

# Base-Catalyzed Oxidation of Aminotriazole Derivative by Permanganate Ion in Aqueous Alkaline Medium: A Kinetic Study

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**ABSTRACT:** Kinetic investigation on the oxidation of one of the aminotriazole derivatives, namely *N,N*-dimethyl-*N'*-(4*H*-1,2,4-triazol-3-yl) formamidine (ATF) by permanganate ion in alkaline medium has been performed at a constant ionic strength of 0.1 mol dm<sup>-3</sup> and at 25 °C. The progress of the reaction was followed spectrophotometrically. Both spectroscopic and kinetic evidences reveal formation of a 1:1 intermediate complex between the oxidant and substrate. The influence of pH on the oxidation rate indicated that the reaction is base-catalyzed. The reaction shows first order dependence with respect to [MnO<sub>4</sub><sup>-</sup>], and fractional-first order dependences on both [ATF] and [OH<sup>-</sup>]. Increasing ionic strength and dielectric constant did not affect the reaction rate. Addition of small amounts of alkali-metal ion catalysts was found to accelerate the oxidation rate and the order of effectiveness of the ions was: Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup>. The final oxidation products of ATF were identified as 3-aminotriazole, dimethyl amine and carbon dioxide. A plausible reaction mechanism consistent with the kinetic observations is proposed, and the reaction constants involved in the different steps of the mechanism have been evaluated. The activation parameters with respect to the slow step of the reaction, along with thermodynamic quantities of the equilibrium constants are calculated and discussed.

**KEYWORDS:** Permanganate, Oxidation, Kinetics, Mechanism, Aminotriazole.

## I. INTRODUCTION

Permanganate ion is a strong oxidizing agent in different media which still remains as one of the most important, eco-friendly and powerful multi-electron oxidants. It is stable in acidic, neutral, and slightly alkaline solutions, but it is disproportionate in strongly alkaline medium to form hypomanganate(V) and manganate(VI) short-lived transient species [1]. Permanganate can exist in various oxidation states, among which +7 is its highest oxidation state, which occurs in the oxo-compounds like MnO<sub>4</sub><sup>-</sup>, Mn<sub>2</sub>O<sub>7</sub>, MnO<sub>3</sub>F. Out of which, MnO<sub>4</sub><sup>-</sup> is the most commonly used well-known oxidant species to carry out kinetic studies in acidic, neutral and alkaline media [1].

In the last decades, formamidine derivatives have achieved commendable importance due to their very broad spectrum of biological activity. The biochemical potentialities of formamidines include monoamine oxidase inhibitors [2,3], adrenergic, neurochemical receptors [4,5] and prostaglandin E<sub>2</sub> synthesis [6]. The *N,N*-dialkyl derivatives are highly

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effective acaricides and the most rewarding of these studies resulted in discovery of the acaricide insecticide chlordimeform. 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 [7].

Although, permanganate ion in alkaline media has been used as a potent oxidant for various organic molecules [8-17], no reports are available in the literature on the kinetics and mechanism of oxidation of aminotriazole derivatives by this oxidant. In view of the above aspects, the title reaction was investigated in detail. The objectives of the present study are to establish the optimum conditions affecting oxidation of the aminotriazole derivative (ATF), elucidate plausible reaction mechanism and characterize the oxidation products.

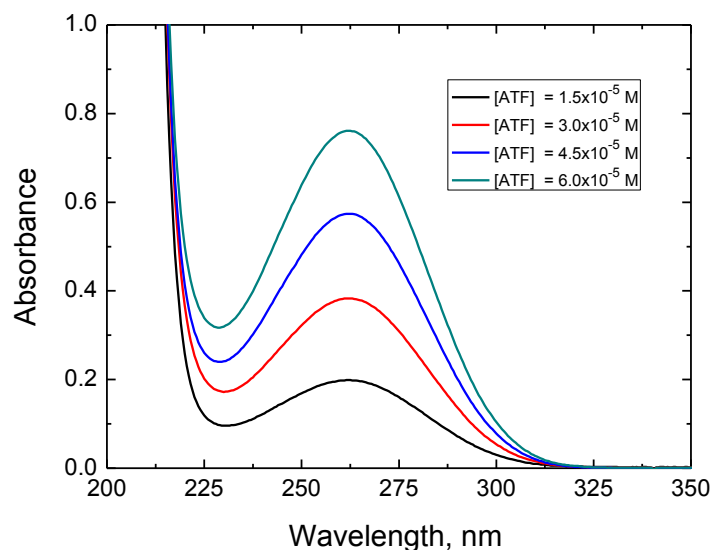
## II. EXPERIMENTAL

### Materials

All chemicals employed in the present work were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water. A fresh solution of aminotriazole derivative (ATF) was prepared as reported elsewhere [8]. The solution of potassium permanganate was prepared and standardized as reported earlier [18]. Sodium hydroxide, sodium perchlorate and *t*-butyl alcohol were used to vary the alkalinity, ionic strength and dielectric constant in the reaction medium, respectively.

