

Kinetic Study of UV Peroxidation of Bis(2-chloroethyl) Ether in Aqueous Solution

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Experimental data from the UV peroxidation of bis(2-chloroethyl) ether (DCEE) in aqueous solution indicated the rate equation is $0.163[\text{DCEE}]^{0.61}[\text{H}_2\text{O}_2]^{0.54}$. Important intermediates identified are 2-chloroethyl acetate, an enolic tautomer of 2-chloroethyl acetate, 2-chloroethoxyethene, 2-chloroethanol, acetaldehyde, ethylene oxide, and chloroethene. All the intermediates could be reduced to undetectable levels after 30 min of irradiation when DCEE/ H_2O_2 initial ratio of 1/10 was used. A reaction mechanism with complex pathways through both the attack of hydroxy free radical and the direct photolysis on DCEE was proposed. Intermediate identification and the rate equation suggested that the pathways in which DCEE is attacked by hydroxy free radicals are predominant. The rate equation derived from this mechanism predicted the peroxidation of DCEE is half-order with respect to both DCEE and H_2O_2 concentrations.

Introduction

The groundwater aquifer underneath a chemical manufacturing plant in Southeast Texas has been contaminated by the leachate from its landfill. At least 17 chlorinated hydrocarbon contaminants have been detected in the groundwater. An air-stripping unit followed by a thermal catalytic oxidation unit is currently being operated on-site to remove all of the chlorinated compounds from the contaminated groundwater. Based on computer simulations, the current air flow rate used in the air-stripping unit is about 10 times higher than the calculated flow rate if bis(2-chloroethyl) ether (DCEE) is excluded. This excessive air flow rate has caused maintenance problems and a higher energy consumption. It was proposed to treat the contaminated groundwater by air stripping to remove the volatile compounds and by UV/ H_2O_2 oxidation to destruct the low-volatility compounds such as DCEE (Huang et al., 1994a). A feasibility study of this process has been initiated and reported recently (Huang et al., 1994b). It was found that the UV peroxidation rate of DCEE was faster than those of chloroethanes. These photo-oxidation rates were found to be insensitive to temperature, salinity, alkalinity, and pH of the solution. In this paper we will concentrate on the kinetic study of the photooxidation of DCEE by UV/ H_2O_2 since DCEE is the major compound in the residue solution after stripping.

Experiment

A medium-pressure, mercury, immersion lamp with a 1-L borosilicate glass reaction vessel (ACE Glass Inc.) was used in the study. Figure 1 shows the schematic diagram of the photochemical oxidation unit. Of the total energy radiated from the lamp (175.8 W), approximately 40–48% is in the ultraviolet portion of the

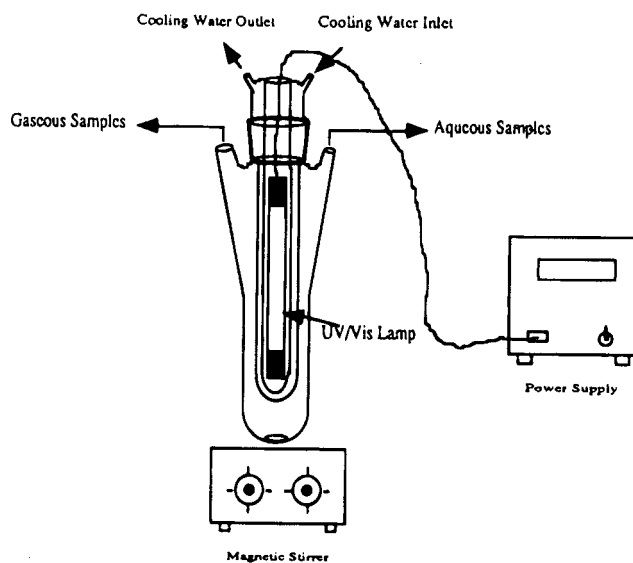


Figure 1. Schematic diagram of the photochemical oxidation reactor.

spectrum, 40–43% is in the visible, and the balance is in the infrared. All the experiments were conducted in a completely mixed, batch mode. The water temperature was maintained at 20 °C through a recirculation of cooling water and the pH was kept at 7 by use of a phosphate buffer solution. The concentration of DCEE studied was about 1.55×10^{-3} M (222 ppm), which represented its concentration in the contaminated groundwater.

The concentration of DCEE were analyzed using a gas chromatograph (GC) (Varian Model 3500) equipped with a purge-and-trap concentrator (Tekmar Model LSC 2000), a flame-ionization detector, and a 15-m AT-1701 Microbore column (J&W Scientific). The concentration of H_2O_2 was measured using a modified titration method (Liu, 1994). A gas chromatograph (HP Model 5890) equipped with a mass spectrometer detector (MS) (HP

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Table 1. Kinetic Data for DCEE Degradation^a

time (min)	DCEE	H ₂ O ₂	DCEE	H ₂ O ₂	DCEE	H ₂ O ₂	DCEE	H ₂ O ₂
[DCEE] ₀ = Constant								
0	1.5538	15.427	1.5538	9.6053	1.5538	6.0638	1.5538	1.4553
5	0.1221	11.327	0.2865	6.7915	0.7034	4.73	1.138	1.2126
10	0.0116	6.5732	0.0352	4.4144	0.1684	3.5171	0.6767	0.7035
15	0	4.6085	0.0107	2.8921	0.0523	2.1321	0.4835	0.2668
30	0	0.8235	0	0.7762	0	0.2668	0.2963	0
[H ₂ O ₂] ₀ = Constant								
0	0.8786	8.9097	1.2405	8.6144	2.508	8.5406	3.2915	8.6144
5	0.017	4.7256	0.1635	6.3991	0.3417	6.1532	1.4447	6.4485
10	0	3.2241	0.0115	3.4459	0.0467	4.0612	0.5036	4.4303
15	0	1.9444	0	2.2397	0.0108	2.215	0.2064	2.9782
30	0	0	0	0	0	0.2462	0.0331	0.6153

^a All the kinetic data shown here are in millimolar concentrations.

