

Behavior of By-products during Direct-photodegradation Treatment of Trichloroethylene. Effect of Oxygen Concentration on Production of By-products

Shin Yamamoto,* Takashi Amemiya, Masayuki Murabayashi, and Kiminori Itoh

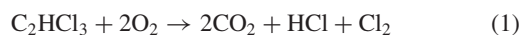
Graduate School of Environment and Information Sciences, Yokohama National University, Hodogaya-ku, Yokohama 240-8501

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During direct-photodegradation treatment of trichloroethylene by a low-pressure mercury lamp in a dry air atmosphere, slightly degradable by-products are produced; this production is the most serious issue associated with such treatment. We observed the acceleration of by-products degradation with decrease in an oxygen concentration in a treatment atmosphere.

Soil and groundwater have been polluted with volatile organic chlorinated compounds (VOCCs) such as trichloroethylene (TCE) and tetrachloroethylene discharged into the environment as an industrial waste. These pollutions have been considered to be of grave environmental concern for several decades.¹ Among many remedies against the pollutions, direct-photodegradation by UV light has been suggested as an effective method of treating VOCCs^{2,3} since it is well known that chlorinated ethylenes such as TCE are degraded very fast in gaseous phase⁴ due to a homogeneous chain reaction with chlorine radical.⁵ When the photodegradation is used as a method of treating VOCCs, a principal issue arises, namely, how efficiently slightly-degradable by-products such as carbon monoxide (CO), dichloroacetyl chloride (DCAC), and phosgene can be degraded; if a low-pressure mercury lamp (LML, wavelength: 254 and 185 nm), which emits vacuum UV light, is employed as a light source for the photodegradation, the treatment of ozone formed from oxygen is also required.⁶ In particular, the photodegradation of CO is extremely difficult⁷ and is therefore the most serious issue regarding the photodegradation of VOCCs. To the best of our knowledge, however, hardly any studies on the photodegradation of these by-products have been reported from an environmental perspective.

In this study, we chose to use TCE as an object material of photodegradation treatment in gaseous phase, and we investigated the treatment of by-products formed during the TCE photodegradation. A circulation-type of photodegradation apparatus (made of Pyrex glass and Teflon)⁸ was employed and an LML (Sen Lights Corp., 10 W, light intensity: 3.75 W at 254 nm and 0.75 W at 185 nm) was used as a light source. A FT-IR spectrometer (Perkin Elmer, Spectrum GX) was used to measure the concentrations of the reactant and products. The TCE photodegradation in our experiment was carried out in a dry air atmosphere. The light intensity at 185 nm is reduced owing to the absorption by oxygen in the air. While oxygen in a treatment atmosphere is indispensable for oxidation of TCE as shown in the following Eq 1, during the photodegradation treatment carried out in the air atmosphere, the oxygen concentration (approximately 21 vol % = 9.4 mol·m⁻³) is much higher than that required for the TCE concentration at issue (mostly < 10⁴ ppm = 0.45 mol·m⁻³).



Consequently, a possibility that the light intensity at 185 nm is reduced wastefully is present and therefore the efficiency of photodegradation treatment should be raised by the decrease in an oxygen concentration to less than 21 vol %. The variation in an oxygen concentration is, however, considered to influence photodegradation of by-products chemically as well as physically; in aqueous phase, the efficiencies of dissolved oxygen on VOCCs photodegradation have been reported.⁹ We carried out photodegradation of TCE under conditions with various oxygen concentrations prepared by mixing oxygen and nitrogen as 1 atm, and investigated into the behavior of the by-products. The initial concentration of TCE was approximately 0.06 mol·m⁻³ and it was almost completely degraded for < 0.5 min of the treatment at = 0.1 vol % oxygen concentration; at < 0.1 vol %, however, a small amount of TCE still remained at 0.5 min after the beginning of the treatment. The infrared absorption spectrum of TCE observed under an initial condition and these of by-products at 20 min after the beginnings of TCE photodegradation treatments that are carried out at 100, 20, 1.0, and < 0.1 vol % oxygen concentrations are shown in Figure 1. Under the conditions of = 0.1 vol % oxygen concentration, carbon dioxide (CO₂), CO, HCl, and phosgene were observed; these amounts of phosgene are < 10% of the maximum amounts formed under each condition. Then, 100 ± 6% as carbon balances were obtained under these conditions. However,

