Environ. Sci. Technol. 2000, 34, 1229−1233

Acetone-Photosensitized Reduction of Carbon Tetrachloride by 2-Propanol in Aqueous Solution

ERIC A. BETTERTON*

Department of Atmospheric Sciences, University of Arizona, Tucson, Arizona 85721-0081

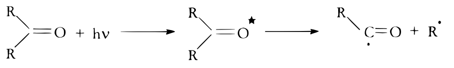
NADIA HOLLAN, ROBERT G. ARNOLD, STEFAN GOGOSHA, KRISTA MCKIM, AND ZHIJIE LIU

Department of Chemical and Environmental Engineering, University of Arizona, Tucson, Arizona 85721

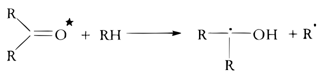
Simple carbonyl chromophores can be used to facilitate the solar-promoted reductive dehalogenation of halo-organics. Here we describe the kinetics and mechanism of the reductive dehalogenation of carbon tetrachloride (CT) to chloroform (CF) in the presence of aqueous acetone and 2-propanol, which is added as a hydrogen donor. The reaction is rapid in sunlight, stoichiometrically converting 3 mM CT to CF in approximately 2 min. Under typical conditions (0.69 M acetone, 5.7 M 2-propanol, 3 mM CT) using a 75 W Xe lamp, the observed zero-order reaction occurs at a rate of 2.7×10^{-6} M s^{-1}. The mechanism appears to become first order in CT near the end of the reaction. The zero-order reaction rate increased with both acetone- and 2-propanol concentration and also with absorbed light intensity. Other combinations of carbonyls, alcohols, and halogenated organics are also effective.

Introduction

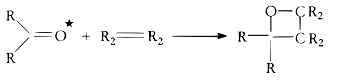
Carbonyl photochemistry, both in the gas and liquid phases, has been studied in remarkable detail over the course of several decades and has been the subject of numerous articles and reviews (e.g., see refs *1−7*, and references therein). As a result, ketones are well-known to undergo three types of photochemical reactions: (i) Type I cleavage of a bond α to the carbonyl chromophore (eq 1), (ii) intermolecular and intramolecular hydrogen abstraction (eq 2); and (iii) addition of the excited-state carbonyl to olefins (eq 3).



(1)



(2)



(3)

Here we focus solely on the H-abstraction reaction and how it may be employed to reductively dehalogenate carbon tetrachloride (CT) in a photocatalytic system.

The electron distribution in the excited states plays a crucial role in determining chemical reactivity (*1−4*). Both S_1 and T_1 states are n, π^* in character, meaning that the unpaired n-orbital electron is localized at the O-atom, while the lone π^*-orbital electron is delocalized over the functional group. The result is that the O-atom is radical-like, behaving much like an alkoxy radical in H-abstraction reactions.

In the presence of molecular oxygen, ketones can be used to sensitize the photooxidation of alcohols (*4, 5*). Oxygen insertion into the alcohol results in the formation of a hydroxyhydroperoxide that readily hydrolyzes in aqueous solution to generate a new carbonyl (as distinct from the original photosensitizer) and hydrogen peroxide. Although the reaction is normally viewed as photooxidation of the alcohol substrate, it can just as easily be viewed as photoreduction of O_2. In principle, this photochemical system should be capable of reducing many target species besides O_2, depending on the redox potential of the target.

Here we apply some of the fundamental knowledge gained on ketone photochemistry over the past four decades to the problem of remediating solvent-contaminated water. Specifically, we describe, apparently for the first time, the kinetics and mechanism of the photosensitized reductive dehalogenation of carbon tetrachloride to chloroform (CF) by 2-propanol (iP) in the presence of acetone (A) in aqueous solution. The rate of reduction is extremely rapid (e.g., 3 mM CT can be destroyed in 2 min by exposure to sunlight), and quantum yields are high. The overall reaction is

$$CCl_4 + (CH_3)_2CHOH \rightarrow CHCl_3 + (CH_3)_2CO + HCl \qquad \Delta G° = -115 \text{ kJ mol}^{-1} \quad (4)$$

Although the liquid-phase photolysis of 1,4-dichlorobutane (DCB) is sensitized by singlet (n,π^*) acetone, the process reportedly occurs by collisional deactivation of excited acetone by DCB and not via H-atom abstraction (*8, 9*).

