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Ru(III), Os(VIII), Pd(II) and Pt(IV) catalysed oxidation of glycyl–glycine by sodium *N*-chloro-*p*-toluenesulfonamide: comparative mechanistic aspects and kinetic modelling

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The Ru(III)/Os(VIII)/Pd(II)/Pt(IV)-catalysed kinetics of oxidation of glycyl–glycine (Gly-Gly) by sodium *N*-chloro-*p*-toluenesulfonamide (chloramine-T; CAT) in NaOH medium has been investigated at 308 K. The stoichiometry and oxidation products in each case were found to be the same but their kinetic patterns observed are different. Under comparable experimental conditions, the oxidation-kinetics and mechanistic behaviour of Gly-Gly with CAT in NaOH medium is different for each catalyst and obeys the underlying rate laws:

$$\text{Rate} = k\,[\text{CAT}]_t\,[\text{Gly-Gly}]^0\,[\text{Ru(III)}][\text{OH}^-]^x$$
$$\text{Rate} = k\,[\text{CAT}]_t[\text{Gly-Gly}]^x\,[\text{Os(VIII)}]^y[\text{OH}^-]^z$$
$$\text{Rate} = k\,[\text{CAT}]_t[\text{Gly-Gly}]^x\,[\text{Pd(II)}][\text{OH}^-]^y$$
$$\text{Rate} = k\,[\text{CAT}]_t[\text{Gly-Gly}]^0\,[\text{Pt(IV)}]^x[\text{OH}^-]^y$$

Here, Ts = $CH_3C_6H_4SO_2$- and *x, y, z* < 1 in all the cases. The anion of CAT, $CH_3C_6H_4SO_2NCl^-$, has been postulated as the common reactive oxidising species in all the cases. Under comparable experimental conditions, the relative ability of these catalysts towards oxidation of Gly-Gly by CAT are in the order: Os(VIII) > Ru(III) > Pt(IV) > Pd(II). This trend may be attributed to the different d-electronic configuration of the catalysts. Further, the rates of oxidation of all the four catalysed reactions have been compared with uncatalysed reactions, under identical experimental conditions. It was found that the catalysed reaction rates are 7- to 24-fold faster. Based on the observed experimental results, detailed mechanistic interpretation and the related kinetic modelling have been worked out for each catalyst. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: Ru(III)/Os(VIII)/Pd(II)/Pt(IV) catalysis; oxidation-kinetics; glycyl–glycine; chloramine-T; alkaline medium

INTRODUCTION

The chemistry of *N*-haloamines is of interest due to their diverse chemical behaviour.[1] These compounds resemble hypohalites in their oxidative behaviour and they are more stable than hypohalites.[2,3] Consequently, these compounds react with a wide range of functional groups and effect a variety of molecular changes.[1] The prominent member of this class of compounds is sodium *N*-chloro-4-methylbenzenesulfonamide, commonly known as chloramine-T (*p*-$CH_3C_6H_4SO_2NClNa\cdot 3H_2O$ and abbreviated as CAT). Mechanistic aspects of many of its reactions have been well documented.[1,4–6] However, a very little information is available in the literature on CAT reactions with dipeptides.

Dipeptides are useful biomaterials in many biological, pharmaceutical, analytical and synthetic applications. Glycyl–Glycine (Gly-Gly) is the first member of the dipeptide series and a review of literature reveals that there are many reports on the kinetics of its hydrolysis.[7,8] It has also been oxidised by manganese-(III),[9] bromamine-T,[10] bromamine-B[11] in acid medium. However, literature survey revealed that there are no efforts being made from the kinetic and mechanistic viewpoints on the oxidation of Gly-Gly by *N*-haloamines in alkaline medium. Hence, there was a need for understanding the oxidation mechanism of this dipeptide in alkaline medium, so that this study is expected to throw some light on the mechanism of metabolic conversion of Gly-Gly in the biological systems. Hence, the present kinetic study gives an impetus, as the Gly-Gly is a biologically important substrate. Also, no one has examined the role of platinum group metal ions as catalysts in *N*-haloamine oxidation of Gly-Gly.

The studies on the use of platinum group metal ions, either alone or binary mixtures, as catalysts in many redox reactions, have been gaining interest.[12] Common platinum group metal ions employed in homogeneous catalysis involving redox reactions are Ruthenium (III) chloride (Ru(III)), Osmium(VIII) oxide (Os(VIII)), Palladium(II) chloride (Pd(II)), Platinum(IV) chloride (Pt(IV)), Iridium(III) chloride (Ir(III)) and Rhodium(III) chloride (Rh(III)). The mechanisms of these catalysis are quite complicated due to the formation of different intermediate complexes, free radicals and differing oxidising states of these catalysts.[13,14]

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Although many complexes of these metal ions with various organic and inorganic substances have been reported, an extensive literature survey reveals the absence of comprehensive studies on the oxidation-kinetics and mechanism of dipeptides by any of these catalysts. Consequently, such studies provide an insight into the interaction of metal ions with the substrate in biological systems.

This background instigated us to carry out the title reaction in order to interpret the mechanism and to understand the catalytic redox chemistry of Gly-Gly in the presence of platinum group metal ions. Preliminary experimental results revealed that the reactions of Gly-Gly with CAT in alkaline medium without a catalyst were sluggish, but the reactions become facile in the presence of a micro quantity of platinum group metal ions like Ru(III), Os(VIII), Pd(II) and Pt(IV). The main objectives of the present investigation are to: (i) elucidate plausible mechanisms, (ii) deduce appropriate rate laws, (iii) ascertain the various reactive species, (iv) assess the relative rates of catalysts, (v) understand the catalytic redox chemistry of Gly-Gly in the presence of platinum group metal ions, (vi) find the catalytic efficiency of catalysts and (vii) compare the reactivity with that under uncatalysed oxidation.

EXPERIMENTAL

Materials

Chloramine-T (Merck) was purified by the method of Morris *et al.*[3] An aqueous solution of CAT was prepared, standardised iodometrically and stored in amber coloured, stoppered bottles to prevent photochemical deterioration.[3] The concentration of stock solutions was periodically determined. Chromatographically pure Gly-Gly (Merck) was used as received. Aqueous solutions of desired strength were prepared whenever required. Ruthenium trichloride (Merck), palladium chloride (Arora-Matthey) and platinum chloride (SD Fine Chem Ltd.) solutions were prepared in 20 mM HCl while osmium tetroxide (BDH) was prepared in 20 mM NaOH. Allowance for the amount of acid/alkali present in the catalyst solutions was made while preparing the reaction mixtures for kinetic runs. The ionic strength of the system was maintained constant at a high value (0.3 mol dm^{-3}) using a concentrated solution of $NaClO_4$ in order to swamp the reaction wherever the effect is noticed. The permittivity of the reaction mixture was altered by the addition of methanol in varying proportions (v/v), and the values of the dielectric constant of water–methanol mixtures as reported in the literature[15] were employed. Solvent isotope studies were made in D_2O (99.4% purity) supplied by Bhabha Atomic Research Center, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout. UV-3101 PC UV–Vis-NIR Scanning Spectrophotometer was used for studying the formation of various complexes. Regression analysis of the experimental data was carried out on an f_x-100W scientific calculator to obtain the regression coefficient, *r*.

Kinetic measurements

The reactions were carried out under pseudo-first-order conditions ($[\text{substrate}]_0 \gg [\text{oxidant}]_0$) at constant temperature in glass-stoppered Pyrex boiling tubes coated black on outside surface to eliminate any photochemical effects. The oxidant and requisite amount of substrate, NaOH, Ru(III)/Os(VIII)/Pd(II)/Pt(IV) catalyst, $NaClO_4$ (wherever mentioned) solutions and water (to keep the total volume constant for all runs), were taken in the tube and thermostatted at 308 K until thermal equilibrium was attained. A measured amount of CAT solution, which was also thermostatted at the same temperature, was rapidly added to the mixture and was shaken intermittently for uniform concentration. The progress of the reaction was monitored by iodometric determination of unreacted CAT in 5 ml of aliquots of the reaction mixture withdrawn at different time intervals. The course of the reaction was studied for more than two half-lives. The pseudo-first-order rate constants (k' s^{-1}) calculated from the linear plots of log [CAT] *versus* time were reproducible within ±3–5%.

Stoichiometry

Different ratios of CAT to Gly-Gly in the presence of 1.0×10^{-2} mol dm^{-3} NaOH and 1.0×10^{-5} mol dm^{-3} catalyst were equilibrated at 308 K for 24 h. The unreacted oxidant in the reaction mixture was determined iodometrically. The analysis showed that one mole of Gly-Gly reacts with two moles of oxidant for all the catalysed reactions, confirming to the following stoichiometry:

$$\begin{aligned} NH_2CH_2CONHCH_2COOH + 2TsNClNa + 3H_2O &\rightarrow 2HCHO + 2CO_2 \\ &+ 2NH_3 + 2TsNH_2 + 2Na^+ + 2Cl^- \end{aligned} \tag{1}$$

where $Ts = CH_3C_6H_4SO_2$.

Product analysis

The reaction mixtures (1 mol of Gly-Gly and 2 moles of CAT in the presence of 1.0×10^{-2} and 1.0×10^{-5} mol dm^{-3} catalyst) were allowed to progress for 2–3 h under stirred condition at 35 °C. After completion of the reaction (monitored by TLC), the reaction products were extracted with ether. Formaldehyde and *p*-toluenesulfonamide (PTS) are identified as the main oxidation product of Gly-Gly and reduction product of CAT, respectively. Evaporation of the ether layer was followed by column chromatography on silica gel (60–200 mesh) using gradient elution (from dichloromethane to chloroform). After initial separation, the products were further purified by recrystalisation.