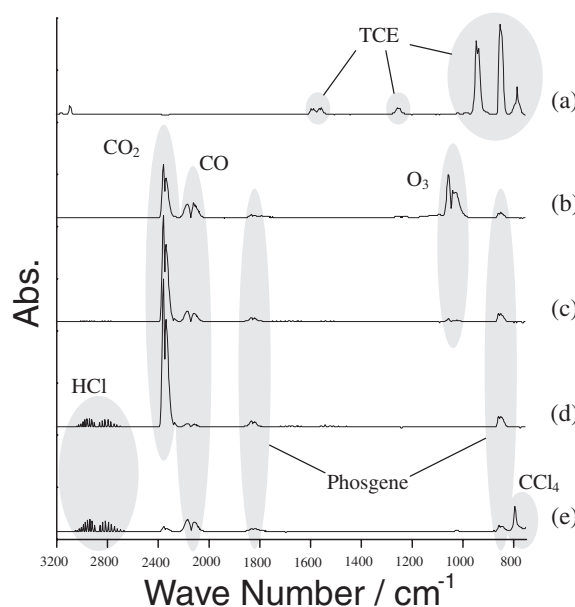


Figure 1. Infrared absorption spectrum of reactants. (a) is that of TCE under the initial condition, and (b), (c), (d), and (e) are these of by-products generated at 100, 20, 1.0, and < 0.1 vol % oxygen concentration, respectively.

no amount of CO_2 was generated but carbon tetrachloride was observed at < 0.1 vol % oxygen concentration. Under this condition, further, a carbon balance also reduced to $< 50\%$; this may be due to low oxygen concentration. The concentrations of CO and CO_2 generated in atmospheres containing various concentrations of oxygen (0.1 to 100 vol %) are shown in Figure 2. The concentration of CO was decreased with decreasing the oxygen concentration from 100 to 3.0 vol %, and a steep increase of CO production was observed at < 1.0 vol % oxygen concentration; meanwhile, the concentration of CO_2 shows an opposite behavior to that of CO toward the oxygen concentration. Consequently, the condition of 1.0 to 3.0 vol % oxygen concentration has been found to be most efficient for oxidation of CO to CO_2 during the TCE photodegradation. The minimum concentration of CO was approximately $0.01 \text{ mol}\cdot\text{m}^{-3}$ observed at 3.0 vol % oxygen concentration; this CO concentration is 1/5 of that generated under the condition of air atmosphere. Since light from the LML cannot be absorbed by CO, the decrease of CO observed with decreasing the oxygen concentration would be incomprehensible; this phenomenon is presumably, however, because chlorine-atom generated in the treatment atmosphere, which can oxidize CO,¹⁰ increased with decreasing the oxygen concentration. Figure 3 shows variations in a degradation-time for 95% of DCAC and in that of phosgene during TCE photodegradation treatment with changing the oxygen concentration;

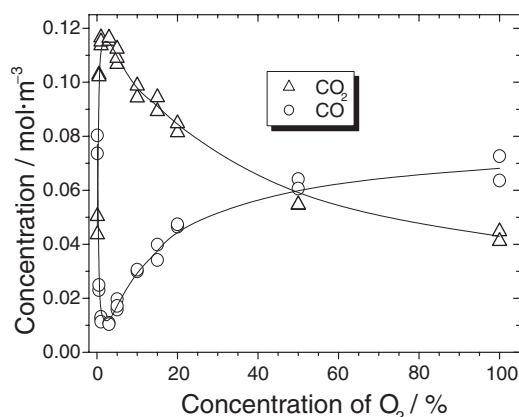


Figure 2. Variations in the productions of CO and CO_2 with changing oxygen concentration.

