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Permanganate Oxidation of Benzimidazole and Benzthiazole Derivatives in Diluted Sulfuric Acid Medium: Kinetics and Mechanistic Aspects

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Abstract

The kinetics of oxidation of *N,N*-dimethyl-*N'*-(1*H*-benzimidazol-2-yl) formamidine (BIF) and *N,N*-dimethyl-*N'*-(benzthiazol-2-yl) formamidine (BTF) by permanganate ion in diluted sulfuric acid medium has been investigated spectrophotometrically at a constant ionic strength of 0.2 mol dm⁻³ and at a temperature of 25°C. The reactions of both organic reductants with permanganate ion showed a first order dependence with respect to [MnO₄⁻] and fractional-first order dependences with respect to both hydrogen ion and reductants concentrations. Increasing either ionic strength or dielectric constant of the reactions media had no significant effect on the oxidation rates. Manganese(II) ion was found to auto-catalyze the oxidation reactions with less than unit order dependences. The final oxidation products of BIF and BTF were identified by both spectroscopic and chemical tools as 2-aminobenzimidazole and 2-aminobenzthiazole, respectively, in addition to dimethylamine and carbon dioxide. Under comparable experimental conditions, the oxidation rate of BIF was higher than that of BTF. A plausible reactions mechanism has been suggested and the reaction constants involved in the mechanism have been evaluated. The activation parameters with respect to the second order rate constants have been computed and discussed.

1. Introduction

Benzimidazole and benzthiazole derivatives are significant heterocyclic organic compounds which have been a topic of interest for research for over a century because they have important biological activities and a broad spectrum of pharmaceutical and industrial applications. Benzimidazole structure is a part of the nucleotide portion of vitamin B₁₂ and the nucleus in some drugs such as proton pump inhibitors and anthelmintic agents. Benzimidazole and its derivatives are widely employed as intermediates in the synthesis of vital organic compounds including pharmaceuticals, agrochemicals, dyes, photographic chemicals, corrosion inhibitors, epoxy curing agents, adhesives and plastic modifiers. Benzthiazole derivatives have been developed for the

treatment of muscle relaxants, diabetes, tuberculosis, epilepsy, analgesia, inflammation and viral infection [1-3]. They were showed inhibitory effect against human laryngocarcinoma [4], anticancer [5, 6], antitumoractivity [7], fungicidal activities [8], antihelmintic [9], antiviral [10], and antimicrobial activity [11]. The benzimidazolyl- and benzthiazolyl-formamidine derivatives reacts with heterocyclic amines to give biologically active heterocyclic compounds [12]. On the other hand, The oxidative cleavage of formamidine derivatives is quite important, since the *N,N*-dialkyl-formamidine group is one of the most versatile protecting groups, especially in biosynthetic applications.

Oxidation reactions are considered as a significant field in organic synthesis. The permanganate ion is considered as the most important oxidizing agent in acidic, neutral and alkaline media. It is extensively used for oxidation of organic compounds [13-30], and it is an important source of mechanistic information. It is stable in neutral and slightly alkaline media, but it disproportionates in strongly alkaline media to form blue hypomanganate(V) and green manganate(VI), which are short-lived transient species [19-23].

Although the kinetics of oxidation of benzimidazolyl-formamidine (BIF) and benzthiazolyl-formamidine (BTF) derivatives by permanganate ions have been investigated in aqueous alkaline medium [16], there are no reports describing their oxidation kinetics by this oxidant in different media. A detailed study of the title reactions was therefore undertaken in order to understand the effect of the medium on the oxidation kinetics and mechanism.

2. Materials and Methods

2.1. 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. Stock solutions of benzimidazolyl-formamidine (BIF) and benzthiazolyl-formamidine (BTF) derivatives were prepared as described elsewhere [16]. A fresh solution of potassium permanganate was prepared and standardized as reported [31]. Sulfuric acid and sodium sulfate were used to provide the required acidity and ionic strength, respectively, and acetic acid was used to study the effect of dielectric constant.

2.2. Kinetic Measurements

All kinetic measurements were performed under pseudo-first order conditions where a large excess of BIF or BTF was present over permanganate ion. The ionic strength of the reactions media was adjusted to 0.2 mol dm^{-3} . The reactions temperature (25°C) was controlled to within $\pm 0.1^\circ\text{C}$. The solutions of permanganate oxidant and the mixtures containing BIF or BTF and sulfuric acid were separately thermostated for about 2 h. Then, the permanganate solution

was added to the mixtures. The progress of the reactions was followed by recording the decrease in the absorbance of permanganate ion as a function of time at its absorption maximum ($\lambda = 525 \text{ nm}$), whereas the other constituents of the reactions mixtures did not absorb significantly at this wavelength as shown in Fig. 1. The absorbance measurements were made in a thermostated Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. Time-resolved spectra during the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid solutions were illustrated in Fig. 1a, b, respectively. The Figure shows gradual disappearance of the permanganate band at $\lambda = 525 \text{ nm}$ as a result of its reduction by organic substrates.

