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Transition Metal Chemistry

ISSN 0340-4285
Volume 39
Number 4

Transition Met Chem (2014) 39:379-386
DOI 10.1007/s11243-014-9811-3

TRANSITION
METAL
CHEMISTRY
An International Journal

4
Vol. 39-No. 4
MAY 2014
39(4) 361–486
ISSN 0340-4285
2014

Springer

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Kinetic and mechanistic investigations on the oxidation of *N*'-heteroaryl unsymmetrical formamidines by permanganate in aqueous alkaline medium

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Received: 14 December 2013 / Accepted: 19 February 2014 / Published online: 27 February 2014

Abstract Kinetic studies on the oxidation of two substituted azinyl formamidines (Azn-Fs), namely *N*,*N*-dimethyl-*N*'-(pyrimidin-2-yl) formamidine (Pym-F) and *N*,*N*-dimethyl-*N*'-(pyridin-2-yl) formamidine (Py-F), by alkaline permanganate have been performed by spectrophotometry. The spectroscopic and kinetic evidence reveals the formation of 1:1 intermediate complexes between the oxidant and substrates. The influence of pH on the oxidation rates indicated that the reactions are base-catalyzed. The reactions show identical kinetics, being first order each in $[MnO_4^-]_0$ and $[\text{Azn-F}]_0$, but with a fractional first-order dependence on $[OH^-]$. The effect of temperature on the reaction rate has been studied. Increasing ionic strength has no significant effect on the rate. The final oxidation products of Pym-F and Py-F were identified as 2-aminopyrimidine and 2-aminopyridine, respectively, in addition to dimethyl amine and carbon dioxide. Under comparable experimental conditions, the oxidation rate of Py-F is higher than that of Pym-F. A reaction mechanism adequately describing the observed kinetic behavior is proposed, and the reaction constants involved in the different steps of the mechanism have been evaluated. The activation parameters with respect to the rate-limiting step of the reactions, along with thermodynamic quantities, are presented and discussed.

Introduction

Interest in the tri-substituted formamidines of general structure (**I**), shown in Scheme 1, has increased in the last decades, due to their very broad spectrum of biological activity. The biochemical potentialities of formamidines include monoamine oxidase inhibitors [1, 2], adrenergic, neurochemical receptors [3, 4] and prostaglandin E_2 synthesis [5]. Formamidines are also noted for their complexation with transition metals [6, 7] and usage as auxiliaries in asymmetric synthesis [8, 9] and as electrophiles [10]. The *N*,*N*-dialkyl derivatives are highly effective acaricides, and the most rewarding of these studies resulted in discovery of the acaricide insecticide chlordimeform, structure (**II**), Scheme 1.

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. The azine moiety is a common structural subunit in a large number of natural products and synthetic compounds with important biological activities [11].

Although permanganate ion in alkaline media has been used extensively as a potent oxidant for many organic molecules [12–16], to the best of our knowledge, the kinetics of oxidation of azinyl formamidines (Azn-Fs) by permanganate, or indeed by any other oxidants, have not yet been reported. This observation prompted us to investigate the

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Electronic supplementary material The online version of this article (doi:10.1007/s11243-014-9811-3) contains supplementary material, which is available to authorized users.

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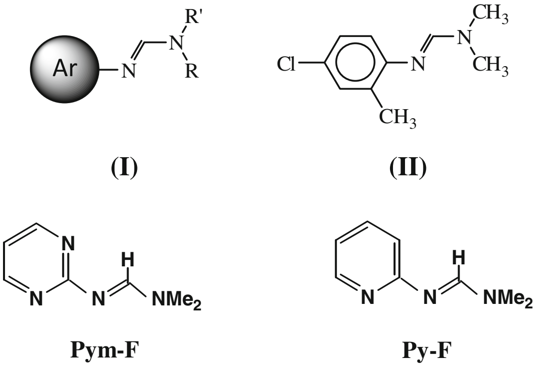


(I) (II)

Pym-F Py-F

Scheme 1 Structure of some azinyl formamidines

kinetics and mechanism of oxidation of two substituted Azn-Fs, namely *N*,*N*-dimethyl-*N*'-(pyrimidin-2-yl) formamidine (Pym-F) and *N*,*N*-dimethyl-*N*'-(pyridin-2-yl) formamidine (Py-F), Scheme 1, by alkaline permanganate. The objectives of the present investigation are to establish optimum conditions affecting oxidation of Azn-Fs, elucidate a plausible oxidation mechanism and characterize the oxidation products.

