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Modeling the response of a control-released ion-selective electrode and employing it for the study of permanganate oxidation kinetics†

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Although polymeric membrane ion-selective electrodes (ISEs) based on outward ion fluxes have been found analytically useful, there is still a lack of a theoretical framework for this detection system. In this study, we attempted to model the response of this kind of permanganate ISE and employed this ISE to analyze the rapid $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction. This response is attributed to H_2O_2 oxidation with MnO_4^- that is released from the inner solution to the membrane surface layer. The results show that the experimental data can be fitted well to the proposed model that is elucidated mathematically from the viewpoint of chemical kinetics. The second-order rate constant is determined at a near neutral pH and is in agreement with the acid dissociation law to provide the specific value of $370 \text{ M}^{-1} \text{ s}^{-1}$. The kinetic mechanism was then investigated by performing DFT calculations. Via analysis of the Mn–O bond length and the HOMO orbital, it has been found that the studied redox system functions similarly as the so-called hydrogen abstraction mechanism with an energy barrier of $24.5 \text{ kcal mol}^{-1}$. This study is considered to be the first report on the simulation of MnO_4^- attack at the O–H bond. On the basis of the transition state theory and previous studies on MnO_4^- attack at the C=C and C–H bonds, the relationship between the experimental rate constant and computational energy barrier is finally constructed. The result indicates the validity of our proposed method and makes the control-released ISE a very promising platform to study the kinetics.

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Introduction

Polymeric membrane ion-selective electrodes (ISEs) are one of the most important analytical tools widely used for the analysis of environmental and biological samples.¹ They have received significant attention owing to the attractive features including high selectivity, ease of handling, and relatively low-cost.^{2,3} Recently, these well-established potentiometric sensors have undergone a quiet revolution to reach the detection limits in the sub-nanomolar levels.^{4,5} Inspired by this, many innovative sensing schemes have been proposed for a broad range of targets over the last few years.^{6–8} Accompanied by the technological advances, great emphasis has also been placed on

understanding the mechanism of potentiometric response of the ISE.⁹

To date, it has been fully realized that the transmembrane concentration gradient can cause ion flux across the polymeric interface and thus deteriorate the detection limit of the ISE by perturbing the ion concentration at the phase boundary.^{10,11} Although the ion flux cannot be entirely eliminated, this characteristic of ISE has been recently found to be useful for applications in polyion sensors,¹² pulstrodes,¹³ switchtrodes,¹⁴ and ion-channel biosensors.¹⁵

Recently, a novel ISE system has been exploited using outward ion flux (efflux) in the direction of the sample solution under zero-current conditions.^{16–18} In this case, the ISE membrane can play the critical roles of both a polymer matrix for reagent release and a sensitive transducer for potentiometric detection. Particularly, our group has developed an ionophore-free permanganate ISE that utilizes outward ion fluxes through the membrane to provide control-released substrates for monitoring the analytes of interest.^{16,19} Previous studies have shown that the design based on permanganate release allows a sensitive and reproducible detection of reductants including ascorbate and dopamine. However, the application of this technique is still limited since all reductants that can efficiently

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react with permanganate ions may produce measured potential interference.

This is obviously disadvantageous for the analysis of complex samples, but advantageous for the study of permanganate oxidation kinetics under controllable conditions. Because the potential responses are mainly attributed to the consumption of permanganate ion on the membrane surface layer, this permits the selective and continuous observation of the rapid permanganate oxidation process. In comparison, the spectrophotometric method together with the stopped-flow technique would be restricted by the disturbance from the *in situ* formed colloidal manganese oxide.²⁰ Consequently, it is necessary to model the response behavior of the control-released permanganate ISE with respect to the chemical principle of the reaction.

Herein, we attempted to investigate the theoretical foundation of the efflux permanganate ISE under zero-current conditions for the first time and then employed this ISE as a research platform to study the permanganate oxidation kinetics. As a proof-of-concept experiment, hydrogen peroxide (H_2O_2) was chosen to be the objective analyte. Note that the permanganate titration has long been recognized as a reliable procedure for H_2O_2 determination.²¹ Additionally, the corresponding reaction kinetics has been investigated in an acidic aqueous solution by stopped-flow spectrophotometry.²² By the construction of a theoretical model, the ionophore-free permanganate ISE may have the opportunity to extend its utilization to describe the related reaction routes at a near neutral pH. To gain a deeper insight into the reaction mechanism, the density functional theory (DFT) calculation is adopted thereafter to explain the reaction mechanism.^{23,24} The obtained results were further used to confirm and explain the outcome of the experimental study.

