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Oxidation of chlorinated ethenes by potassium permanganate: a kinetics study

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Abstract

The kinetics of oxidation of perchloroethylene (PCE), trichloroethylene (TCE), three isomers of dichloroethylene (DCE) and vinyl chloride (VC) by potassium permanganate (KMnO₄) were studied in phosphate-buffered solutions of pH 7 and ionic strength ~0.05 M and under isothermal, completely mixed and zero headspace conditions. Experimental results have shown that the reaction appears to be second order overall and first order individually with respect to both KMnO₄ and all chlorinated ethenes (CEs), except VC. The degradation of VC by KMnO₄ is a two-consecutive-step process. The second step, being the rate-limiting step, is of first order in VC and has an activation energy (E_a) of 7.9 ± 1 kcal mol⁻¹. The second order rate constants at 20°C are 0.035 ± 0.004 M⁻¹ s⁻¹ (PCE), 0.80 ± 0.12 M⁻¹ s⁻¹ (TCE), 1.52 ± 0.05 M⁻¹ s⁻¹ (*cis*-DCE), 2.1 ± 0.2 M⁻¹ s⁻¹ (1,1-DCE) and 48.6 ± 0.9 M⁻¹ s⁻¹ (*trans*-DCE). The E_a and entropy (ΔS^\ddagger) of the reaction between KMnO₄ and CEs (except VC) are in the range of 5.8–9.3 kcal mol⁻¹ and -33 to -36 kcal mol⁻¹ K⁻¹, respectively. Moreover, KMnO₄ is able to completely dechlorinate CEs, and the increase in acidity of the solution due to CE oxidation by KMnO₄ is directly proportional to the number of chlorine atoms in CEs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Potassium permanganate; Trichloroethylene; Perchloroethylene; Kinetics; Activation energy

1. Introduction

Permanganate has been recently evaluated as an oxidant for the remediation of aquifers contaminated with perchloroethylene (PCE), trichloroethylene (TCE) and their biodegradation products such as *cis*-dichloroethylene (DCE) and vinyl chloride (VC). Early laboratory

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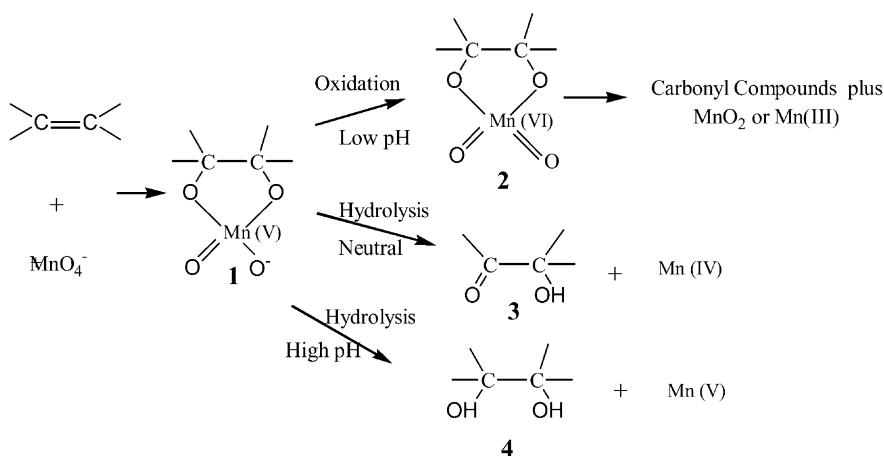
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and pilot scale studies have shown that permanganate can rapidly degrade TCE and PCE in aqueous solutions [1–5] or soil environments [6–11]. These early works indicate that the in situ permanganate oxidation technology could be a promising remediation alternative for the sites that are contaminated with chlorinated ethenes (CEs).

Kinetic information on the reactions of permanganate with CEs is warranted for the optimization of remediation system design and the modeling of treatment progress. While the kinetics of oxidation of TCE by potassium permanganate (KMnO_4) has been thoroughly studied [3,4], the literature lacks kinetic data for other CEs. This study was thus aimed at determining the kinetic parameters (e.g. reaction order, rate constant and activation parameters) of the oxidation of PCE, TCE, three isomers of DCEs and VC by KMnO_4 through a series of well-controlled batch experiments. Additionally, the extent of CE dechlorination and change in acidity of the solutions due to CE oxidation by KMnO_4 were also investigated. The presented kinetic data would enable the remediation engineers to predict the reaction rates of CEs with permanganate under various subsurface conditions (e.g. temperature and oxidant concentration) during the remediation application.

2. Permanganate oxidation kinetics

The oxidation of TCE by KMnO_4 appears to proceed in a strikingly similar way to the alkenes–permanganate reaction [12]. It is proposed that permanganate rapidly reacts with ($\text{C}=\text{C}$) double bonds to form a cyclic hypomanganate(V) ester intermediate at the initial step of the reactions (Scheme 1) [12–16]. Subsequent reactions involve competition between permanganate (further oxidation pathway) and hydroxyl ions (hydroxylation pathway) for the initial hypomanganate ester intermediate. The different reaction pathways may result in the formation of carbonyl compounds, glycols, ketones and carboxylic acids,



Scheme 1. Reaction pathways of oxidation of alkenes with permanganate (adapted after Lee and Brownridge, 1974).

strongly depending on pH and oxidant concentration. The reaction appears to be first order in both the oxidant and the reductant (i.e. TCE and alkenes), and the degradation of CEs by permanganate oxidation appears to be independent of both pH and ionic strength [3,17]. The pseudo-first order rate constants of oxidation of CEs by KMnO_4 reported by Yan and Schwartz [3] indicate that chlorine atoms in CE structures may induce significant steric and electronic effects that hinder the formation of the initial intermediate.