Experimental

Materials

Azinyl formamidines were synthesized by heating a mixture of 10 mmol of 2-aminopyrimidine or 2-aminopyridine in dry benzene and dimethylformamide dimethylacetal (DMF-DMA) (30 mmol) in dry benzene under reflux for 8 h. The solvent was then removed *in vacuo,* and the crude products were dried and purified either by chromatography or recrystallization to afford the corresponding formamidine derivatives Pym-F and Py-F, respectively. The identities of Pym-F and Py-F were confirmed by their elemental analysis and spectral data. For example, the ^{1}H NMR spectrum of Pym-F displayed two singlets at δ 3.09–3.12 ppm due to the *N*,*N*-dimethyl protons, a singlet at δ 8.60 ppm due to the olefinic proton, a triplet at ca. 6.76 ppm due to the pyrimidine-*CH*-5 protons, a doublet at δ 8.43 ppm assigned to pyrimidine-*CH*-4 and a doublet at δ 8.49 ppm for the pyrimidine-*CH*-6 protons.

The solution of potassium permanganate was prepared and standardized as reported earlier [17]. All other chemicals used were of analytical grade, and double distilled water was used throughout the work. Sodium hydroxide solution was used to provide the required alkalinity. The ionic strength (I) was maintained constant (0.1 mol dm^{-3}) using NaClO$_4$ as an inert electrolyte. The reaction temperature was controlled to within ±0.1 °C.

Kinetic measurements

Kinetic runs were performed under pseudo-first-order conditions, such that in general, the Azn-Fs were present in large excesses over permanganate at a constant ionic strength and temperature. Some additional experiments were conducted under second-order conditions of [Azn-F] $\leq$ [MnO$_4^-$] in order to check the data obtained from the pseudo-first-order kinetics; the results were found to be in a good agreement with each other within the experimental errors, indicating the reproducibility of the measurements.

The absorbance measurements were made in a thermostatted cell compartment at the desired temperature on a Shimadzu UV-1800 PC automatic scanning double-beam spectrophotometer fitted with a program controller using cells of path-length 1 cm. The course of the reactions was followed up to not less than two half-lives by recording the decrease in the absorbance of permanganate ion at $\lambda = 525$ nm, its absorption maximum, as a function of time. It was verified that there is no interference from other reagents at this wavelength. All experiments were studied in triplicate, and the rate constants were reproducible to within ±3 %.

Results

Stoichiometry and product analysis

Reaction mixtures containing an excess of permanganate over Azn-Fs were mixed at [OH$^-$] = 0.03 and $I = 0.1$ mol dm^{-3} and allowed to react in the dark for about 24 h at 25 °C. The remaining [MnO$_4^-$] in each case was analyzed periodically by both titrimetric and spectrophotometric techniques. The results revealed that 2.00 ± 0.11 mol of permanganate were consumed by 1.0 mol of Azn-F, according to the following stoichiometric equations;

$$\begin{aligned} \mathrm{R{-}N=CH{-}NMe_2} &+ \mathrm{2MnO_4^-} + \mathrm{2OH^-} \\ &= \mathrm{R{-}NH(CO)NMe_2} + \mathrm{2MnO_4^{2-}} + \mathrm{H_2O} \end{aligned} \qquad (1)$$

$$\begin{aligned} &\mathrm{R{-}NH(CO)NMe_2} + \mathrm{H_2O} \\ &= \mathrm{R{-}NH_2} + \mathrm{Me_2NH} + \mathrm{CO_2} \end{aligned} \qquad (2)$$

where R–N = CH–NMe$_2$ is the Azn-F, R–NH(CO)NMe$_2$ is 1,1-dimethyl-3-(azin-2-yl) urea as an intermediate product and R-NH$_2$ is the corresponding 2-amino azine. The above stoichiometric equations are consistent with the results of product analysis. The intermediate product 1,1-dimethyl-3-(azin-2-yl) urea was confirmed by spectral data. The ^{1}H NMR spectrum displayed two singlets due to the methyl group protons in the range of δ 3.12 ppm, a triplet

