J. Chem. Sci., Vol. 117, No. 1, January 2005, pp. 33–42. © Indian Academy of Sciences.

Kinetic, mechanistic and spectral investigation of ruthenium (III)-catalysed oxidation of atenolol by alkaline permanganate (stopped-flow technique)

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MS received 10 October 2003; revised 26 December 2003

Abstract. Kinetics of ruthenium (III) catalyzed oxidation of atenolol by permanganate in alkaline medium at constant ionic strength of 0·30 mol dm^3 has been studied spectrophotometrically using a rapid kinetic accessory. Reaction between permanganate and atenolol in alkaline medium exhibits 1 : 8 stoichiometry (atenolol : $KMnO_4$). The reaction shows first-order dependence on [permanganate] and [ruthenium (III)] and apparently less than unit order on both atenolol and alkali concentrations. Reaction rate decreases with increase in ionic strength and increases with decreasing dielectric constant of the medium. Initial addition of reaction products does not affect the rate significantly. A mechanism involving the formation of a complex between catalyst and substrate has been proposed. The active species of ruthenium (III) is understood as $[Ru(H_2O)_5OH]^{2+}$. The reaction constants involved in the different steps of mechanism are calculated. Activation parameters with respect to the slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated.

Keywords. Kinetics; permanganate; stopped-flow technique; oxidation of atenolol; ruthenium(III) catalysis.

1. Introduction

Permanganates ions oxidize a greater variety of substrates and find extensive applications in organic syntheses,[1–7] especially after the advent of phase-transfer catalysis,[3,4,6] which permits the use of solvents such as methylene chloride and benzene. Kinetic studies constitute an important source of mechanistic information on the reaction, as demonstrated by results referring to unsaturated acids in both aqueous[1,3,7] and non-aqueous media.[8]

During oxidation by permanganate, it is evident that the Mn(VII) in permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium[9] used for the study. In strongly alkaline media, the stable reduction product[10,11] is the manganate ion, MnO_4^{2-}. No mechanistic information is available to distinguish between direct one-electron reduction to Mn(VI) (scheme 1) and one in which a hypomanganate is formed in a two-electron step followed by rapid reaction[12] (scheme 2).

4-(2-Hydroxy-3-isopropylaminopropoxy)phenyl-acetamide commercially known as atenolol (ATN), a *b*-adrenoreceptor blocking agent, is commonly used

$$\mathrm{Mn(VII)} + S \xrightarrow{k_1^1} \mathrm{Mn(VI)} + S^\bullet,$$

$$\mathrm{Mn(VII)} + S^\bullet \xrightarrow{k_2^1} \mathrm{Mn(VI)} + \text{products},$$

$$\text{where } S = \text{substrate},\ k_2^1 \gg k_1^1.$$

Scheme 1.

$$\mathrm{Mn(VII)} + S \xrightarrow{k_3^1} \mathrm{Mn(V)} + \text{products},$$
$$\mathrm{Mn(VII)} + \mathrm{Mn(V)} \xrightarrow{k_4^1} 2\ \mathrm{Mn(VI)},$$

$$\text{where } S = \text{substrate},\ k_4^1 \gg k_3^1.$$

Scheme 2.

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as antihypertensive drug.[13] It is also used for anti-angina treatment to relieve symptoms, improve tolerance and as an anti-arrhythmic to regulate heartbeat and present infections. It is also used in management of alcohol withdrawal, in anxiety states, migraine prophylaxis, hyperthyroidism and tremors.

Ruthenium (III) acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium.[14] The catalysis mechanism can be quite complicated due to the formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The kinetics of fast reaction between ruthenate (VII), RuO_4^-, and manganate (VI), i.e. MnO_4^{2-}, have been studied,[15] where the reaction is presumed to proceed via an outer-sphere mechanism. The uncatalysed reaction between atenolol and permanganate in an alkaline medium has been studied previously.[16] A microscopic amount of ruthenium (III) is sufficient to catalyze the reaction and a variety of mechanisms are possible. Herein, we describe the results of the title reaction in order to understand the active species of oxidant, reductant and catalyst in such media and to arrive at a plausible mechanism.

2. Experimental

2.1 *Devices*

Since the initial reaction was too fast to be monitored by the usual methods, kinetic measurements were performed on a Peltier accessory (temperature control) attached Varian Cary 50 Bio UV–Vis spectrophotometer connected to a rapid kinetic accessory (HI-Tech SFA-12). IR, NMR, fluorimetry and mass spectral studies were performed by Nicolet Impact-410 FT IR, Brucker 300 MHz, and Pesciex Qstar Polsar LC-MS/MS-TOF.

2.2 *Materials: Chemicals and catalyst*

All chemicals used were of reagent grade. Solution of atenolol (M/s SS Antibiotics Pvt Ltd, Aurangabad, India) was prepared by dissolving the appropriate amount of recrystalised sample in double distilled water**.** The solution of $KMnO_4$ (BDH) was prepared by dissolving the appropriate amounts of sample in doubly distilled water and standardized[17] against $(CO_2H)_2$. K_2MnO_4 solution was prepared as described by Carrington and Symons[18] as follows: A solution of $KMnO_4$ was heated to boiling in 8·0 mol dm^{-3} KOH solution until a green colour appeared. The solid formed on cooling was recrystallised from the same solvent. Using the required amount of recrystallised sample, a stock solution of K_2MnO_4 was prepared in aqueous KOH. The solution was standardized by measuring the absorbance on a Peltier accessory (temperature control) attached Varian Cary 50 Bio UV–Vis spectrophotometer with a 1 cm quartz cell at 608 nm ($e = 1530 \pm 20$ dm^3 mol^{-1} cm^{-1}).

