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Applications of electrochemical ferrate(VI) for degradation of trichloroethylene in the aqueous phase

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ABSTRACT

The degradation of trichloroethylene (TCE) by ferrate generated from electrochemical synthesis has been studied. The degradation efficiency of TCE in aqueous solution was observed at various pH (3, 7, 11), ferrate dosages (5, 8, 11, 13, 15 and 17 mg/L), and temperature (10, 25, 35 and 50˚C). The experimental results showed that TCE removal efficiency increased with an increase in ferrate dosages. For the effect of pH, the highest value of k_{app}, 893.54 $\mathrm{M^{-1}s^{-1}}$, was observed at pH 7. The TCE degradation pathways have been proposed based on the intermediate products such as ethyl chloride, dichloroethylene, chloroform, 1,1-dichloropropene, trichloroacetic acid and trichloroethane, and $\mathrm{Cl^-}$ was identified as an end product.

Keywords: Ferrate(VI); Trichloroethylene; Reaction pathway; Intermediate study

1. Introduction

Trichloroethylene (TCE) is a volatile organic compound that has been proven to cause liver damage and kidney failure in humans, and was assessed as carcinogenic to animals. TCE is produced worldwide in very large quantities due to its extensive use in the chemical industry. Leakage from storage tanks and, sometimes, improper disposal practices led to soil, groundwater, and surface water contamination with TCE. Consequently, TCE is listed as a priority pollutant in the US EPA Chemical Contaminant List and is strictly regulated in drinking water to a maximum contaminant level of 0.005 mg/L [1]. The application of oxidizing chemicals in treatment of drinking water and wastewater continues to be an active topic of scientific research and an interest to water utility practitioners. This arises from the continuing need to meet higher water quality objectives and to employ treatment chemicals that are cost-effective and which lead to a low level of by-product formation. Thus, in recent years, considerable attention has been paid to the study of chlorine dioxide, potassium permanganate, ozone, ozone/H_2O_2 and UV/H_2O_2. Of Particular interest are those chemicals which are able to contribute to a variety of treatment objectives. In this respect, salts of the ferrate(VI) ion, $\mathrm{FeO_4^{2-}}$, have the ability to act as both oxidant and primary coagulant [2]. Ferrate(VI) has been of great interest because of its role as an oxidant and hydroxylating agent in industrial and water

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treatment processes, such as the development of a "super iron" battery, green chemistry synthesis, and non-chlorine oxidation for pollutant remediation [3–12]. Ferrate(VI) provides an environmentally benign, high-energy density cathode for batteries [13–15]. Selective oxidations by ferrate(VI) can be complete oxidation reaction in shorter time periods than oxidations carried out by permanganate and chromate [16,17]. Iron, unlike chromium and manganese, is considered non-toxic; therefore, ferrate(VI) can make industrial processes more environmentally benign by achieving cleaner technologies. In addition, ferrate(VI) is an emerging water-treatment disinfectant and coagulant, which does not cause the concerns of disinfectant by-products associated with currently used chemicals such as free chlorine and chloramines [18–22]. The kinetics of reactions of inorganic and organic compounds with ferrate(VI) indicate that degradation of contaminants would be complete in milliseconds to seconds. The products of the oxidation of compounds studied are relatively non-toxic [23–26]. Also, ferrate(VI) does not react with bromide ion, unlike ozone; so carcinogenic bromate ion is not produced in the treatment of bromide-containing water. In addition, ferrate(VI) acts as a strong oxidant to degrade a wide range of compounds present in wastewater and industrial effluents [3,27,28].

In general, there are three methods for the synthesis of ferrate: (1) the electrochemical method by anodic oxidation of iron in an alkaline electrolyte solution. The production yield is revealed to be strongly dependent on the electrolyte concentration and current density; (2) the dry methods by which various iron-oxide containing minerals are melted under extremely alkaline and aerobic conditions. This method proves to be quite dangerous and difficult, since the synthesis process could cause detonation at elevated temperature; and (3) the wet method by which an iron salt is oxidized under extremely alkaline condition by either hypochlorite or chlorine [29]. The main advantage of the electrochemical synthesis in comparison to the other two methods is the high purity of the product and the utilization of an electron as a so-called "clean oxidant". In addition, this approach results in a substantial reduction of the amount of solvents needed to produce ferrate of high purity [30]. The objective of this study is to evaluate the electrochemical ferrate(VI) process for the decomposition of refractory and toxic TCE. The effect of the parameters such as ferrate dosage, pH and temperature was investigated. The study of intermediates was implemented to find out the degradation pathways of TCE by ferrate(IV).

