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ORIGINAL ARTICLE

Kinetic, mechanistic, and spectroscopic studies of permanganate oxidation of azinylformamidines in acidic medium, with autocatalytic behavior of manganese(II)

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Abstract The kinetics of permanganate oxidation of two substituted azinylformamidines (Azn-Fs), namely *N,N*-dimethyl-*N*′-(pyridin-2-yl)formamidine (Py) and *N,N*-dimethyl-*N*′-(pyrimidin-2-yl)formamidine (Pym), in sulfuric acid were investigated using conventional spectrophotometry. Kinetic evidence for the formation of 1:1 intermediate complexes between the oxidant and substrates was obtained. The reactions of both substrates with permanganate showed similar kinetics, i.e. first order in $[MnO_4^-]_0$ and fractional-first-order with respect to both $[\text{Azn-F}]_0$ and $[H^+]$. The initial product, Mn^{2+}, was found to autocatalyze the oxidation process. Changes in the ionic strength and dielectric constant of the medium had no significant effect on the rate. The final oxidation products of Py and Pym were identified as 2-aminopyridine and 2-aminopyrimidine, respectively, in addition to dimethylamine and carbon dioxide. A plausible reaction mechanism is suggested and the reaction constants involved in the mechanism were evaluated.

1. Introduction

The permanganate ion is an important oxidizing agent in neutral, alkaline, and acidic media. It is one of the most versatile and vigorous oxidants and is extensively used for oxidation of organic [1–9] and inorganic [10–22] compounds in acidic media, and is an important source of mechanistic information [23]. It is stable in neutral and slightly alkaline solutions, but it decomposes in strongly alkaline media to form blue hypomanganate(V) and green manganate(VI), which are short-lived transient species [24,25]. In alkaline, neutral, or weakly acidic

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solutions, Mn^{VII} is reduced to Mn^{IV}. In acidic media, the permanganate ion can exist in several different forms, namely $HMnO_4$, $H_2MnO_4^+$, and Mn_2O_7. The redox reaction mechanism is inner-sphere or outer-sphere [26,27], depending on the nature of the reductant. In general, the reduction of permanganate ion in an acidic medium gives either Mn^{IV} or Mn^{II}; the reduction potential of the Mn^{VII}/Mn^{IV} couple is 1.695 V and that of the Mn^{VII}/Mn^{II} couple is 1.51 V [28]. In strongly acidic media, Mn^{VII} is reduced, ultimately forming Mn^{II}, but the species that has the main role as a potential oxidant depends on the nature of the substrate and the pH of the medium [22,24,29–33,23,34–36].

Trisubstituted formamidines have attracted increasing interest in recent decades, because of their very broad spectrum of biological activities. The biochemical roles of formamidines include monoamine oxidase inhibitors [37,38], adrenergic and neurochemical receptors [39,40], and participation in prostaglandin E_2 synthesis [41]. The *N,N*-dialkyl derivatives are highly effective acaricides, and the most important result was the discovery of the acaricide insecticide chlordimeform. The oxidative cleavage of formamidines is important, because the *N,N*-dialkylformamidine group is one of the most versatile protecting groups, especially in biosynthetic applications. The azine moiety is a common structural subunit in a large number of natural products and synthetic compounds with important biological activities [42].

Although the kinetics of the oxidation of the azinylformamidine (Azn-F) derivatives *N,N*-dimethyl-*N′*-(pyridin-2-yl)formamidine (Py) and *N,N*-dimethyl-*N′*-(pyrimidin-2-yl)formamidine (Pym) by permanganate ions have been studied in aqueous alkaline solution [43], there are no reports describing their oxidation kinetics when other oxidants are used. A detailed study of the title reaction was therefore undertaken in order to understand the effect of the medium on the kinetics, with a view to assigning a mechanistic pathway for the reactions.

2. Experimental

2.1. Materials

Reagent-grade chemicals were used. Stock solutions of Azn-Fs were synthesized and identified as described elsewhere [43]. A permanganate stock solution was prepared by dissolving potassium permanganate in water, and it was standardized by titration against oxalic acid. Stock solutions of other reagents were prepared by dissolving the appropriate amounts of the samples in the required volumes of double-distilled water. Sulfuric acid and sodium sulfate were used to provide the required acidity and ionic strength, respectively. The reaction temperature was controlled within ±0.1 °C.

