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Spectrophotometric Study of Osmium (VIII) Catalyzed Oxidation of Carbamazepine by Permanganate Ions in Aqueous Acidic Medium: A Kinetic and Mechanistic Approach

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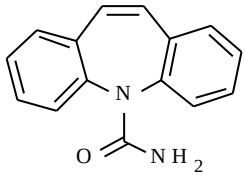
ABSTRACT

Oxidation kinetics of carbamazepine (CBZ) by permanganate ions in aqueous acid solutions at 25 °C at ionic strength of 0.12 mol dm^{-3} have been investigated by spectrophotometrically. The stoichiometry is 1:1, i. e., one mole of carbamazepine consumes one mole of permanganate ions. The order of the reaction with respect to manganese (VII) and osmium (VIII) concentration was unity while order with respect to carbamazepine was less then unity over the concentration range studied. The rate increased with an increase in acid concentration. The reaction rates revealed that the Os (VIII) catalyzed reaction was about 10-fold faster than the uncatalyzed path. A tentative mechanism consistent with the kinetics has been proposed. The reaction constants involved in the different steps of the reaction mechanism were calculated. Kinetic experiments propose that $HMnO_4$ is the reactive permanganate species and $[OsO_4(OH)_2]^{2-}$ is the reactive Os (VIII) species.

1. Introduction

Carbamazepine (CBZ, 5H-Dibenzene[b,f]azepine-5-carboxamide) is an anticonvulsant. It is widely used in the treatment of epilepsy, neuralgic pain and bipolar affective disorder. The drug is a carbamylated iminostilbene, structurally related to the tricyclic antidepressants [1]. The main oxidative pathway involves the formation of more than seven metabolites; the main metabolite is carbamazepine-10, 11-epoxide which possesses anticonvulsant properties similar to those of CBZ [2]. It is metabolized by CYP3A enzyme, which is present in the intestinal wall and in the liver. Overall the treatment with CBZ is effective and safe. However, approximately 30 - 40% of epileptic patients do not respond very well to the treatment [3].

Clinical trials demonstrate that CBZ can be prescribed for other conditions such as central nervous system and gastrointestinal system, causing sedation, ataxia, dizziness, nausea, vomiting, constipation and diarrhea. Long-term treatment with CBZ may modify plasma lipids, changes the concentration of sex hormones, produces hyponatremia, increases appetite and causes weight-gain, reduces the number of white blood cells and induces several allergic reactions [4, 5]. It also seems to be an effective and applicative drug in patients with psychiatric illness [6, 7]. The structure of carbamazepine is as shown in Scheme 1.



Scheme 1 Structure of carbamazepine

Potassium permanganate ion is widely used as an oxidizing agent in synthetic as well as in analytical chemistry [8] and according to Insutai et.al, it has several advantages as an analytical reagent [9]. In general, reduction of the permanganate, in acid media goes to either Mn (IV) or Mn (II) having the reduction potential [10] of the couple Mn (VII)/ Mn (IV): 1.695 V and Mn (VII)/Mn (II): 1.51 V. Oxidation by permanganate finds extensive application in organic synthesis [11]. During oxidation by permanganate, it is evident that permanganate is reduced to different oxidation states in acidic, alkaline and neutral media. The manganese chemistry involved in these multistep redox reactions is an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long lifetimes, and oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanisms, including the nature of intermediates. In acid medium it exists in different forms viz., $HMnO_4$, $H_2MnO_4^+$, $HMnO_3$, and Mn_2O_7 and depending on the nature of the reductant, the oxidant has been assigned both the inner sphere and outer sphere mechanism pathways in their redox reactions [12, 13]. Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation states. In recent years the use of transition metal ions such as ruthenium, osmium, palladium, manganese, chromium, iridium, either alone or as binary mixtures as catalysts in various redox processes has attracted considerable interest [14].

The role of osmium (VIII) as a catalyst in some redox reactions has been reviewed [15]. Even though the mechanism of catalysis depends on the nature of the substrate, the oxidant and experimental conditions it has been shown that metal ions operate as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Osmium (VIII) catalysis in redox reactions involves different degrees of complexity, due to the formation of different intermediate complexes and different oxidation states of osmium. There is no report on the kinetics of oxidation of carbamazepine in acid media with oxidant but except in one case [16]. It is also observed that there is lack of literature on the catalyzed oxidation of this drug by any oxidant in an acid media. We have observed that osmium (VIII) catalyzes the oxidation of carbamazepine by permanganate ions in acid medium in micro-sized amounts. In view of the potential pharmaceutical importance of carbamazepine, to know the active species of Mn (VII) and catalyst Os (VIII), and the complexity of the reaction, a detailed study of the title reaction becomes important. The present investigation is aimed at checking the reactivity of carbamazepine toward permanganate ions in osmium (VIII) catalyzed reactions and to arrive at the plausible mechanisms.

