

## PAINT SOLVENT TO FOOD ADDITIVE: AN ENVIRONMENTAL ROUTE OF DEHALOGENATION FOR 4-CHLOROBENZOTRIFLUORIDE

CORAJ. YOUNG,<sup>†</sup> RODOLFO F. GÓMEZ BIAGI,<sup>†</sup> MICHAEL D. HURLEY,<sup>‡</sup> TIMOTHY J. WALLINGTON,<sup>‡</sup> and SCOTT A. MABURY\*<sup>†</sup><sup>†</sup>Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada<sup>‡</sup>Ford Motor Company, Mail Drop SRL-3083, Dearborn, Michigan 48121, USA

(Received 30 January 2008; Accepted 17 April 2008)

**Abstract**—In an effort to reduce volatile organic compounds (VOCs) in paint solvents, replacements containing non-VOC compounds have been proposed. One such compound is 4-chlorobenzotrifluoride (CBTF), for which environmental fate studies have not been conducted. The objective of the present study was to determine the products of the atmospheric oxidation of CBTF and the aqueous fate of these products. Smog chamber experiments were performed to measure the kinetics and mechanism of atmospheric oxidation. A rate constant of  $2.22 (\pm 0.30) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was determined for the reaction of hydroxyl radicals with CBTF in 700 Torr of air at 296 K. Using offline sampling and gas chromatography coupled to mass spectroscopic analysis, it was determined that 2-chloro-5-trifluoromethylphenol (*o*-CTFP) was the primary product of CBTF atmospheric oxidation. Aqueous photolysis of *o*-CTFP in deionized water proceeded at a rate of  $1.3 (\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ , corresponding to a half-life of  $1.5 \pm 0.1 \text{ h}$  and a quantum yield of  $6.6 (\pm 0.4) \times 10^{-4}$ . The mechanism of photolysis was investigated using liquid chromatography coupled to tandem mass spectrometry, which suggested that degradation of *o*-CTFP occurred via photonucleophilic displacement of chlorine, followed by photoinduced hydrolysis of the trifluoromethyl group to yield 3,4-dihydroxybenzoic acid (an approved food additive considered to be nontoxic).

**Keywords**—4-Chlorobenzotrifluoride Atmospheric oxidation Dihydroxybenzoic acid Aqueous photolysis

## INTRODUCTION

Recognition that volatile organic compounds (VOCs) are important contributors to ozone production and local air quality degradation has led to regulations that limit VOC emissions. Sources of VOCs include vehicle emissions, gasoline evaporation, paint, and other solvents. Paint solvents can be a major contributor and have been estimated to make up to 46% of VOCs in an urban area [1]. As a result, effort has been made to reduce VOCs in paint solvents. Proposed replacement products typically utilize low-boiling compounds that fall outside the definition of VOC and can be used without restriction [2,3]. One such compound is 4-chlorobenzotrifluoride (CBTF), which is not considered a VOC by the U.S. Environmental Protection Agency [4]. This compound has been the subject of only one environmental fate study in which it was shown to have an atmospheric lifetime of approximately 50 d [5]. This implies that it will be subject to atmospheric transport prior to degradation and, consequently, will not contribute to ozone production at ground level in urban areas [4,5]. Prior to large-scale use of CBTF, further information on its environmental fate is needed. The goal of the present study was to provide such information.

Atmospheric degradation of CBTF is dominated by reaction with hydroxyl radicals [5]. The reactions of hydroxyl radicals with aromatic compounds proceed via addition to the aromatic ring, hydrogen abstraction from C–H bonds in substituents on the aromatic ring, and addition to  $>\text{C}=\text{C}<$  bonds in substituents on the aromatic ring [6,7]. The substituents in CBTF are unreactive toward OH radicals; hence, reaction is expected to

proceed via formation of the OH–CBTF adduct. The atmospheric fate of the adduct is expected to be reaction with molecular oxygen leading to a complex mixture of products with phenolic compounds as major products [6,8]. The oxidation products will be less volatile and more water soluble than the parent compound and are likely to be susceptible to wet deposition. Once in the aqueous environment, we hypothesize that the atmospheric products will be subject to photolysis to yield a salicylic acid derivative, 2,4-dihydroxybenzoic acid (2,4-DHBA), or its isomer, 3,4-DHBA (Fig. 1).

Salicylic acid is best known as the precursor to acetylsalicylic acid (aspirin). This compound itself is known to have anti-inflammatory and pain-reducing properties and is commonly used in skin treatments, specifically for the treatment of warts, acne, and other skin conditions [9]. Salicylic acid can be derived from natural sources and is found in natural waters at low parts-per-billion levels despite effective removal of wastewater by treatment plants (up to 99%) [10]. Salicylic acids and DHBAs are approved for use as food additives and have been shown to be nontoxic at the levels used for these purposes [11].

The objective of the present study was to examine the environmental fate of the non-VOC solvent, CBTF. Specifically, the potential for environmental dehalogenation through atmospheric oxidation and the aqueous photolysis were studied.