2.2. Kinetic measurements

Kinetic measurements were conducted under pseudo-first-order conditions; a large excess of Azn-F over permanganate ion concentration was maintained. The ionic strength, I, of the reaction mixture was adjusted to 0.3 mol dm^{-3}. Solutions of permanganate and the mixture containing Azn-F and acid were separately thermostated for about 2 h. The permanganate solution was then added to the mixture. Absorbance measurements were performed using a Shimadzu UV-1800 PC automatic scanning double-beam instrument, which had a cell compartment kept at constant temperature. The reactions were followed by measuring the absorbance of permanganate in the reaction mixture at its absorption maximum, $\lambda = 525$ nm, as a function of time. The kinetic runs monitored up to at least three half-lives of the reaction completion. The effect of dissolved oxygen on the reaction rate was checked by monitoring the reaction in a nitrogen atmosphere. No significant difference between the results obtained under nitrogen and in the presence of air was observed.

3. Results

3.1. Stoichiometry and identification of products

Different reaction mixtures containing an excess of Azn-Fs over permanganate were mixed at $[H^+] = 0.1$ and $I = 0.3$ mol dm^{-3}, and allowed to react in the dark for about 6 h at 20 °C. The remaining MnO_4^- concentration was determined spectrophotometrically at 525 nm. The results confirm that the stoichiometry of the overall reaction holds for the following stoichiometric equations:

$$5R{-}N{=}CH{-}NMe_2 + 2MnO_4^- + 6H^+ = 5R{-}NH(CO)NMe_2 + 2Mn^{2+} + 3H_2O \qquad (1)$$

$$R{-}NH(CO)NMe_2 + H_2O = R{-}NH_2 + HNMe_2 + CO_2 \qquad (2)$$

where $R{-}N{=}CH{-}NMe_2$ is the Azn-F, $R{-}NH(CO)NMe_2$ is an intermediate product, i.e. 1,1-dimethyl-3-(azin-2-yl)urea, and $R{-}NH_2$ is the corresponding 2-aminoazine. The above stoichiometric equations are consistent with the results of product analysis. The presence of the intermediate product 1,1-dimethyl-3-(azin-2-yl)urea was confirmed by the ^1H NMR spectrum shown in Fig. 1(a). Furthermore, the IR spectrum showed an NH band at ca. 3320 cm^{-1} (spectrum not shown). The final 2-aminoazine products were isolated after completion of the reaction and identified based on their ^1H NMR spectra (Fig. 1b). In addition, the IR spectrum showed two bands assigned to the NH_2 group, at 3420 and 3380 cm^{-1}. Dimethylamine and carbon dioxide were identified using a spot test [44] and lime water [45], respectively.

3.2. Spectroscopic changes

Fig. 2(a and b) shows the spectral scans during acidic permanganate oxidation of Azn-Fs; gradual disappearance of the MnO_4^- bands at $\lambda = 525$ nm was observed. Previous studies [46–48] showed that manganese(IV) ions absorb in the region 400–650 nm. Fig. 1 shows no features in this wavelength area, meaning that MnO_2 is not a reaction product. Furthermore, as no absorption increases and decreases were observed at 418 nm, it is concluded that Mn^{IV} ions do not act as an oxidizing agent.

3.3. Reaction–time curves

The reaction–time curves for the overall reactions were sigmoid, as shown by the example in Fig. 3. The initial rates were slow,