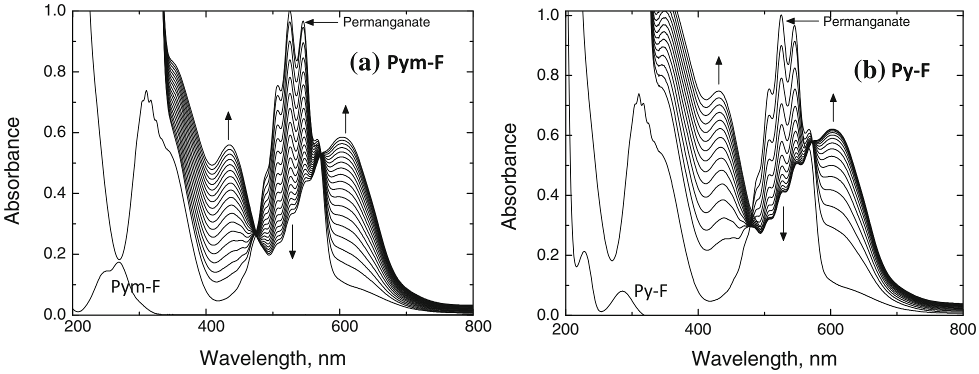


Fig. 1 **a**, **b** Spectral changes for the oxidation of azinyl formamidines by alkaline permanganate. [Azn-F] = 8×10^{-3}, $[MnO_4^-] = 4 \times 10^{-4}$, $[OH^-] = 0.03$ and $I = 0.1$ mol dm^{-3} at 25°C. Scanning time intervals = 1 min

in the range of δ 7.16 ppm for the pyrimidine-*CH*-5 protons, a doublet at δ 8.60 ppm due to the pyrimidine-*CH*-4 and pyrimidine-*CH*-6 protons, and a broad signal at δ 10.90 ppm from the NH proton. Furthermore, the IR spectrum showed an NH band at ca. 3320 cm^{-1} (spectrum not shown). The final 2-amino azine products were also isolated after completing the reaction courses and were confirmed by their spectral data. The ^{1}H NMR spectrum displayed a triplet at ca. δ 6.50 ppm due to the pyrimidine-*CH*-5 protons and a doublet at δ 8.20 ppm due to the pyrimidine-*CH*-4 and pyrimidine-*CH*-6 protons. In addition, the IR spectrum showed two bands assigned to the NH_2 group at 3,420 and 3,380 cm^{-1}. Dimethyl amine was identified by a spot test [18], the intermediate $Mn^{VI}O_4^{2-}$ by its visible spectrum and carbon dioxide by lime water [17].

Spectral changes

The spectral scans obtained during the oxidation of Azn-Fs by alkaline permanganate are shown in Fig. 1a, b. The Figure shows a gradual decay of the MnO_4^- band at 525 nm with corresponding growth of new intermediate absorption maxima at wavelengths of 606 and 435 nm. The band at 606 nm 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 [20]. The appearance of two isosbestic points at 575 and 473 nm during the course of reaction indicates the interconversion of MnO_4^- to both $Mn^{VI}O_4^{2-}$ and MnO_2, respectively [21, 22]. The yellow color persisted after completion of the oxidation reactions, then finally, dispersed brown MnO_2 sol was observed, confirming that the hypomanganate(V) formed and subsequently decomposed to Mn^{IV} sol. The latter was coagulated by aging to give a colloidal precipitate of $Mn^{IV}O_2$. The absence of a hypomanganate(V) intermediate band around 700 nm is explained as due to rapid disproportionation of Mn^{V} [23, 24]. 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.

Reaction orders

The orders (n) of these oxidation reactions were determined from the slopes of plots of the observed first-order rate constants (k_{obs}) versus concentration (C) in logarithm coordinates ($\log k_{obs} = n \log C$) by varying the concentrations of permanganate, Azn-F and alkali in turn while keeping all other concentrations and conditions constant.

Under pseudo-first-order conditions of $[\text{Azn-F}]_0 \gg [MnO_4^-]_0$ at constant $[\text{Azn-F}]_0$, $[OH^-]$ and temperature, plots of ln absorbance versus time were linear, showing first-order dependence of the rates on $[MnO_4^-]_0$. The values of k_{obs} remained unaffected with changes in $[MnO_4^-]_0$ as listed in Table 1, confirming the first-order kinetics in $[MnO_4^-]_0$.

On the other hand, increasing $[\text{Azn-F}]_0$ was found to accelerate the reaction rates, Table 1. Plots of k_{obs} versus $[\text{Azn-F}]_0$ gave straight lines passing through the origin, substantiating a first-order dependence of the rates on $[\text{Azn-F}]_0$. Furthermore, the second-order rate constants ($k' = k_{obs}/[\text{Azn-F}]_0$) were nearly the same for the two Azn-F, establishing the first-order dependence on $[\text{Azn-F}]_0$.