## MATERIALS AND METHODS

*Chemicals*

All chemicals were analytical reagent grade and were used as received. All authentic standards (CBTF, 98%; 2-chloro-5-trifluoromethylphenol [*o*-CTFP], 96%; and 3,4-DHBA) were obtained from Sigma-Aldrich (Oakville, ON, Canada). Smog

\* To whom correspondence may be addressed (smabury@chem.utoronto.ca).

Published on the Web 4/29/2008.

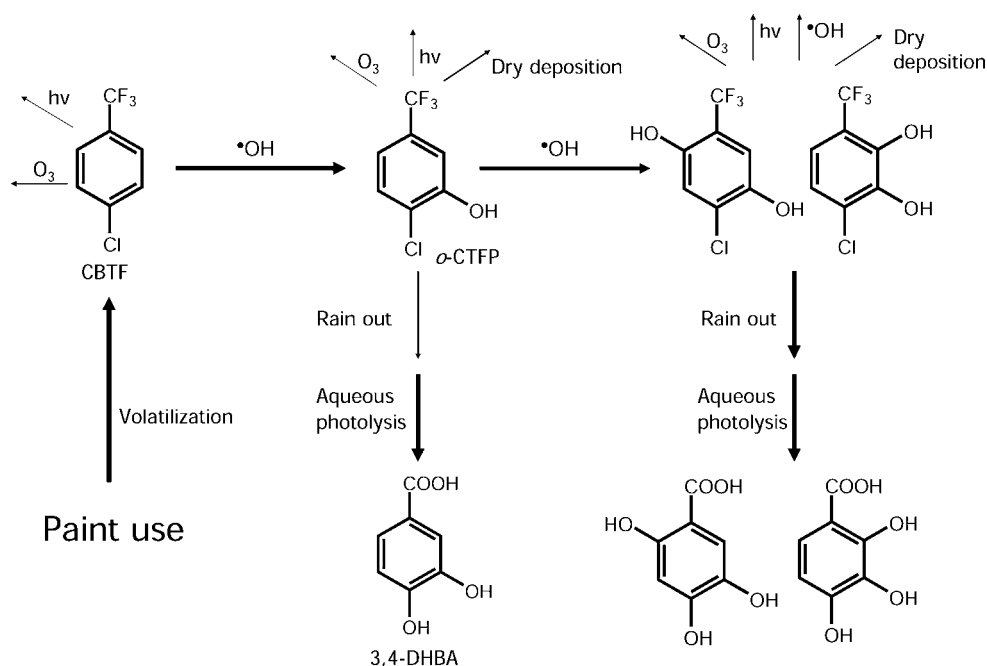


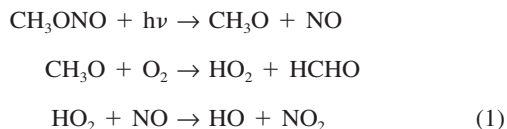
Fig. 1. Potential environmental pathway of dehalogenation for 4-chlorobenzotrifluoride (CBTF) to 2-chloro-5-trifluoromethylphenol (*o*-CTFP) and 3,4-dihydroxybenzoic acid (3,4-DHBA).

chamber experiments were performed in zero air diluent (Michigan Airgas, Bay City, MI, USA). All water used was Barnstead E-pure<sup>®</sup> water (Dubuque, IA, USA) with a resistivity of 18 M $\Omega$  cm<sup>-1</sup>. Solvents used were of high-performance liquid chromatography (HPLC) grade and were obtained from EMD Biosciences (through VWR International, Mississauga, ON, Canada).

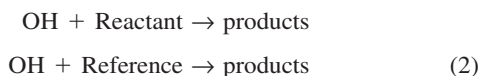
#### Atmospheric oxidation

Experiments were performed in a 140-L Pyrex<sup>®</sup> reactor interfaced to a Mattson Sirius 100 Fourier transform infrared spectrometer (Madison, WI, USA). The reactor was surrounded by 22 fluorescent black lamps (GE F15T8-BL, General Electric, Fairfield, CT, USA) that were used to photochemically initiate OH product studies. Reaction progress was monitored using Fourier transform infrared spectroscopy, with an infrared pathlength of 27 m and a spectral resolution of 0.25 cm<sup>-1</sup>. Infrared spectra were derived from 32 co-added interferograms. Liquid reagents were subjected to repeated freeze, pump, and thaw before introduction into the chamber via a calibrated volume. Smog chamber methods are similar to those that have been described previously [12].