2. Materials and methods

2.1. Materials

The chemicals used in these studies were reagent grade or higher purity. Electrochemical ferrate(VI) was synthesized and analyzed using the method in the previous works [31–34]. TCE was obtained from the Wako Pure Chemical Industries (Ltd., Japan). The purity of the organic compound was 99.5%. Stock of TCE was prepared in a stirred glass flask, which was sealed by Teflon-covered rubber stopper to prevent organic vapor from escaping.

2.2. Experiments

Experiments were conducted in a closed, zero-head space, glass reactor, sealed with Teflon-covered rubber stoppers and operated in the batch mode. Temperature inside the reactor was kept at a preselected value. A pH meter was used to control the pH at constant value.

2.3. Analytical methods

TCE in 0.4 mL sample from the reactor was extracted using the headspace extraction method and analyzed with gas chromatography (Technologies Co. 4890D) equipped with a Rxi-5 ms column ($L = 30$ m, internal diameter = 0.25 μm), and an electron capture detector (ECD). The temperatures of the injection port and detector were 250 and 280℃, respectively. The temperature program began at 50℃, followed by a 10℃/min ramp until a temperature of 150℃ was reached, then followed by a 20℃/min ramp until a final temperature of 250℃ was reached. The gas chromatography/mass spectrometry (GC/MS) technique was used to analyze reaction intermediates. GC/MS analysis was performed with Mass Spectrometer Systems (GCMS-QP2010Plus, Shimadzu, Japan) and an AT-1 capillary column (60 m × 0.32 mm I.d × 1.0 μm film thickness). The injection port temperature was 300℃ and the column temperature, initially 35℃, was held constant for 10 min, followed by 8℃/min ramp until a temperature of 120℃ was reached and held for 10 min, then followed by 12℃/min ramp until a temperature of 180℃ was reached and held for 7 min, and followed by 15℃/min ramp until a final temperature of 230℃ was reached.

3. Results and discussion

3.1. Effect of pH

The effect of pH on TCE degradation is shown in Fig. 1. The effect of pH was tested at pH 3, 7, and 11.

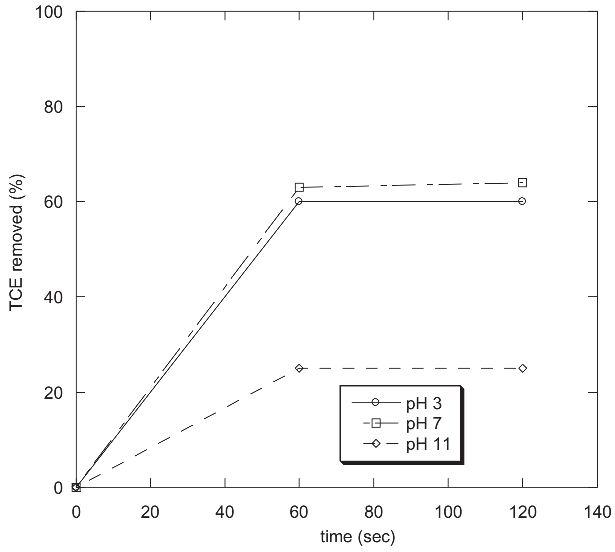

Fig. 1. Effect of pH on the TCE removal of (%) by ferrate. (Experimental conditions: $C_o = 1$ ppm, $[FeO_4^{2-}] = 13$ mg/L, Temp. = 25 ± 1°C.)

Fig. 2 shows the relationship between ferrate exposure and TCE decomposition (C/C_o) by ferrate in pH variations. The ferrate exposure is the time-integrated concentration of ferrate due to the instability and the k_{app} is the apparent second-order rate constant [35]. The k_{app} value of 893.54 $M^{-1}s^{-1}$ was obtained from the slope of the plots ferrate exposure and ln C/C_o of TCE at pH 7, while pH 3 and 11 was 435.23 and 351.36 $M^{-1}s^{-1}$ [35].