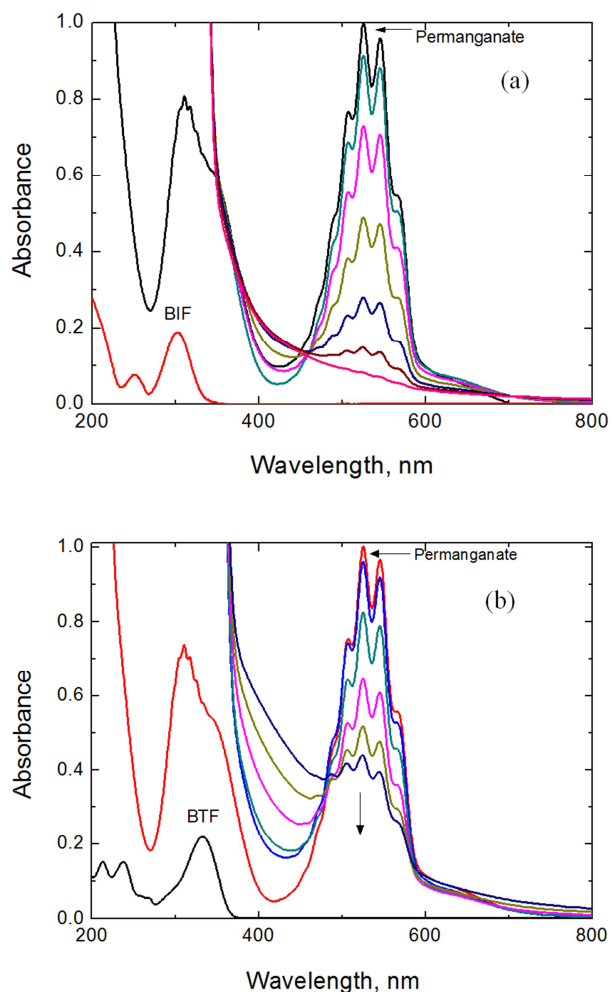


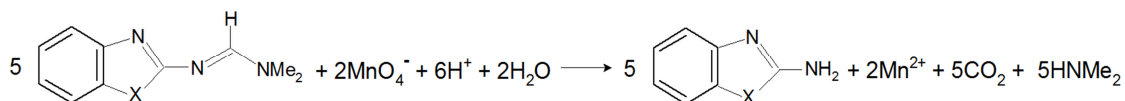
Figure 1. Time-resolved spectra in the oxidation of: (a) BIF, and (b) BTF by permanganate ion in diluted sulfuric acid medium; $[S] = 6.0 \times 10^{-3}$, $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{H}^+] = 5.0 \times 10^{-2}$, and $I = 0.2 \text{ mol dm}^{-3}$ at 25°C . Scanning time interval = 1 min.

3. Result and Discussion

3.1. Reactions Stoichiometry and Products Identification

Various sets of the reactions mixtures containing different initial concentrations of the reactants at constant $[\text{H}^+]$ and

ionic strength were equilibrated in dark. The unreacted permanganate concentration was estimated by both titrimetric and spectrophotometric techniques. The results indicate



where X = NH for benzimidazolyl-formamidine (BIF) and X = S for benzthiazolyl-formamidine (BTF).

The above stoichiometric equation is consistent with the results of products identification, where the final oxidation products of BIF and BTF were identified by both spectroscopic and chemical tools as described elsewhere [16, 32, 33] as 2-aminobenzimidazole and 2-aminobenzthiazole, respectively, in addition to dimethylamine and carbon dioxide. Dimethylamine was identified by spot tests [33] and carbon dioxide by lime water.

3.2. Reaction–Time Curves

The reactions–time curves throughout the entire range of reactions, illustrated in Figure 2, were found to consist of two stages. The initial stage was found to be slow (induction period), followed by an increase in the oxidation rates over longer times (auto-acceleration period). As the reactions are of catalytic nature, it obeys the rate expression: $(A_t - A_\infty) = B_0 e^{-k_s t} + P_0 e^{-k_f t}$ where k_s and k_f are the observed first order rate constants for the induction and auto-acceleration periods, respectively, A_t and A_∞ are the absorbance at times t and infinity; while B_0 and P_0 represent the absorbance change for the slow and fast reacting species, respectively. The rate constants were obtained by drawing a straight line through the slow-time linear portion (k_s) of the first order plot and extrapolating the time back to zero time (B_0). The rate of oxidation for the auto-acceleration period, k_f , was obtained from plots of the form: $\ln[(A_t - A_\infty) - (A_\infty - A_t)] - t$ where the quantity $(A_t - A_\infty)$ represents the experimental point and $(A_\infty - A_t)$ is the extrapolated one at time t [34]. The values of k_s and k_f were calculated by the least-squares method and were reproducible to within 3-4%. The orders of reactions with respect to the reactants were determined from the slopes of the $\log k_s$ versus \log (Conc.) plots by varying the concentrations of the reductants and acid, in turn, while keeping other conditions constant.

