

# Carbon isotope fractionation during degradation of benzene, trichloroethene, and tetrachloroethene under ultraviolet light

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Stable carbon isotope fractionation factors associated with the degradation of benzene, trichloroethene (TCE), and tetrachloroethene (PCE) under ultraviolet light (254 nm) have been measured experimentally using simple and inexpensive quartz reaction vessels equipped with a syringe valve and septum. Carbon isotope enrichment factors of  $\epsilon_{\text{benzene}} = -6.2 \pm 0.3\text{‰}$ ,  $\epsilon_{\text{TCE}} = -6.8 \pm 0.2\text{‰}$ , and  $\epsilon_{\text{PCE}} = -4.1 \pm 0.2\text{‰}$  were obtained. The results demonstrate that the simple and inexpensive experimental design used in this study has potential application to determine isotope enrichment factors associated with degradation under conditions more representative of important atmospheric processes, and hence has future application to the study of the behavior of important trace gases such as non-methane hydrocarbons and other volatile organic compounds in the atmosphere.

Keywords: carbon, isotope, fractionation, ultra-violet, degradation

## INTRODUCTION

The emission of volatile organic compounds (VOCs) such as non-methane hydrocarbons (NMHCs), halogenated VOCs, and oxygenated VOCs to the atmosphere has lead to environmental concerns such as health risks associated with air pollution (e.g., World Health Organization, 2000), and the involvement of these compounds in various atmospheric chemistry reactions (e.g., Atkinson, 1985, 2000; Fuentes *et al.*, 2000). Since the first measurements of  $\delta^{13}\text{C}$  of atmospheric VOCs by Rudolph *et al.* (1997), there has been continued development of analytical methodologies to determine the isotopic composition of NMHCs and VOCs (e.g., Archbold *et al.*, 2005; Komatsu *et al.*, 2005; Pupek *et al.*, 2005), and a remarkable proliferation of the application of stable isotope analysis to study the behavior of large number of VOCs during atmospheric processes e.g., Tsunogai *et al.* (1999), Rudolph and Czuba (2000), Rudolph *et al.*, (2002, 2003), Saito *et al.* (2002), and Thompson *et al.* (2002, 2003), with a recent comprehensive review by Goldstein and Shaw (2003). Critical data required for the interpretation of stable isotope measurements of atmospheric VOCs are

the isotopic fractionation factors associated with processes that remove these compounds from the atmosphere, such as direct photolysis, reaction with ozone, and reaction with OH-radicals, in particular. A database of carbon and also hydrogen isotope enrichment factors is currently developing in the literature, with the majority of studies to date concerned with carbon isotope fractionation during reaction with OH radicals, which is one of the most important mechanisms for the degradation of NMHCs and VOCs in the troposphere (Rudolph *et al.*, 2000; Iannone *et al.*, 2003, 2004; Anderson *et al.*, 2004a, b).

To date, the technique used to measure stable isotope enrichment factors associated with atmospheric processes (described in detail by Anderson *et al.*, 2003) requires a relatively complex experimental methodology. The objective of this study is to develop a simple and inexpensive alternative methodology for determining these isotope enrichment factors. The simplified technique has been investigated by measuring the carbon isotope fractionation factor associated with the degradation by ultraviolet light of a NMHC (benzene), and two chlorinated VOCs (trichloroethene, TCE, and tetrachloroethene, PCE) of environmental concern.

## EXPERIMENTAL METHODS

Experiments were conducted in custom-fabricated 100 ml reaction vessels (Fig. 1). These reaction vessels consist of a lower portion of fused silica tube to allow transmittal of ultraviolet light, while the upper portion con-

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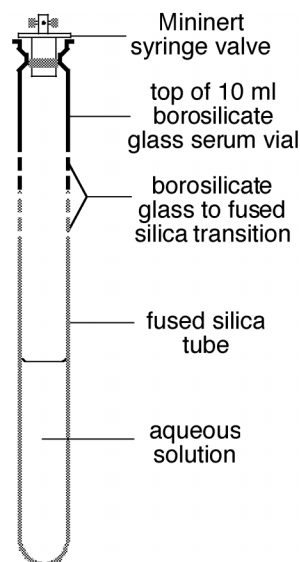