The Ru(III) solution was prepared by dissolving a known weight of $RuCl_3$ (sd Fine-Chem) in HCl (0·20 mol dm^{-3}). Hg was added to the Ru(III) solution, to reduce any Ru(IV) formed during the preparation of the Ru(III) stock solution, which was set aside for 24 h. The Ru(III) concentration was then assayed by EDTA titration.[19]

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. NaOH and $NaClO_4$ were used to provide the required alkalinity and to maintain the ionic strength respectively.

2.3 *Kinetic measurements*

All kinetic measurements were performed under pseudo-first order conditions with excess of [atenolol] over [MnO_4^-] at a constant ionic strength of 0·30 mol dm^{-3}. The reaction was initiated by mixing previously thermostatted solutions of MnO_4^- and atenolol, which also contained the necessary quantities of Ru(III), NaOH and $NaClO_4$, to maintain the required alkalinity and ionic strength respectively. The temperature was uniformly maintained at 25 ± 0.1°C. The course of reaction was followed by monitoring the decrease in the absorbance of MnO_4^- in a 1 cm quartz cell of Peltier accessory (temperature control) attached Varian Cary 50 Bio UV–Vis spectrophotometer connected to a rapid kinetic accessory (Hi-Tech SFA-12), at its absorption maximum of 526 nm as a function of time. The application of Beer's law to permanganate at 526 nm is verified, giving $e = 2083 \pm 50$ dm^3 mol^{-1} cm^{-1} (literature $e = 2200$ dm^3 mol^{-1} cm^{-1}). The first-order rate constants, (k_c) were evaluated by the plots of log (A_t–A_∞) versus time by fitting the data to the expression $A_t = A_\infty + (A_0 - A_\infty)e^{-kc.t}$, where A_t, A_0 and A_∞ are absorbances of permanganate at time t, 0 and ∞ respectively. The first-order plots in almost all cases are linear to 80% completion of the reaction and k_c is reproducible within ±5%. During the course of measurements, the solution changes from violet to blue and then to green. The spectrum of the green solution is identical to that of MnO_4^{2-}. It is probable that the blue color originates from the violet of permanganate and the green from the manganate, excluding the accumulation of hypomanganate. It is also evident from figure 1 that the absorbance of permanganate decreases at 526 nm whereas the absorbance of manganate increases at 608 nm.

The effect of dissolved oxygen on the rate of reaction was studied by preparing the reaction mixture and following the reaction in an atmosphere of N_2. No significant difference is observed, between the results. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate has no effect on reaction rate. However, fresh solutions were used during the experiments.

In view of the modest concentration of alkali used in the reaction medium, attention was also given to the effect of the surface of the reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on the rate.

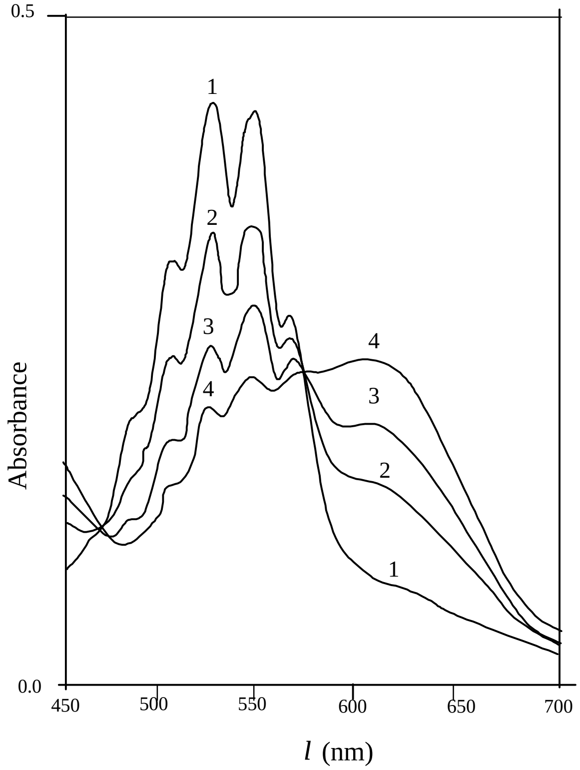


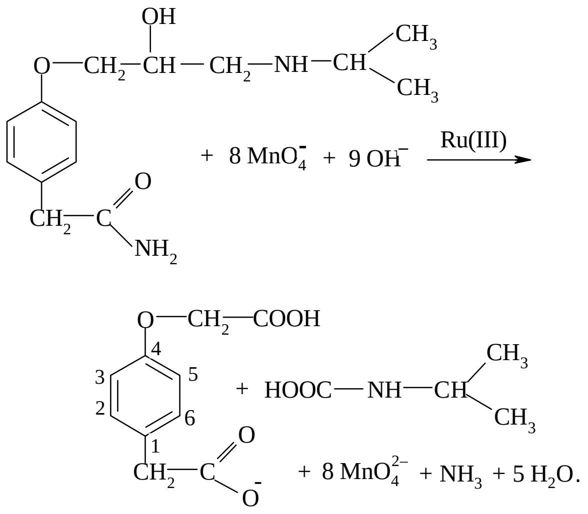
Figure 1. Spectroscopic changes occurring in the Ru(III) catalysed oxidation of atenolol by permanganate with [ATN] = $1·5 \times 10^{-3}$, $[MnO_4] = 1·5 \times 10^{-4}$ [Ru(III)] = $1·0 \times 10^{-6}$, $[OH^-] = 0·05$, and $I = 0·30$ mol dm^{-3} at 25°C, scanning time interval = 120 s.