Model 5970), a sample concentrator (Envirochem 810A), and a 25-m HP Ultra-2 capillary column was used to identify oxidation intermediates in all of the reactions.

The chemical solution of DCEE used in this experiment was ordered from Aldrich Company and was 99% pure. The impurities were identified as 1,2-dichloroethane (1,2-DCA) for almost 1% and 1,1,2-trichloroethane (1,1,2-TCA) for trace amount. This DCEE chemical solution was used for the preparation of the reaction solution without further purification.

Rate Equation of DCEE UV Peroxidation

The rate equation may be determined by using either the integral method or the initial rate method which is usually not as accurate as the integral method. However, in the reaction of DCEE by UV/H₂O₂ many intermediates have been produced and degraded again. This complex reaction makes the integral method approach almost impossible, so the initial rate method was used in this study. The kinetic data gained by the initial rate method are listed in Table 1.

The experimental rate equation may be written in the following form:

$$\frac{-d[\text{DCEE}]_0}{dt} = k[\text{DCEE}]_0^a [\text{H}_2\text{O}_2]_0^b \quad (1)$$

where [DCEE]₀ is the initial concentration of DCEE, [H₂O₂]₀ is the initial concentration of H₂O₂, and *t* is the oxidation time in minutes. If [DCEE]₀ is kept at a constant, eq 1 becomes

$$\frac{-d[\text{DCEE}]_0}{dt} = k'[\text{H}_2\text{O}_2]_0^b \quad (2)$$

where $k' = k[\text{DCEE}]_0^a$. Take a logarithmic function of both sides of eq 2 to obtain

$$\ln \frac{-d[\text{DCEE}]_0}{dt} = \ln k' + b \ln [\text{H}_2\text{O}_2]_0 \quad (3)$$

Using eq 3 and the data shown in Table 1, a plot of $\ln\{-d[\text{DCEE}]_0/dt\}$ versus $\ln [\text{H}_2\text{O}_2]_0$ gives a linear relation as shown in Figure 2. The slope of the straight line, the reaction order *b*, is 0.54 ± 0.05 , and the intercept of the plot, the value of $\ln k'$ ($= \ln\{k[\text{DCEE}]_0^a\}$) is -5.854 . On the other hand, if [H₂O₂]₀ is constant, eq 1 becomes

$$\frac{-d[\text{DCEE}]_0}{dt} = k''[\text{DCEE}]_0^a \quad (4)$$

where $k'' = k[\text{H}_2\text{O}_2]_0^b$. Take a logarithmic function of both sides of eq 4 to obtain

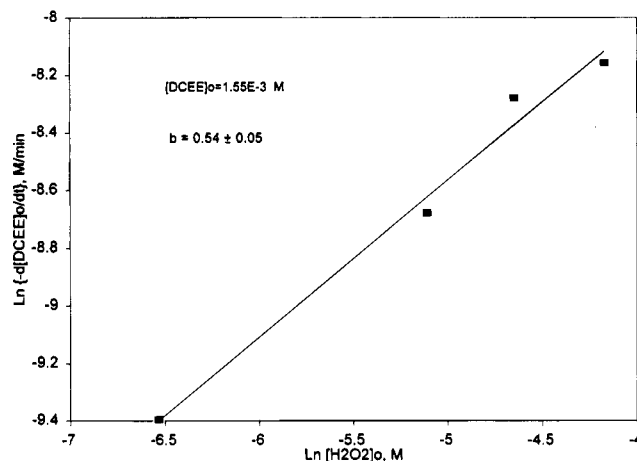


Figure 2. $\ln\{-d[\text{DCEE}]_0/dt\}$ versus $\ln [\text{H}_2\text{O}_2]_0$ at temperature = 20 °C and pH = 7.

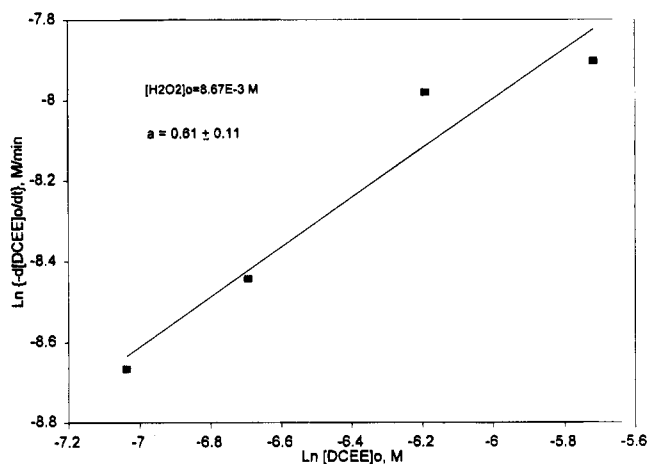


Figure 3. $\ln\{-d[\text{DCEE}]_0/dt\}$ versus $\ln [\text{DCEE}]_0$ at temperature = 20 °C and pH = 7.

