

A Study of the Kinetic and Mechanism of Oxidation of Pyrazole Derivative by Permanganate Ion in Neutral Medium and the Effect of Metal Ion Catalysts

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Abstract: Oxidation of methylaminopyrazole formamidine (MAPF) by permanganate ion was studied spectrophotometrically in neutral medium in the presence of phosphate buffer solution. The stoichiometry of the reaction was found to be 3: 2 (MAPF: MnO_4^-). The oxidation reaction showed a first order kinetics with respect to $[MnO_4^-]$ and a fractional-first order dependence with respect to $[MAPF]$. Addition of small amounts of some metal ions increased the oxidation rate and the order of catalytic efficiency was: $Ag(I) > Cu(II) > Al(III)$. The suggested oxidation mechanism involves formation of a 1:1 intermediate complex between permanganate ion and MAPF. The formed complex decomposes in the rate-determining step to yield a free radical derived from MAPF and an intermediate Mn(VI). The free radical is attacked by Mn(VI) species to give rise to the final oxidation products which were identified by both spectroscopic and chemical tools as methylaminopyrazole, dimethylamine and carbon dioxide. The rate-law expression was deduced and the reaction constants involved in the different steps of the suggested mechanism were evaluated. The activation parameters of the rate constant of the slow step along with the thermodynamic quantities of the formation constant of the intermediate complex were evaluated and discussed.

Keywords: Methylaminopyrazole Formamidine, Oxidation, Permanganate, Kinetics, Mechanism

1. Introduction

Formamidines have very broad spectrum of biological activity [1, 2] and their derivatives are highly effective acaricides [3, 4]. The oxidative cleavage of formamidines is quite important, since the *N,N*-dialkyl formamidine group is one of the most versatile protecting groups, especially in biosynthetic applications. Furthermore, complexes of metal ions with organic ligands containing N, S or O are well known [5-9]. The presence of heteroatom in such ligands plays a key role when coordinated with transition metal ions. Such complexes exhibit remarkable biological activity against certain microbes, viruses and tumors [10, 11]. Fawzy et al. [12-14] studied the kinetics of oxidation of methylaminopyrazole formamidine (MAPF) in acidic media by cerium (IV) in perchloric acid medium [12] and by

chromic acid in sulfuric acid medium [13], and in alkaline medium by hexacyanoferrate (III) [14] and in all cases the final oxidation products were identified as methylaminopyrazole, dimethylamine and carbon dioxide.

Permanganate ion is an efficient oxidant in acidic, neutral and alkaline media [15-28] which is still considered as one of the most important, eco-friendly and powerful multi-electron oxidants employed in the kinetic studies [29]. The mechanism of oxidation by this multivalent oxidant depends not only on the substrate but also on the medium used for the study. On the other hand, transition metal ions have been widely used as homogeneous catalysts for oxidation of organic and inorganic substrates [30-32]. Kinetic investigations on the homogeneous catalyzed oxidation of organic compounds are considered to be a significant field of chemistry

because of the role played by metals in biological systems.

Although the kinetics of oxidation of methylaminopyrazole formamidine by some oxidants have been investigated in both acidic [12, 13] and alkaline [14] media, there are no reports describing its oxidation kinetics by permanganate ion. The present study deals with the oxidative behavior of methylaminopyrazole formamidine by permanganate ion in neutral medium in order to establish the effect of changing the oxidant and medium on the oxidation kinetics of such organic substrate and to elucidate a plausible oxidation mechanism.

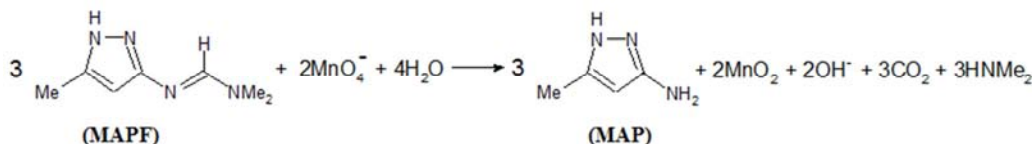
2. Materials and Methods

2.1. Materials

All chemicals used throughout the present work were of reagent grade and doubly distilled water was used in all preparations. The solution of methylaminopyrazole formamidine was freshly prepared by dissolving the sample in doubly distilled water. A fresh solution of potassium permanganate was prepared and standardized as reported [29]. Phosphate buffer solution was used to maintain the neutral medium.