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2. Experimental Methods

2.1 Chemicals and Solutions

The solutions were prepared in water which had been twice distilled in an all glass unit in the presence of potassium permanganate. Reagent grade chemicals were used. Carbamazepine (CBZ) was purchased from Sigma, (molecular weight = 110.1, purity ≥ 99.0%, mp = 191 - 192 °C, bioavailability = 100%, protein binding = 70 - 80%, biological half-life = 36 h for single dose and excretion = urine (72%), feces (28%)). A stock solution of carbamazepine was prepared by dissolving in ethanol (alcohol). Permanganate (MnO^-_4) stock solution was obtained by dissolving potassium permanganate (Glaxo, Analar) in water and standardized by titrating against oxalic acid [17]. A standard stock solution of Os (VIII) was prepared by dissolving OsO_4 (Johnson Matthey) in 0.50 mol dm^{-3} NaOH. The concentration of Os (VIII) was ascertained [18, 19] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce (IV) solution in an acidic medium. Always freshly prepared and standardized MnO^-_4 solutions were used in the kinetics. The manganese (II) solution was made by dissolving manganese sulphate (AR) in water. The acetic acid (CDH) solution was prepared by dissolving it in water. Na_2SO_4 (AR) and H_2SO_4 (AR) were used to provide the required ionic strength and acidity respectively.

2.2 Instruments Used

(i). For kinetics measurements, a UV-vis spectrophotometer (Shimadzu-1800, Japan) was used.
(ii). For pH measurements, an Elico pH meter model LI120 was used.

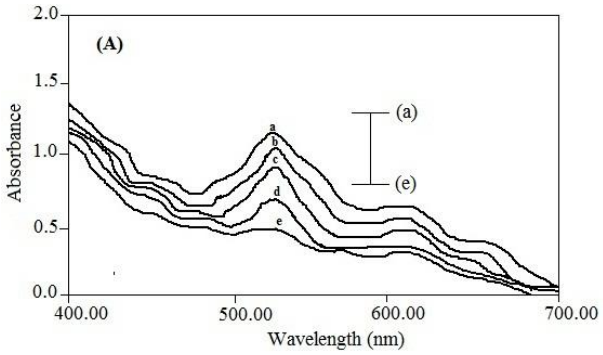


Fig. 1a UV-vis. Spectral changes during the oxidation of carbamazepine by acidic permanganate at 298 K, $[MnO_4^-] = 5 \times 10^{-5}$, [CBZ] = 5×10^{-4}, $[H^+] = 0.05$, [Os(VIII)] = 8.0×10^{-7} and $I = 0.12$ mol dm^{-3} with scanning times of: (*a*) 0.5, (*b*) 1.0, (*c*) 1.5, (*d*) 2.0, (*e*) 2.5 min

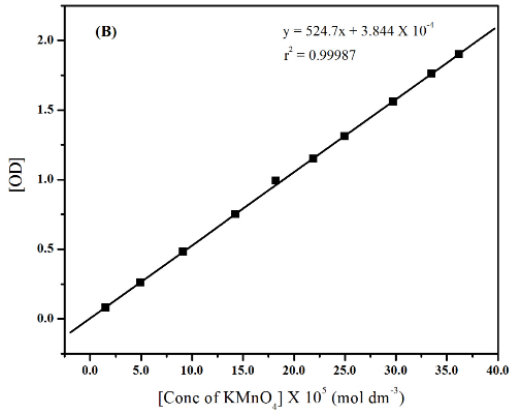


Fig. 1b The Beer's law verification between 1.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} of permanganate ion concentration at 525 nm

2.3 Kinetic Measurements

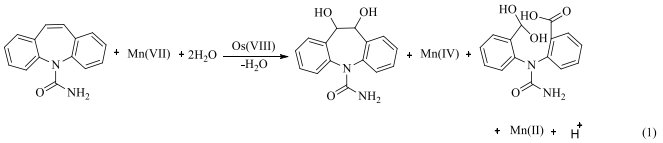
The kinetics was followed under pseudo-first order conditions with CBZ concentration greater than permanganate ion concentration at constant ionic strength, i.e., $I = 0.12$ mol dm^{-3}. The reaction was initiated by mixing thermally equilibrated (25.0 ± 0.1 °C) solutions of carbamazepine and permanganate which has also contained the required amounts of sodium sulphate, sulphuric acid and osmium (VIII). The progress of the reaction was followed by measuring the absorbance of unreacted permanganate ion concentration in the reaction mixture at its maximum absorption wavelength, 525 nm, as a function of time. It was verified that other constituents of the reaction mixture do not absorb significantly at this wavelength. The application of Beer's law was verified between 1.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} of permanganate ion concentration at 525 nm had been verified and the molar extinction coefficient, ε, was found to be 2388 ± 50 dm^3 mol^{-1} cm^{-1} (literature value ε = 2400 dm^3 mol^{-1} cm^{-1}) [20].

