Treatment of gas-phase trichloroethene in air by the UV/O$_3$ process

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Abstract

The reaction behavior of the photolysis of gas-phase trichloroethene (TCE) in the presence of ozone was studied. The temporal distributions of TCE and chlorinated intermediates under various operating conditions were studied and described in terms of a two-step consecutive dechlorination kinetic model. The enhancement of UV light intensity would promote the decomposition of TCE more effectively than the addition of ozone. The presence of ozone contributed more to the dechlorination of chlorinated intermediates than of TCE by the UV/O$_3$ process. © 1997 Elsevier Science B.V.

Keywords: Photolysis; UV/O$_3$ process; Trichloroethene

1. Introduction

Emissions of volatile organic compounds (VOCs) into the atmosphere have the potential to cause adverse effects on human health and environment [1,2]. As a result, increasingly stringent environmental regulations have created a growing demand for alternative abatement methods for a variety of VOCs. Conventional methods for treating VOCs from gas streams, including absorption, adsorption, condensation and incineration (thermal and catalytic), have various drawbacks. They can be expensive and, in some case, may create hazardous byproducts which must be dealt with off site.

In view of the constraints of existing air pollution control technologies that remove

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VOCs from gas streams, it would be beneficial to develop a process that removes VOCs in relatively low concentrations from gas streams in a more cost effective and environmentally safe manner. The combination of the use of ultraviolet light and ozone has been attracting extensive attention and is considered to be a possible alternative for removal of refractory organics in aqueous bodies [3–5]. Recently, some researchers have extended the application of the UV/O_3 process and focus on the treatment of VOCs in air streams [6–8]. The UV/O_3 process is considered attractive because it might carry treatment to completion: VOCs are ultimately converted to carbon dioxide, water and inorganic species. The oxidation mechanisms of VOCs in the presence of light and ozone include direct photolysis, oxidation, and a combination of both photolysis and oxidation. The relative contribution of these mechanisms to the decomposition of gas-phase organics depends on the wavelength and intensity of UV irradiation, the concentration and type of organics, the concentration of ozone added and the presence of moisture [9].

McGregor et al. [6] evaluated the use of an air-phase UV oxidation process to treat the VOC-laden off gas from an air stripper and found the process to be more cost effective than GAC adsorption for the control of VOC emissions. Blystone et al. [7] observed the effective removal and decomposition of several VOCs (trichloroethene, perchloroethene, 1,1-dichloroethene, chloroform and methylene chloride) by a xenon flash lamp. A full-scale air emission control system (> 95% removal) for TCE has been constructed, capable of continuous treatment of at least 300 scfm with a residence time of about 2 s. Buckley et al. [8] used a Solarchem high power density lamp to treat toluene and trichloroethene in air streams. It was found that the treatment of toluene required the addition of ozone as a light absorber to generate hydroxyl radicals (the EE/O_g value is between 0.5 and 1.5), whereas trichloroethene could be treated directly by direct photolysis (the EE/O_g value is 0.05). Bhowmick and Semmens [9] used ultraviolet light photooxidation for treating the off gas (five volatile chlorinated alkanes and alkenes) from air stripping. By comparison, both photolysis and oxidation are important mechanisms in the destruction of trichloroethene (TCE) and perchloroethene (PCE) with 185 nm and 254 nm radiation, although the shorter wavelength light is significantly more effective. The effect of supplemental ozone improves the kinetics of TCE and PCE oxidation, and an ozone concentration of $2-3\,\mathrm{mg\,l^{-1}}$ appears to give optimum performance.

Trichloroethene (C_2HCl_3) is a solvent commonly used for many industrial operations and frequently found as a contaminant in waters. It has also often been used as a target pollutant to compare the treatment efficiency between various advanced oxidation processes. In previous work, most of the studies on the decomposition of VOCs by ultraviolet radiation in the presence of ozone were mainly based on phenomenological descriptions of the removal of parent pollutants. However, the study of the effect of operating factors on the decomposition of organic intermediates is scarce. The objective of this study is to investigate the effect of process variables on the decomposition of TCE and chlorinated organic intermediates in air streams by both direct photolysis and the UV/O_3 process. The distribution and temporal behavior of TCE and chlorinated intermediates were studied and described in terms of a two-step consecutive dechlorination kinetic model combined with a mass balance of chlorine.