The influence of alkali on the rate was studied at various $[OH^-]$, keeping all other reactant concentrations constant. The rate constants increased with increasing alkali concentration (Table 1), suggesting that the oxidation reactions are base-catalyzed. Plots of k_{obs} versus $[OH^-]$ were linear with nonzero intercepts, suggesting that these reactions are fractional first order in $[OH^-]$. Furthermore, plots of $\log k_{obs}$ versus $\log [OH^-]$ were linear with less than unit slopes showing fractional orders with respect to $[OH^-]$.

Effects of ionic strength and temperature

The effect of ionic strength was studied by varying the concentration of $NaClO_4$ in the reaction medium at constant concentrations of alkali, Azn-F and permanganate. It was found that variation in ionic strength had no significant effect on the rates.

To investigate the effect of temperature, the kinetic experiments were conducted at 288, 293, 298 and 303 K, keeping other experimental conditions constant. The experimental results indicated that the oxidation rates are greater at higher temperatures (Table 2). The activation parameters associated with the oxidation reactions were calculated using Arrhenius plots of ln k versus 1/T according to the equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

where $R = 8.314$ J mol^{-1} K^{-1}.

Table 1 Influence of [MnO$_4^-$], [Azn-F] and [OH$^-$] on the first-order rate constants (k_{obs}) in the oxidation of azinyl formamidines by alkaline permanganate at 25°C

10^4 [MnO$_4^-$] mol dm^{-3}	10^3 [Azn-F] mol dm^{-3}	10^2 [OH$^-$] mol dm^{-3}	10^5 k_{obs} s^{-1}	
			Pym-F	Py-F
2.0	8.0	3.0	111	291
3.0	8.0	3.0	109	295
4.0	8.0	3.0	110	290
5.0	8.0	3.0	113	287
6.0	8.0	3.0	108	288
4.0	4.0	3.0	58	146
4.0	6.0	3.0	86	208
4.0	8.0	3.0	110	290
4.0	10.0	3.0	141	355
4.0	12.0	3.0	172	424
4.0	8.0	1.0	62	161
4.0	8.0	2.0	92	235
4.0	8.0	3.0	110	290
4.0	8.0	4.0	127	342
4.0	8.0	5.0	151	421

Experimental error = ± 3%

The activation enthalpy, $\Delta H^{\neq}$, and activation entropy, $\Delta S^{\neq}$, can be determined from the Eyring equation;

$$\ln k = \ln \frac{k_B T}{h} + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \quad \text{or}$$

$$\ln \frac{hk}{k_B T} = \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{R}\frac{1}{T}$$

where k_B is the Boltzmann constant and h is the Planck constant. The temperature dependence was found to fit both the Eyring and Arrhenius equations.

Polymerization study

To test for the participation of the free radicals in these reactions, the reaction mixtures were mixed with known quantities of acrylonitrile monomer and kept for 24 h under nitrogen. On dilution with methanol, a white precipitate was 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.

Discussion

It has been reported [25, 26] that permanganate ion in aqueous alkaline medium 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

$$\text{MnO}_4^- + \text{OH}^- \overset{K_1}{\rightleftharpoons} [\text{MnO}_4 \cdot \text{OH}]^{2-} \tag{3}$$

This is consistent with the apparent order of less than unity in OH$^-$. The formation of [MnO$_4$·OH]$^{2-}$ in alkaline medium in the present systems is further supported by plots

Table 2 Effect of temperature on the first-order rate constants (10^5 k_{obs} s^{-1}) in the oxidation of azinyl formamidines by alkaline permanganate

10^3 [Asn] mol dm^{-3}	10^2 [OH$^-$] mol dm^{-3}	Temperature (K)							
		Pym-F				Py-F			
		288	293	298	303	288	293	298	303
4	3	36	45	58	75	80	113	149	201
6	3	51	65	86	112	119	167	208	283
8	3	70	88	110	145	154	221	290	393
10	3	90	112	141	185	183	263	355	497
12	3	103	133	172	220	244	312	424	528
8	1	34	43	55	74	81	104	131	168
8	2	53	69	92	105	131	178	223	245
8	3	70	88	110	145	154	221	290	393
8	4	81	103	127	174	221	278	352	434
8	5	91	118	154	199	263	323	421	476