The kinetic runs were followed more than 85% completion of the reaction. The spectral changes during the chemical reaction for the standard condition at 298 K are shown in Fig. 1a. It is evident from the figure that the concentration of permanganate decreases. Regression analysis of experimental data to obtained and it shows a linear relationship with the linear regression equation y = 524.7x + 3.844 × 10^{-4}, relative regression coefficient (r^2 = 0.99987) and the standard deviation (S = 0.00109), which was performed with Microsoft Office Excel 2007 as show in Fig. 1b.

3. Result and Discussion

3.1 Stoichiometry and Product Analysis

Different sets of reaction mixtures containing varying ratios of carbamazepine to MnO_4^- and a constant amount of Os (VIII) were mixed in the presence of 0.05 mol dm^{-3} $[H^+]$ maintaining a constant ionic strength, I = 0.12 mol dm^{-3}, were kept for 24 h at room temperature. The results indicate that 1 mol of MnO_4^- consumed 1 mol of carbamazepine. Thus it is shows 1:1 stoichiometry as given in Eq. (1).



The reaction products were identified as 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide, Mn^{4+}, 2-(1-(2-(dihydroxymethyl)phenyl)ureido)benzoic acid, Mn^{2+}. The main reaction products were confirmed by LC-MS/MS and also by probable mechanism. Mn^{2+} was identified by UV-visible spectroscopy and spot test [21]. The 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide product was confirmed by its ESI(+) MS-m/z^a at 271 and ESI(+) MS^2-m/z at 253*, 210. Another product 2-(1-(2-(dihydroxymethyl)phenyl)ureido) benzoic acid was confirmed by its ESI(+) MS-m/z^a at 303 and ESI(+) MS^2-m/z at 285*, 267 [16].

3.2 Reaction Orders

As the permanganate oxidation of carbamazepine in acidic medium proceeds with a measurable rate in the presence of the catalyzed (k_C) reaction. Hence the reaction orders have been determined from the slopes of $\log_{10} k_C$ versus $\log_{10}$ (concentration) plots by varying the concentrations of CBZ, H^+ and catalyst Os (VIII) in turn, while keeping the others constant. The uncatalyzed reaction was followed under the condition $[MnO_4^-] = 5 \times 10^{-5}$, [CBZ] = 5×10^{-4} and $[H^+] = 0.05$ maintaining a constant I = 0.12 mol dm^{-3}. The rate constant of the uncatalyzed reaction (k_U) was obtained by the plot of $\log_{10}$ (absorbance) versus time by following the progress of the reaction spectrophotometrically at 525 nm.

3.3 Evaluation of Pseudo First Order Rate Constants

The oxidant, permanganate $[MnO_4^-]$, concentration was varied in the range of 1.0 x 10^{-5} - 10.0 x 10^{-4} mol dm^{-3}. The observed pseudo-first order rate constants, (k_C), were determined from the $\log_{10}$ (absorbance) versus time plots. The plots were linear up to 85% completion of reaction ($r \geq 0.9727$, $S \leq 0.0040$). The sensibly constant pseudo-first order rate constants, k_C, indicate that the order with respect to $[MnO_4^-]$ was unity (Table 1).

3.4 Effect of Varying [CBZ]

The effect of variation of carbamazepine on the rate of reaction was studied in the concentration range, 1.0 x 10^{-4} - 10.0 x 10^{-3} mol dm^{-3}, at constant concentration of MnO_4^-, H^+ and ionic strength, i.e., I = 0.12 mol dm^{-3} in the presence of the Os (VIII) catalyst. At constant temperature the k_C values increased with increases in [CBZ] (Table 1) ($r \geq 0.9818$, $S \leq 0.0852$). The value of the slope of the plot of $\log_{10} k_C$ versus $\log_{10}$ [CBZ] was found to be less than unity indicating less than unit order with respect to [CBZ].

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Table 1 Effect of variation of [MnO_4^-], [CBZ], [H^+], [SO_4^{2-}] and [Os(VIII)] on the oxidation of carbamazepine by permanganate in aqueous acidic medium at 298 K and I = 0.12 mol dm^{-3}

