Photoreduction of 1,1,2-Trichlorotrifluoroethane Initiated by TiO₂ Particles

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Reductive dehalogenation of 1,1,2-trichlorotrifluoroethane (CFC 113) takes place upon illumination of airfree suspensions of TiO_2 particles containing formate ions. Chloride ions and 1,2-dichlorotrifluoroethane (HCFC 123a) are the main reaction products. Reaction rates increase with increasing concentration of CFC even beyond the solubility limit of the Freon in water. Evidence is presented that a chain transformation of the Freon takes place in formate solutions. The results are explained assuming that reduction of the Freon proceeds via a radical chain mechanism, which involves participation of CFC and formate species located on as well as next to the oxide surface.

Introduction

Reactions of organic compounds initiated by illumination of semiconductor particles in solution continue to receive considerable interest.^{1,2} Oxidation processes have been frequently studied, since they may offer a simple method for the elimination of undesirable chemicals.^{3–8} Reduction reactions have received less attention; most of these studies have examined the dynamics of interfacial electron transfer.^{1,2} Photoinitiated transformations usually involve radical reactions. Radicals form when substrates present next to or on the particle surface are attacked by holes, electrons, or other reactive species formed upon exposure of the particles to light.⁹ Except for chain processes,^{5,10–12} the photoreactions proceed with low quantum efficiencies.^{1–4}

Earlier studies have shown that efficient reductive dehalogenations of organic halides take place in deoxygenated alcohols through free radical chain reactions.^{13–15} Chain reductions of fluoro halides in homogeneous solution have been observed occasionally.^{14,16–18} Only a few heterogeneous photoreductive dehalogenations have been investigated. Reductions of CCl₄ and CHBr₃ occurred in suspensions of TiO₂-containing electron donors;^{19,20} halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) was photoreduced in aqueous solutions of alcohols containing platinized TiO₂ particles.²¹ The efficiencies of these transformations are limited because of fast competing processes such as charge carrier recombination reactions. However, higher efficiencies seem achievable in cases where illumination of the semiconductors may initiate chain dehalogenation reactions.

The photocatalyzed reduction of fluoro halides was used to test this concept. Light-initiated reductions are interesting as possible ways to modify chlorofluorocarbons (CFCs). These chemicals interfere with the natural stratospheric cycle of ozone²² and are currently being replaced by their hydrogensubstituted analogs (HCFCs).²³ The photoreduction of 1,1,2trichlorotrifluoroethane (CFC 113) was examined in this study. Air-free aqueous suspensions of TiO₂ particles were utilized to initiate the reactions, and efforts were made to improve the efficiency of the reduction process. Formate ions were selected as electron donors because the Freon was efficiently reduced in acetonitrile solutions containing HCO_2^- ions.¹⁶ In the present report kinetic evidence is presented that the photoreduction of CFC 113 proceeds via a radical chain mechanism involving the electron donor.

Experimental Section

Chemicals were reagent grade (Aldrich, Fisher or PCR) and were not further purified. The water used in all preparations was obtained from a Milli-Q/RO system (Millipore). TiO₂ particles from Degussa (P-25, 30 nm average diameter) were used in this study. Aqueous suspensions of the semiconducting material containing sodium formate were prepared in the photochemical reactors and then degassed with N₂ for at least 20 min. Liquid CFC 113 was deaerated using the freeze– pump–thaw method and subsequently injected into the degassed TiO₂ suspensions. Prior to illumination the mixtures were equilibrated by stirring in the dark for several minutes.

Irradiations were performed at room temperature using borosilicate glass vessels (internal volume 168 mL) as photochemical reactors. The vessels contained 130 mL of the suspensions, which were stirred continuously during illumination. A PTI 1010 S system with a 150 W Xe arc lamp was utilized as a light source. Infrared radiation was filtered with a 10 cm water filter and an IR-absorbing filter. For irradiations with multiple wavelengths, the light was filtered with a Kopp GS-7-60 filter (320 $\leq \lambda \leq$ 385 nm). The effect of light intensity (I_0) on the reaction rates was investigated with an Oriel 340 nm narrow-band filter for $I_0 < 3 \times 10^{-7}$ M (*hv*) s⁻¹ and with the GS-7-60 filter for higher intensities. Neutral density filters were employed to adjust I_0 ; actinometry was performed with Aberchrome 540.²⁴ Efficiencies of the photoreactions are given in terms of photonic efficiency (ζ), which corresponds to the rate of product formation divided by the rate of incident photons.^{4b} The reported values of ζ were not corrected for photon losses due to scattering of light in the TiO₂ suspensions. Optical determinations were carried out using a Hitachi U-2000 spectrophotometer.

