



Oxidation of inorganic compounds by aqueous permanganate: Kinetics and initial electron transfer steps



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ABSTRACT

In this study, the kinetics of the reactions between aqueous permanganate (Mn(VII)) and selected inorganic compounds (e.g. KSCN, NaNO₂, Na₂SO₃, Na₂S₂O₃, KI, N₂H₄, H₂O₂, and NH₂OH) were investigated in aqueous solutions at pH 5–9 with excess pyrophosphate (L) by detecting the decay of Mn(VII) using a stopped-flow technique. With excess L, soluble Mn(III)L rather than MnO₂ was generated, which had negligible interference on examining the change of the absorbance of Mn(VII) at 525 nm (~45 M⁻¹ cm⁻¹ for Mn(III)L vs 2500 M⁻¹ cm⁻¹ for Mn(VII)). The reactions of Mn(VII) with Na₂SO₃, Na₂S₂O₃, KSCN, NaNO₂, and KI (referred to as S_A) exhibited second-order kinetics. Comparatively, the reactions of Mn(VII) with N₂H₄, H₂O₂, and NH₂OH (referred to as S_B) showed two-phase kinetics (i.e., an initial lag phase and a secondary fast phase), and the second-order rate constants (k_1 , M⁻¹ s⁻¹) were calculated in the initial phase. In the second phase, Mn(III)L reacted with S_B producing Mn(II), and then Mn(II) reacted fast with Mn(VII) producing Mn(III)L. The kinetics of the reaction between Mn(II) and Mn(VII) with excess L at pH 4–9 were examined and the loss rate of Mn(VII) increased with increasing pH value. The species-specific second-order rate constants (k_{1i} , M⁻¹ s⁻¹) for the reactions of Mn(VII) with inorganic compounds were determined by the experimental k_1 values. Furthermore, a linear free energy relationship (LFER) was found ($\log(k_{1i}) = 2.86 - 1.90E_{(2)}$) between $\log k_{1i}$ and 2-e⁻ reduction potentials for inorganic species (i.e., SO₃²⁻, S₂O₃²⁻, SCN⁻, H₂O₂, NH₂OH, I⁻, and N₂H₄) while only NO₂⁻ showed 1-e⁻ transfer process, indicating highly active aqueous manganese intermediates (Mn(V) and Mn(VI)) formed in situ upon Mn(VII) reduction.

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1. Introduction

Permanganate (Mn(VII)), a well-known chemical oxidant, has been paid more attention during water treatment in surface water to control odor/taste, algal toxins, and the formation of disinfection byproducts due to its wide reactivity with electron-rich organic moieties such as olefins and phenols as well as its properties of low cost, ease of handling, and stability [1–10]. In addition, Mn(VII) can also be used in the in situ chemical oxidation (ISCO) to remediate polluted groundwater with organic (e.g., trichloroethene, tetrachloroethene, and methyl *t*-butyl ether) and inorganic contaminants (e.g., arsenite) [11,12].

The kinetics of the reactions between Mn(VII) and organic compounds have already been widely studied, nevertheless, there was little information for the reactions between Mn(VII) and inorganic

compounds [13–16]. Since many types of inorganic compounds exist in natural waters, the reactions of Mn(VII) with inorganic compounds are also important in the application of Mn(VII) oxidation. Hence, the kinetics of the oxidation of several inorganic ions by Mn(VII) were studied in this article, including compounds of sulfur (SO₃²⁻, S₂O₃²⁻, SCN⁻), nitrogen (NH₂OH, NO₂⁻), oxygen (H₂O₂), metal (manganese(II), arsenite(III)), and halogen (I⁻). In drinking water treatment, the reactions of H₂O₂, NO₂⁻, I⁻, and manganese(II) are of interest. NO₂⁻ is a relevant environmental factor in natural waters [17,18]. Up to now, the kinetics of the reaction between Mn(VII) and nitrite were only studied at acidic pH [19], therefore, the kinetic study at neutral pH value should also be examined. During the oxidation of I⁻ by Mn(VII), iodinated disinfection byproducts (IDPBs) could be produced [20,21], hence, this reaction kinetics were very important. Though Van Benschoten et al. studied the kinetics of the reaction between Mn(VII) and Mn(II) [22], no kinetics were examined in the presence of complexing ligands. Also, a previous study showed the formation of soluble

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Mn(III) by mixing Mn(VII) and Mn(II) with excess ligands [23], hence, these kinetics were deserved to be studied. SCN^- is widely found in mining wastewater, and its toxicity include the inhibition of enzymes and the danger in mammalian blood [24,25]. No information about the kinetics of the reaction between Mn(VII) and SCN^- was found, but they are important to be studied. A stock solution of colloidal manganese dioxide was prepared according to the fast reaction between Mn(VII) and $\text{S}_2\text{O}_3^{2-}$ [26], but little information on the rate constants were reported. NH_2OH is always used as the common quenching agent in oxidation process, and also acts as an intermediate product formed during nitrification and ammonium oxidation in natural waters [27,28]. Nevertheless, this kinetics were rarely studied yet. Waldemer et al. [12] reported that to examine the kinetics of Mn(VII) oxidation, manganese products MnO_2 could flocculate into particles, hence, excess phosphate were dosed to prevent the interference. However, the molar absorptivity of MnO_2 with phosphate was different in different conditions. Therefore, a novel method to examine this kinetics is also essential to be developed.

To understand the mechanisms of one-electron or two-electron transfer process in ferrate (Fe(VI)) oxidation, the obtained rate constants for the reactions of Fe(VI) with inorganic compounds were correlated with reduction potentials [29–40]. By this manner, high oxidation states of iron, Fe(V) and Fe(IV) , have been postulated as intermediates involved in Fe(VI) oxidation. Similarly, this method may also be used to speculate the possible manganese intermediates in the oxidation of inorganic compounds by Mn(VII).