It is too soon to determine if carbonyl-photosensitized treatment systems will be of any practical use, but ongoing work (to be reported elsewhere) shows that the system is effective for a wide range of halogenated alkanes and alkenes. Combinations of other carbonyls (aromatic and aliphatic aldehydes and ketones) and alcohols are also useful.

Experimental Section

Materials. Deionized water was further purified to >18MΩcm by passage through a Millipore Milli-Q system. Acetone (Fisher, HPLC grade), 2-propanol (Mallinckrodt, AR), and carbon tetrachloride (ACROS, 99.8%) were all used as received. Other ketones and alcohols tested in this study were all >99% purity (Aldrich), except for 2,3-butanedione (biacetyl) which was 97% (Aldrich). GC/FID analysis showed that the 2-propanol contained traces of acetone (0.3mM) which was taken into account in analyzing the results of the subsequent photolysis experiments.

Methods. Polar organics (acetone and 2-propanol) were determined in the headspace by gas chromatography (GC) (Hewlett-Packard 5880; DB-WAXETR 30m × 1.5 mm; He; isothermal 60 °C; FID; HP5880A integrator), while halogenated organics were determined in pentane extracts (2.5 μL: 1.27 mL) by GC/ECD (Hewlett-Packard 7673 auto injector; HP 5790; DB 624 30m × 1.5 mm; He, isothermal 40−100 °C, depending on analyte; HP 3392A integrator). Unidentified peaks were analyzed by GC/MS (Varian 3400; Finnigan MAT700 ion trap detector; Megabore DB-5 60 m). Chloride, the only anion detected, was determined by ion chromatography (IC) (Dionex DX-100; AG4A, AS4A; 0.85 mM Na_2-

---

* Corresponding author phone: (520)621-2050; fax: (520)621-6833; e-mail: better@atmo.arizona.edu.

10.1021/es9902120 CCC: $19.00

CO_3 eluant). Electronic absorption spectra of ketones and solvents were recorded on a Hitachi U-2000 spectrophotometer using 1 cm rectangular quartz cuvettes. Hydrogen peroxide was determined spectrophotometrically after addition of titanium sulfate (*10*).

Solar photolysis experiments were performed by exposing the contents of a sealed 17-mL borosilicate glass serum vial (Wheaton) to sunlight. The vial was placed over a darkened surface and supported at an angle perpendicular to the solar beam. The diameter of the cylindrical vial was 2.5 cm. Acetone has a low extinction coefficient where the n-π^* band overlaps with the solar spectrum (see later) resulting in relatively high transmission (>10%T) for the solar experiments, which were therefore probably not light-limited, in contrast to the experiments conducted with the Xe arc lamp source. The actinic flux (≈295−320 nm) reaching the contents of the vial was estimated to be ≈6×10^{15} photon s^{-1}, after accounting for the transmittance of the glass wall (determined by UV−visible spectrophotometry) but ignoring possible effects of reflection and refraction.

Most experiments were conducted using an Oriel 75W Xe arc lamp assembly consisting of a fused silica collimating lens, a 10-cm IR water filter, a 400-nm cut off filter to remove visible light, an adjustable iris diaphragm, and a fiber input adapter which focused light onto a ≈1 m × 1 mm core optical fiber (3M Corp.). The fiber passed through a septum into a 17-mL glass vial reactor. Some cladding (2−4 mm) was removed from the fiber tip that was positioned 3.0 or 3.7 cm above the bottom of the vial, depending on the liquid volume (13.7 or 17.0 mL). The contents were stirred with a glass-coated magnetic stir bar. Reactions were studied only at room temperature (≈25 °C).