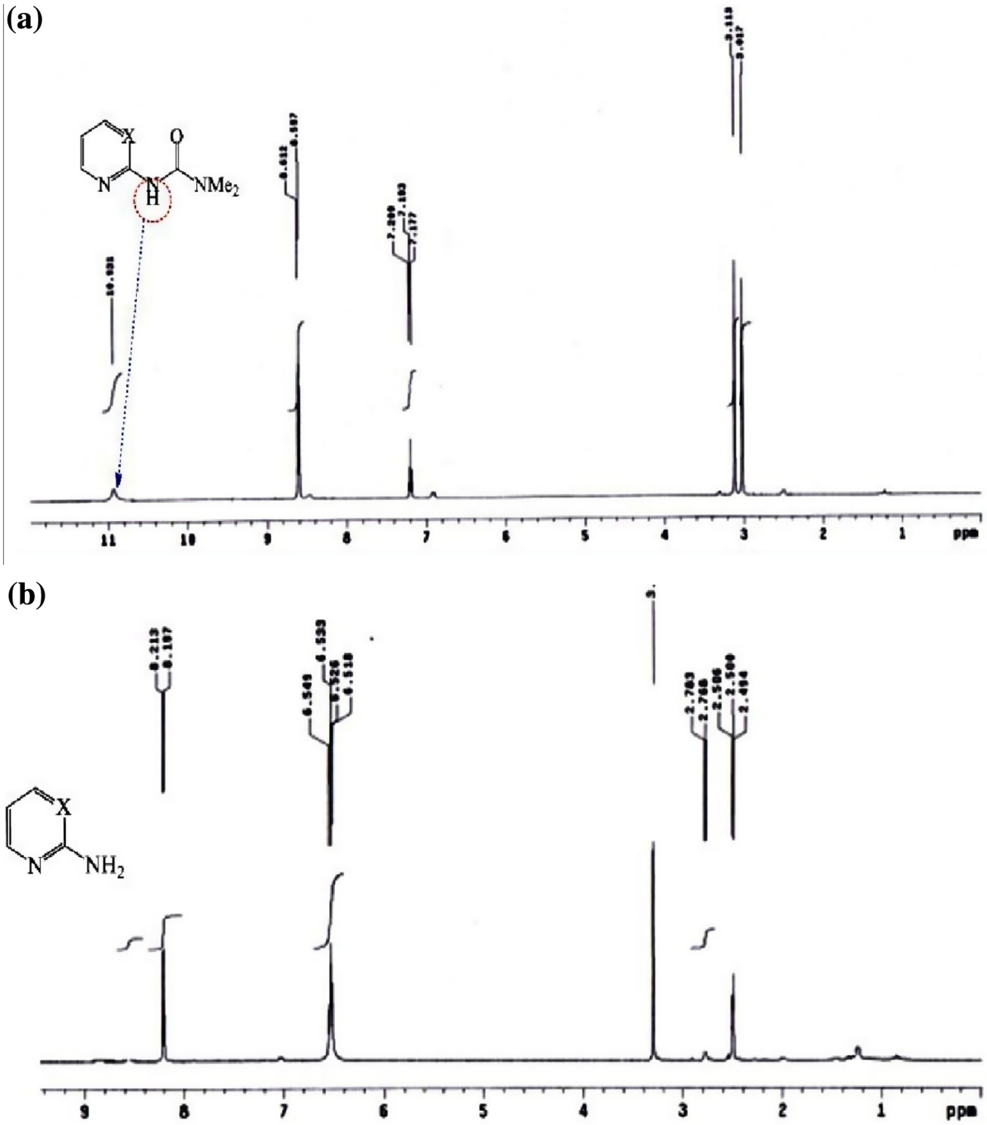


Figure 1 ^{1}H NMR spectra of formed intermediate (a) and azine product (b).

followed by an increase in the oxidation rates over longer time periods. The pseudo-first-order rate constants, k_{obs}, were calculated as the slopes of the plots by considering the initial straight line region. The values of k_{obs} were reproducible to within 4% and were the average of at least three to four kinetic runs.

3.4. Rate dependence on oxidant concentration

The order with respect to permanganate ion concentration was determined by studying the reaction rate at different initial permanganate ion concentrations, $[MnO_4^-]_0$, in the range $(1–6) \times 10^{-4}$ mol dm^{-3}, at constant concentrations of both substrate and sulfuric acid, and fixed ionic strength and temperature. The observed pseudo-first-order rate constants, k_{obs}, were almost constant (Table 1), indicating first-order dependence with respect to permanganate ion concentration.

3.5. Rate dependence on reductant concentration

The effect of changing the reductant (Azn-F) concentration on the reaction rate was studied in the concentration range 4.0×10^{-3} to 1.4×10^{-2} mol dm^{-3}, at constant concentrations of permanganate and acid, and at constant ionic strength. It was observed that k_{obs} increases with increasing reductant concentration (Table 1). The slopes of the linear plots of ln k_{obs} versus ln [S] (Fig. 4) were less than unity (0.96 and 0.98), which indicates that the reactions are fractional-first-order with respect to Azn-F concentration.

3.6. Rate dependence on acid concentration

Kinetic measurements were performed in sulfuric acid solutions with different [H$^+$] and constant [MnO_4^-], [Azn-F], ionic strength, and temperature, to clarify the influence of [H$^+$] on