Fig. 1. Custom-fabricated reaction vessels used for degradation by ultraviolet light experiments. Reactor dimensions: length 30 cm, diameter 2.5 cm.

sists of the top part of a 10 ml borosilicate glass serum vial. Forty ml of distilled, deionized water was added to each reaction vessel, which was then capped with a Mininert valve (Vici Precision Sampling Co. Inc., Baton Rouge, LA). Neat chlorinated compounds (TCE, 99+% anhydrous; PCE, 99+% anhydrous; Sigma-Aldrich, Milwaukee, WI) or benzene (99.7+%; Wako Pure Chemicals Ltd., Tokyo, Japan) were added by means of a pipetting syringe (Hamilton Co., Reno, NV) via the Mininert valve to provide dissolved concentrations of 30 mg/l (TCE, PCE) or 40 mg/l (benzene), and the solution and headspace were allowed to reach equilibrium. The reaction vessels were exposed to an ultraviolet lamp with a wavelength of  $253.7 \pm 0.5$  nm for time periods up to 700 minutes (Fig. 2). Light flux was not measured. All experiments were conducted at a room temperature of  $23 \pm 2^\circ\text{C}$ . Control experiments, and reaction vessels that were not actively being exposed to ultraviolet light, were shielded with aluminum foil in order to reduce exposure to any ambient ultraviolet light. The experiments were not pH-buffered.

Organic compound concentrations and  $\delta^{13}\text{C}$  compositions were determined using a headspace technique (Slater *et al.*, 1999; Hunkeler and Aravena, 2000). Headspace samples of 0.1–1.0 ml were taken from the reaction vessel using a Pressure-Lok gastight syringe (Vici Precision Sampling Co. Inc., Baton Rouge, LA) via the Mininert valve, and injected into a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a 0.32 mm ID  $\times$  0.25  $\mu\text{m}$  film thickness  $\times$  60 m long HP-5TA column

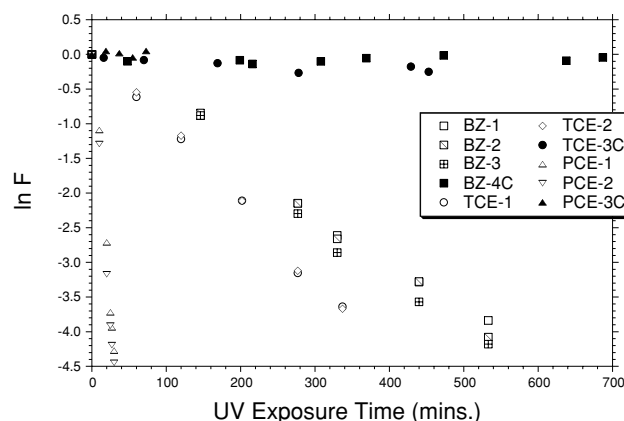


Fig. 2. Rate data for the degradation of benzene, TCE, and PCE by ultraviolet light.  $F$  is the fraction of compound remaining ( $=\text{concentration at time } t / (\text{initial concentration})$ ). Open symbols represent active experiments with UV exposure, closed symbols represent control experiments with no UV exposure.