In a typical photolysis experiment, 13.7 mL of an aqueous mixture of 2-propanol (5.7 M) and acetone (0.69 M) was added to the vial, purged with N_2 or He for 10−20 min, and sealed with a Teflon-coated rubber septum. No significant loss of acetone due to volatilization could be detected by GC/FID over this time period. The vial was wrapped in aluminum foil to protect the contents from light prior to injecting the desired amount of CT. The reaction was initiated by exposure to light (solar or Xe arc lamp). Liquid-phase samples were withdrawn at known intervals and analyzed by GC or IC. The high solubility of CT in the alcoholic solution obviated the problem of significant headspace losses.

The photon flux into the solution from the end of the optical fiber, determined by ferrioxalate actinometry, was 5.1×10^{15} photon s^{-1}, assuming an average quantum yield of 1.22 over the photoactive wavelength range of 200−400 nm (*12*). However, we were primarily interested in the flux absorbed by the n-π^* electronic band (≅210−310 nm), which was estimated in the following way. The water in the 10-cm IR filter was replaced with 0.22 M aqueous acetone (optical depth = [acetone] × path length = 2.2 M cm), and the ferrioxalate actinometry was repeated. The flux absorbed by the acetone n-π^* band was found to be 6.6×10^{14} photon s^{-1}, i.e., 13% of the original incident flux. By arranging all subsequent Xe lamp experiments to maintain a reactor optical depth of 2.2 M cm (e.g., 0.69 M acetone × 3.2 cm), the photolytically active flux, I_A, was always known to be 6.6×10^{14} photon s^{-1} (7.5×10^{-8} M s^{-1}).

Results and Discussion

Using the Xe lamp, the disappearance of CT was typically accompanied by stoichiometric production of CF (Figure 1a), Cl^-, and H^+ (data not shown). The reaction was zero-order in CT until about 90% completion after which the reaction order appeared to change, possibly becoming first-order near the end. This is more easily seen during the photoreduction of a more recalcitrant target such as CF (Figure 1b). As expected, the reduction rates for CT (2.7 ± 0.1 μM s^{-1}) and CF (3.0 ± 0.1 μM s^{-1}) were similar under these low-intensity light conditions. It should be noted that this was not the case during solar photolysis when the zero-order rates were dependent on the nature of the target halocarbon (Table 1). The quantum yield for CT loss (Φ_{CT}) was ≈30, indicating the existence of an efficient chain reaction. Here we define $\Phi_{CT} = (-d[CT]/dt)/I_A$, during the zero-order period.