Experimental

Chemicals and reagents

Tridodecylmethylammonium chloride (TDMAC), 2-nitrophenyl octyl ether (*o*-NPOE), and high-molecular weight poly(vinyl chloride) (PVC) were obtained from Fluka AG (Buchs, Switzerland). Other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Aqueous solutions were prepared by dissolving the appropriate salts in freshly deionized water (18.2 MΩ cm specific resistance) obtained using a Pall Cascada laboratory water system. The pH measurements were conducted using a Leici pH meter coupled with a combined electrode (Shanghai Apparatus Co. Ltd.) that was calibrated at pH 4.00, 6.86, and 9.18 before use.

Preparation of membranes and electrodes

The ionophore-free permanganate ISE was prepared according to the previous procedures.¹⁶ Briefly, 240 mg of the membrane component containing 10 wt% TDMAC, 65 wt% *o*-NPOE, and 25 wt% PVC was dissolved in 2.5 mL of tetrahydrofuran (THF). The resulting solution was then transferred into a glass ring of 36 mm diameter fixed on a glass plate to allow the solvent to evaporate completely to obtain a homogeneous membrane, as

shown in Fig. S1 in the ESI.† For each ISE, a disk of 7 mm diameter was punched from the obtained membrane and glued to a PVC tube with a THF/PVC slurry. A 0.08 M potassium permanganate solution containing 0.02 M NaCl was added to each electrode as the inner filling solution. Before the measurements, these electrodes were activated by conditioning them in 0.1 M NaCl for 3 days. This pretreatment was used to make permanganate anion (MnO_4^-) enter the ionophore-free ISE membrane from the inner filling solution and combine with tridodecylmethylammonium cation (TDMAC^+) *via* ion-exchange between MnO_4^- and Cl^- . After this step, the TDMAC^+ sites were considered to be fully saturated by MnO_4^- , which not only could maintain the relatively stable MnO_4^- concentration in the membrane phase but could also facilitate the continuous ion flux from the inner filling solution to the sample solution.

EMF measurements

Potentiometric measurements were carried out at 25 °C using an LK2006 electrochemical workstation (Tianjin, China) with a saturated calomel electrode as a reference electrode in the galvanic cell: SCE//sample solution/ISE membrane/inner filling solution/AgCl/Ag. The 20 mL sample solutions were prepared with 0.1 M NaCl as the background electrolyte and adjusted with NaOH or HCl to the required pH. For each measurement, the ionophore-free permanganate ISE was first taken out from the condition solution, rinsed with water, and immersed in the sample solution under vigorous magnetic stirring to obtain a potential baseline. The potential change was then initiated by adding a certain amount (200 μL) of H_2O_2 and was determined continuously with time.

Computational details

The density functional theory (DFT) calculation was performed using the Gaussian 16 package program.²⁵ The B3LYP model together with the LanL2DZ basis set for the manganese atom and 6-31+G(d) basis set for other atoms were employed throughout this study. The solvent effect of water was taken into account using the IEFPCM model. It is worth mentioning that the abovementioned method has been utilized successfully in the mechanistic study of permanganate oxidation in an aqueous solution.²⁰ The geometry was initially optimized, and the vibrational frequency was then calculated to determine the nature of the stationary point and the critical energy parameters. The transition state was further confirmed by intrinsic reaction coordinate (IRC) analysis. The Cartesian coordinates could be found in the ESI.† Based on the optimized structures, the corresponding wave functions were also analyzed.^{23,24} The three-dimensional diagrams of the optimized structure, the highest occupied molecular orbital (HOMO), the bond critical point (BCP) in the hydrogen bond path, and the spin density were constructed with Avogadro.

Model development

As shown in Fig. 1, MnO_4^- can diffuse through the polymeric membrane when the ISE is immersed in the sample solution.