### Kinetic Measurements

All kinetic runs were followed under pseudo-first order conditions with ATF in at least a 10-fold excess over that of permanganate. The reaction was initiated by mixing the previously thermostatted solutions of permanganate and ATF that also contained the required amounts of NaOH and NaClO<sub>4</sub>. The progress of reaction was followed by monitoring the decrease in absorbance of permanganate, as a function of time, at  $\lambda = 526$  nm, its absorption maximum, whereas the other constituents of the reaction mixtures do not absorb significantly at this wavelength. The applicability of Beer's law for ATF ion in alkaline medium (0.05 mol dm<sup>-3</sup>) at its absorption maximum,  $\lambda = 262$  nm, has been verified giving  $\epsilon = 12673 \pm 51$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> (Fig. 1). The absorbance measurements were made in a thermostatted quartz cell of a pathlength 1 cm on a Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer fitted with a wavelength program controller.



**Fig. 1:** Absorption spectra of various concentrations of ATF in 0.05 mol dm<sup>-3</sup> sodium hydroxide solution 25 °C.

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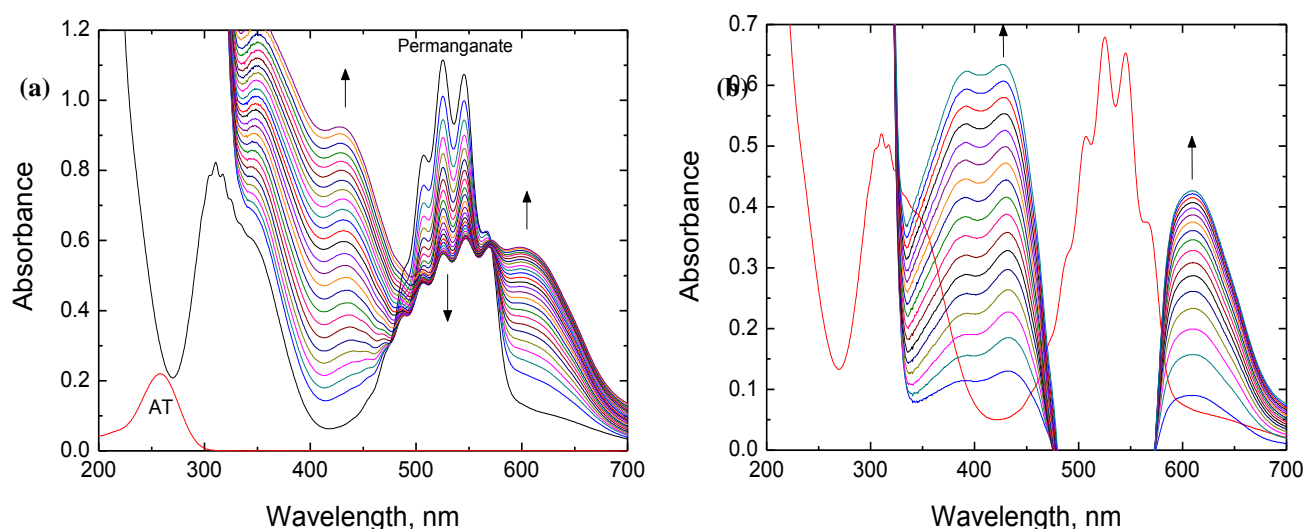
First order plots of  $\ln$  (absorbance) versus time were found to be straight lines up to at least 85% of the reaction completion and the pseudo-first order rate constant values were calculated as the gradients of such plots. Average values of at least two independent determinations of the rate constant were taken for the analysis. The rate constants were reproducible to within 4%. The order of reaction with respect to the reactants were determined from the slopes of the  $\log k_{\text{obs}}$  versus  $\log(\text{concentration})$  plots by varying the concentrations of substrate and base, in turn, while keeping other conditions constant.

Few kinetic runs were carried out after bubbling purified nitrogen and compared with those taken under air, and the results were found to be the same. Thus the dissolved oxygen does not have any effect on the rate constant.

### III. EXPERIMENTAL RESULTS

#### Time-resolved spectra

The spectral scans during the oxidation of ATF by alkaline permanganate are shown in Fig. 2(a,b). Figure 2a shows a gradual decay of the permanganate band at 526 nm with a corresponding growth of new intermediate absorption maxima at wavelengths of 606 and 435 nm. The band at 606 nm, shown in Fig. 2a and b, corresponds to the transient manganate(VI) species [19]. The formation of a manganate(VI) intermediate was also consistent with the green color observed as the reaction proceeded [1]. The appearance of two isosbestic points at 575 and 473 nm during the course of reaction indicates the interconversion of  $\text{MnO}_4^-$  to both  $\text{Mn}^{\text{VI}}\text{O}_4^{2-}$  and  $\text{MnO}_2$ , respectively [20]. The yellow color persisted after completion of the oxidation reactions, then finally dispersed brown  $\text{MnO}_2$  sol, was observed, confirming that the hypomanganate(V) formed and subsequently decomposed to  $\text{Mn}^{\text{IV}}$  sol. The latter was coagulated by aging to give a colloidal precipitate of  $\text{Mn}^{\text{IV}}\text{O}_2$ . When the concentration of manganate(VI) intermediate builds up, a slow decay of the intermediate takes place to give rise to the final oxidation products.



**Fig. 2(a,b):** Time-resolved spectra during the oxidation of ATF by alkaline permanganate.  $[\text{ATF}] = 0.02$ ,  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.05$  and  $I = 0.1 \text{ mol dm}^{-3}$  at  $25^\circ\text{C}$ . Scan time intervals = 1 min. b) Reference cell ( $\text{MnO}_4^-$  and  $\text{OH}^-$  of the same reaction mixture concentration).