10^5 [MnO_4^-] (mol dm^{-3})	10^4 [CBZ] (mol dm^{-3})	0.05 [H^+] (mol dm^{-3})	0.04 [SO_4^{2-}] (mol dm^{-3})	10^7 [Os(VIII)] (mol dm^{-3})	10^2 K_C (s^{-1}) Found	10^2 K_C (s^{-1}) Calculated
1.0	5.0	0.05	0.04	8.0	3.26	3.27
3.0	5.0	0.05	0.04	8.0	3.27	3.35
5.0	5.0	0.05	0.04	8.0	3.32	3.42
7.0	5.0	0.05	0.04	8.0	3.31	3.42
10.0	5.0	0.05	0.04	8.0	3.30	3.42
5.0	1.0	0.05	0.04	8.0	1.55	1.55
5.0	3.0	0.05	0.04	8.0	2.31	2.34
5.0	5.0	0.05	0.04	8.0	2.79	2.80
5.0	7.0	0.05	0.04	8.0	2.85	2.84
5.0	10.0	0.05	0.04	8.0	3.03	3.09
5.0	5.0	1.0	0.04	8.0	1.80	1.79
5.0	5.0	3.0	0.04	8.0	2.42	2.42
5.0	5.0	5.0	0.04	8.0	2.79	2.81
5.0	5.0	8.0	0.04	8.0	2.93	2.90
5.0	5.0	10.0	0.04	8.0	3.10	3.19
5.0	5.0	0.05	1.0	8.0	1.13	1.16
5.0	5.0	0.05	4.0	8.0	1.17	1.16
5.0	5.0	0.05	6.0	8.0	1.19	1.16
5.0	5.0	0.05	8.0	8.0	1.14	1.16
5.0	5.0	0.05	10.0	8.0	1.14	1.16
5.0	5.0	0.05	0.04	5.0	1.54	1.54
5.0	5.0	0.05	0.04	8.0	2.88	2.87
5.0	5.0	0.05	0.04	10.0	3.45	3.44
5.0	5.0	0.05	0.04	30.0	8.64	8.63
5.0	5.0	0.05	0.04	50.0	14.60	14.59

3.5 Effect of Varying [H$^+$] and [SO$^{2-}_4$]

The actual concentration of [H^+] and [SO^{2-}_4], i.e., [H^+]$_f$ and [SO^{2-}_4]$_f$, were calculated using the bisulfate dissociation constant [22]. As the reaction was carried out in sulfuric acid the effect of [H^+] on the reaction rate was studied by varying the H^+ ion concentration in the range of 1.0 x 10^{-2} - 10.0 x 10^{-1} mol dm^{-3} at constant concentration of MnO^-_4, CBZ and at fixed ionic strength, i.e., I = 0.12 mol dm^{-3} in the presence of the Os (VIII) catalyst. The apparent order in [H^+] obtained was less than unity. At constant temperature, it was found that the k_C values increased with increases in [H^+] (Table 1) ($r \geq 0.9915$, $S \leq 0.0596$).

The effect of SO^{2-}_4 concentration on the reaction system was studied by varying the concentration of Na_2SO_4 in the range of 1.0 x 10^{-2} - 10.0 x 10^{-1} mol dm^{-3} with all other reaction conditions kept constant. It was observed that [SO^{2-}_4] did not have any significant effect on the reaction rate (Table 1).

3.6 Effect of Varying [Osmium (VIII)]

The effect of osmium(VIII) was studied by varying the [Os (VIII)] from 5.0 x 10^{-7} - 50.0 x 10^{-6} mol dm^{-3} at constant concentration of MnO^-_4, CBZ, H^+ and a constant ionic strength, i.e., I = 0.12 mol dm^{-3}. The order in [Os (VIII)] was found to be unity from the linearity of the plot of k_C versus [Os (VIII)] (Table 1) ($r \geq 0.9989$, $S \leq 0.0028$) (Fig. 2).

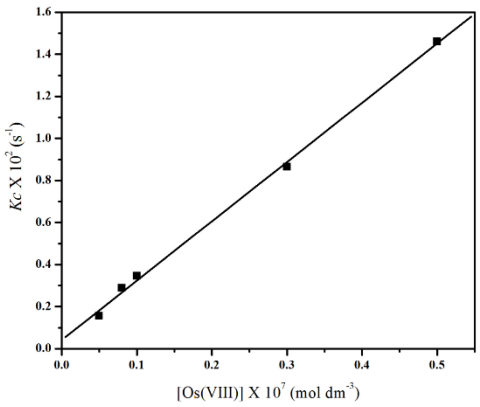


Fig. 2 Unit order plot of [Os(VIII)] versus K_C

3.7 Effect of Varying Ionic Strength (I) and Dielectric Constant (D)

At constant concentrations of reactants and at other conditions, i.e., MnO^-_4, CBZ, H^+ and Os (VIII) kept constant the ionic strength was varied between 0.01 and 0.1 mol dm^{-3} by varying the concentrations of sodium sulphate. It was found that there was no significant effect of ionic strength on the rate of reaction.

The effect of dielectric constant of the medium (D) was varied by varying the acetic acid-water percentage with all other conditions kept constant. With increase in acetic acid content in the reaction medium, the rate of reaction decreased. The plot of $\log_{10} k_C$ versus 1/D was linear with negative slope (Fig. 3).

