

Kinetics of the Degradation of 1,4-Dioxane Using Persulfate

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Recibido el 21 de julio de 2006; aceptado el 19 de enero de 2007

Abstract. The kinetics of oxidation of 1,4-dioxane by persulfate ions in aqueous media was investigated at different temperature, oxidant concentration and pH. Experimental results indicated that 1,4-dioxane degradation follows a pseudo-first-order decay model. Under the experimental conditions the reaction has an activation energy of 21.0 kcal/mol. Temperature and persulfate concentration significantly accelerate the 1,4 dioxane degradation, however, increasing pH (over the range of 3-11) decreased the rate.

Keywords: 1,4-dioxane, persulfate, degradation, kinetics.

Resumen. Se investigó la cinética de oxidación de 1,4-dioxano con iones persulfato en medio acuoso a diferente temperatura, concentración del oxidante y pH. Los resultados experimentales indican que la degradación de 1,4-dioxano sigue una cinética de pseudo-primer orden. La energía de activación de la reacción es de 21.0 kcal/mol bajo las condiciones experimentales. Tanto la temperatura como la concentración de persulfato aceleran significativamente la degradación de 1,4 dioxano, sin embargo, incrementando el pH (3-11) disminuye la velocidad.

Palabras clave: 1,4-dioxano, persulfato, degradación, cinética.

Introduction

1,4-dioxane is a cyclic ether and a problematic water pollutant that has major impacts on human health and the environment. It is used widely in industry as a solvent for many organic and inorganic compounds. It is also produced as a byproduct in many industrial processes such as ethylene glycol, ethylene oxide, and polyethylene tetraphthalate manufacturing [1, 2]. Moreover 1,4-dioxane is a known carcinogen to animals and a suspected carcinogen to humans, and hence, is classified as a hazardous compound and a priority pollutant [3]. If not removed from industrial wastewater effluent, 1,4-dioxane appears as a xenobiotic constituent of groundwater and drinking water [4].

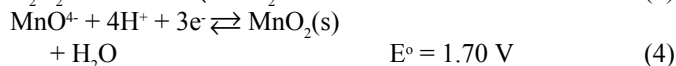
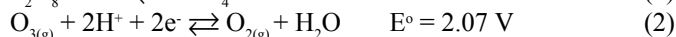
In Mexico there has not yet been established a Federal drinking water standard or maximum contaminant level (MCL) for 1,4-dioxane; the same situation is found in the United State of America since EPA (Environmental Protection Agency) has not established a MCL. However in California has set an advisory Action Level (AL) of 3 ppb. An AL reflects calculations for acceptable risks based on best available data. Since there is no Federal standard, the states of Michigan, Maine and Massachusetts have set safety levels at 85 ppb, 70 ppb and 50 ppb, respectively [5].

Conventional water and wastewater treatment processes [6] include chemical treatment, air stripping, carbon adsorption, and biological treatment. These processes are generally ineffective in removing 1,4-dioxane because of its high aqueous solubility and resistance to biodegradation. There is currently very little data on the removal of 1,4-dioxane in conventional biological wastewater treatment plants. However, the available information on biodegradation, sorption, and air stripping suggest that removal efficiencies for 1,4-dioxane will be very low. The advanced oxidation processes (AOP), which use the hydroxyl radical as the oxidant, can achieve substantial

reductions in 1,4-dioxane. Ozone (O_3) and hydrogen peroxide (H_2O_2) have been used for the degradation of 1,4-dioxane [4, 7-10]. Some studies have shown that hydrogen peroxide can also be used in combination with ferrous ion (Fenton's reagent) to degrade 1,4-dioxane; for example Klecka and Gonsior [11] observed a 97% reduction in 1,4-dioxane after 10 h of incubation in Fenton's reagent with a 12:1 ratio of H_2O_2 to 1,4-dioxane. Interestingly, Maurino et al. [12] found that sodium peroxydisulfate combined with UV light was more effective in degrading 1,4-dioxane than UV light with H_2O_2 .