Fig. 1 Schematic of the ionophore-free permanganate ISE under the zero-current condition and the MnO_4^- flux from the membrane phase to the membrane surface layer (i.e., J_{in}) and further into the sample bulk (i.e., J_{out}).

This is attributed to the transmembrane concentration gradient under the zero-current condition.⁹ It has been well-established that the ionophore-free permanganate ISE can exhibit a high discrimination ability towards other anions such as thiocyanate, nitrate, and chloride.¹⁶ Therefore, the observed potentiometric response (E) serves as an indication of the MnO_4^- activity ($\alpha_{\text{MnO}_4^-}$) on the membrane surface layer:

$$E = E^0 - \frac{RT}{F} \ln \alpha_{\text{MnO}_4^-} \quad (1)$$

In the absence of a reductant, the change in E is mainly related to the MnO_4^- flux from the membrane phase to the membrane surface layer (i.e., J_{in}). The E value will approach to be stable gradually when J_{in} equals to the MnO_4^- flux diffusing further into the sample bulk (i.e., J_{out}). This is actually the steady-state process with a constant $\alpha_{\text{MnO}_4^-}$ released at the membrane surface layer.

After the addition of a reductant (i.e., H_2O_2) to the sample solution, an efficient redox reaction occurs, and the $\alpha_{\text{MnO}_4^-}$ at the membrane surface layer is decreased; thus, the measured potential from E_0 at time = 0 to E_t at time = t is increased:

$$\Delta E = E_t - E_0 = -\frac{RT}{F} \ln \frac{\alpha_{\text{MnO}_4^-,t}}{\alpha_{\text{MnO}_4^-,0}} \quad (2)$$

At the initial stage, the reaction rate is significant, whereas the MnO_4^- flux remains at a low level as the steady-state process (i.e., $J_{\text{in}} = J_{\text{out}}$). The E variation (ΔE) with time (Δt) should be merely attributed to the consumption of MnO_4^- by H_2O_2 . This is analytically useful and can be modelled mathematically from the kinetic point of view hereinafter.

By speculating that the MnO_4^- oxidation of H_2O_2 is a simple bimolecular reaction, the decay rate of $\alpha_{\text{MnO}_4^-}$ can be expressed by the following second-order equation:

$$-\frac{d\alpha_{\text{MnO}_4^-}}{dt} = k\alpha_{\text{MnO}_4^-}\alpha_{\text{H}_2\text{O}_2} = k\gamma_{\text{MnO}_4^-}C_{\text{MnO}_4^-}\gamma_{\text{H}_2\text{O}_2}C_{\text{H}_2\text{O}_2} \quad (3)$$

where α , γ , and C represent the activities, the activity coefficients, and the concentrations of the corresponding species,

respectively; k represents the second-order rate constant. The integration of eqn (3) provides

$$\ln \frac{\alpha_{\text{MnO}_4^-,t}}{\alpha_{\text{MnO}_4^-,0}} = -k\gamma_{\text{H}_2\text{O}_2}C_{\text{H}_2\text{O}_2}\Delta t \quad (4)$$

Considering the Debye–Hückel rule with the Güntelberg approximation, the activity coefficient of the neutral molecule can be taken as unity ($\gamma_{\text{H}_2\text{O}_2} = 1$), thus indicating the equivalent of $C_{\text{H}_2\text{O}_2}$ to $\alpha_{\text{H}_2\text{O}_2}$.²⁶ If H_2O_2 is applied in a large excess (e.g. at least 5 folds) of MnO_4^- , $C_{\text{H}_2\text{O}_2}$ can be considered as approximately constant. Eqn (4) is thus simplified and transformed into a pseudo-first-order kinetic model as follows:

$$\ln \frac{\alpha_{\text{MnO}_4^-,t}}{\alpha_{\text{MnO}_4^-,0}} = -k_p\Delta t \quad (5)$$

where k_p is the pseudo-first-order rate constant equaling to $kC_{\text{H}_2\text{O}_2}$. Upon substituting eqn (5) into (2), we obtained

$$\frac{dE}{dt} = \frac{\Delta E}{\Delta t} = \frac{RT}{F}k_p \quad (6)$$

From eqn (6), the potential change rate (dE/dt) at the initial stage is found to be a function of k_p , which is further proportional to $C_{\text{H}_2\text{O}_2}$.

