

## 알칼리성 용매에서 과망간산에 의한 세프포독심 프록세틸의 산화의 분광광도법적 조사: 속도론적 연구

Aftab Aslam Parwaz Khan, Ayaz Mohd, Shaista Bano, and K. S. Siddiqi\*  
Department of Chemistry, Aligarh Muslim University, Aligarh, 202002, (U. P.) India  
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## Spectrophotometric Investigation of Oxidation of Cefpodoxime Proxetil by Permanganate in Alkaline Medium: A Kinetic Study

Aftab Aslam Parwaz Khan, Ayaz Mohd, Shaista Bano, and K. S. Siddiqi\*  
Department of Chemistry, Aligarh Muslim University, Aligarh, 202002, (U. P.) India  
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**요약.** 일정한 이온 세기의 알칼리 용액에서 과망간산에 의한 프포독심 프록세틸(Cefpodoxime Proxetil)의 산화의 속도론적 경로가 분광광도법적으로 연구되었다. 그 반응은 과망간산 이온 농도에서 일차 속도론적으로 나타났으며, 프포독심 산과 알칼리 농도에서 단일 이하의 차수를 나타내었다. 용매의 이온 세기가 증가함에 따라 속도도 증가하였다. 산화 반응은 프포독심 산과 함께 복합체를 형성하는 알칼리-과망간산 종들을 통하여 진행된다. 반응물을 만들기 위해서 프포독심 산의 자유 라디칼과 과망간산의 다른 분자 사이의 빠른 반응에 이어서 다음 분해가 천천히 진행된다. 다양한 온도에서 반응의 조사는 제안하는 메커니즘의 느린 단계를 고려한 활성화 변수들의 결정할 수 있게 하고 일차 속도론을 따른다. 제안하는 메커니즘과 유도된 속도 법칙들은 관찰된 속도들과 일치하였다.

**주제어:** 프포독심 프록세틸, 과망간산, 속도론, 열역학

**ABSTRACT.** A Kinetics pathway of oxidation of Cefpodoxime Proxetil by permanganate in alkaline medium at a constant ionic strength has been studied spectrophotometrically. The reaction showed first order kinetics in permanganate ion concentration and an order less than unity in cefpodoxime acid and alkali concentrations. Increasing ionic strength of the medium increase the rate. The oxidation reaction proceeds via an alkali-permanganate species which forms a complex with cefpodoxime acid. The latter decomposes slowly, followed by a fast reaction between a free radical of cefpodoxime acid and another molecule of permanganate to give the products. Investigations of the reaction at different temperatures allowed the determination of activation parameters with respect to the slow step of proposed mechanism and follows first order kinetics. The proposed mechanism and the derived rate laws are consistent with the observed kinetics.

**Keywords:** Cefpodoxime proxetil, Permanganate, Kinetics, Thermodynamics

### INTRODUCTION

Cefpodoxime proxetil (CFP) is one of the several new cepheims administered orally as inactive esters of the antibiotic Cefpodoxime. It is (1-[isopropoxy-carbonyl]oxy) ethyl ester of (z)-7-[2-(2-amino-1,3-

thiazol-4-yl)-2-methoxyiminoacetamido]-3-methoxymethyl-3-cephem-4-carboxylic acid) (Fig. 1). CFP is an ester prodrug of Cefpodoxime acid (CFA), where a proxetil radical is attached to CFA. It is an orally absorbed, broad spectrum, third generation cephalosporin ester implicated in the treatment of