Formaldehyde, the oxidation product of Gly-Gly was detected by spot tests[16] and estimated as its 2,4-DNP derivative.[17] The amount of formaldehyde was calculated from the weight of hydrazone formed in the presence of each catalyst and the yield of the formaldehyde was found to be 75–80%. Further, the melting point of the 2,4-DNP derivative of formaldehyde was found to be 165 °C (Lit. m.p. 166 °C). It was also observed that formaldehyde does not undergo further oxidation under the prevailing kinetic conditions.

The reduction product of CAT, PTS ($TsNH_2$), was detected by TLC.[18] It was further confirmed by its melting point of 139 °C (Lit m.p. 137–140 °C). Further, PTS has been quantitatively estimated[17] by its reaction with xanthydrol to yield the corresponding *N*-xanthyl-*p*-toluenesulfonamide. In a typical experiment, equal quantities of separated PTS and xanthydrol (0.20 g) were dissolved in 10 ml of glacial acetic acid. The reaction mixture was stirred for 3 min at laboratory temperature and allowed to stand for 90 min. The derivative was filtered, recrystalised with dioxane/

Table 1. Effect of varying reactant concentrations on the reaction rate at 308 K

		$10^4\,k'$ (s^{-1})			
10^3 $[CAT]_0$ (mol dm^{-3})	10^2 $[Gly\text{-}Gly]_0$ (mol dm^{-3})	Ru(III)	Os(VIII)	Pd(II)	Pt(IV)
0.20	1.00	5.69	10.11	3.16	4.20
0.50	1.00	5.74	9.98	3.10	4.29
1.00	1.00	5.78	10.0	3.12	4.26
2.00	1.00	5.70	10.1	3.00	4.21
4.00	1.00	5.81	10.0	3.20	4.30
1.00	0.50	5.70	7.41	2.14	4.21
1.00	1.00	5.78	10.0	3.12	4.26
1.00	2.00	5.71	14.1	4.46	4.20
1.00	3.00	5.80	17.40	5.51	4.19
1.00	4.00	5.79	20.1	6.56	4.30

$[NaOH] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[catalyst] = 1.00 \times 10^{-5}$ mol dm^{-3}; $I = 0.30$ mol dm^{-3} (in case of Ru(III) catalysis).

water (3:1) and dried at room temperature. This was weighed and the recovery of PTS in all the cases is found to be 80–85%. The liberated CO_2 and NH_3 were identified by conventional lime water and Nessler's reagent tests, respectively.

RESULTS

Kinetic orders

The kinetics of oxidation of Gly-Gly by CAT was investigated at several initial concentrations of the reactants in NaOH medium in the presence of Ru(III), Os(VIII), Pd(II) and Pt(IV) catalysts at 308 K under identical experimental conditions. Despite the fact that the stoichiometry and oxidation products were same in all the catalysed reactions, the oxidation kinetic behaviour was different. All the reactions were carried out under pseudo-first-order conditions, wherein $[Gly\text{-}Gly]_0 \gg [CAT]_0$.

Under the pseudo-first-order conditions of $[Gly\text{-}Gly]_0 \gg [CAT]_0$, with other reaction conditions remaining constant, the order in $[CAT]_0$ was found to be unity in all the four catalysed reactions, as indicated by the linearity of the plots of log [CAT] *versus* time ($r > 0.9948$). Further, the linearity of these plots with constancy of the slopes obtained at various $[CAT]_0$ indicated a first-order dependence of the reaction rate on $[CAT]_0$. The pseudo-first-order rate constants (k') obtained are given in Table 1. Under the same experimental conditions, the rate of the reaction increased in $[Gly\text{-}Gly]_0$ (Table 1) for Os(VIII)- and Pd(II)-catalysed reactions and plots of log k' *versus* log [Gly-Gly] were found to be linear ($r > 0.9925$) with fractional slopes of 0.47 and 0.54, respectively, indicating a fractional-order dependence on $[Gly\text{-}Gly]_0$ in both cases. Further, the intercepts of the plots of k' *versus* $[Gly\text{-}Gly]_0$ in these cases were linear ($r > 0.9889$) which confirmed a fractional-order dependence of rate on $[Gly\text{-}Gly]_0$ in both the reactions. But the orders in $[Gly\text{-}Gly]_0$ were found to be zero in case of Ru(III) and Pt(IV) catalysis (Table 1).

The rate of the reaction increased with increasing [NaOH] (Table 2) in all the cases. The log–log plots of rate *versus* [NaOH] ($r > 0.9901$) showed that the orders in $[OH^-]$ were less than unity (0.37–0.73), indicating a fractional-order dependence of rate on $[OH^-]$ in all the four catalysed reactions. The reaction rate increases with the increase in [Ru(III)] and [Pd(II)] and log–log

Table 2. Effect of varying NaOH and catalyst concentrations on the reaction rate at 308 K

		$10^4\,k'$ (s^{-1})			
10^2 [NaOH] (mol dm^{-3})	10^5 [catalyst] (mol dm^{-3})	Ru(III)	Os(VIII)	Pd(II)	Pt(IV)
0.20	1.00	2.41	5.42	1.06	2.26
0.50	1.00	4.00	7.61	2.01	3.17
1.00	1.00	5.76	10.0	3.12	4.26
2.00	1.00	8.41	13.6	5.76	5.47
4.00	1.00	12.2.	17.7	9.01	7.06
1.00	0.20	1.14	3.00	0.74	1.16
1.00	0.50	2.86	6.10	1.47	2.51
1.00	1.00	5.76	10.00	3.12	4.26
1.00	2.00	11.6	17.7	6.41	7.67
1.00	4.00	23.2	29.6	12.61	14.0

$[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[Gly\text{-}Gly]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}; $I = 0.30$ mol dm^{-3} (in case of Ru(III) catalysis).

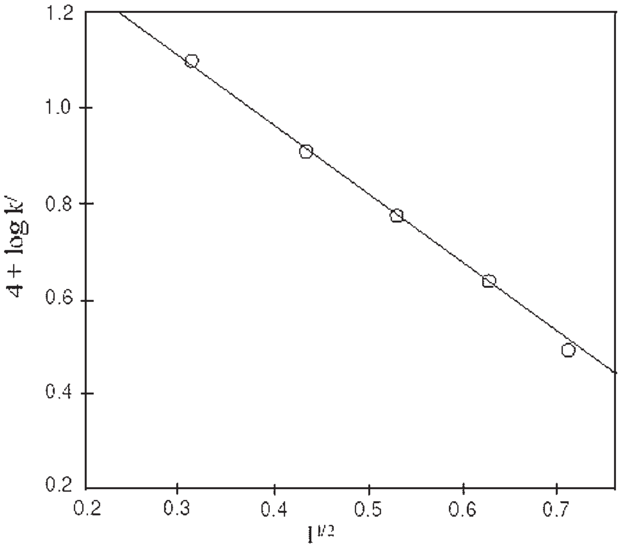


Figure 1. Plot of log k' *versus* $I^{1/2}$

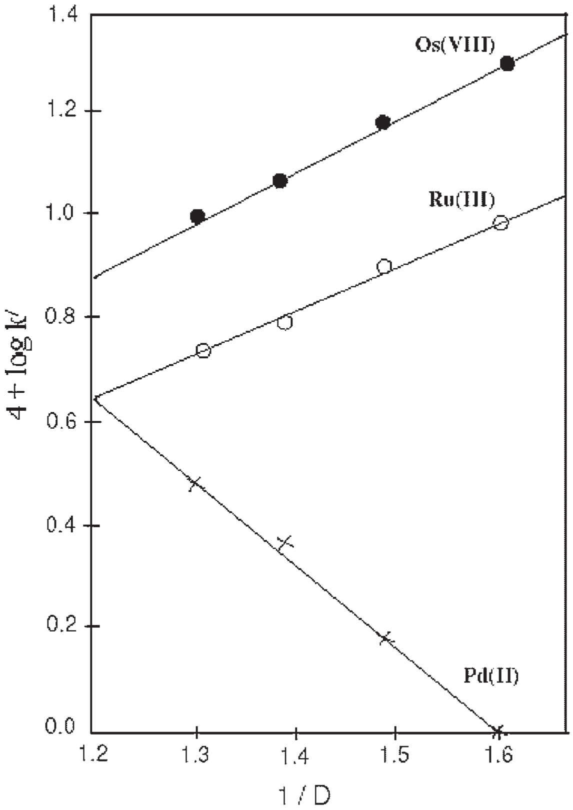


Figure 2. Plots of log k' *versus* $1/D$

plots of rate *versus* [catalyst] were found to be linear ($r > 0.9905$) with a slope of unity, indicating a first-order dependence of rate on [Ru(III)] and [Pd(II)]. Whereas in case of [Os(VIII)] and [Pt(IV)] catalysis, such plots were linear ($r > 0.9965$) with slopes less than unity (0.80–0.85), indicating fractional-order kinetics in [Os(VIII)] and [Pt(IV)]. All these results are recorded in Table 2.

Addition of PTS to the reaction mixture retards the rate in Pt(IV) catalysis and the rate constants at 4.0, 8.0, 14.0 and 20.0×10^{-4} [PTS] mol dm^{-3} were 4.26, 3.80, 2.92 and 2.45×10^{-4} s^{-1}, respectively. Further, a plot of log k' *versus* log [PTS] was linear ($r = 0.9899$) with a negative slope of 0.25, indicating a negative fractional-order dependence of the rate on [PTS]. It also indicates that PTS is involved in a fast pre-equilibrium to the rate-limiting step in the proposed scheme for the Pt(IV) catalysis. But the rate was unaffected by the addition of PTS in other catalysed reactions and it signifies that the PTS is not involved in any step prior to the rate-limiting step in the schemes proposed.

An increase in ionic strength of a reaction system by the addition of $NaClO_4$ decreased the rate of the reaction and the rate constants at 0.1, 0.2, 0.3, 0.4 and 0.5 mol dm^{-3} ionic strength were 12.8, 8.11, 5.76, 4.21 and 3.11×10^{-4} s^{-1}, respectively, in case of Ru(III) catalysis. Further, a plot of log k' *versus* $I^{1/2}$ gave a straight line (Fig. 1; $r = 0.9926$) with a negative slope of 1.5. But variation of ionic strength showed negligible effect on the rate of the reaction in other catalysed reactions. Hence, only in case of Ru(III)-catalysed reaction, the ionic strength of the medium was maintained at a constant concentration of 0.30 mol dm^{-3} of $NaClO_4$ for kinetic runs in order to swamp the reaction.