Concentrations of Cl⁻ and F⁻ ions were monitored in situ using a Radiometer K601 mercurous sulfate reference electrode and ion-selective electrodes (Orion). Calibration curves were obtained before each kinetic run with suspensions identical to those used during the illuminations. Using this procedure ensured that halide ions adsorbed on the surface of the particles were accounted for. Each experiment was performed at least twice, and in most cases, the results deviated by less than 10%. Measurements of pH were accomplished with a Radiometer GK 273920S electrode containing a saturated K_2SO_4 solution. Radiometer pH meters models PHM 84 and PHM 95 were used in the potentiometric determinations. The data were acquired after stopping the irradiation to avoid artifacts generated by

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Figure 1. Plot of [Cl⁻] vs time in degassed suspensions with (a) 0.5, (b) 0.2, and (c) 0.1 g L⁻¹ TiO₂; $I_0 = 1 \times 10^{-6}$ M (*hv*) s⁻¹, pH = 7.1, 0.077 M HCO₂⁻, and 2 mL of CFC 113.

direct illumination of the electrodes. Immersion of the electrodes into the suspensions was achieved via glass joints located on the top of the reactors. The electrodes were tightly fitted through perforated septa, and degassing of the suspensions proceeded after sealing the joints with these septa.

Identification of volatile products was carried out by analysis of CH_2Cl_2 extracts of the aqueous phase and by headspace analysis; both sampling methods gave the same results. GC– MS measurements were conducted on a Finnigan 9500 GC equipped with either a Porapaq-Q or a 5% Fluorocol column (Supelco), in conjunction with a Finnigan 3300 MS instrument.

Results

Illumination of degassed suspensions of TiO₂ containing formate ions and CFC 113 generated Cl- ions and small amounts of F⁻ ions. Figure 1 shows the variation in [Cl⁻] during irradiation (320 $\leq \lambda \leq$ 385 nm) of suspensions saturated with the CFC that contained 7.7×10^{-2} M HCO₂⁻ ions and several concentrations of semiconductor particles. A linear increase in the concentration of Cl- ions with increasing time was noticed after an initial period of 5-8 min. Formation of chloride ions was slow during this initial period and obeyed no simple rate law; the initial formation rate was less than 10% of the rate observed at longer times. Very low concentrations of F^{-} ions were measured at short times, with a rate smaller by a factor of 10 than the formation rate of Cl⁻ ions. The length of the initial slow process remained unaffected by increases in the degassing time. Similar two-step processes occurred in all experiments with the Freon; the kinetic results presented in this report correspond to data collected at times longer than the initial period of slow reaction. During the second step, formation of Cl⁻ ions always followed zero-order kinetics, and the slopes of the straight lines in the plots of [Cl⁻] vs time were used to obtain zero-order rate constants (k_0) for the light-induced reduction process. While F⁻ ions were also detected at longer reaction times, their concentrations were less than 1% of the [Cl⁻]. In addition, formation of H⁺ ions occurred during the photoreactions, but only small decreases in the pH of the suspensions were measured due to the buffering effect exerted by the formate ions. Since it was not possible to fit the fluoride and H⁺ data to any simple kinetic model, these results were not further analyzed. Irradiation of suspensions containing acetate instead of HCO₂⁻ yielded Cl⁻ ions as well, but the reactions were 30 times slower than those performed with HCO_2^- ions. Halide ion generation via postirradiation reactions was not detected in any of the experiments.

Shown in Figure 2 is the variation of k_0 with molar concentration of Freon at [CFC 113] $\leq 9 \times 10^{-4}$ M. The zero-



Figure 2. Variation of k_0 as a function of Freon concentration in systems at pH = 7.5 with 0.5 g L⁻¹ TiO₂ and 0.5 M HCO₂⁻; $I_0 = 9.4 \times 10^{-7}$ M ($h\nu$) s⁻¹. The inset corresponds to experiments where the volume of Freon added exceeded the solubility limit.



Figure 3. Dependence of the zero-order rate constant for Cl⁻ ion formation on [HCO₂⁻] in suspensions with 0.5 g L⁻¹ TiO₂ and 2 mL of CFC 113; $I_0 = 9.1 \times 10^{-7}$ M ($h\nu$) s⁻¹.

order rate constant increased slowly with increasing [Freon] at concentrations lower than 7×10^{-4} M , followed by a steep rise at the higher concentration. Results from experiments where larger amounts of CFC 113 were injected into the suspensions are presented in the inset. The limiting solubility of this Freon in water is 9×10^{-4} M (22 μ L of Freon in 130 mL solution).²⁵ Formation of two phases occurred when the amounts of CFC added exceeded the solubility limit, and a large number of small Freon droplets were generated upon stirring of the suspensions. In spite of this, k_0 increased rapidly with increasing volume of CFC even beyond the limit of solubility. Increases in the reaction rate leveled off at 2 mL of Freon added, and k₀ was constant thereafter. The TiO₂ particles remained dispersed in the aqueous phase for systems where two phases were formed, and negligible reduction of CFC 113 occurred in the absence of the semiconductor. Consequently, formation of chloride ions at the [Freon] of the inset was due to reactions taking place in the aqueous phase containing the oxide particles.

