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Kinetics and mechanism of oxidation of 1,10-phenanthroline by alkaline permanganate

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ABSTRACT: The kinetics of the oxidation of 1,10-phenanthroline (1,10-phen) by permanganate were investigated in alkaline medium. A first-order, fractional-order and zero-order dependence of the rate each in [MnO_4^-], [1,10-phen] and [OH^-], respectively, was observed. The data suggest that the oxidation proceeds via the formation of a complex between 1,10-phen and MnO_4^- which decomposes in a slow step to yield the free radical of 1,10-phen, followed by a fast step to give 2,2′-bipyridy1 3,3′-dicarboxaldehyde. The reaction constants involved in the mechanism were evaluated. There was good agreement between the observed and calculated rate constants under varying conditions of the experiments. The activation parameters were calculated with respect to the slow step of the mechanism. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; mechanism; oxidation; permanganate; 1,10-phenanthroline

INTRODUCTION

During oxidation by permanganate, it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. Furthermore, the mechanism by which this multivalent oxidant oxidizes a substrate depends not only on the substrate but also on the medium[1] used for the study. In strongly alkaline medium the stable reduction product[2,3] of permanganate ion is manganate ion, MnO_4^{2-}. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) (Scheme 1) and a mechanism, in which a hypomanganate is formed in a two-electron reduction followed by rapid oxidation of hypomanganate ion[4] (Scheme 2).

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k_1'} \mathrm{Mn(VI)} + \mathrm{S}^{\cdot}$$

$$\mathrm{Mn(VII)} + \mathrm{S}^{\cdot} \xrightarrow{k_2'} \mathrm{Mn(VI)} + \text{products}$$

$$\mathrm{S} = \text{substrate}; k_2' \gg k_1'$$

Scheme 1

$$\mathrm{Mn(VII)} + \mathrm{S} \xrightarrow{k_3'} \mathrm{Mn(V)} + \text{products}$$

$$\mathrm{Mn(VII)} + \mathrm{Mn(V)} \xrightarrow{k_4'} 2\mathrm{Mn(VI)}$$

$$\mathrm{S} = \text{substrate}; k_4' \gg k_3'$$

Scheme 2

1,10-phenanthroline (1,10-phen) is a well known complexing agent which forms various coordination complexes with different metal ions. Its use in analytical chemistry as an oxidation–reduction indicator is extensive. Fedorova and Berdnikov[5] carried out the oxidation of 1,10-phenanthroline by H_2O_2 in aqueous solution and reported that the oxidation product was 2,2′-bipyridyl 3,3′-dicarboxaldehyde. Wimmer and Wimmer[6] reported the facile synthesis of 2,2′-bipyridyl 3,3′-dicarboxylic acid by vigorous oxidation of 1,10-phen by alkaline permanganate, but did not carry out a mechanistic study. In view of the lack of reports in the literature on the oxidation of 1,10-phen (except Refs 5 and 6) and in continuation of work in our laboratory[7] on alkaline permanganate oxidation, we selected 1,10-phen as a substrate for oxidation and obtained the major oxidation product as 2,2′-bipyridyl 3,3′-dicarboxaldehyde. The present study involved the title reaction to investigate the redox chemistry of permanganate in such media and to arrive at a plausible mechanism.

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EXPERIMENTAL

Materials. 1,10-Phenanthroline and potassium permanganate (BDH) were of analytical grade and their solutions were prepared by dissolving the requisite amounts in doubly distilled hot and cold water, respectively. The concentration of potassium permanganate was ascertained by titrating it against standard oxalic acid.[8] A solution of K_2MnO_4 was prepared[9] as follows: potassium permanganate solution was refluxed in aqueous 8 mol dm^{-3} KOH until a green colour developed and the solid K_2MnO_4 formed on cooling was recrystallized from the same solvent. Weighing out an appropriate amount of sample, a stock solution of K_2MnO_4 was prepared in aqueous KOH. The concentration of K_2MnO_4 was ascertained by measuring its absorbance at 608 nm ($\epsilon = 1530 \pm 20$ dm^3 mol^{-1} cm^{-1}) using a Hitachi model 150–20 spectrophotometer.