(Hewlett-Packard, Palo Alto, CA). The oven temperature program was  $40^\circ\text{C}$  for 6 minutes, increase to  $160^\circ\text{C}$  at  $30^\circ\text{C}/\text{minute}$ , and hold at  $160^\circ\text{C}$  for 1 minute. Compound-specific isotope analysis was conducted using a Finnigan delta S mass spectrometer combined with the HP5890 GC through a microvolume combustion ceramic reactor tube (0.5 mm ID  $\times$  1.5 mm OD  $\times$  34 cm) operated at  $840^\circ\text{C}$ . The reactor tube was loaded with three Cu wires (0.5 mm diameter  $\times$  30 cm long) and one Pt wire (0.5 mm diameter  $\times$  30 cm long), and the Cu wires were pre-oxidized to form CuO before use by heating at  $540^\circ\text{C}$  under an  $\text{O}_2$  gas flow for three days. Combustion performance was monitored by periodic checks using standard samples. The ion currents of the resulting  $\text{CO}_2$  for  $m/z$  44, 45 and 46 were recorded every 0.125 sec. Concentrations were quantified by integrating the  $m/z$  44 peak, and normalizing to  $m/z$  44 peak areas determined before exposure to ultraviolet light. Concentration measurements had a typical reproducibility of  $\pm 5\%$ . Isotope analyses were compared against external  $\text{CO}_2$  isotope standards using ISODAT software, and  $\delta^{13}\text{C}$  values are reported in the usual  $\delta$  notation relative to the VPDB standard. The reproducibility of isotope analyses is dependent upon concentration, with a reproducibility of 0.3‰ for initial concentrations, and a typical reproducibility of 1‰ at low concentrations ( $<1\%$  of starting concentration). Values of  $\delta^{13}\text{C}$  measured for compounds in the vapor phase are assumed to be the same as values for dissolved compounds, as the vapor-dissolved phase isotope fractionation factor is insignificant ( $<0.5\%$ ; Slater *et al.*, 1999), and is assumed to be constant during the course of the experiment.

Table 1. Reaction rate ( $k$ ) and carbon isotope enrichment factors ( $\epsilon$ ) results for ultraviolet light (254 nm) degradation experiments of benzene (BZ), trichloroethene (TCE), and tetrachloroethene (PCE)

| Expt. # | Initial concn.<br>(mg/l) | rate, $k$<br>(min <sup>-1</sup> ) | $r^2$ | $\epsilon \pm \text{SE}^{(a)}$<br>(‰) | $r^2$ | $\delta^{13}\text{C}_{t-i}^{(b)}$<br>(‰) | $\delta^{13}\text{C}_{50}^{(c)}$<br>(‰) | $\delta^{13}\text{C}_{90}^{(c)}$<br>(‰) |
|---------|--------------------------|-----------------------------------|-------|---------------------------------------|-------|------------------------------------------|-----------------------------------------|-----------------------------------------|
| BZ-1    | 40                       | 0.0075                            | 0.99  | -6.5 ( $\pm 0.3$ )                    | 0.99  | +25.7                                    | +4.5                                    | +15.1                                   |
| BZ-2    | 40                       | 0.0078                            | 0.99  | -6.3 ( $\pm 0.3$ )                    | 0.99  | +26.4                                    | +4.4                                    | +14.6                                   |
| BZ-3    | 40                       | 0.0082                            | 0.99  | -5.7 ( $\pm 0.3$ )                    | 0.99  | +24.4                                    | +4.0                                    | +13.2                                   |
| BZ-4C   | 40 (control)             |                                   |       |                                       |       | $\pm 0.1$                                |                                         |                                         |
| TCE-1   | 30                       | 0.011                             | 1.00  | -7.0 ( $\pm 0.2$ )                    | 1.00  | +25.3                                    | +4.9                                    | +16.2                                   |
| TCE-2   | 30                       | 0.011                             | 1.00  | -6.6 ( $\pm 0.2$ )                    | 0.99  | +23.9                                    | +4.6                                    | +15.3                                   |
| TCE-3C  | 30 (control)             |                                   |       |                                       |       | $\pm 0.1$                                |                                         |                                         |
| PCE-1   | 30                       | 0.15                              | 0.99  | -4.0 ( $\pm 0.2$ )                    | 0.99  | +17.0                                    | +2.8                                    | +9.3                                    |
| PCE-2   | 30                       | 0.16                              | 0.99  | -4.3 ( $\pm 0.1$ )                    | 1.00  | +19.2                                    | +3.0                                    | +10.0                                   |
| PCE-3C  | 30 (control)             |                                   |       |                                       |       | $\pm 0.2$                                |                                         |                                         |

<sup>(a)</sup>SE = standard error.