OH radicals were produced by the photolysis of CH<sub>3</sub>ONO in air:



In relative rate experiments, the following reactions take place:



It can be shown that:

$$\ln\left(\frac{[\text{Reactant}]_{t_0}}{[\text{Reactant}]_t}\right) = \frac{k_{\text{Reactant}}}{k_{\text{Reference}}}\ln\left(\frac{[\text{Reference}]_{t_0}}{[\text{Reference}]_t}\right) \quad (3)$$

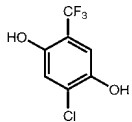
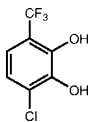
where [Reactant]<sub>t<sub>0</sub></sub>, [Reactant]<sub>t</sub>, [Reference]<sub>t<sub>0</sub></sub>, and [Reference]<sub>t</sub> are the concentrations of the reactant and reference compounds at times *t*<sub>0</sub> and *t*, and *k*<sub>Reactant</sub> and *k*<sub>Reference</sub> are the rate constants for the reactant and the reference. The reaction mixture used to determine *k*(OH + CBTF) consisted of 6.2 mTorr of CBTF, 100 mTorr of CH<sub>3</sub>ONO, and 5.0 mTorr of C<sub>2</sub>H<sub>2</sub> in 700 Torr of air diluent.

Product studies were performed by collecting offline samples of the gas phase for product analysis initially and after 10 and 20 min of ultraviolet (UV) irradiation. The reaction mixture for product studies consisted of 32.3 mTorr of CBTF and 207 mTorr of CH<sub>3</sub>ONO. Samples were collected by pulling 2.5 to 3 L of chamber air through XAD cartridges (Amberlite XAD-2, 400/200 mg purchased from Sigma-Aldrich) at a rate of approximately 1 L min<sup>-1</sup>. Sampling cartridges were purchased from Sigma-Aldrich and were used without modification. The XAD cartridges were extracted using two 5-ml portions of ethyl acetate, which were combined and blown down to 1 ml using a nitrogen evaporator. Separate extraction of breakthrough sorbent indicated the main XAD sorbent was capturing all the analytes of interest. Samples were analyzed using an Agilent 6890 gas chromatograph and detected with an Agilent 5973 inert mass selective detector operating in electron impact mode (70 eV, Santa Clara, CA, USA). Analytes were separated with a DB-5 column (Restek, 0.25  $\mu$ m, 15 m  $\times$  0.25 mm) using a temperature program starting at 70°C, followed by an increase of 15°C min<sup>-1</sup> to 150°C and an increase of 8°C min<sup>-1</sup> to 200°C. Analytes were detected in total ion monitoring mode.

#### Aqueous photochemistry

Photochemical experiments were conducted in a Suntest CPS photosimulator (Atlas, Chicago, IL, USA) equipped with a Xe lamp as the UV source and special glass filters restricting the transmission of wavelengths below 290 nm. However, even with the presence of these filters, there was a slight bleed of wavelengths below 290 nm, leading to inexact match of the

Table 1. Calculated physical properties for 4-chlorobenzotrifluoride (CBTF), 2-chloro-5-trifluoromethylphenol (*o*-CTFP), and proposed environmental degradation products [13,14]

	CBTF	<i>o</i> -CTFP		
Vapor pressure (Pa)	769	26	0.04	0.61
Water solubility (mol L <sup>-1</sup> )	2.4 × 10 <sup>-4</sup>	9.9 × 10 <sup>-2</sup>	Miscible	6.5 × 10 <sup>-3</sup>
Log air-water partitioning coefficient (log <i>K</i> <sub>AW</sub> )	0.13	-3.98	-8.13	-6.17
Log octanol-water partitioning coefficient (log <i>K</i> <sub>OW</sub> )	2.88	2.57	1.63	2.01
Log octanol-air partitioning coefficient (log <i>K</i> <sub>OA</sub> )	2.74	3.14	9.78	8.18
Lifetime for atmospheric reaction with OH	50 d <sup>a</sup>	138 h <sup>b</sup>	14 h <sup>b</sup>	14 h <sup>b</sup>

<sup>a</sup> Determined in the present study and by Atkinson et al. [5].

<sup>b</sup> Determined using the method of Kwok and Atkinson [15].

simulated spectrum with actinic radiation. The lamp was set to maximum intensity (765 W m<sup>-2</sup>). Cold water flowed through the photosimulator to maintain an internal temperature close to room temperature. Solutions were prepared in deionized water or pH 4 or 9 buffers. Reactions were performed in large quartz vessels with approximately 100 ml of solution for product studies at a 50-ppm (260 μM) initial concentration. Kinetic studies were performed in smaller quartz tubes, with approximately 10 ml of solution and a 4-ppm (20 μM) initial concentration. Dark controls were maintained for all studies. Samples were stored at 4°C prior to analysis.

#### Analytical methods

Ultraviolet absorption spectra were recorded using a Hewlett-Packard 8452A diode array spectrophotometer (Palo Alto, CA, USA). High-performance liquid chromatography with UV detection analyses were performed at room temperature using a Waters 600S chromatograph fitted with a C18 column (5 μm, 250 × 4.6 mm, Milford, MA, USA). A 20-μl injection of each sample was done using a Waters 717 autosampler. Analytes were detected with a Waters 996 photodiode array detector. Analysis of CTFP was performed at 280 nm under 1-ml min<sup>-1</sup> isocratic conditions of 70% acetonitrile and 30% water.