Experimental error = ±4 %

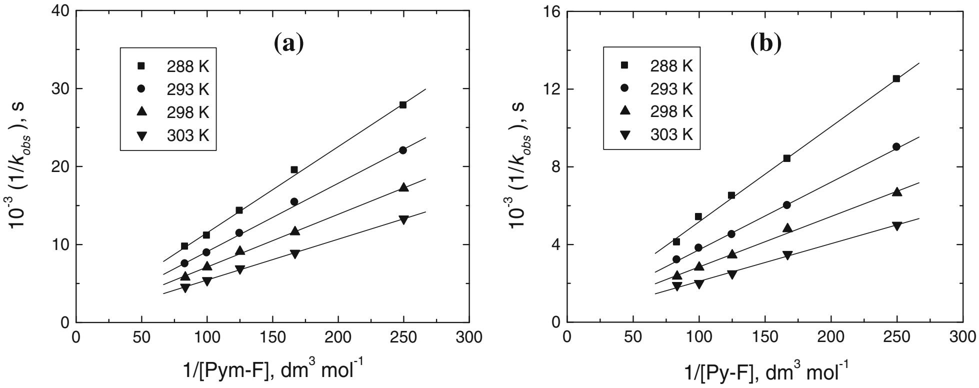
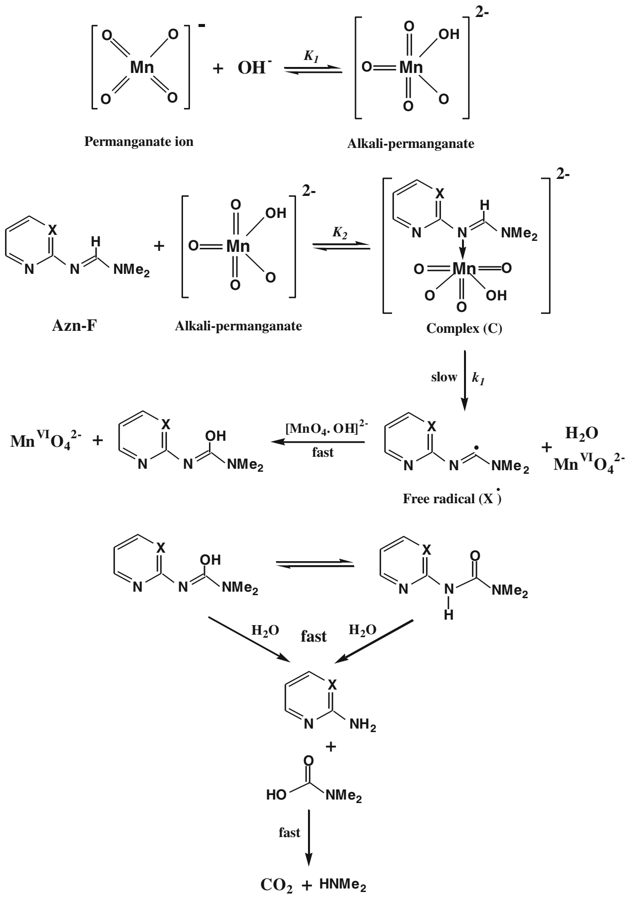


Fig. 2 **a**, **b** Double reciprocal plots for the formation of the intermediate complexes in the oxidation of (**a**) Pym-F and (**b**) Py-F by alkaline permanganate at different temperatures. $[MnO_4^-] = 4 \times 10^{-4}$ and $[OH^-] = 0.03$ mol dm^{-3}



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

Scheme 2 Mechanism of oxidation of azinyl formamidines by alkaline permanganate

of $1/k_{obs}$ versus $1/[OH^-]$ shown in Fig. 3a, b, which are linear with positive intercepts.

Many investigators [14–16, 19, 26] 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. 1a, b. Also, the linearity of the plots between $1/k_{obs}$ and 1/[Azn-F], Fig. 2a, b, is considered to provide kinetic evidence in favor of possible formation of a transient complex between oxidant and substrate similar to the well-known Michaelis–Menten [27] mechanism for enzyme–substrate reactions. On the other hand, the observed negligible effect of ionic strength on the reaction rate implies the association of an ion and a neutral molecule [19, 28].

