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ABTS as an Electron Shuttle to Enhance the Oxidation Kinetics of Substituted Phenols by Aqueous Permanganate

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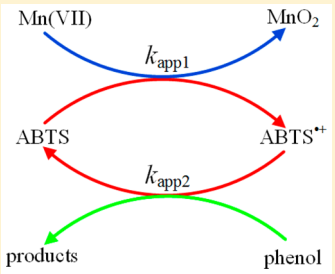
Supporting Information

ABSTRACT: In this study, it was, interestingly, found that 2,2′-azino-bis(3-ethylbenzothiazoline)-6-sulfonate (ABTS), a widely used electron shuttle, could greatly accelerate the oxidation of substituted phenols by potassium permanganate (Mn(VII)) in aqueous solutions at pH 5−9. This was attributed to the fact that these substituted phenols could be readily oxidized by the stable radical cation ($ABTS^{\bullet+}$), which was quickly produced from the oxidation of ABTS by Mn(VII). The reaction of Mn(VII) with ABTS exhibited second-order kinetics, with stoichiometries of ∼5:1 at pH 5−6 and ∼3:1 at pH 7−9, and the rate constants varied negligibly from pH 5 to 9 ($k = (9.44 \pm 0.21) \times 10^4\ M^{-1}\ s^{-1}$). Comparatively, the reaction of $ABTS^{\bullet+}$ with phenol showed biphasic kinetics. The second-order rate constants for the reactions of $ABTS^{\bullet+}$ with substituted phenols obtained in the initial phase were strongly affected by pH, and they were several orders of magnitude higher than those for the reactions of Mn(VII) with substituted phenols at each pH. Good Hammett-type correlations were found for the reactions of $ABTS^{\bullet+}$ with undissociated ($\log(k) = 2.82-4.31\sigma$) and dissociated phenols ($\log(k) = 7.29-5.90\sigma$). The stoichiometries of (2.2 ± 0.06):1 ($ABTS^{\bullet+}$ in excess) and (1.38 ± 0.18):1 (phenol in excess) were achieved in the reaction of $ABTS^{\bullet+}$ with phenol, but they exhibited no pH dependency.



INTRODUCTION

Over the past decades, permanganate (Mn(VII)) has received much more attention as a chemical oxidant to control odor and taste, algal toxins, and the formation of disinfection byproducts during water treatment due to the properties of ease of handling, stability, and low cost, as well as its wide reactivity with electron-rich organic moieties such as phenols and olefins.[1−10] In addition, Mn(VII) has also been applied in in-situ chemical oxidation (ISCO) to remediate contaminated groundwater and soil.[11]

Recently, it was found that manganese dioxide (MnO_2) formed in situ upon the decomposition of Mn(VII) could accelerate the reactions of Mn(VII) with phenols.[4,5] A surface catalytic mechanism was proposed to account for the observed promoting effect of MnO_2, where the formation of surface precursor complexes between organic pollutants and surface active sites of MnO_2 was involved.[4,5] In addition, Zhang et al. reported that ceria-supported ruthenium ($Ru(III)/CeO_2$), a heterogeneous catalyst, could enhance the oxidation of butylparaben by Mn(VII).[12] This was explained by the fact that Ru(III) was oxidized by Mn(VII) to produce reactive Ru(VI) and Ru(VII) intermediates, which could participate in butylparaben degradation. However, MnO_2 can act as a catalyst to enhance Mn(VII) oxidation only at an acidic pH, and Ru is a precious metal in spite of its effectiveness over a wide pH range.

In this study, we will present a novel and efficient oxidation process involving Mn(VII) with metal-free ABTS (2,2′-azino-bis(3-ethylbenzothiazoline)-6-sulfonate) as a catalyst over a wide pH range. In fact, ABTS as a simple synthetic electron shuttle has been widely used as a redox mediator in enzymatic catalysis (e.g., laccase).[13−16] A stable green radical, $ABTS^{\bullet+}$, once formed from laccase oxidation of ABTS, has much higher reactivity than laccase itself. For instance, several groups reported that ABTS could promote laccase oxidation of polycyclic aromatic hydrocarbons (e.g., anthracene, pyrene, phenanthrene, and benzo[a]-pyrene),[17−19] pentachlorophenol,[20] and hydroxy polychlorinated biphenyls.[21] Camarero et al. and Murugesan et al. demonstrated that this approach was also effective in paper-pulp-bleaching wastewater treatment.[22−24] Hence, it seems likely that ABTS can also serve as a catalyst in the oxidation of micropollutants by Mn(VII), where ABTS and $ABTS^{\bullet+}$ form a catalytic cycle.

This study was conducted to examine whether ABTS could act as a catalyst to promote the oxidation of substituted phenols by Mn(VII). To this end, the kinetics and stoichiometries of the reactions of Mn(VII) with ABTS, and $ABTS^{\bullet+}$ with substituted

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phenols were investigated at pH 5−9 (i.e., pH = 5, 6, 7, 8, and 9) first. Furthermore, the Hammett-type correlations were developed for the reactions of $ABTS^{\bullet+}$ with undissociated and dissociated phenols and compared with those of other water-treatment oxidants. Finally, the effects of trace levels of ABTS on the oxidation of substituted phenols by Mn(VII) as well as other oxidants (i.e., ferrate (Fe(VI)) and hypochlorous acid (HOCl)) were examined in synthetic and natural waters. In addition, detailed kinetic and mechanistic aspects for the reaction of Mn(VII) with ABTS, a model system for the initial one-electron transfer process, obtained in this study were expected to provide useful information for a better understanding of the fates of manganese intermediates involved in Mn(VII) oxidation, as did in the case of Fe(VI) by Lee et al.[25]