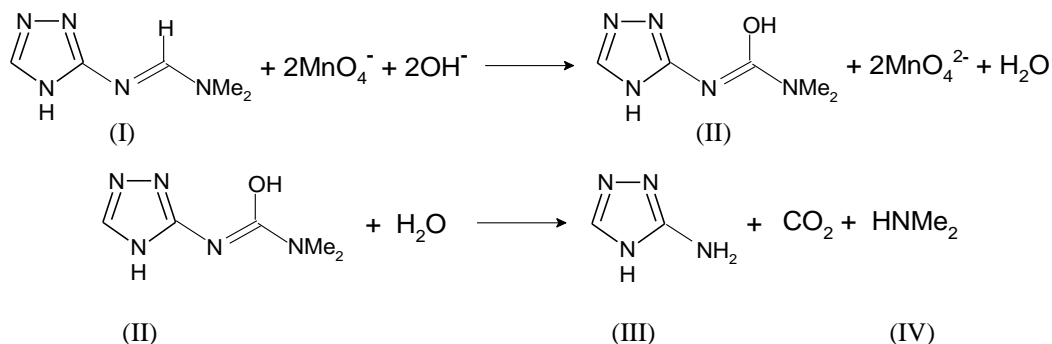
#### Stoichiometry and product analysis

The stoichiometry was determined spectrophotometrically at  $[\text{OH}^-] = 0.05$  and  $I = 0.1 \text{ mol dm}^{-3}$  which indicates the consumption of two permanganate ions for one molecule of ATF to yield the oxidation products as shown in the following Scheme,

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**SCHEME 1:** Stoichiometric equations for the oxidation of ATF by alkaline permanganate

where the compounds (I), (II), (III) and (IV) are ATF, 1,1-dimethyl-2-hydroxy-3-(4H-1,2,4-triazol-3-yl) formamide as an intermediate product, aminotriazole and dimethyl amine, respectively. The above stoichiometric equations are consistent with the results of product analysis as described elsewhere [8]. Aminotriazole and dimethylamine were identified by liquid chromatography [21] and spot tests [22], respectively, and carbon dioxide by lime water.

### Rate dependence on $[\text{MnO}_4^-]$

Permanganate oxidant was varied in the concentration range of  $1.0 \times 10^{-4}$  to  $8.0 \times 10^{-4}$  mol  $\text{dm}^{-3}$  while other reactant concentrations were kept constant. The pH and temperature were also kept constant. It has been observed that plots of  $\ln$  (absorbance) versus time were linear up to about 85% of the reaction completion. Furthermore, the increase in the oxidant concentration does not alter the oxidation rate of ATF (Table 1). These results indicate that the order of reaction with respect to the oxidant is confirmed to be one.

### Rate dependence on [ATF]

The observed first order rate constant was determined at different initial concentrations of the reductant ATF keeping others constant. A plot of  $k_{\text{obs}}$  versus [ATF] was found to be linear with a positive intercept (Figure not shown) confirming the fractional-first order dependence with respect to ATF concentration.

### Rate dependence on $[\text{OH}^-]$

The influence of alkali on the rate was studied at various  $[\text{OH}^-]$ , keeping all other reactant concentrations constant. The rate constant increased with increasing alkali concentration (Table 1), suggesting that the oxidation reaction is base-catalyzed. A plot of  $k_{\text{obs}}$  versus  $[\text{OH}^-]$  was also linear with a non-zero intercept, suggesting that the order of reaction in  $[\text{OH}^-]$  was fractional-first. Furthermore, a plot of  $\log k_{\text{obs}}$  versus  $\log [\text{OH}^-]$  was linear with less than unit slope showing fractional order with respect to  $[\text{OH}^-]$ .

### Rate dependence on ionic strength and dielectric constant

The effect of ionic strength was studied by varying the concentration of  $\text{NaClO}_4$  in the reaction medium at constant concentrations of alkali, ATF and permanganate. It was found that variation in ionic strength had no any significant effect on the rate as observed from the data listed in Table 1.

The dielectric constant of the medium,  $D$ , was varied by varying the *t*-butyl alcohol–water content (0–40 %) in the reaction mixture with all other conditions being constant. The  $D$  values were calculated from the equation:  $D = D_w V_w + D_B V_B$ , where  $D_w$  and  $D_B$  are dielectric constants of pure water and *t*-butyl alcohol, respectively, and  $V_w$  and  $V_B$  are the volume fractions of components water and *t*-butyl alcohol, respectively, in the total mixture. The data clearly reveal that the decrease in dielectric constant of the solvent mixture, i.e. increase the *t*-butyl alcohol content did not alter the reaction rate.

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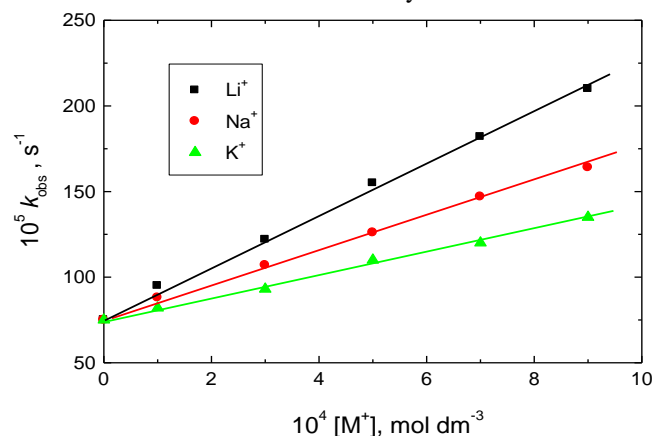
**TABLE 1:** Effect of variation of  $[\text{MnO}_4^-]$ ,  $[\text{ATF}]$  and  $[\text{OH}^-]$  on the first order rate constant ( $k_{\text{obs}}$ ) in the oxidation of ATF by alkaline permanganate at 25 °C.