3. Experimental section

3.1. Materials

KMnO_4 solutions of the required concentrations were prepared by dissolving KMnO_4 (reagent grade, Fisher Scientific, Pittsburgh, PA) in deionized (DI) water. Stock solutions of aqueous-phase TCE and DCEs were individually prepared in 40 ml volatile organic analysis (VOA) vials by equilibrating the excess of these chemicals (97–99+% purity, Fisher Scientific) with DI water. Because significant amount of PCE stock solutions were used in the experiments, they were prepared with phosphate-buffered solutions (instead of DI water) to avoid their impacts on the ionic strength and pH of the buffer solution in the reactor. The solutions in the 40 ml VOA vials were vigorously shaken and then left to stand for 24 h prior to transferring the aqueous-phase portions to other 40 ml VOA vials that were preserved at 4°C for further use. A VC stock solution of ~6.4 mM was prepared by diluting a VC standard solution of 31.9 mM (VC in methanol, quantitative validation, Chem Service, West Chester, PA) with methanol. The phosphate-buffered solution of pH 7 was prepared by mixing 1.85 g l⁻¹ of dibasic sodium phosphate (Na_2HPO_4 , 100.7%, Fisher Scientific) and 1.52 g l⁻¹ of monobasic sodium phosphate (NaH_2PO_4 , 99.2%, J.T. Baker, Phillipsburg, NJ) in DI water. The pH values of phosphate-buffered solutions were adjusted with 1N sodium hydroxide, (NaOH, ACS grade, Fisher Scientific) and perchloric acid, (HClO_4 , 70%, Fisher Scientific), whenever required. A solution (1N) of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, reagent grade, J.T. Baker) was used as a quenching reagent to stop the CE–permanganate reactions in samples [5].

3.2. Analysis

A gas chromatograph (HP GC-5890 Series II) equipped with a capillary column (0.25 mm × 60 m, J&W DB-624), a flame ionization detector, a purge & trap (Tekmar ALS 2016) and a concentrator (Tekmar LSC 2000) was used to analyze the CEs in samples that were quantified using the internal standard method. Chloride was analyzed by using an ion chromatograph (Dionex DX-500) equipped with an ion exchange column (Dionex 4 mm AS9H). KMnO_4 concentrations were measured by a spectrophotometer (Milton Roy Spectronic 601) at a wavelength (λ) of 526 nm. For the measurement of KMnO_4 concentration, the samples after being collected were immediately filtered with 0.45 μm syringe filters (13 mm PVDF membrane, Analytical Sales and Service) and measured for the absorbance at $\lambda = 526$ nm. All the pH measurements were made using a pH meter (Accumet, Fisher Scientific).

3.3. Kinetic experiments

The experiments of oxidation of PCE, TCE, 1,1-DCE and *cis*-DCE by KMnO_4 were conducted in a zero headspace batch system that comprised of a 100 ml gas-tight glass syringe connected to a sampling/injecting syringe by means of a control valve and luer-lock fittings (Fig. 1). The solution in the reactor had a constant pH value (by using phosphate-buffered solutions of $I \sim 0.05 \text{ M}$) and was under completely mixed and isothermal conditions (by placing the reactor on a magnetic stirring plate inside an incubator maintained at a desired temperature) during the experiment. The system was maintained in a zero headspace condition by moving the plungers of both the sampling and reactor syringes simultaneously during the injection of reactants or sampling to avoid CE loss due to evaporation during the experiment. A typical experiment involved adding 90–100 ml of phosphate-buffered solutions and a teflon-coated stir bar into a 100 ml syringe. The plunger was inserted to displace the air inside the syringe. An appropriate volume (determined based on the CE solubility; for instance 10 ml for PCE, 1.5 ml for TCE and less than 0.5 ml for DCEs) of CE stock solutions was then injected using a small gas-tight syringe and the contents were then mixed for 15 min on a magnetic stirrer that was placed inside an incubator. The first sample ($\sim 2.4 \text{ ml}$) was collected to determine the initial CE concentration. Following the initial sampling, the reaction was initiated by an injection of an appropriate volume of KMnO_4 solution (5, 10, 20, 30 or 40 g l^{-1}). Several samples were collected during the run to monitor the variation in CE concentration with time. Additional parameters including KMnO_4 , chloride and pH were measured only in the beginning and at the end of the experiment so that the change in reaction volume due to sampling was less than 5%. Samples collected for the analysis of CE and chloride were quenched immediately after sampling with sodium thiosulfate (1N) to stop the CE–permanganate reactions. CE samples were analyzed immediately after quenching. Several experiments were run in duplicate to ascertain the repeatability of the experimental procedures.

The kinetic experiments of oxidation of *trans*-DCE and VC by KMnO_4 were conducted in a set of 4.8 ml VOA vials due to their short half-lives (e.g. a few seconds under the

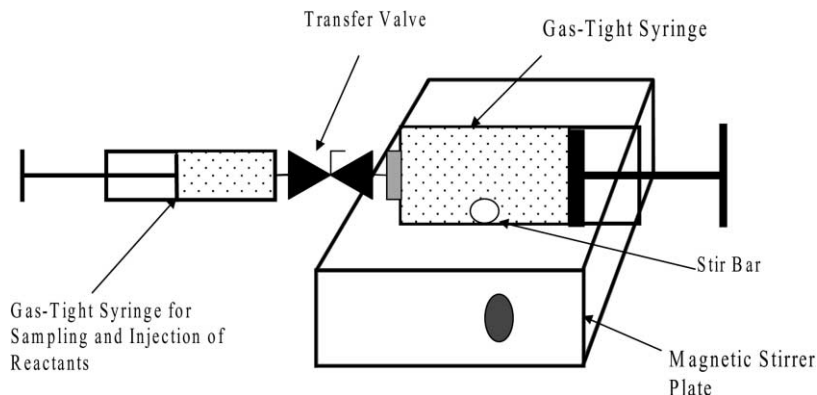


Fig. 1. The batch system used for the study of kinetics of oxidation of chlorinated ethenes by KMnO_4 .

experimental conditions). In a typical run, 10 vials (including one KMnO_4 vial, two substrate control vials and seven sample vials) were filled with 4.7 ml of KMnO_4 -in-buffer solutions (for the sample and KMnO_4 control vials) or a buffer-only solution (for the substrate control vials). These vials and the required reagents were placed in an incubator maintained at a desired temperature for 2 h. One vial at a time was then injected with 20 μl of *trans*-DCE (or 50 μl of VC) stock solution, manually shaken for 3–5 s, and then returned to the incubator. After a desired reaction time, one vial at a time was taken out of the incubator, quenched with 5 μl of 1N $\text{Na}_2\text{S}_2\text{O}_3$ solution and immediately analyzed for the target compound.