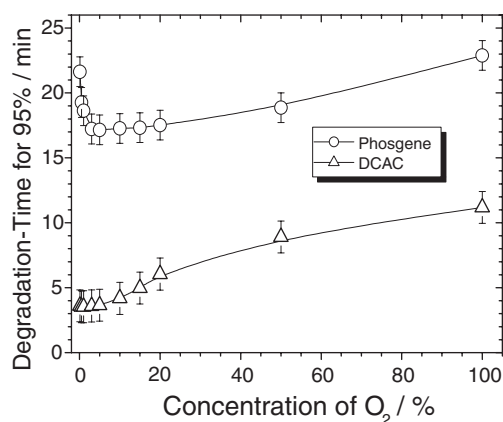


Figure 3. Variations in the degradation-times for 95% of DCAC and phosgene with changing oxygen concentration.

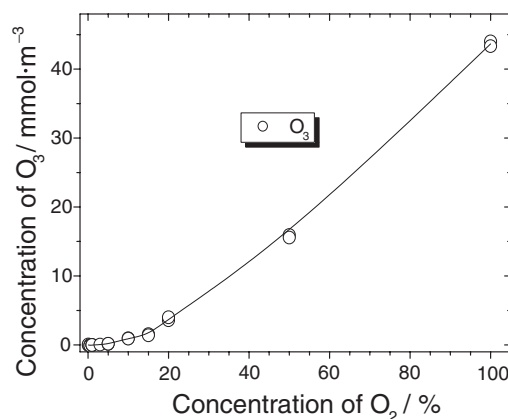


Figure 4. Variation in the production of ozone with changing oxygen concentration.

these times are for degrading 95% of the maximum amounts formed under each condition. These results represent that the highest degradation rate of DCAC and that of phosgene are obtained at ca. 1 vol % and at 3.0 to 5.0 vol % oxygen concentrations, respectively. The increases in the degradation rates of these two by-products are considered to be due to not only the increase in the light intensity at 185 nm but also the influence on chemical kinetics because increases in the degradation-time were observed at the region of low oxygen concentration. Moreover, the degradation-time of phosgene increased rapidly at < 3.0 vol % oxygen concentration, and the decrease in degradation-time of phosgene observed with decreasing the oxygen concentration from 100 to 5.0 vol % was more sluggish than that of DCAC. Such differences between the behavior of DCAC and that of phosgene are considered to be due to photo-formation of phosgene; the rate of phosgene photo-formation has been reported to be higher, the lower an oxygen concentration is.¹¹ Finally, the concentrations of ozone formed under the condition of various oxygen concentrations are shown in Figure 4. A decrease in the formed concentration of ozone was observed with decreasing oxygen concentration.

In consequence of these results, the decrease of oxygen concentration to ca. 3 vol % is found to be effective in the by-products degradation during the TCE photodegradation treatment.

References

- 1 J. M. Symons, T. A. Bellar, J. K. Carswell, J. DeMarco, K. L. Kropp, G. G. Robeck, D. R. Seeger, C. J. Slocum, B. L. Smith, and A. A. Stevens, *J.—Am. Water Works Assoc.*, **67**, 634 (1975).
- 2 M. Bhowmick and M. J. Semmens, *J.—Am. Water Works Assoc.*, **86**, 86 (1994).
- 3 W. R. Haag and M. D. Johnson, *Environ. Sci. Technol.*, **30**, 414 (1996).
- 4 R. Gürtler, U. Möller, S. Sommer, H. Müller, and K. Kleinermanns, *Chemosphere*, **29**, 1671 (1994).
- 5 E. Sanhueza, I. C. Hisatsune, and J. Heicklen, *Chem. Rev.*, **76**, 801 (1976).
- 6 H. Matsutani, M. Hashimoto, and M. Hashimoto, *Mizu Kankyo Gakkaishi*, **21**, 29 (1998).
- 7 S.-I. Yamaguti, T. Iwaizumi, Y. Mitsui, and S. Tsuda, *Combust. Sci. Technol.*, **133**, 107 (1998).
- 8 S. Yamamoto, K. Itoh, and M. Murabayashi, *Electrochemistry*, **70**, 425 (2002).
- 9 H. Shirayama, Y. Tohezo, and S. Taguchi, *Water Res.*, **35**, 1941 (2001).
- 10 G. K. Rollefson and C. W. Montgomery, *J. Am. Chem. Soc.*, **55**, 4036 (1933).
- 11 G. K. Rollefson, *J. Am. Chem. Soc.*, **55**, 148 (1933).