Regression analysis of experimental data to obtain the regression coefficient *r* and standard deviation *S* of points from the regression line was done using a Pentium-IV personal computer.

3. Results

3.1 *Stoichiometry and product analysis*

Reaction mixtures containing an excess permanganate concentration over atenolol and constant [ruthenium (III)], 0·05 mol dm^{-3} NaOH, and adjusted to ionic strength of 0·30 mol dm^{-3} was allowed to react for 6 h. at 25 ± 0.1°C. The remaining permanganate was then analysed spectrophotometrically. The results indicated that eight moles of MnO_4^- are consumed by one mole of atenolol as given by the reaction:



(1)

For identification of the products, the reaction mixture containing excess of atenolol was kept to allow completion of reaction. The reaction product, 4-carboxy methoxy phenyl acetic acid, was extracted with ether and recrystallised from aqueous alcohol, and its purity checked by HPLC. 4-Carboxy methoxy phenyl acetic acid was also characterised by its IR spectrum, which showed a band at (*u*) 1690 cm^{-1} due to acid >C=O stretch and a broad band at 2845 cm^{-1} due to O–H stretch. It was further characterised by ^{1}H NMR spectrum (DMSO), where it showed a singlet at 9·6 *d* due to two carboxylic OH's, a doublet (J = 9 Hz) at 6·94 *d* due to C_3- and

C_5-protons, another doublet (J = 9 Hz) at 7·20 ***d*** due to C_2- and C_6-protons, a singlet at 3·53 ***d*** due to methylene protons of ph-CH_2- and another singlet at 4·58 ***d*** due to methylene protons of ph-O-CH_2- respectively. Mass spectra ESI technique (solvents: acetonitrile + water + ammonium acetate) gave (M^+ + 17) (ammoniated) 228 and (M^+) m/z 211. Ammonia was identified by use of Nessler's reagent.[20] The product, Ni(II), remained in the aqueous layer and it was identified by its dimethyl glyoxime complex.[21]

N-(isopropyl) amino carboxylic acid, which is soluble in water, was identified by the spot test.[22] It was observed that the 4-carboxy methoxy phenyl acetic acid and N-(isopropyl) amino carboxylic acid do not undergo further oxidation under the present kinetic conditions.

3.2 *Spectrofluorimetric studies*

The fluorescence study was carried out in methanol as solvent for good dissolution of the pure and product compound. No interference of the solvent methanol was seen in the fluorescent study. Fluorescence studies of pure compound atenolol and the product of the reaction of atenolol with permanganate in presence of ruthenium (III) catalyst in aqueous alkaline medium were carried out. Excitation for the atenolol was observed at 370 nm and emission now at 411 nm with intensity 106. Excitation of the product was observed at 370 nm and emission was at 416 nm with considerable decrease in fluorescent intensity to 36·62, due to quenching.

3.3 *Reaction orders*

As permanganate oxidation of atenolol in alkaline medium proceeds with measurable rate in the absence of ruthenium (III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T – k_U$. Hence, the reaction orders have been determined from the slopes of log k_C vs log concentration plots by varying the concentrations of reductant, Ru(III), and alkali in turn, while keeping the others constant.

Potassium permanganate concentration was varied in the range of $2{\cdot}0 \times 10^{-5}$ to $2{\cdot}0 \times 10^{-4}$ mol dm^{-3}, and the linearity of plots of log absorbance vs time ($r \geq 0{\cdot}9998$, $S \leq 0{\cdot}0131$) up to 85% completion of the reaction (figure 2) indicate a reaction order of unity in [MnO_4^-]. This is also confirmed by variation of [MnO_4^-], which did not result in any change in the pseudo first-order rate constants, k_C (table 1). The substrate concentration was varied in the range $1{\cdot}0 \times 10^{-3}$ to $1{\cdot}0 \times 10^{-2}$ mol dm^{-3} at 25°C, while keeping all other reactant concentrations and conditions constant, including ruthenium (III) catalyst. The kc values increased with increase in concentration of atenolol indicating an apparently less than unit order dependence on [atenolol] (table 1).

Ruthenium (III) concentration was varied in the $8{\cdot}0 \times 10^{-7}$ to $8{\cdot}0 \times 10^{-6}$ mol dm^{-3} range, at constant concentration of permanganate, atenolol, alkali and ionic strength. The order in [Ru(III)] is found to be unity (table 1) from the linearity of the plots of log kc vs log [Ru(III)] ($r \geq 0{\cdot}9995$, $S \leq 0{\cdot}0122$). The effect of alkali on the reaction has been studied at constant concentrations of atenolol, potassium permanganate, ruthenium (III) and a constant ionic strength of 0·30 mol dm^{-3}. The rate constants increased with increasing [alkali] and the order less than unity (table 1).