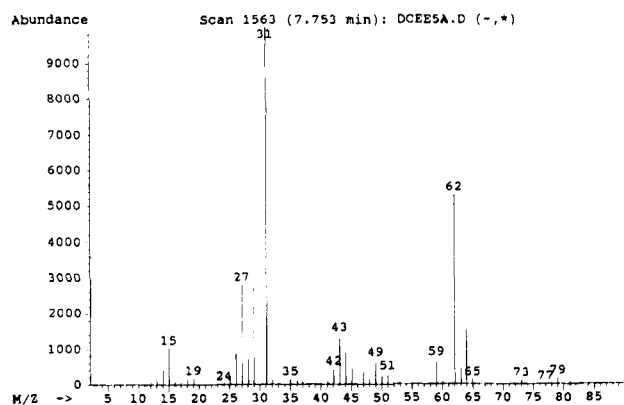
$$\ln \frac{-d[\text{DCEE}]_0}{dt} = \ln k'' + a \ln [\text{DCEE}]_0 \quad (5)$$

Using eq 5 and the data shown in Table 1, a plot of $\ln\{-d[\text{DCEE}]_0/dt\}$ versus $\ln [\text{DCEE}]_0$ gives a straight line as can be seen from Figure 3. The slope of the straight line equals the value of *a* ($= 0.61 \pm 0.11$), the reaction order with respect to [H₂O₂]₀, and the intercept of the plot gives the value of $\ln k''$ ($= -4.318 = \ln\{k[\text{H}_2\text{O}_2]_0^b\}$).

The reaction rate constant, *k*, can be obtained from the values of *a* and $\ln\{k'\}$ and also from the values of *b* and $\ln\{k''\}$. The calculated *k* is 0.151 from *k'* and 0.175 from *k''* with an average value of $0.163 \text{ M}^{-0.15} \text{ min}^{-1}$. Finally, the rate equation of DCEE photooxi-

Table 2. List of Identified Intermediates from DCEE Photooxidation

GC retention time, min	GC/MS retention time, min	intermediates
1.60	2.697	chloroethene
2.12	2.756	ethylene oxide
3.13	2.771	acetaldehyde
3.85	5.632	2-chloroethanol
5.67	7.180	2-chloroethoxyethene
6.12	7.753	2-chloroethyl 1-hydroxyethenyl ether
9.28	9.895	2-chloroethyl acetate

**Figure 4.** Mass spectrum of the GC peak at 6.12 min retention time.

dation by $\text{UV}/\text{H}_2\text{O}_2$ can be obtained as

$$\frac{-d[\text{DCEE}]_0}{dt} = 0.163[\text{DCEE}]_0^{0.61}[\text{H}_2\text{O}_2]_0^{0.54} \quad (6)$$

Intermediate Identification for DCEE UV Peroxidation

The intermediates produced during the peroxidation of DCEE in this study were identified by using a purge-and-trap concentrator followed by GC/MS and are listed in Table 2. All the GC and MS spectra may be found in a thesis (Liu, 1994) and are omitted in this paper. The mass spectra (m/e) of each intermediate listed in Table 2 match very well (83–96%) with the standard mass spectra in the NIST MS ChemStation Library, except for the peak at GC/MS retention time of 7.753 min. This peak was identified as chloroethene by the computer library match, but the quality of the mass spectrum match is only 53%. Even more, the peak of the standard chloroethene reagent in gas chromatograms is at a retention time of 1.60 min. Therefore, chloroethene is not considered as the byproduct of this peak. The enolic tautomer of 2-chloroethyl acetate is a possible byproduct of this peak according to a study of reaction mechanism as will be discussed. Also, the fragments of this enolic tautomer of 2-chloroethyl acetate (shown in Table 3) match those in the GC/MS spectrum (shown in Figure 4).

Figure 5 shows a series of gas chromatograms of DCEE reacted with $\text{UV}/\text{H}_2\text{O}_2$ and Figure 6 shows a series of gas chromatograms of DCEE reacted with UV only. It can be seen from the initial time of these two figures that the reagent DCEE is not pure. The major impurity compound, shown by the peak at GC retention time of 3.65 min, is identified as 1,2-DCA. The concentration of this impurity is less than 1.55×10^{-5} M. The peak area of 1,1,2-TCA (GC retention time = 7.18) increases from 5306 ($t = 0$) to 253 715 ($t = 5$ min) for $\text{UV}/\text{H}_2\text{O}_2$ reaction system and from 3310 ($t = 0$) to

Table 3. 2-Chloroethyl 1-Hydroxyethenyl Ether Fragment List

M / e	Fragment
14 → 15	$\text{H}-\dot{\text{C}}-\text{H}$
26	$\text{H}-\dot{\text{C}}-\text{C}-\text{H}$ and $\text{:C}=\text{C}-\text{H}$
27	$\text{H}-\dot{\text{C}}-\text{C}-\text{H}$
28 → 29	$\text{H}-\text{C}-\text{C}-\text{H}$
30 → 31	$\text{H}-\text{C}-\text{O}-\text{H}$ and $\text{H}-\text{C}-\text{OH}$
43	$\text{H}-\text{C}-\text{C}-\text{O}-\text{H}$ and $\text{H}-\text{C}-\text{OH}$
49/51	$\text{H}-\text{C}-\text{Cl}$ and $\text{H}-\text{C}-\text{H}$
59	$\text{H}-\text{C}-\text{O}-\text{H}$ and $\text{H}-\text{C}-\text{Cl}$
62/64	$\text{H}-\text{C}-\text{C}-\text{H}$ and $\text{H}-\text{C}-\text{Cl}$
79/81	$\text{H}-\text{C}-\text{C}-\text{O}-\text{H}$ and $\text{H}-\text{C}-\text{Cl}$

28 670 ($t = 30$ min) for UV irradiation only. This increase in TCA does not result from DCEE degradation because TCA has been identified as an intermediate from the $\text{UV}/\text{H}_2\text{O}_2$ oxidation of DCA (Liu, 1994), which is an impurity in DCEE solution. Although the peak area of TCA is relatively large, the actual concentration is not. For example, the peak area of 253 715 corresponds to 5.62×10^{-6} M (0.7 ppm) TCA in aqueous solution.