All other reagents were of analytical grade and their solutions were prepared by dissolving the appropriate amount in doubly distilled water. NaOH and $NaClO_4$ were utilized to maintain the required alkalinity and ionic strength, respectively.

Kinetics. Kinetic measurements were carried out under pseudo-first-order conditions where [1,10-phen] was always $\geq$10-fold in excess over $[MnO_4^-]$ at a constant ionic strength of 1.0 mol dm^{-3}. The reaction was initiated by mixing the required quantities of previously thermostated solutions of 1,10-phen and permanganate which also contained appropriate quantities of NaOH and $NaClO_4$ to maintain the required alkalinity and ionic strength respectively, at a constant temperature of 23.0 ± 0.1 °C. The progress of the reaction was followed by measuring the disappearance of MnO_4^- in a 1 cm quartz cell of a Hitachi model 150–20 spectrophotometer at its absorption maximum of 526 nm. Earlier it was verified that there is negligible interference from other reaction species at this wavelength. The application of Beer's law for permanganate at 526 nm had earlier been verified giving $\epsilon = 2080 \pm 50$ dm^3 mol^{-1} cm^{-1}.

The pseudo-first-order rate constants were obtained from the plots of $\log[MnO_4^-]$ versus time; the plots were linear up to 75% completion of the reaction and k_{obs} values were reproducible within ±5%. During the progress of the reaction, the colour of the solution changed from violet to blue and further to green. The spectrum of the green solution was identical with that of an authentic sample of MnO_4^{2-}. Hence it is concluded that the blue colour originates from the violet of MnO_4^- and green of MnO_4^{2-}, excluding the accumulation of hypomanganate. The formation of Mn(VI) was also evidenced by Fig. 1, where the absorbance of Mn(VII) decreases at 526 nm and that of Mn(VI) increases at 608 nm during the course of the reaction.

In view of the modest concentration of alkali used in the reaction medium, attention was also given on the effect of the surface of reaction vessel on the kinetics. The use of polythene or acrylic ware and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on reaction rates.