EXPERIMENTAL SECTION

Standards and Reagents. Phenol, 4-chlorophenol, 4-bromophenol, 4-carboxyphenol, 4-methylphenol, and 4-fluorophenol were all obtained from Sigma-Aldrich with a purity of 99%. Suwannee River Humic Acid (SRHA) was obtained from International Humic Substances Society. Other chemicals of analytical grade or higher were purchased from Sigma-Aldrich and Sinopharm Chemical Reagent Co., Ltd. Deionized water (18.2 MΩ·cm) was obtained by the passage of distilled water through a Millipore Milli-Q water purification system. A natural water sample was taken from Songhua River in Harbin, China (DOC = 6.4 mg C/L, alkalinity =190 mg/L as $CaCO_3$, and pH = 7.8). After filtering through the glass fiber filters of 0.7 μm nominal pore size (Whatman GF/F), this water was buffered to pH 8 with borate buffer (10 mM) and stored at 4 °C.[8]

Weighed amounts of potassium permanganate crystals were dissolved to make Mn(VII) stock solutions, which were standardized spectrophotometrically by the direct 525 nm method (ε = 2500 (M^{-1} cm^{-1})). Potassium ferrate (K_2FeO_4) with high purity was prepared by the method of Thompson et al.[26] Solid samples of K_2FeO_4 were dissolved in borate buffered solutions (pH ≈ 9.1) to make stock solutions of Fe(VI), which were determined by the direct 510 nm method (ε = 1150 (M^{-1} cm^{-1})) after filtration to remove ferric particulates.[27,28] Stock solutions of HOCl were prepared by diluting a commercial solution (5.2% active chlorine) and were determined by iodometry.[29] ABTS stock solutions were freshly prepared by dissolving ABTS solids into deionized water.[25,30,31] $ABTS^{\bullet+}$ stock solutions were freshly prepared following the suggestion of Re et al.[32] by the stoichiometric reaction between ABTS and potassium persulfate ($K_2S_2O_8$) and were standardized spectrophotometrically at 415 nm (ε = 34000 (M^{-1} cm^{-1})).[30,31]

Reaction Kinetics and Stoichiometries. All of the experiments were performed over the pH range of 5−9 (i.e., pH = 5, 6, 7, 8, and 9) at 25 ± 1 °C. The following buffers (10 mM) were used: sodium acetate for pH 5−6 (i.e., pH = 5 and 6), and sodium borate for pH 7−9 (i.e., pH = 7, 8, and 9). Although the buffering capacities were weak for pH 6 and 7, pH values changed negligibly during the reactions. MOPS and phosphate with much stronger buffering capacities for pH 6 and 7 were not used due to their interferences with Mn(VII) reactions.[4]

The reaction kinetics of Mn(VII) with ABTS were investigated by monitoring the formation of $ABTS^{\bullet+}$ at 415 nm with a stopped-flow spectrophotometer, where the pseudo-first-order reaction conditions with ABTS in excess were maintained. To eliminate the interference of the accumulation of MnO_2 formed in situ at pH 7−9, we added excess sodium pyrophosphate into the reaction solutions, where soluble Mn(III) rather than MnO_2 was formed.[33] The molar absorption coefficient of Mn(III)−pyrophosphate complex at 415 nm was so low (~50 (M^{-1} cm^{-1}) for Mn(III)−pyrophosphate versus 34 000 (M^{-1} cm^{-1}) for $ABTS^{\bullet+}$) that its contribution to the absorbance at 415 nm was negligible.[31] Similarly, the reaction kinetics of $ABTS^{\bullet+}$ with substituted phenols were examined at pH 5−9 (i.e., pH = 5, 6, 7, 8, and 9) by monitoring the decay of $ABTS^{\bullet+}$ at 415 nm with stopped-flow spectrophotometer, where the pseudo-first-order reaction conditions with substituted phenols in excess were maintained.

The stoichiometries for the reaction of Mn(VII) with ABTS at pH 5−9 (i.e., pH = 5, 6, 7, 8, and 9) were determined in the absence and presence of pyrophosphate by monitoring the production of $ABTS^{\bullet+}$ at 415 nm with a UV−vis spectrometer. Sufficient time was allowed for the reactions to reach completion (i.e., Mn(VII) was consumed completely). In the absence of pyrophosphate, $ABTS^{\bullet+}$ was detected after filtering through 0.45 μm glass fiber filters to eliminate the interference of MnO_2. Similar procedures were used to examine the stoichiometries for the reaction of $ABTS^{\bullet+}$ with phenol.

Further experiments were conducted to examine the effects of ABTS in trace levels on the oxidation kinetics of selected substituted phenols in synthetic or natural water by Mn(VII). Reactions were initiated by quickly spiking Mn(VII) into pH-buffered solutions containing one selected phenolic compound and ABTS at desired concentrations, where the pseudo-first-order reaction conditions were maintained with Mn(VII) in excess. Samples were collected periodically and quenched with ascorbic acid before high-performance liquid chromatography (HPLC) analysis. Comparatively, the effects of ABTS on the oxidation of phenol by Fe(VI) or HOCl in synthetic water were also examined following the same procedure as that in the case of Mn(VII).

All experiments were conducted in duplicates or triplicates, and the average data and their standard deviations were shown.

Analytical Methods. Phenols were determined using a HPLC equipped with a Waters symmetry C18 column, a Waters 717 autosampler, and a Waters 2487 dual λ detector. The measurement of UV−vis spectra was performed on a Cary 300 spectrometer. A stopped-flow spectrophotometer (SX20, Applied Photophysics Ltd.) equipped with both photodiode array (PDA) and photomultiplier tube (PMT) detectors was used to carry out the kinetic studies.