Results and discussion

Experimental modeling of the potentiometric response

Fig. 2 displays a representative profile of the potentiometric response with time obtained in this study. As discussed in the model development, the potentiometric response first reached a stable value, serving as an indication of a steady-state process (i.e., $J_{\text{in}} = J_{\text{out}}$), which meant a constant $\alpha_{\text{MnO}_4^-}$ at the membrane surface layer. By adding a small aliquot of H_2O_2 to the sample solution, MnO_4^- on the membrane surface layer was consumed; thus, the $\alpha_{\text{MnO}_4^-}$ value was decreased, and the

Fig. 2 A representative profile of the potentiometric response with time by adding $C_{\text{H}_2\text{O}_2} = 33 \mu\text{M}$. Inset: the corresponding linear fitting to the model proposed by eqn (6).

measured potential was increased. It is worthy to note that the $\alpha_{\text{MnO}_4^-}$ -value at the membrane surface layer is in the range from 0.1 to 1.0 μM , whereas in the sample bulk, it is below 1.4 nM in 1 min (*i.e.* 80 nM in 1 h).¹⁶ Therefore, the prerequisite for maintaining the pseudo-first-order condition should be satisfied using at least 5 μM H_2O_2 . This is confirmed by the result shown in the inset of Fig. 2, where the potential change rate (dE/dt) at the initial stage can be fitted well to eqn (6); this illustrates the reasonability of the proposed model. The linear relationship also confirmed a first-order dependence on $\alpha_{\text{MnO}_4^-}$ and gave the k_p value from the fitting slope. Note that the initial stage is present for a short time. The deviation between the actual and ideal potential will become larger and can be attributed to the increased J_{in} caused by the greater transmembrane concentration gradient. The increased J_{in} is apt to inhibit the consumption of MnO_4^- by H_2O_2 to reach a new steady-state process. Consequently, the abovementioned analysis was only performed at the initial stage when the steady-state process was still valid.

The variation of k_p under different reaction condition was then examined. In Fig. 3, the determined k_p was found to increase with the increasing $C_{\text{H}_2\text{O}_2}$ added to the sample solution. The positive linear correlation with a zero intercept indicated a first-order dependence on $C_{\text{H}_2\text{O}_2}$. The reaction between MnO_4^- and H_2O_2 was thus concluded to be of first-order with respect to each reactant and second-order in total, which was in accordance with the results obtained for other permanganate oxidation reactions.^{20,27} The second-order rate constant (k) could be calculated by dividing the k_p value by $C_{\text{H}_2\text{O}_2}$. Obviously, this is the reaction basis for the potentiometric response of the ionophore-free permanganate ISE under the zero-current condition. Although its analytical working range was solely limited to 5–66 μM , which was not superior to that of the titration method,²¹ the ionophore-free permanganate ISE together with the constructed theoretical model (eqn (6)) offered a very promising alternative to study the rapid

permanganate oxidation kinetics. This is mainly attributed to the inherent advantages, including the high selectivity for MnO_4^- and continuous monitoring without a quenching step, of the ISE. The similar ISE system has also been successfully employed to detect the enzyme activity.^{17,18} Hence, this study may provide a possibility of studying other reactions by controlling the release of suitable reagents such as antigens or toxins.^{28,29}

The inset of Fig. 3 shows the obtained k values in correspondence to different pH conditions, which are usually ascribed to the distribution of the acid-base species of the reactants.^{27,30} On the basis of the acid dissociation constants ($\text{p}K_a = -2.25$) of $\text{HMnO}_4/\text{MnO}_4^-$ and ($\text{p}K_a = 11.75$) $\text{H}_2\text{O}_2/\text{HO}_2^-$,^{31,32} there should be only one reaction pathway involving the reacting species of MnO_4^- and H_2O_2 in the near neutral pH range. This is supported by the relatively stable k values of 381 $\text{M}^{-1} \text{s}^{-1}$, 378 $\text{M}^{-1} \text{s}^{-1}$, and 351 $\text{M}^{-1} \text{s}^{-1}$ at the pH values of 6, 7, and 8, respectively. The corresponding specific second-order rate constant was then averaged to be 370 $\text{M}^{-1} \text{s}^{-1}$ for the $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction. This level of reaction rate constant is higher than that reported for the oxidation of most organic compounds with MnO_4^- .³³ Therefore, if the $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction is involved in the treatment of environmental contaminants, it would occur first and may play a critical role in the enhancement of the reaction efficiency by forming a highly reactive intermediate. However, only the kinetic result was not sufficient to make us account for the reaction mechanism. In general, MnO_4^- prefers to react with the electron-rich moiety through oxygen addition, hydrogen abstraction, and electron transfer.^{20,27} For the electrophilic attack of H_2O_2 by MnO_4^- , the primary reactive site is hard to be predicted. This is mainly attributed to the structural simplicity of H_2O_2 , thus hindering a complete disclosure of the reaction mechanism.