3.4 *Effect of relative permittivity and ionic strength*

The effect of relative permittivity (e_T) on the rate constant has been studied by varying the *t*-butanol–

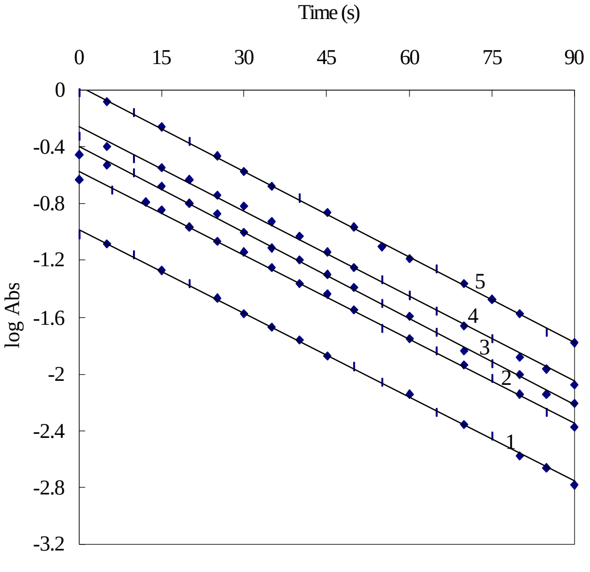


Figure 2. First-order plots of Ru(III)-catalysed oxidation of permanganate by atenolol in aqueous alkaline medium at 25°C. [MnO_4^-] × 10^4 (mol dm^{-3}); (1) 0·2, (2) 0·4, (3) 1·0, (4) 1·5, (5) 2·0.

Table 1. Effect of variation of [$KMnO_4$], [ATN], [Ru(III)] and [OH] on Ru(III)-catalysed oxidation of atenolol by $KMnO_4$ in aqueous alkaline media at 25°C and I = 0·30 mol dm^{-3}.

$10^4[MnO_4]$ (mol dm^{-3})	10^3[ATN] (mol dm^{-3})	10^6[Ru(III)] (mol dm^{-3})	[OH^-] (mol dm^{-3})	10^2 (s^{-1})			
				k_T	k_u	$k_{c\ \mathrm{expt.}}$	$k_{c\ \mathrm{cal.}}$
0·2	1·5	1·0	0·05	4·64	1·12	3·52	3·48
0·4	1·5	1·0	0·05	4·66	1·14	3·52	3·48
1·0	1·5	1·0	0·05	4·67	1·13	3·54	3·48
1·5	1·5	1·0	0·05	4·65	1·16	3·49	3·48
2·0	1·5	1·0	0·05	4·62	1·09	3·53	3·48
1·5	1·0	1·0	0·05	3·63	0·86	2·77	2·70
1·5	1·5	1·0	0·05	4·65	1·16	3·49	3·48
1·5	3·0	1·0	0·05	6·99	2·04	4·95	5·02
1·5	6·0	1·0	0·05	10·0	3·54	6·46	6·47
1·5	1·0	1·0	0·05	13·5	5·54	7·93	7·41
1·5	1·5	0·8	0·05	3·97	1·16	2·81	2·78
1·5	1·5	1·0	0·05	4·65	1·16	3·49	3·48
1·5	1·5	2·0	0·05	8·21	1·16	7·05	6·95
1·5	1·5	4·0	0·05	15·3	1·16	14·2	13·9
1·5	1·5	8·0	0·05	29·4	1·16	28·3	28·0
1·5	1·5	1·0	0·02	2·50	0·58	1·92	1·87
1·5	1·5	1·0	0·05	4·65	1·16	3·49	3·48
1·5	1·5	1·0	0·08	6·07	1·50	4·57	4·43
1·5	1·5	1·0	0·10	6·50	1·60	4·90	4·86
1·5	1·5	1·0	0·20	8·00	2·01	5·99	6·08

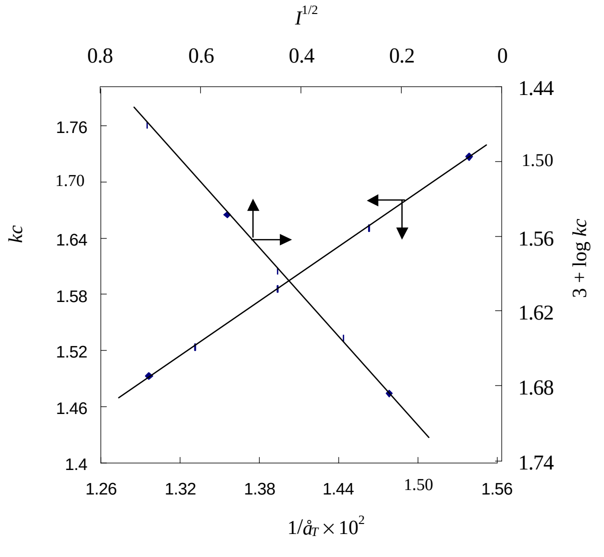


Figure 3. Plots of log k_c vs $I^{1/2}$ and log k_c vs $1/e_T$. [ATN] = 1·5 × 10^{-3}, [MnO_4^-] = 1·5 × 10^{-4}, [Ru(III)] = 1·0 × 10^{-6}, [OH^-] = 0·05, and I = 0·30 mol dm^{-3} at 25°C.

water content in the reaction mixture with all other conditions kept constant, including concentration of Ru(III) catalyst. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids.[23] No reaction of the solvent with the oxidant occurs under the experimental conditions employed. The rate constant, k_C, increases with decreasing relative permittivity of the medium. The plot of log k_C vs $1/e_T$ is linear with a positive slope (figure 3) ($r \geq 0·9989$, $S \leq 0·0141$).