3.3. Dependence of the Oxidation Rates on $[\text{MnO}_4^-]$

The effect of permanganate ion oxidant was studied by varying its initial concentration in the range of $(1.0 - 8.0) \times 10^{-4} \text{ mol dm}^{-3}$ at constant concentrations of both reductants and sulfuric acid, and at fixed ionic strength and temperature. The values of k_s were found to be almost constant, Table 1, indicating first order dependence with respect to $[\text{MnO}_4^-]$.

consumption of two moles permanganate ions for five moles of BIF or BTF to yield the final oxidation products as shown in the following equation,

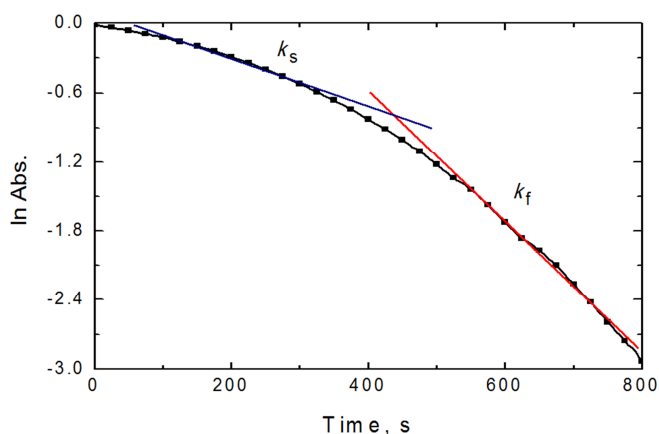


Figure 2. Reaction-time curve in the oxidation of BTF by permanganate ion in diluted sulfuric acid medium. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{BTF}] = 6.0 \times 10^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2}$, and $I = 0.2 \text{ mol dm}^{-3}$ at 25 °C.

3.4. Dependence of the Oxidation Rates on $[\text{S}]$

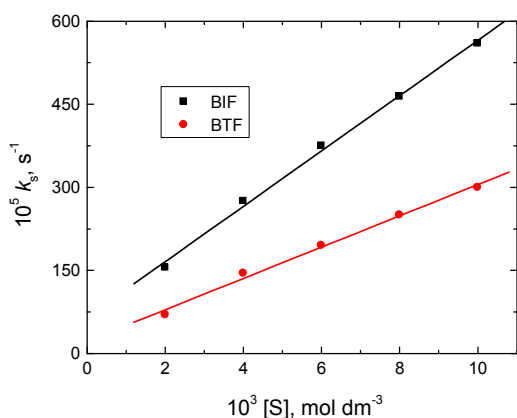
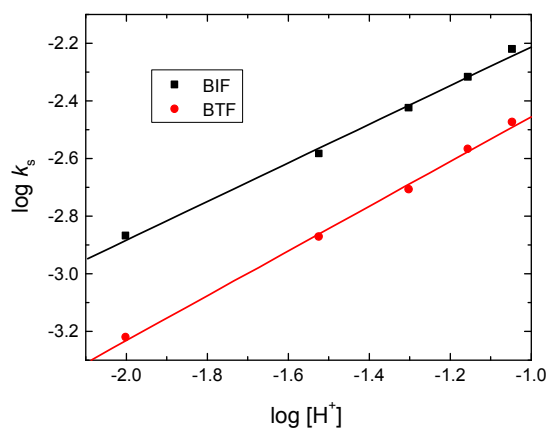
The reductants BIF and BTF (abbreviated by S) were varied in the concentration range $(2.0 - 10.0) \times 10^{-3} \text{ mol dm}^{-3}$, at constant concentrations of permanganate ion and acid, and at constant ionic strength and temperature. It was observed that k_s increased with increasing reductants concentrations as listed in Table 1. The plots of k_s versus $[\text{BIF}]$ and $[\text{BTF}]$ were linear with positive intercepts as shown in Figure 3 confirming the fractional-first order dependences with respect to reductants concentrations.