Theoretical modeling of the reaction mechanism

In addition to the experimental approach, the mechanism of the $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction was also studied computationally. The potential energy profile is shown in Fig. 4, where the reported energy value is normalized using the reactants (*i.e.*, $\text{MnO}_4^- + \text{H}_2\text{O}_2$) as the zero-point. The transition state (TS) was then obtained with the energy barriers of 24.5 kcal mol^{-1} from the zero-point and 21.0 kcal mol^{-1} from the reactant complex

Fig. 3 The plot of pseudo-first-order rate constant (k_p) as a function of $C_{\text{H}_2\text{O}_2}$ at pH = 7. Inset: the second-order rate constant (k) measured at the pH equal to 6, 7, and 8 with $C_{\text{H}_2\text{O}_2} = 33 \mu\text{M}$.

Fig. 4 The Gibbs free-energy profile (kcal mol^{-1}) of the reaction between MnO_4^- and H_2O_2 .

(RC). The imaginary frequency at $251.6i\text{ cm}^{-1}$ was the stretching motion of the hydrogen and oxygen atoms of H_2O_2 towards the two corresponding oxygen atoms of MnO_4^- . By passing through the TS, a product complex (PC) was found with an energy level of $12.7\text{ kcal mol}^{-1}$. It should be mentioned herein that the wave function of PC is not stable. A more reasonable structure (PC(T)) in the triplet spin state can be obtained with an energy level of 5.2 kcal mol^{-1} , which is 7.5 kcal mol^{-1} lower than that of the PC. The result indicates the generation of hypomanganate(v) species product, which is supported by the localization of nearly two electrons (spin density equaling to 1.65) on the manganese atom of PC(T), as shown in Fig. 5c.

The reaction resembles the MnO_4^- oxidation of alkanes *via* a so-called hydrogen abstraction mechanism.^{34,35} In the reaction process (Fig. 4), the hydrogen atom of H_2O_2 is clearly transferred to one oxygen atom of MnO_4^- ; this causes the elongation of the corresponding Mn–O bond from $1.609\text{ \AA}$ in RC to $1.722\text{ \AA}$ in TS and to $1.806\text{ \AA}$ in PC. Moreover, another involved Mn–O bond was elongated from $1.590\text{ \AA}$ in RC to $1.598\text{ \AA}$ in TS and to $1.824\text{ \AA}$ in PC due to the immediate collapse of the oxygen atom of H_2O_2 . The HOMO orbitals of RC, TS, and PC were then analyzed, as shown in Fig. 5a, due to their reliability in understanding the chemical reactivity.^{20,35} For RC, the HOMO orbital was mainly distributed on the oxygen atoms of both MnO_4^- and H_2O_2 ; this confirmed their involvements in the $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction. As the reaction proceeded, the HOMO orbital of TS was found at the OOH group in H_2O_2 and the manganese atom in MnO_4^- . The result suggested the breaking of the O–H bond and the production of a radical OOH and a manganate(vi) center in TS. Finally, the HOMO orbital of PC was located almost on the manganese atom of MnO_4^- ; this implied the formation of the hypomanganate(v) center, which was consistent with the result of the spin density analysis.