Figure 3 illustrates the variation of k_0 as a function of formate ion concentration. The zero-order rate constant for the formation of Cl⁻ ions increased with increasing concentration of electron donor until [HCO₂⁻] = 0.5 M and remained constant thereafter. In these experiments the initial pH of the suspensions was determined by each particular concentration of formate ions (the "natural" pH values) and changed from 5.4 to 7.7 as [formate] increased. A few additional experiments were performed at an initial pH = 7.3; significant increases in k_0 occurred only at [HCO₂⁻] < 2 × 10⁻² M. Attempts to fit the data of Figures 2



Figure 4. Changes in k_0 as a function of pH in suspensions containing 0.1 mL CFC 113 and 0.5 g L⁻¹ TiO₂; $I_0 = 7.8 \times 10^{-7}$ M ($h\nu$) s⁻¹. (\bigcirc) [HCO₂⁻] + [HCO₂H] = 0.1 M; (\blacktriangle) [HCO₂⁻] = 0.1 M, pH adjusted with buffers; (\square) 0.025 M HCO₂⁻, pH adjusted with HClO₄ or NaOH.

and 3 with single adsorption site Langmuir-type kinetic models were unsuccessful.^{4a} Also, no linear correlations were obtained from log-log plots of these results.

Figure 4 illustrates the variations of the zero-order rate constant as a function of pH in suspensions with 0.5 g L^{-1} TiO₂ and 0.1 mL of Freon. At pH > 9 high concentrations of formate caused interferences in the potentiometric determinations of halide ions. Experiments were therefore performed at $pH \le 9$ and with $[HCO_2^{-}] \le 0.1$ M, conditions that ensured a proper operation of the ion-selective electrodes. A "natural" pH of 7.3 was typical for suspensions containing 0.1 M formate. In the top curve (O), initial pH values lower than 7.3 were established by mixing appropriate amounts of NaHCO₂ with formic acid so that $[HCO_2^-] + [HCO_2H] = 0.1$ M, whereas pH values above 7.3 were obtained by addition of NaOH to suspensions with 0.1 M NaHCO₂. The rate of Cl⁻ ion formation increased sharply with increasing pH, reaching a maximum at pH = 6. Further increases in pH induced a decrease in k_0 until pH = 8.1, after which k_0 remained constant.

The curve labeled with closed triangles (\blacktriangle) corresponds to solutions in which the pH was fixed by buffers such as phthalate $(5 \times 10^{-2} \text{ M} + \text{acid or base for } 4 \le \text{pH} \le 5), \text{H}_2\text{PO}_4^- (5 \times 10^{-2} \text{ M} + 10^{-2} \text{ M}$ $10^{-2} \text{ M} + \text{base for } 6 \le \text{pH} \le 8.1$), and borax $(1.3 \times 10^{-2} \text{ M})$ + acid for pH = 9). Smaller rate constants were obtained in these systems, and k_0 increased slowly with increasing pH until a maximum was reached at pH = 7.3 (the pH in the absence of buffers). Above this pH k_0 dropped first and then remained constant. With exception of the data measured at pH = 7.3, similar results were obtained when the pH of suspensions containing 2.5×10^{-2} M formate was adjusted with HNO₃ and NaOH or with buffers. In the curve labeled with open squares (\Box) the suspensions contained 2.5 \times 10⁻² M NaHCO₂, and the pH was adjusted with HClO₄ and NaOH. The rate increased with pH reaching a maximum at the "natural" pH (6.8); it decreased until pH = 8.1 and then remained constant. However, below pH = 6.8 the Freon photoreduction was about 2.5 times faster than in systems with buffers. Evidence that ClO_4^- ions affected the reduction process was obtained by irradiating suspensions at pH = 7.3 containing 0.5 g L^{-1} TiO₂, 0.1 M NaHCO₂, and 0.1 mL of CFC 113. A rate constant of $k_0 = 1.8$ imes 10⁻⁷ M s⁻¹ was determined in the presence of 5 imes 10⁻² M NaClO₄, which is 50% of the value in the absence of perchlorate.

The CFC photoreduction was also followed as a function of the mass of TiO_2 dispersed in the formate solutions. It turned out that the rates depended in an unusual way on the amount



Figure 5. Dependence of ζ (Cl⁻) on the amount of dispersed TiO₂ at pH = 7.3 with 0.1 M HCO₂⁻ and 2 mL of CFC 113: curve *a*, $I_0 = 6 \times 10^{-8}$ M (*hv*) s⁻¹; curve *b*, $I_0 = 8.5 \times 10^{-7}$ M (*hv*) s⁻¹.