RESULTS AND DISCUSSION

$ABTS^{\bullet+}$ Formation in the Reaction of Mn(VII) with ABTS. *Stoichiometries.* The apparent stoichiometric relationships in the reaction of Mn(VII) with ABTS were determined by the ratio (r_1) of $ABTS^{\bullet+}$ produced ($\Delta ABTS^{\bullet+}$) to Mn(VII) consumed (ΔMn(VII)) over the wide pH range of 5−9 in the absence and presence of pyrophosphate, respectively.

(1). Without Pyrophosphate. In the absence of pyrophosphate, 5 μM Mn(VII) reacted with ABTS in excess (i.e., [ABTS] = 100−300 μM) yielding 25 μM and 15 μM $ABTS^{\bullet+}$ at pH 5−6 and pH 7−9, respectively. These data suggested that Mn(II) (i.e., aqua-Mn^{2+}) was the final manganese product at pH 5−6, while the colloidal MnO_2 product was formed at pH 7−9. The higher stoichiometries at pH 5−6 were mainly due to the fact that colloidal MnO_2 could readily oxidize ABTS, which was confirmed in the experiments (data were not shown).

The possible pathways for the generation of $ABTS^{\bullet+}$ from the reaction between Mn(VII) and ABTS are proposed. First, the

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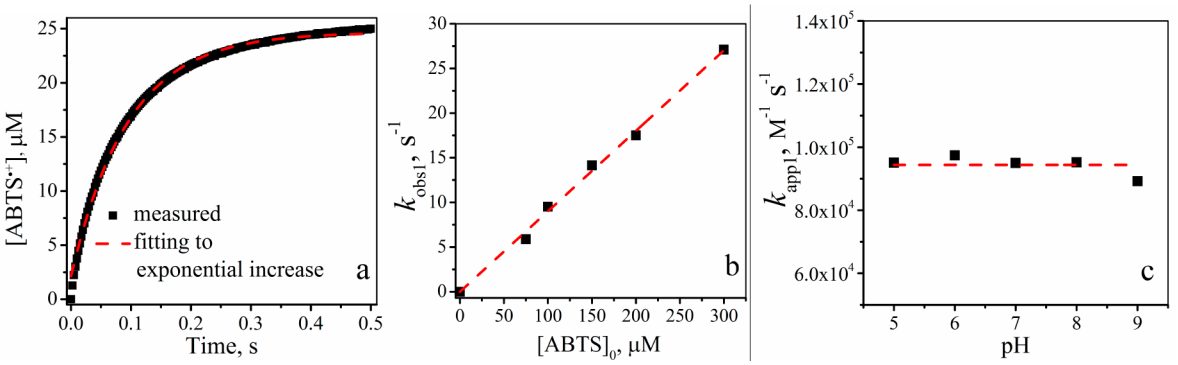

Figure 1. Formation of $ABTS^{\bullet+}$ (415 nm) from the reaction of Mn(VII) (5 μM) with ABTS (100 μM) at pH 5 (a), a linear plot of the pseudo-first-order rate constants (k_{obs1}) for the formation of $ABTS^{\bullet+}$ vs ABTS concentration at pH 5 (b), and the second-order rate constants (k_{app1}) for the reaction of Mn(VII) with ABTS over the pH range of 5−9 (c). The black symbols represent the experimental data, and the red dashed lines represent the model prediction.

oxidation of ABTS by Mn(VII) via a one-electron transfer process produces $ABTS^{\bullet+}$ and Mn(VI) (eq 1).

$$\mathrm{Mn(VII)} + \mathrm{ABTS} \xrightarrow{\mathrm{pH=5-9}} \mathrm{Mn(VI)} + \mathrm{ABTS}^{\bullet+} \quad (1)$$

Then, Mn(VI) may react with ABTS, forming Mn(V) (eq 2) or self-decay into Mn(V) and Mn(VII) (eq 3).[34−36]

$$\mathrm{Mn(VI)} + \mathrm{ABTS} \xrightarrow{\mathrm{pH=5-9}} \mathrm{Mn(V)} + \mathrm{ABTS}^{\bullet+} \quad (2)$$

$$2\mathrm{Mn(VI)} \xrightarrow{\mathrm{pH=5-9}} \mathrm{Mn(V)} + \mathrm{Mn(VII)} \quad (3)$$

Mn(V) may also participate in the oxidation of ABTS, producing $Mn(IV)_{aqua}$ (i.e., aqua-MnO^{2+}) (eq 4) or self-decompose into Mn(VI) and $Mn(IV)_{aqua}$ (eq 5).[37−39]

$$\mathrm{Mn(V)} + \mathrm{ABTS} \xrightarrow{\mathrm{pH=5-9}} \mathrm{Mn(IV)_{aqua}} + \mathrm{ABTS}^{\bullet+} \quad (4)$$

$$2\mathrm{Mn(V)} \xrightarrow{\mathrm{pH=5-9}} \mathrm{Mn(VI)} + \mathrm{Mn(IV)_{aqua}} \quad (5)$$

Then, $Mn(IV)_{aqua}$ hydrolyzes into colloidal MnO_2 quickly without a complexing ligand (eq 6).[39,40]

$$\mathrm{Mn(IV)_{aqua}} \xrightarrow[\mathrm{hydrolysis}]{\mathrm{pH=5-9}} \mathrm{MnO_2} \quad (6)$$

At acidic pH, colloidal MnO_2 can readily oxidize ABTS producing Mn(III) (i.e., aqua-Mn^{3+}) (eq 7).[40]

$$\mathrm{MnO_2} + \mathrm{ABTS} \xrightarrow{\mathrm{pH=5,6}} \mathrm{Mn(III)} + \mathrm{ABTS}^{\bullet+} \quad (7)$$