<sup>(b)</sup> $\delta^{13}\text{C}_{f-i}$  is the change in  $\delta^{13}\text{C}$  over the course of an active experiment (i.e.,  $\delta^{13}\text{C}_{\text{final}} - \delta^{13}\text{C}_{\text{initial}}$ ), or  $1\sigma$  variation of ( $\delta^{13}\text{C}_{\text{time } t} - \delta^{13}\text{C}_{\text{initial}}$ ) measurements for control experiments. Control experiments analyzed for the same time duration as the active experiments.

<sup>(c)</sup> $\delta^{13}\text{C}_{50}$  and  $\delta^{13}\text{C}_{90}$  are the calculated changes in  $\delta^{13}\text{C}$  for 50% and 90% degradation, respectively.

## RESULTS

### Degradation rate

Degradation rate data are presented in Fig. 2, and the results are summarized in Table 1. All active experiments yielded degradation rates that are first-order with respect to organic compound concentration, which is consistent with previous work using ultraviolet light at 254 nm (Frischherz *et al.*, 1986; Sundstrom *et al.*, 1986; Weir *et al.*, 1987), although experiments conducted under similar conditions, i.e., without the presence of additional oxidants such as  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , or catalysts such as  $\text{TiO}_2$  or  $\text{UO}_2^{2+}$ , are relatively rare (Legrini *et al.*, 1993). The degradation rate for benzene was the slowest of the three compounds studied, while the degradation rate for PCE was faster than for TCE. The faster degradation rate for PCE vs. TCE is consistent with the work of Frischherz *et al.* (1986), and is also consistent with the possibility of direct photolysis as the dominant degradation mechanism, as PCE has a higher molar absorptivity than TCE at 254 nm (Perkampus, 1992). Unfortunately, direct comparison of measured degradation rates amongst these studies is not possible, as the light flux was not measured. Nonetheless, for experiments conducted under broadly similar conditions, a pseudo first-order reaction rate for benzene degradation of  $0.0078 \text{ min}^{-1}$  measured in this study compares to a previous value of  $0.0145 \text{ min}^{-1}$  (Weir *et al.*, 1987), and a pseudo first-order reaction rate for TCE degradation rate of  $0.011 \text{ min}^{-1}$  measured in this study compares to a previous value of  $0.0315 \text{ min}^{-1}$  (Sundstrom *et al.*, 1986).

### Isotope fractionation associated with degradation

If the products of the degradation reaction do not back-react or isotopically exchange with the reactant,  $\delta^{13}\text{C}$ -concentration data are expected to follow a Rayleigh fractionation trend, described by:

$$\delta = (\delta_i + 1000)F^{(\alpha-1)} - 1000 \quad (1)$$

where  $\delta$  is the isotopic composition of the organic compound (benzene, TCE, or PCE) at time  $t$ ,  $\delta_i$  is the initial isotopic composition of the organic compound,  $F$  is the fraction of the organic compound remaining (=concentration at time  $t$ /initial concentration), and  $\alpha$  is the isotope fractionation factor associated with the degradation reaction. Rearrangement of (1) gives:

$$\ln[(\delta + 1000)/(\delta_i + 1000)] = (\alpha - 1)\ln F. \quad (2)$$

Hence, if the  $\delta^{13}\text{C}$ -concentration data follows a Rayleigh fractionation trend, a plot of  $\ln[(\delta + 1000)/(\delta_i + 1000)]$  vs.  $\ln F$  should give a straight line with a slope of  $(\alpha - 1)$ , and pass through the origin. The isotope enrichment factor,  $\epsilon$ , is calculated using:

$$\epsilon = 1000(\alpha - 1). \quad (3)$$

Values of  $\ln[(\delta + 1000)/(\delta_i + 1000)]$  vs.  $\ln F$  are plotted in Figs. 3–5 (benzene, TCE, PCE, respectively), and the experimental results are summarized in Table 1. Values of  $\alpha$  have been calculated using best fit lines for  $\ln[(\delta + 1000)/(\delta_i + 1000)]$  vs.  $\ln F$  for all data points collected

