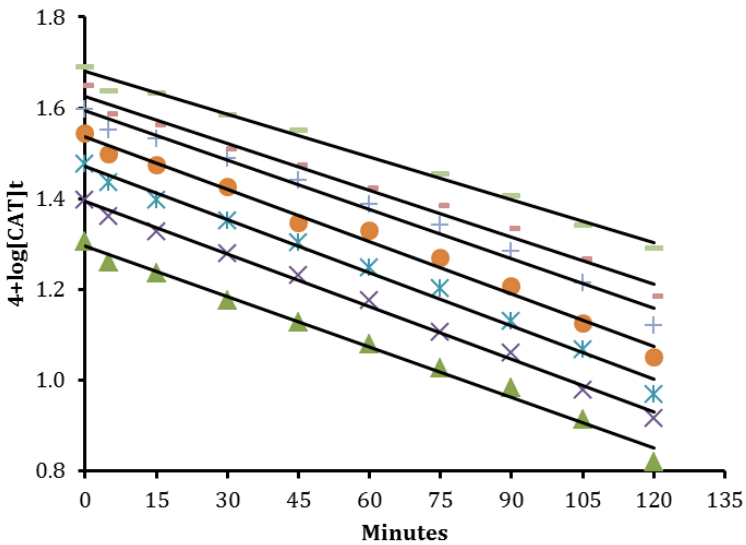


Figure 1 Pseudo First Order Plots in Osmium(VIII) catalyzed oxidation of phenylphosphinic acid by chloramine-T
[PhP] = 5.0×10^{-2} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-5} mol dm^{-3};
[OH^-] = 0.10 mol dm^{-3}; 45°C;
[CAT] = ▲, 2.0×10^{-3} ; ×, 2.5×10^{-3} ; ✳, 3.0×10^{-3} ; ●, 3.5×10^{-3} ;
+ 4.0×10^{-3} ; -, 4.5×10^{-3} ; –, 5.0×10^{-3} mol dm^{-3}

Table 1 Pseudo first order rate constants (k', s^{-1}) and second order rate constants (k, dm^3 mol^{-1} s^{-1}) in the reaction of Chloramine-T and Phenylphosphinic acid

10^2 [PhP] = 5.0 mol dm^{-3}; 10^5 [Os(VIII)] = 5.0 mol dm^{-3}; [OH^-] = 0.10 mol dm^{-3}; 45°C

10^3 [CAT], mol dm^{-3}	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
10^4 k´, s^{-1}	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54	1.54
k, dm^3 mol^{-1} s^{-1}	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1

Phenylphosphinic acid dependence

The concentration of phenylphosphinic acid was also varied from 2.0×10^{-3} to 10.0×10^{-3} mol dm^{-3} at constant concentrations of other reaction ingredients viz. [CAT]= 2.0×10^{-3} mol dm^{-3}, [Os(VIII)] = 5.0×10^{-5} mol dm^{-3} and [OH^-] = 0.075, 0.10 and 0.125 mol dm^{-3} respectively and also at 45, 50, 55 and 60°C, respectively. The rate initially increased with increasing concentration of the substrate and tended to attain a limiting value at higher concentrations (**Figure 2**).

Such a rate dependence of the substrate concentration appears to be complex corresponding to the following empirical rate equation (2).

$$-\frac{d[CAT]}{dt} = \frac{A[PhP][Os(VIII)][CAT]}{B + C[PhP]} \quad (2)$$

where, 'A', 'B' and 'C' are empirical rate constants.