3.4. Determination of kinetic parameters

Generally, when reaction mechanisms are unknown, the rate law describing a particular chemical reaction can be deduced from experimentally measured time–concentration data for one or all of the reactants [18,19]. Kinetic rate methods including the differential method, the integral method and the initial rate method are commonly used to abstract kinetic parameters for developing rate laws [18,20]. The reactions were expected to be first order in both CE and permanganate based on early kinetic studies on the oxidation of alkenes and CEs by permanganate [3,5,15,21,22]. The integral method that was commonly selected for the reactions of known reaction order with respect to reactants was used to determine the rate parameters. The rate law for the degradation of CEs by KMnO_4 was assumed to be the form of Eq. (1).

$$-r_{\text{CE}} = k_{(a+b)} [\text{KMnO}_4]^a [\text{CE}]^b \quad (1)$$

where $-r_{\text{CE}} = -d[\text{CE}]/dt$ is the rate expression for CEs, $k_{(a+b)}$ the overall rate constant, 'a' and 'b' the reaction order in KMnO_4 and CE, respectively and are assumed to be one for both *a* and *b*. Under the conditions of KMnO_4 in excess of CEs, Eqs. (2) and (3) can be derived from Eq. (1).

$$-r_{\text{CE}} = k_1 [\text{CE}] \quad (2)$$

$$k_1 \approx k_2 [\text{KMnO}_4]_0 \quad (3)$$

where k_1 is the pseudo-first order rate constant (s^{-1}) for CEs, k_2 the second order rate constant ($\text{M}^{-1} \text{s}^{-1}$), $[\text{KMnO}_4]_0$ the initial KMnO_4 concentration (M). The above hypotheses are verified through the experimental data. Moreover, due to the strong oxidizing strength of permanganate, several parallel side reactions are virtually inevitable while KMnO_4 oxidizes CEs [23–25]. The experiments were therefore designed to collect seven to nine data values in the early stages of the reactions (e.g. within one to six half-lives of CE degradation) to minimize the errors induced from side reactions.

3.5. Extent of CE dechlorination and changes in acidity

The extent of CE dechlorination (based on the recovery of chloride produced from the reactions) and change in acidity of the solutions (based on the amount of protons produced from the oxidation per mole of CEs) due to the CE–permanganate reactions were studied. The experiments were conducted in a set of VOA vials with full capacity near 23.8 ml. Five

replicated experiments for each of the substrates were performed. A typical run involved filling five vials with 21.7–23.7 ml of KMnO_4 solution (1.6 mM) prepared with DI water, followed by an injection of 50–2000 μl of the CE stock solutions (all prepared with DI water) into the vials through the PTFE-lining septa in the vial cap. With a small air bubble remaining, the contents of the vials were manually mixed for ~ 30 s and the vials were then placed on a shaker inside an incubator maintained at 20°C . The experimental time was set to be sufficient so as to result in 99% degradation of the CE, estimated based on the rate constant obtained from the previous kinetics study. Changes in pH and chloride in the samples were determined by comparing the data observed in the sample vials with those in a control vial (i.e. with no CE injection). Two additional vials filled with the same volume of DI water instead of KMnO_4 solution were used to determine the initial CE concentration.

4. Results and discussion

4.1. Reaction order and rate constants

The kinetics of oxidation of CEs by KMnO_4 was investigated. The experiments were conducted in the phosphate-buffered solution of pH 7.0 and $I \sim 0.05$ M at the initial ratio of $[\text{KMnO}_4]_0/[\text{CE}]_0$ greater than 10 under isothermal, completely mixed and zero headspace conditions. The data of the degradation of PCE, TCE and three isomers of DCEs by KMnO_4 over the course of the reactions were fit with a first order decay model (because the degradation pattern for VC deviated from that of other CEs, the results of VC– KMnO_4 reactions are discussed in a later section). A typical graph showing the degradation of PCE, TCE and three isomers of DCEs by KMnO_4 during the experiments is presented in Fig. 2.

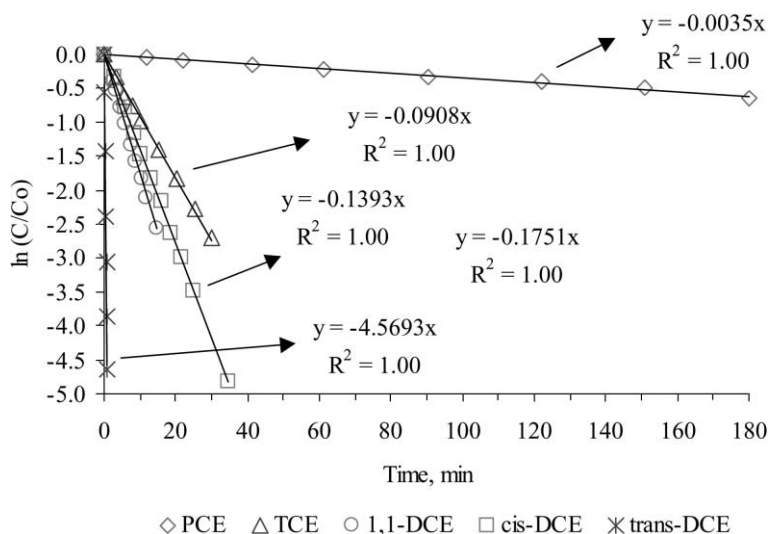


Fig. 2. Degradation of PCE, TCE, *cis*-DCE, 1,1-DCE and *trans*-DCE by KMnO_4 . $[\text{CE}]_0 \sim 0.1$ mM; $[\text{KMnO}_4]_0 \sim 1.6$ mM; pH = 7.0 (phosphate buffer, $I \sim 0.05$ M); 20°C .