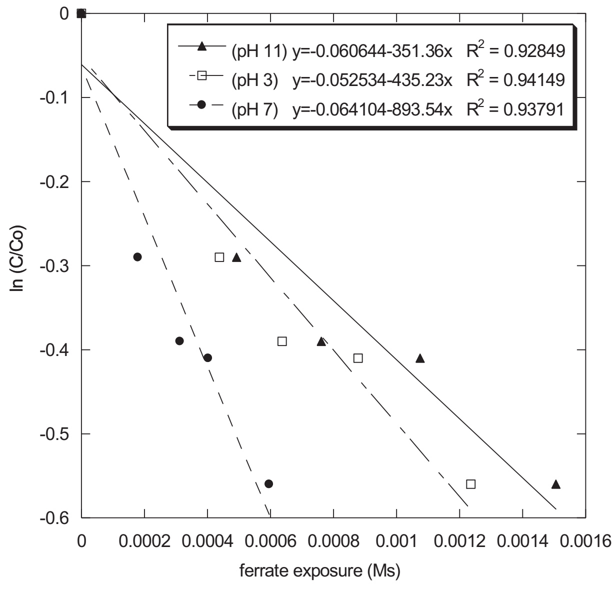

Fig. 2. Rate TCE degradation by ferrate in pH variations. (Experimental conditions: $C_o = 1$ ppm, $[FeO_4^{2-}] = 13$ mg/L, Temp. = 25 ± 1°C.)

According to the previous studies on ferrate reaction with organic compound, second-order reaction rate constants have been obtained. The second-order reaction rate law can be described by Eq. (1).

$$-\mathrm{d}[\mathrm{TCE}]/\mathrm{d}t = k_{\mathrm{app}}[\mathrm{FeO}_4^{2-}][\mathrm{TCE}] \tag{1}$$

Eq. (1) is rearranged and d[TCE]/dt is integrated to become Eq. (2)

$$\mathrm{Ln}(\mathrm{TCE}]/[\mathrm{TCE}]_0) = -k_{\mathrm{app}}\int_0^t [\mathrm{FeO}_4^{2-}]dt$$

where the $\int_0^t [\mathrm{FeO}_4^{2-}]\mathrm{d}t$ is the concentration of ferrate exposure, and the k_{app} is the apparent second-order reaction rate constant [35–37].

Ferrate is a powerful oxidizing agent throughout the entire pH range with a reduction potential varying from +2.2 to +0.7 V in acidic and basic solution. Ferrate (VI) ion is reduced rapidly to Fe(III) and oxygen in strong acids [9]. Decreasing pH caused the decomposition of ferrate(VI) by itself, and consequently reduced the reaction rate of ferrate with TCE [38,39].

At pH 7, the reaction proceeded very fast and TCE decomposition reached 64% after 2 min. At pH 11, the degradation efficiency of TCE was only 25% after 2 min. Among the different conditions of pH, the highest degradation efficiency of TCE was obtained at pH 7 and the lowest was obtained at pH 11, the alkaline condition.

3.2. Effect of ferrate dosage

The effect of the ferrate dosage on the degradation of TCE is shown in Fig. 3. The TCE degradation efficiency increased with an increase in ferrate dosage. It has been reported that the degradation efficiency increased with increasing of ferrate(VI) dosage and the degradation of TCE strongly depended on the dosage of ferrate added to the reactor in previous studies [38–40]. From the experiments, the amount of the ferrate(VI) added to the reactor definitely affected the TCE degradation efficiency, and the proportional relationship was also observed between ferrate dosage and degradation efficiency of TCE (Fig. 4).