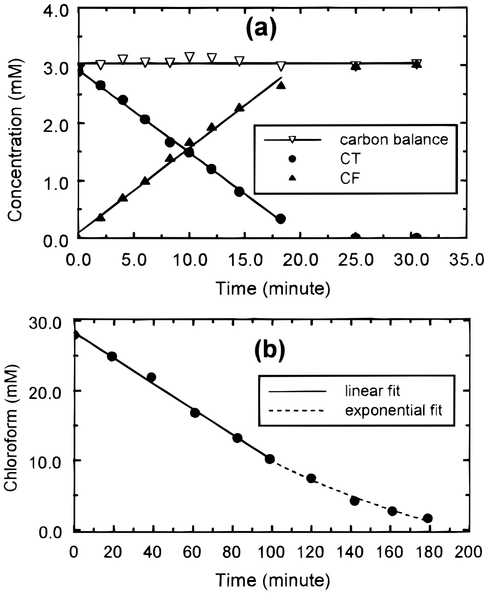


FIGURE 1. (a) Results of a typical experiment showing mainly zero-order acetone-photopromoted reduction of carbon tetrachloride to chloroform (75 W Xe lamp, $I_A = 6.6 \times 10^{14}$ photon s^{-1}; [A] = 0.69 M; [iP] = 5.7 M; optical depth = 2.2 M cm; anoxic). Linear regression parameters for CT loss rate: slope = −(1.43 ± 0.03) × 10^{-1}; intercept = 2.92 ± 0.03; $r^2 = 0.998$; $n = 9$. (b) Results of a similar experiment showing reduction of 10-fold higher initial chloroform concentration that begins as a zero-order decay but apparently becomes first-order after approximately 100 minutes. Linear regression parameters for CF loss rate: slope = −(1.8 ± 0.06) × 10^{-1}; intercept = (2.83 ± 0.03) × 10^{1}; $r^2 = 0.996$; $n = 6$. Exponential fit parameters for CF loss rate: $y = (1.1 \pm 0.2)) \times 10^2 \times \exp[-(2.3 \pm 0.1) \times 10^{-2}]x$; $r^2 = 0.983$; $n = 5$.

The generally accepted mechanism (*4*) for the photosensitized reduction of O_2 forms the basis for our proposed mechanism for the CT-containing system.

$$A + h\nu \rightarrow A^* \quad I_A \tag{R1}$$

$$A^* + iP \rightarrow 2iP^\bullet \quad k_2 = 9.7 \times 10^5\ M^{-1}\ s^{-1}\ (\mathit{15, 20}) \tag{R2}$$

$$iP^\bullet + CT \rightarrow A + CT^\bullet + HCl \quad k_3 = 1.8 \times 10^8\ M^{-1}\ s^{-1}\ (\mathit{18, 19}) \tag{R3}$$

$$CT^\bullet + iP \rightarrow CF + iP^\bullet \quad k_4 \approx 1.4 \times 10^2\ M^{-1}\ s^{-1}\ (\mathit{17}) \tag{R4}$$

$$2iP^\bullet \rightarrow A + iP \quad k_5 \approx 4 \times 10^8\ M^{-1}\ s^{-1}\ (\mathit{14}) \tag{R5}$$

$$\text{NET:} \quad iP + CT \rightarrow A + CF + HCl$$

Excitation occurs in the first step, where ground-state acetone (A) absorbs a photon, undergoes an n-π^* transition to the short-lived excited singlet state (S_1), and rapidly undergoes intersystem crossing (10^9 s^{-1} (*1, 16, 17*)) to triplet state (T_1) A* with a quantum efficiency close to unity. Although the overlap of the acetone n-π^* electronic absorption band (≅210−310 nm) with the solar spectrum at the earth's surface is not great (Figure 2), it is sufficient to promote rapid

TABLE 1. Comparison of Photopromoted Zero-Order Loss Rates for Some Chloroalkanes and -alkenes under Comparable Conditions in Sunlight[a]

target species	relative rate
CCl_4 (CT)	1.0
$CHCl_3$ (CF)	$(1.4 \pm 0.1) \times 10^{-1}$
CCl_3CHCl_2 (PCA)	$(5.1 \pm 0.41) \times 10^{-1}$
$CHCl_2CHCl_2$ (1,1,2,2-TECA)	$(1.48 \pm 0.03) \times 10^{-2}$
CCl_3CHCl_2 (1,1,1,2-TECA)	$(5.1 \pm 0.41) \times 10^{-1}$
$CHCl_2CH_2Cl$ (1,1,2-TCA)	$(3.0 \pm 0.5) \times 10^{-3}$
CCl_3CH_3 (1,1,1-TCA)	$(2.12 \pm 0.04) \times 10^{-1}$
$CHCl_2CH_3$ (1,1-DCA)	$(3.9 \pm 0.4) \times 10^{-1}$
$CHCl{=}CCl_2$ (TCE)	$(4.2 \pm 0.7) \times 10^{-2}$
$CCl_2{=}CCl_2$ (PCE)	$(6 \pm 3) \times 10^{-2}$

[a] 0.69 M acetone; 5.7 M 2-propanol; 8:30 a.m. local time, 8/16/97. Under these conditions the absolute rate for CT reduction was 1.0×10^{-5} M s^{-1}.