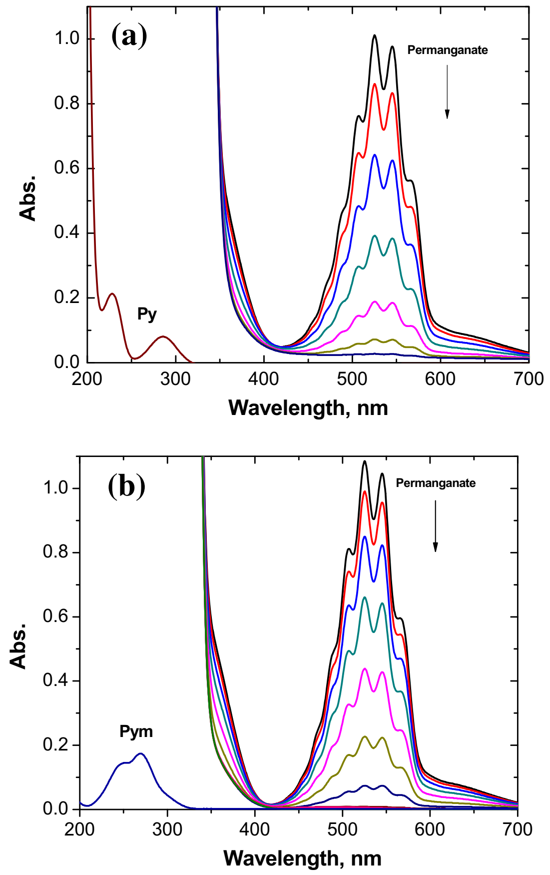


Figure 2 (a and b) Spectroscopic changes in oxidation of Azn-Fs by permanganate in sulfuric acid medium; [Azn-F] = 0.01, $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$, and $I = 0.3\ mol\ dm^{-3}$, at 20 °C. Scanning time interval = 1 min.

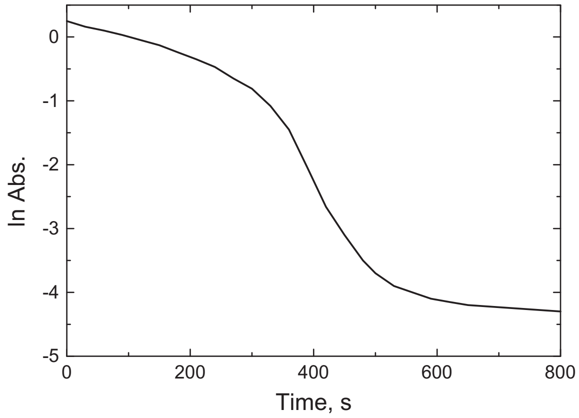


Figure 3 Ln(absorbance) versus time curves for oxidation of Pym by permanganate in sulfuric acid medium. [Pym] = 0.01, $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$, and $I = 0.3\ mol\ dm^{-3}$, at 20 °C.

the reaction and to elucidate the reaction mechanisms. An increase in acid concentration accelerated the reactions, suggesting that the oxidation reactions were acid catalyzed. Under our experimental conditions, the plots of k_{obs} versus $[H^+]$ were linear, with positive intercepts on the k_{obs} axes, as shown in Fig. 5, confirming that the reaction order with respect to $[H^+]$ was less than unity. Some experiments were performed in perchloric acid solutions, but the reactions were very slow.

3.7. Rate dependence on manganese(II) concentration

Mn^{2+} is one of the oxidation products, therefore its effects on the reaction rates were investigated in the concentration range $(2–10) \times 10^{-3}\ mol\ dm^{-3}$, with other reagent concentrations and conditions kept constant. The k_{obs} values increased with increasing $[Mn^{2+}]$. The orders with respect to $[Mn^{2+}]$ were less than unity, as shown in Fig. 6.

3.8. Influences of ionic strength and dielectric constant

The ionic strength was varied from 0.3 to 1.0 mol dm^{-3}, using sodium sulfate, at constant concentrations of Azn-F and MnO_4^-, and at constant pH and temperature. Increasing the ionic strength had a negligible effect on the reaction rate. Similarly, at constant concentrations of reactants and with other conditions constant, the concentration of *t*-butyl alcohol was varied from 0% to 40% (v/v) in the reaction medium. Changing the dielectric constant of the medium did not have any significant effect on the reaction rate.

3.9. Free-radical tests

To test for the participation of free radicals in these reactions, the reaction mixtures were mixed with known quantities of acrylonitrile monomer and kept for 6 h under nitrogen. On dilution with methanol, a white precipitate formed, indicating the participation of free radicals in the oxidation reactions. Blank experiments carried out with either MnO_4^- or Azn-Fs alone with acrylonitrile did not induce polymerization under the same experimental conditions.

4. Discussion

The reaction rate enhancement with increasing acid concentration, with an apparent order of less than unity in $[H^+]$, suggests the formation of a more powerful oxidant, namely permanganic acid [49–51], by the following equilibrium:

$$MnO_4^- + H^+ \overset{K_1}{\rightleftharpoons} HMnO_4 \tag{3}$$

where K_1 is the protonation constant of permanganate ion.

The negligible effects of both the ionic strength and the dielectric constant of the medium on the rates indicate that the reactions occur between two neutral molecules [52], i.e. between Azn-F substrates and permanganic acid. However, the linearity of the plots of $1/k_{obs}$ versus 1/[S] (Fig. 7) is considered to be kinetic evidence of possible formation of an intermediate complex between the oxidant and the substrates, similar to the well-known Michaelis–Menten [53] mechanism for enzyme–substrate reactions. The failure to detect such an intermediate complex spectrophotometrically may be due to low concentration of the reactants used, leading to lower absorptivity of the formed complex, and/or fast subsequent decomposition of the intermediate compared with its formation.