3.3. Effect of temperature

Fig. 5 shows the effect of steady-state solution temperature on TCE decomposition. The effect of temperature was observed at four different temperature

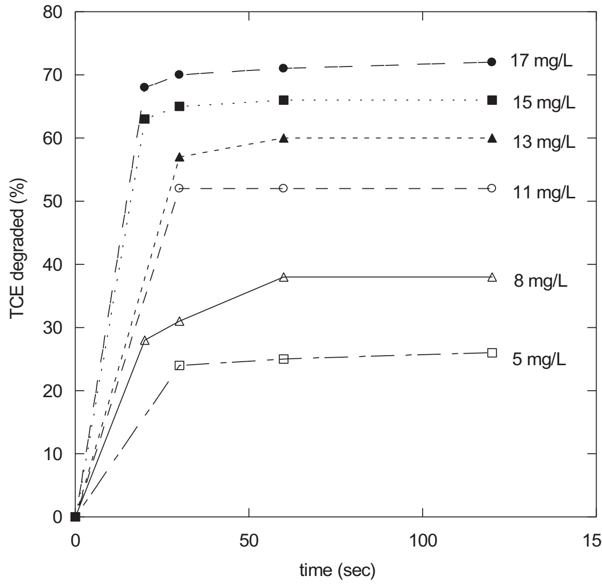

Fig. 3. Effect of the ferrate [FeO_4^{2-}] dosage on removal of TCE (%). (Experimental conditions: $C_o = 1$ ppm, pH = 3.0, Temp. = 25 ± 1˚C.)

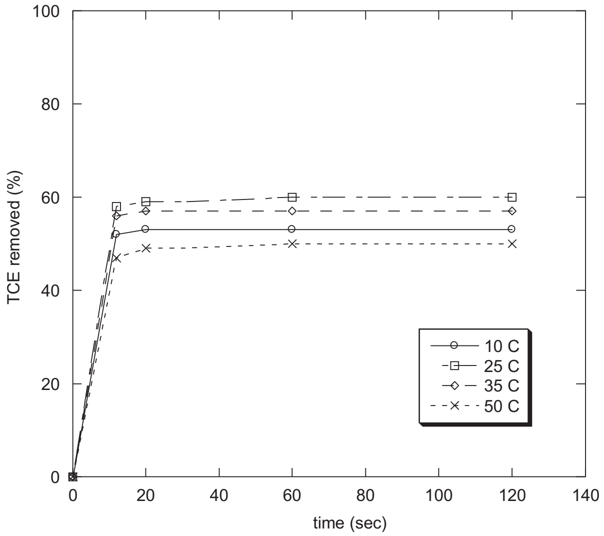

Fig. 5. Effect of the temperature on removal of TCE (%) by ferrate. (Experimental conditions: $C_o = 1$ ppm, [FeO_4^{2-}] = 13 mg/L, pH = 3.0.)

conditions (10, 25, 35, and 50˚C). The TCE degradation efficiency increased from temperature 10 to 25˚C, but decreased from temperature 25 to 50˚C. Increasing temperature caused self-decomposition of ferrate and reduced the ferrate concentration to react with TCE. The temperature has been reported as one of the most significant parameters, its effect on ferrate stability has been observed in the previous researches. Increasing temperature caused an enhancement of the homogeneous ferrate decomposition kinetics [41–43]. The activation energy for TCE degradation reaction was 5.27 kJ/mole, as measured by Arrhenius equation:

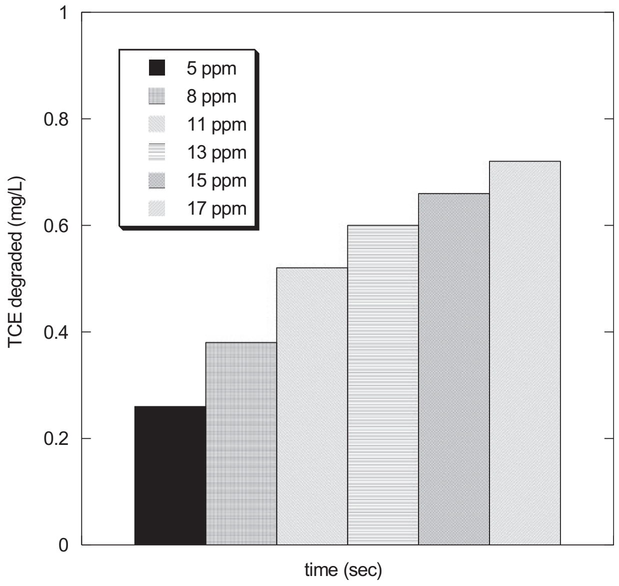

Fig. 4. TCE degraded (mg/L) in various ferrate dosages. (Experimental condition: $C_o = 1$ ppm, Temp. = 25 ± 1˚C, contact time 2 min.)