Figure 6. Light intensity effect on ζ (Cl⁻) in suspensions at pH = 7.3 that contained 0.1 M HCO₂⁻, 0.5 g L⁻¹ TiO₂, and 2 mL of CFC 113. The inset is a log-log plot of these results.

of suspended oxide and also on the light intensity. Therefore, comparisons between results of different experiments were simplified by using photonic efficiencies of Cl⁻ ion generation $(\zeta(Cl^{-}))$ instead of rate constants. The data are presented in Figure 5; curve a corresponds to experiments where the 340 nm narrow-band filter was utilized, with a light intensity of 6 $\times 10^{-8}$ M (hv) s⁻¹. Low efficiencies were determined at 0.01 and 0.1 g L⁻¹ TiO₂ with ζ (Cl⁻) = 0.01 and 0.04, respectively. The efficiencies increased substantially with increasing amounts of dispersed oxide, reached a maximum of $\zeta(Cl^{-}) = 2.9$ in the presence of 0.5 g L^{-1} TiO₂, and dropped somewhat thereafter. Less pronounced variations in $\zeta(Cl^{-})$ with increasing amounts of dispersed oxide took place at the higher light intensity of curve b ($I_0 = 8.5 \times 10^{-7} \text{ M} (h\nu) \text{ s}^{-1}$). The efficiencies varied between $0.1 \leq \zeta(Cl^{-}) \leq 0.3$; they increased slowly with increasing amounts of TiO2 until a maximum was reached at 0.5 g/L. As in the case of curve a, $\zeta(Cl^{-})$ decreased for suspensions containing higher amounts of oxide particles.

Illustrated in Figure 6 is the influence of light intensity on the yield of photoreduction. The highest photonic efficiency of $\zeta(Cl^-) = 2.9$ occurred at $I_0 = 6 \times 10^{-8}$ M ($h\nu$) s⁻¹ and decreased continuously as the light intensity increased to a value of $\zeta(Cl^-) = 0.39$ at $I_0 = 9.1 \times 10^{-7}$ M ($h\nu$) s⁻¹. Shown in the inset is a plot of log $\zeta(Cl^-)$ vs log I_0 , which yielded a straight line with a slope of -0.64. The values of $\zeta(Cl^-)$ remained unchanged when sealed vessels without electrodes were employed in the irradiations. This means that leakage of traces of air into the suspensions was not significant in the experiments performed with electrodes. In another experiment, a degassed suspension consisting of 0.5 g L⁻¹ TiO₂, 0.1 M NaHCO₂, and 2 mL of CFC 113 was first exposed to a high light intensity ($I_0 = 9 \times 10^{-7}$ M ($h\nu$) s⁻¹) for 20 min. This procedure ensured the photoreduction of traces of O₂ that may remain adsorbed on the surface of the particles even after degassing.²⁶ The preirradiated sample was then illuminated using a lower intensity of $I_0 = 6 \times 10^{-8}$ M ($h\nu$) s⁻¹. A substantial improvement was achieved, because $\zeta(Cl^-)$ was 3.7 in the preilluminated sample whereas $\zeta(Cl^-) = 2.9$ in a similar experiment but without preirradiation (Figure 6).

Volatile products of the photoreduction were identified by GC/MS analysis of suspensions containing 0.5 g/L TiO₂, 0.1 M NaHCO₂, and 2 mL of CFC 113, illuminated with $I_0 = 1.2$ \times 10⁻⁶ M (*hv*) s⁻¹. These determinations showed that 1,2dichlorotrifluoroethane (HCFC 123a) was generated in this reaction. Traces of a byproduct, chlorotrifluoroethylene (CFC 1113), were also found, but the dimer (CClF-CF₂Cl)₂ was not detected. As expected, no CO2 was detected during headspace analysis because it is present mainly as bicarbonate in these suspensions (pH = 7.3), which chemisorbs on the oxide surface.³ Attempts made to quantify the yields of HCFC 123a and CFC 1113 failed because their Henry's law constants and their solubilities in the two phases (H2O-saturated CFC 113 and water saturated with Freon) are unknown. The presence of CFC 1113 as one of the products indicated that CFC 113 was, in part, reduced via a two-electron reaction since the olefin is the expected product of this type of reaction.²⁷ Furthermore, the photoreduction of halothane in air-saturated systems containing platinized TiO₂ particles proceeds via two consecutive electron transfer steps to form the olefin 2-chloro-1,1-difluoroethylene, as well as Br⁻ and F⁻ ions.²¹ This process is in competition with a one-electron reduction reaction that yields Br- and trifluoroacetate ions.