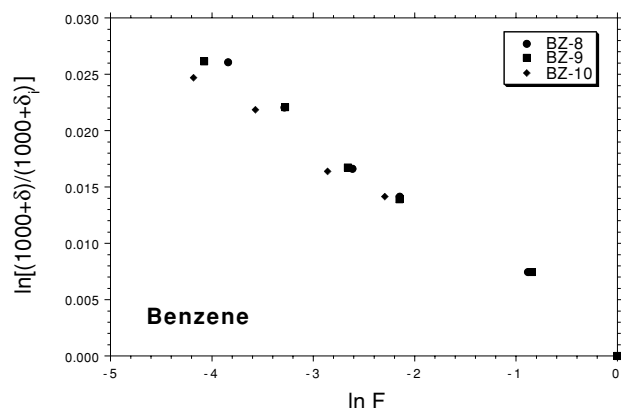


Fig. 3. Isotope fractionation data, presented as  $1000[(1000 + \delta)/(1000 + \delta_i)]$  vs. extent of reaction, presented as  $\ln F$ , during degradation of benzene by ultraviolet light.

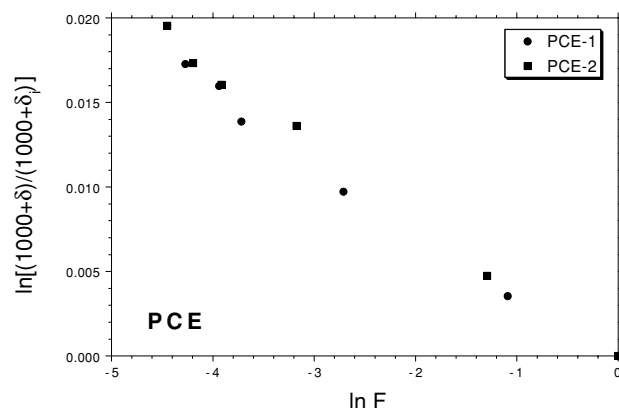


Fig. 5. Isotope fractionation data, presented as  $1000[(1000 + \delta)/(1000 + \delta_i)]$  vs. extent of reaction, presented as  $\ln F$ , during degradation of PCE by ultraviolet light.

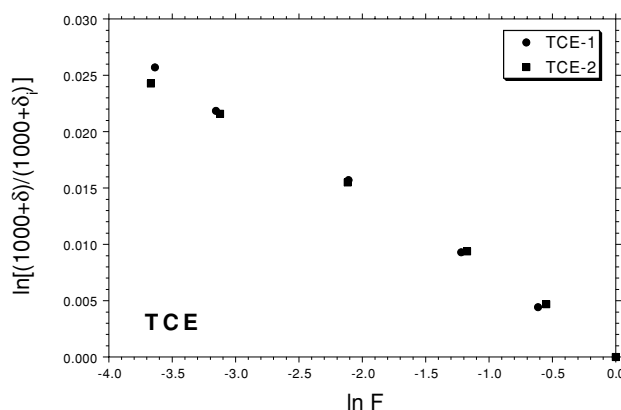


Fig. 4. Isotope fractionation data, presented as  $1000[(1000 + \delta)/(1000 + \delta_i)]$  vs. extent of reaction, presented as  $\ln F$ , during degradation of TCE by ultraviolet light.

for each experiment. All active experiments show a significant and progressive  $^{13}\text{C}$  enrichment in the value of  $\delta^{13}\text{C}$  for the residual reactant compound during the course of the experiment ( $\delta^{13}\text{C}_{\text{final}} - \delta^{13}\text{C}_{\text{initial}} = +17$  to  $+26\text{‰}$ ). All experiments yielded excellent values of  $r^2$  for the linear least-squares fits to the data, with values of  $r^2$  ranging from 0.99 to 1.00, indicating that the results are well-described by a Rayleigh fractionation model. Measurements of  $\epsilon$  show good reproducibility, and yield average values of  $-6.2\text{‰}$  for benzene ( $1\sigma = 0.3\text{‰}$ ),  $-6.8\text{‰}$  for TCE ( $1\sigma = 0.2\text{‰}$ ), and  $-4.1\text{‰}$  for PCE ( $1\sigma = 0.2\text{‰}$ ).