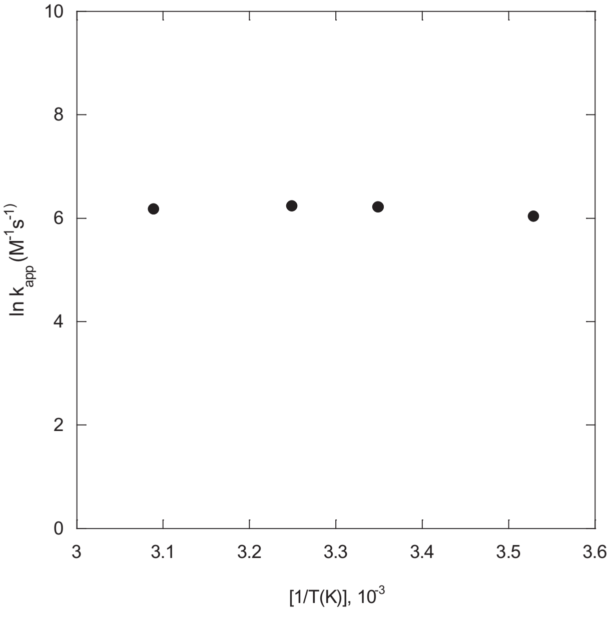

Fig. 6. k_{app} of TCE degradation by ferrate in various temperatures. (Experimental conditions: $C_o = 1$ ppm, [FeO_4^{2-}] = 13 mg/L, Temp. = 25 ± 1˚C.)

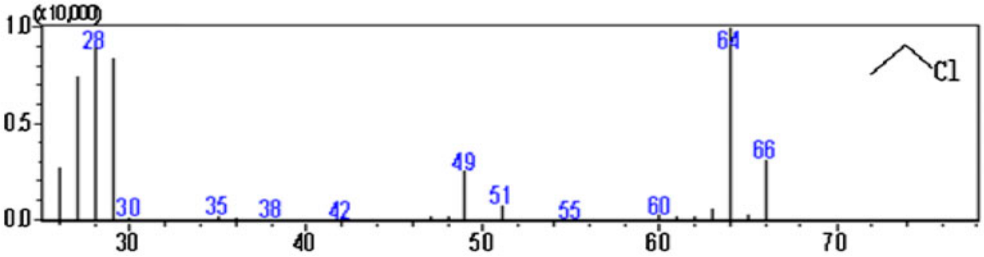

Fig. 7(a). Mass spectrum of ethyl chloride. (Ret. time: 3.627 min.)

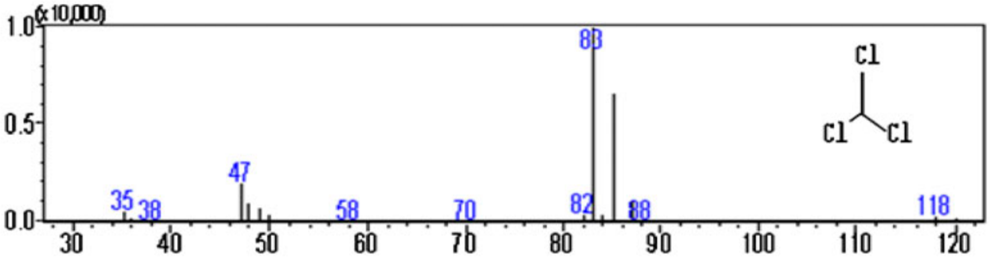

Fig. 7(b). Mass spectrum of dichloroethylene. (Ret. time: 4.519 min.)