Efforts were therefore made to determine the importance of the consecutive two-electron process using 1,1,1-trichlorotrifluoroethane (CFC 113a) instead of CFC 113. Reduction of CFC 113a via a two-electron process is expected to generate Cl⁻ and F⁻ ions in a ratio of [Cl⁻]/[F⁻] = 1/1 according to the steps

$$\operatorname{CCl}_3 - \operatorname{CF}_3 + \operatorname{e}^- \to \operatorname{^{\bullet}CCl}_2 - \operatorname{CF}_3 + \operatorname{Cl}^-$$
(1)

$$^{\bullet}\mathrm{CCl}_2 - \mathrm{CF}_3 + \mathrm{e}^- \to \mathrm{CCl}_2 = \mathrm{CF}_2 + \mathrm{F}^-$$
(2)

Experiments with CFC 113a were carried out by illuminating suspensions containing 2 mL of this Freon at $I_0 = 6 \times 10^{-8}$ M ($h\nu$) s⁻¹. The variations of the chloride and fluoride ion concentrations with time are presented in Figure 7. Both [Cl⁻] and [F⁻] increased linearly with time, with formation photonic efficiencies of ζ (Cl⁻) = 1.5 and ζ (F⁻) = 0.08. Hence, ζ (Cl⁻) $- \zeta$ (F⁻) = 1.42 is the yield of Cl⁻ ions generated by a reaction different from the consecutive two-electron-transfer process represented by reactions 1 and 2. It follows that the two-electron reaction channel contributed with only 5.3% to the overall reduction process of the CFC. This conclusion is supported by GC/MS data which identified 2,2-dichloro-1,1,1-trifluoro-ethane (HCFC 123) as the main reduction product. Only very small amounts of the product of reaction 2, the olefin 1,1-dichloro-2,2-difluoroethylene (CFC 1112a), were found.

A few photoreductions of CFC 113 were performed in the presence of air. The rate of Cl^- ion formation decreased by 50% after injecting 3 mL of air into a degassed TiO₂ suspension prephotolyzed for 40 min. Also, generation of F⁻ ions was 5 times faster after the addition of oxygen as compared with the initial rate of air-free suspensions. On the other hand, in air-



Figure 7. Changes in [Cl⁻] and [F⁻] as a function of illumination time for a suspension at pH = 7.3 that contained 2 mL of CFC 113a, 0.1 M HCO₂⁻, and 0.5 g L⁻¹ TiO₂, with $I_0 = 6 \times 10^{-8}$ M (*hv*) s⁻¹.

saturated (but sealed) suspensions the rates of chloride ion formation were about 170 times lower than those of degassed samples. Furthermore, [F⁻] increased linearly with time, and formation of Cl⁻ and F⁻ ions occurred with the same rate. However, in all air-saturated samples the rate of chloride ion formation increased abruptly at about 90 min. After this time the halide ion generation proceeded with the same rates as the second step in degassed suspensions. This means that O₂ was consumed in the first 90 min during the decay of the Freon, but the CFC was photoreduced as in air-free systems once the O₂ molecules were eliminated. Obviously, the transformation of the Freon in the absence of oxygen is different from the pathway involving O₂, which enhances generation of F⁻ ions and suppresses formation of Cl⁻ ions. While the decay of CFC 113 in the presence of oxygen was not further investigated, we suspect that the faster release of F⁻ in these samples results from a process similar to the photoreduction of halothane with air that yields trifluoroacetate ions.²¹

Discussion

Photoreactions of chlorofluorocarbons have not been observed in TiO₂ suspensions that are free of electron donors because the oxidizing species photogenerated in the semiconductor particles are unable to attack C-Cl or C-F bonds.²⁸ The information gathered in this study shows that CFC 113 is dechlorinated in illuminated anaerobic TiO₂ suspensions containing HCO₂⁻ ions as electron donors through a photoreduction process. A slow step takes place during the first 8 min, where formation of chloride ions is 10 times faster than generation of F⁻ ions. At longer times a faster zero-order step is observed, with rates of Cl⁻ ion generation that are more than 100 times higher than the rates of F^- ion formation. The slow initial step is probably related to the presence of small amounts of O₂ in the suspensions. Observations made with air-containing systems support this assumption, since similar two-step processes occur in these systems. Initially, the Cl⁻ ion formation is slow in the presence of air, but production of fluoride ions can reach rates that are equal to those of Cl^{-} ions. Once the O_2 molecules are consumed, the rates of halide ion formation are the same as during the second step of air-free samples; that is, formation of Cl⁻ ions is fast whereas generation of F⁻ ions is much slower. Evidently, O₂ inhibits the reduction of the Freon; the inhibition period is short in degassed solutions due to the very small amounts of O₂ present in these samples.