The reactions of persulfate (also known as peroxydisulfate and peroxodisulfate) ions with various organic and inorganic compounds have been extensively studied [13, 14]. Persulfate oxidation is generally conducted under heat, photo or metal-catalyzed conditions because the oxidation rates can be greatly accelerated. High reactive species such as sulfate radicals ($SO_4^{\cdot-}$) and hydroxyl radicals ($HO^{\cdot}$) are generated as a result of photolysis or heat decomposition of persulfate ions in aqueous media [15-20]. Ultraviolet (UV) light, heat or some metal catalysts are also able to oxidize many organic substances into carbon dioxide. This has led to the use of the UV-persulfate or heated-persulfate oxidation as a standard method for the determination of total organic carbon (TOC) in water and wastewater [21]. Oxidation of large biological molecules such as proteins and monoclonal antibodies proceeds rapidly, while other compounds such as 4-butanol, 2-propanol, acetic acid, acetonitrile, tartaric acid etc. are relatively more difficult to oxidize [21]. However, increasing the temperature or the oxidant concentration, which could increase the production rate of free radicals, can generally enhance the reaction rate.

In aqueous solutions, the standard reduction potential [22] for the half-cell persulfate ion is 2.01 V (Eq. 1), this is comparable to the reduction of ozone ($E^\circ = 2.07$ V), hydrogen peroxide ($E^\circ = 1.78$ V) and permanganate ion ($E^\circ = 1.70$ V) (Eqs. 2-4):



Since hydrogen peroxide and ozone have relatively short-lifetimes in aqueous media as compared to persulfate, then persulfate may be more effective in oxidizing organic substances. In this study sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) without and with addition of Ag^+ ion was studied as a potential alternative oxidant for the degradation of 1,4-dioxane. The kinetics and several factors influencing the 1,4-dioxane degradation were studied. Kinetic parameters including reaction order, rate constant, activation energy (E_a) and parameters of transition state as: enthalpy ($\Delta H^\ddagger$), energy ($\Delta G^\ddagger$) and entropy ($\Delta S^\ddagger$) are calculated. The influence of temperature, oxidant concentration and pH on 1,4-dioxane degradation by persulfate is presented.

Materials and Methods

ACS-grade sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), 1,4-dioxane ($\text{C}_4\text{H}_8\text{O}_2$) and acetonitrile HPLC grade were supplied by Aldrich. All solutions were prepared with deionized (DI) water from SYBON/Barnstead purification system model 02610.

The experiments were carried out in a jacketed reaction beaker (500 ml), for better controlling the temperature of the reaction, equipped with a magnetic stirrer and a stop-cork through which a thermometer, a gas outlet and a tube for withdrawing samples, were installed. The gas outlet tube passed through a 1.0 M $\text{Ba}(\text{OH})_2$ solution for detecting the formation of CO_2 during the course of the degradation of 1,4-dioxane. Stirring and the temperature of the reacting solution were kept constant throughout the experiment. Temperature was controlled with a VWR heated/refrigerated circulator, model 1166. Sample solutions withdrawn from the reactor at reaction times of 0, 5, 10, 20, 30, 40, 60, 90 and 120 minutes, were immediately analyzed for 1,4-dioxane concentration using a High Performance Liquid Chromatography (HPLC) apparatus (Hewlett Packard, model 1090) with spectrophotometric detection at 200 nm wavelength as reported by Scalia *et al.* [23]. Acetonitrile - water (50% v/v) was used as eluent at 1 ml/min and sample injections of 10 μL were separated on a C18 reversed-phase column (Altech, 10 cm) at room temperature.

Results and Discussion

Degradation kinetics of 1,4-dioxane by persulfate.