The results in Fig. 2 indicate that the reaction order is first order with respect to PCE, TCE and all DCEs when reacting with KMnO_4 , as evidenced by the linear correlation relationship (e.g. $R^2 \sim 1$) among the data points for all runs. The observed pseudo-first order rate constants, half-lives and corresponding experimental conditions are shown in Table 1. Under the experimental conditions (e.g. $\text{KMnO}_4 = 1.6 \text{ mM}$ at 20°C), the half-lives of PCE, TCE, *cis*-DCE, 1,1-DCE and *trans*-DCE were approximately 202, 8, 5, 4, and 0.15 min, respectively. The results indicate that the rate of reaction between KMnO_4 and CEs decreased as the number of chlorine atoms in CEs increased, revealing that the chlorine atoms had a significant influence on the CE degradation rate. The rate constants for the oxidation of CEs with KMnO_4 at temperatures 10, 15, 20 and 25°C were also determined. It is evident that the reaction rate increases with the increase in temperature for all the CEs (Table 1).

Initially, the method of excess (e.g. TCE was used in excess of KMnO_4 in the experiments) was employed to investigate the reaction order with respect to KMnO_4 . However, because under high concentrations of TCE solutions KMnO_4 was rapidly consumed and the reaction formed brown colloidal MnO_x , monitoring the KMnO_4 concentration with time

Table 1

Rate constants for the oxidation of PCE, TCE, 1,1-DCE, *cis*-DCE and *trans*-DCE with KMnO_4 (1.6 mM) in phosphate-buffered solutions (pH 7; $I \sim 0.05 \text{ M}$) at various temperatures^a

[Substrate] ₀ ($\times 10^{-3} \text{ M}$)	R^2	Temperature ($^\circ\text{C}$)	k_1 ($\times 10^{-4} \text{ s}^{-1}$)	Half-life (min)	k_2^c ($\text{M}^{-1} \text{ s}^{-1}$)
PCE (0.13)	0.99	10	0.33	350.00	0.021
PCE (0.13)	0.99	15	0.48	240.00	0.030
PCE (0.13) ^b	1.00/0.99	20	0.57/0.56	201.67	0.036/0.035
PCE (0.12)	1.00	25	0.80	145.00	0.051
TCE (0.12)	1.00	10	8.53	13.54	0.53
TCE (0.14)	1.00	15	11.32	10.21	0.72
TCE (0.11) ^b	1.00/0.99	20	15.13/14.67	7.63	0.95/0.93
TCE (0.14)	1.00	25	18.83	6.13	1.19
1,1-DCE (0.11)	1.00	10	20.6	5.67	1.30
1,1-DCE (0.06)	1.00	15	25.4	4.50	1.61
1,1-DCE (0.12)	1.00	20	29.2	4.00	2.08
1,1-DCE (0.09)	1.00	25	39.0	3.00	2.47
<i>cis</i> -DCE (0.14)	1.00	10	13.0	8.83	0.82
<i>cis</i> -DCE (0.13)	1.00	15	16.8	6.83	1.06
<i>cis</i> -DCE (0.07) ^b	1.00/0.99	20	23.2/22.5	5.00	1.47/1.42
<i>cis</i> -DCE (0.13)	1.00	25	28.1	4.17	1.78
<i>trans</i> -DCE (0.11)	0.99	10	533	0.22	33.7
<i>trans</i> -DCE (0.10)	1.00	15	632	0.18	40.0
<i>trans</i> -DCE (0.05) ^b	1.00/0.99	20	760/749	0.15	48.0/47.4
<i>trans</i> -DCE (0.11)	1.00	25	897	0.13	56.8

^a The KMnO_4 concentration in C/C_0 at the end of the runs: >90% (PCE); >85% (TCE); >87% (1,1-DCE); >89% (*cis*-DCE); 90% (*trans*-DCE).

^b The experiment was conducted in duplicate.

^c k_2 is calculated by $k_2 = k_1/[\text{KMnO}_4]_0$.

by spectrophotometric methods was difficult due to the interference from MnO_x particles. One alternative approach (based on Eq. (3)) was adopted to investigate the reaction order in KMnO_4 . As implied by Eq. (3), under constant temperature and pH the pseudo-first order rate constant, k_1 , is proportional to $[\text{KMnO}_4]_0$ when a relatively constant KMnO_4 concentration is maintained during the reaction. The slope of the line in the plot of $\ln k_1$ versus $\ln[\text{KMnO}_4]_0$ will be close to one if the reaction is first order in KMnO_4 . A set of experiments involving the oxidation of CEs by various excess concentrations of KMnO_4 (the remaining KMnO_4 concentrations at the end of the runs are shown in Table 2) were performed, and the results are shown in Fig. 3. The slopes of the lines in Fig. 3 range from 0.99 to 1.04, demonstrating that it is first order with respect to KMnO_4 when reacting with CEs. The rate law for the CEs oxidation by KMnO_4 can be written as Eq. (4). The second order rate constants (k_2) calculated using Eq. (3) are presented in Tables 1 and 2.