2. Experimental

The photoreaction system employed in this research, depicted schematically in Fig. 1, contained a plug flow annular photoreactor made entirely of Pyrex glass with an effective volume of 0.95 l. The photoreactor consisted of one 1.5 cm i.d. quartz tube housing a UVP-XX-15S 254 nm low pressure mercury UV lamp with approximately 5.3 W maximum output. The temperature inside the photoreactor was maintained at 40°C by an externally mounted insulated nichrome wire heater controlled by a variable voltage transformer. The light intensity of the UV lamp was adjusted by a variable voltage transformer and detected by a Spectroline model DRC-100X digital radiometer combined with a DIX-254 radiation sensor. Fig. 2 compares the emission spectrum of the low pressure mercury UV lamp with the absorption spectra of TCE [8]. It was shown that TCE would absorb strongly in the deep UV region. The production of ozone was controlled by changing the power input to a Fischer 502 ozone generator, and the flow rate of the inlet oxygen gas was kept at 50 l h^{-1}.

The temperature of the TCE solvent-containing bottle, which was used as the gas-phase TCE source by the vacuum extraction method, was adjusted by an externally mounted insulated nichrome wire heater controlled by a variable voltage transformer to give the desired concentration of TCE. The TCE-laden air stream mixed with the O_2/O_3 stream from the ozone generator at the gas mixer before being directed into the reactor and the retention time was controlled at 22 s by the flowmeter of the gas mixer. The humidity of the mixed stream was kept at 73% by adjusting the flowrate of the carrier gas into the deionized water bottle. When the temperature, flowrate, pressure and humidity in the reactor reached a steady state, the UV lamp was turned on to initiate the photoreaction. The inlet and effluent concentration of TCE was analyzed by a China Chromatograph model 8700 gas chromatograph equipped a 4 m × 1/8″ Supelcoport 1% sp-1240-DA 100/120 column and using a flame ionization detector and a six-way gas sampling valve. The effluent stream was directed into the absorption unit, which used 400 ml of deionized water as an absorbent to trap the soluble species (e.g. HCl) and any species hydrolyzed to HCl (e.g. phosgene) [10]. The concentration of chloride ions in the absorption bottle was analyzed with a Dionex model DX-100 ionic chromatograph. The standard deviations of the concentrations of TCE determined by GC/FID and chloride
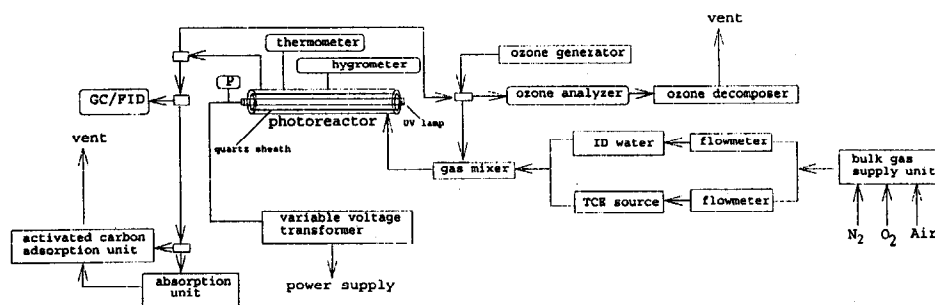

Fig. 1. Schematic representation of the experimental apparatus employed for the photooxidation studies.
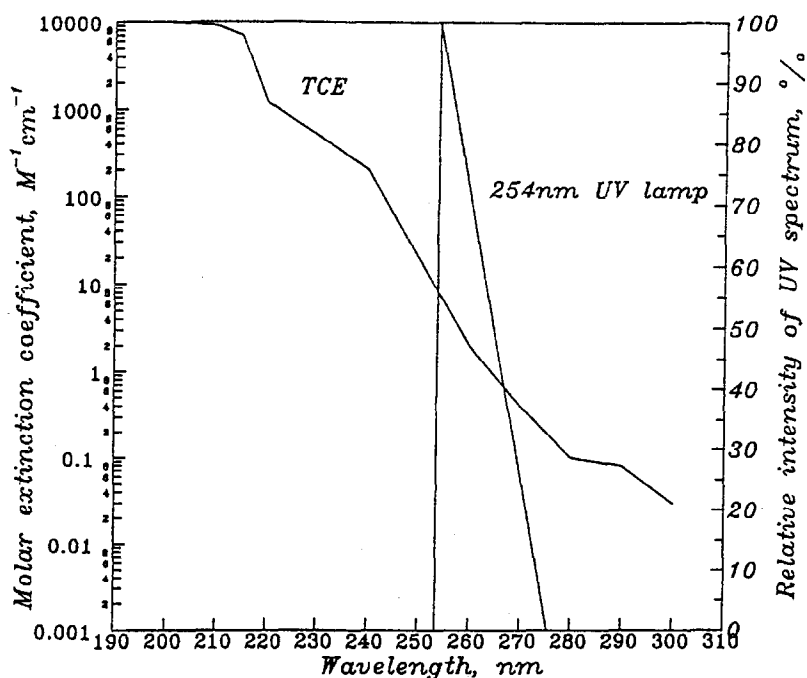
Fig. 2. The emission spectrum of the low pressure mercury UV lamp and the absorption spectra of TCE.