Mechanism of DCEE UV Peroxidation

The reaction pathways of the photooxidation of DCEE by $\text{UV}/\text{H}_2\text{O}_2$ are very complicated and may be subdivided into two mechanistic pathways: (1) the direct photochemical fragmentation of DCEE itself and (2) those involving hydroxy free radicals which are formed from the photodissociation of hydrogen peroxide. Once the intermediates (either free radicals or molecules) are formed, they could be degraded further by photolysis or by hydroxy free radical attack until the final products of carbon dioxide and water.

The photochemical oxidation reaction in aqueous solution is usually a free radical reaction. Free radical

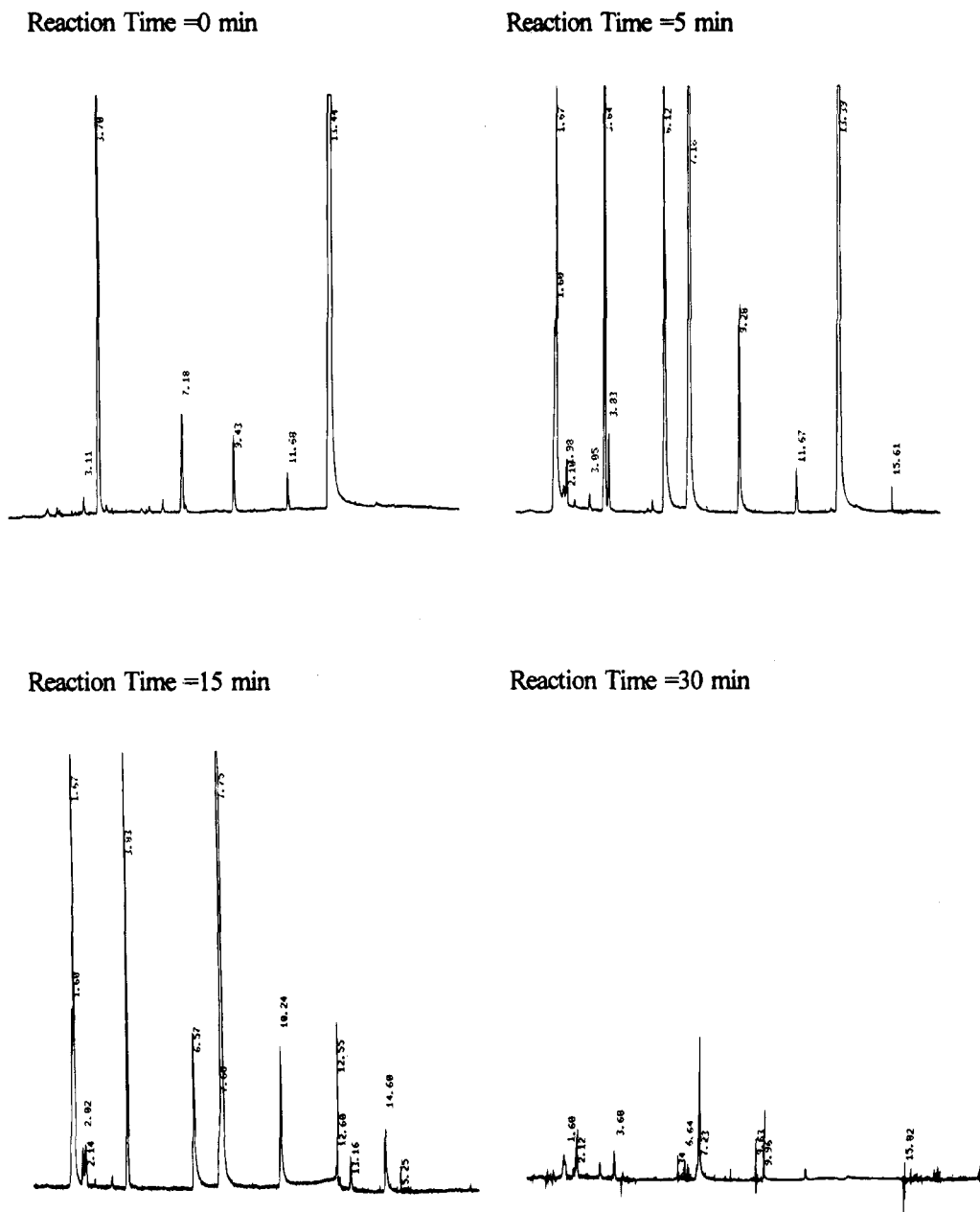


Figure 5. Gas chromatograms: DCEE reacted with UV/H₂O₂. Initial concentration of DCEE = 2.59×10^{-3} M. Initial H₂O₂/DCEE ratio = 10.

reactions may be divided into three main types: initiation, propagation, and termination (Pryor, 1966). The initiation reactions of the proposed mechanism, which form free radicals, are the photochemical dissociation of H₂O₂ (S1), and cleavages of C–Cl (through S2) and C–O bonds (through S3) of DCEE as can be seen in Scheme 1.

Reaction step 1 (S1) takes place very fast due to a low O–O bond energy (33.3 kcal/mol compared with 76.0 and 79.6 kcal/mol of C–Cl and C–O bond energies, respectively) (Moelwyn-Hughes, 1961). From this information, it is not difficult to understand why the rate of DCEE photochemical degradation in the presence of H₂O₂ is faster than degradation without H₂O₂ (compare Figure 5 with Figure 6). The hydroxy free radical, •OH, is a very strong oxidant. It is second only to fluorine in oxidative power. The free radicals 2-(β-chloroethoxy)ethyl (1), chloroethoxy (2), and chloroethyl (3) may be degraded further under the attack of either hydroxy free radicals and/or UV photolysis in the propagation steps.