Then, the intermediate product, Mn(III), reacts with ABTS, forming Mn(II) (eq 8) or disproportionates into Mn(II) and $Mn(IV)_{aqua}$ (eq 9).[33]

$$\mathrm{Mn(III)} + \mathrm{ABTS} \xrightarrow{\mathrm{pH=5,6}} \mathrm{Mn(II)} + \mathrm{ABTS}^{\bullet+} \quad (8)$$

$$2\mathrm{Mn(III)} \xrightarrow{\mathrm{pH=5,6}} \mathrm{Mn(II)} + \mathrm{Mn(IV)_{aqua}} \quad (9)$$

Thus, it is not difficult to understand that Mn(II) was generated as the final manganese product at acidic pH, while MnO_2 colloids were formed at neutral and alkaline pH.

(2). With Pyrophosphate (L). In the presence of pyrophosphate (i.e., 100 and 200 μM), the r_1 values were 5:1 and 4:1 at pH 5 and pH 6−9, respectively. These results indicated that Mn(II) (i.e., pyrophosphate-complexed Mn^{2+}) was the final manganese product at acidic pH 5, while the soluble Mn(III) (i.e., pyrophosphate-complexed Mn^{3+}) product was formed at pH 6−9.[33] The higher stoichiometry at pH 5 was mainly ascribed to the fact that soluble Mn(III) could readily oxidize ABTS (eq 10), which was also confirmed in the experiments (data were not shown).

$$\mathrm{Mn(III)} + \mathrm{ABTS} \xrightarrow[\mathrm{(L)}]{\mathrm{pH=5}} \mathrm{Mn(II)} + \mathrm{ABTS}^{\bullet+} \quad (10)$$

Soluble Mn(III) may be formed via a one-electron transfer process from $Mn(IV)_{complexed}$ (i.e., pyrophosphate-complexed MnO^{2+}) (eq 11).

$$\mathrm{Mn(IV)_{complexed}} + \mathrm{ABTS} \xrightarrow[\mathrm{L}]{\mathrm{pH=5-9}} \mathrm{Mn(III)} + \mathrm{ABTS}^{\bullet+} \quad (11)$$

It is reasonable that $Mn(IV)_{complexed}$ is generated in the presence of pyrophosphate (eq 12), which may retard the hydrolysis of $Mn(IV)_{aqua}$ into colloidal MnO_2.

$$\mathrm{Mn(IV)_{aqua}} \xrightarrow[\mathrm{L}]{\mathrm{pH=5-9}} \mathrm{Mn(IV)_{complexed}} \quad (12)$$

The possible occurrence of $Mn(IV)_{complexed}$ was consistent with the studies of von Gunten and Reisz et al.[38,39] These authors found that in the reaction of Mn(II) with ozone in distilled water, colloidal MnO_2 was observed without a complexing ligand, while Mn(VII) was generated with complexing ligands (e.g., polyphosphate and oxalate) via a complexed MnO^{2+} intermediate.[38,39] Hence, it can be rationalized by assuming that the oxidation of ABTS by $Mn(IV)_{complexed}$ is faster than its hydrolysis into nonreactive colloidal MnO_2. Pathways for the formation of $Mn(IV)_{aqua}$ in the reaction between Mn(VII) and ABTS in the presence of pyrophosphate are similar to those in the absence of pyrophosphate (eqs 1−5).

Comparatively, Lee et al. found that the stoichiometric factor (i.e., 1) of the reaction between Fe(VI) and ABTS was less than the theoretical one (i.e., 3).[25,31] This result was explained by the fact that Fe(V) formed upon one-electron reduction of Fe(VI) by ABTS self-decayed quickly (to Fe(III) and H_2O_2) rather than was involved in the formation of $ABTS^{\bullet+}$.[25] This finding was markedly different from the reaction between Mn(VII) and ABTS, where manganese intermediates, as the sequential one-electron equivalent reducing products of Mn(VII) by ABTS, all participated in the oxidation of ABTS.

Kinetics. Figure 1a typically shows the $ABTS^{\bullet+}$ production from the reaction of 5 μM Mn(VII) with 100 μM ABTS at pH 5 as a function of time. The kinetic data followed exponential rate law (red dashed line in Figure 1a), indicating that the reaction

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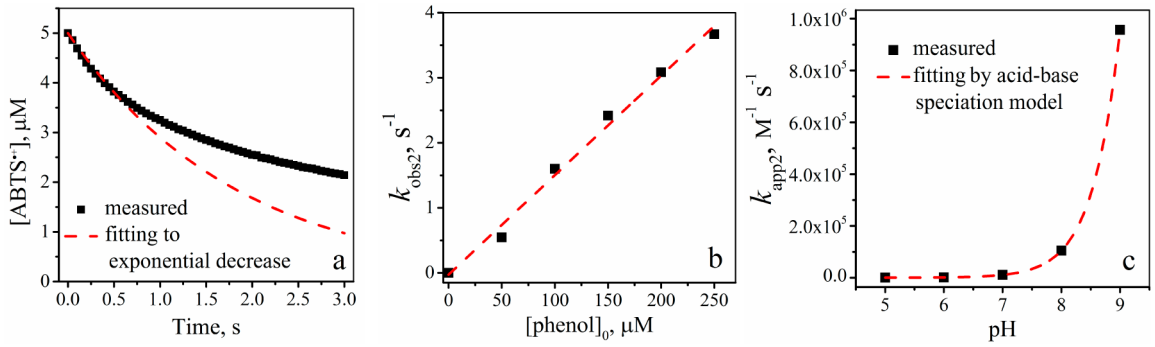