The effect of dielectric constant of the medium on the reaction rate was studied by adding methanol (0–30% v/v) to the reaction mixture, while keeping other experimental conditions constant. The rates were found to increase with increase in MeOH content in case of Ru(III)- and Os(VIII)-catalysed reactions and the plots of log k' versus $1/D$ were linear (Fig. 2; $r > 0.9979$) with positive slopes. But in the case of Pd(II) catalysis, the slope of such a plot was negative (Fig. 2; $r = 0.9990$). However, negligible influence of variation of dielectric constant on the rate was observed in case of Pt(IV) catalysis. All these results were recorded in Table 3. The rate remained constant with the addition of Cl^- or Br^- ions in

Table 3. Effect of varying dielectric constant of the medium on the reaction rate at 308 K

		$10^4\ k'$ (s^{-1})			
% MeOH (v/v)	*D*	Ru(III)	Os(VIII)	Pd(II)	Pt(IV)
0	76.73	5.76	10.0	3.12	4.26
10	72.37	6.81	12.3	2.41	4.30
20	67.48	9.00	15.2	1.61	4.20
30	62.71	12.01	20.0	1.00	4.16

$[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[Gly\text{-}Gly]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}; $[NaOH] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[catalyst] = 1.00 \times 10^{-5}$ mol dm^{-3}; $I = 0.30$ mol dm^{-3} (in case of Ru(III) catalysis).

Table 4. Temperature dependence on the reaction rate and values of activation parameters for the oxidation of Gly-Gly by CAT in the presence and absence of catalyst

	$10^4\ k'$ (s^{-1})			
Temperature (K)	Ru(III)	Os(VIII)	Pd(II)	Pt(IV)
298	2.84	5.69	1.20	1.79 (0.11)
303	3.74	7.82	2.01	2.71 (0.22)
308	5.76	10.0	3.12	4.26 (0.41)
313	8.08	14.0	5.11	6.61 (0.81)
318	11.6	18.2	8.00	9.59 (1.41)
E_a (kJ mol^{-1})	58.6	42.7	75.7	68.2 (108)
$\Delta H^{\neq}$ (kJ mol^{-1})	56.0 ± 0.02	39.6 ± 0.01	73.1 ± 0.02	65.3 ± 0.06 (106 ± 0.10)
$\Delta G^{\neq}$ (kJ mol^{-1})	95.0 ± 0.09	93.1 ± 0.16	95.8 ± 0.2	95.0 ± 0.12 (101 ± 0.21)
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-125 ± 0.21	-173 ± 0.21	-75.3 ± 0.10	-96.2 ± -0.21 (15.7 ± 0.41)
log *A*	9.69 ± 0.11	4.17 ± 0.01	9.33 ± 0.10	8.20 ± 0.01 (14 ± 0.09)

$[CAT]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[Gly\text{-}Gly]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}; $[NaOH] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[catalyst] = 1.00 \times 10^{-5}$ mol dm^{-3}; $I = 0.30$ mol dm^{-3} (in case of Ru(III) catalysis).
Values in the parentheses refer to oxidation of Gly-Gly by CAT in the absence of catalyst. Experimental conditions are the same as in footnote without catalyst.

the form of NaCl or NaBr (1.0×10^{-2}–5.0×10^{-2} mol dm^{-3}). As a dependence of the rate on hydroxyl ion concentration was noted, solvent isotope studies were made using D_2O for all the four catalysed reactions. Studies of the reaction rate in D_2O medium for Ru(III)-, Os(VIII)-, Pd(II)- and Pt(IV)-catalysed reactions revealed that $k'(H_2O)$was equal to 5.70×10^{-4}, 10.0×10^{-4}, 3.12×10^{-4} and 4.26×10^{-4} s^{-1}, and $k'(D_2O)$ was $6.7.0 \times 10^{-4}$, 11.2×10^{-4}, 3.85×10^{-4} and 4.85×10^{-4} s^{-1}, respectively. The solvent isotope effect, $k'(H_2O)/k'(D_2O)$ was found to be 0.88, 0.89, 0.81 and 0.88 for the four cases.

The reaction was studied at different temperatures (298–318 K), keeping other experimental conditions constant. From the linear Arrhenius plots of log k' versus $1/T$ ($r > 0.9904$), values of activation parameters for the overall reaction were evaluated (Table 4). The addition of the reaction mixtures to aqueous acrylamide monomer solutions did not initiate polymerisation, indicating the absence of *in situ* formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions but without the oxidant, CAT.

DISCUSSION

Chloramine-T acts as an oxidising agent in both acidic and alkaline solutions. The oxidation potential of CAT-PTS redox couple varies[19] with the pH of the medium, having values of 1.139 V at pH 0.65, 0.778 V at pH 7.0 and 0.614 V at pH 9.7. Chloramine-T behaves like a strong electrolyte[2] in aqueous solutions, and depending on the pH of the medium, it furnishes different equilibria in solutions.[2,19–21] The possible oxidising species in acidified CAT solutions[2,19–21] are the conjugate-free acid TsNHCl, the dichloramine-T $TsNCl_2$, the hypochlorous acid HOCl and also perhaps H_2O^+Cl. In alkaline CAT solutions, $TsNCl_2$ does not exist[22,23] and hence the expected reactive species are TsNHCl, $TsNCl^-$, HOCl and OCl^-.

Hardy and Johnston[19] have reported the establishment of the following equilibria in alkaline solution of CAT:

$$TsNCl^- + H_2O \rightleftharpoons TsNHCl + OH^- \qquad (2)$$

$$TsNHCl + H_2O \rightleftharpoons TsNH_2 + HOCl \qquad (3)$$

If HOCl were to be the primary oxidising species as indicated in Eqn (3), a first-order retardation of rate by added PTS would be expected. However, no such effect was noticed in the present study. If TsNHCl is the reactive species, retardation of the rate by $[OH^-]$ is expected (Eqn (2)), which is also contrary to the experimental observations. Hence, in the present investigation, the rate of the reaction is accelerated by OH^- ions clearly indicates that the anion $TsNCl^-$ is the most likely oxidising species involved in the oxidation of Gly-Gly by CAT in all the four catalysed reactions.

Mechanism and rate law of Ru(III) catalysis

Ru(III) chloride acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium.[24–26] Under the experimental conditions $[OH^-] \gg [Ru(III)]$ and the fact that $[OH^-]$ increases the rate, ruthenium (III) is mostly present as the hydroxylated species $[Ru(H_2O)_5OH]^{2+}$ and its formation in the following equilibrium is of importance in the reaction:

$$[Ru(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Ru(H_2O)_5OH]^{2+} + H_2O \qquad (4)$$

Hence, the hydroxylated species $[Ru(H_2O)_5OH]^{2+}$ complex ion of ruthenium(III) has been assumed to be the reactive catalysing species. Similar equilibria have been reported between Ru(III)-catalysed oxidation of several other substrates with various oxidants in alkaline medium.[13,27–29]

The existence of a complex between the catalyst and oxidant was evidenced from the UV–Vis spectra of both Ru(III) and

Ru(III)-CAT mixture, in which a shift of Ru(III) from 352.6 to 338 nm was observed, indicating the formation of a complex (Fig. 3). Such type of oxidant–catalyst complex formation has also been reported in other studies.[30,31]

Further, for a general equilibrium

$$\mathrm{M} + n\mathrm{S} \overset{K}{\rightleftharpoons} (\mathrm{MS}_n) \qquad (5)$$

between two metal species, M and MS_n having different extinction coefficients, Ardon[32] has derived the following:

$$\frac{1}{\Delta A} = \frac{1}{[\mathrm{S}]^n\{1/\Delta E[\mathrm{M}_{\mathrm{Total}}]K\}} + \frac{1}{\Delta E[\mathrm{M}_{\mathrm{Total}}]} \qquad (6)$$

where K is the formation constant of the complex, [S] is the concentration of CAT, ΔE is the difference in extinction coefficient between two metal species, $[\mathrm{M}]_{\mathrm{Total}}$ is the total concentration of metal species and ΔA is the absorbance difference of solution containing no S and one that contains a certain concentration of S represented by [S]. Equation (6) is valid provided that [S] is so much greater than $[\mathrm{M}]_{\mathrm{Total}}$ that the amount of S tied up in the complex is negligible or it is subtracted from the initial concentration of S. According to Eqn (6), a plot of $1/\Delta A$ *versus* 1/[S] or $1/[\mathrm{S}]^2$ should be linear with an intercept in case of 1:1 or 1:2 type of complex formation between M and S. The ratio of intercept to slope of this linear plot gives the value of K.

Ruthenium (III) in NaOH medium containing CAT showed an absorption peak at 338 nm ($\lambda_{\max}$ for the complex). The complex formation studies were made at this $\lambda_{\max}$ of 338 nm. In a set of experiments, the solutions were prepared by taking different amounts of CAT (2.0×10^{-4}–4.0×10^{-3} mol dm^{-3}) at constant amounts of $\mathrm{RuCl_3}$ (1.0×10^{-5} mol dm^{-3}) and NaOH (1.0×10^{-2} mol dm^{-3}) at 308 K. The absorbance of these solutions was measured at 338 nm. The absorbance of the solution in the absence of CAT was also measured at the same wavelength. The difference of these absorbances (with and without CAT) gives the differential absorbance, ΔA. A plot of $1/\Delta A$ *versus* 1/[CAT] was linear ($r = 0.9944$) with an intercept suggesting the formation of a 1:1 complex between CAT and Ru(III) catalyst. Similar type of behaviour for the formation of complex has been reported in earlier works.[18,32,33] Further, the plot of log ($1/\Delta A$) *versus* log (1/[CAT]) was also linear ($r = 0.9801$) and from the slope and intercept of the plot of $1/\Delta A$ *versus* 1/[CAT], the value of the formation constant, K, of the complex was deduced; it was found to be 6.06×10^2.