Liquid chromatography–tandem mass spectrometry analysis was performed using a Waters 616 LC pump and 600 controller with detection by a Micromass Quattro Micro<sup>®</sup> MS/MS detector in negative ion mode (Cheshire, UK). A mobile phase of 80% methanol and 20% water and a cone voltage of 35 V were used. Triplicate 10-μl loop injections were made, and the following mass-to-charge ratios (*m/z*) were monitored: 196, 178, 172, 157, and 154.

#### Phase distribution and environmental fate modeling

Physical properties of 4-CBTF, *o*-CTFP, and hypothesized atmospheric oxidation products of *o*-CTFP were estimated using the SPARC online calculator ([ibmlc2.chem.uga.edu/sparc/](http://ibmlc2.chem.uga.edu/sparc/)) [13,14], as no relevant experimentally determined properties were available. Calculated properties are shown in Table 1. Where values for reaction with hydroxyl radical were not available, the method of Kwok and Atkinson [15] was used to estimate these rates. Values were input to a level III fugacity model [16] ([www.trentu.ca/academic/aminss/envmodel/](http://www.trentu.ca/academic/aminss/envmodel/)) under default environmental conditions, with advection removed as a source of loss.

## RESULTS AND DISCUSSION

### Atmospheric oxidation

The reactivity of CBTF toward hydroxyl radicals was measured relative to that of C<sub>2</sub>H<sub>2</sub>. By monitoring the loss of CBTF and C<sub>2</sub>H<sub>2</sub> when mixtures containing these compounds were exposed to hydroxyl radicals in 700 Torr of air at 296 K, a rate constant ratio  $k(\text{OH} + \text{CBTF})/k(\text{OH} + \text{C}_2\text{H}_2) = 0.263 \pm 0.035$  was derived. Quoted uncertainties are two standard deviations from the regression analysis, together with estimated uncertainties in the infrared analysis. The rate constant ratio can be placed on an absolute basis using  $k(\text{OH} + \text{C}_2\text{H}_2) = 8.45 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  [17] to give  $k(\text{OH} + \text{CBTF}) = (2.22 \pm 0.30) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This result is in agreement with the value of  $k(\text{OH} + \text{CBTF}) = (2.3 \pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reported by Atkinson et al. [5]. Using a global-weighted OH concentration of 10<sup>6</sup> molecules cm<sup>-3</sup>, we estimate that the atmospheric lifetime of CBTF is approximately 50 d, which agrees with the lifetime determined by Atkinson et al. [5].

Atmospheric oxidation of CBTF should result primarily in OH addition products that are either *ortho*- or *meta*-substituted (relative to the chlorine substituent): *o*-CTFP and 3-chloro-6-trifluoromethylphenol (*m*-CTFP). To verify this hypothesis and determine whether one or the other product is formed, offline samples were taken, extracted, and analyzed by gas chromatography with mass spectrometric analysis (GC-MS). Chromatographic resolution of structural isomers is often analytically challenging. In this case, the presence of an intramolecular hydrogen bond in the *meta*-substituted product is expected to lead to different physical properties, which should affect retention on a gas chromatography column and lead to chromatographic separation. Authentic standards were only available for *o*-CTFP, so a comparative isomer study was performed using trifluorocresol. Analysis of *o*- and *m*-trifluorocresol using the same gas chromatography method described previously demonstrated the different behavior of the two products (Fig. 2). The *o*-trifluorocresol elutes much earlier due to the presence of an intramolecular hydrogen bond that reduces the polarity of the compound, which increases vapor pressure and reduces interactions with the column, subsequently reducing the retention time. Isomers of CTFP would be expected to behave in a similar manner to trifluorocresol isomers, with the *m*-CTFP isomer eluting much earlier than *o*-CTFP. Analysis of smog chamber extracts by GC-MS revealed the presence of a single peak, which had the same retention time as the *o*-CTFP

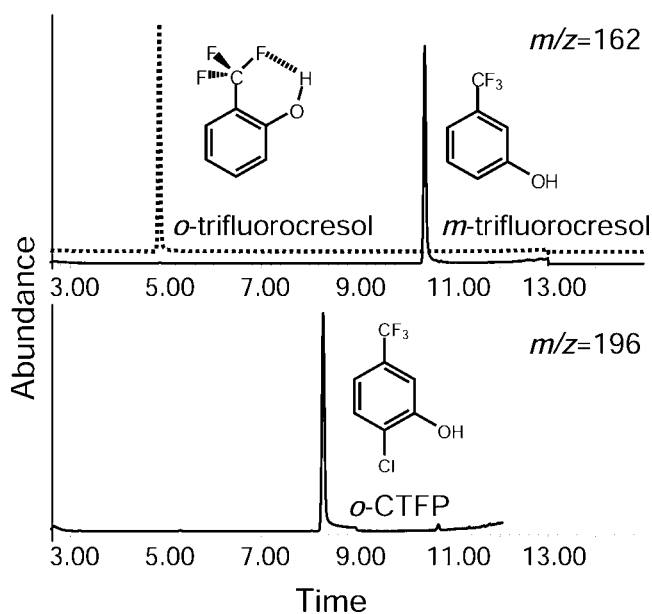


Fig. 2. Gas chromatography with mass spectrometric analysis chromatograms for 2-chloro-5-trifluoromethylphenol (*o*-CTFP) and *o*- and *m*-trifluorocresol in electron impact mode.

standard. No other peaks were visible in the GC-MS chromatogram for the smog chamber extract, suggesting that no *m*-CTFP was formed from atmospheric oxidation of CBTF and that the primary product of atmospheric oxidation of CBTF was *o*-CTFP. This is consistent with structure-activity relationship predictions, which suggest that the position *ortho* to the chlorine should be more than three times more reactive to OH addition than the *meta* position [15].