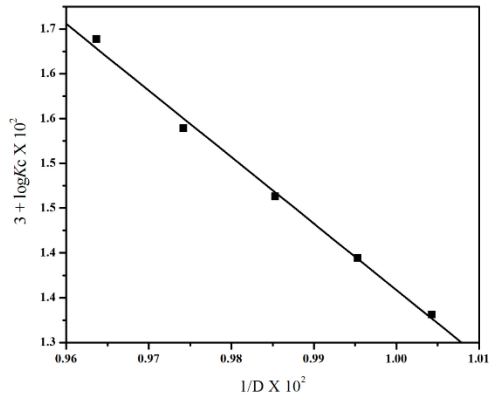


Fig. 3 Effect of dielectric constant of the medium on the oxidation of carbamazepine at 298 K

3.8 Effect of Initially Added Products

Initially added products, 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide, Mn^{4+}, 2-(1-(2-(dihydroxymethyl) phenyl)ureido)benzoic acid, Mn^{2+} did not have any significant effect on the rate of reaction.

Thus, from the observed experimental results, the rate law for the Os(VIII) catalyzed reaction is gives as:

$$\text{Rate} = k_C[MnO^-_4]^{1.0}[CBZ]^{0.66}[H^+]^{0.52}[Os(VIII)]^{1.0}$$

3.9 Effect of Temperature (T)

The kinetics was studied at four different temperatures: 298 K, 303 K, 308 K and 313 K under varying concentration of carbamazepine, acid, permanganate ions and ionic strength, i.e., I = 0.12 mol dm^{-3} in the presence of the Os (VIII) catalyst. The rate constants, (k), of the slow step of Scheme 3 were obtained from the plots of [Os (VIII)]/k_C versus 1/[CBZ] at four different temperatures. The values are given in Table 2. The activation parameters for the rate determining step were obtained by the least-squares method from a plot of $\log_{10} k_C$ versus 1/T and are presented in Table 2.

Table 2 Activation parameters and thermodynamic quantities for the osmium (VIII) catalyzed oxidation of CBZ by permanganate in aqueous acidic medium with respect to the slow step of Scheme 3. [MnO_4^-] = 5.0 × 10^{-5}, [CBZ] = 5.0 × 10^{-4}, [H^+] = 0.05, [Os(VIII)] = 8.0 × 10^{-7} and I = 0.12 mol dm^{-3}

(a) *Effect of temperature*

Temperature (K)	10^{-4} k (dm^3 mol^{-1} s^{-1})
298	0.41
303	0.54
308	0.69
313	0.80

(b) *Activation parameters (Scheme 3)*

Parameter	value
Ea (kJ mol^{-1})	36.5 ± 3.0
$\Delta H^{\#}$ (kJ mol^{-1})	34.0 ± 0.6
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-41.6 ± 3
$\Delta G^{\#}$ (kJ mol^{-1})	43.4 ± 5
$\text{Log}_{10}A$	11.0 ± 0.3

(c) *Effect of temperature on K_1 and K_2 for the osmium(VIII) catalyzed oxidation of CBZ by permanganate in aqueous acidic medium*

Temperature (K)	10^{-1} K_1 (dm^3 mol^{-1})	10^{-2} K_2 (dm^3 mol^{-1})
298	4.18	5.73
303	3.83	8.13
308	3.20	11.38
313	1.89	14.20

(d) *Thermodynamic quantities using K_1 and K_2*

Thermodynamic quantities	Values from K_1	Values from K_2
ΔH (kJ mol^{-1})	-52.9	63.22
ΔS (J K^{-1} mol^{-1})	-142.3	259.7
ΔG_{298} (kJ mol^{-1})	-5.16	-19.01

3.10 Catalytic Activity

It has been pointed out by Moelwyn-Hughes [23] that in the presence of catalyst the uncatalyzed and catalyzed reactions proceed simultaneously, so that,

$$k_T = k_U + K_C[O_S(VIII)]^x \quad (2)$$

Here k_T is the observed pseudo first –order rate constant in the presence of [Os(VIII)] catalyst; k_U the pseudo first-order rate constant for uncatalyzed reaction; K_C the catalytic constant; and 'x' the order of the reaction with respect to [Os (VIII)]. In the present investigations; x values for the standard run were found to be unity.

Then, the value of K_C is calculated using the equation,

$$K_C = \frac{k_T - k_U}{Os(VIII)^x} = \frac{k_C}{Os(VIII)^x} \text{ Where } k_T - k_U = k_C \quad (3)$$

The values of K_C were evaluated for Os (VIII) catalyst at different temperatures and were found to vary at different temperatures. Further, plots of $\log_{10} K_C$ versus $1/T$ were linear and the values of energy of activation and other activation parameters with reference to the catalyst were computed. These results are summarized in Table 3. The value of K_C is 0.81×10^3 at 298 K.