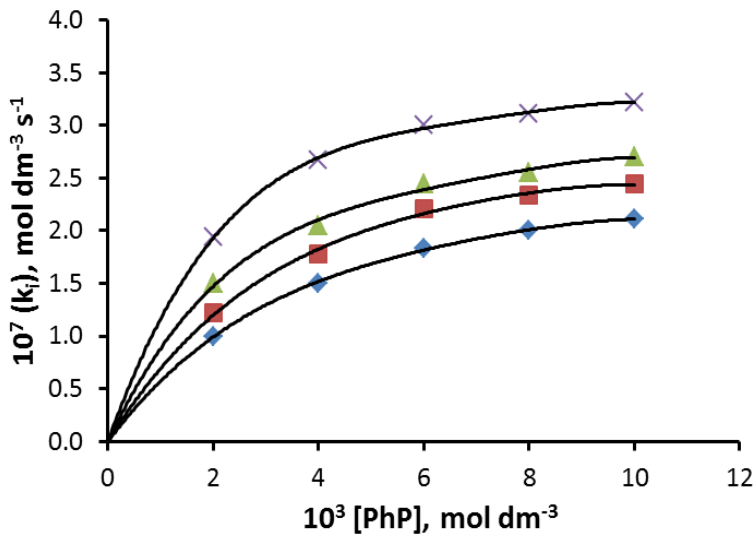


Figure 2 Variation of phenylphosphinic acid in Os(VIII) catalysed chloramine-T reaction
[CAT] = 2.0×10^{-3} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-5} mol dm^{-3};
[OH^-] = 0.075 mol dm^{-3}; ♦, 45°C; ■, 50°C; ▲, 55°C; X , 60°C

Osmium(VIII) dependence

The concentration of Osmium(VIII) was varied from 1.0×10^{-5} to 10.0×10^{-5} mol dm^{-3} at fixed concentrations of other reaction ingredients viz. [CAT] = 2.0×10^{-3} mol dm^{-3}, [PhP] = 2.0×10^{-2} mol dm^{-3} and [OH^-] = 0.10 mol dm^{-3} at 45°C. The plot of first order rate constants (k´, s^{-1}) against the concentration of the catalyst yielded a straight line passing through the origin ascribing first order with respect to the catalyst.

Hydroxide ion dependence

The concentration of hydroxide ion was varied from 2.0×10^{-2} to 1.0×10^{-1} mol dm^{-3} at fixed concentrations of other reaction ingredients viz. [CAT] = 2.0×10^{-3} mol dm^{-3}, [PhP] = 5.0×10^{-2} mol dm^{-3}, [Os(VIII)] = 5.0×10^{-5} mol dm^{-3} and I = 0.5 mol dm^{-3} at 45, 50 and 55°C respectively. The rate decreases with increasing hydroxide ion concentration.

Effect of ionic strength (I)

The effect of ionic strength was studied by employing sodium nitrate at fixed concentrations of other reaction ingredients viz. [CAT] = 2.0×10^{-3} mol dm^{-3}, [PhP] = 5.0×10^{-2} mol dm^{-3}, [Os(VIII)] = 5.0×10^{-5} mol dm^{-3} and [OH^-] = 0.10 mol dm^{-3} at 45°C. The rate remains unchanged with the changing concentration of sodium nitrate, such an observation eliminated any possibility of interaction of similarly charged species of the reactants.

Effect of toluene-p-sulfonamide

The concentration of toluene-p-sulfonamide was varied in the range (1.0×10^{-3} - 1.0×10^{-2}) mol dm^{-3} keeping constant concentrations of other reaction ingredients viz. [CAT] = 2.0×10^{-3} mol dm^{-3}, [PhP] = 5.0×10^{-2} mol dm^{-3}, [Os(VIII)] =

5.0×10^{-5} mol dm^{-3} and [OH^-] = 0.10 mol dm^{-3} at 45°C. The rate remains unaffected by the change in concentration of the sulfonamide. Such an effect of the toluene-p-sulfonamide as a product eliminates its involvement in any equilibrium preceded by the rate determining step.

Effect of chloride ion

The concentration of chloride ion was varied from 0.02 to 0.50 mol dm^{-3} at fixed concentrations of other reaction ingredients viz. [CAT] = 2.0×10^{-3} mol dm^{-3}, [PhP] = 5.0×10^{-2} mol dm^{-3}, [Os(VIII)] = 5.0×10^{-5} mol dm^{-3} and [OH^-] = 0.10 mol dm^{-3} at 45°C. The rate remains unchanged.