In view of the above facts, a detailed mechanism for Ru(III)-catalysed oxidation of Gly-Gly by CAT in alkaline medium is shown in Scheme 1.

The total concentration of CAT is $[\mathrm{CAT}]_\mathrm{t}$, then

$$[\mathrm{CAT}]_\mathrm{t} = [\mathrm{TsNHCl}] + [\mathrm{TsNCl}^-] \qquad (7)$$

By substituting for [TsNHCl] from equilibrium (i) of Scheme 1 in Eqn (7) and solving for $[\mathrm{TsNCl}^-]$, one obtains

$$[\mathrm{TsNCL}^-] = \frac{K_1[\mathrm{CAT}]_\mathrm{t}[\mathrm{OH}^-]}{[\mathrm{H_2O}]+K_1[\mathrm{OH}^-]} \qquad (8)$$

From the slow and rate-determining step (rds) of Scheme 1,

$$\mathrm{Rate} = -\mathrm{d}[\mathrm{CAT}]_\mathrm{t} = k_2[\mathrm{TsNCl}^-][\mathrm{Ru(III)}] \qquad (9)$$

By substituting for $[\mathrm{TsNCl}^-]$ from Eqn (8) into Eqn (9), the following rate law is obtained:

$$\mathrm{Rate} = \frac{-\mathrm{d}[\mathrm{CAT}]_\mathrm{t}}{\mathrm{dt}} = \frac{K_1k_2[\mathrm{CAT}]_\mathrm{t}[\mathrm{Ru(III)}][\mathrm{OH}^-]}{[\mathrm{H_2O}] + K_1[\mathrm{OH}^-]} \qquad (10)$$

Rate law (10) is in good agreement with the experimental results.

Since rate $= k'[\mathrm{CAT}]_\mathrm{t}$, Eqn (10) can be transformed into

$$k' = \frac{K_1k_2[\mathrm{Ru(III)}][\mathrm{OH}^-]}{[\mathrm{H_2O}] + K_1[\mathrm{OH}^-]} \qquad (11)$$

$$\frac{1}{k'} = \frac{[\mathrm{H_2O}]}{K_1k_2[\mathrm{Ru(III)}][\mathrm{OH}^-]} + \frac{1}{k_2[\mathrm{Ru(III)}]} \qquad (12)$$

Based on Eqn (12), a plot of $1/k'$ *versus* $1/[\mathrm{OH}^-]$ at constant $[\mathrm{CAT}]_0$, $[\text{Gly-Gly}]_0$, [Ru(III)] and temperature was found to be linear ($r = 0.9822$). From the values of slope and intercept of such a plot, the equilibrium constant (K_1) and decomposition constant (k_2) were calculated and found to be 7.90×10^4 and 11.1 dm^3 mol^{-1} s^{-1}, respectively.

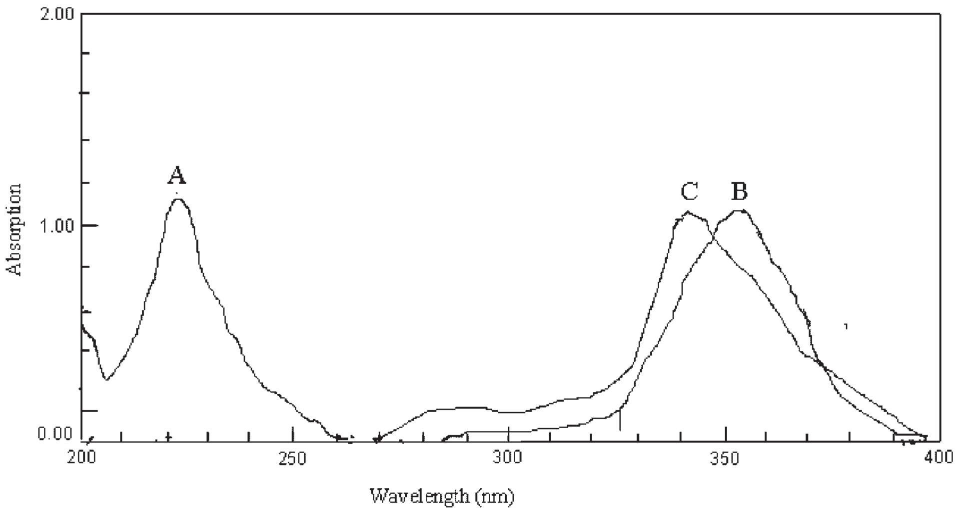
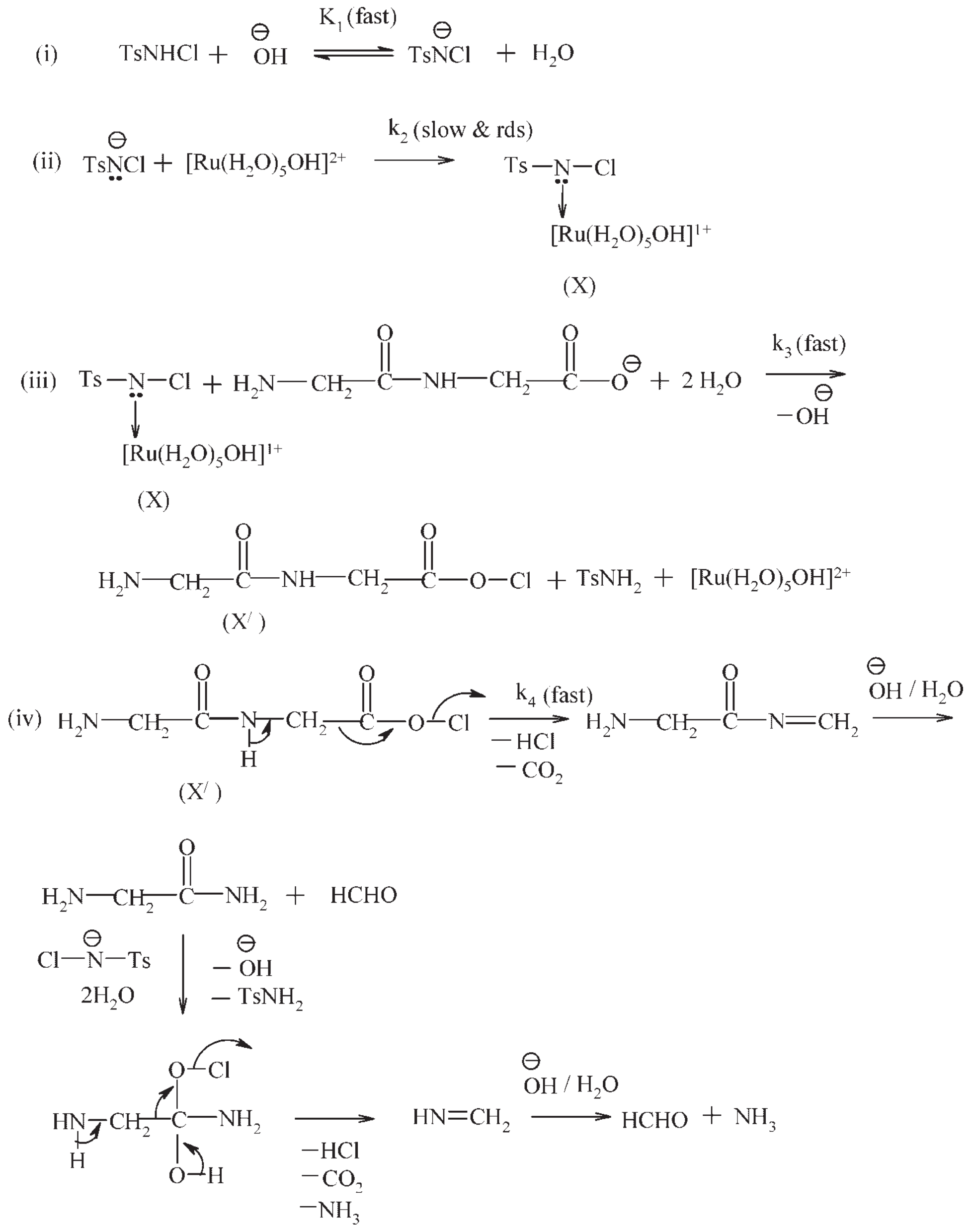


Figure 3. UV–Vis spectra of (A) CAT, (B) Ru(III) and (C) CAT + Ru(III) in NaOH medium



Scheme 1. A detailed mechanistic scheme for Ru(III)-catalysed oxidation of Gly-Gly by CAT

The proposed mechanism and the derived rate law are substantiated by the following experimental facts:

For a reaction involving a fast pre-equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O since D_3O^+ and OD^- are two to three times stronger acids and stronger bases,[34–36] respectively, than H_3O^+ and OH^- ions. In the present study, the observed solvent isotope effect of $k'(H_2O)/k'(D_2O) < 1$ is due to the greater basicity of OD^- compared to OH^- and is conforming to the fact. However, the magnitude of increase of rate in D_2O is small ($k'(H_2O)/k'(D_2O) = 0.88$) compared to the expected value of 2 to 3 times greater, which can be attributed to the fractional-order dependence of rate on $[OH^-]$.

