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TIO_2 MEDIATED PHOTOOXIDATION OF TRICHLOROETHYLENE AND TOLUENE DISSOLVED IN FLUOROCARBON SOLVENTS

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ABSTRACT:

Titanium dioxide mediated photodegradation of trichloroethylene (TCE) and toluene dissolved in a fluorocarbon solvent (Galden® HT110) was demonstrated. The photodegradation of TCE yielded dichloroacetic acid as a major intermediate. The TCE reaction kinetics and high photoefficiency suggest autocatalysis and/or a radical chain reaction mechanism. Photooxidation of toluene is a first-order reaction. Membrane-assisted solvent extraction of TCE from water to the fluorocarbon solvent was demonstrated, and the combination of photooxidation and extraction form the basis for a novel two-stage process for the removal and destruction of organic contaminants from water.

INTRODUCTION:

TiO_2-catalyzed photooxidation is one of a number of advanced oxidation processes under consideration for the destruction of organic compounds dissolved or dispersed in aquatic media [1-6]. The process is ordinarily employed by irradiating a suspension of particulate TiO_2 in aqueous solution with photons of energy equal to or greater than the band gap of the semiconductor. Electronic excitation produces an excess of valence band holes (h_s^+) and conduction band electrons (e_s^-) at the surface of TiO_2, and the reaction of h_s^+ with surface H_2O is thought to produce hydroxyl radicals ($OH\cdot$). The reaction of oxygen with e_s^- produces $O_2^{\cdot -}$ which undergoes further reaction to also produce hydroxyl radicals. These OH radicals function as indiscriminate oxidants of organic compounds. The reaction of these nonselective oxidants and direct reaction of organic compounds with the surface holes and electrons are the pathways by which illuminated semiconductors catalyze the destruction of organic pollutants in water.

The utilization of TiO_2 catalyzed photooxidation to destroy bulk organic waste chemicals is limited by the low solubility of most organic compounds in water. Hydroxyl radicals will react with both saturated and unsaturated hydrocarbons, and thus any hydrocarbon solvent or surfactant [7] added to water to increase the solubility of organic compounds may be degraded as well. To broaden the application of TiO_2 photocatalysis and to increase its efficiency, we have investigated the photodegradation of trichloroethylene (TCE) and toluene in fluorocarbon solvents.

Fluorocarbons are well known for their extreme chemical stability under severe oxidizing conditions due to the stability of fluorine-carbon bonds [8,9]. Our interest in these solvents is further enhanced by their ability to dissolve oxygen and their immiscibility with water. The latter property makes possible extractive separations of water-borne contaminants into the fluorocarbon solvents followed by destruction of the contaminants directly in the solvents. The ability to concentrate the TCE before illumination appeared to us to be a promising avenue toward increasing overall photoefficiency. To support this idea, we report results of a membrane-assisted extraction of TCE from an aqueous solution to a fluorocarbon solvent. These experiments are important since they are the basis for a novel waste-treatment process in which the extraction of organic compounds from aqueous solution is combined with photocatalyzed destruction. This is the first report of TiO_2-catalyzed photooxidation employing an inert fluorocarbon solvent, and the first use of a two-phase system for the photodestruction of organic-soluble contaminants.

EXPERIMENTAL SECTION:

Fluorocarbon solvents (perfluorooctane and Galden® HT110) and perfluorinated surfactants were obtained from PCR, Inc. (Gainesville, Florida). The semiconductor powder (TiO_2) was a gift of Degussa (Grade P25). All other chemicals used in this study were of reagent grade or higher purity and were used without further purification. Solutions for photolysis were prepared by adding 10 mg TiO_2 and 0.1 mL trichloroethylene (TCE) or toluene to a mixture of 9 mL of fluorocarbon and 1 mL of water. Photochemical reactions were carried out in a 25 mL Pyrex Erlenmeyer flask covered with a thin Pyrex watchglass, and the mixture was rapidly stirred using a magnetic stirrer and spinbar arrangement. UV illumination was provided by two 15 W black light blue tubes (F15T8/BLB, General Electric). The lamps emit between 300 and 400 nm and have a maximum at 366 nm. Reaction vessels were placed directly under the tubes at a distance of 7 cm, and the 10 mL suspension received 4.51×10^{16} photons/sec as measured by ferrioxalate actinometry. The source of oxygen in these photooxidation reactions was air.