$10^4 [\text{MnO}_4^-]$ mol dm <sup>-3</sup>	$10^2 [\text{ATF}]$ mol dm <sup>-3</sup>	$10^2 [\text{OH}^-]$ mol dm <sup>-3</sup>	$I$ mol dm <sup>-3</sup>	$10^5 k_{\text{obs}}$ s <sup>-1</sup>
<b>1.0</b>	2.0	5.0	0.10	73.4
<b>2.0</b>	2.0	5.0	0.10	76.6
<b>4.0</b>	2.0	5.0	0.10	75.0
<b>6.0</b>	2.0	5.0	0.10	74.1
<b>8.0</b>	2.0	5.0	0.10	77.8
4.0	<b>0.5</b>	5.0	0.10	28.2
4.0	<b>1.0</b>	5.0	0.10	47.0
4.0	<b>2.0</b>	5.0	0.10	75.0
4.0	<b>3.0</b>	5.0	0.10	101.8
4.0	<b>4.0</b>	5.0	0.10	128.3
4.0	2.0	<b>1.0</b>	0.10	36.1
4.0	2.0	<b>3.0</b>	0.10	57.7
4.0	2.0	<b>5.0</b>	0.10	75.0
4.0	2.0	<b>7.0</b>	0.10	87.9
4.0	2.0	<b>9.0</b>	0.10	102.5
4.0	2.0	5.0	<b>0.1</b>	75.0
4.0	2.0	5.0	<b>0.2</b>	77.3
4.0	<b>2.0</b>	<b>5.0</b>	<b>0.3</b>	77.1
4.0	2.0	5.0	<b>0.4</b>	75.3
4.0	2.0	5.0	<b>0.5</b>	76.7

Experimental error = ±4%

### Rate dependence on alkali-metal ion catalysts

Chlorides of some selected alkali metal ions such as  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  were added to the reaction medium at identical concentrations at constant other variables. The experimental observations show that presence of such cations accelerates the reaction rate. The order of effectiveness of the cations was:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ . A plot of  $k_{\text{obs}}$  versus electrolyte concentration exhibits a non-zero rate at zero electrolyte concentration as shown in Fig. 4.



**Fig. 3:** Influence of alkali-metal cations on the first order rate constant in the oxidation of ATF by alkaline permanganate.  $[\text{ATF}] = 0.02$ ,  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$ ,  $[\text{OH}^-] = 0.05$  and  $I = 0.1$  mol dm<sup>-3</sup> at 25 °C.

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## Rate dependence on temperature

To investigate the effect of temperature, the kinetic experiments were conducted at five temperatures (15 - 35 °C) keeping other conditions constant. The experimental results indicated that the oxidation rate was found to increase with raising temperature. The activation parameters of the rate constant of the slow step of the reaction ( $k_1$ ) along with thermodynamic parameters of the equilibrium constants involved in the reaction mechanism are evaluated and are listed in Tables 2 and 3.

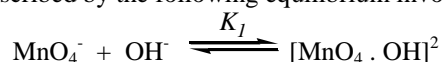
## Test for free radical intermediate

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 in the absence of ATF did not induce polymerization under similar conditions. This indicates that the reaction was routed through free radical path.

## IV. DISCUSSION

Permanganate ion,  $\text{MnO}_4^-$ , 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. Simandi *et al.* [23,24] reported that at  $\text{pH} > 12$ , the reduction product of  $\text{Mn}^{\text{VII}}$  is stable  $\text{Mn}^{\text{VI}}$  and no further reduction is observed. However, on prolonged standing, the green  $\text{Mn}^{\text{VI}}$  is reduced to  $\text{Mn}^{\text{IV}}$  under our experimental conditions. Permanganate in alkaline media exhibits various oxidation states, such as  $\text{Mn}^{\text{VII}}$ ,  $\text{Mn}^{\text{V}}$  and  $\text{Mn}^{\text{VI}}$ . 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 permanganate solution from the violet  $\text{Mn}^{\text{VII}}$  ion to green  $\text{Mn}^{\text{VI}}$  ion through the blue  $\text{Mn}^{\text{IV}}$  ion has been observed.

In aqueous alkaline medium [25,26] permanganate ion first combines with alkali to form an alkali-permanganate species in a pre-equilibrium step, as described by the following equilibrium involving the equilibrium constant  $K_1$ ,



This is consistent with the apparent order of less than unity in  $\text{OH}^-$ . The formation of  $[\text{MnO}_4 \cdot \text{OH}]^2$  in alkaline medium in the present systems is further supported by plots of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  shown in Fig. 5, which are linear with positive intercepts.