The ionic strength (I) effect on the reaction rates has been described according to the theory of Bronsted and Bjerrum,[37] which postulates the reaction through the formation of an activated complex. According to this theory, the effect of ionic strength on the rate for a reaction involving two ions is given by the relationship:

$$\log k' = \log k_0 + 1.02 Z_A Z_B I^{1/2} \tag{13}$$

Here, Z_A and Z_B are the valency of the ions A and B, and k and k_0 are the rate constants in the presence and absence of the added electrolyte, respectively. A plot of log k' against $I^{1/2}$ should be linear with a slope of 1.02 $Z_A Z_B$. If Z_A and Z_B have similar signs, the quantity $Z_A Z_B$ is positive and the rate increases with the ionic strength, having a positive slope, while if the ions have dissimilar charges, the quantity $Z_A Z_B$ is negative and the rate would decrease with the increase in ionic strength, having a negative slope. In the present case, a primary salt effect is observed as the rate decreases with increase in ionic strength of medium,[37] supporting the involvement of ions of opposite sign in the rate-limiting step (Scheme 1). The Debye–Huckel plot of log k' against $I^{1/2}$ gave a straight line with a slope of -1.5. In the present system, two positive ions and one negative ion are involved in the rate-limiting step (Scheme 1) and the expected slope of -2 has not been found. This may be due to the fact that the ionic strength employed in the present investigation is beyond the formal Debye–Huckel limiting law. Alternatively, there could be formation of ion pairs in concentrated solutions, as suggested by Bjerrum.[37]

In the present case, addition of methanol to the reaction mixture increased the reaction rate. The effect of changing solvent composition on the rate of reaction has been described in detail in various monographs[38–44] and a plot of log k' *versus* $1/D$ was linear, with a positive slope. The dependence of the rate constant on the dielectric constant of the medium is given by the following:

$$\ln k' = \ln k'_0 - \left(\frac{NZ_AZ_Be^2}{DRTr_{\neq}}\right) \tag{14}$$

In this equation, k'_0 is the rate constant in a medium of infinite dielectric constant, Z_Ae and Z_Be are the total charges on the ions A and B, $r_{\neq}$ is the radius of the activated complex, R, T and N have their usual meanings. This equation predicts a linear plot of log k' *versus* $1/D$ with a negative slope if the charges on the ions are of the same sign and a positive slope if they are of opposite sign. The positive dielectric effect observed in the present study (Table 3) clearly supports[41] the involvement of dissimilar charges in the rate-limiting step (Scheme 1).

It was felt reasonable to compare the reactivity of CAT towards Gly-Gly in the absence of Ru(III) catalyst, under identical experimental conditions, in order to evaluate the catalytic efficiency of Ru(III). The reactions were carried out at different temperatures (298–318 K) and from the plots of log k' *versus* $1/T$ ($r > 0.9914$), activation parameters are evaluated for the uncatalysed reactions also (Table 4). However, the Ru(III)-catalysed reactions were found to be about 14 times faster than uncatalysed reactions. The activation parameters evaluated for the catalysed and uncatalysed reactions explain the catalytic effect on the reaction. The catalyst Ru(III) forms a complex (X) with the oxidant, which increases the oxidising property of the oxidant than without Ru(III). Further, the catalyst Ru(III) suitably modifies the reaction path by lowering the energy of activation (Table 4).

It has been pointed out by Moelwyn-Hughes[45] that, even in presence of the catalyst, the uncatalysed reactions also proceed simultaneously, so that

$$k_1 = k_0 + K_C[\text{catalyst}]^x \tag{15}$$

Here, k_1 is the observed pseudo-first-order rate constant obtained in the presence of Ru(III) catalyst and k_0 is that for the uncatalysed reaction, K_C is the catalytic constant and x is the order of the reaction with respect to [Ru(III)]. In the present investigation, 'x' value was found to be unity. Then the value of K_C is calculated using the Eqn (16):

$$K_C = k_1 - \frac{k_0}{[\text{Ru(III)}]^x} \tag{16}$$

The values of K_C have been evaluated at different temperatures (298–318 K) and K_C was found to vary with temperature. Further, a plot of log K_C *versus* $1/T$ was linear ($r = 0.9992$) and the values of energy of activation and other activation parameters for the Ru(III) catalyst were computed and are summarised in Table 5.

The proposed mechanism is supported by the observed moderate values of energy of activation and other thermodynamic parameters. The fairly high positive values of the free energy of activation and of the enthalpy of activation suggest that the transition state is highly solvated, while fairly high negative entropy of activation (Table 4) indicates the formation of a rigid associated transition state. Addition of the reduction product of CAT, PTS, did not alter the rate, indicating its non-involvement in the pre-equilibrium with the oxidant. Similarly, addition of halide ions has no effect on the rate indicating that there is no role for halide ions in the reaction. All these observations support the proposed mechanism.

Mechanism and rate law of Os (VIII) catalysis

Osmium tetroxide is known to be an efficient catalyst in the oxidation of several organic compounds by various oxidants in aqueous alkaline medium.[29,46–48] It has been shown that osmium is stable in its +8 oxidation state and exists in the

Table 5. Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values

	K_C			
Temperature (K)	Ru(III)	Os(VIII)	Pd(II)	Pt(IV)
298	27.3	5.57	0.61	2.98
303	35.2	7.59	1.00	4.42
308	53.5	9.58	1.52	6.84
313	72.7	13.2	2.41	10.4
318	102	16.8	3.70	14.5
E_a (kJ mol^{-1})	51.0	39.2	68.2	59.8
$\Delta H^{\neq}$ (kJ mol^{-1})	48.4 ± 0.01	36.7 ± 0.06	65.5 ± 0.01	57 ± 0.1
$\Delta G^{\neq}$ (kJ mol^{-1})	65.5 ± 0.16	69.7 ± 0.14	74.5 ± 0.12	70.3 ± 0.24
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	-54.6 ± 0.13	-106 ± 0.14	-28.9 ± 0.10	-43.0 ± -0.61
log A	10.3 ± 0.10	7.66 ± 0.01	11.7 ± 0.11	10.6 ± 0.10

$[\text{CAT}]_0 = 1.00 \times 10^{-3}$ mol dm^{-3}; $[\text{Gly-Gly}]_0 = 1.00 \times 10^{-2}$ mol dm^{-3}; $[\text{NaOH}] = 1.00 \times 10^{-2}$ mol dm^{-3}; $[\text{catalyst}] = 1.00 \times 10^{-5}$ mol dm^{-3}; $I = 0.30$ mol dm^{-3} (in case of Ru(III) catalysis).

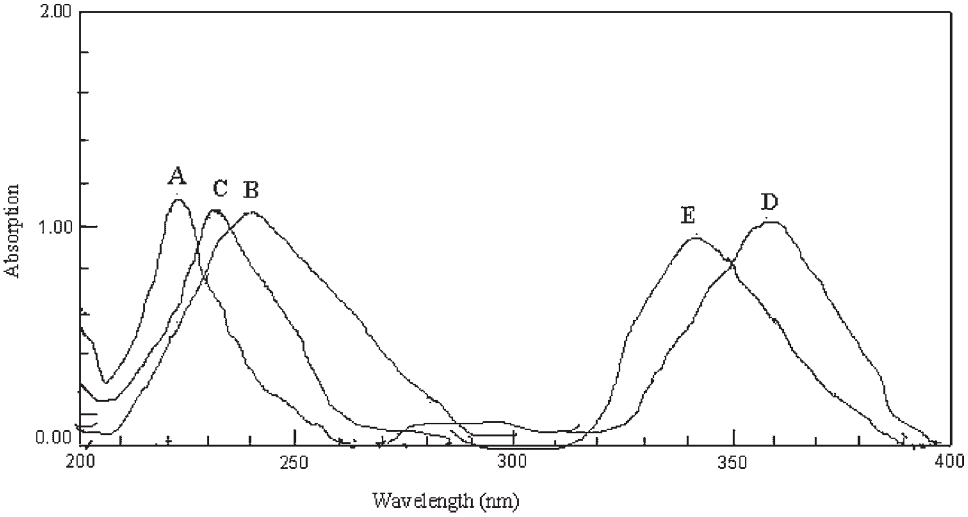


Figure 4. UV–Vis Spectra of (A) CAT, (B) Gly-Gly and (C) CAT + Gly-Gly, (D) Pd(II) and (E) Pd(II) + CAT + Gly-Gly in NaOH medium

following equilibria:[49–55]

$$OsO_4 + OH^- + H_2O \rightleftharpoons [OsO_4(OH)(H_2O)]^- \qquad (17)$$

$$[OsO_4(OH)(H_2O)]^- + OH^- \rightleftharpoons [OsO_4(OH)_2]^{2-} + H_2O \qquad (18)$$

The complexes $[OsO_4(OH)(H_2O)]^-$ and $[OsO_4(OH)_2]^{2-}$, which can be reduced to $[OsO_2(OH)_4]^{2-}$, with octahedral geometries are less likely to form higher coordination species with the oxidant/substrate. It is more realistic to postulate OsO_4, which has tetrahedral geometry,[50] as the active catalyst species than can effectively form a complex with the oxidant/substrate species. Spectroscopic evidence for the complex formation between CAT and Gly-Gly was obtained from UV–Vis spectra of Gly-Gly, CAT and a mixture of both (Fig. 4). Absorption maxima in alkaline medium appear at 236 nm for Gly-Gly, 223 nm for CAT and 227 nm for a mixture of both. A bathochromic shift of 4 nm from 223 to 227 nm of CAT suggests that complexation occurs between CAT and Gly-Gly.

Furthermore, the first-order dependence of rate on $[CAT]_0$ and fractional-order dependence on each of $[Gly\text{-}Gly]_0$, $[OH^-]$ and [Os(VIII)] indicate that the intermediate complex formed from the oxidant and substrate, which interacts with the catalyst. The possible oxidising species here would be $TsNCl^-$. In the light of these considerations, the Gly-Gly-CAT oxidation mechanism is formulated as given in Scheme 2 to explain all the observed experimental results.