Inhibitions induced by oxygen and photonic efficiencies higher than 1 are typical of chain reactions, such as radical polymerizations initiated by semiconductor particles.¹⁰ Also, the reduction of the Freon in acetonitrile solutions with formate ions is believed to follow a chain mechanism,¹⁶ and as in that system, the photoreduction of CFC 113 on the TiO₂ particles vields mainly HCFC 123a. Hence, it seems logical to assume that light induces a chain reduction of the Freon in the oxide suspensions. The results of Figure 2 are consistent with this assumption. Although some Freon is probably adsorbed on the oxide surface, the data obtained at [CFC 113] $\leq 9 \times 10^{-4}$ M suggest that the amounts of adsorbed Freon are very small, because the solubility limit of CFC 113 does not seem to be affected by the presence of the TiO_2 particles in the aqueous solutions. Slow reductions take place below the solubility limit since, as in the case of chain photopolymerizations,¹⁰ efficient chain reactions are not sustained at low [substrate]. The rate of the photoreduction increases significantly above the solubility limit. Phase separation occurs at [CFC 113] > 9 \times 10⁻⁴ M, and we observed formation of small Freon droplets during stirring, some of which probably exist next to the oxide surface. We speculate that a large number of CFC molecules in these droplets are therefore available to participate in the chain process, which induces a drastic increase in k_0 .

The data of Figure 3 show that formate ions act as efficient electron donors in the photoreductions. Higher values of k_0 result upon increasing [HCO₂⁻], suggesting that these ions participate in the chain reduction of the Freon. HCO₂⁻ ions adsorbed on the oxide surface, or located next to it, react with holes or •OH radicals to yield reducing radicals.²⁹ Due to the acidic nature of $^{\circ}CO_2H$ radicals (pK_a = 1.4),³⁰ oxidation of formate ions in our systems (pH \ge 3) mainly yields $^{\circ}CO_2^{-1}$ radicals. These radicals are strong reductants ($E^0 = -1.8$ V for $CO_2/CO_2^{-})^{30}$ and have been used as reducing agents in the TiO₂-initiated photoreduction of metal ions.³¹ While •CO₂radicals are capable of reducing CFC 113 (half-wave potential = -1.21 V),²⁷ the radicals formed by oxidation of acetate ions do not seem to behave as reducing agents,³² which explains the smaller rates of Freon reduction when acetate was the electron donor. Thus, formate not only suppresses charge carrier recombination by reacting with the oxidizing species but also forms radicals that participate in the reduction of CFC 113. Increases in the [HCO₂⁻] yield higher concentrations of electron donor available to scavenge 'OH radicals and holes, as well as faster reductions of the Freon.

Participation of the ${}^{\circ}CO_2^{-}$ radicals in the transformation of CFC 113 is consistent with results from an earlier study showing that these radicals initiate the chain reduction of CF₃-CHBrCl in homogeneous solutions.¹⁷ As in the case of CFC 113, a hydrogen-substituted derivative (CF₃-CH₂Cl) is the main product of the reduction of halothane in formate solutions. We therefore propose the following mechanism for the chain reduction of the Freon on illuminated TiO₂ particles:

$$\mathrm{TiO}_{2} + h\nu \rightarrow \mathrm{h_{vb}}^{+} + \mathrm{e_{cb}}^{-}$$
(3)

$$h_{vb}^{+} + e_{cb}^{-} \rightarrow heat$$
 (4)

$$H_2O + h_{vb}^{+} \rightarrow OH + H^{+}$$
(5)

$$h_{vb}^{+}/OH + HCO_{2}^{-} \rightarrow OO_{2}^{-} + H^{+}/H_{2}O$$
 (6)

$$\mathrm{TiO}_{2} + ^{\bullet}\mathrm{CO}_{2}^{-} \rightarrow \mathrm{e_{cb}}^{-} + \mathrm{CO}_{2}$$
(7)

$$CCl_2F-CF_2Cl + e_{cb}^{-} \rightarrow CClF-CF_2Cl + Cl^{-}$$
 (8)

$$CCl_2F - CF_2Cl + {}^{\bullet}CO_2^{-} \rightarrow {}^{\bullet}CClF - CF_2Cl + Cl^{-} + CO_2 \quad (9)$$

$$^{\bullet}CCIF - CF_2CI + HCO_2^{-} \rightarrow ^{\bullet}CO_2^{-} + HCCIF - CF_2CI$$
(10)

$$CClF - CF_2Cl + e_{cb}^{-} \rightarrow CClF = CF_2 + Cl^{-}$$
(11)