#### Kinetics and mechanism of aqueous photolysis

*Ortho*-chlorotrifluoromethylphenol is expected to undergo photonucleophilic displacement of chlorine and photolysis of trifluoromethyl to yield 3,4-DHBA. *Ortho*-chlorotrifluoromethylphenol was observed to degrade in aqueous solutions. No significant loss of *o*-CTFP was detected in dark controls, which eliminates sorption and thermal and hydrolytic processes as contributors to observed degradation. Although trifluoromethylphenols have been shown to be subject to hydrolysis in the absence of light to yield semiquinones, the *meta* isomer was demonstrated to be stable in the dark [18], which is consistent with the results of the current experiment. Direct photolysis kinetics were measured, and results are shown in Table 2. The observed first-order rate constant for degradation in deionized water (pH 5.5) was  $1.3 (\pm 0.1) \times 10^{-4} \text{ s}^{-1}$ , corresponding to a half-life of  $1.5 \pm 0.1 \text{ h}$ . This is not an absolute half-life, as it was determined under conditions not identical to actinic conditions. However, the corresponding quantum yield for this reaction, determined using *p*-nitroanisole and pyridine as chemical actinometers, was calculated as  $6.6 (\pm 0.4) \times 10^{-4}$  and is independent of the intensity of light used. This reaction was generally faster than rates observed for other trifluoromethyl phenyl compounds. Direct photolysis kinetics of fluoxetine has been measured using a setup identical to that used in this experiment and yielded a rate constant of  $3.5 (\pm 0.3) \times 10^{-6} \text{ s}^{-1}$  and a quantum yield of  $4.2 (\pm 1.5) \times 10^{-5}$  [19]. Acifluorfen has also been shown to be less photoactive, with a quantum yield of  $1.8 \times 10^{-4}$  [20]. In contrast, the rate constant was somewhat slower than those measured for non-

Table 2. Kinetics and quantum yield of direct photolysis for 2-chloro-5-trifluoromethylphenol

	Rate constant ( $\text{s}^{-1}$ )	Half-life (h)	Quantum yield
pH 4	$7.1 (\pm 0.2) \times 10^{-5}$	$2.7 \pm 0.1$	$3.8 (\pm 0.1) \times 10^{-4}$
pH 5.5 (deionized)	$1.3 (\pm 0.1) \times 10^{-4}$	$1.5 \pm 0.1$	$6.6 (\pm 0.4) \times 10^{-4}$
pH 9	$1.8 (\pm 0.1) \times 10^{-3}$	$0.11 \pm 0.01$	$9.7 (\pm 0.9) \times 10^{-3}$

substituted chlorophenols. Quantum yields for 2-chlorophenol have been measured as 0.0437 [21] and 0.03 [22,23], although neither was measured under actinic conditions.

Photolysis rates of *o*-CTFP were comparable in deionized water (pH 5.5) and at pH 4 but were faster at pH 9. Under pH 9 conditions, the degradation rate was measured as  $1.8 (\pm 0.1) \times 10^{-3} \text{ s}^{-1}$ , with a corresponding quantum yield of  $9.7 (\pm 0.9) \times 10^{-3}$ . This was slower than the previously measured quantum yields for 2-chlorophenol at high pHs of 0.30 (fully deprotonated form) [22] and 0.32 (pH 11) [24]. Two potential explanations could justify the observed increased rate at a higher pH. First, it is well established that increasing the pH above the  $\text{p}K_a$  of a phenol increases the direct photolysis rate constant due to a redshift in the UV-visible absorbance of the compound [18,24,25]. A redshifted UV-visible spectrum for *o*-CTFP was observed in a pH 9 buffer relative to deionized water. It is also possible that a faster rate at pH 9 could be due to a base-catalyzed mechanism. Proposed mechanisms for photonucleophilic displacement of chlorine in 4-chlorophenol involve loss of chlorine as the rate-determining step and subsequent formation of a carbene [23]. This would not be affected by hydroxide concentration, apart from the effect on ionization of the phenol. Similarly, it has been shown that once *p*-trifluoromethylphenol is mostly deprotonated, increasing pH has no further effect on the rate of hydrolysis [26]. These two pieces of evidence suggest that the faster rate of photolysis of *o*-CTFP at high pH is due to redshifting of the absorption spectrum. Although the light source utilized for aqueous photolysis experiments does have minimal bleed into the UV region, this would not be expected to affect the mechanism of degradation. The UV-visible spectrum of *o*-CTFP at pH 5.5 shows a small peak from 258 to 300 nm, which presumably drives the observed reactivity. The main region of absorption of *o*-CTFP occurs far within the UV region, beginning at 236 nm, and is unlikely to be excited under the conditions of these experiments.