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, $[MnO_4{\cdot}OH]^{2-}$, on the Azn-F substrate (S), leading to the formation of a complex (C) in a prior equilibrium step;

$$S + [MnO_4 \cdot OH]^{2-} \overset{k_2}{\rightleftharpoons} \left[S - Mn^{VI}O_4 \cdot OH\right]^{2-}(C) \qquad (4)$$

where K_2 is the formation constant of this complex.

In this complex, one electron is transferred from the Azn-F substrate to permanganate. Slow cleavage of the complex leads to the formation of a free radical intermediate derived from the substrate (S˙) and manganate(VI) transient species

$$\left[S - Mn^{VI}O_4 \cdot OH\right]^{2-}(C) \xrightarrow[slow]{k_1} S^{\cdot} + Mn^{VI}O_4^{2-} + H_2O \qquad (5)$$

The intermediate (S) is rapidly attacked by another alkali-permanganate species to yield an intermediate product, 1,1-dimethyl-3-(azin-2-yl) urea, as follows:

$$S^{\cdot} + [MnO_4 \cdot OH]^{2-} \xrightarrow{fast} \text{Intermediate product} + Mn^{VI}O_4^{2-} \qquad (6)$$

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

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

According to this mechanism, the rate of disappearance of the permanganate ion or the formation of the

Table 3 Values of the rate constants of the slow step (k_1) and the equilibrium constants (K_1 and K_2) in the oxidation of azinyl formamidines by alkaline permanganate at different temperatures

Constant	Temperature (K)							
	Pym-F				Py-F			
	288	293	298	303	288	293	298	303
$10^3\ k_1$, s^{-1}	2.41	3.16	4.64	6.62	3.16	3.98	5.07	6.43
K_1, $dm^3\ mol^{-1}$	18.90	17.31	15.62	13.71	21.84	20.41	18.62	15.97
K_2, $dm^3\ mol^{-1}$	8.89	8.09	7.27	6.41	19.54	18.36	15.56	13.32

Experimental error = ±4 %

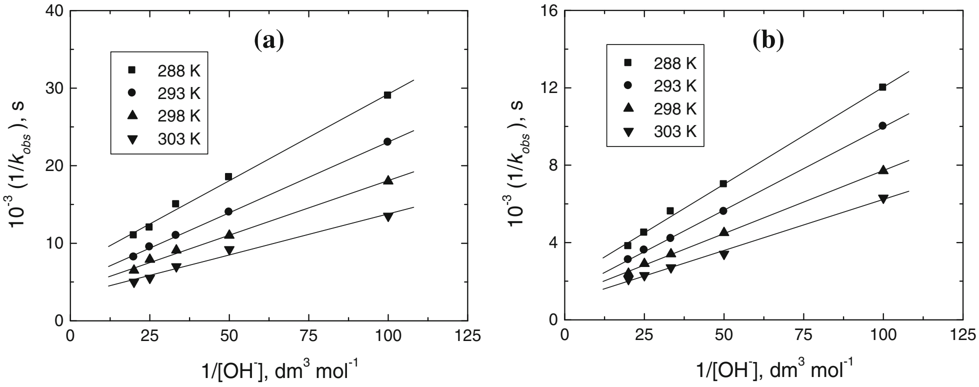


Fig. 3 **a**, **b** Plots of $1/k_{obs}$ versus $1/[OH^-]$ for the formation of the intermediate complexes in the oxidation of (**a**) Pym-F and (**b**) Py-F by alkaline permanganate at different temperatures. [Azn-F] = 8×10^{-3} and $[MnO_4^-] = 4 \times 10^{-4}$ mol dm^{-3}

intermediate complexes can be expressed by the following rate law:

$$\text{Rate} = \frac{-d\left[MnO_4^-\right]}{dt} = \frac{+d[S-Mn^{VI}O_4\cdot OH^{2-}]}{dt} = k_1\left[S-Mn^{VI}O_4\cdot OH^{2-}\right] \tag{8}$$

The variation in the rate of complex formation with the substrate, hydroxyl ion and oxidant concentrations can be deduced ("Appendix") to give the following equation

$$\text{Rate} = \frac{k_1K_1K_2[S][OH^-]\left[MnO_4^-\right]}{1+K_1[OH^-]+K_1K_2[S][OH^-]} \tag{9}$$

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

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

Comparing Eqs. (9) and (10), after rearrangement we obtain

$$\frac{1}{k_{obs}} = \left(\frac{1+K_1[OH^-]}{k_1K_1K_2[OH^-]}\right)\frac{1}{[S]} + \frac{1}{k_1} \tag{11}$$

According to Eq. (11), the relationship between $1/k_{obs}$ and 1/[S] at constant $[OH^-]$ should be linear with positive intercept on the $1/k_{obs}$ axis. The experimental results satisfy this requirement at different temperatures as shown in Fig. 2a, b. From the intercepts of these plots, values of the rate constant of the slow step (k_1) were evaluated and are listed in Table 3.