2.2. Kinetic Measurements

The kinetic runs were followed under pseudo-first order conditions where MAPF was present in a large excess over that of permanganate ion oxidant. Initiation of the reaction was done by mixing the formerly thermostatted solutions of permanganate and MAPF



The above stoichiometric equation is consistent with the results of product identification which performed by both spectroscopic and elemental tools as described elsewhere [33, 34]. Similar oxidation products were obtained in earlier works [12-14].

3.2. Time-Resolved Spectra

Time-resolved spectra throughout oxidation of methylaminopyrazole formamidine by permanganate ion in neutral medium in the presence of phosphate buffer solution are shown in Figure 1. The Figure shows a gradual disappearance of permanganate band at $\lambda = 525$ nm with the appearance of two isosbestic points at wavelengths of 507 and 578 nm.

substrate that also contained the required amounts of phosphate buffer solution. The course of the reaction was followed by monitoring the decay in the absorbance of permanganate ion as a function of time at its absorption maximum ($\lambda = 525$ nm), whereas the other constituents of the reaction mixture did not absorb considerably at the determined wavelength. The absorption measurements were done in a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. First order plots of $\ln(\text{absorbance})$ versus time were recorded to be straight lines up about two-half lives of the reaction completion and the observed first order rate constants (k_{obs}) were calculated as the gradients of such plots. At least two independent kinetic runs of the rate constants were taken for the analysis. The rate constants were reproducible to within $\pm 3\%$. Some kinetic runs were performed under purified nitrogen and compared with those taken under air, and the results were the same. Thus, dissolved oxygen did not affect the oxidations rates.

3. Results

3.1. Reaction Stoichiometry and Products Characterization

Various sets of the reaction mixtures containing different amounts of permanganate ion and MAPF in the presence of phosphate buffer were allowed to react for about 24 h for completion of the reaction. The unreacted $[\text{MnO}_4^-]$ was determined spectrophotometrically at 525 nm. The results indicated that two moles of permanganate ions consumed three moles of MAPF to yield the oxidation products as shown in the following equation,

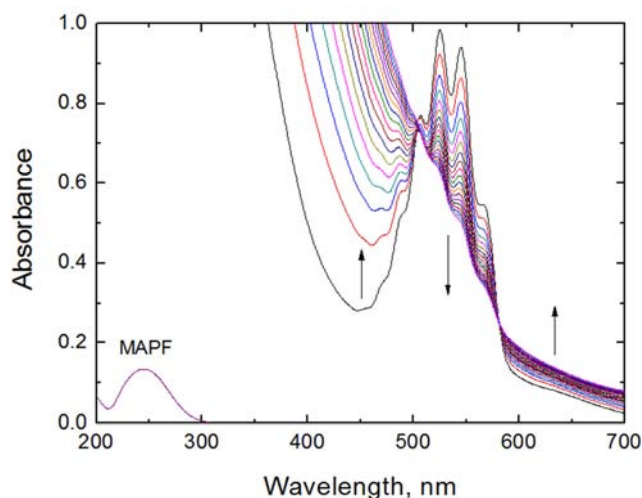


Figure 1. Time-resolved spectra throughout oxidation of methylaminopyrazole formamidine by permanganate ion in neutral medium. $[\text{MAPF}] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C . Scan time intervals = 1.0 min.

3.3. Effect of $[MnO_4^-]$

The effect of permanganate concentration on the oxidation rate of methylaminopyrazole formamide was studied by varying its concentration in the range of $(2.0 - 12.0) \times 10^{-4} \text{ mol dm}^{-3}$ at fixed MAPF concentration and temperature. The order with respect to $[MnO_4^-]$ was found to be unity, as plots of $\ln(\text{absorbance})$ versus time were linear up to about two-half lives of the reaction completion. The first order dependence with respect to $[MnO_4^-]$ was also confirmed by the non-variation of the observed first order rate constant (k_{obs}) at various $[MnO_4^-]$ while keeping others constant.