As mentioned earlier, there are two possible modes of degradation of *o*-CTFP under aqueous photolysis conditions: Through photonucleophilic displacement of chloride ion and through photolysis and hydrolysis of the trifluoromethyl group to a carboxylic acid (Fig. 3). It is expected that both of these processes occur to yield 3,4-DHBA, but the kinetics and dominance of the preceding processes are unclear. To elucidate the degradation mechanism, photolysates were analyzed using HPLC-UV and liquid chromatography-tandem mass spectrometry. Degradation of *o*-CTFP throughout the experimental period was monitored by HPLC-UV, while liquid chromatography-tandem mass spectrometry was used to observe potential products of photolysis in diluted photolysate. Authentic standards were unavailable for the products, and as a result, methods were based on optimization to *o*-CTFP in the mass spectrometer. Stable fragments were not obtained over the available range of collision energies, so only parent ions could

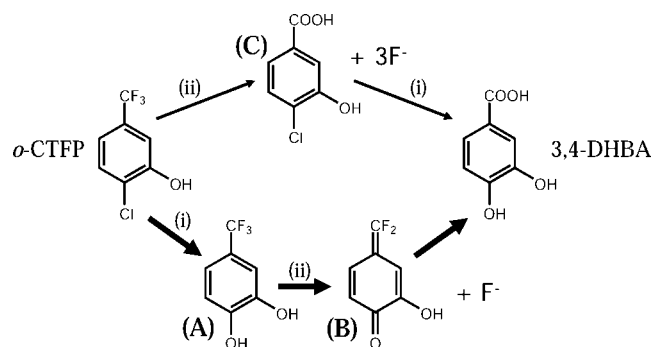


Fig. 3. Proposed mechanisms for the aqueous photolysis of 2-chloro-5-trifluoromethylphenol (*o*-CTFP) in deionized water to 3,4-dihydroxybenzoic acid (3,4-DHBA). Thick arrows indicate the mechanism supported by our experiments.

be observed. As *o*-CTFP was degraded,  $m/z$  177 and smaller amounts of  $m/z$  157 appeared (Fig. 4). Mass-to-charge ratio 177 presumably corresponds to the product of photonucleophilic displacement of chlorine (compound A in Fig. 3). This product was observed to increase over the first 9 h of experiment and then begin decreasing. Studies have shown that *ortho*- and *para*-substituted trifluoromethylphenols can hydrolyze to form semiquinones [18]. The  $m/z$  157 likely corresponds to a semiquinone formed from the loss of hydrogen fluoride (compound B in Fig. 3). The presence of the fluorinated quinone was corroborated by the similarity in the production trend compared to compound A, which would be expected given that compound A is the source of compound B. Ellis and Mabury [18] observed that 33% of the *p*-trifluoromethylphenol degraded immediately, with or without irradiation, to form the semiquinone. They also observed their photolysate to be opaque, inferring the production of a polymer from the semiquinones. In contrast, in the current experiment, all photolysates were clear and compound B was present at a much lower level than that of compound A. However, since authentic standards were not available for the compounds, it was impossible to determine their relative responses and, consequently, concentrations. Over the course of the experiment, there were no observable levels of  $m/z$  171 (compound C in Fig. 3), which would be the mass expected if degradation of the trifluoromethyl group occurred prior to photonucleophilic displacement of the chlorine. As levels of compound A and compound B decreased, a small amount of 153 formed. This mass corresponds to the 3,4-DHBA that would be formed due to both photonucleophilic displacement of chlorine and degradation of the trifluoromethyl group.

As discussed earlier, the direct photolysis rate of *o*-CTFP is faster than that of trifluoromethyl-substituted compounds but slower than that of unsubstituted chlorophenols. Trifluoromethyl groups are electron withdrawing and consequently deactivating to many types of reactions. Assuming photonucleophilic displacement of 2-chlorophenol proceeds via a similar mechanism to 4-chlorophenol, the rate-limiting step is the formation of a carbene intermediate. A carbene formed from *o*-CTFP would be destabilized by the trifluoromethyl group relative to a carbene formed from a chlorophenol and would form at a slower rate. This is suggestive of the displacement of chlorine being the first and rate-determining step. These observations lend support to the first process occurring initially as the rate-determining step in the loss of *o*-CTFP to form