Figure 2. Decay of $ABTS^{\bullet+}$ (5 μM) in the presence of phenol (50 μM) at pH 7 (a), a linear plot of the pseudo-first-order rate constants (k_{obs2}) in the initial phase for the decay of $ABTS^{\bullet+}$ vs phenol concentration at pH 7 (b), and pH-dependent second-order rate constants (k_{app2}) for the reaction of $ABTS^{\bullet+}$ with phenol (c). The black symbols represent the experimental data, and the red dashed lines represent the model predictions.

was first-order with respect to the Mn(VII) concentration. Pseudo-first-order rate constants (k_{obs1}, s^{-1}) were calculated by the exponential regression (with the SX20 operating software) of $ABTS^{\bullet+}$ production kinetic curves according to Lee's method.[25] The k_{obs1} values were found to vary linearly with ABTS concentrations (75−300 μM) (Figure 1b), suggesting a first-order dependence on ABTS concentration. Hence, the reaction of Mn(VII) with ABTS could be described by the second-order kinetics (Text S1), with the apparent second-order rate constants (k_{app1}, M^{-1} s^{-1}) obtained by dividing the k_{obs1} value by ABTS concentration. As shown in Figure 1c, the k_{app1} value changed negligibly at pH 5−9 (~9.44×10^4 M^{-1} s^{-1}). Comparatively, Lee et al. found that the reaction of Fe(VI) with ABTS was also first-order with respect to each reactant but varied significantly over the pH range of 1.5−10.[25]

Reaction of $ABTS^{\bullet+}$ with Phenol. *Kinetics.* Figure 2a shows a typical time course of the oxidation kinetics of 50 μM phenol by 5 μM $ABTS^{\bullet+}$ at pH 7. Interestingly, the decay of $ABTS^{\bullet+}$ exhibited biphasic kinetics (i.e., an initial phase and a secondary lag phase). Similar biphasic kinetics for the reactions of $ABTS^{\bullet+}$ with catechin, ferulic acid, and coniferyl alcohol were also found by Tian et al.[41]

In the initial phase, the loss rate of $ABTS^{\bullet+}$ followed the pseudo-first-order kinetics with excess phenol, indicating the first-order with respect to $ABTS^{\bullet+}$. Measured pseudo-first-order rate constants (k_{obs2}, s^{-1}) varied linearly with phenol concentrations (50−250 μM) (Figure 2b), demonstrating a first-order with respect to phenol concentration. Hence, the reaction of $ABTS^{\bullet+}$ with phenol displayed the second-order kinetics in the initial phase (Text S2), and the apparent second-order rate constants (k_{app2}, M^{-1} s^{-1}) were provided in Figure 2c. It was shown that the k_{app2} value significantly increased with the increase of solution pH from 5 to 9 (5.4×10^2 to 9.57×10^5 (M^{-1} s^{-1})). This pH dependency of k_{app2} could be explained by parallel reactions of $ABTS^{\bullet+}$ ($ABTS^{\bullet+}$; $pK_a < 0$) with acid−base species of phenol ($pK_a = 9.99$).[42,43] Accordingly, the k_{app2} value is given by

$$k_{app2} = \sum_{j=1,2}^{i=1} k_{ij}\alpha_i\beta_j \quad (13)$$

where α_i and β_j represent the fractions of $ABTS^{\bullet+}$ and phenol present as the species i and j at a given pH, respectively, and the k_{ij} value represents the species-specific second-order rate constant for each i and j pair. The k_{ij} values (k_{11} and k_{12}) were determined by a nonlinear least-squares regression (acid−base speciation model) of the experimental k_{app2} values (Figure 2c). The result showed that the k_{11} value (4.74×10^2 (M^{-1} s^{-1})) was much lower than the k_{12} value (1.03×10^7 (M^{-1} s^{-1})), which was consistent with the fact that the protonated phenol (PhOH) was considerably less reactive than the phenolate anion (PhO^-).[44−47]

In the secondary phase, the loss rate of $ABTS^{\bullet+}$ slowed as the reaction progressed and deviated from the pseudo-first-order kinetics, which might be attributed to the gradual accumulation of unreacted ABTS ($ABTS_u$). The inner-electron-exchange process between $ABTS^{\bullet+}$ and ABTS, with an electron-exchange rate constant of $(4 \pm 1) \times 10^7$ (M^{-1} s^{-1}) in neutral aqueous solution, was found by Scott et al.[42] Hence, it was likely that $ABTS_u$ had the inhibiting effect on the reaction of $ABTS^{\bullet+}$ with phenol. To verify this, we conducted experiments to examine the effect of $ABTS_u$ on the oxidation of phenol by $ABTS^{\bullet+}$ with different ratios of additional $ABTS_u$ to initial $ABTS^{\bullet+}$ (i.e., $m = 0/1$, $1/1$, $2/1$, $3/1$, $4/1$, $5/1$, and $9/1$) (discussed in Text S2 in detail). The results (Figure 3) showed that the consumption rate

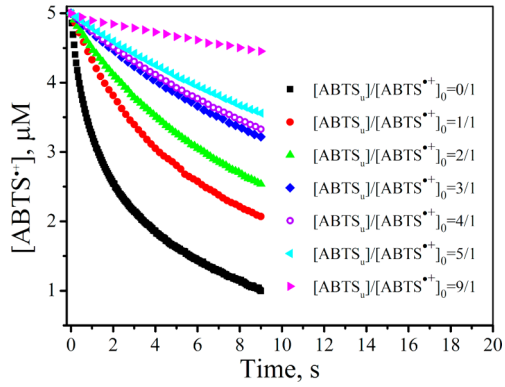

Figure 3. Decay of $ABTS^{\bullet+}$ (5 μM) with different ratios of [$ABTS_u$] to [$ABTS^{\bullet+}$]$_0$ in the presence of phenol (50 μM) at pH 7.

of $ABTS^{\bullet+}$ by phenol significantly decreased with the increase in m value. Similar suppressive effects of $ABTS_u$ over the wide pH values were shown in Figure S1.