$$C_2HCl_3 + 1.5\ O_2 + H_2O \text{----------->}\ 2\ CO_2 + 3HCl \qquad (1)$$
$$C_7H_8 + 9\ O_2\ \text{------------------->}\ 7\ CO_2 + 4\ H_2O \qquad (2)$$

The complete photooxidation of 10 mL of 0.1 M TCE (1.1 mmol) requires 176 mL of air at STP (35 mL of pure oxygen). Therefore, reactions were carried out with the flask loosely covered, and control experiments indicated that the loss of TCE by evaporation was < 30 % and that of toluene was not significant under ambient temperature.

Analyses for TCE, toluene, and reaction intermediates were performed by gas chromatography using a Hewlett-Packard gas chromatograph (Model 5890) with dual capillary columns (J&W DB-1 columns, 30 m x 0.25 mm, 0.25 mm) and flame ionization detectors. Samples were analyzed following dissolution into hexane solvent containing 1 mM 2-bromobutane as an internal standard. The column temperature was maintained at 50 ^{o}C for TCE and programmed as follows for toluene: 50 ^{o}C for 1 min, increased to 100 ^{o}C at 10 ^{o}C/min and maintained at 100 ^{o}C for 1 min. Chloride, fluoride, and chlorinated acetic acids were analyzed in aqueous solution with a Dionex ion chromatograph with IonPac AS5A anion column and post-column self-regenerating suppresser. Samples were eluted with 15 mM NaOH.

RESULTS AND DISCUSSION:

The TiO_2 catalyzed photooxidation of TCE and toluene was studied in a dispersion in which fluorocarbon solvents constituted the major component. The solvents employed were perfluorooctane or Galden®. The latter is a perfluorinated polyether having the composition $CF_3[\{OCF(CF_3)CF_2\}_x(OCF_2CF_2)_y]OCF_3$ and an average molecular weight 580. The irradiated solution also contained 10% (v/v) water, which is not miscible with the fluorocarbon solvents. The TiO_2 particles appeared to be present either in the aqueous phase or at the liquid-liquid interface as evidenced by the milky white appearance of the aqueous phase and a clear fluorocarbon phase. During irradiation, the mixture was rapidly stirred to disperse the two liquid phases.

A number of solubility considerations governed our approach and the interpretation of the data. The solubility of TCE in the fluorocarbon solvents is much higher than the solubility of the TCE in water. The saturation solubility of TCE in water is 8 mM [10], whereas the solubility of TCE was determined to be 730 mM in Galden® and 960 mM in perfluorooctane (unpublished results). From GC measurements, the partition coefficients of TCE between fluorocarbon solvents and water, which are slightly concentration dependent, were between 40 and 50 for Galden® and between 50 and 60 for perfluorooctane, respectively. The solubility of oxygen in

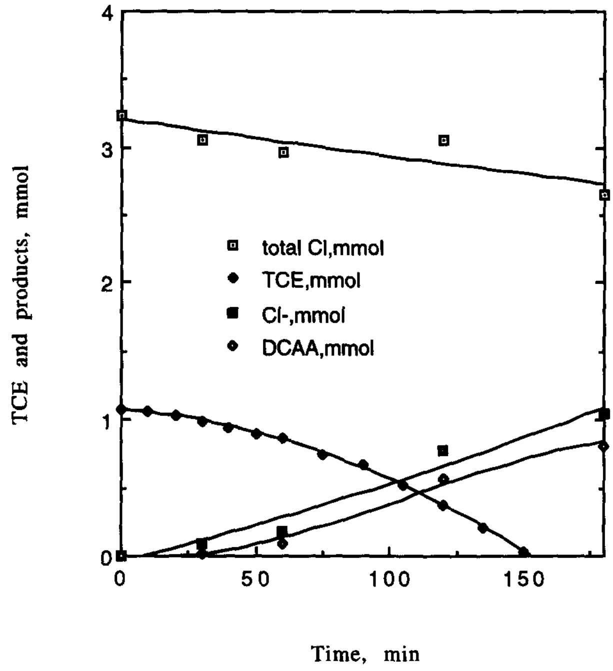

Figure 1. Photodegradation of 0.1 mL TCE in 9 mL Galden® and 1 mL water with 10 mg TiO_2 showing the amounts of TCE, the intermediates and the final products as a function of photolysis time.