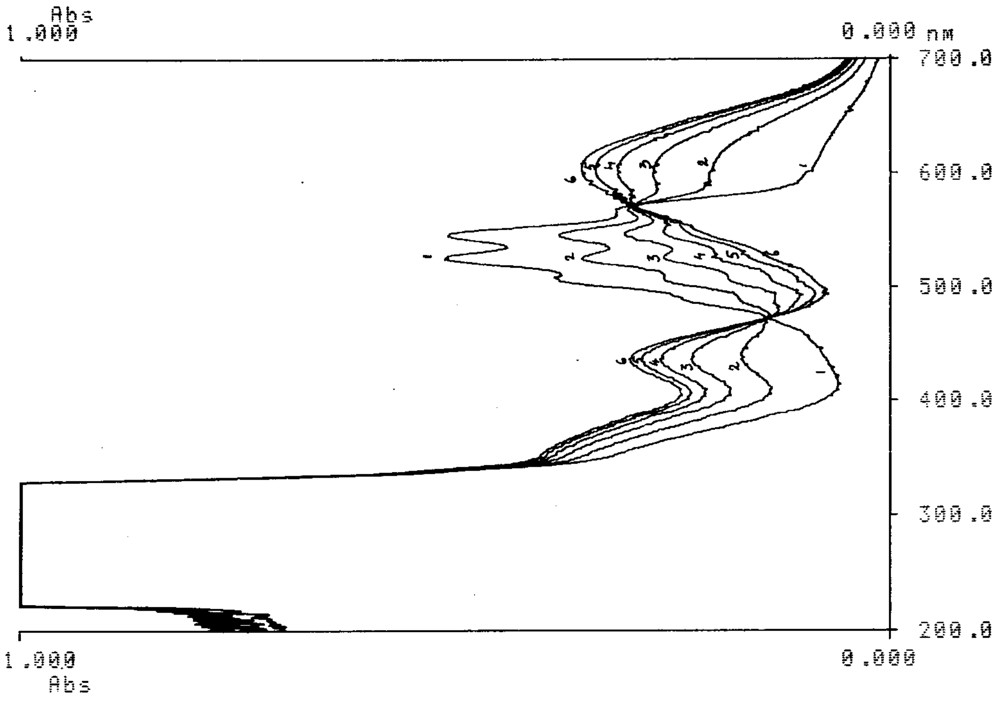


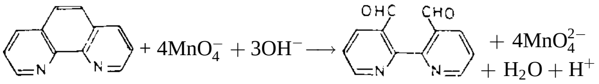
Figure 1. Spectral changes in the oxidation of 1,10-phen by permanganate with $[MnO_4^-] = 2.0 \times 10^{-4}$, $[1,10\text{-phen}] = 2.0 \times 10^{-3}$ and $[OH^-] = 0.50$, $I = 1.0$ mol dm^{-3} at 23 °C and with a scanning time interval of 2 min

Some kinetic runs were also carried out in an atmosphere of nitrogen to understand the effect of dissolved oxygen on the rate of reaction. There was no significant difference in the results obtained under a nitrogen atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in basic media, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. However, fresh solutions were used while carrying out the kinetic study.

RESULTS

Stoichiometry

Different sets of reaction mixtures containing excess [MnO_4^-] over [1,10-phen] were mixed in the presence of 0.5 mol dm^{-3} alkali adjusted to an ionic strength of 1.0 mol dm^{-3} and kept for 12 h. in an inert atmosphere. The remaining permanganate was then determined spectrophotometrically. The results indicated that 1 mol of 1,10-phen consumed 4 mol of permanganate as in Eqn. 1. The main oxidation products were identified as 2,2′-bipyridyl 3,3′-dicarboxaldehyde and manganate. The aldehyde was confirmed by the formation of crystalline hydrazone with 2,4-dinitrophenylhydrazine and the formation of a white crystalline precipitate with dimedone[10]. The presence of dicarboxaldelyde was confirmed by formation of a pink dye on the addition of hydrazine hydrate. Further confirmation was obtained from the UV–visible spectrum of the reaction mixture, which showed an absorption band at 325 nm (n → π^* transitions) due to the carbonyl group of the aldehyde.



(1)

It was observed that the dicarboxaldehyde did not undergo further oxidation under the present kinetic conditions, since the test for the probable oxidation product of an aldehyde, i.e. acid, was negative.

Reaction order

The reaction orders were determined from the slopes of $\log k_{obs}$ versus log(concentration) plots, by varying the concentration of MnO_4^-, 1,10-phen and alkali in turn while keeping the others constant.

Effect of permanganate

The permanganate concentration was varied in the range 4.0×10^{-5}–4.0×10^{-4} mol dm^{-3} at a constant concentration of 1,10-phen and alkali maintaining a constant ionic strength of 1.0 mol dm^{-3}. The non-variation of the pseudo-first-order rate constants at various concentrations of MnO_4^- indicate that the order in [permanganate] is unity (Table 1). This was also confirmed from the linearity of the plots of log[MnO_4^-] versus time.

Table 1. Effect of [1,10-phen], [MnO_4^-] and [OH^-] on the oxidation of 1,10-phen by alkaline permanganate at 23 °C, I = 1.0 mol dm^{-3}

[1,10-phen] $\times 10^3$ (mol dm^{-3})	[MnO_4^-] $\times 10^4$ (mol dm^{-3})	[OH^-] (mol dm^{-3})	$k_{obs} \times 10^3$ (s^{-1})	
			Expt.[a]	Calc.[a]
0.5	2.09	0.5	0.90	1.03
1.0	2.09	0.5	1.91	1.78
2.0	2.09	0.5	2.70	2.81
2.5	2.09	0.5	3.35	3.18
3.0	2.09	0.5	3.60	3.48
5.0	2.09	0.5	4.34	4.30
2.0	0.40	0.5	2.70	2.81
2.0	0.80	0.5	2.71	2.81
2.0	1.55	0.5	2.72	2.81
2.0	2.09	0.5	2.69	2.81
2.0	4.00	0.5	2.71	2.81
2.0	2.09	0.1	2.23	2.81
2.0	2.09	0.3	2.30	2.81
2.0	2.09	0.5	2.68	2.81
2.0	2.09	0.7	2.49	2.81
2.0	2.09	1.0	2.68	2.81

[a] Experimental and calculated. Error ±4%.