The total effective concentration of CAT is

$$[CAT]_t = [TsNHCl] + [TsNCl^-] + [X^{II}] + [X^{III}] \qquad (19)$$

By substituting for [TsNHCl], $[TsNCl^-]$ and $[X^{II}]$ from steps (i), (ii) and (iii) of Scheme 2 in Eqn (19) and solving for $[X^{III}]$, we get

$$[X^{III}] = \frac{K_5K_6K_7[CAT]_t[Gly-Gly][Os(VIII)][OH^-]}{[H_2O] + K_5[OH^-] + K_5K_6[Gly-Gly][OH^-]\{1 + K_7[Os(VIII)]\}} \qquad (20)$$

From the slow and rds of Scheme 2,

$$Rate = \frac{-d[CAT]_t}{dt} = k_8[X^{III}] \qquad (21)$$

By substituting for $[X^{III}]$ from Eqn (20) into Eqn (21), the following rate law was obtained:

$$Rate = \frac{K_5K_6K_7k_8[CAT]_t[Gly-Gly][Os(VIII)][OH^-]}{[H_2O] + K_5[OH^-] + K_5K_6[Gly-Gly][OH^-]\{1 + K_7[Os(VIII)]\}} \qquad (22)$$

Since rate $= k'[CAT]_t$, Eqn (22) can be transformed into

$$k' = \frac{K_5K_6K_7K_8[Gly-Gly][Os(VIII)][OH^-]}{[H_2O] + K_5[OH^-] + K_5K_6[Gly-Gly][OH^-]\{1 + K_7[Os(VIII)]\}} \qquad (23)$$

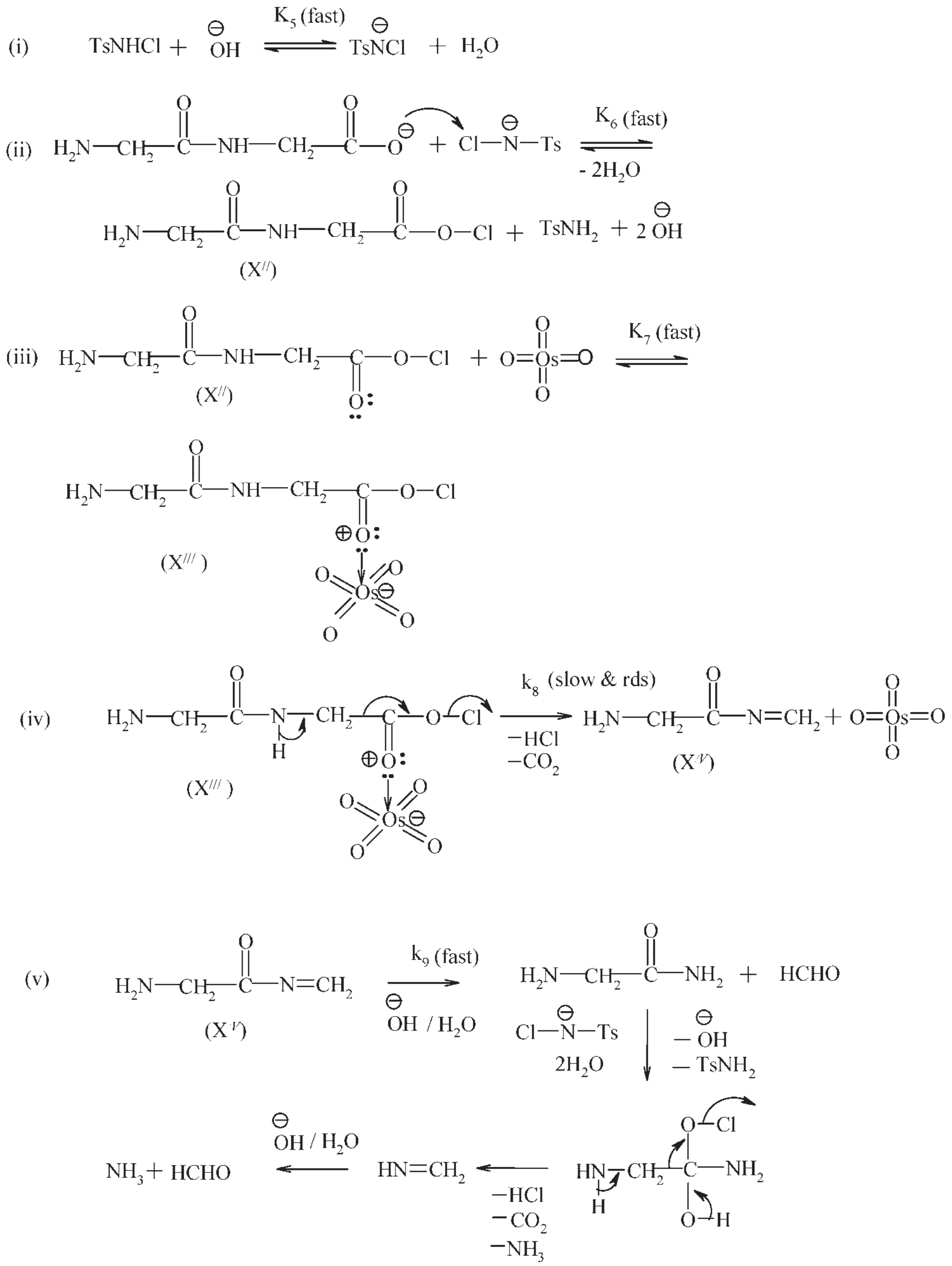
Scheme 2 and the rate law (23) are supported by the following facts:

Solvent isotope studies show that $k'(H_2O)/k'(H_2O) < 1$. This is generally correlated with the fact that OD^- ion is a stronger base than OH^- and in base catalysed reactions, enhancement of rate in D_2O medium is expected[34–36] and the same is noticed in the present study. In the present investigation, a plot of log k' *versus* $1/D$ is linear with a positive slope supporting the proposed Scheme 2, where a positive ion and a dipole[43,56] are involved in the rate-limiting step. The negligible influence of variation of the ionic strength, addition of PTS and halide ions on the rate of the reaction, and also the evaluated activation parameters are in good agreement with the mechanism proposed and the rate law derived.

The reactivity of CAT towards Gly-Gly in the absence of Os(VIII) catalyst was compared with the Os(VIII)-catalysed reaction, under identical set of experimental conditions. Rate constants revealed that the Os(VIII)-catalysed reactions are 24-fold faster than uncatalysed reactions (Table 4). The values of K_C were determined at different temperatures and from a plot of log K_C *versus* 1/T ($r = 0.9948$), values of activation parameters for Os(VIII) catalyst were computed (Table 5).

Mechanism and rate law of Pd(II) catalysis

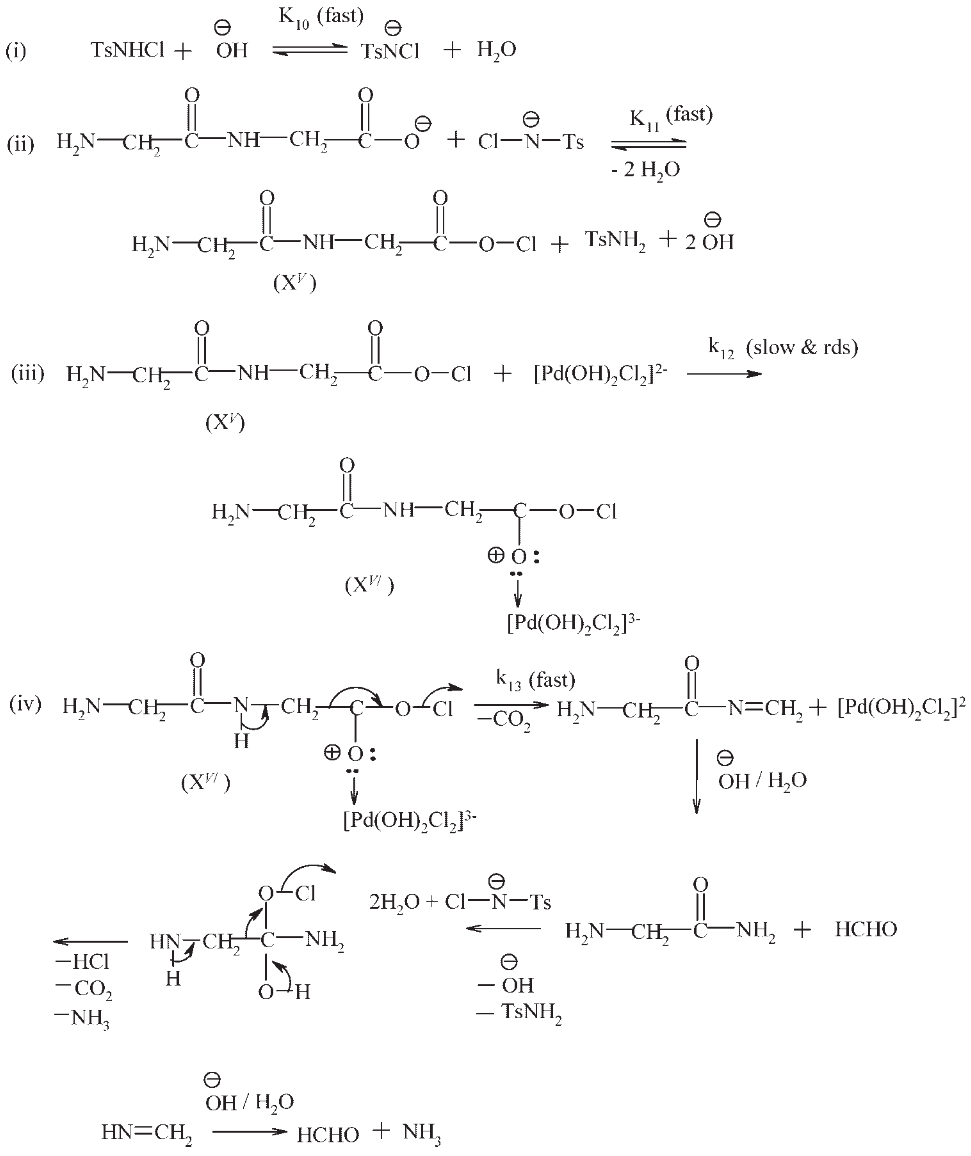
Palladium (II) chloride catalysis has been observed during various redox reactions and the reactions in the presence of Pd(II) have also shown a complex kinetics. Generally, the palladium



Scheme 2. A detailed mechanistic scheme for Os(VIII)-catalysed oxidation of Gly-Gly by CAT

complexes are somewhat less stable, from both kinetic and thermodynamic sense, than their platinum analogous. It is known to exist as different complexes in alkaline solutions[13,57–59] and the possible Pd(II) complex species are $[Pd(OH)Cl_3]^{2-}$, $[Pd(OH)_2Cl_2]^{2-}$ and $[Pd(OH)_4]^{2-}$. The species $[Pd(OH)_3Cl]^{2-}$ and $[Pd(OH)_4]^{2-}$ are not commonly found as they are insoluble. Further, the rate increases with the increase in $[OH^-]$ and there was no effect of $[Cl^-]$ on the rate of reaction which clearly rules out $[Pd(OH)Cl_3]^{2-}$ as the reactive species. Hence, $[Pd(OH)_2Cl_2]^{2-}$ complex ion has been assumed to be the reactive species in the present study.