3.5. Dependence of the Oxidation Rates on $[\text{H}^+]$

In order to clarify the effect of $[\text{H}^+]$ on the oxidation rates to elucidate the oxidation mechanism, kinetic runs were performed at different hydrogen ion concentrations in the range of $(1.0 - 10.0) \times 10^{-2} \text{ mol dm}^{-3}$ at constant other conditions. Increasing acid concentration was found to accelerate the oxidation rates, suggesting that the oxidation reactions were acid-catalyzed. Under our experimental conditions, the plots of $\log k_s$ versus $\log [\text{H}^+]$ were linear with slopes of 0.71 and 0.79 for BIF and BTF, respectively (Fig. 4) confirming that the orders of the reactions with respect to $[\text{H}^+]$ were fractional-first.

Table 1. Effect of variation of $[MnO_4^-]$, $[S]$, $[H^+]$ and I on the observed first order rate constants (k_s) in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium.

$10^4 [MnO_4^-]$ (mol dm ⁻³)	$10^3 [S]$ (mol dm ⁻³)	$10^2 [H^+]$ (mol dm ⁻³)	I (mol dm ⁻³)	$10^5 k_s$ (s ⁻¹)	
				BIF	BTF
1.0	6.0	5.0	0.2	377.1	196.0
2.0	6.0	5.0	0.2	363.9	193.2
4.0	6.0	5.0	0.2	373.8	195.4
6.0	6.0	5.0	0.2	381.0	188.9
8.0	6.0	5.0	0.2	384.1	201.8
4.0	2.0	5.0	0.2	154.9	69.4
4.0	4.0	5.0	0.2	275.0	145.3
4.0	6.0	5.0	0.2	373.8	195.4
4.0	8.0	5.0	0.2	464.3	250.1
4.0	10.0	5.0	0.2	559.7	297.4
4.0	6.0	1.0	0.2	135.6	58.9
4.0	6.0	3.0	0.2	260.3	134.1
4.0	6.0	5.0	0.2	373.8	195.4
4.0	6.0	7.0	0.2	478.6	269.8
4.0	6.0	9.0	0.2	593.9	335.5
4.0	6.0	5.0	0.2	373.8	195.4
4.0	6.0	5.0	0.3	383.1	191.6
4.0	6.0	5.0	0.4	366.0	201.7
4.0	6.0	5.0	0.5	371.4	198.3
4.0	6.0	5.0	0.6	364.3	183.7

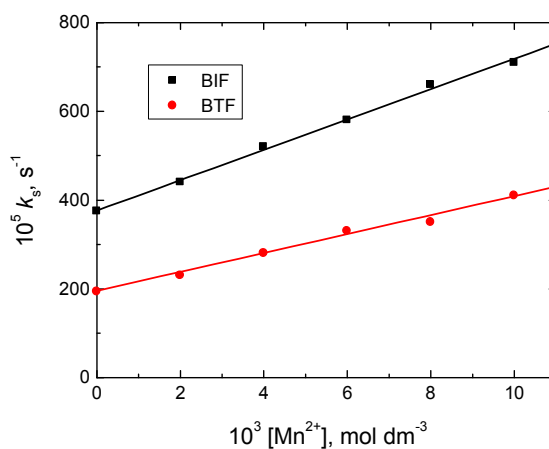
Experimental error $\pm 3\%$ **Figure 3.** Effect of reductants concentration, $[S]$, on the observed first order rate constant of the slow stage (k_s) in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[H^+] = 5.0 \times 10^{-2}$ and $I = 0.2$ mol dm⁻³ at 25°C.**Figure 4.** Plots of $\log k_s$ versus $\log [H^+]$ in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[S] = 6.0 \times 10^{-3}$ and $I = 0.2$ mol dm⁻³ at 25°C.

3.6. Effect of Ionic Strength and Dielectric Constant

The ionic strength was varied from 0.2 to 0.6 mol dm⁻³ using sodium sulfate at constant concentrations of other reactants and temperature. Increasing the ionic strength had a negligible effect on the oxidation rates as listed in Table 1. Furthermore, at constant concentrations of reactants and with other conditions constant, the concentration of acetic acid was varied from 0% to 40% (v/v) in the reactions media. Changing the dielectric constant of the media did not have any significant effect on the oxidation rates.

3.7. Dependence of the Oxidation Rates on $[Mn^{II}]$

The effect of manganese(II) ion, as one of the oxidation products, on the oxidation rates was examined by addition of

**Figure 5.** Effect of added $[Mn^{II}]$ on the rates of oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[MnO_4^-] = 4.0 \times 10^{-4}$, $[S] = 6.0 \times 10^{-3}$, $[H^+] = 5.0 \times 10^{-2}$ and $I = 0.2$ mol dm⁻³ at 25°C.

different concentrations of $\text{Mn}^{\text{II}}\text{SO}_4$ in the range of at fixed other conditions. The experimental observations indicated that the oxidation rates increased with increasing $[\text{Mn}^{2+}]$ with a complete disappearance of the induction period and the orders with respect to $[\text{Mn}^{2+}]$ were less than unity, as shown in Figure 5.