Effect of 1,10-phenanthroline

The concentration of 1,10-phen was varied in the range 5.0×10^{-4}–5.0×10^{-3} mol dm^{-3} keeping all other conditions constant. The order in [1,10-phen] was *ca* 0.5 (Table 1).

Effect of alkali

To study the effect of [OH^-] on the rate of reaction, [OH^-] was varied in the range 0.1–1.0 mol dm^{-3} at constant concentrations of permanganate and 1,10-phen, maintaining a constant ionic strength of 1.0 mol dm^{-3}. The rate constants remained constant with increase in concentration of alkali, indicating that the order in [OH^-] is zero (Table 1).

Effect of ionic strength

To study the effect of ionic strength, the concentration of sodium perchlorate was varied from 0.5 to 1.5 mol dm^{-3} at constant concentrations of oxidant, substrate and

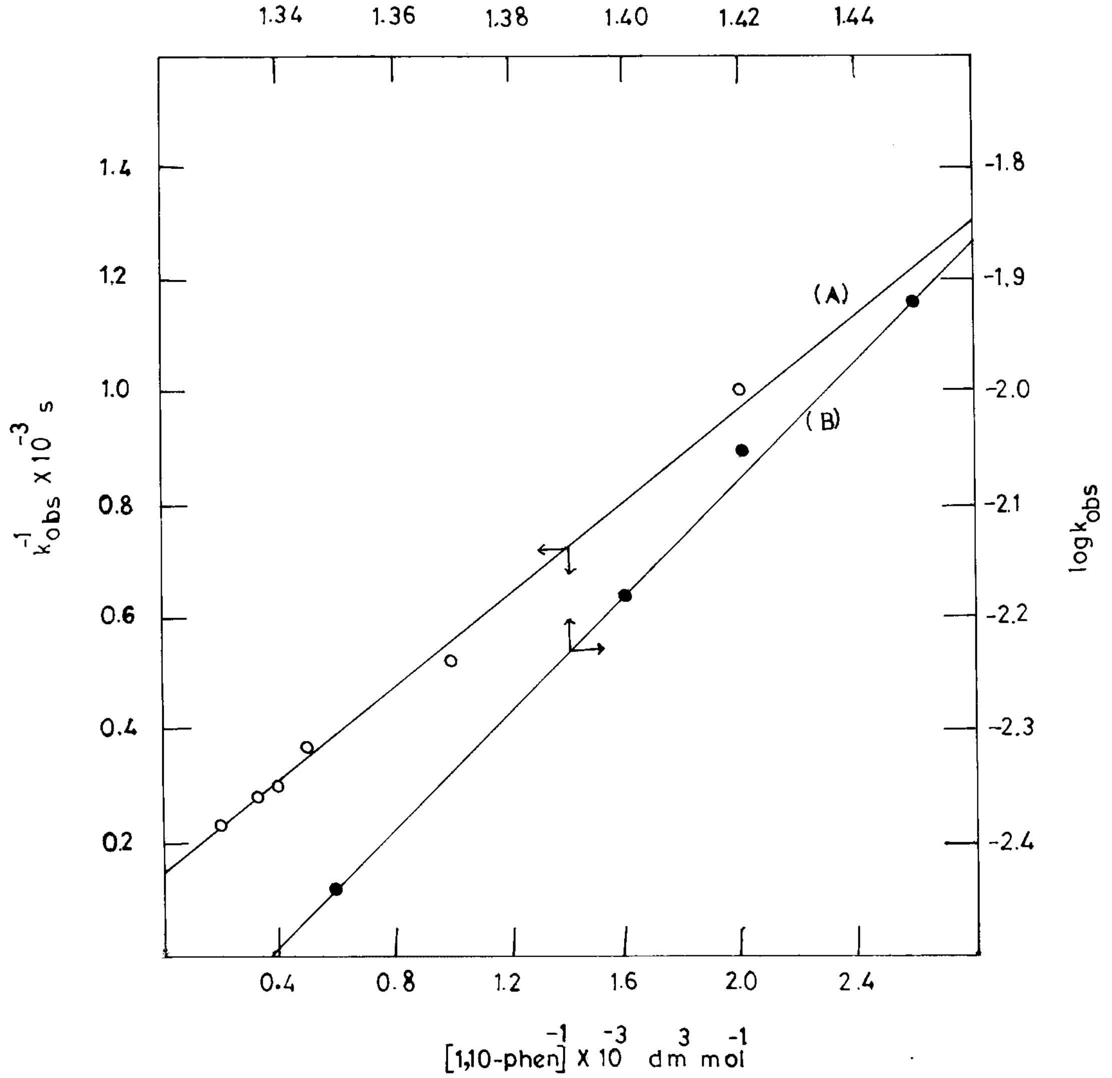
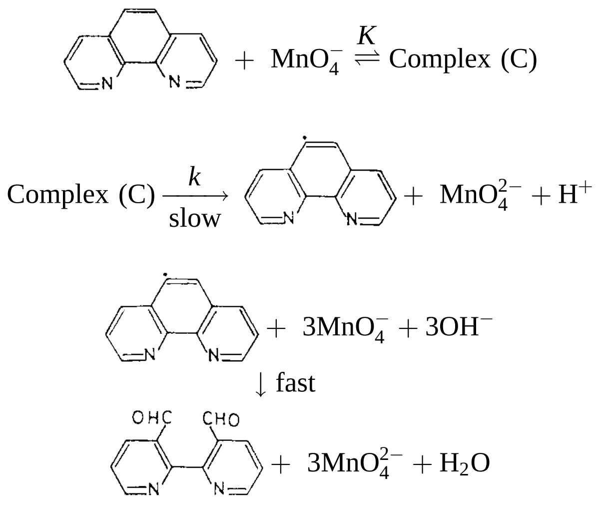