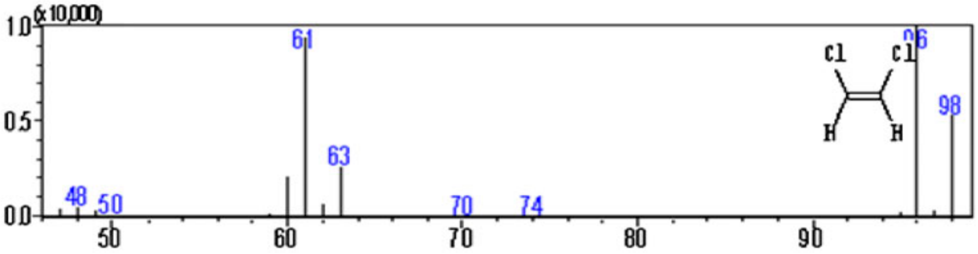

Fig. 7(c). Mass spectrum of chloroform. (Ret. time: 6.978 min.)

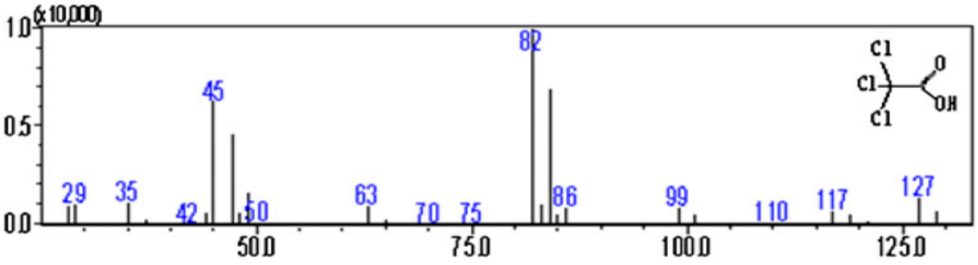

Fig. 7(d). Mass spectrum of trichloroacetic acid. (Ret. time: 13.448 min.)

$$\ln\frac{rate_1}{rate_2} = -\frac{ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

Fig. 6 shows the k_{app} values in the temperature range from 10 to 45℃ with the concentration of ferrate, 13 mg/L in acidic condition. The highest value of $k_{\mathrm{app},}$ 504.01 $M^{-1}s^{-1}$ was obtained in 25℃.

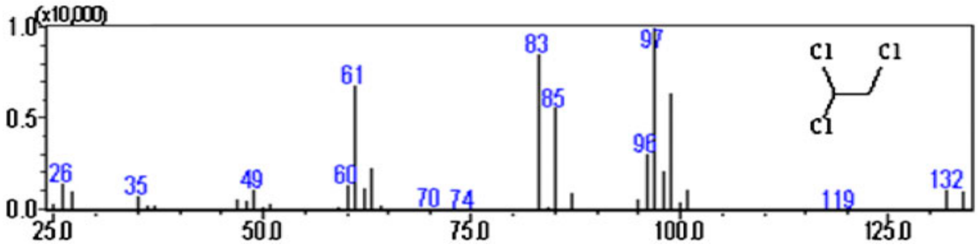

Fig. 7(e). Mass spectrum of trichloroethane. (Ret. time: 14.681 min.)