3.8. Effect of Temperature

The rates of oxidation reactions of both organic reductants were measured at five different temperatures in the range of 15 - 35°C at constant concentrations of the reactants and other conditions being constant. The results indicate that the rate constants increased with rise in temperature. The activation parameters of the second order rate constant (k_2) are calculated using Eyring and Arrhenius equations and are listed in Table 2.

Table 2. Activation parameters of the second order rate constants (k_2) in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{S}] = 6.0 \times 10^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2}$ and $I = 0.2 \text{ mol dm}^{-3}$ at 25°C.

Organic Reductant	ΔS^\ddagger J mol ⁻¹ K ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔG^\ddagger_{298} kJ mol ⁻¹	E_a^\ddagger kJ mol ⁻¹
BIF	-88.91	29.05	55.45	31.77
BTF	-107.03	32.71	64.60	35.01

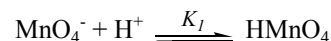
3.9. Polymerization Tests

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

3.10. Reaction Mechanism

Permanganate ion in various media provides excellent results when used in oxidation processes. Manganese(VII) is reduced to Mn^{II} during the oxidation reactions via many manganese species having different oxidation states such as Mn^{VI} , Mn^{V} , Mn^{IV} and Mn^{III} . The appearance of these intermediate oxidation states depends on the reaction conditions and the type of substrate. It was reported [35] that reduction of permanganate ion in an acidic medium gives either Mn^{IV} or Mn^{II} , the reduction potential of the $\text{Mn}^{\text{VII}}/\text{Mn}^{\text{IV}}$ couple is 1.695 V and that of the $\text{Mn}^{\text{VII}}/\text{Mn}^{\text{II}}$ couple is 1.51 V. 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 [36]. Oxidation reactions involving permanganate ion as an oxidant are suggested [13-24] to proceed throughout intermediate complex formation between oxidant and reductant. The formation of manganate(VI) and/or hypomanganate(V) short-lived intermediates may be confirmed by the change in the color of

the solution mixture as the reaction proceeded from purple-pink, Mn^{VII} , to blue, Mn^{V} , to green, Mn^{VI} . The failure to detect Mn^{V} , absence of an absorption maximum around $\lambda = 700 \text{ nm}$, may be interpreted by its extreme short lifetime and undergoing a rapid disproportionation [21, 37]. Also, the enhancement of the reaction rate with increasing acid concentration and the chemistry of potassium permanganate suggest [38, 39] formation of a more powerful oxidant, namely permanganic acid, by the equilibrium:



where K_1 is the protonation constant of permanganate ion. The protonation of permanganate ion shifts the $\text{Mn}^{\text{VII}}/\text{Mn}^{\text{VI}}$ couple to a more positive value (+1.3 V), which makes HMnO_4 a stronger oxidizing agent than MnO_4^- [39].