ions determined by ionic chromatograph were ± 3 ppmv and ± 0.1 ppmv, respectively. The concentration of ozone in air streams was determined by a Seki model SOZ-6003 UV photometric ozone analyzer. The TCE solvent was supplied in analytical grade (purity 99.5%) by Merck and was used without any further purification.

3. Results and discussion

The decomposition of TCE in air streams by direct photolysis and the UV/O_3 process was investigated under various UV light intensities and ozone dosages to characterize the removal of the TCE and chlorinated intermediates. The distribution and temporal behavior of TCE and chlorinated intermediates were extensively monitored in order to determine the completeness of decomposition. In this work, the concentrations of TCE, chloride ion (generated from soluble species such as HCl and any species hydrolyzed to HCl, e.g. phosgene) and chlorinated intermediates were used to establish the elemental mass balance of chlorine during the reaction [11].

Mass balance of chlorine

$$[TCE]_{Cl,0} = [TCE]_{Cl} + [Interme]_{Cl} + [Cl^-] \tag{1}$$

where

$[TCE]_{Cl,0}$ the total initial amount of TCE as chlorine, $mg\,l^{-1}$
$[TCE]_{Cl}$ the amount of TCE as chlorine, $mg\,l^{-1}$

Fig. 3. Decomposition pathways of TCE by the UV/O_3 process.

[Interme]$_{Cl}$ the amount of chlorinated intermediates as chlorine, $mg\,l^{-1}$
[Cl^-]   the amount of chloride ions trapped by the absorption bottle, $mg\,l^{-1}$

The amount of chlorinated intermediates, [Interme]$_{Cl}$, was calculated as the difference between the total initial amount of TCE as chlorine, [TCE]$_{Cl,0}$, and the amount of TCE as chlorine, [TCE]$_{Cl}$, plus [Cl^-]. Fig. 3 illustrates schematically the decomposition pathways of TCE by the UV/O_3 process, based on the findings of the previous studies [8,10]. The TCE is postulated to be destroyed by UV light, ozone and hydroxyl radicals and produces chlorinated intermediates and final products (e.g. H_2O, HCl, CO_2). A simplified two-step consecutive dechlorination model was used to describe the temporal behavior of TCE and other reacting species during the reaction in this work:

$$[TCE]_{Cl} \longrightarrow [Interme]_{Cl} \longrightarrow \quad \longrightarrow HCl$$
$$\searrow HCl$$

(2)

In the first step of the reaction, TCE was dechlorinated to become chlorinated intermediates and HCl. Then the chlorinated intermediates were dechlorinated to HCl and other non-chlorine-containing species by the UV/O_3 process. Each step of the reaction was assumed as a first-order and irreversible reaction in a steady-state plug flow reactor. Thus, the pseudo-first-order decomposition rate constant k_{TCE} of TCE can be calculated by:

$$k_{TCE} = \ln(C_{a0}/C_{af})/\tau$$

(3)

where

C_{a0} the initial concentration of TCE, ppmv
C_{af} the effluent concentration of TCE, ppmv
τ the retention time of the reaction, s