UV–Vis spectral studies revealed that there is transient existence of complex between CAT and Gly-Gly in alkaline medium for Pd(II) catalysis. Absorption maxima were appeared at 223 nm for CAT, 236 nm for Gly-Gly and 227 nm for mixture of both (Fig. 4). The formation of other complex between CAT + Gly-Gly mixture and Pd(II) was also informed from UV–Vis spectral studies. Absorption maxima in alkaline medium appeared at 356 nm for Pd(II), 227 nm for CAT + Gly-Gly and 340 nm for Pd(II) and CAT + Gly-Gly mixture confirmative the existence of complex between Pd(II) and CAT + Gly-Gly mixture. The complex formation studies have been made for Pd(II) and CAT + Gly-Gly mixture at 340 nm in alkaline medium. A plot of $1/\Delta A$ *versus* 1/[CAT] ($r = 0.9910$) with an intercept suggests the formation of 1:1 complex between Pd(II) and CAT + Gly-Gly mixture. Further, the 1:1 complex formation was also evidenced



Scheme 3. A detailed mechanistic scheme for Pd(II)-catalysed oxidation of Gly-Gly by CAT

from the linearity of the plot log 1/Δ*A* *versus* log 1/[CAT] ($r = 9899$). From the slope and intercept of the plot 1/Δ*A* *versus* 1/[CAT], the value of formation constant, *K* was found to be 3.5×10^2.

Furthermore, the kinetic data led the authors to assure that $TsNCl^-$ is the reactive species of CAT. On the basis of the experimental findings, Scheme 3 is proposed for CAT oxidation of Gly-Gly in the presence of Pd(II) in alkaline medium.

The total effective concentration of CAT is

$$[CAT]_t = [TsNHCl] + [TsNCl^-] + [X^V] \tag{24}$$

By substituting for [TsNHCl] and $[TsNCl^-]$ from steps (i) and (ii) of Scheme 3 in Eqn (24) and solving for $[X^V]$, one gets

$$\text{Rate} = \frac{K_{10}K_{11}K_{12}[CAT]_t[Gly-Gly][OH^-]}{[H_2O] + K_{10}[OH^-] + K_{10}K_{11}[Gly-Gly][OH^-]} \tag{25}$$

From the slow and rds of Scheme 3,

$$\text{Rate} = \frac{-d[CAT]_t}{dt} = k_{12}[X^V][Pd(II)] \tag{26}$$

By substituting for $[X^V]$ from Eqn (25) into Eqn (26), the following rate law is derived:

$$\text{Rate} = \frac{K_{10}K_{11}K_{12}[CAT]_t[Gly-Gly][Pd(II)][OH^-]}{[H_2O] + K_{10}[OH^-] + K_{10}K_{11}[Gly-Gly][OH^-]} \tag{27}$$

The rate law (27) satisfies all the experimental observations and hence the proposed mechanism and the derived rate law are valid.

Since rate $= k'[CAT]_t$, Eqn (27) can be transformed into

$$k' = \frac{K_{10}K_{11}K_{12}[Gly-Gly][Pd(II)][OH^-]}{[H_2O] + K_{10}[OH^-] + K_{10}K_{11}[Gly-Gly][OH^-]} \tag{28}$$

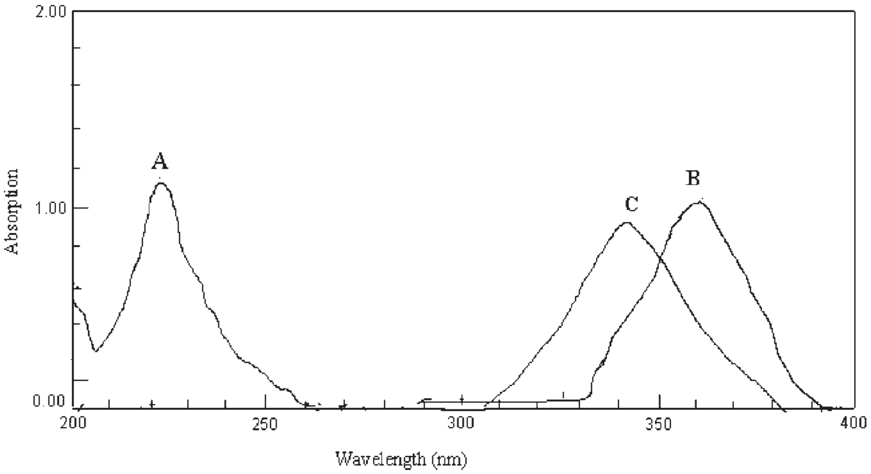


Figure 5. UV–Vis spectra of (A) CAT, (B) Pt(IV) and (C) Pt(IV) + CAT in NaOH medium

Rate of reaction decreases on decreasing dielectric constant of the medium. This observed solvent effect leads to the reported conclusion,[43] that the decrease in dielectric constant should decrease the reaction rate for the reaction involving a negative ion and dipolar molecule as shown in Scheme 3, which substantiates the proposed mechanism. The increase of reaction rate in D_2O medium supports the proposed mechanism since it is well known that OD^- is a stronger base than OH^-[34–36] ion and hence exerts a stronger acceleration effect on the reaction. The proposed mechanism is also supported by the activation parameters and also negligible effect of PTS, halide ions and ionic strength on the rate of the reaction. Further, energy of activation of Pd(II)-catalysed and -uncatalysed reactions were computed and it was found that Pd(II)-catalysed reactions were nearly eightfold faster than uncatalysed reactions (Table 4). The values of K_C and activation parameters for Pd(II) catalyst were determined (Table 5) by the plot of log K_C *versus* $1/T$ ($r = 0.9981$).

Mechanism and rate law of Pt(IV) catalysis

Pt(IV) catalysis during variety of redox-reactions is well reported in the literature.[13,33,60,61] Chloroplatinic acid, $H_2(PtCl_6)$, is the starting material in platinum(IV) chemistry. In aqueous solution, chloroplatinic acid ionises[13,33,62] as follows:

$$H_2[PtCl_6] \rightleftharpoons [PtCl_6]^{2-} + 2H^+ \tag{29}$$

In an alkaline medium (pH > 8), $[PtCl_6]^{2-}$ changes to $[PtCl_5(OH)]^{2-}$ in a fast step[33,60,62] and follows as

$$[PtCl_6]^{2-} + OH^- \rightleftharpoons [PtCl_5(OH)]^{2-} + Cl^- \tag{30}$$

Further ligand (Cl^-) replacements from $[PtCl_5(OH)]^{2-}$ is also reported:[33,60,62]

$$[PtCl_5(OH)]^{2-} + OH^- \rightleftharpoons [PtCl_4(OH)_2]^{2-} + Cl^- \tag{31}$$

However, the dihydroxy platinum (IV) species is quite unstable[33,63] in aqueous solutions and therefore consequently under the present experimental conditions $[PtCl_5(OH)]^{2-}$ may act as the reactive species of Pt(IV) in alkaline medium. Similar equilibrium have been reported in the Pt(IV)-catalysed oxidation of several substrates using various oxidants in alkaline medium.[60–62]

The formation of a complex between Pt(IV) and oxidant was evidenced from UV–Vis spectra of both Pt(IV), and Pt(IV)-CAT in which a shift of Pt(IV) from 360 to 347 nm was observed, indicating the formation of a complex (Fig. 5). According to Eqn (6), a plot of $1/\Delta A$ *versus* 1/[CAT] ($r = 0.9912$) with an intercept suggests the formation of 1:1 complex between Pt(IV) and CAT. Further, the plot of log $1/\Delta A$ *versus* log 1/[CAT] was also linear ($r = 9816$). From the slope and intercept of the plot $1/\Delta A$ *versus* 1/[CAT], the value of formation constant, *K*, of the complex was found to be 4.29×10^2.

Based on the experimental results, it is likely that $TsNCl^-$ itself acts as the reactive oxidant species in the present case also. Considering the above facts and all the observed experimental data, the reaction Scheme 4 can be suggested for Pt(IV)-catalysed oxidation of Gly-Gly by CAT in alkaline medium.