Figure 2. (A) Plot of $1/k_{obs}$ versus 1/[1,10-phen]. Conditions as in Table 1. (B) Plot of log k_{obs} versus $1/D$. Conditions: $[MnO_4^-] = 2.09 \times 10^{-4}$, $[1,10\text{-phen}] = 2.0 \times 10^{-3}$, $[OH^-] = 0.50$ and $I = 1.0$ mol dm^{-3}

alkali. It was found that the ionic strength had no significant effect on the rate of reaction.

Effect of solvent polarity

The relative permittivity (D) effect was studied by varying the percentage of *tert*-butanol–water content in the reaction medium with all other conditions being kept constant. Attempts to measure D failed. However, it was calculated from the values for pure liquids as described earlier.[11] The inertness of the solvent with respect to the oxidant was checked under the experimental conditions. The rate constants k_{obs} increased with increase in the content of *tert*-butanol or decrease in the dielectric constant of the medium (Fig. 2). The plot of logk_{obs} vs $1/D$ was linear with a positive slope (Fig. 2).



Scheme 3

Table 2. Thermodynamic activation parameters (with respect to slow step of Scheme 3) of oxidation of 1,10-phenanthroline by alkaline permanganate

E_a	12.8 ± 1.3 kJ $\mathrm{mol^{-1}}$
$\Delta S^{\neq}$	-252 ± 25 J $\mathrm{K^{-1}\,mol^{-1}}$
$\Delta H^{\neq}$	10.3 ± 1.0 kJ $\mathrm{mol^{-1}}$

Effect of initial addition of products

The addition of various amounts of reaction products had no significant effect on the rate of the reaction.

Test for free radicals

To test the intervention of free radicals in the reaction mixture, the latter was mixed with acrylonitrile monomer and kept for 24 h in an inert atmosphere. On dilution with methanol a white precipitate was formed, indicating the presence of free radicals.