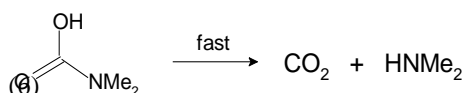
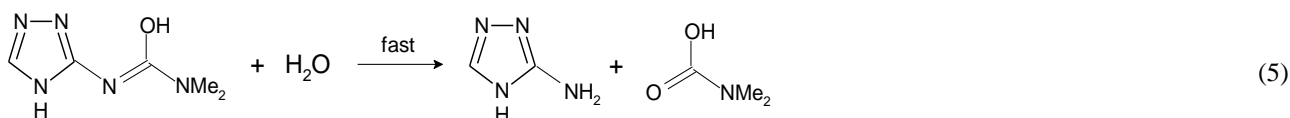
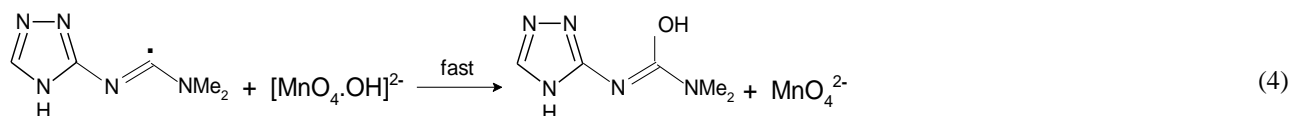
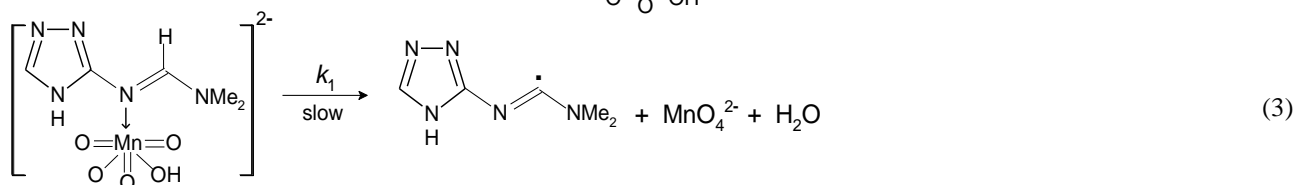
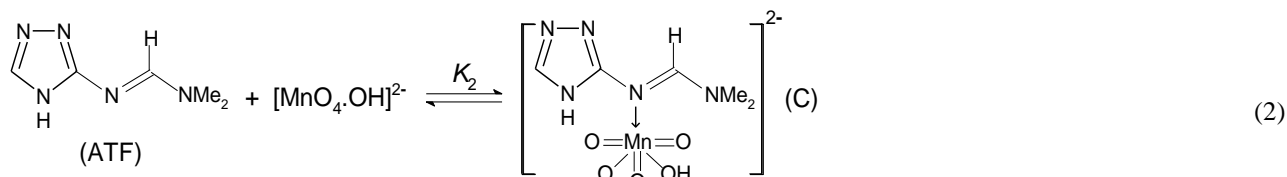
Many investigators [8-17] have suggested that most of the oxidation reactions by permanganate ion in neutral and alkaline media proceed through intermediate complex formation between the oxidant and substrate. Spectroscopic evidence for such a complex was obtained from the UV-Vis spectra, Fig. 2(a,b). Also, the linearity of the plots between  $1/k_{\text{obs}}$  and  $1/[\text{ATF}]$ , Fig. 4, is considered as a kinetic evidence in favour of possible formation of a transient complex between oxidant and substrate similar to the well-known Michaelis-Menten mechanism [27] for enzyme-substrate reactions. On the other hand, the observed negligible effect of ionic strength and dielectric constant of the medium on the reaction rate implies the association of an ion and a neutral molecule [19].

In view of the above arguments, the reaction mechanism shown in Scheme 2 may be suggested. This involves attack of the active species of permanganate,  $[\text{MnO}_4 \cdot \text{OH}]^2$ , on ATF substrate leading to the formation of a complex (C) in a prior equilibrium step. In this complex, one electron is transferred from the ATF substrate to permanganate. Slow cleavage of the complex leads to the formation of a free radical intermediate derived from the substrate ( $\text{ATF}^\cdot$ ) and manganate(VI) transient species. The intermediate ( $\text{ATF}^\cdot$ ) is rapidly attacked by another alkali-permanganate species to yield an intermediate product, 1,1-dimethyl-2-hydroxy-3-(4H-1,2,4-triazol-3-yl) formamidine. In a further fast step, the intermediate product is hydrolyzed to give the final oxidation products. Scheme 2 can be depicted as follows,

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### SCHEME 2: Mechanism of oxidation of ATF by alkaline permanganate

The relationship between reaction rate and substrate, hydroxyl ion and oxidant concentrations can be deduced (Appendix A) to give the following equation,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{ATF}] [\text{OH}^-] [\text{MnO}_4^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{ATF}] [\text{OH}^-]} \quad (7)$$

Under pseudo-first order condition the rate law can be expressed by Eq. (8)

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-] \quad (8)$$

Comparing equations (7) and (8) and with rearrangement we obtain the following equations,

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1 + K_1 [\text{OH}^-]}{k_1 K_1 K_2 [\text{OH}^-]} \right) \frac{1}{[\text{ATF}]} + \frac{1}{k_1} \quad (9)$$