It is worth mentioning that chloride ion catalyzes a large number of reactions of chloramine-T including those of hypophosphite and phosphite in acidic medium [22]. However, Cl^- catalysis is missing in reactions of CAT in alkaline medium. Such a difference of Cl^- catalysis indicates that chloramine-T species in acidic and alkaline media react in a different manner. In fact such an effect of chloride ion on the rate had been considered to be a diagnostic approach in making distinction between $RNCl^-$ and RNHCl species of CAT. Since RNHCl considered to be an acidic CAT species which is responsible for Cl^- catalysis via [$RNHCl^{\square+}$....$Cl^{\square-}$] species, $RNCl^-$ being basic CAT species does not show the presence of such a species. Therefore, $RNCl^-$ to be the reactive form of CAT in alkaline medium is justified if such an effect of Cl^- on rate is any guide to make a difference between RNHCl and $RNCl^-$ species of chloramine-T.

Discussion

Chloramine-T being sodium salt is a strong electrolyte [23, 24] in aqueous solution and speciates as governed by equilibria (3) to (7) in acid medium.

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \quad (3)$$
$$RNCl^- + H^+ \rightleftharpoons RNHCl \quad (4)$$
$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2 \quad (5)$$
$$RNHCl + H_2O \rightleftharpoons HOCl + RNH_2 \quad (6)$$
$$HOCl \rightleftharpoons OCl^- + H^+ \quad (7)$$

All these species such as RNHCl, $RNCl_2$ and HOCl are present only in acidic medium [25-27]. Since the order with respect to CAT is one and rate is not affected by toluene-p-sulfonamide, the equilibria (5) and (6) are ruled out. Equilibrium (7) conforms to hydroxide ion catalysis contrary to what is observed in the title reaction. If calculations made by Bishop and Jennings [23] on the decinormal solutions of chloramine-T are any guide, the concentration of $RNCl^-$ is significantly more predominant than [RNHCl] in alkaline medium.

Phenylphosphinic acid similar to hypophosphite is also monobasic and as such $C_6H_5HPO_2^-$ appears to be the most likely species in alkaline medium.

$[OsO_4(OH)_2]^{2-}$ is reported to be a red solution of osmium tetraoxide in strongly alkaline solution [28], the species $[OsO_4(OH)_2]^{2-}$ is converted into $[OsO_3(OH)_3]^-$ in dilute alkaline solution as reported by Sauerbrum and Sandell [29]. Since rate decreases with increasing concentration of hydroxide-ion, all the species subsequent to $[OsO_3(OH)_3]^-$ must be less reactive. Furthermore, an intense brown-red colour appeared in the reaction mixture on mixing solutions of Phenylphosphinic acid and Osmium(VIII) at ~ 5°C whereas mixture of either of these reagents with CAT did not exhibit any colour change. It is worth mentioning that chelate formation between CAT and Osmium(VIII) is reported in the oxidation of α-hydroxy acids without adducing any kinetic and/or spectral evidence. The kinetics results of this study, however, do not support such a chelate formation in osmium(VIII) catalyzed oxidation of phenylphosphinic acid in alkaline medium.

Thus considering experimental observations viz. first order with respect to [CAT] and [Os(VIII)] respectively, complex dependence on phenylphosphinic acid and inverse dependence on hydroxide ion concentration, a reaction mechanism consisting of following steps (8) to (12) can be envisaged.

$$[OsO_3(OH)_3]^- + OH^- \underset{}{\overset{K_1}{\rightleftharpoons}} [OsO_4(OH)_2]^{2-} + H_2O \quad (8)$$

$$[OsO_3(OH)_3]^- + PhP^- \overset{K_2}{\rightleftharpoons} [OsO_3(OH)_3(PhP)]^{2-} \quad (9)$$

$$[OsO_4(OH)_2]^{2-} + PhP^- \overset{K_3}{\rightleftharpoons} [OsO_4(OH)_2(PhP)]^{3-} \quad (10)$$

$$[OsO_3(OH)_3(PhP)]^{2-} + RNCl^- \xrightarrow{k_1,\ H_2O} [OsO_3(OH)_4] + PhPO_3^{2-} + RNH_2 + HCl \quad (11)$$

$$[OsO_4(OH)_2(PhP)]^{3-} + RNCl^- \xrightarrow{k_2,\ H_2O} [OsO_4(OH)_2]^{2-} + PhPO_3^{2-} + RNH_2 + HCl \quad (12)$$