## DISCUSSION

The isotope enrichment factors for benzene, TCE, and PCE have been quantified for many biological, chemi-

cal, and physical processes e.g., Harrington *et al.* (1999), Poulson and Drever (1999), Poulson and Naraoka (2002), Schmidt *et al.* (2004) and references therein. However, this study is the first to quantify the isotope enrichment factor associated with degradation in the presence of ultraviolet light at 254 nm. Previous studies have quantified the carbon isotope enrichment factor associated with benzene degradation caused by OH-radicals generated by the photolysis of isopropyl nitrite by ultraviolet light in the wavelength range 320 to 400 nm, and measured values of  $-8.1 \pm 0.8\text{‰}$  (Rudolph *et al.*, 2000) and  $-7.5 \pm 0.5$  (Anderson *et al.*, 2004b). In the absence of compounds such as  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  (the experimental conditions of this study), OH radicals are not generated by ultraviolet light at 254 nm, which suggests that a different degradation mechanism may have operated in this study. The probable differences in degradation mechanisms for this study vs. the studies of Rudolph *et al.* (2000) and Anderson *et al.* (2004b) precludes any meaningful comparison of measured isotope enrichment factors. Experimental determination of the degradation mechanism, or mechanisms, was beyond the scope of the present study, and is not available in the literature, in part due to the paucity of experiments conducted in the absence of catalysts or additional oxidants (Legrini *et al.*, 1993). However, as PCE has a higher molar absorptivity than TCE at 254 nm (Perkampus, 1992), the faster degradation rate of PCE vs. TCE suggests that direct photolysis may be a possible degradation mechanism.

Isotope fractionation factors are typically considered to decrease as reaction rates increase (e.g., Goldhaber and Kaplan, 1975; Mariotti *et al.*, 1988), and the data for the two chlorinated ethenes from this study is consistent with this relationship, as the carbon isotope enrichment factor for PCE ( $\epsilon_{\text{PCE}} = -4.1$ ) is significantly smaller than the enrichment factor for TCE ( $\epsilon_{\text{TCE}} = -6.8$ ), which is associ-

ated with the PCE degradation rate being much faster than the TCE degradation rate (Fig. 2). Comparison of fractionation factors and degradation rates for TCE and PCE vs. benzene is not appropriate due to the different molecular structures of the chlorinated ethenes vs. the aromatic benzene ring, which may result in these two classes of compounds having very different degradation mechanisms.

Potentially, the isotope enrichment factors determined in this study could be used to help monitor the efficiency of remediation processes that use ultraviolet light at 254 nm to degrade contaminant compounds in water. In practice, such an application is unlikely as the use of ultraviolet light alone to remediate contaminant compounds is not a very efficient process, and such a process could monitor degradation efficiency more cheaply and easily by measuring contaminant concentrations alone.

Despite the fact that the results obtained in this study are not directly applicable to the study of the behavior of VOCs in the atmosphere, the excellent reproducibility and linear regression coefficients of the experimental results (Figs. 2–5, Table 1) in this study demonstrates that the experimental design used here has potential as a simple and inexpensive alternative to the method described by Anderson *et al.* (2003). The experimental design used here is similar to the design of Anderson *et al.* (2003) in that the reactor is a batch reactor under ultraviolet light, and that isotope analysis is performed using a gas chromatograph-combustion-isotope ratio mass spectrometer (GC-C-IRMS) system that is available from a number of commercial vendors. The experimental design used in this study differs from Anderson *et al.* (2003) in that a simplified sampling scheme using a gas-tight syringe and a Mininert syringe valve has been employed in this study. Modification of the experimental design used in this study to perform degradation experiments more representative of conditions under which atmospheric VOCs are degraded (i.e., degradation by OH radicals) appears to be relatively straightforward, and future work is planned in this direction as well as performing degradation experiments under conditions similar to previous studies, so that a more direct comparison of experimentally-determined isotope enrichment factors can be performed. In addition, it is hoped that our simple and inexpensive experimental design will facilitate and encourage further determination of isotope enrichment factors for different VOCs, different isotope systematics (e.g., hydrogen and chlorine), and different environmental conditions by other investigators.

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