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1}{k_1 K_1 K_2 [\text{ATF}]} \right) \frac{1}{[\text{OH}^-]} + \left( \frac{1}{k_1 K_2 [\text{ATF}]} + \frac{1}{k_1} \right) \quad (10)$$

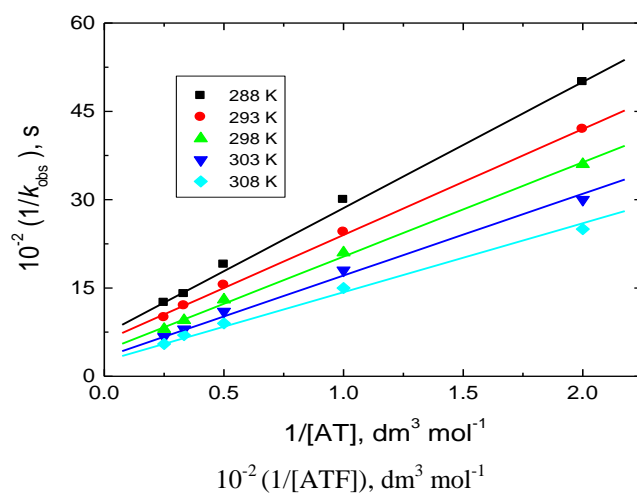
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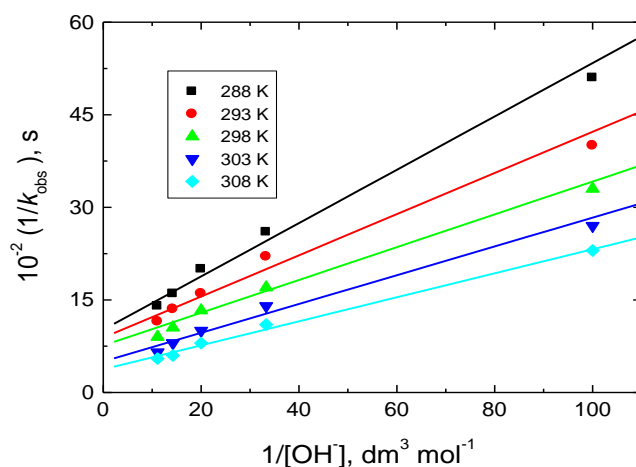
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According to Eq. (9), the relationship between  $1/k_{\text{obs}}$  and  $1/[\text{ATF}]$  at constant  $[\text{OH}^-]$  should be linear with positive intercept on the  $1/k_{\text{obs}}$  axis. The experimental results satisfy this requirement at different temperatures as shown in Fig. 4. From the intercepts of these plots, values of the rate constant of the slow step ( $k_1$ ) are evaluated and are listed in Table 2.

Also, regarding to Eq. (10), plots of  $1/k_{\text{obs}}$  against  $1/[\text{OH}^-]$  at constant  $[\text{ATF}]$  also should give straight lines with positive intercepts on  $1/k_{\text{obs}}$  axis, as was experimentally observed, Fig. 5. Values of the equilibrium constants  $K_1$  and  $K_2$  at different temperatures were calculated from the slopes and intercepts of Fig. 3 (and the obtained  $k_1$  values) and are also listed in Table 3. The obtained values of  $K_1$  are in a good agreement with those reported in the literature [8,10,17].



**Fig. 4:** Plots of  $1/k_{\text{obs}}$  versus  $1/[\text{ATF}]$  in the oxidation of ATF by alkaline permanganate at different temperatures.  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$  and  $[\text{OH}^-] = 0.05$  and  $I = 0.1 \text{ mol dm}^{-3}$ .



**Fig. 5:** Plots of  $1/k_{\text{obs}}$  versus  $1/[\text{OH}^-]$  in the oxidation of ATF by alkaline permanganate at different temperatures.  $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$  and  $[\text{ATF}] = 0.02$  and  $I = 0.1 \text{ mol dm}^{-3}$ .