Equation (11) can be rearranged to

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1K_1K_2[S]}\right)\frac{1}{[OH^-]} + \left(\frac{1}{k_1K_2}\frac{1}{[S]} + \frac{1}{k_1}\right) \tag{12}$$

Regarding Eq. (12), plots of $1/k_{obs}$ against $1/[OH^-]$ at constant [S] also should give straight lines with positive intercepts on the $1/k_{obs}$ axis, as was experimentally observed, Fig. 3a, b. Values of the first and second equilibrium constants K_1 and K_2 at different temperatures were calculated from the slopes and intercepts of Fig. 3a, b (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 [15, 16].

The activation parameters for the rate constants of the slow step (k_1) were calculated using Eyring and Arrhenius plots, as given in Table 4. Furthermore, the thermodynamic parameters of the equilibrium constants were also determined using a Van't Hoff's plot and are listed in Table 5.

From Table 4, the obtained large negative values of $\Delta S^{\neq}$ suggest that the reactants give transition states which are more ordered than the reactants, due to loss of degrees of freedom.

Table 4 Activation parameters associated with the slow step (k_1) in the oxidation of azinyl formamidines by alkaline permanganate

Substrate	Parameter				
	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$E_a^{\neq}$ kJ mol^{-1}	A mol^{-1} s^{-1}
Pym-F	−131.19	47.20	86.24	43.66	2.30×10^3
Py-F	−181.66	31.81	85.34	34.28	5.16×10^3

Experimental error = ±4 %

Table 5 Thermodynamic parameters associated with the equilibrium constants (K_1 and K_2) in the oxidation of azinyl formamidines by alkaline permanganate

Substrate	Equilibrium constant	Parameter		
		ΔH° kJ mol^{-1}	$\Delta G^{\circ}{}_{298}$ kJ mol^{-1}	ΔS° J mol^{-1} K^{-1}
Pym-F	K_1	−15.39	−6.80	−28.83
	K_2	−15.74	−4.91	−36.34
Py-F	K_1	−14.82	−7.24	−25.42
	K_2	−19.85	−6.80	−43.79

Experimental error = ±4 %

This is also supported by the very small frequency factors A [29]. The experimental values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were both favorable for electron transfer processes. Again, the positive values of both $\Delta H^{\neq}$ and $\Delta G^{\neq}$ indicate endothermic formation of the intermediate. The observed modest values of $\Delta H^{\neq}$ and the higher rate constants for the slow step indicate that the reactions occur via an inner-sphere mechanism [30]. This accords with the suggested transition states which are consistent with formation of intermediate complexes via an inner-sphere electron transfer mechanism. This mechanism is also consistent with the proposition made by Stewart and co-workers [19, 28] for ionic transition states in oxidation of many organic substrates by permanganate. They reported that the entropy of activation tends to be more positive for reactions with outer-sphere mechanisms, whereas it is more negative for reactions of the inner-sphere type. On the other hand, comparison of the thermodynamic parameters listed in Table 5 with those obtained for the slow steps of the reactions show that the reactions before the rate-determining steps are fairly fast and involve low activation energies [31].

Appendix

According to the suggested mechanism,

$$\text{Rate} = \frac{-\mathrm{d}\left[\mathrm{MnO_4^-}\right]}{\mathrm{d}t} = \frac{+\mathrm{d}\left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right]}{\mathrm{d}t} = k_1\left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right] \tag{A1}$$

From reaction (3)

$$K_1 = \frac{\left[\mathrm{MnO_4\cdot OH^{2-}}\right]}{\left[\mathrm{MnO_4^-}\right]\left[\mathrm{OH^-}\right]} \tag{A2}$$

$$\text{Therefore, } \left[\mathrm{MnO_4\cdot OH^{2-}}\right] = K_1\left[\mathrm{MnO_4^-}\right]\left[\mathrm{OH^-}\right] \tag{A3}$$

From reaction (4)

$$K_2 = \frac{\left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right]}{[\mathrm{S}]\left[\mathrm{MnO_4\cdot OH}\right]^{2-}} \tag{A4}$$

$$\text{Therefore, } \left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right] = K_2[\mathrm{S}]\left[\mathrm{MnO_4\cdot OH^{2-}}\right] \tag{A5}$$