Typical reaction rates of oxidation of 1,4-dioxane versus time at various temperatures and initial concentrations of oxidant are presented in Figures 1 and 2, respectively. Figure 1 shows the 1,4-dioxane decay at four different temperatures (25, 30, 40 and 50 $^\circ\text{C}$) with constant initial 1,4-dioxane and persulfate

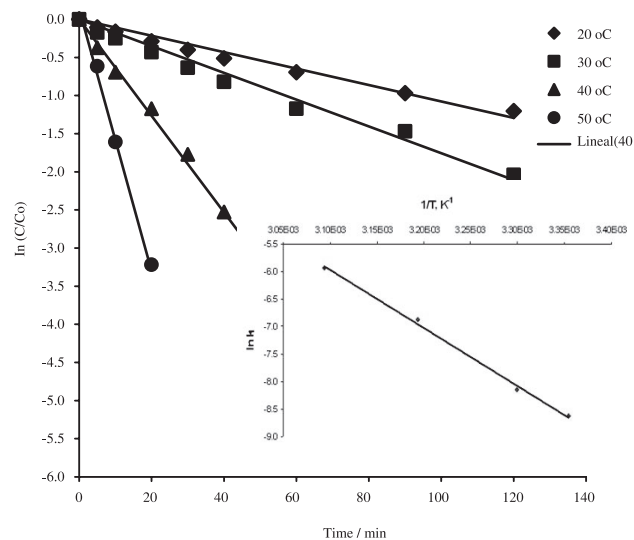


Fig. 1. Effect of temperature on the degradation of 1,4-dioxane by persulfate. Insert: Plot of $\ln k_1$ vs $1/T$ for E_a estimation using Arrhenius equation. $[\text{1,4-dioxane}]_0 = 1.13 \text{ mM}$; $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mM}$; $\text{pH} \sim 7$.

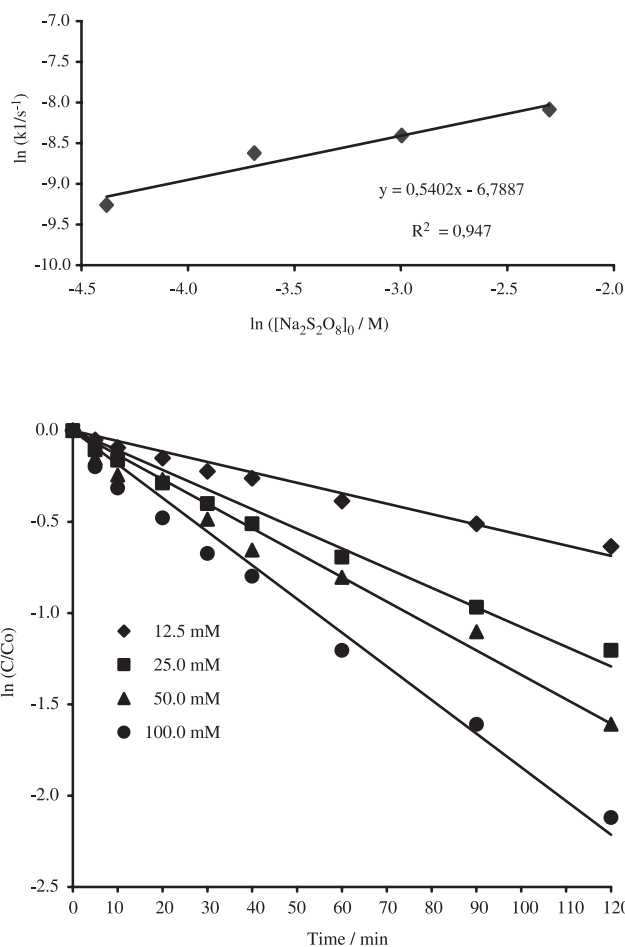


Figure 2. Effect of $\text{Na}_2\text{S}_2\text{O}_8$ concentration on 1,4-dioxane degradation rate. Insert: Plot of $\ln k_1$ vs $\ln [\text{Na}_2\text{S}_2\text{O}_8]_0$. $[\text{1,4-dioxane}]_0 = 1.13 \text{ mM}$; $\text{pH} \sim 7$; Temperature = 25 $^\circ\text{C}$.

concentrations at 1.13 mM and 25.00 mM respectively. Figure 2 shows the 1,4-dioxane decay at four different initial persulfate concentrations (12.5, 25.0, 50.0 and 100.0 mM) at an ambient temperature of 25 °C and using an initial 1,4-dioxane concentration of 1.13 mM in all cases.