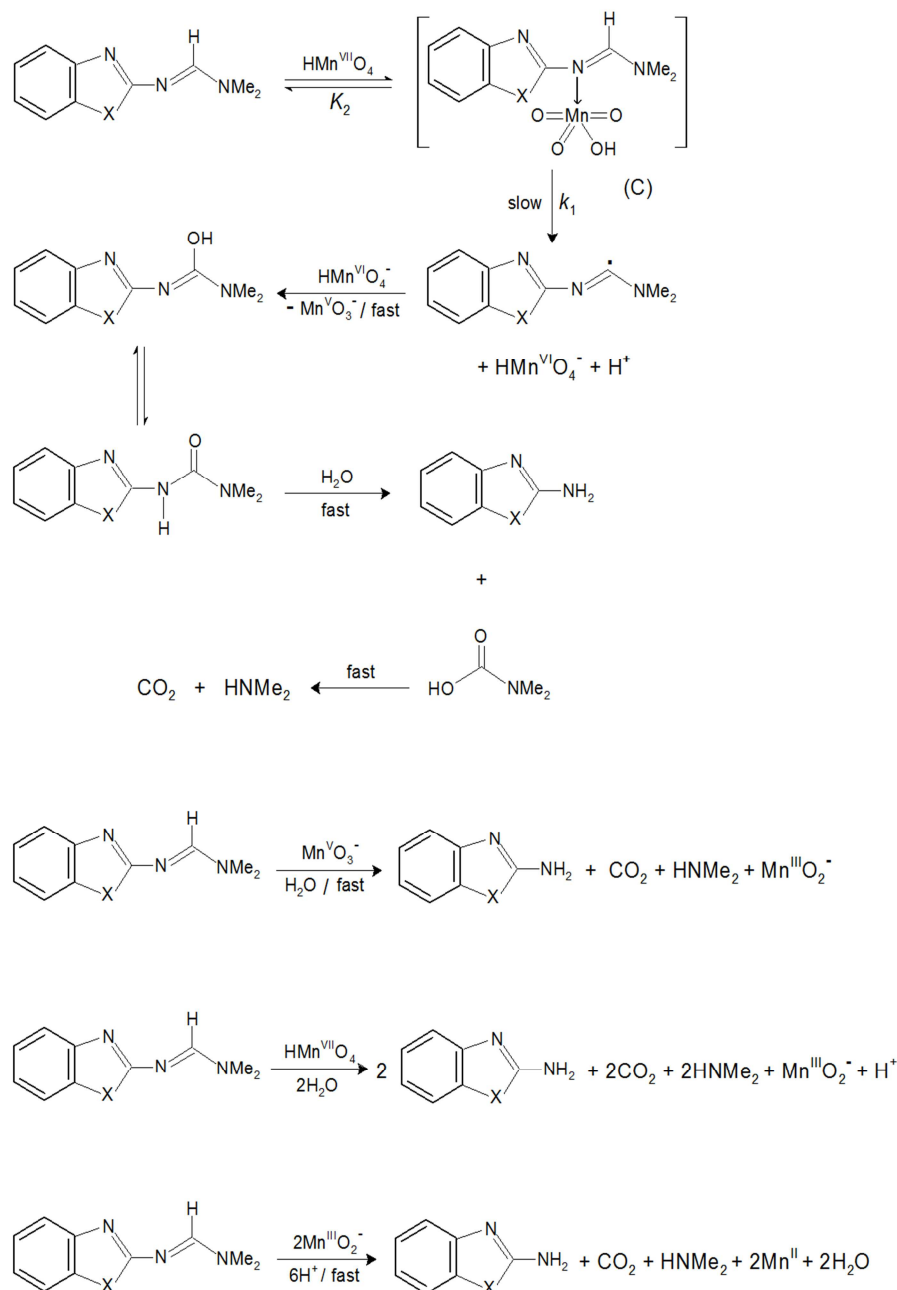
The present reactions between the investigated organic reductants (BIF and BTF) and permanganate ion in diluted sulfuric acid medium have a stoichiometry of 5: 2 (reductant: permanganate) with a first order dependence on $[\text{MnO}_4^-]$ and fractional-first order dependences with respect to both $[\text{H}^+]$ and [reductant]. The fractional-first order dependences on $[\text{H}^+]$ suggests protonation of permanganate ion to form a more powerful oxidant (permanganic acid) in the first step of the suggested mechanism. Also, the less-than-unit order dependences with respect to reductants concentrations suggests formation of intermediate complexes between reductants and permanganate ion in the pre-equilibrium step. The kinetic evidence for complexes formation was obtained from the plots of $1/k_s$ versus $1/[\text{S}]$ which they were found to be linear with positive intercepts on $1/[\text{S}]$ axes as shown in Figure 6, similar to the well-known Michaelis–Menten mechanism for enzyme–substrate reactions [40]. On the other hand, the negligible effects of both ionic strength and dielectric constant of the reactions media on the oxidation rates indicate that the reactions occur between two neutral molecules [41, 42], i.e. between organic reductant and permanganic acid.

In view of the above arguments, the following reactions mechanism, Scheme 1, can be suggested. The mechanism involves attack of the powerful permanganic acid on one mole of organic reductant in a pre-equilibrium step to give an intermediate complex (C). The cleavage of such complex leads to formation of a free radical derived from organic reductant and an intermediate Mn^{VI} species. Such intermediate is rapidly attacked by manganate(VI) ion to yield the corresponding secondary alcohol, as an intermediate product, and Mn^{V} species. The intermediate product is rapidly hydrolyzed to give the final oxidation products. In a further fast step, the intermediate Mn^{V} being very active and unstable reacts with another organic reductant to yield again the final oxidation products and an intermediate Mn^{III} species. This step is followed by reactions between two molecules of organic reductants and one molecule of permanganic acid giving other oxidation products and another Mn^{III} species. The last step is the reaction between the fifth molecule of organic reductant and two produced

Mn^{III} species leading to formation of the oxidation products of organic reductant and Mn^{II} as the final oxidation product of permanganate, satisfying the observed reactions stoichiometry.