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

$$\left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right] = K_1K_2[\mathrm{S}]\left[\mathrm{OH^-}\right]\left[\mathrm{MnO_4^-}\right] \tag{A6}$$

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

$$\text{Rate} = k_1K_1K_2[\mathrm{S}]\left[\mathrm{OH^-}\right]\left[\mathrm{MnO_4^-}\right] \tag{A7}$$

The total concentration of the substrate is given by

$$[\mathrm{S}]_\mathrm{T} = [\mathrm{S}]_\mathrm{F} + \left[\mathrm{S-Mn^{VI}O_4\cdot OH^{2-}}\right] \tag{A8}$$

where $[\mathrm{S}]_\mathrm{T}$ and $[\mathrm{S}]_\mathrm{F}$ stand for total and free concentrations of the substrate.

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

$$[\mathrm{S}]_\mathrm{T} = [\mathrm{S}]_\mathrm{F} + K_1K_2[\mathrm{S}]_\mathrm{F}\left[\mathrm{OH^-}\right]\left[\mathrm{MnO_4^-}\right] \tag{A9}$$

$$[\mathrm{S}]_\mathrm{T} = [\mathrm{S}]_\mathrm{F}\left(1 + K_1K_2\left[\mathrm{OH^-}\right]\left[\mathrm{MnO_4^-}\right]\right) \tag{A10}$$

Therefore,

$$[\mathrm{S}]_\mathrm{F} = \frac{[\mathrm{S}]_\mathrm{T}}{1 + K_1K_2[\mathrm{OH^-}][\mathrm{MnO_4^-}]} \tag{A11}$$

Similarly,

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{T}} = [\mathrm{MnO_4^-}]_{\mathrm{F}} + [\mathrm{MnO_4 \cdot OH^{2-}}] + [\mathrm{S - Mn^{VI}O_4 \cdot OH^{2-}}] \tag{A12}$$

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

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{T}} = [\mathrm{MnO_4^-}]_{\mathrm{F}} + 1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{S}][\mathrm{OH^-}]\left[\mathrm{MnO_4^-}\right]_{\mathrm{F}} \tag{A13}$$

$$\left[\mathrm{MnO_4^-}\right]_{\mathrm{F}} = \frac{\left[\mathrm{MnO_4^-}\right]_T}{1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{S}][\mathrm{OH^-}]} \tag{A14}$$

And $\left[\mathrm{OH^-}\right]_{\mathrm{T}} = [\mathrm{OH^-}]_{\mathrm{E}} + [\mathrm{MnO_4 \cdot OH^{2-}}]$ (A15)

$$[\mathrm{OH^-}]_{\mathrm{F}} = \frac{[\mathrm{OH^-}]_{\mathrm{T}}}{1 + K_1\left[\mathrm{MnO_4^-}\right]} \tag{A16}$$

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

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{S}][\mathrm{OH^-}]\left[\mathrm{MnO_4^-}\right]}{\left(1 + K_1K_2[\mathrm{OH^-}]\left[\mathrm{MnO_4^-}\right]\right)\left[1 + K_1\left[\mathrm{MnO_4^-}\right]\right]\left(1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{S}][\mathrm{OH^-}]\right)} \tag{A17}$$

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

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{S}][\mathrm{OH^-}]\left[\mathrm{MnO_4^-}\right]}{1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{S}][\mathrm{OH^-}]} \tag{A18}$$

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

$$\text{Rate} = \frac{-\mathrm{d}\left[\mathrm{MnO_4^-}\right]}{\mathrm{d}t} = k_{\mathrm{obs}}\left[\mathrm{MnO_4^-}\right] \tag{A19}$$

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

$$k_{\mathrm{obs}} = \frac{k_1K_1K_2[\mathrm{S}][\mathrm{OH^-}]}{1 + K_1[\mathrm{OH^-}] + K_1K_2[\mathrm{S}][\mathrm{OH^-}]} \tag{A20}$$

and with rearrangement it becomes

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

Equation (A21) can be rearranged to be

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{1}{k_1K_1K_2[\mathrm{S}]}\right)\frac{1}{[\mathrm{OH^-}]} + \left(\frac{1}{k_1K_2}\frac{1}{[\mathrm{S}]} + \frac{1}{k_1}\right) \tag{A22}$$

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