$$-r_{\text{CE}} = k_2 [\text{KMnO}_4][\text{CE}] \quad (4)$$

Table 2

Rate constants for the oxidation of PCE, TCE, 1,1-DCE, *cis*-DCE and *trans*-DCE with various concentrations of KMnO_4 solutions in phosphate-buffered solutions (pH 7; $I \sim 0.05 \text{ M}$) at 20°C^a

[Substrate] ₀ ($\times 10^{-3} \text{ M}$)	$[\text{KMnO}_4]_0$ ($\times 10^{-3} \text{ M}$)	R^2	k_1 ($\times 10^{-4} \text{ s}^{-1}$)	k_2^c ($\text{M}^{-1} \text{ s}^{-1}$)
PCE (0.13) ^b	1.6	0.99/1.00	0.57/0.56	0.036/0.035
PCE (0.12)	3.2	1.00	1.03	0.033
PCE (0.13)	4.7	0.99	1.50	0.032
PCE (0.13)	6.3	1.00	2.32	0.037
Mean value $\pm 95\%$ confidence interval of k_2 at $20^\circ\text{C} = 0.035 \pm 0.004 \text{ M}^{-1} \text{ s}^{-1}$				
TCE (0.10)	1.6	1.00	13.4	0.84
TCE (0.19)	3.2	0.98	23.3	0.74
TCE (0.18)	4.7	0.97	36.7	0.78
TCE (0.12)	6.3	0.97	56.2	0.89
Mean value $\pm 95\%$ confidence interval of k_2 at $20^\circ\text{C} = 0.80 \pm 0.12 \text{ M}^{-1} \text{ s}^{-1}$				
1,1-DCE (0.12)	0.8	0.99	16.5	2.08
1,1-DCE (0.11)	1.6	1.00	29.2	1.84
1,1-DCE (0.09) ^b	2.4	1.00/1.00	51.0/49.2	2.15/2.07
1,1-DCE (0.11)	3.2	1.00	68.2	2.16
Mean value $\pm 95\%$ confidence interval of k_2 at $20^\circ\text{C} = 2.1 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$				
<i>cis</i> -DCE (0.07)	0.8	0.99	12.1	1.53
<i>cis</i> -DCE (0.14) ^b	1.6	1.00/0.99	23.2/22.5	1.47/1.42
<i>cis</i> -DCE (0.14)	2.4	1.00	36.5	1.54
<i>cis</i> -DCE (0.14)	3.2	1.00	48.4	1.53
Mean value $\pm 95\%$ confidence interval of k_2 at $20^\circ\text{C} = 1.52 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$				
<i>trans</i> -DCE (0.05)	0.8	1.00	388	49.1
<i>trans</i> -DCE (0.11) ^b	1.6	1.00/0.99	760/749	48.0/47.4
<i>trans</i> -DCE (0.11)	2.4	1.00	1143	48.2
<i>trans</i> -DCE (0.11)	3.2	1.00	1550	49.0
Mean value $\pm 95\%$ confidence interval of k_2 at $20^\circ\text{C} = 48.6 \pm 0.9 \text{ M}^{-1} \text{ s}^{-1}$				

^a TCE data are abstracted from the study by Huang et al. (1999). The KMnO_4 concentration in C/C_0 at the end of the runs: $>90\%$ (PCE); $>85\%$ (TCE); $>87\%$ (1,1-DCE); $>89\%$ (*cis*-DCE); 90% (*trans*-DCE).

^b The experiment was conducted in duplicate.

^c k_2 is calculated by $k_2 = k_1/[\text{KMnO}_4]_0$.

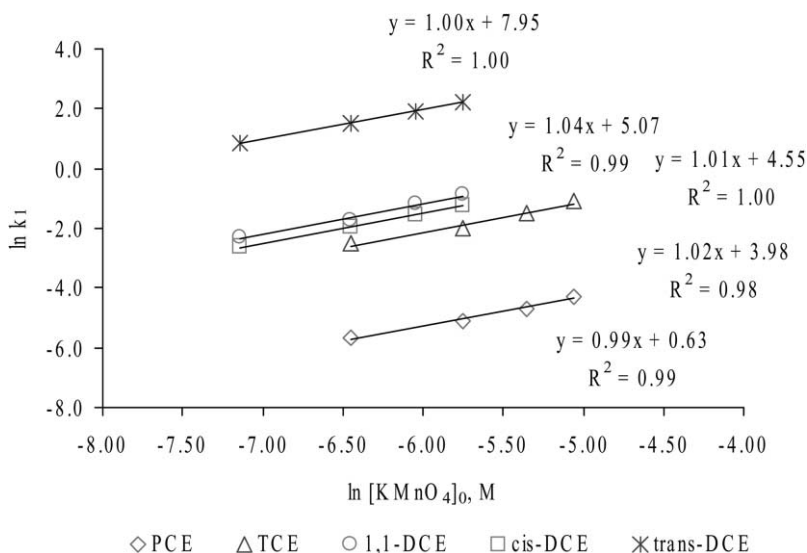


Fig. 3. Plot of $\ln k_1$ vs. $\ln[\text{KMnO}_4]_0$ for determining the reaction order (the slope) with respect to KMnO_4 in the reaction between CEs and KMnO_4 . $[\text{CE}]_0 \sim 0.1 \text{ M}$; $[\text{KMnO}_4]_0$ 0.8–6.3 mM; pH = 7.0; $I \sim 0.05 \text{ M}$; 20°C.