The effect of ionic strength was studied by variation of the $NaClO_4$ concentration in the reaction medium. The ionic strength was varied from 0·05 to 0·5 mol dm^{-3} at constant concentrations of permanganate, atenolol, ruthenium (III) and alkali. It is found that the rate constant decreases with increasing concentration of $NaClO_4$. The plot of log k_C vs $I^{1/2}$ is linear with a negative slope (figure 3) ($r \geq 0·9997$, $S \leq 0·0112$).

3.5 *Effect of initially added products*

The initially added products, such as manganate, and 4-carboxy methoxy phenyl acetic acid, do not have any significant effect on the rate of the reaction.

Table 2. Thermodynamic activation parameters for Ru(III)-catalysed oxidation of alkaline permanganate by atenolol in alkaline media with respect to the slow step of scheme 3.

(a) *Effect of temperature*

Temp. (K)	298	303	308	313	318
$k \times 10^{-5}$ (dm^3 mol^{-1} s^{-1})	2.10	2.31	2.51	2.75	2.99

(b) *Effect of temperature on K_1 in Ru(III)-catalysed oxidation of alkaline permanganate by atenolol in alkaline medium*

Temp. (K)	298	303	308	313	318
K_1(dm^3 mol^{-1})	15.0	18.3	21.6	25.1	29.4

(c) *Activation parameters*

Parameters	E_a (kJ mol^{-1})	log A	$\Delta H^\#$ (kJ mol^{-1})	$\Delta S^\#$ (JK^{-1} mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})
Catalysed reaction	13·7 ± 0·7	7·74 ± 0·4	11·2 ± 0·6	–25·1 ± 1·3	18·8 ± 1·0
Uncatalysed reaction[16]	24 ± 3	–	21 ± 3	–200 ± 10	82 ± 4

(d) *Thermodynamic quantities for the first equilibrium of scheme 3*

Thermodynamic quantities	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})	ΔG (kJ mol^{-1})
Values	25·9 ± 1·4	110 ± 6	–7·8 ± 0·4

3.6 *Test for free radicals*

To test for the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 24 h under nitrogen atmosphere. On dilution with methanol, white precipitate of polymer was formed, indicating that intervention of free radicals in the reaction does occur. The blank experiment of reacting either permanganate and ruthenium (III) or atenolol and ruthenium (III) alone with acrylonitrile did not induce polymerization under the same conditions. Initially added acrylonitrile decreases the rate indicating free radical intervention, as in the earlier work.[24]

3.7 *Effect of temperature*

Rates of reaction were measured at different temperatures under varying atenolol concentrations. Rate of reaction increases with increase of temperature. The rate constants, k, of the slow step of scheme 3 are obtained from the slope of the plot of [Ru(III)]/kc vs 1/[atenolol] ($r \geq 0.9996$, $S \leq 0.0121$) and used to calculate the activation parameters. The values of k (dm^3 mol^{-1} s^{-1}) are given in table 2. The activation parameters corresponding to these constants were evaluated from the plot of log k vs $1/T$ ($r \geq 0.9989$, $S \leq 0.0135$) and are tabulated in table 2.

4. Discussion

Permanganate ion, MnO$_4^-$, is a powerful oxidant in aqueous alkaline media. As it exhibits many oxidation states, the stoichiometric results and pH of the reaction media play important roles. Under the prevailing experimental conditions at pH > 12, the reduction product of Mn(VII), i.e. Mn(VI), is stable and further reduction of Mn(VI) might be stopped.[10,11] Diode array rapid scan spectrophotometric (DARSS) studies have shown that at pH > 12, the product of Mn(VII) is Mn(VI) and no further reduction is observed as reported by Simandi *et al*.[10] However, on prolonged standing, the green Mn(VI) is reduced to Mn(IV) under our experimental conditions.

Permanganate in alkaline media exhibits various oxidation states, such as Mn(VII), Mn(V) and Mn(VI). The colour of the solution changes from violet to blue and further to green excluding the accumulation of hypomanganate. The violet colour originates from the pink of the permanganate and the blue from the hypomanganate during the course of the reaction. Colour change in the KMnO$_4$ solution from the violet Mn(VII) ion to the dark green Mn(VI) ion through the blue Mn(IV) ion has been observed.