Based on the experimental observations, a mechanism can be suggested that involves attack of the powerful oxidant,

Table 1 Influence of $[MnO_4^-]$, [Azn-F], and $[H^+]$ on the first-order rate constants, k_{obs}, in the oxidation of Azn-Fs by permanganate in sulfuric acid medium at 20 °C and $I = 0.3$ mol dm^{-3}.*

10^4 $[MnO_4^-]$, mol dm^{-3}	10^2 [Azn-F], mol dm^{-3}	$[H^+]$, mol dm^{-3}	10^4 k_{obs}, s^{-1}	
			Py	Pym
1.0	1.0	0.10	24.1	20.8
2.0	1.0	0.10	24.7	21.9
3.0	1.0	0.10	23.4	21.3
4.0	1.0	0.10	24.5	21.5
5.0	1.0	0.10	24.9	22.1
6.0	1.0	0.10	25.6	21.9
4.0	0.4	0.10	11.4	9.6
4.0	0.6	0.10	15.4	12.8
4.0	0.8	0.10	19.8	17.1
4.0	1.0	0.10	24.5	21.6
4.0	1.2	0.10	29.2	25.9
4.0	1.4	0.10	34.3	28.7
4.0	1.0	0.01	3.9	3.1
4.0	1.0	0.02	6.2	5.6
4.0	1.0	0.05	13.2	11.4
4.0	1.0	0.10	24.5	21.6
4.0	1.0	0.15	33.6	32.2
4.0	1.0	0.20	43.1	41.4

* Experimental error ± 4%.

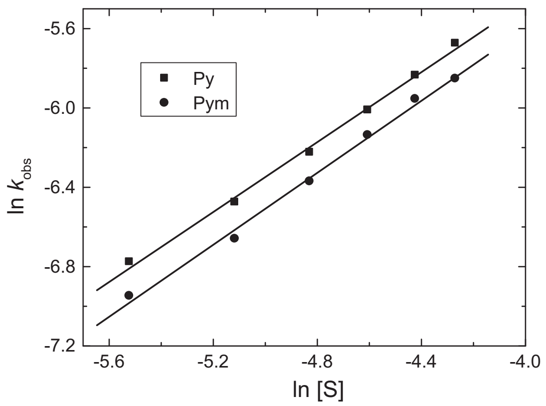


Figure 4 Plots of lnk_{obs} versus ln[S] in the oxidation of Azn-Fs by permanganate in sulfuric acid medium. $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$, and $I = 0.3$ mol dm^{-3}, at 20 °C.

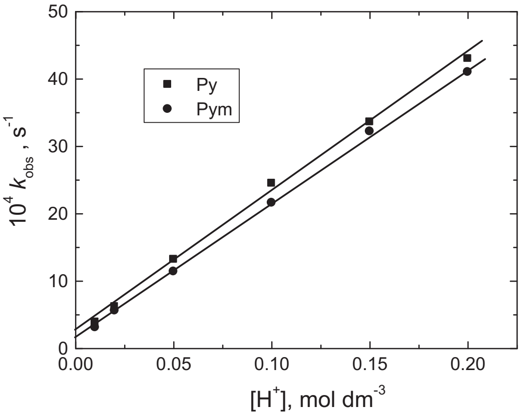


Figure 5 Plots of k_{obs} versus $[H^+]$ in oxidation of Azn-Fs by permanganate in sulfuric acid medium. [Azn-F] = 0.01, $[MnO_4^-] = 4 \times 10^{-4}$, and $I = 0.3$ mol dm^{-3}, at 20 °C.

$HMnO_4$, on the Azn-F substrate (S), leading to formation of a complex (C) prior to the rate-determining step:

$$S + HMnO_4 \overset{K_2}{\rightleftharpoons} [S\text{–}HMnO_4](C) \qquad (4)$$

followed by cleavage of the complex to form a free-radical substrate and manganate(VI) intermediates:

$$[S\text{–}HMnO_4] \xrightarrow[\text{slow}]{k_1} S^{\cdot} + HMn^{VI}O_4^- + H^+ \qquad (5)$$

The intermediate ($S^{\cdot}$) is rapidly attacked by the manganate(VI) ion of the oxidant to yield an intermediate product, 1,1-dimethyl-3-(azin-2-yl)urea, as follows:

$$S^{\cdot} + HMnO_4^- \xrightarrow{\text{fast}} \text{intermediate product} + MnO_3^- \qquad (6)$$

In a further fast step, the intermediate product is hydrolyzed to give the final oxidation products:

$$\text{Intermediate product} + H_2O \xrightarrow{\text{fast}} \text{final products} \qquad (7)$$

Mn^V is very unstable in strong acidic media, therefore it will be converted to Mn^{II} and Mn^{VII} by rapid disproportionation, as follows:

$$5MnO_3^- + 6H^+ \rightarrow 3MnO_4^- + 2Mn^{2+} + 3H_2O \qquad (8)$$

Multiplying Eqs. (3)–(7) by a factor of five and then summing them with Eq. (8) results in an overall reaction with the stoichiometry satisfied.