To the best of our knowledge, this is the first report on the theoretical study of MnO_4^- attack at the O–H bond. The reaction mechanism is similar to the so-called hydrogen abstraction process with a hydrogen atom transfer to one oxygen atom of MnO_4^- and two electrons transfer from the oxygen atom of H_2O_2 to the manganese center of MnO_4^- . It is worth noting that the MnO_4^- oxidation of H_2O_2 may also occur at the O–O bond. However, all attempts failed with an immediate departure of

H_2O_2 away from MnO_4^- (data is not shown). This may be attributed to the electrostatic repulsive effect between the oxygen atoms of MnO_4^- and H_2O_2 although the more negative electrostatic potential usually means the more electron-rich region being susceptible to the electrophilic attack.²⁰ By contrast, the reaction pathway for the MnO_4^- oxidation of the O–H bond should be facilitated by the presence of a hydrogen bond ($\text{Mn}\cdots\text{O}\cdots\text{H}\cdots\text{O}$). The result was supported by the topology analysis, as shown in Fig. 5b, where a bond path with a bond critical point (BCP) was observed between O and H atoms in RC.^{23,24} The positive Laplacian of electron density ($\nabla^2\rho = 0.127$ in a.u.) and negative electron energy density ($H = -0.475 \times 10^{-3}$ in a.u.) at BCP suggested a closed-shell interaction and the strong bonding strength, whereas the negative ratio of local kinetic energy density (G) to local potential energy density (V) equaling to 0.985 (*i.e.*, $-G/V$) in the range of 0.5–1.0 was indicative of the partially covalent character.

On the basis of the abovementioned analysis results, we could finally try to construct a relationship between the experimental rate constant (average value k_A was used herein) and the computational energy barrier (ΔG^{++}), as depicted in Fig. 6 and Table S1.† In previous studies, the permanganate attacks at the C=C double bond and the C–H bond have been carefully studied.^{34–36} The kinetic information is also available for the related compounds including perchloroethylene (PCE), trichloroethylene (TCE), *trans*-dichloroethylene (*trans*-DCE), ethanol, and toluene.³³ Therefore, the corresponding transition states and ΔG^{++} were calculated using the same method as used in this study and compared with those of H_2O_2 . In Fig. 6, the Eyring plot of $\ln k_A$ versus ΔG^{++} was found to be significantly linear with a coefficient of 0.966. The tendency is in accordance with the transition state theory stating that a higher energy barrier usually implies a lower reaction rate.²⁰ This result suggested the good agreement of the experimental and theoretical data and further indicated the validity of our kinetic research platform based on the control-released ISE.

Fig. 5 The plots of (a) the HOMO (isovalue = 0.1) of RC, TS, and PC; (b) the BCP (yellow point) in the hydrogen bond path of RC; and (c) the spin density (isovalue = 0.02) of PC(T).

Fig. 6 Eyring correlation of the experimental rate constant with the computational energy barrier for different permanganate oxidation reactions in an aqueous solution at 25°C .

Conclusions

In summary, the response of the polymeric membrane ISE based on the controlled release of permanganate has been theoretically elucidated for the first time. The obtained model was then used to analyze the rapid permanganate oxidation kinetics at a near neutral pH. The potentiometric response is attributed to the consumption of MnO_4^- by H_2O_2 on the membrane surface layer and elaborated mathematically from the viewpoint of chemical kinetics. A good fit is obtained for the experimental data; this illustrates the reasonability of the proposed model. The positive linear relationship between k_p and $C_{\text{H}_2\text{O}_2}$ can be considered as the calibration curve for the analysis and as the reaction basis for the potentiometric detection. The second-order rate constant is relatively stable at the pH values of 6, 7, and 8; this can be explained by the distribution of the acid–base species of the reactants. To gain a deeper insight into the kinetic mechanism, the $\text{MnO}_4^-/\text{H}_2\text{O}_2$ reaction is simulated by the DFT calculation. It has been found that the MnO_4^- oxidation of H_2O_2 resembles the so-called hydrogen abstraction mechanism; this can be supported by the analysis of the Mn–O bond length and the HOMO orbital. To the best of our knowledge, this is the first report on the theoretical study of MnO_4^- attack at the O–H bond. The experimental rate constant and the computational energy barrier could be finally correlated by constructing the Eyring plot based on the transition state theory and the previous studies on MnO_4^- attack at the C=C and C–H bonds. Considering the fact that MnO_4^- has been widely applied in preparing functional substances and removing the emerging pollutants, the proposed ISE technique appears to be very promising for investigating the kinetic process in water by excluding the spectral interference.

Conflicts of interest

There are no conflicts to declare.

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