Figures 1 and 2 indicate that 1,4-dioxane was rapidly degraded by persulfate under the experimental conditions. For example, in a persulfate solution of 25.0 mM at 40 and 50°C, the half-life time of 1,4-dioxane was less than half hour (Table 1). It is evident, from Figures 1 and 2, that the reaction rate was significantly influenced by temperature and oxidant concentration. The higher the temperature and oxidant concentration resulted in faster 1,4-dioxane degradation.

The rate of 1,4-dioxane degradation can be expressed using the following equation:

$$-\frac{d[1,4\text{-dioxane}]}{dt} = k [1,4\text{-dioxane}]^x [\text{Na}_2\text{S}_2\text{O}_8]^y \quad (5)$$

Where $-\frac{d[1,4\text{-dioxane}]}{dt}$ is the rate of reaction, k is the rate constant and $[1,4\text{-dioxane}]$ and $[\text{Na}_2\text{S}_2\text{O}_8]$ are the concentrations of 1,4 dioxane and persulfate, respectively. x and y are the parameters representing the order of the reaction with respect to each component. Since the concentration of persulfate is in excess, Eq. (5) can be simplified to Eqs. (6) and (7).

$$-\frac{d[1,4\text{-dioxane}]}{dt} = k_1 [1,4\text{-dioxane}]^x \quad (6)$$

$$\text{With } k_1 = k[\text{Na}_2\text{S}_2\text{O}_8]^y \quad (7)$$

where k_1 is the pseudo- x -order rate constant. If the reaction is first order with respect 1,4-dioxane concentration ($x = 1$) then the plot of $\ln \frac{[1,4\text{-dioxane}]}{[1,4\text{-dioxane}]_0}$ versus time should be linear with slope = $-k_1$ as shown in Figures 1 and 2.

The results of a series of kinetics experiments under various conditions (i.e., different temperature, oxidant concentration and pH) are presented in Tables 1-3. Pseudo-first-order rate constants (k_1) of 1,4-dioxane degradation at pH 7 and initial concentration of 1,4 dioxane and persulfate of 1.13 and 25.00 mM respectively at 25, 30, 40 and 50 °C were 1.80×10^{-4} , 2.93×10^{-4} , 10.30×10^{-4} and $26.50 \times 10^{-4} \text{ s}^{-1}$ respectively (Table 1). These numbers show that at 50 °C the 1,4-dioxane degradation rate by persulfate oxidation is comparable with the degradation of this compound using TiO_2/UV oxidation at pH 11 ($33.33 \times 10^{-4} \text{ s}^{-1}$) or using $\text{H}_2\text{O}_2/\text{UV}$ oxidation ($20.00 \times 10^{-4} \text{ s}^{-1}$), but smaller than the degradation rate using persulfate/UV ($73.00 \times 10^{-4} \text{ s}^{-1}$) as reported Maurino et al. [12].

The activation energy was determined based on the data shown in Table 1 and using the Arrhenius equation ($k = A \exp -E_a/RT$), where “ A ” is the frequency factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. The insert of Figure 1 shows a plot of $\ln k$ vs $1/T$ in the temperature range of 25-50 °C, the E_a for the reaction of 1,4-dioxane with persulfate is 21.0 kcal/mol. Similar value were

Table 1. Rate constants of oxidation of 1,4-dioxane by persulfate under various temperatures. $[1,4\text{-dioxane}]_0 = 1.13 \text{ mM}$; $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mM}$; $\text{pH}_0 \sim 7$.