previously thermostated solutions of  $MnO_4^-$  and (CFA), which also contained required quantities of NaOH and  $NaClO_4$  to maintain alkaline medium and ionic strength, respectively. The temperature was maintained at 25 °C. The reaction was monitored by the decrease in absorbance of  $MnO_4^-$ , at its absorption maximum of 525 nm. Earlier it was verified that there is no interference from other reagents at this wavelength. Application of Beer's Law for permanganate at 525 nm had earlier been verified, giving  $\epsilon$ , was found to be  $2083 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . The reaction was followed more than three half lives. The first order rate constants  $k_{obs}$  were evaluated by plots of  $\log [MnO_4^-]$  vs. time. The first order plots in almost all cases were linear up to 85% of the reaction and  $k_{obs}$  were reproducible at 525 nm and an increasing absorbance of Mn(VI) at 610 nm during the course of the reaction (Fig. 5). The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in nitrogen atmosphere. No significant difference between the results obtained under nitrogen and in the presence of air was observed. Added carbonate had also no effect on the reaction rate. Regression analysis of experimental data to obtain the regression coefficient  $r$  and the standard deviation  $S$  of points from the regression line was performed using a Microsoft excel-2007 program.

## RESULTS

The absorption spectrum of CFP was exhibited two peaks at 270 and 345 nm (Fig. 3).<sup>18</sup> After addition of potassium permanganate in the same medium is oxidized the (CFA) and exhibits a green colour of manganate ion, appears which absorbs at 610 nm. It was empirically found that the blue colour originated from a mixture of violet  $MnO_4^-$  and green

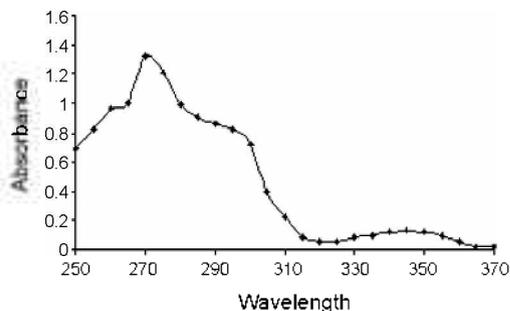


Fig. 3. Absorption spectrum of CFP.

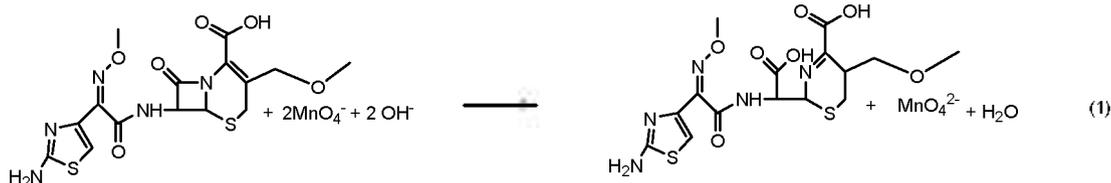
colour  $MnO_4^{2-}$  rather than form the formation of hypomanganate. The formation of Mn(VII) was also evidence by the decrease of the absorbance of Mn(VII) at 525 nm and the increase of that of Mn(VI) at 610 nm during the course of reaction (Fig. 5). The intensity of the colour increases with time and hence a kinetic method based on the spectrophotometric measurement was developed.

### Stoichiometry of the reaction

The reaction mixture containing an excess of permanganate over (CFA) were mixed in the presence of  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  NaOH and at constant ionic strength  $I = 0.10 \text{ mol dm}^{-3}$  were kept in a closed container under a nitrogen atmosphere at 25 °C. After 1 h the manganese (VII) concentration was assayed by measuring the absorbance at 610 nm. The results indicated that 2 mols of manganese (VII) consumed 1 mol of (CFA). Therefore, the reaction mechanism is proposed on the basis of the literature background<sup>19</sup> and our experimental study as shown in eq 1.

### Reaction order

The reaction order were evaluated from the slope of  $\log k_{obs}$  versus  $\log$  concentration plots by the varying concentration of (CFA) and alkali keeping other factors constant.



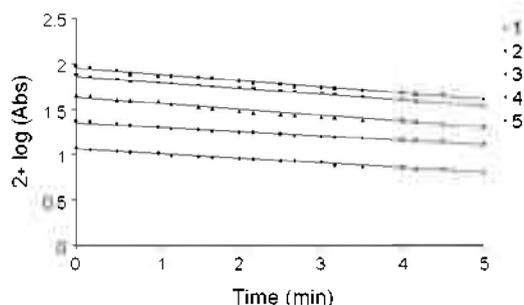


Fig. 4. First order plots for the oxidation of CFA by alkaline  $\text{MnO}_4^-$  at  $25^\circ\text{C}$ ;  $[\text{CFA}] = 1.0 \times 10^{-3}$ ;  $[\text{OH}^-] = 2 \times 10^{-2}$ ;  $I = 0.10/\text{mol dm}^{-3}$ ;  $[\text{Mn(VII)}] \times 10^4 \text{ mol dm}^{-3}$ : (1) 0.6, (2) 0.8, (3) 1.0, (4) 2.0, and (5) 3.0.