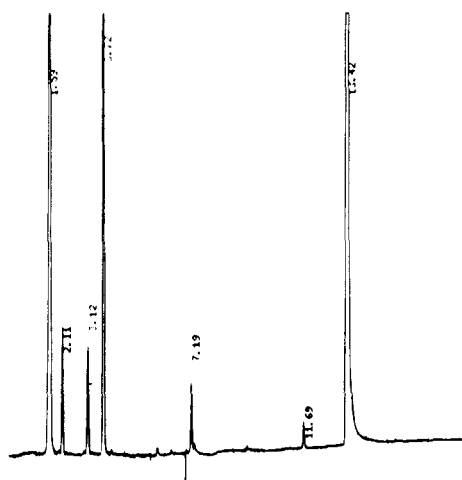
In a propagation step, a free radical is reacted to form another free radical.

The 2-(β-chloroethoxy)ethyl radical (1) may go through two independent pathways, S4 and S5, as shown in Scheme 1. Under the irradiation of UV light, radical (1) further fragments (through S4) to produce intermediate [4], ethylene, and the chloroethoxy radical (2). Through S5, radical (1) may lose a hydrogen atom to form 2-chloroethoxyethene [5], which has been identified by GC/MS (Table 2). The intermediate [4] has never been detected in our experiment. This could be due to its high volatility nature.

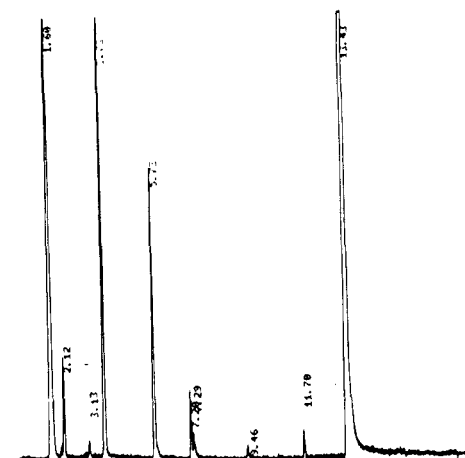
Besides the photolysis reaction, the DCEE molecules may also be under the attack of hydroxyl free radical to form chloroethoxy free radical (2) and 2-chloroethanol [6], which has been identified by GC/MS (Table 2). This direct attack of hydroxy free radical on DCEE is indicated by the reaction step S6 (shown in Scheme 1).

The chloroethoxy radical (2) can go through two reaction pathways to form other byproducts as proposed

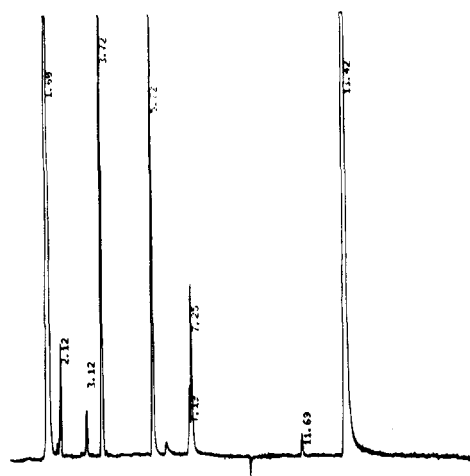
Reaction Time = 0 min



Reaction Time = 5 min



Reaction Time = 15 min



Reaction Time = 30 min

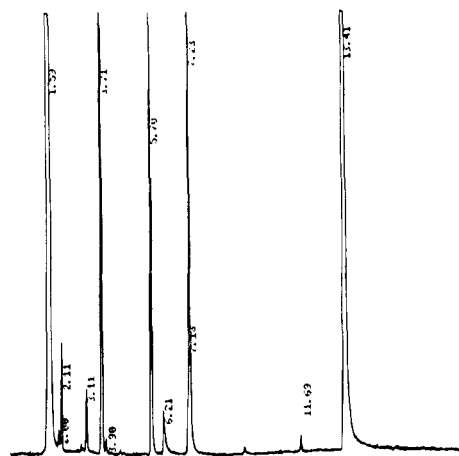


Figure 6. Gas chromatograms: DCEE reacted with UV only. Initial concentration of DCEE = 1.32×10^{-3} M.