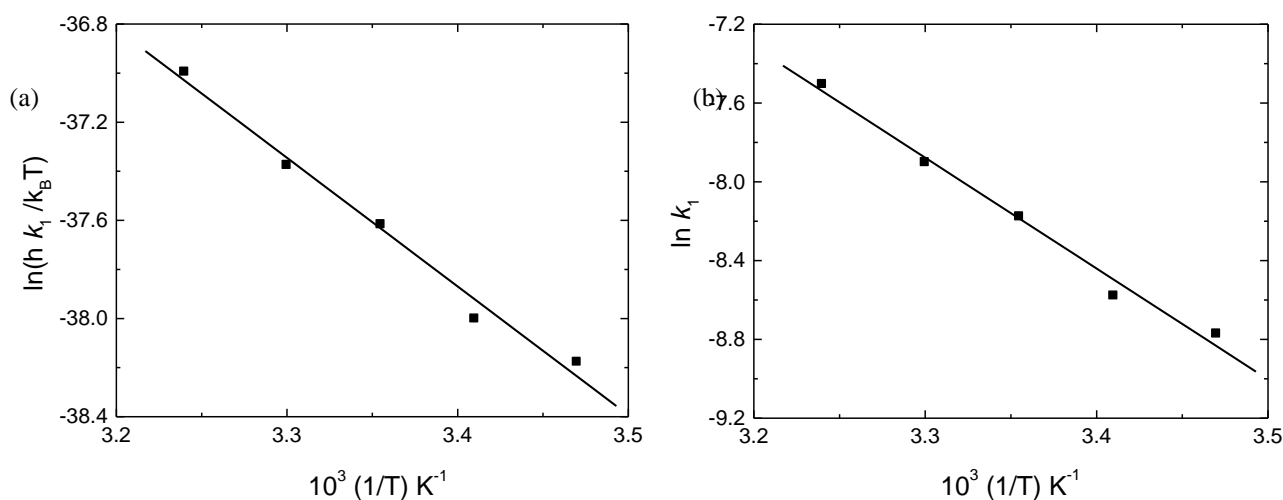


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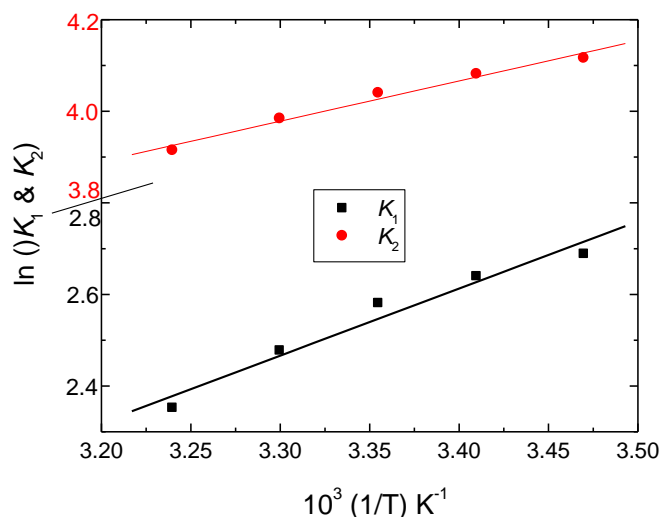
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The activation parameters of the rate constants of the slow step ( $k_1$ ) were calculated using Eyring (Fig. 6) and Arrhenius (Fig. 7) plots, as given in Table 3. Furthermore, the thermodynamic parameters of the equilibrium constants were also determined using van't Hoff's plot (Fig. 8) and are listed in Table 3.



**Fig 6(a,b):** a) Eyring and a) Arrhenius plots of  $k_1$  in the oxidation of ATF by alkaline permanganate.  $[MnO_4^-] = 4.0 \times 10^{-4}$ ,  $[ATF] = 0.02$  and  $I = 0.1 \text{ mol dm}^{-3}$ .



**Fig. 7:** van't Hoff plots of  $K_1$  and  $K_2$  in the oxidation of ATF by alkaline permanganate.  $[MnO_4^-] = 4.0 \times 10^{-4}$ ,  $[ATF] = 0.02$  and  $I = 0.1 \text{ mol dm}^{-3}$ .

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**TABLE 2:** Values of the rate constant of the slow step ( $k_1$ ) at different temperatures and its associated activation parameters in the oxidation of ATF by alkaline permanganate

Rate Constant ( $s^{-1}$ )	Temperature (K)					Activation parameters			
	288	293	298	303	308	$\Delta S^\ddagger$ ( $J mol^{-1} K^{-1}$ )	$\Delta H^\ddagger$ ( $kJ mol^{-1}$ )	$\Delta G^\ddagger_{298}$ ( $kJ mol^{-1}$ )	$E_a^\ddagger$ ( $kJ mol^{-1}$ )
$10^4 k_1$	15.51	18.79	28.11	36.91	55.17	-94.78	59.78	88.02	63.68

Experimental error =  $\pm 4\%$

**TABLE 3:** Values of the equilibrium constants ( $K_1$  and  $K_2$ ) at different temperatures and their thermodynamic quantities in the oxidation of ATF by alkaline permanganate

Equilibrium Constant ( $dm^3 mol^{-1}$ )	Temperature (K)					Thermodynamic parameters		
	288	293	298	303	308	$\Delta H^\circ$ ( $kJ mol^{-1}$ )	$\Delta G^\circ_{298}$ ( $kJ mol^{-1}$ )	$\Delta S^\circ$ ( $J mol^{-1} K^{-1}$ )
$K_1$	14.71	14.01	13.22	12.18	10.83	-12.14	-6.40	-19.26
$K_2$	61.30	59.23	56.81	53.70	50.11	-7.32	-10.01	9.02

Experimental error  $\pm 5\%$

The obtained large negative values of  $\Delta S^\ddagger$  indicate that there is a decrease in the randomness during the oxidation process. This leads to the formation of compacted intermediate complex and such activated complex is more ordered than the reactants due to loss of degree of freedom [28]. The experimental values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favorable for electron-transfer process [29]. Again, the positive values of  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  indicate endothermic formation of the intermediate and its non-spontaneity, respectively.

On the other hand, the enhancement of oxidation rate upon addition of small amounts of alkali-metal ion catalysts, have interpreted [30-34] on the basis of specific effects of metal ions in terms of bridging which facilitates electron transfer in redox systems, while Wahl [35,36] and his co-workers have interpreted specific effects in terms of complex formation.

### V. CONCLUSIONS

1. In alkaline medium, the title reaction was observed to proceed through formation of a 1:1 intermediate complex between oxidant and substrate and the reaction was base-catalyzed.
2. Addition of small amounts of alkali-metal ion catalysts was found to accelerate the oxidation rate and the order of effectiveness of the ions was:  $Li^+ > Na^+ > K^+$ .
3. The final oxidation products were identified as 3-aminotriazole, dimethyl amine and carbon dioxide.
4. The mechanism consistent with the obtained experimental observation was proposed and the reaction constants involved in the mechanism have been evaluated.
5. The activation parameters with respect to the slow step of the reaction, along with thermodynamic quantities of the equilibrium constants are calculated and discussed.