The total effective concentration of CAT is

$$[CAT]_t = [TsNHCl] + [TsNCl^-] + [X^{VII}] + [X^{VIII}] \tag{32}$$

By substituting for [TsNHCl], $[TsNCl^-]$ and $[X^{VII}]$ from steps (i), (ii) and (iii) of Scheme 4 in Eqn (32) and solving for $[X^{VIII}]$, we get

$$[X^{VIII}] = \frac{K_{14}K_{15}K_{16}[CAT]_t[Pt(IV)][OH^-][H_2O]}{[TsNH_2]\{[H_2O] + K_{14}[OH^-] + K_{14}K_{15}[Pt(IV)][OH^-]\} + 1} \tag{33}$$

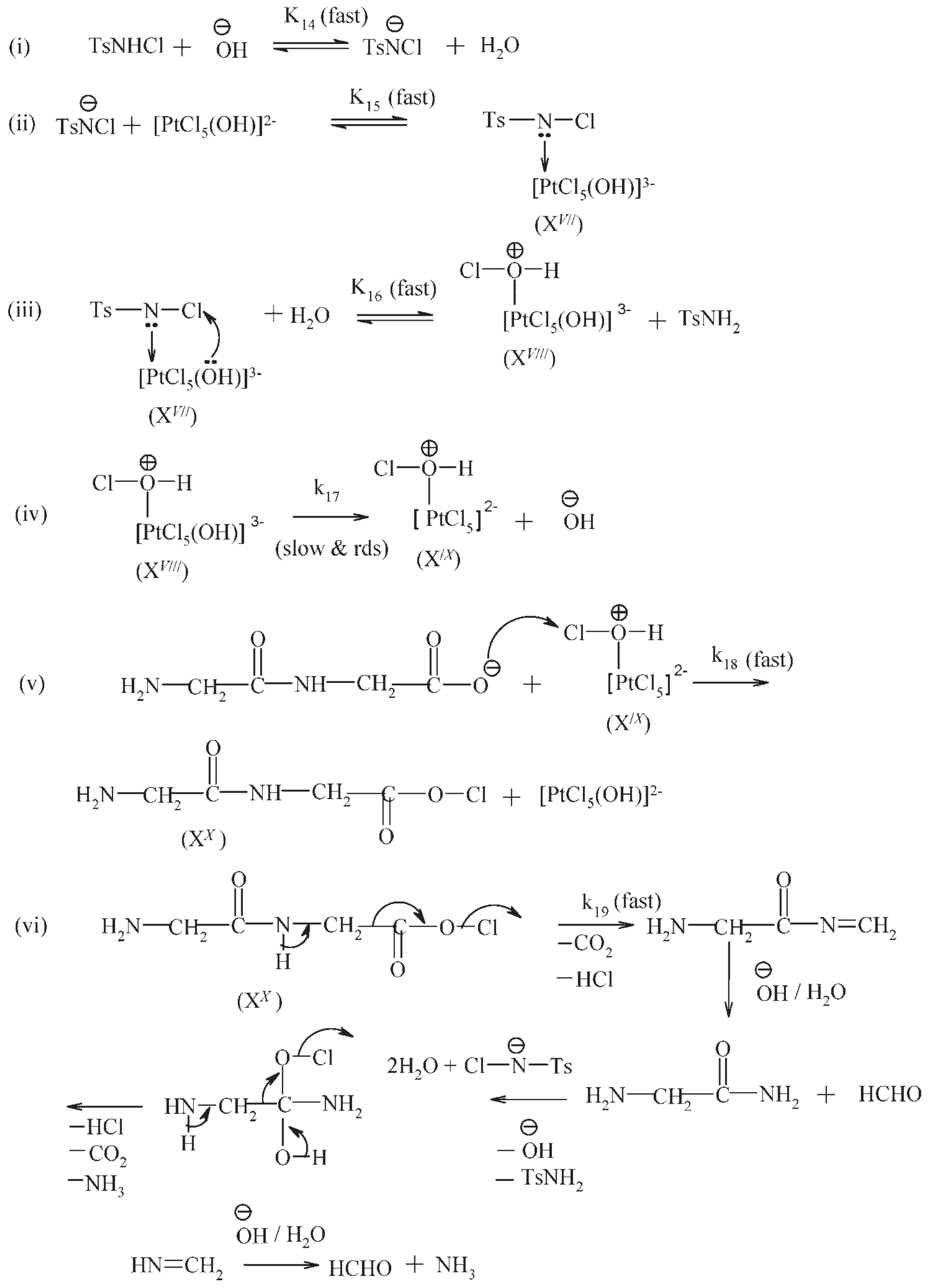
From the slow and rds (iv) of Scheme 4,

$$\text{Rate} = \frac{-d[CAT]_t}{dt} = k_{17}[X^{VIII}] \tag{34}$$

By substituting for $[X^{VIII}]$ from Eqn (33) into Eqn (34), the following rate law is governed:

$$\text{Rate} = \frac{K_{14}K_{15}K_{16}k_{17}[CAT]_t[Pt(IV)][OH^-][H_2O]}{[TsNH_2]\{[H_2O] + K_{14}[OH^-] + K_{14}K_{15}[Pt(IV)][OH^-]\} + 1} \tag{35}$$

The rate law (35) is in complete agreement with the experimental observations.



Scheme 4. A detailed mechanistic scheme for Pt(IV)-catalysed oxidation of Gly-Gly by CAT

Since rate $= k'[\mathrm{CAT}]_t$, Eqn (35) can be transformed into Eqn (36):

$$k' = \frac{K_{14}K_{15}K_{16}k_{17}[\mathrm{CAT}]_t[\mathrm{Pt(IV)}][\mathrm{OH}^-][\mathrm{H_2O}]}{[\mathrm{TsNH_2}]\{[\mathrm{H_2O}] + K_{14}[\mathrm{OH}^-] + K_{14}K_{15}[\mathrm{Pt(IV)}][\mathrm{OH}^-]\} + 1} \tag{36}$$

The observed dielectric and isotope effects are in accordance with the theories of Amis[43] and Collins and Bowman,[34] respectively. The negligible influence of ionic strength of the medium and of added halide ions on the rate of the reaction, and also the observed activation parameters further corroborate with the suggested mechanism. Catalytic constants and activation parameters with reference to Pt(IV) catalyst have been computed (Table 5). Pt(IV)-catalysed reactions showed 10-fold faster than the uncatalysed reactions (Table 4). The values of k_0 obtained from the experiment ($0.41 \times 10^{-4}\ \mathrm{s}^{-1}$) and by the plot of k' *versus* Pt(IV) ($0.39 \times 10^{-4}\ \mathrm{s}^{-1}$) were consistent with each other, indicating that both Pt(IV)-catalysed and -uncatalysed reactions take place simultaneously.

We thought, it is worthwhile to compare the rate of oxidation of Gly-Gly in the presence of these four catalysts with that of uncatalysed reaction (in the absence of catalyst), under identical experimental conditions. It was found that the catalysed reactions are 7- to 24-fold faster than the uncatalysed reaction. For the catalysed reactions, it is seen from the Table 4 that the activation energy is highest for the slowest reaction and vice versa. From the inspection of rate constants and the values of energy of activation (Table 4), the relative reactivity of these catalysts during the oxidation of Gly-Gly by CAT in alkaline medium is in the order: Os(VIII) > Ru(III) > Pt(IV) > Pd(II). This may be attributed to the d-electronic configuration of the metal ions. Osmium having d^0 electronic configuration has greater catalytic efficiency to oxidise the substrate compared to the other metal ions used in the present study. Thus, the catalytic efficiency decreases as the number of electrons in the d-orbital increases. Pd(II) having d^8 electronic configuration is expected to have least catalytic efficiency among the catalysts used. It is likely that during the course of the reaction the metal ion momentarily undergo reduction when the oxidant/oxidant-substrate complex is attached to the metal ions and after this the metal ion gets back to its original valence state as shown in Schemes 1–4. Ru(III) and Pt(IV) having d^5 and d^6 electronic configuration, respectively, exhibit intermediate catalytic efficiency in the present study. Hence, based on d-electronic configuration of the metal ions, the reactivity decreases as the number of electrons increases in the d-orbital as d^0 (Os(VIII)) > d^5 (Ru(III)) > d^6 Pt(IV) > d^8 (Pd(II)). Consequently, the observed catalytic trend: Os(VIII) > Ru(III) > Pt(IV) > Pd(II) is based on the d-electronic configuration of the metal ions.

Furthermore, efforts were made to compare the main salient features of the kinetic data of this paper with the results reported[64] for the oxidation of glycine (monomer of gly-gly) by CAT in alkaline medium. Gowda and Mahadevappa have reported the kinetics of oxidation of several amino acids by CAT in both acid and alkaline media.[64] Rate of oxidation of glycine shows first-order dependence each in $[CAT]_0$ and $[Glyine]_{0,}$ and inverse fractional-order in $[OH^-]$. But in the present investigation, the oxidation of gly-gly exhibits a first-order kinetics in $[CAT]_0$ and fractional-order in $[OH^-]$ for all the four catalysed reactions, whereas zero and fractional-order in $[gly\text{-}gly]_0$, and first and fractional order in [catalyst] for various catalysed reactions studied. The stoichiometry of the reaction was found to be 1:2 for both glycine and gly-gly. It was also found that the $E_a = 108$ and 62.0 kJ mol^{-1} for gly-gly (Table 4) and glycine,[64] respectively, revealed that the reaction is faster in glycine compared to gly-gly. This can be attributed to the involvement of different oxidising species TsNHCl and HOCl in the oxidation of glycine, and $TsNCl^-$ in the case of gly-gly. The facts presented above compel us to conclude that the present study in many respects differ from the reported studies[64] that is the kinetics of oxidation of glycine by CAT in alkaline medium.

CONCLUSIONS

The kinetic patterns of Ru(III)/Os(VIII)/Pd(II)/Pt(IV)-catalysed oxidation of Gly-Gly by CAT in NaOH medium were found to be different and the catalytic efficiency of these platinum group metal ions increases in the order: Os(VIII) > Ru(III) > Pt(IV) > Pd(II). This trend may be attributed to different d-electronic configuration of the catalysts. Further, the rates of oxidation of Gly-Gly for all the catalysed reactions have been compared with uncatalysed reaction and found that the catalysed reactions are 7- to 24-fold faster. Catalytic constants and activation parameters with reference to each catalyst have been computed. Based on the observed experimental results, detailed mechanistic interpretation and the related kinetic modelling have been worked out for each catalyst. It can be concluded that Ru(III)/Os(VIII)/Pd(II)/Pt(IV) acts as efficient catalysts in the oxidation of Gly-Gly brought about by CAT in alkaline medium.

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