Such a mechanism leads to the rate law (13) or (14) –

$$-\frac{d[CAT]}{dt} = \frac{[CAT][Os(VIII)][PhP](k_1K_2 + k_2K_1K_3[OH^-])}{1 + K_1[OH^-] + K_2[PhP] + K_1K_3[OH^-][PhP]} \quad (13)$$

Where, [CAT] and [Os(VIII)] are the gross analytical concentrations of chloramine-T and catalyst respectively. [PhP] is free equilibrium concentration of phenylphosphinic acid.
Or

$$k = \frac{[PhP](k_1K_2 + k_2K_1K_3[OH^-])}{1 + K_1[OH^-] + K_2[PhP] + K_1K_3[OH^-][PhP]} \quad (14)$$

Where 'k' is an observed second order rate constant

Since the limiting rate is not obtained even at sufficiently high concentrations of hydroxide ion, the second term in the numerator does not contribute much to the overall rate of the reaction. Thus reduces the rate law (14) to (15).

$$k = \frac{k_1K_2[PhP]}{1 + K_1[OH^-] + K_2[PhP] + K_1K_3[OH^-][PhP]} \quad (15)$$

The double reciprocal of eqn (15) on re-arrangement yields eqn (16)

$$1/k = \frac{1 + K_1[OH^-]}{k_1K_2[PhP]} + \left(\frac{1}{k_1} + \frac{K_1K_3[OH^-]}{k_1K_2}\right) \quad (16)$$

A plot of 1/k versus 1/[PhP] was made from eqn (16) that yielded a straight line with non-zero intercept (Figure 3). The calculated Intercept (I_1) and slope (S_1) evaluated from this plot are given by eqns (17) and (18) respectively.

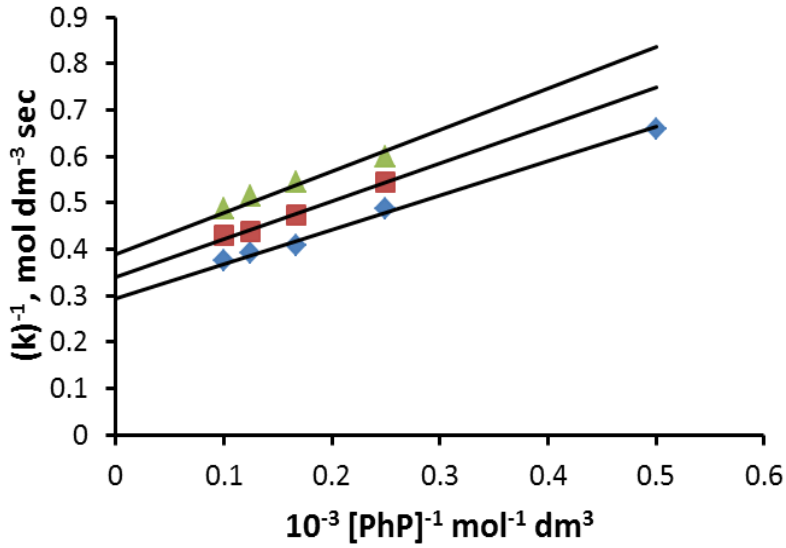


Figure 3 Plot of $(k)^{-1}$ versus $[PhP]^{-1}$ in the reaction of CAT and phenylphosphinic acid catalyzed by osmium(VIII). [CAT] = 2.0×10^{-3} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-5} mol dm^{-3}; [OH^-] = ♦, 0.075 mol dm^{-3}; ■, 0.10 mol dm^{-3}; ▲, 0.125 mol dm^{-3}; 55°C

$$(I_1) = \frac{1}{k_1} + \frac{K_1 K_3 [OH^-]}{k_1 K_2} \tag{17}$$

And

$$(S_1) = \frac{1}{k_1 K_2} + \frac{K_1}{k_1 K_2}[OH^-] \tag{18}$$

Further plots of (I_1) versus [OH^-] and (S_1) versus [OH^-] respectively also yielded straight lines with non-zero intercepts (Figures 4 and 5) the values of k_1 and K_1 to be (6.7) dm^3 mol^{-1} s^{-1} and (34±2) dm^3 mol^{-1} at 55°C were obtained.