Table 3 Values of the catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values. $[MnO_4^-] = 5.0 \times 10^{-5}$, [CBZ] = 5.0×10^{-4}, $[H^+] = 0.05$, [Os (VIII)] = 8.0×10^{-7} and $I = 0.12$ mol dm^{-3}

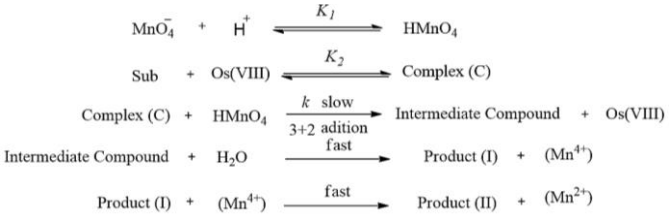
Temperature (K)	$10^{-3} K_C$
298	0.81
303	1.10
308	1.39
313	1.71
Ea (kJ mol^{-1})	45
$\Delta H^{\#}$ (kJ mol^{-1})	41.3
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-28.2
$\Delta G^{\#}$ (kJ mol^{-1})	48.3
$\text{Log}_{10}A$	12.7

The active species of permanganate in aqueous acid solution may be deduced from the dependence of the rate on $[H^+]_f$ in the reaction medium. The noticeable order of the reaction in $[H^+]_f$ is significantly less than unity, which may be an indication of the formation of permanganic acid from permanganate ion. In fact, permanganic acid, $HMnO_4$, is a more efficient oxidant species of manganese (VII) than the permanganate ion [20]. In addition, it has been observed that the reaction rate increased with increase in $[H^+]$ and was tending to attain a limiting value at high acidities. At higher acidities protonation is almost complete, leading to the limiting rate, this indicates that only the protonated form is active. Thus, the acid-permanganate equilibrium can be represented by Eq. (4).

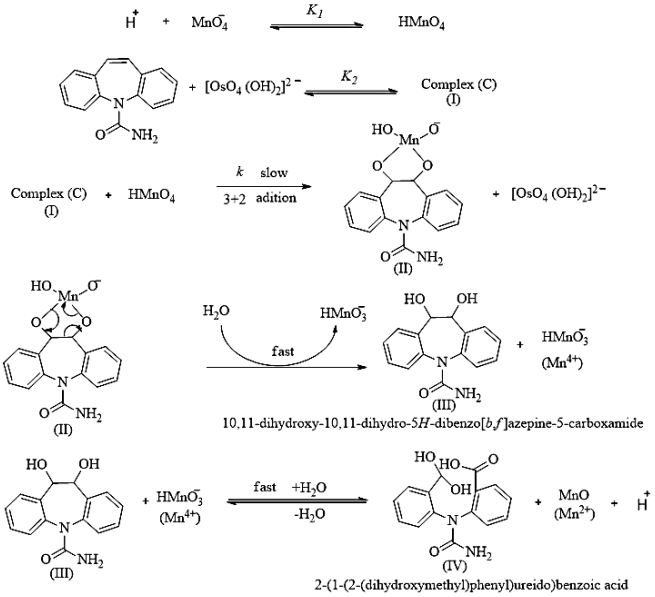
$$MnO_4^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HMnO_4 \quad (4)$$

Osmium catalysts, during the last decade, have provided a new insight in developing chemistry. The osmium (VIII) is known to form different complexes at different OH^- concentrations, $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher concentrations of OH^-, $[OsO_5(OH)]^{3-}$ is significant. At lower concentrations of OH^-, as employed in the present study and since the rate of oxidation increased with increase in $[OH^-]$, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction. Added permanganate retarded the rate. First-order dependency in $[MnO_4^-]$ and catalyst (Os (VIII)) and fractional order in [CBZ] and $[H^+]$ were observed. To explain the observed orders, Scheme 3 has been proposed for the osmium (VIII) catalyzed reaction.

In the present investigation, the reaction between permanganate and CBZ in sulfuric acid has a stoichiometry 1:1 with first orders in permanganate and the catalyst Os(VIII) and fractional orders in [CBZ] and $[H^+]$. The oxidation products were 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide, Mn^{4+}, 2-(1-(2-(dihydroxymethyl) phenyl)ureido)benzoic acid, Mn^{2+}. Based on the experimental results, a probable mechanism can be proposed in which all the observed orders in each constituent, [oxidant], [reductant], [catalyst] and $[H^+]_f$ may be well accommodated. In view of the increase in rate with increases in $[H^+]$ in the prior equilibrium step, H^+ reacts with MnO^-_4 to form the $HMnO_4$ species. $HMnO_4$ species formation is supported in the literature [24]. In the second equilibrium step, carbamazepine reacts with the active osmium (VIII) species to form a complex (C) (I), which further reacts with $HMnO_4$ in a slow step and take 3+2 addition to give intermediate compound of CBZ (II) with regeneration of the catalyst, osmium (VIII). In a fast step, intermediate compound of CBZ (II) hydrolysis to give the product 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide (III) and generating $HMnO^-_3$ (Mn^{4+}) species. Further, the 10,11-dihydroxy-10,11-dihydro-5*H*-dibenzo[*b,f*]azepine-5-carboxamide (III) reacts with the Mn^{4+} species also addition and removal of water to give 2-(1-(2-(dihydroxymethyl)phenyl)ureido)benzoic acid (IV) and MnO (Mn^{2+}), satisfying the stiochiometric observations. The results may be interpreted in the form of Schemes 2 and 3. Similar key steps in the mechanism have been proposed for catalyzed reaction in earlier studies [16, 25].