It is interesting to identify the probable species of ruthenium(III) chloride in alkaline media. Electronic spectral studies[25] have confirmed that ruthenium

(III) chloride exists in hydrated form as $[Ru(H_2O)_6]^{3+}$. In the present study in alkaline media it is quite probable that the species $[Ru(H_2O)_5OH]^{2+}$ might assume the general form $[Ru^{III}(OH)_x]^{3-x}$. The value of x would always be less than six because there are no definite reports of any hexahydroxy species of ruthenium. The remainder of the coordination sphere is filled by water molecules. Hence under the experimental conditions $[OH^-] \gg [Ru^{III}]$, ruthenium (III) is mostly present[26] as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$.

The reaction between permanganate and atenolol in alkaline media in presence of ruthenium (III) has the stoichiometry of 1 : 8 with first-order dependence on $[MnO_4^-]$ and [ruthenium (III)] and less than unit-order dependence on both [alkali] and [atenolol]. No effect of added products is observed. The apparent order of less than unity in $[OH^-]$ may be an indication of the formation of permanganate species as alkali permanganate, $MnO_4.OH^{2-}$, from permanganate ion in a prior-equilibrium step.[27,28] Formation of the $MnO_4.OH^{2-}$ species in alkaline media was further supported by the Michaelis–Menten plot (figure 4) which is linear with a positive intercept. Based on the experimental results, a mechanism can be proposed in which all the observed orders with respect to each constituent such as oxidant, catalyst, reductant and OH^- may be well accommodated. Here the hydroxylated species of ruthenium (III) reacts with ATN to give a complex (C), which reacts with one mole of the alkali permanganate species in a slow step to form a free radical derived from atenolol and the product MnO_4^{2-} with regeneration of catalyst, ruthenium (III). Such complex formation between substrate and catalyst has also been observed in earlier work,[29,30] which is also supported by the observed fractional order in $[OH^-]$ and [atenolol]. The free radical derived from atenolol combines with permanganate species in a fast step to form a diol. This diol reacts with six more moles of permanganate species in further fast steps to yield the products shown in scheme 3.

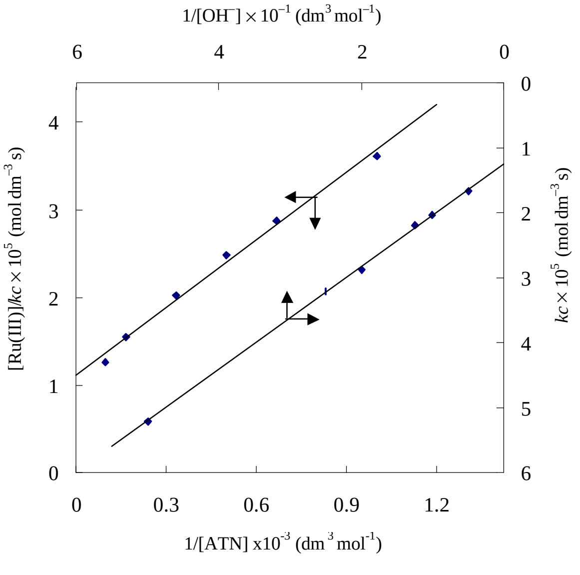


Figure 4. Verification of rate law (2) in the form of (3) (conditions as in table 1).

The probable structure of the complex (C) is given in chart 1.

Spectral evidence for such a catalyst-substrate complex was obtained from the UV-Vis spectra of atenolol and a mixture of ruthenium (III) and atenolol. A hypsochromic shift, $l_{\max}$, of ≈5 nm from 343 to 338 nm is observed together with hyperchromicity at 338 nm.

The thermodynamic quantities for the first equilibrium step in scheme 3 can be evaluated as follows. The hydroxyl ion concentration (as in table 1) is varied at different temperatures. The plots of $[Ru(III)]/k_c$ vs $1/[OH^-]$ ($r \geq 0{\cdot}9999$, $S \leq 0{\cdot}0113$) should be linear as shown in figure 4. From the slopes and intercepts, the values of K_1 are calculated at different temperatures and are given in table 2. A vant Hoff plot was made for the variation of K_1 with temperature [i.e., log K_1 versus $1/T$ ($r \geq 0{\cdot}9998$, $S \leq 0{\cdot}0128$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also given in table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate-limiting step, supporting the fact that the reaction before the rate-determining step is fairly slow and involves high activation energy.[31]

In the presence of catalyst, the reaction is understood to occur in parallel paths with contributions from the uncatalysed and catalysed paths. Thus the