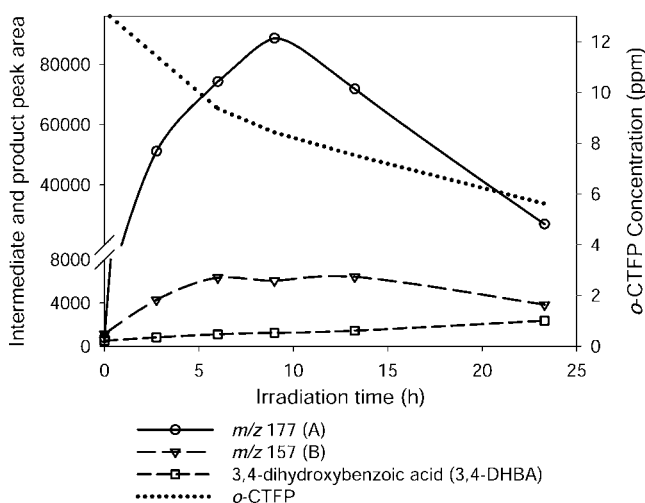


Fig. 4. Liquid chromatography with tandem mass spectrometric detection infusion analysis of photolysis time course fractions shown against high-performance liquid chromatography with ultraviolet analysis of 2-chloro-5-trifluoromethylphenol (*o*-CTFP) degradation. Note that  $m/z$  171 (C) was not detected in any fraction.

compound A, followed more slowly by the second process to yield 3,4-DHBA.

#### Environmental implications

The environmental degradation mechanism for CBTF demonstrated earlier is a rare example of dehalogenation in the environment. However, its relevance increases if it is a dominant environmental fate of CBTF. Given that CBTF is referenced in patents as a paint solvent [2,3], it is expected to be released to the atmosphere. Once in the atmosphere, organic chemicals are subject either to reaction in the gas phase or to partitioning into aerosols and subsequent reaction or deposition. To determine whether CBTF will be found primarily in the gas or aerosol phase, physical properties were estimated and input to a level III fugacity model [16]. Results indicated that more than 99% of CBTF would be present in the gas phase, and as a result, the environmental fate of CBTF is determined by its gas-phase atmospheric fate. The work of Atkinson et al. [5] determined the atmospheric fate of CBTF with respect to photolysis and reaction with hydroxyl radicals and ozone. The measured rate of reaction with hydroxyl radicals was consistent with measurements performed in the present study, corresponding to a lifetime of approximately 50 d. This was significantly faster than their measured rate of reaction with ozone, which corresponds to a lifetime of greater than 8.8 years [5]. Atkinson et al. [5] argue that photolysis is likely to be unimportant compared to reaction with hydroxyl radicals and that the overall atmospheric lifetime of CBTF is close to 50 d. Thus, it seems reasonable to conclude that *o*-CTFP, as a primary product of CBTF reaction with hydroxyl radicals, is a major product of CBTF environmental degradation.

The physical properties of *o*-CTFP were calculated [13,14] (Table 1). In addition, a rate for gas-phase reaction with hydroxyl radicals was calculated using the method of Kwok and Atkinson [15]. These were input to the level III fugacity model [16] with the conditions described earlier. Results indicated that reaction with hydroxyl radicals was the dominant fate of *o*-CTFP, while a small amount of *o*-CTFP would be found in the water phase. Reaction of *o*-CTFP with hydroxyl radicals

yields alcohols, with the added OH at the position *ortho* to the trifluoromethyl group (Fig. 1). The model predicts the dominant fate of both these products would be rain out into aqueous systems, regardless of the rate of atmospheric degradation. Once these compounds were present in an aqueous system, they would likely be subject to the same fate as *o*-CBTF. The additional OH group on the aromatic ring would likely cause greater absorption in the actinic spectrum, suggesting that aqueous photolysis would be an important fate. Photonucleophilic displacement followed by photo-oxidation of the trifluoromethyl group would yield dehalogenated products, trihydroxybenzoic acids.

Restrictions on VOCs provide an incentive to use non-VOC solvents such as CBTF in paints. We show here that CBTF can degrade in the environment into a nontoxic water-soluble product. The addition of chlorine and fluorine to molecules can lead to increased environmental persistence of oxidation products due to their reduced reactivity (for example, in the case of alkanes). Atmospheric oxidation of CBTF, followed by aqueous photolysis, appears to effectively dehalogenate the compound, removing both chlorine and fluorine atoms to yield hydroxybenzoic acids. Although high use of CBTF may have other, unknown effects, the major end products of abiotic degradation of this compound are unlikely to be of environmental significance.

**Acknowledgement**—Thanks to Derek Jackson, Craig Butt, and Joyce Dinglasan-Panlilio. Funding was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC). Thanks to DuPont Summer Internship for funding R.F. Gómez Biagi and NSERC Canada Graduate Scholarship funding for C.J. Young.