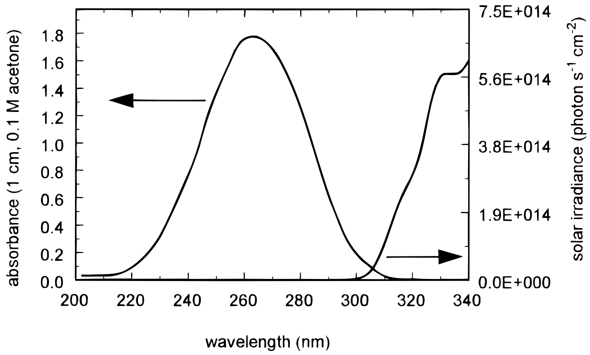


FIGURE 2. Despite the poor overlap of the acetone n-π* band with the calculated solar spectrum at the earth's surface, the rate of carbon tetrachloride reduction is notably rapid in sunlight.

dehalogenation of CT when coupled with the long photochemical chain lengths.

Triplet A* behaves much like an alkoxy radical and so readily abstracts hydrogen from suitable donors (*2*). The rate of H-abstraction from 2-propanol (iP) is much faster than from other potential donors such as water or ground-state acetone (*1, 16*). Consequently, we propose that the chain reaction is initiated only in R2 where two identical 1-hydroxyl-1-methylethyl ketyl (iP•) radicals are generated —one from the alcohol and one from the ketone. If different ketones and/or alcohols are chosen, then two different radicals will be produced.

The iP• radical is a powerful reductant ($(CH_3)_2)CO/(CH_3)_2C^{\bullet}OH = -1.81$ V vs NHE) (*13*) that propagates the chain reaction in R3 where it is proposed that electron donation to CT is accompanied by Cl^- elimination. This is followed by H-atom abstraction by the trichloromethyl radical (CT•) and production of chloroform (CF) in R4.

The only termination step in the proposed mechanism is iP• radical disproportionation (R5). Other possible termination steps include the radical–radical recombination reactions R6, R7, and R8.

$$2CT^{\bullet} \rightarrow C_2Cl_6 \quad k_6 = 3.7 \times 10^8\ M^{-1}\ s^{-1}\ (22) \qquad (R6)$$

$$CT^{\bullet} + iP^{\bullet} \rightarrow CCl_3C(CH_3)_2COH \quad k_7 \qquad (R7)$$

$$2iP^{\bullet} \rightarrow (CH_3)_2C(OH)C(OH)(CH_3)_2 \quad k_8 = k_5/3.4\ (14) \qquad (R8)$$

Since the expected chlorinated products, C_2Cl_6 or $CCl_3C(CH_3)_2OH$, were not detected (<10 nM) by GC/ECD or GC/MS, respectively, and nor was $(CH_3)_2C(OH)C(OH)(CH_3)_2$ detected (<400 nM), we assume that R6, R7, and R8 are unimportant under our experimental conditions.