3.4. Effect of [MAPF]

The reaction rate was measured at different initial concentrations of methylaminopyrazole formamide keeping other conditions constant. It was found that the reaction rate increased with increasing the concentration of MAPF as listed in Table 1. The plots of k_{obs} versus $[MAPF]$, at different temperatures, were found to be linear with positive intercepts on the k_{obs} axes as shown in Figure 2 suggesting that the order with respect to $[MAPF]$ was fractional-first.

Table 1. Effect of $[MnO_4^-]$ and $[MAPF]$ on the observed-first order rate constants (k_{obs}) in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium at 25°C.

$10^4 [MnO_4^-] (\text{mol dm}^{-3})$	$10^3 [MAPF] (\text{mol dm}^{-3})$	$10^5 k_{\text{obs}} (\text{s}^{-1})$
2.0	6.0	91.8
4.0	6.0	92.1
6.0	6.0	94.0
8.0	6.0	93.6
10.0	6.0	90.9
12.0	6.0	92.7
4.0	2.0	51.3
4.0	4.0	74.0
4.0	6.0	92.1
4.0	8.0	112.5
4.0	10.0	128.1
4.0	12.0	142.3

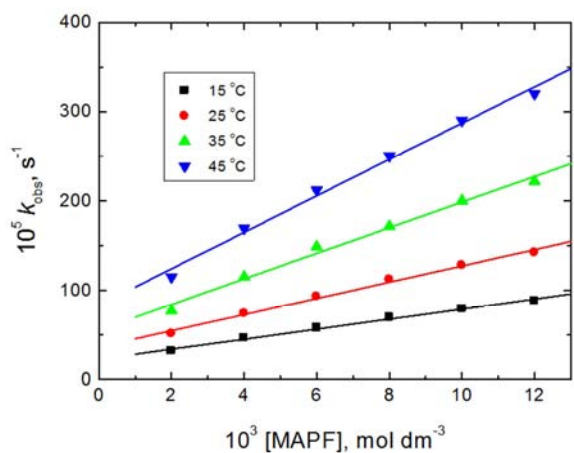


Figure 2. Plots of the observed-first order rate constants (k_{obs}) versus MAPF concentration in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium at different temperatures.

3.5. Effect of Metal Ion Catalysts

The effect of some metal ions with different valences was investigated by addition of small amounts of the salts of Ag(I), Cu(II) and Al(III) to the reaction medium at identical concentrations. The results showed that the reaction rate increased with increasing metal ion concentration and the plots of k_{obs} versus the metal ion concentrations were found to be linear with positive intercepts on the k_{obs} axes as shown in Figure 3. The order of effectiveness of the metal ions was: Ag(I) > Cu(II) > Al(III).

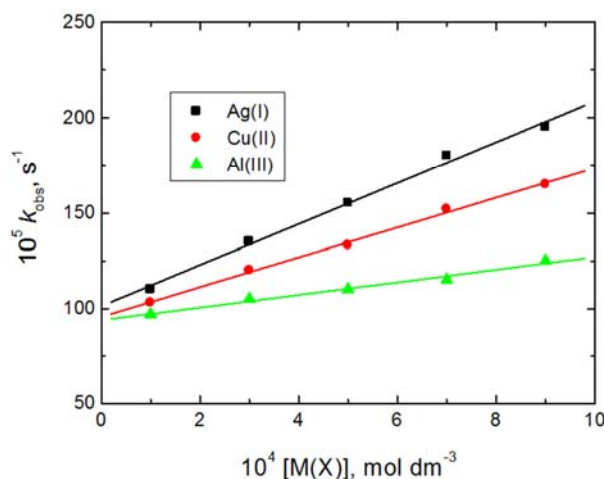


Figure 3. Effect of addition of some metal ions on the rate of oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium. $[MAPF] = 6.0 \times 10^{-3}$, $[MnO_4^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C.