Temperature (°C)	$k_1 \times 10^4 (\text{s}^{-1})$	Half-life (min)
25	1.80	64
30	2.93	39
40	10.30	11
50	26.50	5

Table 2. Rate constants of oxidation of 1,4-dioxane by persulfate under various oxidant concentrations. $[1,4\text{-dioxane}]_0 = 1.13 \text{ mM}$; Temperature = 25 °C; $\text{pH}_0 \sim 7$.

$[\text{Na}_2\text{S}_2\text{O}_8]_0 (\text{mM})$	$k_1 \times 10^4 (\text{s}^{-1})$	Half-life (min)
12.50	0.95	122
25.00	1.80	64
50.00	2.23	52
100.00	3.08	38

Table 3. Rate constants of oxidation of 1,4-dioxane by persulfate under different pH values. $[1,4\text{-dioxane}]_0 = 1.13 \text{ mM}$; $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mM}$; Temperature = 25 °C.

$\text{pH}_{\text{initial}}$	pH_{final}	$K_1 \times 10^4 (\text{s}^{-1})$	Half-life (min)
3	2.70	3.15	37
5	4.40	2.47	47
7	6.80	1.80	64
9	8.70	1.52	76
11	10.80	1.38	84

reported by Huang et al. [24] (24.5 kcal/mol) for methyl *ter*-buthyl ether, Levitt [25] (26.0 kcal/mol) for 2-propanol and Srivastava *et al.* [26] (21.93 kcal/mol) for potassium formate.

Thermodynamic parameters for the transition state like as enthalpy ($\Delta H^\ddagger$), energy ($\Delta G^\ddagger$) and entropy ($\Delta S^\ddagger$) were computed using the following equations [27]:

$$\Delta H^\ddagger = E_a - RT \quad (8)$$

$$\Delta G^\ddagger = RT \ln \frac{\kappa T}{k_1 h} \quad (9)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln \frac{k_1 h}{\kappa T} \quad (10)$$

Where: T is the ambient temperature k_1 is the rate constant at ambient temperature, k is the Boltzman's constant ($1.381 \times 10^{-23} \text{ J/K}$) and h is the Plank's constant ($6.626 \times 10^{-34} \text{ J s}$). Transition state parameters are: $\Delta H^\ddagger = 20.4 \text{ kcal/mol}$, $\Delta G^\ddagger =$

22.6 kcal/mol and $\Delta S^\ddagger = 7.238$ cal/mol-K, indicating that the reaction is endothermic and not a spontaneous reaction.

Four different concentrations of persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) solutions of 12.5, 25.0, 50.0 y 100.0 mM were employed in the experiments to investigate the influence of the oxidant concentration on 1,4-dioxane degradation and is get the real order rate constant. It is evident from Figure 2 that 1,4-dioxane degraded faster at higher concentrations of $\text{Na}_2\text{S}_2\text{O}_8$ solutions as expected. Additionally the insert of Figure 2, where $\ln k_t$ is plotted against $\ln [\text{Na}_2\text{S}_2\text{O}_8]_0$ shows a slope of 0.54 with $R^2 = 0.92$, indicating that the degradation of 1,4-dioxane was directly proportion to initial $\text{Na}_2\text{S}_2\text{O}_8$ concentration and that the real rate constant is 0.0011 s^{-1} . The rate constants are 0.95×10^{-4} , 1.80×10^{-4} , 2.23×10^{-4} and $3.08 \times 10^{-4} \text{ s}^{-1}$ for 12.5, 25.0, 50.0 and 100.0 mM $\text{Na}_2\text{S}_2\text{O}_8$ respectively. The experimental conditions used to obtain this data were $[\text{1,4-dioxane}]_0 = 1.13 \text{ mM}$, temperature = 25°C , pH~7 as are presented in Table 2.