On the other hand, increasing the oxidation rates and disappearance of the induction period upon increasing added Mn^{II} ion may suggest that Mn^{III} and/or Mn^{IV} are the sole

oxidants throughout the auto-acceleration final stage. However, it is difficult to decide whether Mn^{III} or Mn^{IV} was the reactive species in the auto-acceleration period. However, in similar redox reactions involving MnO_4^- as an oxidant, the continuous increase in the oxidation rate with increasing added Mn^{II} in addition to formation of free radicals suggested that Mn^{III} is the more predominant ion [43].



Scheme 1. Mechanism of oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium.

According to the suggested mechanism, the relationship between the oxidation rate and the oxidant, $[MnO_4^-]$, reductant, $[S]$, and hydrogen ion, $[H^+]$, concentrations was derived (see Appendix A) and gave the following equation:

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

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

$$\text{Rate} = \frac{-d[\text{MnO}_4^-]}{dt} = k_s[\text{MnO}_4^-] \quad (2)$$

Comparing Eqs. (1) and (2) and rearrangement gives the following relationship:

$$\frac{1}{k_s} = \left(\frac{1 + K_1[\text{H}^+]}{k_1 K_1 K_2 [\text{H}^+]} \right) \frac{1}{[\text{S}]} + \frac{1}{k_1} \quad (3)$$

$$\frac{1}{k_s} = \left(\frac{1}{k_1 K_1 K_2 [\text{S}]} \right) \frac{1}{[\text{H}^+]} + \left(\frac{1}{k_1 K_2 [\text{S}]} + \frac{1}{k_1} \right) \quad (4)$$

According to Eqs. (3) and (4), other conditions being constant, plots of $1/k_s$ versus $1/[\text{S}]$ at constant $[\text{H}^+]$ and $1/k_s$ versus $1/[\text{H}^+]$ at constant $[\text{S}]$ should be linear with positive intercepts on the $1/k_s$ axes and are indeed found to be so as shown in Figures 6 and 7, respectively. The slopes and intercepts of such plots lead to calculation of the values of k_1 , K_1 and K_2 as listed in Table 3.

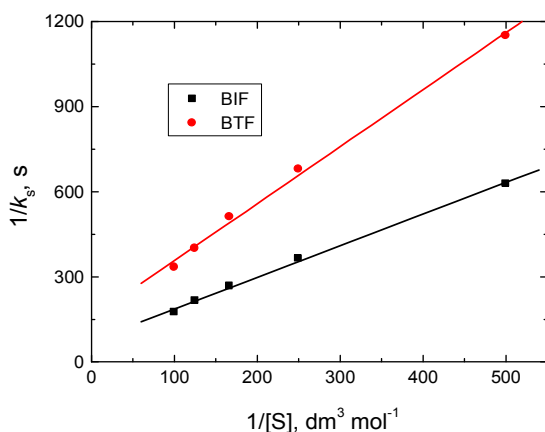


Figure 6. Verification of equation (3) in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{H}^+] = 5.0 \times 10^{-2}$ and $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

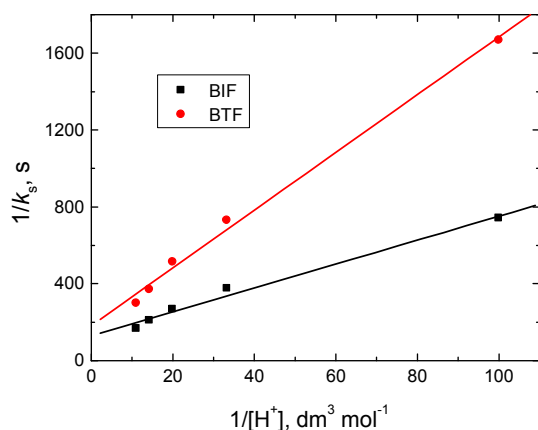


Figure 7. Verification of equation (4) in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{S}] = 6.0 \times 10^{-3}$ and $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

Table 3. Values of k_1 , K_1 and K_2 in the oxidation of BIF and BTF by permanganate ion in diluted sulfuric acid medium. $[\text{MnO}_4^-] = 4.0 \times 10^{-4}$, $[\text{S}] = 6.0 \times 10^{-3}$, $[\text{H}^+] = 5.0 \times 10^{-2}$ and $I = 0.2 \text{ mol dm}^{-3}$ at 25°C .