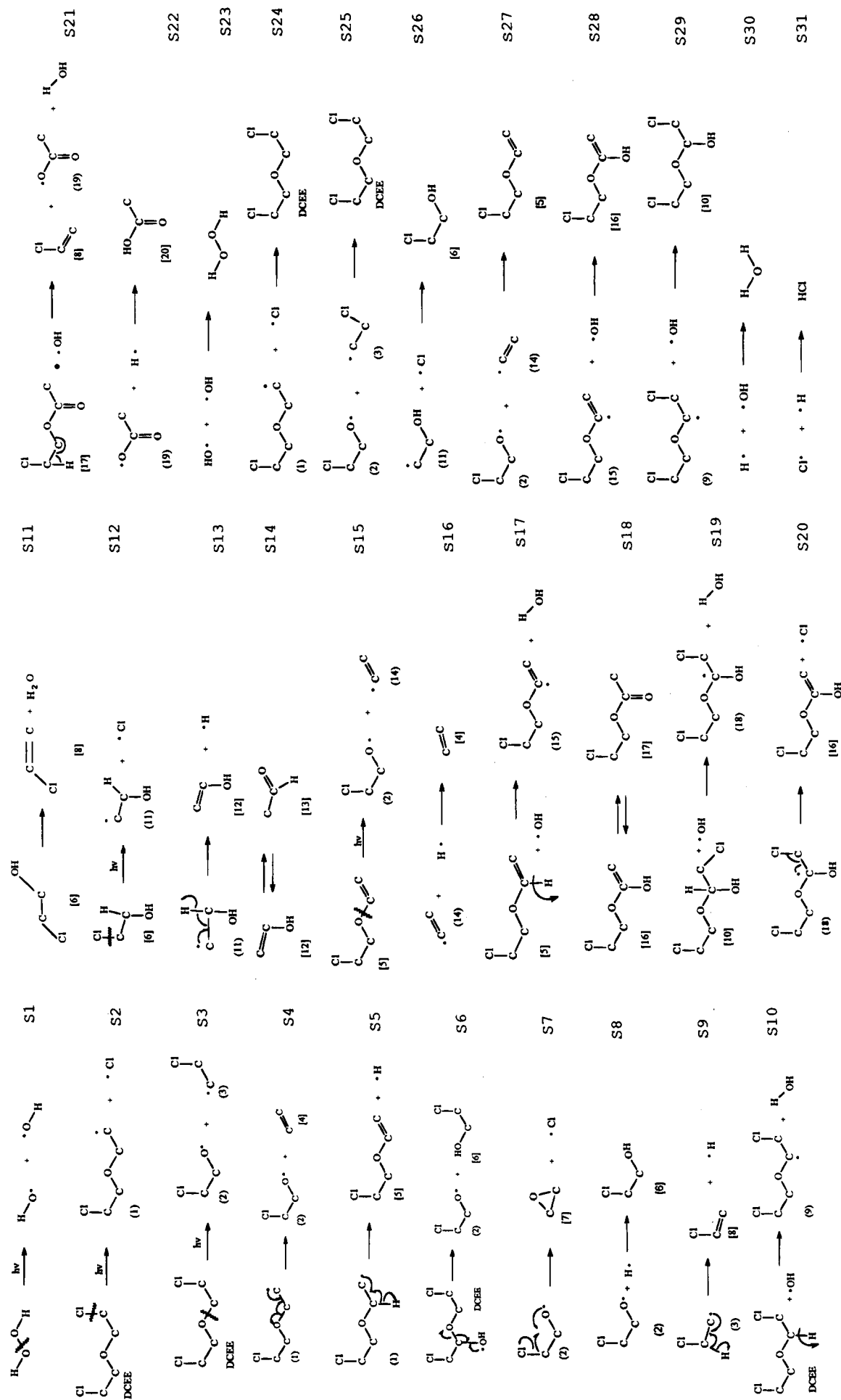
in S7 and S8. The intermediate [7], ethylene oxide, can be rationalized by the intramolecular ring closure of radical (2) through an electron rearrangement as shown by the reaction step S7 in Scheme 1. In S8, the chloroethoxy free radical (2) may react with a hydrogen atom to form 2-chloroethanol [6]. Both intermediates [6] and [7] have been identified by GC/MS (Table 2).

The radical (3), chloroethyl radical, produced in S3, can further fragment, losing a hydrogen atom to form chloroethene (vinyl chloride) [8], which has also been identified by GC/MS. This reaction step is indicated by S9 shown in Scheme 1.

Besides reaction step S6, DCEE molecules can also be attacked by hydroxy free radicals following an abstraction of a hydrogen atom on the α position to the oxygen atom. That would lead to a secondary radical (9) as indicated in the reaction step S10. In the presence of high concentration of $\cdot\text{OH}$, radical (9) is captured easily in a radical termination step which forms 1-hydroxy-*s*-dichloroethyl ether [10]. This reaction is indicated by a free radical termination step S29 shown in

Scheme 1. Evidence for the presence of intermediate [10] is indirect. The molecular ion for this intermediate ($m/e = 158$) was not detected by the GC/MS under any conditions, but two characteristic fragments were found in high abundance for the mass spectrum shown in Figure 4, namely the m/e peak at 31 which is diagnostic for methoxy and hydroxymethyl groups and the m/e peak at 79 and 81 which corresponds to the chloroethoxy fragment. This implies the intermediate identified by the mass spectrum shown in Figure 4 could be the chlorohydrin, 1-hydroxy-*s*-dichloroethyl ether [10], or a similar compound. A close examination of the the GC retention time indicated that the compound of Figure 4 could not be 1-hydroxy-*s*-dichloroethyl ether [10]. Under the reaction conditions, the lifetime of such a compound would be short because of the multitude of degradation pathways which are available. For example, dehydrochlorination initiated by abstraction of the activated hydrogen atom in the intermediate [10] would lead directly to the enolic tautomer [16] of 2-chloroethyl acetate [17]. These reaction steps are depicted in S19,