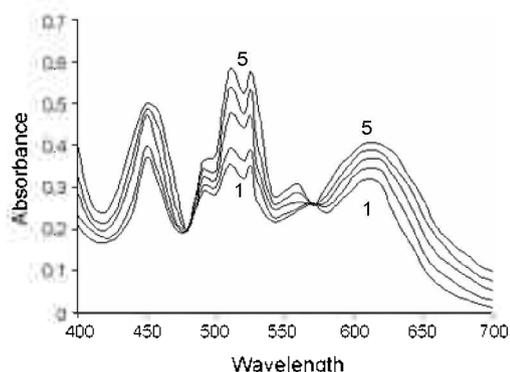


Fig. 5. Spectral changes during the oxidation of [CFA] by alkaline  $\text{MnO}_4^-$  at  $25^\circ\text{C}$ ;  $[\text{Mn(VII)}] = 1.0 \times 10^{-4}$ ,  $[\text{CFA}] = 1.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 2 \times 10^{-2}$ ,  $I = 0.10/\text{mol dm}^{-3}$ .

#### Effect of Concentration of Manganese (VII)

At constant concentration of (CFA),  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ , and alkali,  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , and at constant ionic strength,  $0.10 \text{ mol dm}^{-3}$ . The oxidant  $\text{KMnO}_4$  concentration was varied in the range of  $6 \times 10^{-5}$ – $6 \times 10^{-4} \text{ mol dm}^{-3}$ . All kinetic runs exhibited identical characteristics. The linearity of plots of  $\log(\text{absorbance})$  vs time, for different concentrations of permanganate, indicates order in manganese(VII) concentration as unity (Fig. 4). This was also confirmed by the constant values of pseudo first order rate constants,  $k_{\text{obs}}$ , for different manganese(VII) concentrations (Table 1).

#### Effect of NaOH Concentration

The effect of increasing conc of alkali on the

Table 1. Effect of variation of  $[\text{KMnO}_4]$ ,  $[\text{CFA}]$  and  $[\text{OH}^-]$  on the oxidation of cefpodoxime acid by alkaline  $[\text{KMnO}_4]$  at  $25^\circ\text{C}$  and ionic strength  $I = 0.10/\text{mol dm}^{-3}$

$10^4 \times [\text{KMnO}_4] \text{ mol dm}^{-3}$	$10^3 \times [\text{CFA}] \text{ mol dm}^{-3}$	$10^2 \times [\text{OH}^-] \text{ mol dm}^{-3}$	$10^3 k_{\text{obs}} (\text{S}^{-1})$	$10^3 \text{ kcal} (\text{S}^{-1})$
0.6	3.0	2.0	1.08	1.09
0.8	3.0	2.0	1.09	1.09
1.0	3.0	2.0	1.08	1.09
2.0	3.0	2.0	1.07	1.09
3.0	3.0	2.0	1.10	1.09
4.0	3.0	2.0	1.08	1.09
6.0	3.0	2.0	1.09	1.09
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3.0	0.6	2.0	0.984	0.983
3.0	0.8	2.0	1.05	1.06
3.0	1.0	2.0	1.06	1.07
3.0	1.2	2.0	1.37	1.36
3.0	1.4	2.0	1.60	1.58
3.0	1.6	2.0	1.72	1.73
3.0	1.8	2.0	1.99	1.98
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3.0	3.0	0.6	0.984	0.985
3.0	3.0	0.8	1.03	1.04
3.0	3.0	1.0	1.07	1.06
3.0	3.0	1.2	1.06	1.07
3.0	3.0	1.4	1.60	1.59
3.0	3.0	1.6	1.75	1.76
3.0	3.0	1.8	2.02	2.01