Organic Reductant	$10^3 k \text{ s}^{-1}$	$K_1 \text{ dm}^3 \text{ mol}^{-1}$	$K_2 \text{ dm}^3 \text{ mol}^{-1}$
BIF	13.31	13.78	145.63
BTF	8.11	7.08	272.14

The activation parameters listed in Table 2 may be interpreted as follows. The obtained large negative values of ΔS^\ddagger suggest compactness of the formed complexes and such complexes are more ordered than the reactants due to loss of degrees of freedom [44, 45]. Also, the obtained values of ΔS^\ddagger are within the range of radical reactions. The positive values of both ΔH^\ddagger and ΔG^\ddagger confirm endothermic formation of the intermediate complexes and their non-spontaneities, respectively.

4. Conclusion

The kinetics of oxidation of *N,N*-dimethyl-*N'*-(1*H*-benzimidazol-2-yl) formamidine (BIF) and *N,N*-dimethyl-*N'*-(benzthiazol-2-yl) formamidine (BTF) by permanganate ion in diluted sulfuric acid medium has been investigated. The final oxidation products of BIF and BTF were identified as 2-aminobenzimidazole and 2-aminobenzthiazole, respectively, in addition to dimethylamine and carbon dioxide. Under comparable experimental conditions, the oxidation rate of BIF was higher than that of BTF. A plausible reactions mechanism has been suggested and the activation parameters have been computed and discussed.

Appendix A

According to the suggested mechanism,

$$\text{Rate} = k_1[\text{C}] \quad (\text{A1})$$

$$K_1 = \frac{[\text{HMnO}_4]}{[\text{MnO}_4^-][\text{H}^+]} \quad (\text{A2})$$

Therefore,

$$[\text{HMnO}_4] = K_1[\text{MnO}_4^-][\text{H}^+] \quad (\text{A3})$$

From reaction (4),

$$K_2 = \frac{[\text{C}]}{[\text{S}][\text{HMnO}_4]} \quad (\text{A4})$$

Therefore,

$$[\text{C}] = K_2[\text{S}][\text{HMnO}_4] \quad (\text{A5})$$

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

$$[\text{C}] = K_1 K_2 [\text{S}][\text{H}^+][\text{MnO}_4^-] \quad (\text{A6})$$

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

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

The total concentration of the reductants (S) is given by

$$[S]_T = [S]_F + [C] \quad (A8)$$

where $[S]_T$ and $[S]_F$ stand for total and free concentrations of the substrate.

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

$$[S]_T = [S]_F + K_1 K_2 [S]_F [H^+] [MnO_4^-] \quad (A9)$$

$$[S]_T = [S]_F (1 + K_1 K_2 [H^+] [MnO_4^-]) \quad (A10)$$

Therefore,

$$[S]_F = \frac{[S]_T}{1 + K_1 K_2 [H^+] [MnO_4^-]} \quad (A11)$$

Similarly,

$$[MnO_4^-]_T = [MnO_4^-]_F + [HMnO_4] + [C] \quad (A12)$$

$$Rate = \frac{k_1 K_1 K_2 [S] [H^+] [MnO_4^-]}{(1 + K_1 K_2 [H^+] [MnO_4^-]) (1 + K_1 [MnO_4^-]) (1 + K_1 [H^+] + K_1 K_2 [S] [H^+])} \quad (A17)$$

In view of the low concentration of $[MnO_4^-]$ used, the first and second terms in the denominator of Eq. (A17) both approximate to unity. Therefore, Eq. (17) becomes

$$Rate = \frac{k_1 K_1 K_2 [S] [H^+] [MnO_4^-]}{1 + K_1 [H^+] + K_1 K_2 [S] [H^+]} \quad (A18)$$

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

$$Rate = \frac{-d[MnO_4^-]}{dt} = k_s [MnO_4^-] \quad (A19)$$

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

$$k_s = \frac{k_1 K_1 K_2 [S] [H^+]}{1 + K_1 [H^+] + K_1 K_2 [S] [H^+]} \quad (A20)$$

and with rearrangement it becomes

$$\frac{1}{k_s} = \left(\frac{1 + K_1 [H^+]}{k_1 K_1 K_2 [S] [H^+]} \right) \frac{1}{[S]} + \frac{1}{k_1} \quad (A21)$$

$$\frac{1}{k_s} = \left(\frac{1}{k_1 K_1 K_2 [S]} \right) \frac{1}{[H^+]} + \left(\frac{1}{k_1 K_2 [S]} + \frac{1}{k_1} \right) \quad (A22)$$

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

$$[MnO_4^-]_T = [MnO_4^-]_F + K_1 [MnO_4^-]_F [H^+] + K_1 K_2 [S] [H^+] [MnO_4^-]_F \quad (A13)$$

$$[MnO_4^-]_F = \frac{[MnO_4^-]_T}{1 + K_1 [H^+] + K_1 K_2 [S] [H^+]} \quad (A14)$$

and

$$[H^+]_T = [H^+]_F + [HMnO_4] \quad (A15)$$

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

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

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