Scheme 1. Reaction Steps for DCEE Degradation



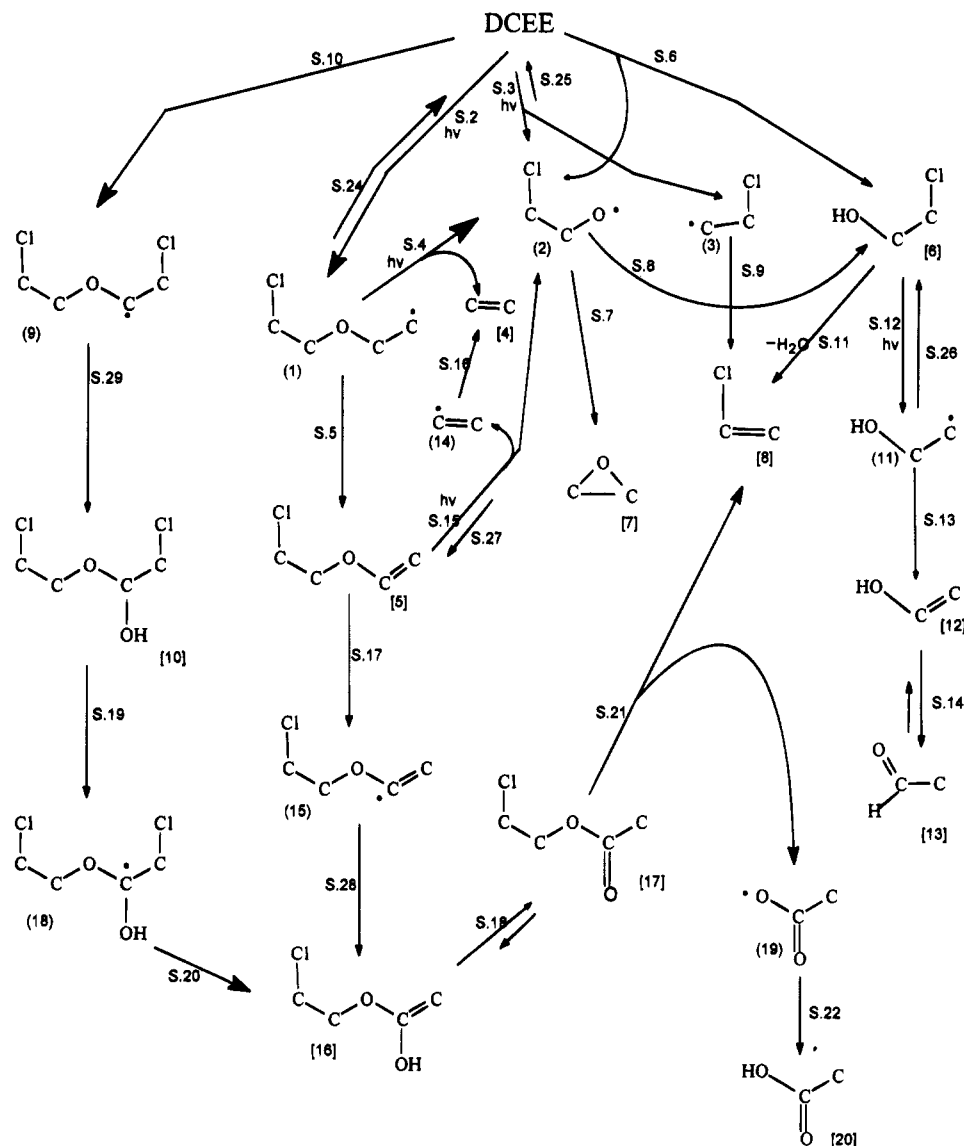


Figure 7. Pathway of DCEE UV peroxidation.

S20, and S18, as can be seen in Scheme 1. The acetate [17] has been identified by GC/MS and the enolic tautomer [16] could be one of the candidates of the intermediate identified by Figure 4. The fragments from this enol [16] match quite well with the mass spectrum shown in Figure 4 as has been discussed in the intermediate identification section.

After the intermediate [6], 2-chloroethanol, is formed, dehydration could occur through either a free radical or an ionic mechanism. This dehydration reaction of 2-chloroethanol to produce chloroethene (vinyl chloride) [8] is shown in step S11. Byproduct [6] may go through a two-step dehydrochlorination reaction (S12 and S13) to form ethenol [12] which is under an enol-aldehyde equilibrium, S14, to produce acetaldehyde [13]. The intermediate acetaldehyde [13] has been identified by GC/MS (Table 2), but the enolic form has not been detected.

The intermediate [5] has been present in a significant quantity during a UV photolysis of DCEE without H_2O_2 (Figure 6). On the other hand, in the presence of H_2O_2 , UV photolysis of DCEE gives a relatively small amount of intermediate [5] (Figure 5). These results suggest a slow photolysis reaction of the intermediate [5] (through S15 and S16) and a fast reaction route, S17 and S28,

through the attack by hydroxy free radicals on intermediate [5]. The reaction route, S15 and S16, is an α -scission followed by an abstraction of hydrogen atom. This reaction route should be much slower than that by OH free radical attack as indicated in S17 and S28. The intermediate [16], 2-chloroethyl 1-hydroxyethenyl ether, an enolic form of 2-chloroethyl acetate [17], may not be stable. But the equilibrium step, S18, may explain the reason why both intermediates [16] and [17] have been detected by GC/MS (Table 2).

The acetate [17] may further fragment through S21, a β -elimination of a hydrogen atom, to form chloroethene [8] and a free radical (19) which rapidly form acetic acid [20] through a hydrogen atom abstraction as indicated by S22 shown in Scheme 1.

The termination reaction in which the radicals are combined may be divided into two groups: (1) reversible steps of the initial reactions as shown in routes S23–S25 and (2) byproduct formation reaction as shown in routes S26–S31.

The reaction pathways discussed in the above may be summarized in Figure 7. The number inside parentheses indicates a free radical while the number inside brackets indicates an intermediate compound or byproduct.

Derivation of Rate Equation from Mechanism of DCEE UV Peroxidation

Each reaction step mentioned above is considered elementary. Therefore, the net reaction rate of DCEE can be written as eq 7. Because the concentration of DCEE in the reacting solution is very low and the concentrations of

$$\frac{-d[\text{DCEE}]}{dt} = k_2[\text{DCEE}] + k_3[\text{DCEE}] + k_6[\text{DCEE}][^{\bullet}\text{OH}] + k_{10}[\text{DCEE}][^{\bullet}\text{OH}] - k_{24}[1][\text{Cl}] - k_{25}[2][3] \quad (7)$$

free radicals [1], [Cl], [2], and [3] are even lower than that of DCEE, the probability of reaction of two free radicals is quite small. Therefore, the last two reaction terms in eq 7 may be neglected when compared with other reaction terms. However, because the concentration of H_2O_2 is relatively high, and the reaction constant of H_2O_2 decomposition (reaction step S1) is large, the reaction rates in which $^{\bullet}\text{OH}$ is involved are not considered zero. From the above discussion, eq 7 can be simplified to:

$$\frac{-d[\text{DCEE}]}{dt} = (k_2 + k_3)[\text{DCEE}] + (k_6 + k_{10})[\text{DCEE}][^{\bullet}\text{OH}] \quad (8)$$