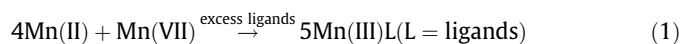
This study was conducted to examine the reaction kinetics of Mn(VII) with inorganic compounds over a pH range of 5–9. To this end, a method to study these kinetics was developed to avoid the interference of MnO_2 by adding excess pyrophosphate (L) first. EDTA and phosphate were also selected to compare these kinetics with pyrophosphate. Then, the second-order rate constants, k ($\text{M}^{-1} \text{s}^{-1}$), for the oxidation of inorganic compounds by Mn(VII) were obtained. Finally, correlations of $\log k$ and reduction potential were used to detect the mechanism of one-electron or two-electron initial transfer process in Mn(VII) oxidation. In addition, this paper offered some useful information for a better understanding of the fates of some high oxidation states of Mn intermediates, Mn(VI) or Mn(V), involved in Mn(VII) oxidation.

2. Materials and methods

2.1. Materials

Deionized water (18.2 $\text{M}\Omega \text{ cm}$) was obtained by purifying distilled water through a Millipore Milli-Q water purification system. Selected inorganic compounds (Sigma-Aldrich) including Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, KSCN, N_2H_4 , NaNO_2 , H_2O_2 , NH_2OH , KI, and MnCl_2 were analytical reagent grade or better without further purification. Other chemicals of analytical grade or higher were purchased from Sinopharm Chemical Reagent Co., Ltd.

Weighed amounts of potassium permanganate crystals were dissolved to make a stock solution, which were standardized spectrophotometrically by 525 nm method ($\epsilon = 2500 \text{ M}^{-1} \text{ cm}^{-1}$). Solutions of Mn(III) complexes were synthesized according to the reaction between Mn(VII) and Mn(II) in excess ligands (Eq. (1)) [23]. Mn(VII) was quickly added to the mixed solutions containing desirable concentrations of Mn(II) and excess ligands (solutions of ligands were adjusted to the desirable pH value with HClO_4 or NaOH before use) following the suggestion of Klewicki et al. [23] by the stoichiometric reaction between Mn(VII) and Mn(II) (Eq. (1)). Mn(III) solutions should be quickly used to avoid their disproportionation.



2.2. Kinetic experiments

All the experiments were conducted over the pH range of 5–9 at 25 ± 1 °C. The following buffers (10 mM) were used: sodium acetate for pH 5–6, and sodium borate for pH 7–9. Although the buffering capacities were weak for pH 6 and 7, pH values changed negligibly during the reactions. 4-morpholinepropanesulfonic acid (MOPS) with much stronger buffering capacity for pH 6 and 7 was not used due to its interference with Mn(VII) reactions.

The reaction kinetics of Mn(VII) with inorganic compounds were investigated by measuring the decrease in absorbance at 525 nm of Mn(VII) with a stopped-flow spectrophotometer in the presence of excess sodium pyrophosphate (1 mM), where the pseudo-first-order reaction conditions with inorganic compounds in excess (see Table S1) were maintained. Similarly, the kinetics of the reactions between Mn(III) complexed by pyrophosphate (Mn(III)L) and inorganic compounds were also studied by determining the decay of Mn(III)L using stopped-flow spectrophotometer, where the pseudo-first-order reaction conditions with inorganic compounds in excess were maintained. Comparatively, the reaction kinetics of inorganic compounds with Mn(VII) in the presence of excess of EDTA and phosphate were also examined following the same procedure as that in the case of pyrophosphate.

2.3. Analytical methods

The determination of UV–vis spectra was conducted on a Cary 300 spectrometer. A stopped-flow spectrophotometer (SX20, Applied Photophysics Ltd, U.K.) equipped with both photomultiplier tube (PMT) and photodiode array (PDA) detectors was used to carry out the kinetic studies.

3. Results and discussion

3.1. Method Development

The kinetics of the reactions between Mn(VII) and inorganic compounds were conducted by monitoring the decay of Mn(VII) at 525 nm using a stopped-flow spectrophotometer, where the pseudo-first-order reaction conditions with inorganic compounds in excess were maintained. As literature discussed previously [12], MnO_2 , as the reduction product of Mn(VII), has interference on measuring the absorbance of Mn(VII) at 525 nm. Although adding excess phosphate could inhibit aggregation of MnO_2 , the absorbance of MnO_2 at 525 nm also needed to be deducted. Molar absorption coefficient (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$) of differing types of MnO_2 might also change [12]. Hence, to eliminate the interference of the accumulation of MnO_2 formed in situ, excess pyrophosphate (i.e., L) was added into the reaction solutions, where Mn(III)L rather than MnO_2 was produced. Since the molar absorption coefficient of Mn(III)L at 525 nm was so low ($\sim 45 \text{ M}^{-1} \text{ cm}^{-1}$ for Mn(III)L versus $2500 \text{ M}^{-1} \text{ cm}^{-1}$ for Mn(VII)) [6], its contribution to the absorbance of Mn(VII) at 525 nm could be neglected.

3.2. Reactions of Mn(VII) with selected inorganic compounds

The reaction kinetics of Mn(VII) with inorganic compounds were conducted under pseudo-first-order conditions in the presence of excess pyrophosphate (i.e., L), where concentration of inorganic compounds were in excess compared to Mn(VII) (see Table S1 for more details). Figs. 1 and S1 show only one phase kinetics in the reactions of Mn(VII) with Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, KSCN,

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