3.1. Direct photolysis of TCE

The effect of UV light intensity on the decomposition of TCE by direct photolysis is shown in Fig. 4. The removal of TCE increased with increasing light intensity. About
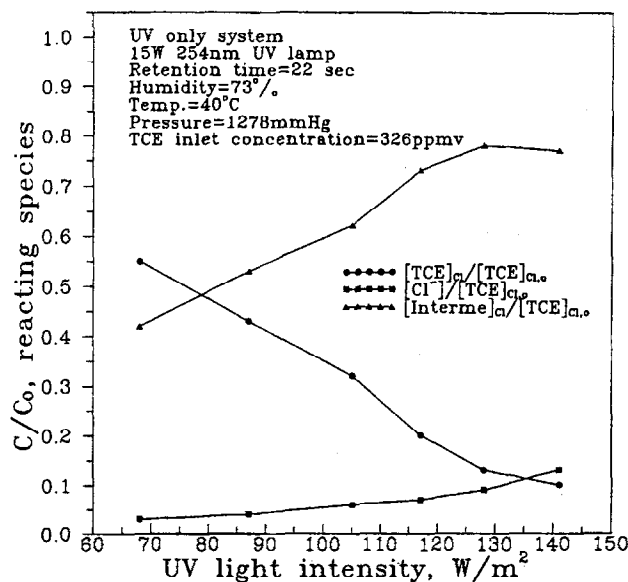
Fig. 4. Effect of UV light intensity on the decomposition of TCE by direct photolysis.

90% removal of TCE could be accomplished at a light intensity of 141 $W m^{-2}$. The formation of chloride ions also increased with increasing light intensity; however, the increment was not as apparent as that of chlorinated intermediates. This indicated that the effect of light intensity on the dechlorination rate of the first step of the model in Eq. (2) was more apparent than that of the second step. That is to say, the dechlorination rate of the chlorinated intermediates by direct photolysis was smaller than that of TCE. Blystone et al. [7] found that the major product from the UV photolysis of TCE was dichloroacetyl chloride (DCAC), a compound about 40 times more toxic than TCE and whose photolysis is about 100 times slower than that of TCE [12]. These findings could reasonably explain the higher formation of chlorinated intermediates produced from the photolysis of TCE at higher light intensity.

The pseudo-first-order decomposition rate constants, $k_{UV.TCE}$, of TCE by direct photolysis at various UV light intensities were calculated and are shown in Table 1. The rate constant equation of TCE with respect to UV light intensity I was regressed and shown to be:

$$k_{UV.TCE} = 0.000122 I^{1.81} \tag{4}$$

The order of UV light intensity in the above rate equation was determined to be 1.81, indicating that radical chain reactions to decompose TCE could apparently occur in this photolytic system.

The electrical energy per order (EE/O_g) for gas-phase systems was used as a measure of the process efficiency and defined as the number of kilowatt-hours required to reduce the concentration of a given pollutant in air by one order of magnitude in 1000

Table 1
The pseudo-first-order decomposition rate constants of TCE by direct photolysis and the UV/O_3 process at various UV light intensities. TCE inlet concentration = 326 ppmv, retention time = 22 s, temperature = 40°C, pressure = 1278 torr, humidity = 73%

UV light intensity($W\,m^{-2}$)	$k_{UV.TCE}(s^{-1})$	$k_{UV/O_3.TCE}(s^{-1})$	$\dfrac{k_{UV/O_3.TCE}}{k_{UV.TCE}}$
68	0.027	0.035	1.29
87	0.038	0.050	1.32
105	0.052	0.065	1.25
117	0.071	0.093	1.31
128	0.086	0.121	1.41
141	0.096	0.159	1.67

standard cubic feet of air [10]. The EE/O_g value can be calculated from the following equation:

$$EE/O_g = \frac{P \times 1000}{R \times 60 \times \log[C_{a0}/C_{af}]} \qquad (5)$$

where P is the lamp power in kW and R is the air flow rate in scfm.

The EE/O_g values of the treatment of TCE by direct photolysis are shown in Fig. 5. It was found that the EE/O_g values decreased with increasing light intensity. The minimum EE/O_g value for the treatment of TCE by direct photolysis was found to be 0.72, which is much larger than that ($EE/O_g = 0.05$) evaluated by Buckley et al. [8]. It
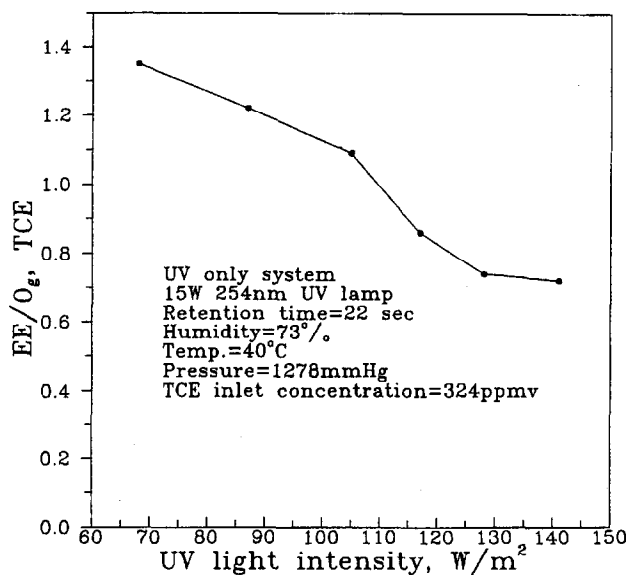