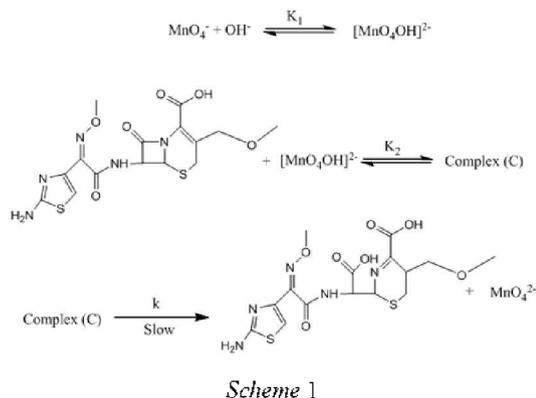
reaction was examined at constant concentration of drug and permanganate ion at  $25^\circ\text{C}$ . The alkali concentration was varied in the range of  $0.6 \times 10^{-2}$  to  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ . The  $k_{\text{obs}}$  values increased with increase in concentration of alkali.

#### Effect of [CFA]

The effect of (CFA) concentration on the reaction was studied at constant concentrations of alkali and permanganate and at a constant ionic strength of  $0.10 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . The substrate, (CFA) was varied in the range of  $5.0 \times 10^{-4}$ – $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ . The  $k_{\text{obs}}$  values increased with increase in concentration of (CFA) (Table 1).

#### Effect of Ionic Strength

The effect of ionic strength was studied by varying the  $\text{NaClO}_4$  concentration from 0.01 to  $0.10 \text{ mol dm}^{-3}$  at constant concentrations of permanganate.



(CFA), and alkali. It was found that increasing ionic strength had no effect on the rate of reaction.

### Effect of temperature

The kinetics was studied at four different temperatures under varying concentrations of (CFA), and alkali, keeping other conditions constant. The rate constants were found to increase with increase in temperature. The rate constant (*k*) of the slow step of Scheme 1 were obtained from the slopes and intercepts of  $1/k_{\text{obs}}$  versus  $1/[\text{CFA}]$  and  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  plots at four different temperatures. The energy of activation corresponding to these rate constants was evaluated from the Arrhenius plot of  $\log k$  versus  $1/T$  and from which other activation parameters were obtained (Table 2).

### Polymerization Study

The possibility of free radicals was examined as follows: the reaction mixture, to which a the reaction mixture with methanol, precipitate resulted, suggesting that the there was participation of free radicals in the reaction.

## DISCUSSION

At the observe experimental condition at  $\text{pH} > 12$  the reductant product of  $\text{Mn(VII)}$  might be stopped.<sup>20,21</sup> Although During our study the colour of the solution undergoes a series of change from blue to green. It is probable that green color originated from the permanganate ion. The spectrum of green solu-

Table 2. Activation and Thermodynamic parameters for the oxidation of cefpodoxime acid by  $\text{KMnO}_4$  in alkaline medium and  $I = 0.10/\text{mol dm}^{-3}$  with respect to slow step of Scheme 1

Temperature (K)	$10^2 k$ ( $\text{S}^{-1}$ )	
(a) Effect of Temperature		
293	2.7	
298	2.9	
303	4.8	
308	5.1	
(b) Activation Prameter values		
$E_a$ ( $\text{kJ mole}^{-1}$ )	65.4	
$\Delta H$ ( $\text{kJ mole}^{-1}$ )	61.7	
$\Delta S^\ddagger$ ( $\text{Jk}^{-1}\text{mole}^{-1}$ )	-120.4	
$\Delta G^\ddagger$ ( $\text{kJ mole}^{-1}$ )	19.11	
Temperature (K)	$K_1$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$10^2 K_2$ ( $\text{dm}^3 \text{mol}^{-1}$ )
(c) Effect of Temperature		
293	15.41	30.14
298	17.74	26.69
303	19.55	20.54
308	21.71	18.76
Thermodynamic Parameters	using $K_1$ values	using $K_2$ values
$\Delta H$ ( $\text{kJ mole}^{-1}$ )	76.5	-61.7
$\Delta S^\ddagger$ ( $\text{Jk}^{-1}\text{mole}^{-1}$ )	128	-63.2
$\Delta G^\ddagger$ ( $\text{kJ mole}^{-1}$ )	-5.6	-6.71