Values of k_2 for the reactions between KMnO_4 and PCE, TCE, *cis*-DCE, 1,1-DCE and *trans*-DCE at 20°C and pH 7 (phosphate buffer, $I \sim 0.05 \text{ M}$) are $0.035 \pm 0.004 \text{ M}^{-1} \text{ s}^{-1}$ (PCE), $0.80 \pm 0.12 \text{ M}^{-1} \text{ s}^{-1}$ (TCE), $1.52 \pm 0.05 \text{ M}^{-1} \text{ s}^{-1}$ (*cis*-DCE), $2.1 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ (1,1-DCE) and $48.6 \pm 0.9 \text{ M}^{-1} \text{ s}^{-1}$ (*trans*-DCE), respectively. The relative degradation rate among CEs by KMnO_4 are PCE < TCE < *cis*-DCE < 1,1-DCE < *trans*-DCE. It is evident that the degradation rate is inversely proportional to the number of chlorine atoms in CEs, suggesting that the chlorine atoms may induce significant steric and electronic effects upon the formation of the initial hypomanganate ester intermediates. The findings are in agreement with what Yan and Schwartz [3] have observed and suggested. The reaction rate does not increase as the electron deficiency of carbon atoms (polarized by chlorine atoms) in CEs increases, supporting that the attack of permanganate on C=C bonds is likely initiated through the electrophilic path as proposed by several early studies [26–28]. Moreover, the degradation rate of *trans*-DCE is nearly 32 times faster than that of *cis*-DCE, indicating that *cis*-DCE may encounter a much greater steric hindrance during the formation of the initial intermediates, most likely occurring when changing from a coplanar structure (with a bond angle 120°) to a tetrahedral (with a bond angle 109°) configuration, which involves changes in bond angle.

4.2. Activation parameters

In order to determine the activation parameters of the reactions between KMnO_4 and CEs, the rate constants at four different temperatures (10, 15, 20 and 25°C) were determined. The second order rate constants at these temperatures (Table 1) were used to calculate the

activation energy using the linearized Arrhenius equation (Eq. (5)).

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

where k is the rate constant, A the frequency factor, E_a the activation energy (kcal mol^{-1}), R the universal gas constant, T the temperature (K). When $\ln k$ is plotted versus $1/T$ as shown in Fig. 4, the slope of the line will give “ $-E_a/R$ ”. It is evident by the high correlation coefficients (e.g. $R^2 = 0.98$ –1.0) of the regression lines in Fig. 4 that the activation energy is nearly constant under the range of studied temperatures. The activation energies for the reactions between KMnO_4 and CEs are $9.3 \pm 0.9 \text{ kcal mol}^{-1}$ (PCE), $8.9 \pm 0.3 \text{ kcal mol}^{-1}$ (TCE), $8.8 \pm 0.5 \text{ kcal mol}^{-1}$ (*cis*-DCE), $6.9 \pm 0.7 \text{ kcal mol}^{-1}$ (1,1-DCE) and $5.8 \pm 0.1 \text{ kcal mol}^{-1}$ (*trans*-DCE) (Table 3). An approximately 10°C increase will increase the oxidation rate by a factor of 1.8 (for PCE) to 1.2 (for *trans*-DCE).

Furthermore, based on the transition state theory the enthalpy (ΔH^*), entropy (ΔS^*) and Gibbs free energy (ΔG^*) of activation were determined using Eqs. (6)–(8), respectively, assuming that the CE– KMnO_4 reactions follow a bimolecular elementary reaction and that ΔH^* and ΔS^* are not functions of temperature in the studied range [29–31].

$$\Delta H^* = E_a - RT \quad (6)$$

$$\Delta S^* = \left(\frac{1}{R}\right) \ln \left(\frac{k_2}{[(kT/h)e^1 e^{-E_a/RT}]} \right) \quad (7)$$

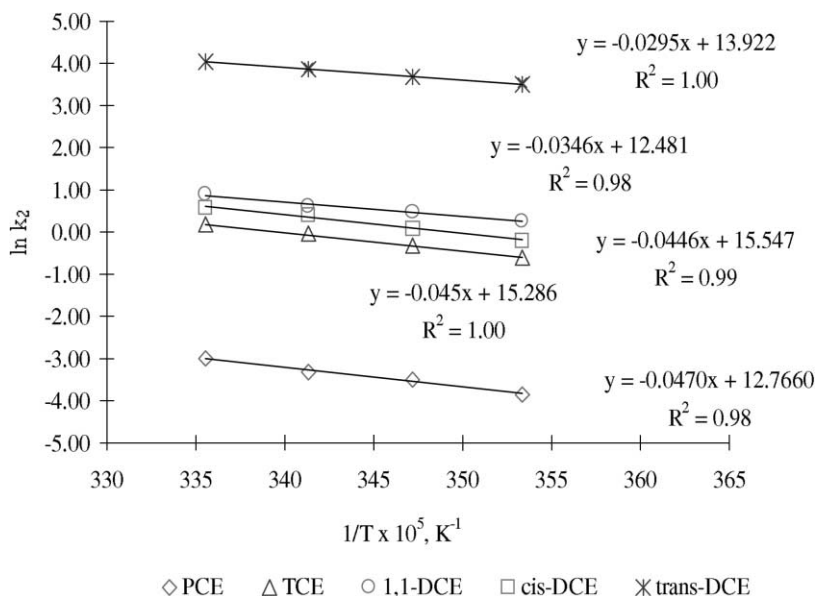


Fig. 4. Plot of $\ln k_2$ vs. $1/T$ for determining the activation energies of oxidation of CEs with KMnO_4 using Arrhenius equation. $[\text{CE}]_0 \sim 0.1 \text{ mM}$; $[\text{KMnO}_4]_0 \sim 1.6 \text{ mM}$; $\text{pH} = 7.0$; $I \sim 0.05 \text{ M}$; 10 – 25°C .