Fig. 5. EE/O_g values for the treatment of TCE by direct photolysis.

was deduced that this result occurred because the Solarchem lamp with strong emission below 240 nm used by the previous researchers has a much higher power (usually 5 kW) than that used in this work.

3.2. Oxidation of TCE by the UV / O₃ process

3.2.1. Effect of ozone dosage

In this work, oxidation of TCE by ozone alone was very slow at room temperature, with the ozone dosage ranging from 36 to 1825 ppmv (O_3/TCE molar ratio = 0.11–5.63). At the reaction condition, the removal of TCE was below 2%. The removal of TCE by UV light in the presence of supplemental ozone at various ozone dosages is shown in Fig. 6. It was found that the addition of ozone had a slight improvement (4–6%) on the removal rate of TCE until the dosage reached 480 ppmv, at which further addition of ozone decreased the removal of TCE. Similar results were reported by Bhowmick and Semmens [9], who studied the decomposition of TCE by the UV/O_3 process and found that the rate of oxidation was increased by 15–30% in relation to an optimum ozone dosage ranging from 933 to 1400 ppmv (2–3 mg l^{-1}). The decomposition of TCE by the UV/O_3 process was assumed to be attributed primarily to direct photolysis as described in the previous section rather than to the attack of hydroxyl radicals generated from the photolysis of ozone. Fig. 7 shows the profiles of the relative light intensity within the photoreactor filled with TCE and ozone at various concentrations according to the Beers law, where the molar extinction coefficients of TCE and ozone are 10 M^{-1} cm^{-1} [7] and 3020 M^{-1} cm^{-1} [13], respectively. It is shown that the absorption of UV light by ozone is increased significantly with ozone concentration and
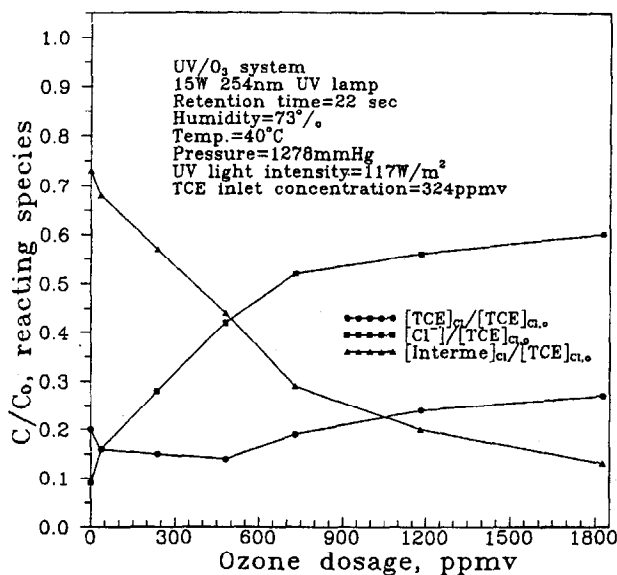

Fig. 6. Effect of ozone dosage on the decomposition of TCE by the UV/O_3 process.
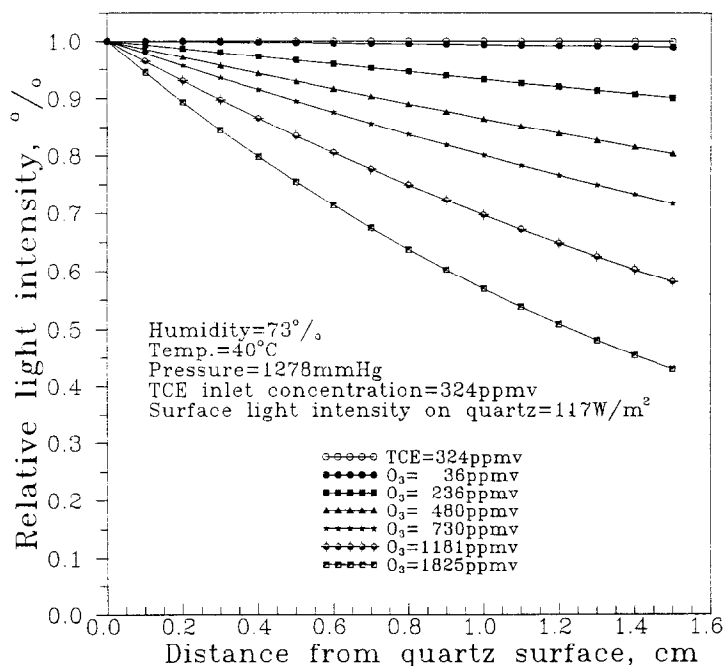
Fig. 7. Inner profiles of the relative light intensity within the photoreactor filled with TCE and ozone at various concentrations, by Beer's law.