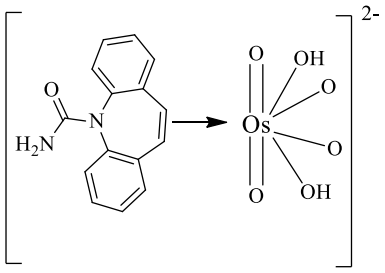


Scheme 2 General scheme for Os (VIII) catalyzed oxidation of carbamazepine by permanganate



Scheme 3 Detailed scheme for Os (VIII) catalyzed oxidation of carbamazepine by permanganate

The probable structure of complex (C) is given below;



From Scheme 3, the rate law (6) can be derived (see Appendix).

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = \frac{kK_1K_2[MnO_4^-][CBZ][H^+][Os(VIII)]}{1+K_1[H^+]+K_1K_2[H^+][CBZ]} \quad (5)$$

$$\frac{\text{Rate}}{MnO_4^-} = k_C = \frac{kK_1K_2[CBZ][H^+][Os(VIII)]}{1+K_1[H^+]+K_1K_2[H^+][CBZ]} \quad (6)$$

The rate law (6) can be rearranged into the following form which is suitable for verification.

$$\frac{[Os(VIII)]}{k_C} = \frac{1}{kK_1K_2[CBZ][H^+]} + \frac{1}{kK_2[CBZ]} + \frac{1}{k} \quad (7)$$

According to Eq. (7), other conditions being constant, plots of $[Os(VIII)]/k_C$ versus $1/[CBZ]$ and $[Os(VIII)]/k_C$ versus $1/[H^+]$ should be linear are found to be in (Fig. 4 and Fig. 5). The slopes and intercepts of such plots lead to the values of K_1, K_2 and k (Table 2). The value of K_1 is in

good agreement with the literature [20]. Using these constants, the rate constants were calculated and compared with the experimental k_C values. There was a sensible agreement with each other (Table 1), which supports the proposed probable mechanism (Scheme 3).

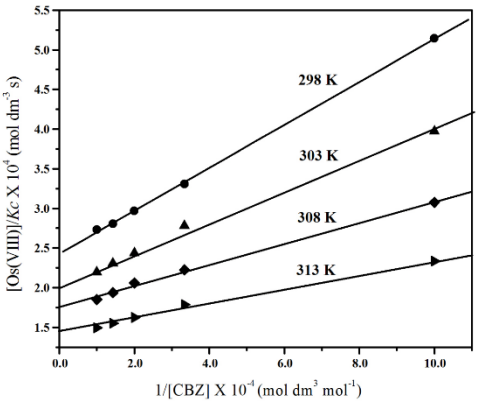


Fig. 4 Verification of rate law (6) for the Os(VIII) catalyzed oxidation of carbamazepine by permanganate. Plot of [Os(VIII)]/k_C versus 1/[CBZ] at four different temperatures (conditions as in Table 1)

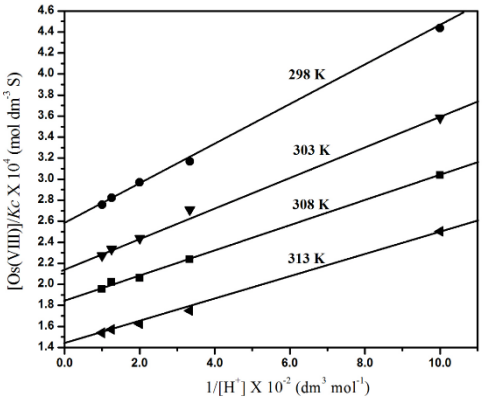


Fig. 5 Verification of rate law (6) for the Os (VIII) catalyzed oxidation of carbamazepine by permanganate. Plot of [Os (VIII)]/k_C versus 1/[H⁺] at four different temperatures (conditions as in Table 1)

The thermodynamic quantities for the different equilibrium steps, in Scheme 3, can be evaluated as follows. The [CBZ] and [H⁺] as in Table 1 were varied at four different temperatures. The plots of [Os (VIII)]/k_C versus 1/[CBZ] and [Os (VIII)]/k_C versus 1/[H⁺]should be linear and are found to be so. From the slopes and intercepts, the values of K_1 and K_2 were calculated at four different temperatures. A vant Hoff's plot was made for the variation of K_1 and K_2 with temperature ($\log_{10} K_1$ versus $1/T$ and $\log_{10} K_2$ versus $1/T$). The values of enthalpy of reaction ΔH, entropy of reaction ΔS and Gibbs energy of reaction ΔG were calculated for the first and second equilibrium steps. These values are given in Table 2. A comparison of the ΔH value, 63.22 kJ mol^{-1} from K_2 with that of $\Delta H^{\#}$, 34.0 kJ mol^{-1} of the rate-limiting step supports that the reaction before the rate determining step is fairly fast as it involves low activation energy [26].