According to this mechanism, the relationship between the reaction rate and the substrate, hydrogen ion, and oxidant

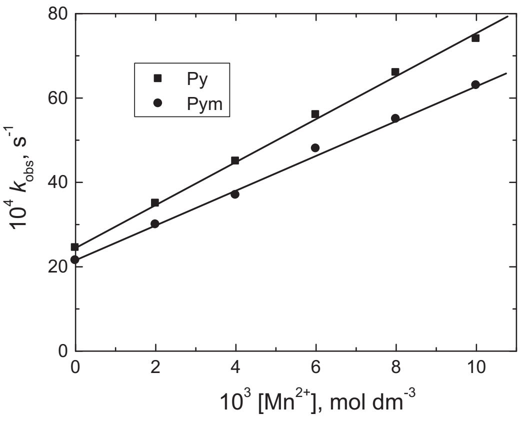


Figure 6 Plots of k_{obs} versus $[Mn^{2+}]$ in oxidation of Azn-Fs by permanganate in sulfuric acid medium. [Azn-F] = 0.01, $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$, and $I = 0.3$ mol dm^{-3}, at 20 °C.

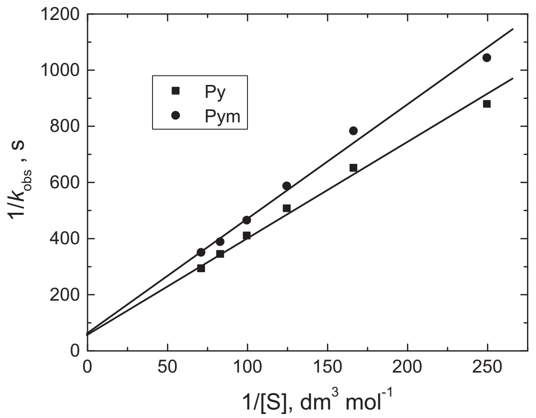


Figure 7 Plots of $1/k_{obs}$ versus 1/[S] in the oxidation of Azn-Fs by permanganate in sulfuric acid medium. $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$ and I = 0.3 mol dm^{-3}, at 20 °C.

concentrations can be deduced (see the Appendix A), to give the following equation:

$$\text{Rate} = \frac{k_1 K_1 K_2 [MnO_4^-][S][H^+]}{1 + K_1[H^+] + K_1 K_2 [S][H^+]} \tag{9}$$

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

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \tag{10}$$

Comparing Eqs. (9) and (10) and rearrangement gives the following relationship:

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2 [H^+]}\right)\frac{1}{[S]} + \frac{1}{k_1} \tag{11}$$

As predicted by Eq. (11), the plots of $1/k_{obs}$ against 1/[S] for the two substrates are linear (Fig. 7). The reciprocals of the intercepts of the plots yield k_1 values of 0.014 dm^3 mol^{-1} s^{-1} for both substrates.

Because the intercepts observed in Fig. 7 are small, Eq. (11) can be simplified to Eq. (12), which is considered to be a suitable rate-law expression:

$$\frac{[S]}{k_{obs}} = \frac{1}{k'}\frac{1}{[H^+]} + \frac{1}{k''} \tag{12}$$

where k' and k'' are the apparent rate constants and are equal $k_1 K_1 K_2$ and $k_1 K_2$, respectively. According to Eq. (12), the plots of $[S]/k_{obs}$ versus $1/[H^+]$ gave good straight lines confirming the suggested mechanism and rate law (Fig. 8); the slopes and intercepts of such plots can be used to calculate the apparent rate constants, k' and k''. The protonation constants of the permanganate ion can be evaluated by dividing k' by k'' ($K_1 = k'/k''$), and were found to equal 0.73 and 0.87 dm^3 mol^{-1} at 20 °C for Pym and Py, respectively, in good agreement with the literature values [14] (0.62 dm^3 mol^{-1} at 25 °C), indicating the validity of the proposed mechanism. The value of the formation constant of the intermediate complex, K_2, was also calculated as 71.42 dm^3 mol^{-1}.