thus inhibits photolysis. The formed amount of chlorinated intermediates generated from the decomposition of TCE by the UV/O_3 process was found to be much less than that by direct photolysis, indicating that hydroxyl radicals could significantly promote the decomposition of chlorinated intermediates. The effect of ozone dosage on the EE/O_g value for treatment of TCE by the UV/O_3 process is shown in Fig. 8. The optimum ozone dosage was found to be 480 ppmv; excessive ozone would reduce the treatment efficiency of TCE by the UV/O_3 process.

3.2.2. Effect of UV light intensity

The effect of UV light intensity on the removal of TCE by the UV/O_3 process is shown in Fig. 9. The removal of TCE increased with increasing light intensity and could reach above 99%. It was found that the formation of chlorinated intermediates showed a slight increment with increasing light intensity. About 50% of the chlorine in the influent TCE could be dechlorinated by the UV/O_3 process in this work, compared to that by direct photolysis which was only 13%.

The pseudo-first-order decomposition rate constants, $k_{UV/O_3 \cdot TCE}$, of TCE by the UV/O_3 process at various UV light intensities were calculated and are shown in Table 1. The rate constant equation of TCE with respect to UV light intensity was regressed and is shown as follows:

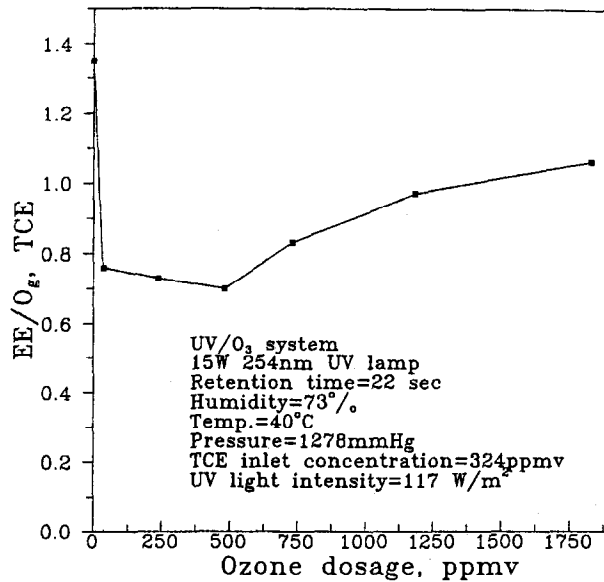$$k_{UV/O_3 \cdot TCE} = 0.0000556 I^{2.05}$$

(6)

Fig. 8. Effect of ozone dosage on the EE/O_g value for the treatment of TCE by the UV/O_3 process.

The order of UV light intensity in the above rate equation was determined to be 2.05, which was slightly larger than that (1.81) by direct photolysis; this indicates that the length of the radical chain reaction to decompose TCE could be promoted by adding ozone to the original photolytic system.
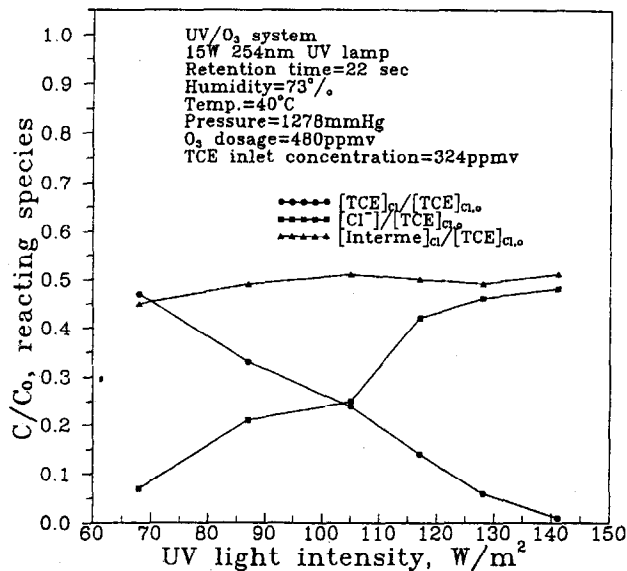