tion was identical to that of  $\text{MnO}_4^{2-}$ . It is probable that the blue color originated from the violet of permanganate and the green from manganate, excluding the accumulation of hypomanganate. It is evident from the (Fig. 5) that the concentration of  $\text{MnO}^+$  decreases at 525 nm due to  $\text{Mn(VII)}$  and increases at 610 nm due to  $\text{Mn(VI)}$ . As the reaction proceeds, slowly yellow turbidity develops, and after keeping for a long time the solution decolorizes and forms a brown precipitate. This suggests that the products formed might have undergone further oxidation resulting in a lower oxidation state of manganese. The results imply that first the alkali combines with permanganate to give an alkali-permanganate species  $[\text{MnO}_4 \cdot \text{OH}]^{2-}$  in a prior equilibrium step, which is in accordance with literature<sup>22-23</sup> and also experimentally observed order

in  $\text{OH}^-$  ion concentration. In the second step  $[\text{MnO}_4\text{-OH}]^{2-}$  combines with CFA to form an intermediate complex. The fractional order with respect to CFA presumably results from the complex formation between oxidant and substrate prior to the slow step. The reaction between permanganate and CFA is supported by Michaelis-Menten plot which is linear with positive intercept which is in agreement with complex formation. Within the complex one-electron is transferred from CFA to Mn(VII). Then this complex (C) decomposes in a slow step to form a species derived from CFA. All the results indicate a mechanism as given in *Scheme 1*.

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = kK_1K_2[\text{MnO}_4^-]_t[\text{CFA}]_f[\text{OH}^-]_f \quad (2)$$

The total  $[\text{MnO}_4^-]$  can be written as

$$\begin{aligned} [\text{MnO}_4^-]_t &= [\text{MnO}_4^-]_f + [\text{MnO}_4\text{-OH}]^{2-} + [\text{Complex}] \\ &= [\text{MnO}_4^-]_f + [\text{MnO}_4^-][\text{OH}^-] + K_1K_2[\text{MnO}_4^-][\text{CFA}][\text{OH}^-] \\ &= [\text{MnO}_4^-]_f (1 + K_1[\text{OH}^-] + K_1K_2[\text{CFA}][\text{OH}^-]) \\ [\text{MnO}_4^-]_f &= \frac{[\text{MnO}_4^-]_t}{1 + K_1[\text{OH}^-] + K_1K_2[\text{CFA}][\text{OH}^-]} \quad (3) \end{aligned}$$

where "t" and "f" stand for total and free. Similarly, total  $[\text{OH}^-]$  can be calculated as

$$\begin{aligned} [\text{OH}^-]_t &= [\text{OH}^-]_f + [\text{MnO}_4\text{-OH}]^{2-} + [\text{Complex}] \\ [\text{OH}^-]_f &= \frac{[\text{OH}^-]_t}{1 + K_1[\text{MnO}_4^-] + K_1K_2[\text{CFA}][\text{MnO}_4^-]} \quad (4) \end{aligned}$$

In view of the low concentrations of  $\text{MnO}_4^-$  and CFA used in the experiment, in eq 4 the terms  $K_1[\text{MnO}_4^-]$  and  $K_1K_2[\text{MnO}_4^-][\text{CFA}]$  can be neglected in comparison with unity.