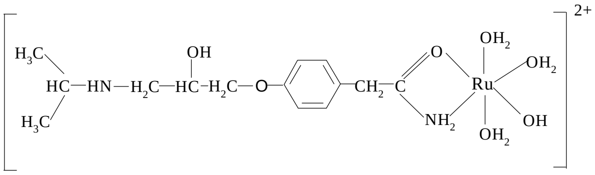
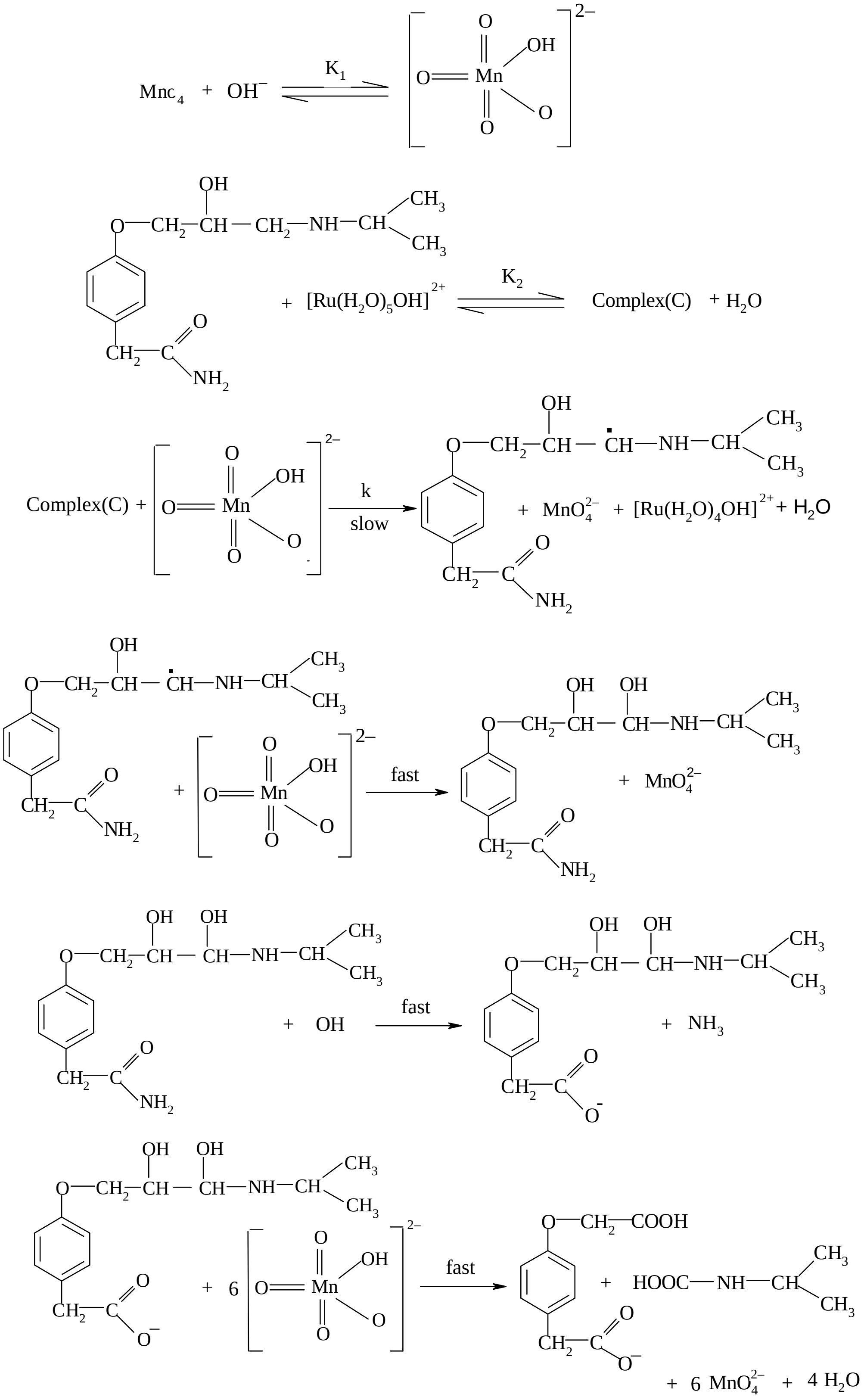


Chart 1.


Mnc4 + OH⁻
K1
2–
Complex(C) + H2O
+ [Ru(H2O)5OH]2+
K2
Complex(C) +
k
slow
+ MnO4 2– + [Ru(H2O)4OH]2+ + H2O
fast
+ MnO4 2–
+ OH
+ NH3
+ 6
+ HOOC—NH—CH
+ 6 MnO4 2– + 4 H2O

Scheme 3.

total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_c) and uncatalysed (k_u) reactions:

$$\text{rate}_{\text{cat}} = \text{rate}_{\text{total}} – \text{rate}_{\text{uncat}}.$$

Scheme 3 leads to the rate law (3) below.

$$\text{Rate} = -\frac{\text{d}[\text{MnO}_4^-]}{\text{d}t} =$$

$$\frac{kK_1K_2[\text{ATN}]_T[\text{MnO}_4^-]_T[\text{Ru(III)}]_T[\text{OH}^-]_T}{(1+K_2[\text{ATN}])(1+K_2[\text{Ru(III)}])(1+K_1[\text{MnO}_4^-])(1+K_1[\text{OH}^-])}. \tag{2}$$

The terms (1 + $K_1[\text{MnO}_4^-]$) and (1 + K_2[Ru(III)]) in the denominator of (2) approximate to unity in view of the low concentrations of MnO_4^- and ruthenium (III) used (omitting the subscripts T and f). In terms of rate constants,

$$\frac{\text{rate}}{[\text{MnO}_4^-]} = k_C = k_T - k_U$$

$$\frac{KK_1K_2[\text{ATN}][\text{Ru(III)}][\text{OH}^-]}{1+K_1[\text{OH}^-]+K_2[\text{ATN}]+K_1K_2[\text{OH}^-][\text{ATN}]}. \tag{3}$$

Equation (3) can be rearranged to the following form, which is used for the verification of the rate law.