Stoichiometries. The stoichiometric relationships in the reaction of $ABTS^{\bullet+}$ with phenol were determined by the ratio (r_2) of $ABTS^{\bullet+}$ consumed ($\Delta ABTS^{\bullet+}$) to phenol lost (Δphenol) over the wide pH range of 5−9. The r_2 value was found to be 2.2 ± 0.06 and 1.38 ± 0.18 in the cases of less and excess phenol, respectively, which changed negligibly with different pH values (Table S3). The finding that the r_2 value was higher than the theoretical value of 1 in both cases suggested that oxidation products of phenol could competitively consume the oxidant

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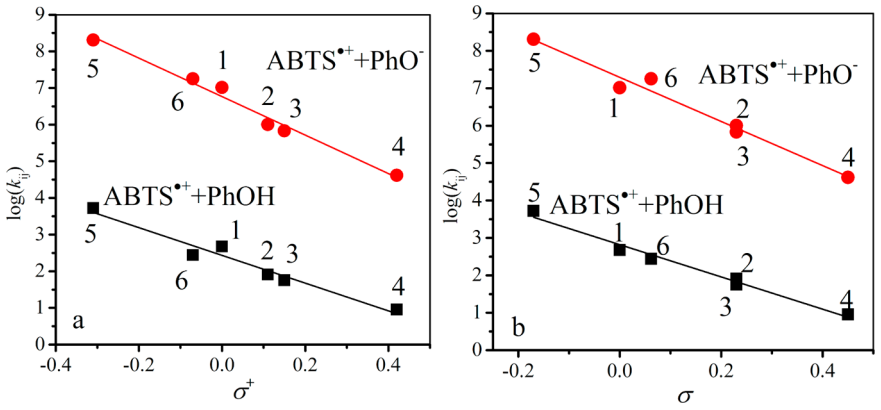

Figure 4. Correlations between the second-order rate constants for the reactions of $ABTS^{\bullet+}$ ($[ABTS_u] = 0\ \mu M$) with undissociated phenols (k_{11}) and dissociated phenols (k_{12}) vs Hammett σ^+ (a) and σ constants (b). The numbers of the compounds from 1 to 6 correspond to phenol, 4-chlorophenol, 4-bromophenol, 4-carboxyphenol, 4-methylphenol, and 4-fluorophenol, respectively.

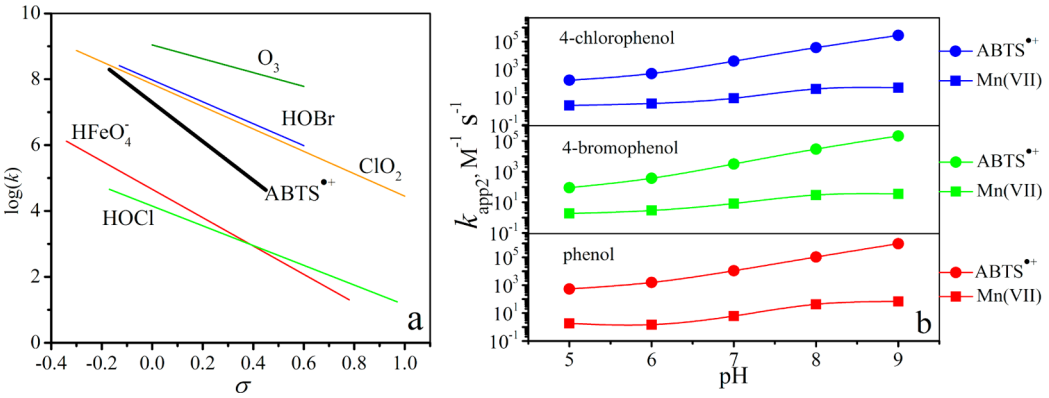

Figure 5. Comparison of the Hammett-type correlations for the reactions of oxidants with dissociated phenols (a) and comparison of the k_{app2} values for the reactions of $ABTS^{\bullet+}$ ($[ABTS_u] = 0\ \mu M$) vs Mn(VII) with phenol, 4-chlorophenol, and 4-bromophenol at pH 5–9 (b). The correlations for O_3, HOBr, ClO_2, $HFeO_4^-$, and HOCl in panel (a) were taken from ref 49, and the k_{app2} values for the reactions of Mn(VII) with phenol, 4-chlorophenol, and 4-bromophenol were taken from refs 4, 52, and8, respectively.

$ABTS^{\bullet+}$. Further, the result that the r_2 value in the case of less phenol (i.e., 2.2 ± 0.06) was higher than that in the case of excess phenol (i.e., 1.38 ± 0.18) might be attributed to the stronger competition of oxidation products of phenol for $ABTS^{\bullet+}$ in the case of less phenol vs excess phenol.