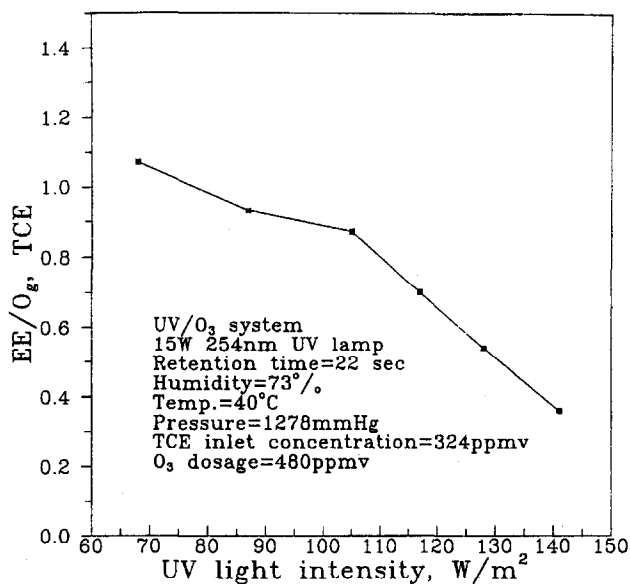Fig. 9. Effect of UV light intensity on the decomposition of TCE by the UV/O_3 process.

Fig. 10. EE/O$_g$ values for the treatment of TCE by direct photolysis and the UV/O$_3$ process.

The EE/O$_g$ values for the treatment of TCE by the UV/O$_3$ process are shown in Fig. 10. It was also found that the EE/O$_g$ values decreased with increasing light intensity, indicating that the increment of photons could prolong the length of the hydroxyl radical oxidation. The minimum EE/O$_g$ value for the treatment of TCE by the UV/O$_3$ process was found to be 0.36, which is half of that by direct photolysis. The treatment efficiency of TCE by the UV/O$_3$ process was found to be superior to that by direct photolysis at various light intensities.

4. Conclusion

The results obtained have shown that direct photolysis and the UV/O$_3$ process are both capable of efficiently decomposing TCE. Oxidation by ozone molecules appeared less important for TCE. The temporal behavior of TCE and other reacting species at various operating conditions in direct photolysis and the UV/O$_3$ process can be explored in terms of the simplified two-step consecutive dechlorination model. The dechlorination of chlorinated intermediates by direct photolysis was found to be much smaller than that of TCE. The finding seemingly limits the practical application of direct photolysis in treating halogenated organics by using a 254 nm low pressure mercury UV lamp. The addition of ozone had a slight improvement (4–6%) on the removal rate of TCE, and an ozone concentration of 480 ppmv appeared to give optimal performance. However, excessive ozone reduces the treatment efficiency of TCE by the UV/O$_3$ process, possibly because ozone can absorb UV light to inhibit the photolysis of TCE. The complete dechlorination of TCE by hydroxyl radicals generated in the UV/O$_3$

process was found to be higher than that by direct photolysis. The oxidized products generated from the decomposition of TCE by photolysis and the UV/O_3 process need to be further identified.

5. Symbols and abbreviations

C_{a0}	initial concentration of TCE, ppmv
C_{af}	effluent concentration of TCE, ppmv
$[Cl^-]$	quantity of chloride ions trapped by the absorption bottle at a desired time interval, $mg\,l^{-1}$
EE/O_g	electrical energy per order for gas-phase systems
I	UV light intensity, $W\,m^{-2}$
$[Interme]_{Cl}$	quantity of chlorinated intermediates as chlorine, $mg\,l^{-1}$
P	lamp power, kW
R	air flow rate, scfm
$[TCE]_{Cl}$	quantity of TCE as chlorine, $mg\,l^{-1}$
$[TCE]_{Cl,0}$	total initial quantity of TCE as chlorine, $mg\,l^{-1}$
τ	retention time of reaction, s

Acknowledgements

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