Thus,

$$[\text{OH}^-]_f = \frac{[\text{OH}^-]_t}{1 + K_1[\text{MnO}_4^-]} \quad (5)$$

Similarly,

$$[\text{CFA}]_f = \frac{[\text{CFA}]_t}{1 + K_1K_2[\text{MnO}_4^-][\text{CFA}]} \quad (6)$$

Substituting equation 3, 5, and 6 in equation 2 and omitting the subscripts, we get

$$\text{Rate} = \frac{kK_1K_2[\text{MnO}_4^-][\text{CFA}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{CFA}][\text{OH}^-]} \quad (7)$$

Equation 7 confirms all the observed orders with respect to different species, which can be verified by rearranging to eq 8.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{kK_1K_2[\text{CFA}][\text{OH}^-]} + \frac{1}{kK_2[\text{CFA}]} + \frac{1}{k} \quad (8)$$

According to eq 8, other conditions being constant, plots of  $1/k_{\text{obs}}$  versus  $1/[\text{CFA}]$  and  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  should be linear and are found to be so (*Figs 6a and 6b*). 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<sup>24</sup> Using these constants, the rate constants were calculated over different experimental conditions, and there is a reasonable agreement between the calculated and the experimental values, which for the proposed mechanism (*Table 1*). The thermodynamic quantities for the first and second equilibrium step of *Scheme 1* can be evaluated as follows: The  $[\text{CFA}]$  and  $[\text{OH}^-]$  as in *Table 1* were varied at four different temperature. The spectral evidence of the complex formation was obtained from UV-Vis spectral study.<sup>25</sup> It is also proved kinetically by the non zero intercept of the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{CFA}]$  ( $r > 0.9997$ ,  $S < 0.0148$ ) (*Fig. 6b*). According to the rate law the plots of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  ( $r > 0.9987$ ,  $S < 0.0124$ ) and  $1/k_{\text{obs}}$  versus  $1/[\text{CFA}]$  ( $r > 0.9998$ ,  $S < 0.0151$ ) should be linear (*Figs 6a and b*) from the slope and intercept, the value of  $k$ ,  $K_1$  and  $K_2$  could be derived as  $2.87 \times 10^{-4}$ ,  $13.8 \text{ dm}^3 \text{ mole}^{-1}$ , and  $22.36 \text{ dm}^3 \text{ mole}^{-1}$  respectively. The rate constant were calculated from these values (*Table 1*) which supports the proposed mechanism. The reaction rate of CFA increased with increasing intensity of the complex. The kinetics was studied at four different temperature and concentration of CFA and NaOH keeping all other conditions constant. The rate constant was found to increase with increasing

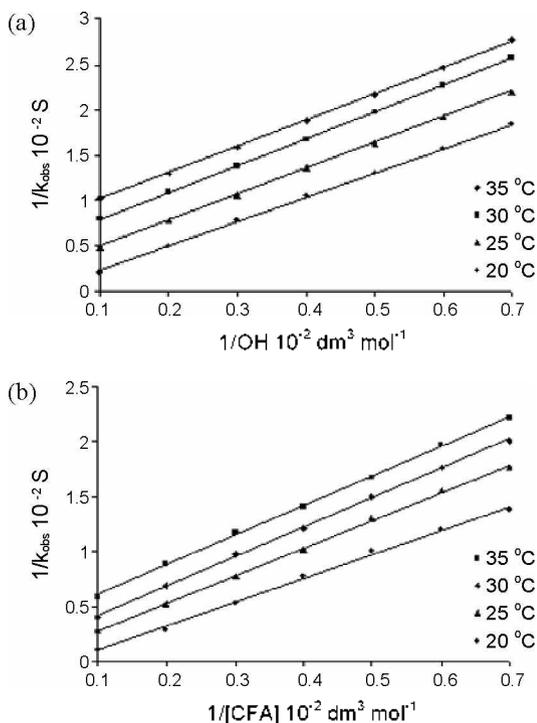


Fig. 6. (a) Rate law plots  $1/k_{obs}$  versus  $1/[OH^-]$  of oxidation of cepodoxime acid by  $KMnO_4$  in alkaline medium at different temperatures (circumstance as in Table 1). (b) Rate law plots  $1/k_{obs}$  versus  $1/[CFA]$  of oxidation of cepodoxime acid by  $KMnO_4$  in alkaline medium at different temperatures (circumstance as in Table 1).