Although formation of chain carriers via reactions 6-9 may vield $^{\circ}CO_{2}^{-}$ and $^{\circ}CCIF-CF_{2}CI$ radicals adsorbed on the oxide surface, some of these species are expected to desorb from the surface and propagate the chain reaction in solution. It is clear that the chain length of this process is short since postirradiation formation of Cl- ions was not detected and because the values of $\zeta(Cl^{-})$ were much smaller than the efficiencies of polymerization.^{10c} This means that the chain process is restricted to the solution region that is within a few nanometers of the TiO₂ surface, and only molecules or radicals that are adsorbed on the surface or close to it can participate in reactions 6-11. Hence, the chain reduction mainly involves CFC molecules located within the interfacial region. Since Freon molecules next to the oxide-solution interface also participate in the chain process, the results of Figures 2 and 3 are not consistent with Langmuir-type kinetic models which assume that only adsorbed substrate is transformed under illumination.33

The reduction is more efficient above the solubility limit of the Freon since CFC molecules from droplets existing next to the TiO₂ particles can diffuse to the interfacial region and participate in the chain process. As in the CdS-initiated photopolymerization of methyl methacrylate in ethylene glycol, where the monomer is phase-separated from the alcoholic phase containing the semiconductor particles,^{10c} the reduction of CFC 113 above the solubility limit is another example of phase transfer photocatalysis. In these processes the reactant is primarily segregated in a liquid phase other than the liquid phase containing the photocatalyst. Transformation of the reactant occurs in two steps: (1) diffusion through the low-solubility medium and (2) chemical reaction next to the semiconductor surface.

The variation of k_0 with pH shown in the top curve of Figure 4 is similar to the dependence of reaction rate on pH for the reduction of CCl₄ in TiO₂ suspensions containing acetate ions as electron donors.^{19a} Increases in k_0 are observed upon increasing the pH from 3 to 6; analogous trends are seen in the other curves. This behavior is related to changes in the amounts of formate ions that are either adsorbed or next to the oxide surface. Positively charged surfaces exist at pH < pzc (pzc =pH at point of zero charge, $6.2 \le pzc \le 6.5$ for TiO₂ P-25).^{3,34} Since the concentration of HCO₂⁻ ions increases as [H⁺] decreases ($pK_a = 3.77$ for HCO₂H), larger amounts of the anions are attracted to the surface at the higher pH values. This leads to a faster step 6 and to more efficient chain reactions. On the other hand, the TiO₂ surface becomes negatively charged upon raising the pH above the pzc. Repulsion between HCO_2^- anions and the oxide particles decreases the concentration of electron donor in the interfacial region, which accounts for the lower rates of reaction at pH > 6 in the top curve. The fact that k_0 remains constant at pH > 8 is an indication that the concentrations of electron donor located either at or next to the TiO₂ surface are high enough to sustain chain processes.

Much lower rates of reaction are observed in curves where the pH was adjusted with buffers (\blacktriangle) or HClO₄ (\Box). Anions such as phthalate, phosphate, borate, and even perchlorate inhibit the photoreduction of CFC 113. Further evidence that these anions affect the chain reaction is that the maximum values of k_0 in these curves occur at the "natural" pH, that is, in the absence of the anions. However, perchlorate, nitrate, and borate ions do not react with ***OH** radicals, but phthalate ions are attacked quickly by ***OH** ($k = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).³⁵ An analogous situation is expected in the case of scavenging of holes, where phthalate ions are probably the only anions that can compete efficiently with HCO₂⁻ for h_{vb}⁺. Thus, the inhibiting effect is not related to the reactivity of the anions toward the light-generated oxidizers. A logical explanation is that addition of buffers or ClO_4^- ions induces a decrease in the concentrations of formate ions and of Freon molecules located within the interfacial region. Lowering the interfacial [HCO_2^-] reduces the rates of reactions 6 and 10. Decreases in the rate of step 6 favor the charge carrier recombination step 4 and inhibit propagation via step 9. On the other hand, reaction 8 and propagation step 9 become slower upon decreasing the CFC concentration in the interfacial region. Consequently, the net effect of adding buffers or anions such as ClO_4^- or NO_3^- is to shorten the length of the chain reaction.

According to the data of Figure 5, $\zeta(Cl^{-})$ increases with increasing amounts of oxide particles at both light intensities, reaching maximum values at 0.5 g L^{-1} TiO₂ followed by a decrease thereafter. A comparison of curves a and b for suspensions containing 0.1 g L^{-1} or less TiO₂ indicates that smaller values of $\zeta(Cl^{-})$ are obtained at the lower light intensity. This is because the probability of a photon striking an oxide particle is low when both the number of suspended particles and the number of photons entering the sample are small. On the other hand, larger amounts of photons are available to excite the oxide particles at the higher I_0 of curve b, resulting in larger photonic efficiencies. Increases in $\zeta(Cl^{-})$ occur above 0.1 g L^{-1} TiO₂, but the reactions are about 9 times more efficient at the lower light intensity. These results are in agreement with the trend shown in Figure 6, where $\zeta(Cl^{-})$ increases with decreasing I_0 . Maximum rates of reaction similar to those of Figure 5 occur at 0.5 g L^{-1} TiO₂ for a variety of photoreactions.³ This effect has been rationalized under the assumption that scattering of light by the particles is very significant above 0.5 g/L TiO₂, which reduces the rate of the processes.