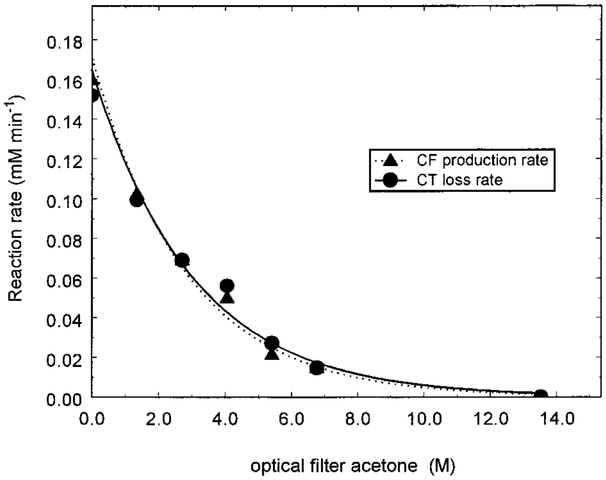


FIGURE 3. The exponential (Beer's law) decrease in carbon tetrachloride loss rate and chloroform production rate as the concentration of acetone in the optical filter was increased demonstrates that the n-π* wavelength range is of prime importance in this system (75 W Xe lamp, $I_A = 6.6 \times 10^{14}$ photon s^{-1}; [A] = 0.69 M; [iP] = 5.7 M; optical depth = 2.2 M cm; anoxic). Exponential fit parameters for CT loss rate: $y = (1.6 \pm 0.2)) \times 10^1 \times \exp[-(3.3 \pm 0.3) \times 10^{-1}]x$; $r^2 = 0.984$; $n = 6$.

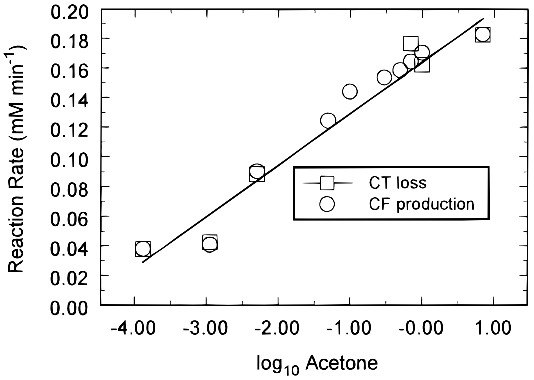


FIGURE 4. Logarithmic increase of reaction rate with acetone concentration when the system is not necessarily light-limited is explained through Beer's law dependence of absorbed light intensity, I_A, in the reactor.

The following experiment showed that it is the n-π* wavelengths that are effective. I_A was varied by filling the IR water filter with a series of aqueous acetone solutions of known concentration to selectively filter out the useful n-π* wavelengths. The resulting plot of reaction rate vs *filter acetone* concentration is exponential at fixed *reactor acetone* concentration (Figure 3) as expected from a consideration of Beer's law.

By contrast, the Beer's law dependence of the absorbed light intensity (I_A) in the reactor results in a logarithmic dependence of the zero-order reaction rate on [A] over a five-order of magnitude concentration range (Figure 4). At sufficiently high [A] the rate should eventually become independent of [A] when every photon is absorbed. However, this could not be demonstrated because it was not possible to prepare a solution that contained more than 6.9 M acetone and yet maintain the required 5.7 M iP (pure acetone has a concentration of 13.6 M). This [A] corresponds to absorption of 99% of the actinic flux.

Using the Xe lamp, the standard reaction is characterized by two phases: an initial period that is zero-order in CT (>90% of the reaction) followed by a second period that is