$$\frac{[\text{Ru(III)}]}{k_C} = \frac{1}{kK_1K_2[\text{ATN}][\text{OH}^-]}$$

$$+\frac{1}{kK_2[\text{ATN}]} + \frac{1}{kK_1[\text{OH}^-]} + \frac{1}{k}. \tag{4}$$

According to (4), the plots of [Ru(III)]/k_c versus 1/[ATN] and [Ru(III)]/k_c versus 1/$[\text{OH}^-]$ ($r \geq 0{\cdot}9996$, $S \leq 0{\cdot}0121$) and ($r \geq 0{\cdot}9999$, $S \leq 0{\cdot}0113$) are linear with an intercept supporting the Ru(III)-atenolol complex, and which is verified in figure 4. From the slope and intercept of such plots, the values of K_1, K_2 and k are calculated to be $15{\cdot}0 \pm 0{\cdot}75$ dm^3 mol^{-1}, $4{\cdot}20 \pm 0{\cdot}21 \times 10^2$ dm^3 mol^{-1} and $2{\cdot}10 \pm 0{\cdot}1 \times 10^5$ dm^3 mol^{-1} s^{-1}. The value of K_1 is in agreement with the earlier value.[32] Using these K_1, K_2 and k values, the rate constants under different experimental conditions were calculated by (3) and compared with experimental data, with which there is good agreement (table 1).

The difference in the activation parameters for the catalysed (k_c) and uncatalysed (k_u) reactions (table 2) explains the catalytic effect on the reaction. The catalyst, Ru(III), forms a complex with atenolol that is more reducible than atenolol itself. Hence, the catalyst lowers the energy of activation. The negative value of $\Delta S^{\#}$ indicates that the complex (C) is more ordered than the reactants.[33] The observed modest enthalpy of activation and the higher rate constant of the slow step (compared to k_c) indicate that the oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by earlier work.[34,35]

The effect of ionic strength on the rate can be understood essentially on the basis of ionic species as in scheme 3. The effect of solvent on the reaction rate has been described in detail in the literature.[36] Increasing the content of *t*-butanol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected interaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of reaction with decreasing dielectric constant may be due to stabilization of the complex (C) at low relative permittivity, which is less solvated than MnO_4^- at higher dielectric constant because of its larger size. Spectrofluorimetric studies reveal that the fluorescence intensity is quenched, which may be due to the electron transfer reaction.[37]

5. Conclusion

It is interesting that the oxidant species $[\text{MnO}_4^-]$ requires a pH > 12 for reaction, below which the system becomes disturbed and the reaction proceeds further to give the reduced product of the oxidant, Mn(IV), which slowly develops yellow turbidity. Hence, it becomes apparent that in carrying out this reaction the role of pH in a reaction medium is crucial. It is also noteworthy that under the conditions studied, the reaction occurs as two successive one-electron reductions (scheme 3) rather than as a two-electron reduction in a single step (scheme 2). Ruthenium (III) is known to be an efficient catalyst especially in alkaline media, a micro amount of ruthenium (III) is sufficient to catalyse the title reaction with measurable rate. The overall mechanistic sequence described here is consistent with products, mechanistic and kinetic studies.

Appendix A

According to scheme 3

$$\text{rate}_{\text{cat}} = \text{rate}_{\text{total}} – \text{rate}_{\text{uncat}}$$

$$= kK_1K_2[\text{ATN}]_f\,[\text{MnO}_4^-]_f\,[\text{OH}^-]_f\,[\text{Ru(III)}]_f. \tag{A1}$$

The total concentration of atenolol $[\mathrm{ATN}]_T$, is given by (subscripts T and f stand for total and free),

$$\begin{aligned}[\mathrm{ATN}]_T &= [\mathrm{ATN}]_f + [\mathrm{C}] \\ &= [\mathrm{ATN}]_f + K_2[\mathrm{ATN}]_f[\mathrm{Ru(III)}] \\ &= [\mathrm{ATN}]_f(1 + K_2[\mathrm{Ru(III)}]).\end{aligned}$$

Therefore,

$$[\mathrm{ATN}]_f = [\mathrm{ATN}]_T/(1 + K_2[\mathrm{Ru(III)}]). \quad \text{(A2)}$$

Similarly,

$$[\mathrm{OH}^-]_f = [\mathrm{OH}^-]_T/(1 + K_1[\mathrm{MnO}_4^-]), \quad \text{(A3)}$$

$$[\mathrm{Ru(III)}]_f = [\mathrm{Ru(III)}^-]_T/(1 + K_2[\mathrm{ATN}^-]), \quad \text{(A4)}$$

$$[\mathrm{MnO}_4^-]_f = [\mathrm{MnO}_4^-]_T/(1 + K_1[\mathrm{OH}^-]). \quad \text{(A5)}$$

Substituting (A2)–(A5) in (A1) we get

$$\text{rate} = -\frac{\mathrm{d}[\mathrm{MnO}_4^-]}{\mathrm{d}t} =$$

$$\frac{kK_1K_2[\mathrm{ATN}]_T[\mathrm{MnO}_4^-]_T[\mathrm{Ru(III)}]_T[\mathrm{OH}^-]_T}{(1+K_2[\mathrm{ATN}])(1+K_2[\mathrm{Ru(III)}])(1+K_1[\mathrm{MnO}_4^-])(1+K_1[\mathrm{OH}^-])}. \quad \text{(A6)}$$

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