The negligible effect of ionic strength on the rate reflects qualitatively the reaction between neutral and positively charged ions, as seen in Scheme 3. Amis [27] has shown that a plot of $\log_{10} k_C$ versus $1/D$ is linear with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for a positive ion-dipole interaction. However, in the present study, an increase in the content of acetic acid in the reaction medium leads to the decrease in the rate of reaction (the plot observed had a negative slope Fig. 3), which is contrary to the Amis theory. Perhaps the effect is countered substantially by the formation of active reaction species to a greater extent in the high relative permittivity media, leading to the net increase in the rate [28]. The negative value of $\Delta S^{\#}$ (−41.61 J K^{-1} mol^{-1}) suggests that the intermediate complex is more ordered than the reactants [29]. The observed modest enthalpy of activation and higher rate constant for the slow step indicate that the oxidation occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations [30-32]. The activation parameters evaluated for the catalyzed reactions explain the catalytic effect on the reaction. The catalyst Os (VIII) forms a complex (C) with substrate, which enhances the reducing property of the substrate more than that without catalyst. Further, the Os (VIII) catalyst modifies the reaction path by lowering the energy of activation.

4. Conclusion

Through the kinetics study, we proposed a simple reaction mechanism for Os (VIII) catalyzed oxidation of carbamazepine by permanganate. For the title reaction, the main active species of permanganate is found to be $HMnO_4$ and the active species of Os (VIII) is found to be $[OsO_4(OH)_2]^{2-}$. The reaction rates revealed that the Os (VIII) catalyzed reaction is about 10-fold faster than the uncatalyzed reaction. It becomes apparent that in carrying out this reaction, the role of reaction medium is crucial. Activation parameters were evaluated for the catalyzed reaction. Catalytic constants and the activation parameters with reference to catalyst were also computed. The overall sequence described here is consistent with probable product, mechanistic and kinetic studies.

APPENDIX

Derivation of Rate Equation

According to Scheme 3,

$$\text{Rate} = \frac{-\mathrm{d}[MnO_4^-]}{\mathrm{d}t} = k[\text{Complex(C)}][HMnO_4]$$
$$= kK_1K_2[CBZ]_f[Os(VIII)]_f[MnO_4^-]_f[H^+]_f \quad \text{(I)}$$

The total concentration of $[MnO^-_4]_T$ is given by,

$$[MnO_4^-]_T = [MnO_4^-]_f + [HMnO_4] + \text{Complex(C)}$$
$$= [MnO_4^-]_f + K_1[H^+][MnO_4^-]_f + K_1K_2[CBZ][H^+][MnO_4^-]_f$$
$$= [MnO_4^-]_f\{1 + K_1[H^+] + K_1K_2[CBZ][H^+]\}$$

and T and f refer to total and free concentrations

$$[MnO_4^-]_f = \frac{[MnO_4^-]_T}{1+K_1[H^+]+K_1K_2[H^+][CBZ]} \quad \text{(II)}$$

Similarly,

$$[H^+]_T = [H^+]_f + [HMnO_4]$$
$$= [H^+]_f + K_1[H^+][MnO_4^-]$$

In view of low concentration of [H⁺] used, the second term can be neglected. Therefore,

Similarly,

$$[H^+]_T = [H^+]_f \quad \text{(III)}$$
$$[CBZ]_T = [CBZ]_f \quad \text{(IV)}$$

Now,

$$Os(VIII)_T = Os(VIII)_f + \text{Complex}$$
$$= Os(VIII)_f + K_2[CBZ][Os(VIII)]_f$$
$$= Os(VIII)_f + \{1 + K_2[CBZ]\}$$
$$Os(VIII)_f = \frac{Os(VIII)_T}{1+K_2[CBZ]}$$

Since the value of second term in the denominator is less than 1, it can be neglected.

Therefore,

$$Os(VIII)_f = [Os(VIII)]_T \quad \text{(V)}$$

Substituting the values of $[MnO^-_4]_f$, $[CBZ]_f$, $[H^+]_f$ and [Os(VIII)] into Eq. (1) and omitting the subscripts, we have,

$$\text{Rate} = \frac{-\mathrm{d}[MnO_4^-]}{\mathrm{d}t} = \frac{kK_1K_2[MnO_4^-][CBZ][H^+][Os(VIII)]}{1+K_1[H^+]+K_1K_2[H^+][CBZ]}$$

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