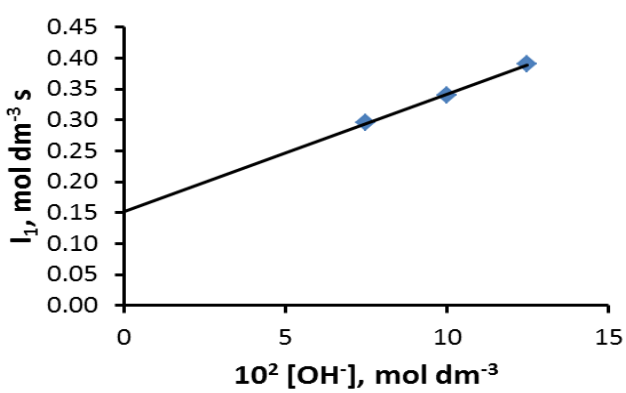


Figure 4 A plot of 'I_1' versus [OH^-]

[CAT] = 2.0×10^{-3} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-5} mol dm^{-3}; 55°C

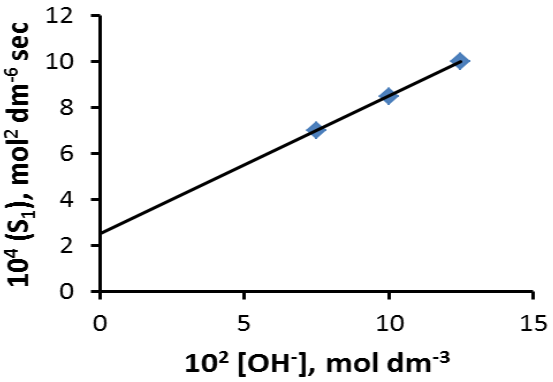
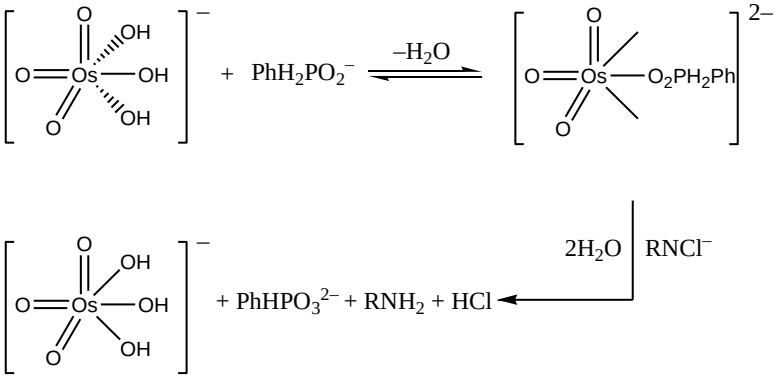


Figure 5 A Plot of 'S_1'Versus [OH$^-$]

[CAT] = 2.0×10^{-3} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-5} mol dm^{-3}; 55°C

So far the mode of reaction events is concerned, a tentative scheme-I can be suggested.



$$HCl + OH^- \longrightarrow H_2O + Cl^-$$

Since kinetic and spectral evidence substantiate complexation between Osmium(VIII) and phenylphosphinic acid, first order dependence with respect to CAT corresponds to formation of a ternary activated complex. Such an activated complex being bulky will disorganized to undergo redox decomposition intramolecularly. It appears that the electron-deficient metal centre being co-ordinated through oxygen to the phenylphosphinic acid anion exposes the latter for preferential external attack by RNCl$^-$ species.

Conclusions

In conclusion, an interaction between chloramine-T and phenylphosphinic acid catalyzed by Osmium(VIII) in alkaline medium is first order with respect to [CAT] and [Os(VIII)] respectively, complex dependence on phenylphosphinic acid and inverse dependence on hydroxide ion concentration. Kinetic and spectral evidence substantiate complexation between Osmium(VIII) and phenylphosphinic acid, first order dependence with respect to CAT corresponds to formation of a ternary activated complex. Also, the speciation of chloramine-T species is discussed in detail and the most probable species has been identified for oxidation of phenylphosphinic acid.

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