Kinetics for the Reactions of Substituted Phenols with $ABTS^{\bullet+}$ and Linear Free Energy Relationships. The apparent second-order rate constants (k_{app2}, $M^{-1}\ s^{-1}$) for the reactions of $ABTS^{\bullet+}$ with different phenolic compounds (phenol, 4-chlorophenol, 4-bromophenol, 4-carboxyphenol, 4-methylphenol, and 4-fluorophenol) were determined by stopped-flow spectrophotometer at pH 5–9. The k_{app2} data were shown in Figure S4. Similar to the case of phenol, the observed pH dependency of k_{app2} for these substituted phenols can be described by eq 13. The calculated specific second-order rate constants, k_{11} and k_{12}, were summarized in Table S4. The Hammett substituent constants (σ^+, σ, and σ^-) were used to predict the effect of the substituents on the rate constants of the substituted phenols.[48] The Hammett-type correlations were analyzed for the obtained k_{11} and k_{12} data. The better Hammett-type correlations were obtained by using σ^+ or σ and shown in Figure 4 (see Text S3 for more details). The linear regressions for both undissociated and dissociated substituted phenols are shown as

$$\log(k_{11}) = 2.43\ (\pm 0.08) - 3.78\ (\pm 0.38)\cdot\sigma^+ \quad R^2 = 0.961 \tag{14}$$

$$\log(k_{12}) = 6.77\ (\pm 0.08) - 5.25\ (\pm 0.34)\cdot\sigma^+ \quad R^2 = 0.983 \tag{15}$$

$$\log(k_{11}) = 2.82\ (\pm 0.07) - 4.31\ (\pm 0.29)\cdot\sigma \quad R^2 = 0.982 \tag{16}$$

$$\log(k_{12}) = 7.29\ (\pm 0.11) - 5.90\ (\pm 0.46)\cdot\sigma \quad R^2 = 0.976 \tag{17}$$

The negative ρ value reflects the sensitivity of the reaction to the substituent effect.[48] Reactions of $ABTS^{\bullet+}$ with dissociated substituted phenols (e.g., $\rho = -5.90$ in the case of σ) were more sensitive to the substituent effect than those with undissociated substituted phenols (e.g., $\rho = -4.31$ in the case of σ).

The Hammett-type correlations of $ABTS^{\bullet+}$ were compared with those of other water treatment oxidants, such as Fe(VI), ozone (O_3), chlorine dioxide (ClO_2), hypobromous acid (HOBr), and HOCl.[45,49−51] Because σ was usually used to obtain Hammett-type correlations for most water treatment oxidants, Hammett-type correlations based on σ rather than σ^+ were compared. Figure 5a shows that most of the k_{12} values of $ABTS^{\bullet+}$ are several orders of magnitude greater than those of Fe(VI) and HOCl but much lower than those of O_3, HOBr, and ClO_2. The Hammett slope for $ABTS^{\bullet+}$ ($\rho = -5.9$) was higher

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than the values obtained for O_3 (ρ = −2.1), HOCl (ρ = −3.0), HOBr (ρ = −3.3), ClO_2 (ρ = −3.4), and Fe(VI) (ρ = −4.3), suggesting that $ABTS^{\bullet+}$ was more sensitive to substitution effects than the other oxidants.

Because no linear free energy relationships for Mn(VII) were found,[1] the k_{app2} values at each pH (rather than the Hammett-type correlation of $ABTS^{\bullet+}$) were compared with those of Mn(VII). As shown in Figure 5b, the k_{app2} values for Mn(VII) at pH 5−9 obtained from the literatures (e.g., phenol, 4-chlorophenol, and 4-bromophenol) were much lower than those for $ABTS^{\bullet+}$.[4,8,52] Hence, it is expected that trace levels of ABTS may catalyze the reactions of Mn(VII) with phenols.

Effect of ABTS on the Oxidation Kinetics of Substituted Phenols by Mn(VII). Further experiments were conducted to examine the effect of ABTS on the oxidation of phenol in synthetic water by Mn(VII). As shown typically in Figure 6, the

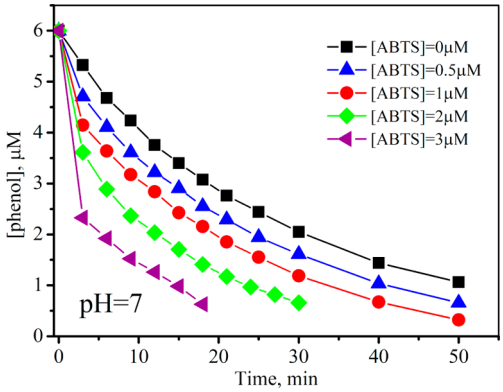

Figure 6. Oxidation kinetics of 6 μM phenol by 70 μM Mn(VII) at pH 7 with different concentrations of ABTS (0−3 μM).

presence of trace levels of ABTS could significantly enhance the oxidation of phenol by Mn(VII) at pH 7. A similar enhancing effect of ABTS was also found on the reactions between Mn(VII) and selected substituted phenols, with an electron-donating substituent (i.e., $-CH_3$) and electron-withdrawing substituents (i.e., −F, −Cl, −Br, and −COOH) (Figure S7). A catalytic role of the $ABTS^{\bullet+}$ and ABTS pair could describe the effect of trace levels of ABTS in promoting Mn(VII) oxidation of phenol. For the catalytic reaction to occur, the formation of $ABTS^{\bullet+}$ by the fast reaction of Mn(VII) with ABTS is necessary. Afterward, phenol is quickly oxidized by $ABTS^{\bullet+}$ with a much higher rate than that for the reaction of Mn(VII) with phenol, which is followed by the regeneration of ABTS.

(1). ABTS Concentration. The enhancing effect of ABTS at different concentrations (0.5−3 μM) was evaluated by comparing the half-life ($t_{1/2}$, min) or pseudo-first-order rate constants (k_{obs3}, min^{-1}). The results indicated that measured $t_{1/2}$ values decreased and calculated k_{obs3} values increased with the increase of the ABTS concentration at each pH 5−9, respectively (Table S5). At a constant pH value, high levels of initial ABTS result in the fast formation of $ABTS^{\bullet+}$ and, thus, the rapid oxidation of phenol by Mn(VII).