4.1. Mechanism of autocatalysis by manganese(II)

The addition of Mn^{2+} ions led to a significant increase in the reaction rates (Fig. 6), suggesting autocatalysis of the oxidation reactions by Mn^{2+}. The catalytic effect of Mn^{2+} can be interpreted in one of two ways: (a) Mn^{2+} may form a complex with the substrate, which is then oxidized by $HMnO_4$, or (b) Mn^{2+} first reduces Mn^{VII} to Mn^{III} and Mn^{IV}, which then accelerate the reaction. The less-than-unity orders in $[Mn^{2+}]$ (Fig. 6) suggest that a complex (C_1) might be formed between the Azn-F substrate and Mn^{2+} in a fast step. The complex is then oxidized by $HMnO_4$ in a slow step [54], according to the following scheme:

$$S + Mn^{2+} \overset{K_3}{\rightleftharpoons} C_1 \tag{13}$$

$$C_1 + HMnO_4 \xrightarrow[\text{slow}]{k_2} HMnO_4^- + Mn^{2+} + H^+ \tag{14}$$

The remaining steps, leading to the final products, resemble those presented in Scheme 1.According to this mechanism, the relationship between the reaction rate and the substrate, hydrogen ion, oxidant, and Mn^{2+} concentrations can be expressed by the following equation:

$$\text{Rate} = \frac{k_2 K_1 K_3 [MnO_4^-][S][H^+][Mn^{2+}]}{(1 + K_1[H^+])(1 + K_3[S] + K_3[Mn^{2+}])} \tag{15}$$

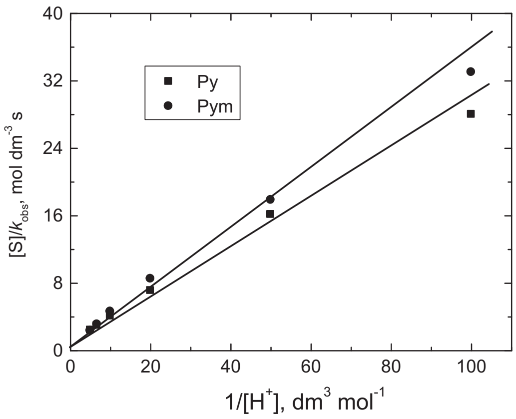
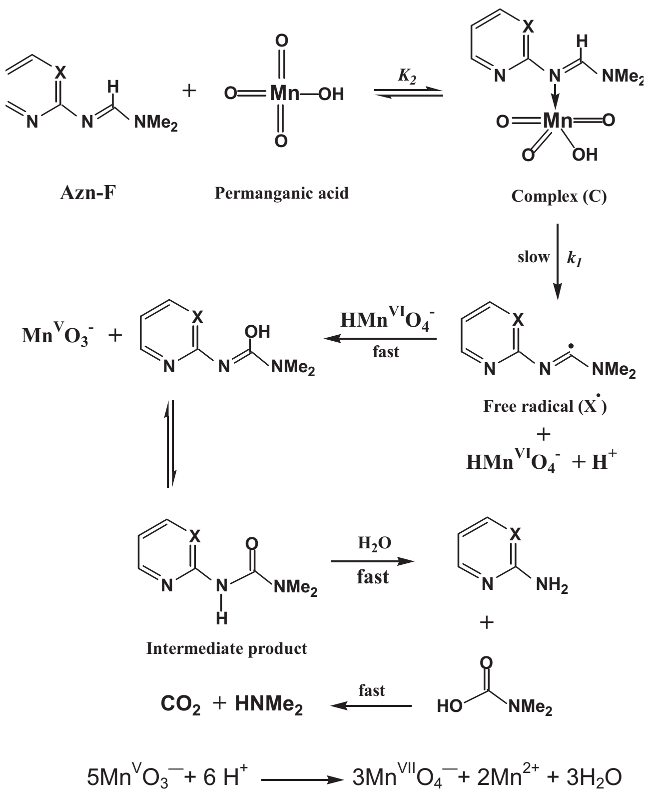


Figure 8 Plots of $[S]/k_{obs}$ versus $1/[H^+]$ in oxidation of Azn-Fs by permanganate in sulfuric acid medium. $[MnO_4^-] = 4 \times 10^{-4}$ and $I = 0.3$ mol dm^{-3}, at 20 °C.



where X = N for Pym-F and X = CH for Py-F

Scheme 1 Mechanism of oxidation of Azn-Fs by permanganate in aqueous acidic medium.

Under pseudo-first-order conditions, the rate law can be expressed by Eq. (10).

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \tag{10}$$

A comparison of Eqs. (10) and (15), and rearrangement, gives the following relationship:

$$\frac{[S]}{k_{obs}} = \left(\frac{1+K_1[H^+]}{k_2K_1K_3[H^+]}\right)\frac{1}{[Mn^{2+}]} + K' \tag{16}$$

As predicted by Eq. (16), the plots of $[S]/k_{obs}$ against $1/[Mn^{2+}]$ for the two substrates are linear (Fig. 9), supporting the validity of the proposed mechanism.