3.6. Effect of Temperature

The oxidation rate was measured at four different temperatures namely, 15, 25, 35 and 45°C at constant concentrations of the reactants and other conditions being constant. The results indicated that raising temperature enhanced the oxidation rate. The activation parameters of the rate constant of the slow step (k) along with thermodynamic quantities of the formation constant involved in the reaction mechanism have been evaluated and listed in Tables 3 and 4.

3.7. Polymerization Test

The involvement of free radicals in the oxidation reaction was examined by initially addition of acrylonitrile to the reaction mixture and keeping in inert atmosphere for about 4 hours. On diluting the reaction mixture with methanol, a white precipitate was formed suggesting that there was participation of free radical in the present reaction. When the experiment was repeated in the absence of MAPF under similar conditions, the test was negative suggesting that the reaction was routed through a free radical path.

4. Discussion

In the permanganate ion, manganese has an oxidation state of VII. It is stable in neutral or slightly alkaline media, but, in a strongly alkaline medium, [29] it disproportionates or

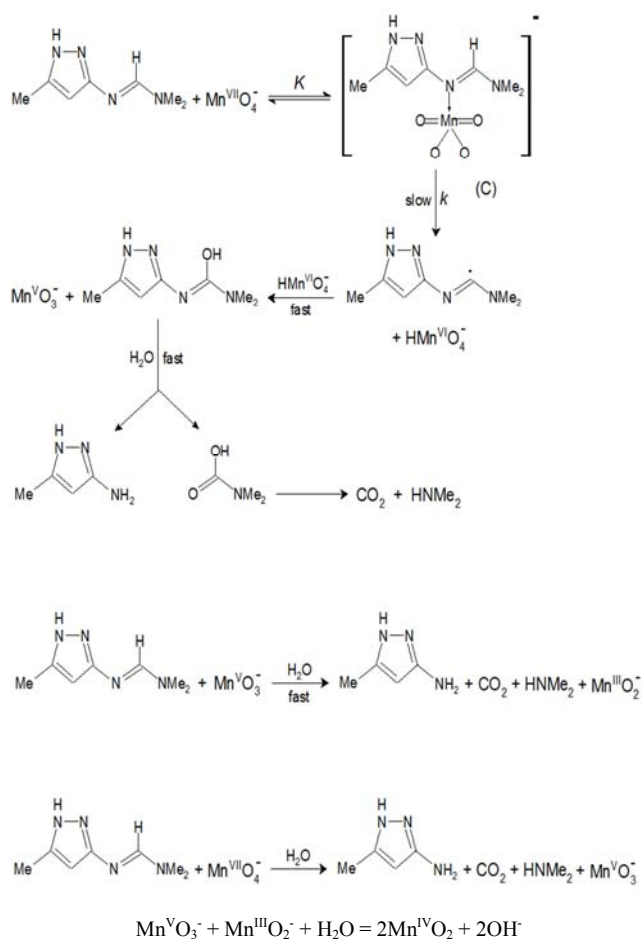
reacts with hydroxide ion to form manganese(V) (hypomanganate) or manganese(VI) (manganate). Manganese(VII) is reduced to Mn(II) during oxidation processes via many manganese species having different oxidation states such as Mn(VI), Mn(V), Mn(IV) and Mn(III). The appearance of these intermediate oxidation states depends upon various reaction conditions and the type of substrate. In neutral or slightly alkaline solutions, permanganate used as a powerful oxidizing agent ($E_0 = +1.23$ V). The formation of manganate(VI) and/or hypomanganate (V) short-lived intermediates may be confirmed by the change in the color of the solution mixture as the reaction proceeded from purple-pink, Mn(VII), to blue, Mn(V), to green, Mn(VI). As the reactions proceed, a yellow turbidity slowly develops and on prolonged standing, the solution turns to colorless with a brown colloidal precipitate, MnO_2 . The failure to detect Mn(V), absence of an absorption maximum around $\lambda = 700$ nm, may be interpreted by its extreme short lifetime and undergoing a rapid disproportionation [20, 35].