Table 3
Activation parameters for the oxidation of five chlorinated ethenes with permanganate

CEs ($\times 10^{-3}$ M)	E_a^a (kcal mol $^{-1}$)	ΔG^{*b} (kcal mol $^{-1}$)	ΔH^{*b} (kcal mol $^{-1}$)	$-\Delta S^{*b}$ (cal mol $^{-1}$ K $^{-1}$)
PCE	9.3 \pm 0.9	19.4	8.8	36
TCE	8.9 \pm 0.3	17.5	8.3	31
<i>cis</i> -DCE	8.8 \pm 0.5	17.2	8.2	30
1,1-DCE	6.9 \pm 0.7	17.0	6.3	36
<i>trans</i> -DCE	5.8 \pm 0.1	15.1	5.2	33

^a Mean value \pm 95% confidence interval.

^b Determined based on the mean value of E_a by Eqs. (6)–(8); $T = 298$ K.

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (8)$$

where k is the Boltzmann constant (1.38×10^{-23} J K $^{-1}$), h the Planck constant (6.63×10^{-34} J s), T the temperature (K). It is evident from Table 3 that the CE–KMnO $_4$ reactions have a relatively low ΔH^* and a large negative ΔS^* . The results are in agreement with several prior studies on alkene–permanganate reactions [13,15]. Since ΔH^* and ΔS^* are the difference in bond energy and entropy, respectively between the reactants and the activated complex, they can be used to deduce the nature of the activated complex. The observed ΔH^* (5.2–8.8 kcal mol $^{-1}$) and ΔS^* (-30 to -36 cal mol $^{-1}$ K $^{-1}$) are comparable to the reported data [e.g. ΔH^* (5.3–7.9 kcal mol $^{-1}$) by Freeman et al. [13]; ΔH^* (5.6 kcal mol $^{-1}$) and ΔS^* (-38 cal mol $^{-1}$ K $^{-1}$) by Lee and Brown [15], indicating that the initial step of the CE–permanganate reactions may proceed via a similar path and activated complex to those of alkene–permanganate reactions.

4.3. Oxidation of vinyl chloride by KMnO $_4$

The oxidation of VC with KMnO $_4$ was studied in phosphate-buffered solutions (pH = 7 and $I \sim 0.05$ M) at the initial ratio of $[\text{KMnO}_4]_0/[\text{VC}]_0$ greater than 10 under isothermal and zero headspace conditions in a set of vials. The degradation of VC over the course of the reaction indicated that KMnO $_4$ rapidly oxidized VC (Fig. 5). However, the degradation pattern was not simply first order in VC as that observed for other CEs when oxidized by KMnO $_4$. The degradation of VC appeared more likely to be a two-consecutive-step process. The rate of the first step (where C/C_0 decreased from 1.0 to ~ 0.5 within 5 s) was much faster and less affected by temperature than that of the second step (where it took ~ 1 min for C/C_0 to decrease from ~ 0.5 to 0.1). The two degradation rates indicate that the reaction was a two-consecutive-step reaction, in which the second step determined the VC degradation rate (Fig. 5). Moreover, the results imply the existence of the initial intermediate, generally believed to be the (2 + 3) cyclic hypomanganate ester formed at the first step of the reaction. A hypothetical process for the degradation of VC by permanganate is proposed below. When permanganate ions encounter VC molecules, the hypomanganate ester intermediates may be rapidly formed because of the low activation energy between the reactants and the activated complex. The first step reaction (i.e. forming the initial intermediate) is, however, gradually

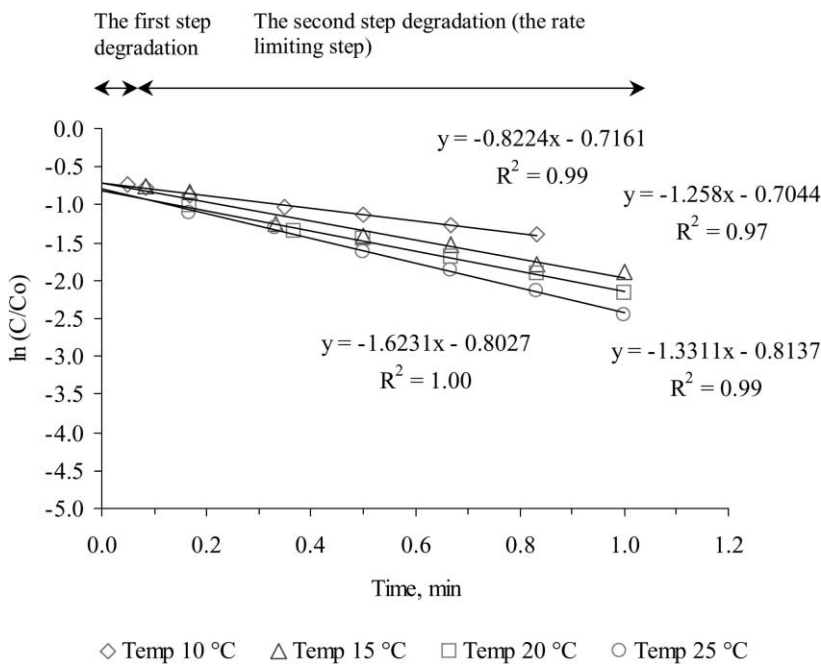


Fig. 5. Degradation of VC by KMnO_4 is a two-step process. The second step, being the rate-limiting step, follows first order decay model. $[\text{VC}]_0 \sim 0.03\text{--}0.08$ mM; $[\text{KMnO}_4]_0 \sim 0.8$ mM; pH = 7.0 (phosphate buffer, $I \sim 0.05$ M); 10–25°C.

inhibited while the concentration of the initial intermediate increases. At a certain point, a reversible balance condition between the reactants and the intermediates is established. Compared to the first step of the reaction, the second step is relatively slow and thus determines the rate of VC degradation (Fig. 5). Although the reaction pattern of VC deviates from that of other CEs, similar behavior has been observed in several alkenes–permanganate reactions [14,22]. The kinetics study of oxidation of cinnamic acid with acidic permanganate reported that in the two-step oxidation process, the second step was first order with respect to the reductant [14].