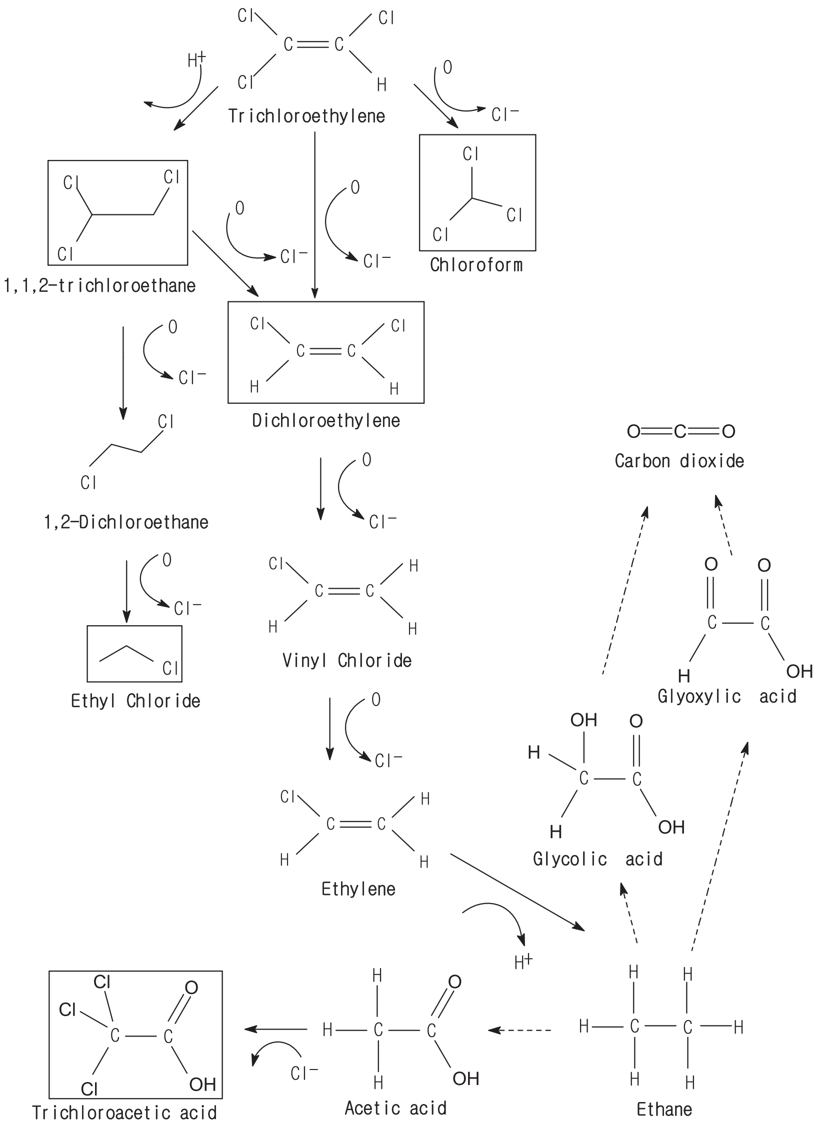

Fig. 8. Reaction pathways for TCE degradation by ferrate. (Species in boxes were detected in the experiments.)

3.4. Identification of TCE intermediates

The mechanism of the reactions between ferrate (VI) and organic/inorganic matters can be divided into three categories. In general, ferrate(VI) was known to allow organic/inorganic matters to be oxidized either by providing oxygen or by taking away electron or hydrogen atom from organic/inorganic matters [3,9,43]. The analysis of the reaction intermediates of TCE proposed reaction pathways to describe the decomposition of TCE by ferrate(VI) in aqueous solution. The reaction started by adding oxygen which is generated from ferrate(VI) [9,44]. The mass spectra of the reaction intermediates of TCE are shown in Fig. 7(a)–(e). The mass spectra were examined with the computer database of the National Institute of Science and Technology mass spectral library. The reaction would mineralize these intermediates to end products such as carbon dioxide and chloride ion. Fig. 8 shows the possible reaction pathways involving oxygen. The first step of the reaction was oxygen transfer and proton addition which yielded the 1,1,2-trichloroethane, dichloroethylene, and chloroform. After first hydrogenation, 1,1,2-trichloroethane could be changed to 1,2-dichloroethane by second oxygen transfer. After second oxygen transfer, 1,2-dichloroethane could be changed to ethyl chloride by third oxygen transfer. And after first oxygen transfer, dichloroethylene could be changed to vinyl chloride by second oxygen transfer. After second oxygen transfer, vinyl chloride could be changed to ethylene by third oxygen transfer. Further decomposition would generate ethane [45–47]. The ethane would be converted to glycolic acid and glyoxylic acid. Then it was proposed that further decomposition of intermediates led to end products like carbon dioxide [48].

4. Conclusion

TCE in aqueous phase could be effectively decomposed by electrochemical ferrate. Degradation efficiency of TCE increased with increasing of ferrate dosage in the range of 5–17 mg/L. Also the rate of TCE oxidation increased with the increase in ferrate dosage. Among three different pH levels (3, 7, 11), the highest rate constant of TCE degradation, $893.54\ M^{-1}s^{-1}$ was obtained at pH 7. The reaction in aqueous solution was affected by the steady-state temperature, and the activation energy value of 5.27 kJ/mole was calculated from the Arrhenius expression for degradation of TCE by ferrate in this controlled reaction condition. Based on the reaction intermediate study, five reaction intermediates have been detected such as ethyl chloride, dichloroethylene, chloroform, trichloroacetic acid, and trichloroethane.

Acknowledgments

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