Appendix A

According to the suggested mechanism,

$$\text{Rate} = k_1[C] \tag{A1}$$

From reaction (3),

$$K_1 = \frac{[HMnO_4]}{[MnO_4^-][H^+]} \tag{A2}$$

$$\text{Therefore,} [HMnO_4] = K_1[MnO_4^-][H^+] \tag{A3}$$

From reaction (4),

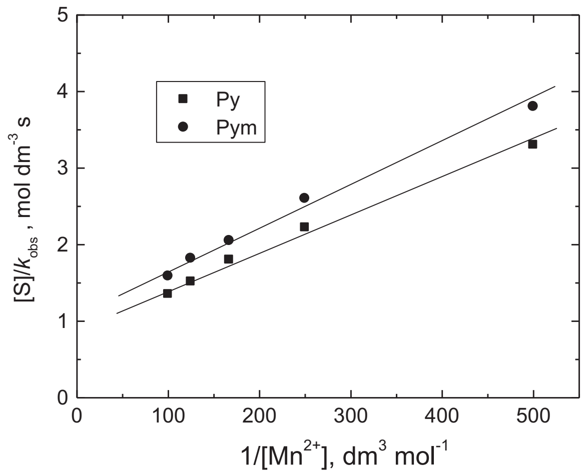


Figure 9 Verification of rate law (15) in the form of Eq. (16) in the oxidation of Azn-Fs by permanganate in sulfuric acid medium. $[MnO_4^-] = 4 \times 10^{-4}$, $[H^+] = 0.1$, and $I = 0.3$ mol dm^{-3}, at 20 °C.

$$K_2 = \frac{[C]}{[S][HMnO_4]} \tag{A4}$$

$$\text{Therefore, } [C] = K_2[S][HMnO_4] \tag{A5}$$

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

$$[C] = K_1K_2[S][H^+][MnO_4^-] \tag{A6}$$

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

$$\text{Rate} = k_1K_1K_2[S][H^+][MnO_4^-] \tag{A7}$$

The total concentration of the substrate is given by

$$[S]_T = [S]_F + [C] \tag{A8}$$

where $[S]_T$ and $[S]_F$ stand for total and free concentrations of the substrate.Substituting Eq. (A6) into Eq. (A8) gives

$$[S]_T = [S]_F + K_1K_2[S]_F[H^+][MnO_4^-] \tag{A9}$$

$$[S]_T = [S]_F(1 + K_1K_2[H^+][MnO_4^-]) \tag{A10}$$

Therefore,

$$[S]_F = \frac{[S]_T}{1 + K_1K_2[H^+][MnO_4^-]} \tag{A11}$$

Similarly,

$$[MnO_4^-]_T = [MnO_4^-]_F + [HMnO_4] + [C] \tag{A12}$$

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

$$[MnO_4^-]_T = [MnO_4^-]_F + K_1[MnO_4^-]_F[H^+] + K_1K_2[S] \times [H^+][MnO_4^-]_F \tag{A13}$$

$$[MnO_4^-]_F = \frac{[MnO_4^-]_T}{1 + K_1[H^+] + K_1K_2[S][H^+]} \tag{A14}$$

$$\text{and } [H^+]_T = [H^+]_F + [HMnO_4] \tag{A15}$$

$$[H^+]_F = \frac{[H^+]_T}{1 + K_1[MnO_4^-]} \tag{A16}$$

Substituting Eqs. A11, A14 and A16 into Eq. (A7) (and omitting the subscripts “T” and “F”) we get

$$\text{Rate} = \frac{k_1K_1K_2[\text{S}][\text{H}^+][\text{MnO}_4^-]}{(1+K_1K_2[\text{H}^+][\text{MnO}_4^-])(1+K_1[\text{MnO}_4^-])(1+K_1[\text{H}^+]+K_1K_2[\text{S}][\text{H}^+])} \tag{A17}$$

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

$$\text{Rate} = \frac{k_1K_1K_2[\text{S}][\text{H}^+][\text{MnO}_4^-]}{1+K_1[\text{H}^+]+K_1K_2[\text{S}][\text{H}^+]} \tag{A18}$$

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

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

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

$$k_{\text{obs}} = \frac{k_1K_1K_2[\text{S}][\text{H}^+]}{1+K_1[\text{H}^+]+K_1K_2[\text{S}][\text{H}^+]} \tag{A20}$$

and with rearrangement it becomes

$$\frac{1}{k_{\text{obs}}} = \left(\frac{1+K_1[\text{H}^+]}{k_1K_1K_2[\text{H}^+]}\right)\frac{1}{[\text{S}]} + \frac{1}{k_1} \tag{A21}$$

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