The degradation of VC in the second step can be modeled with a first order decay equation, as evidenced by the $R^2 \sim 0.99$ of the linear regression lines in Fig. 5. This may imply that a reaction pathway dominates the decomposition of the initial intermediate in the second step. The rate constants for the reactions in the second step (excluding the data observed in the first step of the reaction) at 10, 15, 20, and 25°C were 0.0137, 0.0197, 0.0238 and 0.0286 s^{-1} , respectively (Table 4). Based on these rate constants, the activation energy determined using the Arrhenius equation for the second step is 7.9 ± 1.0 kcal mol^{-1} . Clearly, the degradation rate (0.0238 s^{-1}) for VC in a KMnO_4 solution (0.8 mM) at 20°C at the rate-limiting step is slower than that (0.0388 s^{-1}) for *trans*-DCE. This implies that while the chlorine atoms in CEs hinder the formation of the hypomanganate ester intermediate, they may enhance/destabilize the initial intermediate in the subsequent reactions.

Table 4

Rate constants at the rate-limiting step of oxidation of vinyl chloride with KMnO_4 in phosphate-buffered solutions (pH 7; $I \sim 0.05 \text{ M}$) at various temperatures

Vinyl chloride ($\times 10^{-3} \text{ M}$)	KMnO_4 ($\times 10^{-3} \text{ M}$)	Temperature ($^{\circ}\text{C}$)	k_1 ($\times 10^{-4} \text{ s}^{-1}$)	Half-life (min)
0.08	0.8	10	137	0.84
0.07	0.8	15	197	0.59
0.08	0.8	20	238	0.48
0.03	0.8	25	286	0.40

4.4. Extent of dechlorination and changes in acidity

The extent of dechlorination and change in acidity of the solution for the oxidation of PCE, TCE and three isomers of DCEs with KMnO_4 were investigated. The results show that nearly 100% of chlorine atoms in all the substrates were recovered as chloride in solutions (Table 5), indicating that KMnO_4 is able to completely dechlorinate PCE, TCE and all the DCEs. Chloride may potentially be used as a parameter to estimate the amount of CE destruction by permanganate oxidation in field application. Although it has been reported that chloride may be oxidized into chlorine gas under extreme conditions (e.g. very low pH and high oxidant concentration), it appeared to be very conservative under the experimental conditions.

Examination of the change in acidity of the solution, expressed as $(\text{H}^+)/(\text{substrate})$ in mol per mol (based on the observed changes in pH), when one mole of each of the substrates was oxidized revealed that the order of increase in acidity was $\text{PCE} > \text{TCE} \gg \text{cis-DCE} > 1,1\text{-DCE} \approx \text{trans-DCE}$ (Table 5). The results indicate that the increase in acidity of the solution due to CE oxidation by permanganate is directly proportional to the number of chlorine atoms in CEs. This is most likely because the α -haloalcohols and/or α -haloketones formed during the reactions underwent HCl elimination reactions [17].

Table 5

Extent of dechlorination and change in acidity during the oxidation of PCE, TCE, 1,1-DCE, *cis*-DCE, and *trans*-DCE by KMnO_4 at 20°C

Substrate ($\times 10^{-3} \text{ M}$)	KMnO_4 ($\times 10^{-3} \text{ M}$)	Reaction time (min)	Extent of dechlorination (%) ^{a,b}	$(\text{H}^+)_{\text{prod.}}/(\text{substrate})_{\text{oxid.}}$ (mol mol^{-1}) ^a
PCE (0.13)	1.6	1440	101 ± 6	2.2 ± 0.3 (pH 6.5 \rightarrow 3.4)
TCE (0.12)	1.6	90	102 ± 4	1.3 ± 0.3 (pH 6.5 \rightarrow 3.9)
1,1-DCE (0.16)	1.6	90	100 ± 2	0.02 ± 0.001 (pH 7.1 \rightarrow 5.5)
<i>cis</i> -DCE (0.20)	1.6	90	105 ± 2	0.04 ± 0.01 (pH 7.1 \rightarrow 5.4)
<i>trans</i> -DCE (0.09)	1.6	30	101 ± 9	0.02 ± 0.003 (pH 7.1 \rightarrow 5.8)

^a The average of five replicated experiments $\pm 95\%$ confidence interval.

^b Extent of dechlorination = $[\text{Cl}^-]_{\text{prod.}}/n[\text{CE}]_0$; $[\text{Cl}^-]_{\text{prod.}}$ = produced chloride (mM) from CE oxidation; $[\text{CE}]_0$ = initial CE concentration (mM); n = number of chlorine atoms in CE.

5. Conclusions

The kinetics of the oxidation of six CEs with KMnO_4 was studied. Kinetic parameters including reaction order, rate constant and activation parameters of the reactions between KMnO_4 and PCE, TCE, three isomers of DCEs and VC were determined. The results indicate that the oxidation of PCE, TCE and three isomers of DCEs by KMnO_4 is first order in both the reductant and the oxidant. The rate of reaction between KMnO_4 and CEs decreases as the number of chlorine atoms in CEs increases, most likely due to the hindrance, induced by the chlorine atoms, of the formation of the initial hypomanganate ester intermediate. The activation parameters (e.g. ΔH^* from 5.2 to 8.8 kcal mol⁻¹ and ΔS^* from -30 to -36 cal mol⁻¹ K⁻¹) for the reaction between KMnO_4 and five CEs show that the initial step of the CE-permanganate reactions proceeds via a similar path and activated complex to those of alkene-permanganate reactions. Unlike other CEs, the degradation of VC by KMnO_4 appears to be a two-consecutive-step process. The second step, involving subsequent reactions of the initial intermediate formed during the first step of the reaction, determines the degradation rate. It is of first order in VC and has an E_a of 7.9 ± 1 kcal mol⁻¹.

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