(2). Solution pH. ABTS could enhance the oxidation of phenol by Mn(VII) over a wide pH range (Figure 6 for pH 7 and Figure S8 for other selected pH). Because the reactivity of $ABTS^{\bullet+}$ with phenol increased with the increase of pH value (Figure 2c), it is expected that the promoting effect of ABTS on the oxidation of phenol by Mn(VII) is more significant at high pH than that at low pH. However, the observed enhancing effect of ABTS was not marked in our experiments at alkaline pH (Figure S8). This discrepancy might be attributed to the fact that the higher k_{app2} value than k_{app1} at pH 8 and 9 would result in high ratios of $ABTS_u$ to $ABTS^{\bullet+}$, thus reducing the oxidation rate of phenol by $ABTS^{\bullet+}$.

(3). Phenol Concentration. Further experiments for the oxidation of phenol at different initial concentrations by the Mn(VII) and ABTS combination were examined. The lower initial concentration of phenol was added, and the higher loss rate of phenol was found at a constant pH value and an ABTS concentration (Figure S9). One possible explanation was that the concentrations of phenol had influence on the ratio of $ABTS_u$ to $ABTS^{\bullet+}$ (i.e., low concentrations of phenol resulting in low ratios of $ABTS_u$ to $ABTS^{\bullet+}$; see Text S4 for more details).

The Role of ABTS in the Oxidation of Substituted Phenols by Other Oxidants. The results above suggest that ABTS can accelerate the reactions of Mn(VII) with substituted phenols due to the higher k_{app2} values of their oxidation by $ABTS^{\bullet+}$ versus Mn(VII) (Figure 5b). Similarly, because the rates for the oxidation of substituted phenols by $ABTS^{\bullet+}$ are much higher than those of Fe(VI) and HOCl (Figure 5a), it is expected that ABTS can also catalyze the oxidation by these mild oxidants. To identify this, we conducted experiments to examine the effect of ABTS on the oxidation kinetics of phenol by Fe(VI) and HOCl. As shown in Figure S10a , ABTS greatly accelerated the kinetics of Fe(VI) with phenol as expected. However, no obvious enhancement of ABTS on the reaction of HOCl with phenol (Figure S10b) was found. This was ascribed to the fairly low generation rate of $ABTS^{\bullet+}$ from the reaction of HOCl with ABTS compared to those of Mn(VII) and Fe(VI).[25,30]

Overall, the results obtained in this study suggest that ABTS not only serves as a novel and efficient electron shuttle to catalyze the permanganation process for the treatment of phenolic compounds containing waters over a wide pH range but also acts as a one-electron-transfer probe to provide useful information for the fates of the manganese intermediates in Mn(VII) oxidation. The promoting effect of ABTS on the oxidation kinetics of phenol by Mn(VII) was also confirmed in natural water (Figure S11), suggesting that $ABTS^{\bullet+}$ was not readily quenched by water matrix components. Recent studies have successfully developed the ABTS-modified carbon nanotubes (CNTs) for catalytic technology,[53−57] suggesting that heterogeneous ABTS catalysts (e.g., ABTS-loaded carbons) may be an option for water treatment. This issue needs further investigations by considering redox potential change and mass transfer related to heterogeneous ABTS catalysts. However, the high cost and unknown toxicity of the synthetic mediator, ABTS, may hinder its utilization. Nevertheless, this work brings about the convenience to find out the low-cost and environmentally friendly natural mediators for further development of Mn(VII)-mediator system, as was done in the case of laccase by Gutiérrez et al.[58] Humic substances exist ubiquitously in soils and waters,[59] and they can act as redox mediators participating in various chemical and biochemical processes.[60,61] Previous studies have showed that isolated humic acid (HA) could also greatly accelerate the oxidation of phenols by Mn(VII) under slightly acidic conditions, which was mainly ascribed to its roles as both a reductant and a complexing agent.[4,5,9] On the basis of the results obtained with ABTS, a model mediator,[62,63] it seems likely that HA may also promote Mn(VII) oxidation of phenols under slightly acidic condition through a catalytic mechanism via the pair (HA and HA_{ox}) analogous to the pairing of ABTS and $ABTS^{\bullet+}$ (Figure S12), which needs further studies. In addition,

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because of the high reactivity of $ABTS^{\bullet+}$ with phenolic moieties, it is recommended that the ABTS colorimetric method to quantify water oxidants in trace levels in natural waters or in well-defined laboratory solutions should be conducted under the conditions of acidic pH as well as with ABTS in excess (i.e., a high ratio of $ABTS_u$ to $ABTS^{\bullet+}$) to avoid the appreciable decay of $ABTS^{\bullet+}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03358.

Additional information on the kinetic analysis for the formation of $ABTS^{\bullet+}$ in the reaction of Mn(VII) with ABTS, reaction kinetics between $ABTS^{\bullet+}$ and phenol, linear free-energy relationships, and the effect of different phenol concentrations on phenol oxidation by Mn(VII) and ABTS. Tables showing the constants for reactions of Mn(VII), ABTS, and $ABTS^{\bullet+}$ and stoichiometries of the reaction of $ABTS^{\bullet+}$ with phenol. Figures showing the decay of $ABTS^{\bullet+}$, a linear plot of the pseudo-first-order rate constant for the decay of $ABTS^{\bullet+}$, the second-order rate constant for the reactions of $ABTS^{\bullet+}$ with selected phenolic compounds, correlations between the second-order rate constants for $ABTS^{\bullet+}$ with undissociated phenols, oxidation kinetics, and the effects of ABTS or humic acid on Mn(VII) oxidation. (PDF)

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Notes

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