#### REFERENCES

- Na K, Kim YP, Moon I, Moon K-C. 2004. Chemical composition of major VOC emission sources in the Seoul atmosphere. *Chemosphere* 55:585–594.
- Henry RG. 1998. Zero volatile organic compound compositions based upon organic solvents which are negligibly reactive with hydroxyl radical and do not contribute appreciably to the formation of ground based ozone. European Patent EP0970141. European Patent Office, Munich, Germany.
- St. Clair DJ. 2005. Solvent based, elastomeric coatings with lower VOC. U.S. Patent 724656. U.S. Patent Office, Washington, DC.
- Code of Federal Regulations. 2008. Protection of the environment. CFR 40, Part 51.1. U.S. Government Printing Office, Washington, DC.
- Atkinson R, Aschmann SM, Winer AM, Pitts JN. 1985. Atmospheric gas phase loss processes for chlorobenzene, benzotrifluoride, and 4-chlorobenzotrifluoride, and generalization of predictive techniques for atmospheric lifetimes of aromatic compounds. *Arch Environ Contam Toxicol* 14:417–425.
- Calvert JG, Atkinson R, Becker KH, Kamens RM, Seinfeld JH, Wallington TJ, Yarwood G. 2002. *Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*. Oxford University Press, Oxford, UK.
- Finlayson-Pitts BJ, Pitts JN. 2000. *Chemistry of the Upper and Lower Atmosphere*. Academic Press, San Diego, CA, USA.
- Berndt T, Böge O. 2006. Formation of phenol and carbonyls from the atmospheric reaction of OH radicals with benzene. *Phys Chem Chemical Physics* 8:1205–1214.
- World Health Organization. 1997. WHO model prescribing information: Drugs used in skin diseases. Geneva, Switzerland.
- Fent K, Weston AA, Caminada D. 2006. Ecotoxicology of human pharmaceuticals. *Aquat Toxicol* 76:122–159.
- Mattia A, Renwick AG, Sipes IG, DiNovi M. 2001. Hydroxy- and alkoxy-substituted benzyl derivatives. In *Safety Evaluation of Certain Food Additives and Contaminants*. WHO Food Additives Series 48. World Health Organization, Geneva, Switzerland.
- Mashino M, Ninomiya Y, Kawasaki M, Wallington TJ, Hurley MD. 2000. Atmospheric chemistry of CF<sub>3</sub>CF = CF<sub>2</sub>: Kinetics and mechanism of its reactions with OH radicals, Cl atoms, and ozone. *J Phys Chem A* 104:7255–7260.
- Hilal SH, Carreira LA, Karickhoff SW. 2003. Prediction of the vapor pressure, boiling point, heat of vaporization and diffusion coefficient of organic compounds. *QSAR* 22:565–574.
- Hilal SH, Carreira LA, Karickhoff SW. 2004. Prediction of the solubility, activity coefficient, gas/liquid and liquid/liquid distribution coefficients of organic compounds. *QSAR* 23:709–720.
- Kwok ESC, Atkinson R. 1995. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure–reactivity relationship: An update. *Atmos Environ* 29:1685–1695.
- Mackay D. 2001. *Multimedia Environmental Models: The Fugacity Approach*, 2nd ed. Lewis, Boca Raton, FL, USA.
- Sorensen M, Kaiser EW, Hurley MD, Wallington TJ, Nielsen OJ. 2003. Kinetics of the reaction of OH radicals with acetylene in 25–8000 Torr of air at 296K. *Int J Chem Kin* 35:191–197.
- Ellis DA, Mabury SA. 2000. The aqueous photolysis of TFM and related trifluoromethylphenols: An alternate source of trifluoroacetic acid in the environment. *Environ Sci Technol* 34:632–637.
- Lam MW, Young CJ, Mabury SA. 2005. Aqueous photochemical reaction kinetics and transformations of fluoxetine. *Environ Sci Technol* 39:513–522.
- Vulliet E, Emmeline C, Scrano L, Bufo SA, Chovelon JM, Meallier P, Grenier-Loustalot MF. 2001. Photochemical degradation of acifluorfen in aqueous solution. *J Agric Food Chem* 49:4795–4800.
- Shi Z, Sigman ME, Ghosh MM, Dabestani R. 1997. Photolysis of 2-chlorophenol dissolved in surfactant solutions. *Environ Sci Technol* 31:3581–3587.
- Boule P, Guyon C, Lemaire J. 1982. Photochemistry and environment. IV. Photochemical behaviour of monochlorophenols in dilute aqueous solution. *Chemosphere* 11:1179–1188.
- Grabner G, Richard C, Kohler G. 1994. Formation and reactivity of 4-oxocyclohexa-2,5-dienylidene in the photolysis of 4-chlorophenol in aqueous solution at ambient temperature. *J Am Chem Soc* 116:11470–11480.
- Eriksson J, Rahm S, Green N, Bergman A, Jakobsson E. 2004. Photochemical transformations of tetrabromobisphenol A and related phenols in water. *Chemosphere* 54:117–126.
- Czaplicka M. 2006. Photo-degradation of chlorophenols in the aqueous solution. *J Haz Mater B* 134:45–59.
- Kozachuk DN, Serguchev YA, Fialkov YA, Yagupol'skii LM. 1973. Hydrolysis of trifluoromethyl group attached to aromatic system. IV. Kinetics of alkali hydrolysis of *p*-hydroxybenzotrifluoride and 4-trifluoromethyl-4'-hydroxyazobenzene. *Organicheskoi Khimii* 9:1918–1921.