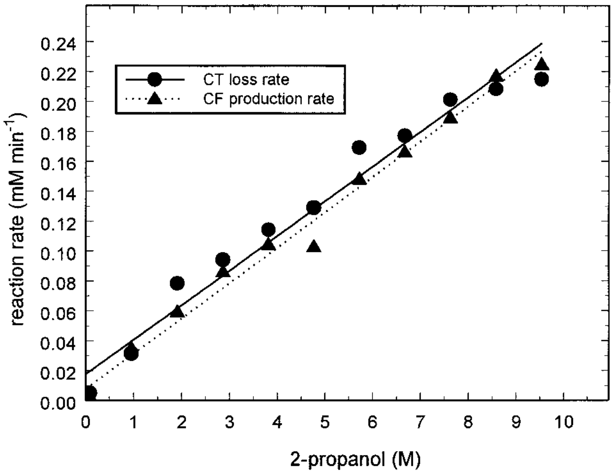


FIGURE 5. Zero-order reaction rates for both carbon tetrachloride loss and chloroform production increase linearly with 2-propanol concentration (75 W Xe lamp, $I_A = 6.6 \times 10^{14}$ photon s^{-1}; [A] = 0.69 M; $[CT]_0 = 3$ mM; optical depth = 2.2 M cm; anoxic). Linear regression parameters for CT loss rate: slope = $(2.3 \pm 0.1) \times 10^{-2}$; intercept = $(1.7 \pm 0.7) \times 10^{-2}$; $r^2 = 0.997$; $n = 12$.

apparently first-order in CT (Figure 1). This suggests the existence of two different rate-limiting steps, depending on [CT]. We consider each phase in turn. During the zero-order period, when [CT] is still high and the propagation steps R3 and R4, in particular, are fast, the overall loss of CT is limited by an earlier step in the mechanism. This is postulated to be R2 because of the observed first-order dependence on [iP] under these conditions (Figure 5). The slope of this plot is therefore equal to k_2A*. Since water and ground-state acetone are both poor H-donors (*1*), initiation reactions equivalent to R2 do not occur in the absence of iP, and the intercept is within 2−3 SDs of zero. No further kinetic information concerning subsequent steps in the proposed reaction mechanism can be extracted from the kinetic data during the zero-order period since R2 is the rate-limiting step.

If we next focus on the second phase (last 10% of the reaction), when [CT] is low due to reduction to CF, the reaction becomes first-order in [CT]. Here it is postulated that a later step in the proposed mechanism, i.e., R4, becomes rate-limiting. This is reasonable since k_4 is 3−5 orders of magnitude smaller than the other second-order rate constants. During this first-order CT period a kinetic analysis becomes more useful. The rate law can be written as

$$\nu = -\mathrm{d[CT]}/\mathrm{d}t = \mathrm{d[CF]}/\mathrm{d}t = k_3[\mathrm{CT}][\mathrm{iP}^\bullet] \tag{7}$$

Under conditions of steady illumination, making pseudo-steady-state assumptions for [A*], [iP$^\bullet$], and [CT$^\bullet$] results in the following rate law.

$$\nu = k_3(2I_A/k_5)^{1/2}[\mathrm{CT}] \tag{8}$$

Thus, under pseudo-steady-state conditions, the reaction becomes first-order in [CT], as observed (Figure 1).

A 120-min time lag was observed before CT reduction began when the reactor was purged with air instead of He. This arises because O_2 is a better iP$^\bullet$ scavenger than CT (*1*−*4*). After the O_2 was consumed by iP oxidation, the degradation of CT proceeded, but at a higher rate than expected based on the results of O_2-free experiments. A rate increase could occur if the O_2 reaction produced more carbonyl chromophore. Hydrogen peroxide should be produced stoichiometrically from the dissolved O_2. The observed H_2O_2 of $\approx 3.5 \times 10^{-6}$ mol was reasonably close to that estimated for the original O_2 contained in the reactor, including the headspace, i.e., 2.6×10^{-6} mol.

The predicted net 1:1 stoichiometric ratio of carbonyl production (R3) compared to CF production (R4) was confirmed by switching to ethanol, which yields acetaldehyde that can more easily be detected against the high background concentration of acetone (instead of 2-propanol which yields acetone). The acetaldehyde concentration was found to increase from zero to 1.2 mM as CF increased to 1.4 mM under our standard conditions.

Other chlorocarbons besides CT can also be dehalogenated via this process. Relative rates of dehalogenation for a series of chlorinated methanes and ethanes, obtained under identical conditions in sunlight, are summarized in Table 1. The substituted methanes were apparently dehalogenated at a rate that was inversely related to the C−Cl bond energy (CT > CF). Among the ethanes, reduction occurred more readily at the most heavily substituted carbon atom. For example, 1,1,1,2-TECA is reduced 30 times faster than 1,1,2,2-TECA, while 1,1,1-TCA reduction was 70 times faster than 1,1,2-TCA. Although PCE and TCE were degraded, no reaction products other than Cl^- could be identified. The expected hydrogenolysis products, TCE and DCE, respectively, were not observed.