Effect of temperature

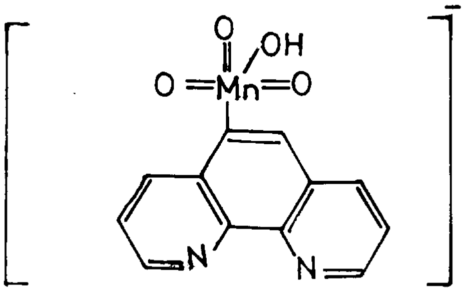
The rate of reaction was measured at different temperatures with various [1,10-phen], keeping other conditions constant. The rate was found to increase with increase in temperature. The rate constants, k, of the slow step of Scheme 3 were obtained from the intercept of plots of $1/k_{\mathrm{obs}}$ versus 1/[1,10-phen] at different temperatures. The values of k were $(6.66 \pm 0.33) \times 10^{-3}$, $(7.26 \pm 0.36) \times 10^{-3}$, $(7.70 \pm 0.38) \times 10^{-3}$ and $(8.35 \pm 0.4) \times 10^{-3}\ \mathrm{s^{-1}}$ at 23, 28, 33 and 38 °C respectively. The activation parameters corresponding to these constants were evaluated from the plot of log$k$ vs $1/T$ and are given in Table 2.

DISCUSSION

The permanganate ion, $\mathrm{MnO_4^-}$, is a powerful oxidizing agent in aqueous alkaline medium. At pH > 12 the reduction product of $\mathrm{MnO_4^-}$, viz $\mathrm{MnO_4^{2-}}$, is stable and further reduction of $\mathrm{MnO_4^{2\,-}}$ might be stopped.[2] Diode-array rapid scan spectrophotometric (DARSS) studies have shown that at pH > 12 the product of the reaction of $\mathrm{MnO_4^-}$ is $\mathrm{MnO_4^{2\,-}}$ with no further reduction, as reported by Simandi *et al.*[2] However, on prolonged standing the reaction mixture turn brown, indicating the reduction of $\mathrm{MnO_4^{2-}}$ to $\mathrm{MnO_2}$ under our experimental conditions.

The reaction between 1,10-phen and permanganate has a stoichiometry of 1:4, with a first-order dependence on $[\mathrm{MnO_4^-}]$, a *ca* 0.5 order dependence on [1,10-phen] and a zero-order dependence on $[\mathrm{OH^-}]$. The kinetic results suggest the formation of a complex between permanganate and 1,10-phen followed by decomposition of the complex in a slow step and a subsequent fast step to yield products. Attempts to obtain spectral (UV–visible) evidence for the phenanthroline–permanganate complex failed. However, the interaction might be feeble, and such complex formation between oxidant and substrate has been reported earlier.[12] The evidence for complex formation was obtained kinetically, i.e. from the non-zero intercept of the plot of $1/k_{\mathrm{obs}}$ versus 1/[1,10-phen] (Fig. 2). The results are in agreement with Scheme 3.

The structure of the complex might be as illustrated.



The fractional-order dependence on [1,10-phen] reveals that 1,10-phen undergoes complexation with permanganate or alkali. Since the order in $[\mathrm{OH^-}]$ is zero, a complex between alkali and 1,10-phen is discounted. The phenanthroline–permanganate complex decomposes in a rate-determining step to give a free radical which reacts further with three molecules of permanganate in subsequent fast steps to yield products. Since permanganate is a one-electron oxidant in alkaline medium, the reaction between 1,10-phen and permanganate would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility (see below). This type of radical intervention has also been observed in the alkaline permanganate oxidation of various organic substrates.[13]

Scheme 3 leads to the rate law

$$-\frac{\mathrm{d}[\mathrm{MnO_4^-}]}{\mathrm{d}t} = \frac{kK[1,10-\mathrm{phen}][\mathrm{MnO_4^-}]}{1 + K[1,10-\mathrm{phen}]} \tag{2}$$

Strictly, the factor $1 + K[\mathrm{MnO_4^-}]$ should also be in the denominator on the right-hand side of Eqn.2, but in view of the low concentration of $\mathrm{MnO_4^-}$ used, this term approximates to unity. Equation 2 can be rearranged to the following form, which is suitable for verification:

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{kK[1,10-\mathrm{phen}]} + \frac{1}{k} \tag{3}$$

According to Eqn.3, a plot of k_{obs}^{-1} vs $[1,10\text{-phen}]^{-1}$ should be linear, which is verified in Fig. 2. The slope and intercept of such a plot lead to the values of K and k at 23 °C of $(356 \pm 18)\ \mathrm{dm^3\ mol^{-1}}$ and $(6.66 \pm 0.30) \times 10^{-3}\ \mathrm{s^{-1}}$, respectively. Using these values, the rate constants at various experimental conditions were calculated and compared with experimental data in Table 1. There is good agreement between the observed and calculated rate constants.