### Appendix A

According to suggested mechanism, and regarding to Eq. (3),

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_1[C] \quad (A1)$$

From reactions (1) and (2),

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$$K_1 = \frac{[\text{MnO}_4 \cdot \text{OH}^{2-}]}{[\text{MnO}_4^-][\text{OH}^-]} \quad (\text{A2})$$

Therefore,

$$[\text{MnO}_4 \cdot \text{OH}^{2-}] = K_1 [\text{MnO}_4^-][\text{OH}^-] \quad (\text{A3})$$

$$K_2 = \frac{[\text{C}]}{[\text{ATF}][\text{MnO}_4 \cdot \text{OH}^{2-}]} \quad (\text{A4})$$

$$[\text{C}] = K_2 [\text{ATF}][\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{A5})$$

Substituting Eq. (A3) into Eq. (A5) leads to,

$$[\text{C}] = K_1 K_2 [\text{ATF}][\text{OH}^-][\text{MnO}_4^-] \quad (\text{A6})$$

Substituting Eq. (A6) into Eq. (A1) yields

$$\text{Rate} = k_1 K_1 K_2 [\text{ATF}][\text{OH}^-][\text{MnO}_4^-] \quad (\text{A7})$$

The total concentration of the ATF is given by,

$$[\text{ATF}]_T = [\text{ATF}]_F + [\text{C}] \quad (\text{A8})$$

where  $[\text{ATF}]_T$  and  $[\text{ATF}]_F$  stand for total and free concentrations of the substrate.

Substituting Eq. (A6) into Eq. (A8) gives

$$[\text{ATF}]_T = [\text{ATF}]_F + K_1 K_2 [\text{ATF}]_F [\text{OH}^-][\text{MnO}_4^-] \quad (\text{A9})$$

$$[\text{ATF}]_T = [\text{ATF}]_F (1 + K_1 K_2 [\text{OH}^-][\text{MnO}_4^-]) \quad (\text{A10})$$

Therefore,

$$[\text{ATF}]_F = \frac{[\text{ATF}]_T}{1 + K_1 K_2 [\text{OH}^-][\text{MnO}_4^-]} \quad (\text{A11})$$

Similarly,

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-]_F + [\text{MnO}_4 \cdot \text{OH}^{2-}] + [\text{C}] \quad (\text{A12})$$

Substituting Eqs. (A3) and (A6) into Eq. (A12) gives,

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-]_F (1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{ATF}]_F [\text{OH}^-]) \quad (\text{A13})$$

$$[\text{MnO}_4^-]_F = \frac{[\text{MnO}_4^-]_T}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{ATF}]_F [\text{OH}^-]} \quad (\text{A14})$$

$$[\text{OH}^-]_T = [\text{OH}^-]_F + [\text{MnO}_4 \cdot \text{OH}^{2-}] \quad (\text{A15})$$

$$[\text{OH}^-]_F = \frac{[\text{OH}^-]_T}{1 + K_1 [\text{MnO}_4^-]} \quad (\text{A16})$$

Substituting Eqs. (A11), (A14) and (A16) into Eq. (A7) (and omitting 'T' and 'F' subscripts) we get,

$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{ATF}]_T [\text{OH}^-]_T [\text{MnO}_4^-]_T}{(1 + K_1 K_2 [\text{OH}^-]_T [\text{MnO}_4^-]_T)(1 + K_1 [\text{MnO}_4^-]_T)(1 + K_1 [\text{OH}^-]_T + K_1 K_2 [\text{ATF}]_T [\text{OH}^-]_T)} \quad (\text{A17})$$

In view of low concentration of  $\text{MnO}_4^-$  used both first and second terms in the denominator of Eq. (A17) can be neglected. Therefore, Eq. (17) becomes,

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$$\text{Rate} = \frac{k_1 K_1 K_2 [\text{ATF}] [\text{OH}^-] [\text{MnO}_4^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{ATF}] [\text{OH}^-]} \quad (\text{A18})$$

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

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_{\text{obs}} [\text{MnO}_4^-] \quad (\text{A19})$$

Comparing Eqs. (A18) and (A19), the following relationship is obtained,

$$k_{\text{obs}} = \frac{k_1 K_1 K_2 [\text{ATF}] [\text{OH}^-]}{1 + K_1 [\text{OH}^-] + K_1 K_2 [\text{ATF}] [\text{OH}^-]} \quad (\text{A20})$$

and with rearrangement, the following equations is obtained,

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1 + K_1 [\text{OH}^-]}{k_1 K_1 K_2 [\text{OH}^-]} \right) \frac{1}{[\text{ATF}]} + \frac{1}{k_1} \quad (\text{A21})$$

$$\frac{1}{k_{\text{obs}}} = \left( \frac{1}{k_1 K_1 K_2 [\text{ATF}]} \right) \frac{1}{[\text{OH}^-]} + \left( \frac{1}{k_1 K_2 [\text{ATF}]} + \frac{1}{k_1} \right) \quad (\text{A22})$$

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