The present reaction between methylaminopyrazole formamide (MAPF) and permanganate ion in neutral medium has a stoichiometry of 3: 2 (MAPF: MnO_4^-) with a first-order dependence on $[MnO_4^-]$ and less than unit order dependence with respect to $[MAPF]$. The less than unit order dependences with respect to $[MAPF]$ suggests formation of an intermediate complex between MAPF and permanganate ion in pre-equilibrium step. Spectral evidence for complex formation was obtained from the UV-Vis spectra (Figure 1). Another support for complex formation is the kinetic evidence as the plots of $1/k_{obs}$ versus $1/[MAPF]$ were linear with positive intercepts on $1/[MAPF]$ axes as shown in Figure 4, similar to the well-known Michaelis-Menten mechanism for enzyme-substrate reactions [36]. Therefore, permanganate ion is suggested to react with one molecule of MAPF in a pre-equilibrium step to give an intermediate complex (C). The cleavage of such complex leads to the formation of a free radical derived from MAPF and an intermediate Mn(VI) species. Such complex is rapidly attacked by manganate(VI) ion to yield the corresponding secondary alcohol, as an intermediate product, and Mn(V) species. The intermediate product is rapidly hydrolyzed to give the final oxidation products. In a further fast step, the intermediate Mn(V) being very active and unstable reacts with another MAPF substrate to yield again the final oxidation products and an intermediate Mn(III) species. This step is followed by a reaction between the last MAPF molecule and one permanganate species giving other oxidation products and another Mn(V) species. Finally, knowing the fact that the species Mn(V) is very unstable, it will attack the intermediate Mn(III) leading to formation of MnO_2 as the final oxidation product of permanganate, satisfying the observed reaction stoichiometry. The proposed mechanism is illustrated in Scheme 1.

The obtained large negative values of ΔS^\ddagger listed in Table 3 suggests that the more plausible mechanism is a one-electron transfer of inner-sphere nature [37]. Also, the large negative

values of ΔS^\ddagger indicate that there is a decrease in the randomness during the oxidation process. This leads to the formation of a compacted intermediate complex and such activated complex is more ordered than the reactants due to loss of degree of freedom. On the other hand, the positive value of ΔH^\ddagger indicates that the complex formation is endothermic. Also, the large positive value of ΔG^\ddagger suggests enhanced formation of the intermediate with increasing temperature as well as to the non-spontaneity of the complex formation.

The enhancement of the oxidation rate upon addition of the investigated metal ions have interpreted [38, 39] by specific effects of metal ions in terms of bridging which facilitates electron transfer in redox systems, while Wahl [40, 41] and his co-workers have interpreted specific effects in terms of complex formation. It was found that metal complex can be more active than the free ligand (MAPF) and can exhibit bioactivity which is not shown by the free ligand.



Scheme 1. Mechanism of oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium.

According to Scheme 1, the oxidation rate can be expressed as follows,

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k[C] \quad (1)$$

Also,

$$K = \frac{[C]}{[\text{MAPF}][\text{MnO}_4^-]} \quad (2)$$

Therefore,

$$[C] = K[\text{MAPF}][\text{MnO}_4^-] \quad (3)$$

Substituting Eq. (3) in Eq. (1) leads to the following equation,

$$\text{Rate} = kK[\text{MAPF}][\text{MnO}_4^-] \quad (4)$$

The total concentration of MAPF substrate is given by,

$$[\text{MAPF}]_T = [\text{MAPF}]_F + [C] \quad (5)$$

where T and F refer to total and free concentrations, respectively.

Therefore,

$$[\text{MAPF}]_F = \frac{[\text{MAPF}]_T}{1 + K[\text{MnO}_4^-]} \quad (6)$$

Similarly,

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-]_F + [C] \quad (7)$$

$$[\text{MnO}_4^-]_F = \frac{[\text{MnO}_4^-]_T}{1 + K[\text{MAPF}]} \quad (8)$$

Substituting Eqs. (6) and (8) into Eq. (4), the following equation is obtained,

$$\text{Rate} = \frac{kK[\text{MAPF}][\text{MnO}_4^-]}{(1 + K[\text{MnO}_4^-])(1 + K[\text{MAPF}])} \quad (9)$$

In view of low concentration of $[\text{MnO}_4^-]$ used, the first term in the denominator of Eq (9) approximate to unity.