Combinations of other carbonyls, including methyl ethyl ketone, 2-pentanone, 4-methyl-2-pentanone, biacetyl, benzophenone, acetophenone, methanol, ethanol, 1-propanol, and 1-butanol, are also effective and are currently under investigation.

Acknowledgments

This publication was made possible by grant number P42 ES004940 from the National Institute of Environmental Health Sciences, NIH with funding provided by EPA. We thank Brian Barbaris and Kristen Taylor for their assistance in the laboratory and Jennifer Slack and Cynthia Malbrough for help in preparing the manuscript.

Literature Cited

(1) Scaiano, J. C. *J. Photochem.* **1973/74**, *2*, 81−118.
(2) Cowan, D. O.; Drisko, R. L. *Elements of Organic Chemistry*; Plenum Press: New York, 1976.
(3) Churio, M. S.; Greal, M. A. *J. Chem. Educ.* **1997**, *74*, 436−438.
(4) Coxon, J. M.; Halton, B. *Organic Photochemistry*, 2nd ed.; Cambridge University Press: London, 1987.
(5) Rubin, M. B. *CRC Handbook of Organic Photochemistry and Photobiology*; Harspool, W. M.; Song, P.-S., Eds.; CRC Press: Boca Raton, 1995; pp 430−436.
(6) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966.
(7) Wagner, P.; Park, B.-S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 2, pp 227−366.
(8) Golub, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 2615−2619.
(9) Golub, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 4925−4926.
(10) Schumb, W. C. *Hydrogen Peroxide*; Reinhold: New York, 1955; pp 548−549.
(11) Seinfeld, J. H. *Atmospheric Chemistry and Physics of Air Pollution*; Wiley-Interscience: New York, 1986.
(12) Rabek, J. F. *Experimental Methods in Photochemistry and Photophysics*; Wiley-Interscience: Chichester, 1982; Part 2, p 944.
(13) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637−1755.
(14) Blank, B.; Henne, A., Laroff, G. P.; Fischer, H. *Pure Appl. Chem.* **1975**, *41*, 475−494.
(15) Porter, G.; Dogra, R. O.; Loutfy, S. E.; Sagumori, S. E.; Yip, R. W. *Faraday Trans.* **1973**, *69*, 1462−1474.
(16) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: 1978; p 91.
(17) Alfassi, Z. B. *Chemical Kinetics of Small Organic Radicals*; CRC Press: Boca Raton, 1988; Vol. 3, pp 41−69.

(18) Stefan, M. L.; Hoy, R. H.; Bolton, J. R. *Environ. Sci. Technol.* **1996**, *30*, 2382−2390.

(19) Steacie, E. W. R. *Atomic and Free Radical Reactions*, 2nd. ed.; Reinhold: New York, 1954; Vol. 1.

(20) Backstrom, H. L. J.; Sandros, K. *J. Chem. Phys.* **1955**, *23*, 2197.

(21) Farhataziz, Ross, A. B. *Selected specific rates of reactions of transients from water in aqueous solution: III. Hydroxyl radical and perhydroxyl radical and their radical ions*; Gov. Doc. # NSRDS-NBS 59; Department of Commerce, National Bureau of Standards: 1977.

(22) Ross, A. B.; Neta, P. *Rate constants for reactions of aliphatic carbon-centered radicals in aqueous solution*. Gov. Doc. # NSRDS-NBS 70; Department of Commerce, National Bureau of Standards: 1982.

Received for review February 22, 1999. Revised manuscript received November 8, 1999. Accepted January 3, 2000.

ES9902120