temperature. The rate constant  $k$  of the slow step of Scheme 1 were obtained from the slope and intercept of  $1/k_{obs}$  versus  $1/[CFA]$  and  $1/k_{obs}$  versus  $1/[OH^-]$  plots at four different temperatures. The activation parameters corresponding to these constant were evaluated from the Arrhenius plot of  $\log k$  versus  $1/T$  and are listed in Table 2. The experimental value of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favorable for electron transfer process. The high negative value of  $\Delta S^\ddagger$  indicate that interaction of the reaction ions of similar charges form an activated complex and is more ordered than the reactants due to loss of degree of freedom.<sup>26</sup> The hydroxyl ion concentration i.e. Table 1 was verified at four different temperature and the  $K_1$  value were determined from a (Fig. 6a) as shown in Table 2. Similarly CFA concentration as in Table 1 was varied at four different temp and

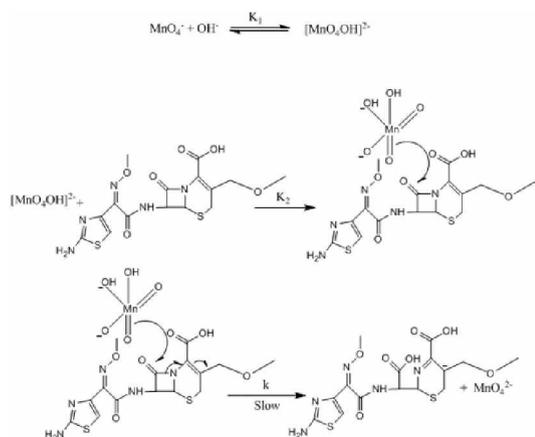
$K_2$  values were determined at each temp (Fig. 6b) as listed in Table 2. The effect of temp on reaction rate is well known and important in the various activation parameters of the reaction product. A Arrhenius plot was made for the variation of  $K_1$  with temperature (i.e.  $\log K_1$  versus  $1/T$ ). The values of the enthalpy change of the first equilibrium step  $K_1$  of the reaction ( $\Delta H$ ), enthalpy of the reaction ( $\Delta S$ ) and free energy of reaction ( $\Delta G$ ) were calculated as listed in Table 2. Similarly thermodynamic parameters for second step  $K_2$  are calculated such as enthalpy: entropy and free energy of activation of the reaction product were calculated using Eyring equation.

$$\log K/T = [\log kb/h + S/2.302R] - \Delta H/2.303RT$$

The plot of  $\log K_2/T$  versus  $1/T$  was linear with correlation coefficient of -0.9996  $\Delta H^\ddagger$  was evaluated from the slope ( $-\Delta H^\ddagger/2.303RT$ ) and  $\Delta S^\ddagger$  from the intercept [ $\log kb/h + S/2.302R$ ] of the compiled Eyring plot. The Gibbs free energy of activation was determined by  $\Delta G^\ddagger = -2.303 RT \log K$  at room temperature. These values are given in Table 2. The proposed mechanism supported by the above thermodynamic parameter. A comparison of the later values (from  $K_2$ ) 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 rate determining step is fairly fast and involves low activation energy.<sup>27</sup> The negative value of indicate that the complex (C) is more ordered than the reactant.<sup>28</sup> A detailed mechanistic explanation is given in Scheme 2.

## CONCLUSION

It is interesting to note that the oxidant species  $[MnO_4^-]$  required a pH > 12 below which the system becomes anxious and the reaction proceeds to Mn(IV) which slowly develops yellow turbidity. The oxidant, manganese(VII), exists in alkali media as alkali-permanganate species  $[MnO_4-OH]^{2-}$ , which takes part in the chemical reaction. The role of hydroxyl ions is essential to the chemical reaction.



Scheme 2. Mechanistic Interpretation for the Oxidation of CFA by Alkaline Permanganate

The given mechanism is consistent with all the experimental evidence. The rate constant of slowest step involved in the mechanism are evaluated and activation parameters with respect to slowest step of reaction were computed. The overall mechanistic sequence described here is consistent with the final product, mechanistic and kinetic studies.

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