Using the pseudo-steady-state hypothesis (Fogler, 1986) for all the free radicals and the byproduct [5], the rate equation, eq 8, can be simplified further to

$$\frac{-d[\text{DCEE}]}{dt} = (k_2 + k_3)[\text{DCEE}] + (k_6 + k_{10})[\text{DCEE}] \left(\frac{-B[\text{DCEE}] + k_{17}k_1[\text{H}_2\text{O}_2] - k_{15}k_{19}[[6]] - k_{17}k_{12}[[10]]}{2(-k_{17}k_{19}[[10]] - k_{17}A[\text{DCEE}])} + \right. \\ \left. \frac{\sqrt{(B[\text{DCEE}] + k_{17}k_1[\text{H}_2\text{O}_2] - k_{15}k_{19}[[6]] - k_{17}k_{12}[[10]])^2 - 4(-k_{17}k_{12}[[10]] - k_{17}A[\text{DCEE}])k_{15}(k_1[\text{H}_2\text{O}_2] + C[\text{DCEE}] - k_{12}[[6]])}}{2(-k_{17}k_{19}[[10]] - k_{17}A[\text{DCEE}])} \right) \quad (9)$$

where

$$A = \frac{k_6k_7 + 2k_{10}k_7 + 2k_{10}k_8'}{k_7 + k_8'} \\ B = \frac{k_8'k_2(k_{15}k_5 + k_{17}K_4)}{(k_4 + k_5)(k_7 + k_8')} - \frac{3k_{17}k_5k_2}{k_4 + k_5} + \frac{k_8'k_6k_{15} + k_8'k_{17}k_3}{k_7 + k_8'} - k_{15}(k_6 + 2k_{10}) - k_3k_{17} \\ C = \frac{k_8'}{k_7 + k_8'} \left(k_3 + \frac{k_4k_2}{k_4 + k_5} \right) - k_3$$

Here, the change of byproduct [5] may be assumed to be zero because the concentration of [5] is very small in the presence of H_2O_2 at the beginning of the reaction (see GC spectra shown in Figure 5). For the reaction without H_2O_2 , the concentration of [5] is large (shown in Figure 6). This implies that [5] is rapidly degraded by H_2O_2 . Therefore, the concentration of byproduct [5] may be considered at steady state during the course of the reaction.

At the initial time period of the reaction, concentrations of intermediates are very small and can be assumed to be zero. Furthermore, B and $(k_2 + k_3)$ are relatively small and may be omitted in eq 9 by comparing with k_1 ,

$$\frac{-d[\text{DCEE}]}{dt} = \frac{k_6 + k_{10}}{2k_{17}A} (k_{17}k_1[\text{H}_2\text{O}_2] + \sqrt{(k_{17}k_1[\text{H}_2\text{O}_2])^2 + 4k_{17}A[\text{DCEE}]k_{15}k_1[\text{H}_2\text{O}_2]}) \quad (10)$$

If $k_{17} \gg k_{15}A$, then eq 10 becomes

$$\frac{-d[\text{DCEE}]}{dt} = \frac{(k_6 + k_{10})k_1}{A} [\text{H}_2\text{O}_2] \quad (11)$$

If $k_{17} \ll k_{15}A$, then eq 10 becomes

$$\frac{-d[\text{DCEE}]}{dt} = (k_6 + k_{10}) \left(\frac{k_{15}k_1}{k_{17}A} \right)^{0.5} [\text{DCEE}]^{0.5} [\text{H}_2\text{O}_2]^{0.5} \quad (12)$$

Kinetic data indicate the degradation reaction of DCEE depends on both DCEE and H_2O_2 concentrations. Besides, the experimental rate equation, eq 6, suggests the reaction is half-order with respect to both DCEE and H_2O_2 concentrations. Therefore, the rate equation obtained in eq 12 is accepted as explaining this reaction. A close look at the relationship $k_{17} \ll k_{15}A$, shows that the attacks of hydroxy free radical on the DCEE molecules, reaction steps S6 and S10, are dominant in this complex reaction mechanism.

Conclusion

Intermediates identified during the UV peroxidation of DCEE suggest a complex reaction mechanism through both the attack of hydroxy free radical and the direct photolysis on DCEE and its derivatives. The rate equation derived from this mechanism indicates the reaction is half-order with respect to both DCEE and H_2O_2 concentrations. This is in good agreement with that measured from the experiment. The derivation of the rate equation from the reaction mechanism shows that the direct attacks of hydroxy free radical on DCEE are dominant in this complex mechanism.

Acknowledgment

Financial support from the Gulf Coast Hazardous Substance Research Center, Beaumont, TX, is appreciated.

Literature Cited

Fogler, H. S. *Elements of Chemical Reaction Engineering*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1986.

- Huang, F. Y. C.; Li, K. Y.; Liu, C. C.; Liu, Z. F. Treatment of Groundwater Contaminated with Chlorinated Hydrocarbons. *Proceedings of Fourth International Symposium on Chemical Oxidation: Technology for the Nineties*, Nashville, TN; 1994a.
- Huang, F. Y. C.; Li, K. Y.; Liu, C. C.; Liu, Z. F.; Liu, P. H. Treatability Studies of Groundwater Contaminated with a High concentration of Bis (chloroethyl)ether. *Proceeding of Fifth Annual West Coast Conference Contaminated Soil and Groundwater*, Longbeach, CA; 1994b.
- Liu, C. C. UV Peroxidation for Selected Chlorinated Hydrocarbons in Aqueous Solution. Master's Thesis, Lamar University, Beaumont, TX, 1994.
- Moelwyn-Hughes, E. A. *Physical Chemistry*. Pergamon Press: New York, 1961.
- Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, Inc.: Boston, 1973.
- Pryor, W. A. *Introduction to Free Radical Chemistry*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1966.

Received for review August 1, 1994

Revised manuscript received January 6, 1995

Accepted March 27, 1995*

IE940472K

* Abstract published in *Advance ACS Abstracts*, May 1, 1995.