Therefore, Eq. (9) becomes,

$$\text{Rate} = \frac{kK[\text{MAPF}][\text{MnO}_4^-]}{1 + K[\text{MAPF}]} \quad (10)$$

Under pseudo-first order conditions, the rate-law can be expressed as,

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}}[\text{MnO}_4^-] \quad (11)$$

Comparing Eqs (10) and (11), and with rearrangement the following relationship is obtained,

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1}{kK} \right) \frac{1}{[\text{MAPF}]} + \frac{1}{k} \quad (12)$$

Equation (12) required that plots of $1/k_{\text{obs}}$ versus $1/[\text{MAPF}]$ to be linear with positive intercepts and are found to be so as shown in Figure 4. Values of the rate constant of

the slow step (k) at different temperatures obtained as reciprocal of the intercepts of such plots are listed in Table 2. The activation parameters of k were calculated from the Eyring and Arrhenius plots and are listed in Table 3. Also, the values of the formation constant K at different temperatures are also calculated from the slopes and intercepts of such plots and are also inserted in Table 2. Furthermore, the thermodynamic parameters of K are evaluated from van't Hoff plot and are inserted in Table 4.

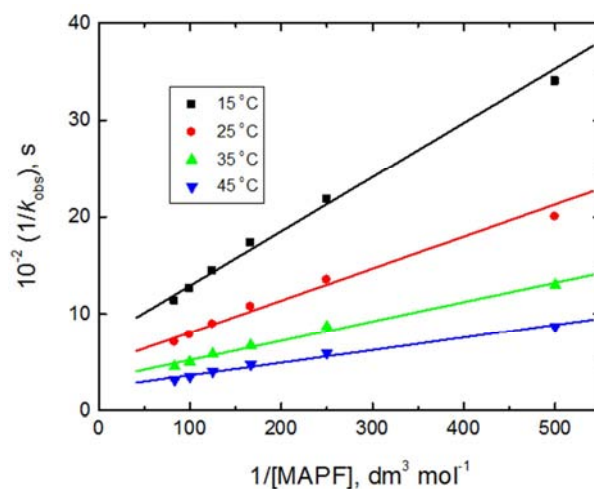


Figure 4. Plots of $1/k_{\text{obs}}$ versus $1/[\text{MAPF}]$ in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium at different temperatures. $[\text{MnO}_4^-] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Table 2. Values of the rate constant of the slow step (k) and the formation constant (K) at different temperatures in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium.

Constant	Temperature (°C)			
	15	25	35	45
$10^3 k \text{ (s}^{-1}\text{)}$	1.37	2.12	3.123	4.34
$K \text{ (dm}^3 \text{ mol}^{-1}\text{)}$	130.35	142.43	160.12	176.92

Table 3. Activation parameters of k in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium.

ΔS^\ddagger $\text{J mol}^{-1}\text{K}^{-1}$	ΔH^\ddagger kJ mol^{-1}	ΔG^\ddagger_{298} kJ mol^{-1}	E_a^\ddagger kJ mol^{-1}
-79.81	27.81	51.59	29.35

Table 4. Thermodynamic parameters associated with K in the oxidation of methylaminopyrazole formamide by permanganate ion in neutral medium.

ΔH° kJ mol^{-1}	ΔG°_{298} kJ mol^{-1}	ΔS° $\text{J mol}^{-1}\text{K}^{-1}$
7.93	-12.26	67.75

5. Conclusions

The kinetics of oxidation of methylaminopyrazole formamide by permanganate ion was studied in neutral medium. Addition of small amounts of some metal ions increased the oxidation rate and the order of catalytic efficiency was: $\text{Ag(I)} > \text{Cu(II)} > \text{Al(III)}$. The reaction mechanism was suggested and the reaction constants

involved in the different steps of the suggested mechanism were evaluated. The activation parameters of the rate constant of the slow step along with the thermodynamic quantities of the formation constant of the intermediate complex were evaluated and discussed.

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