The results of degradation of 1,4-dioxane by persulfate (25.0 mM) at five pH values (i.e. 3, 5, 7, 9 and 11) is shown in Figure 3 and Table 3, it reveals that the rate of 1,4-dioxane degradation by persulfate is pH dependent, the reaction rate was found to decrease with the increase in the pH values. The result is not unexpected because sulfate radicals and hydroxyl radicals decay rapidly due to the reaction with hydroxyl ions as reported by Hayon and McGarvey [19], Singh and Venkatako [28]. These results are also in agreement with finding of Xu *et al.* [29] and Huang *et al.* [24] that in alkaline solutions the carbon dioxide formed from complete oxidation could lead to the formation of bicarbonate and carbonate ions may inhibit the organic compound oxidation.

It is therefore worthwhile to conduct of 1,4-dioxane oxidation at acid conditions since, the halftime of 1,4-dioxane decreases to the half when the pH is lowered from 7 to 3 (Table 3). It is possible that under acidic conditions 1,4-diox-

ane forms oxonium ions as a reactive intermediated that facilitates ring opening and oxidation of the organic compound with the persulfate, while under basic condition such intermediate is not possible to be formed.

Conclusions

In this study the degradation of 1,4-dioxane by persulfate oxidation was investigated. The 1,4-dioxane degradation kinetics and its affecting factors including temperature, oxidant concentration and pH were particularly examined. The 1,4-dioxane degradation was found to be pseudo first order with respect to 1,4-dioxane concentration. Experimental results indicated that the 1,4-dioxane degradation reaction is significantly influenced by temperature, oxidant concentration and pH. Temperature and oxidant persulfate concentration can increase the 1,4-dioxane degradation rate while increasing pH (over the range 3-11) will lead to the opposite.

The activation energy for the degradation reaction of 1,4-dioxane with persulfate is 21.0 kcal/mol. The thermodynamic parameters for the transition state are: $\Delta H^\ddagger = 20.4$ kcal/mol, $\Delta G^\ddagger = 22.6$ kcal/mol and $\Delta S^\ddagger = 7.238$ cal/mol-K, indicating endothermic and not spontaneous reaction.

Acknowledgements

The authors thank Consejo Nacional de Ciencia y Tecnología CONACYT of Mexico (SEP-2004-C01-47959) for financial support for this investigation.

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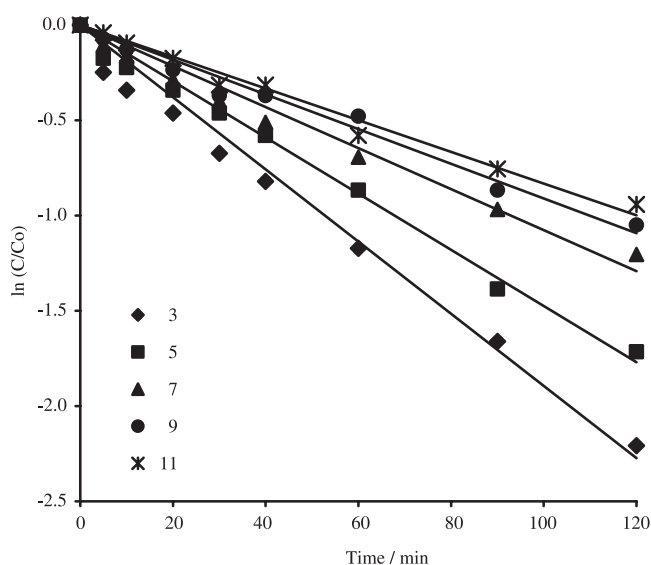


Fig. 3. Effect of initial pH on the 1,4-dioxane degradation rate by persulfate. $[\text{1,4-dioxane}]_0 = 1.13 \text{ mM}$; $[\text{Na}_2\text{S}_2\text{O}_8]_0 = 25.00 \text{ mM}$; Temperature = 25°C .

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