Substantial enhancements in the efficiency of photoinitiated chain polymerizations take place in systems containing high concentrations of semiconductor when the intensity of photons is decreased.¹⁰ The data of Figure 6 indicate that an analogous but less pronounced trend is followed in the photoreduction of CFC 113. Slower charge carrier recombination and termination steps (reactions 4 and 11) occur as I_0 decreases, which results in improvements in the chain length and values of $\zeta(CI^-)$ larger than 1. The rate expression for chloride ion formation is

$$d[Cl^{-}]/dt = R(Cl^{-}) = k(I_0)^{w}[HCO_2^{-}]^{x}[CFC \ 113]^{y}[TiO_2]^{z} (12)$$

where $R(Cl^-)$ is the rate of Cl^- ion formation. Since $\zeta(Cl^-) = R(Cl)/I_0$, and because light intensity was the only changing variable in the experiments of Figure 6, eq 12 can be written as

$$\zeta(\mathrm{Cl}^{-}) = k_{\mathrm{obs}}(I_0)^{w-1} \tag{13}$$

where $k_{obs} = k[\text{HCO}_2^-]^x[\text{CFC 113}]^y[\text{TiO}_2]^z$. Hence, a plot of log $\zeta(\text{Cl}^-)$ vs log(I_0) should yield a straight line with a slope of w - 1. Such a plot is shown in the inset of Figure 6; a value of w = 0.36 is calculated from the slope of the straight line. This reaction order with respect to I_0 is lower than the value of 0.5 predicted by simple mechanisms that assume dimerization of the chain carriers as the main termination channel:^{10b}

$$2R^{\bullet} \rightarrow R - R \tag{14}$$

where $R^{\bullet} = {}^{\bullet}CO_2^{-}$ or ${}^{\bullet}CClF-CF_2Cl$ and R-R are the dimerization products. The fact that GC/MS analysis of illuminated samples failed to detect the dimer (CClF-CF₂Cl)₂, one of the expected products of reaction 14, is another indication that this reaction is not an important termination step. If step 9 proceeds with a rate constant close to that of the reaction between ${}^{\circ}\text{CO}_2^$ and halothane $(k_9 \approx 7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1})$,¹⁷ then combination of two ${}^{\circ}\text{CO}_2^-$ radicals, or of ${}^{\circ}\text{CO}_2^-$ with ${}^{\circ}\text{CClF}-\text{CF}_2\text{Cl}$, via step 14 $(k_{14} \approx 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{17}$ is unable to compete with reaction 9 at our light intensities and [CFC] concentrations.

For chain photopolymerizations, light intensity exponents of less than 0.5 are typical of termination reactions involving chain carriers and primary radicals, the species that initiate the chain transformation.^{10a} We propose an analogous termination reaction for the reduction of CFC 113, which is represented by reaction 11. Supporting this idea are GC/MS results showing that small amounts of the expected product of step 11, CFC 1113, were formed in illuminated suspensions. The data obtained in the photoreduction of CFC 113a also support the proposed mechanism. According to the results of Figure 7 and of GC-MS experiments, this CFC is dehalogenated with a photonic efficiency of $\zeta(Cl^{-}) = 1.5$ to yield the hydrogensubstituted Freon HCFC 123. Interestingly, the contribution of reaction 2 (the termination step in this system) to the overall dehalogenation of CFC 113a can be estimated from $\zeta(F^{-})$. As anticipated for a termination step, the photonic efficiency for fluoride ions is only 0.08, and very small amounts of CFC 1112a are generated. This information indicates that photoreduction of CFC 113a in formate-containing TiO₂ suspensions proceeds via a free radical chain dehalogenation similar to that of CFC 113, and reactions involving electron transfer to Freon radicals act as chain termination steps.

The present study has shown that efficient semiconductorinitiated photoreductions of Freons to form HCFC compounds can be achieved under conditions that favor radical chain reactions. Similar strategies may be useful for the transformation of undesirable materials into valuable chemicals. A remaining problem is the low efficiencies of Freon reduction at high light intensities, which are about 5 times smaller than the values of polymerization.^{10c} Further investigations are needed in order to address this problem, and to explore the possible application of our strategy to other systems.

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