The negligible effect of ionic strength on the rate may be attributed to the interaction between neutral and charged species of 1,10-phen and MnO_4^-, respectively, in the reaction. Increasing the content of *tert*-butanol in the reaction medium leads to an increase in the rate of reaction, which seems to be contrary to the expected interaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of the reaction with decreasing dielectric constant (D) may be due to the stabilization of the monovalent complex (C) at low relative permittivity, which is less solvated than MnO_4^- at higher dielectric constant because of its larger size.

It is interesting that the reactive species of the oxidant, MnO_4^-, required a $\text{pH} > 12$, below which the system is disturbed owing to the formation of a colloidal solution since the reaction will proceed further to give the reduced product of the oxidant, Mn(IV), which slowly develops a yellow turbidity. Hence it is important to note that, in carrying out this reaction, the role of pH in the reaction medium is crucial.

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APPENDIX

Scheme 3 in brief:

$$1,10-\text{phen}+\text{MnO}_4^- \overset{K}{\rightleftharpoons} \text{complex (C)}$$

$$\text{Complex (C)} \xrightarrow[\text{slow}]{k} 1,10-\text{phen}^{\cdot}+\text{MnO}_4^{2-}$$

$$1,10-\text{phen}^{\cdot}+3\text{MnO}_4^-+3\text{OH}^- \xrightarrow{\text{fast}} \text{products}$$

$$\text{Rate} = k[\text{C}] \qquad (\text{A1})$$

$$K = [\text{C}]/[1,10-\text{phen}][\text{MnO}_4^-]$$

Therefore,

$$[\text{C}] = K[1,10-\text{phen}][\text{MnO}_4^-]$$

Equation A1 becomes

$$\text{rate} = kK[1,10-\text{phen}]_\text{f}[\text{MnO}_4^-]_\text{f} \qquad (\text{A2})$$

$$\begin{aligned}
[\text{MnO}_4^-]_\text{T} &= [\text{MnO}_4^-]_\text{f} + [\text{C}]\\
&= [\text{MnO}_4^-]_\text{f} + K[1,10-\text{phen}]_\text{f}[\text{MnO}_4^-]_\text{f}\\
&= [\text{MnO}_4^-]_\text{f}(1 + K[1,10-\text{phen}]_\text{f})\\
[\text{MnO}_4^-]_\text{f} &= [\text{MnO}_4^-]_\text{T}/(1 + K[1,10-\text{phen}]_\text{f}) \qquad (\text{A3})
\end{aligned}$$

$$\begin{aligned}
[1,10-\text{phen}]_\text{T} &= [1,10-\text{phen}]_\text{f} + [\text{C}]\\
&= [1,10-\text{phen}]_\text{f} + K[1,10-\text{phen}]_\text{f}[\text{MnO}_4^-]_\text{f}\\
[1,10-\text{phen}]_\text{f} &= [1,10-\text{phen}]_\text{T}/(1 + K[\text{MnO}_4^-]_\text{f}) \qquad (\text{A4})
\end{aligned}$$

Substituting Eqns A3 and A4 in Eqn.A2, we obtain

$$\text{rate} = \frac{kK[1,10-\text{phen}]_T[\text{MnO}_4{}^-]_T}{(1+K[1,10-\text{phen}]_f)(1+K[\text{MnO}_4{}^-]_f)} \quad \text{(A5)}$$

In view of the low concentration of permanganate used, the term $1 + K[Mn0_4{}^-]_f$ approximates to unity. Hence Eqn. A5 becomes

$$\text{rate} = kK[1,10-\text{phen}]_T[\text{MnO}_4{}^-]_T/(1+K[1,10-\text{phen}]_f)$$

$$\text{rate}/[\text{MnO}_4{}^-] = k_{\text{obs}}$$

$$= kK[1,10-\text{phen}]/(1+K[1,10-\text{phen}])$$

In the above equation, the subscripts T and f stands for total and free, respectively.