fluorocarbon solvents [11] is well known to be many times higher than in water. A highconcentration of oxygen and TCE favors the capture of photochemically generated e_S^--h_S^+ pairs and is expected to contribute to a higher observed photoefficiency (see below). Water is virtually insoluble in the fluorocarbon solvents, and as shown by equation 1, it is an essential reactant in the mineralization of TCE. Furthermore, the oxidation of surface water to OH radicals is one of the principal means of initiating photooxidation [2]. Therefore, we investigated the use of perfluorinated surfactants to increase the solubility of water in the fluorocarbon solvents. Several perfluorinated surfactants were investigated, and the potassium or ammonium salts of perfluorooctanoic acid (at 1% (w/v)) improved either the suspension of water in the fluorocarbon or of the fluorocarbon in water or both. However, these surfactants retarded the photodegradation of TCE under conditions in which the other variables were held constant. Therefore, all further experiments reported here were conducted in the absence of surfactants.

The amounts of TCE and the principal halogen-containing products as a function of irradiation time are shown in Figure 1 for the photooxidation of TCE in Galden®. The quantity of TCE was calculated from its concentration in the fluorocarbon phase and that of dichloroacetic acid (DCAA) from its concentration in the aqueous phase. Control tests showed that the respective concentrations of TCE in the aqueous phase and DCAA in fluorocarbon phase were negligible. The total chlorine content of the system computed from the sum of the quantities of TCE, DCAA, and chloride ion indicates that the major products were accounted for in this product distribution. The near 20% of chlorine content decrease can be attributed to TCE evaporation loss. Dichloroacetic acid was a major intermediate, accounting for more than two thirds of the starting TCE and in fact was observed to be more stable than TCE during photooxidation in Galden®. The high yield of DCAA can be attributed to its distribution into aqueous layer, while major oxidation reactions take place in fluorocarbon layer (see below). The high DCAA yield was in contrast to the photodegradation of TCE in aqueous suspension of TiO_2, where the yield of DCAA never exceeded 1.5% [12].

The fluorocarbon solvent is very stable during the photooxidation of TCE. Fluoride ion is an expected degradation product of aliphatic fluorocarbons, and ion chromatographic analysis of the aqueous solution following photolysis of 90% Galden®, 10% water and 0.1% TiO_2 indicated fluoride ion was not present. The detection limit for fluoride is on the order of 10^{-7} M or lower.

Table I. Average photoefficiencies for photodegradation of TCE and toluene (moles reacted per mole of photons x 100)

time span, min	TCE, %	toluene, %
0-60	41	19
60-120	63	13
120-180	148	13
180-240	41	10

reaction conditions: 10 % water + 89 % Galden® + 1 % TCE or toluene, 1 % TiO_2 (w/v), under ambient temperature.

The apparent photoefficiency (ratio of the number of molecules reacted to the number of photons impinging on the dispersion, uncorrected for light scattering) for degradation of high initial concentration of TCE in the fluorocarbon solvents reaches a value that can not be attained for TCE photodegradation in an aqueous suspension of TiO_2. At lower TCE concentrations, the photoefficiency in aqueous suspension is higher than in the fluorocarbon. The TCE photodegradation efficiency, at an initial TCE concentration of 1 mM, is 15% in aqueous suspension and 1.3% in fluorocarbon. The lower photoefficiency in fluorocarbon system may be attributable to the separation of the TiO_2 phase into the aqueous solution and the TCE into the fluorocarbon solution. Thus, each hydroxyl radical generated on the TiO_2 surface is less likely to react with TCE in the fluorocarbon than with TCE in the aqueous phase. However, there is a limitation that the TCE concentration in aqueous solution can not exceed its solubility (8 mM) while the TCE solubility in fluorocarbons is a factor of 100 times higher. Both literature results [13] and our own experiments show that the apparent photoefficiency as well as the initial reaction rate increase as the initial concentration of TCE increases. For example, the initial apparent photoefficiency increases to 12% at an initial TCE concentration of 11 mM in Galden® and to 40% at an initial TCE concentration of 110 mM. At 110 mM, very high apparent photoefficiencies were observed, especially during the third quarter of the photooxidation reaction where the value approached 150% (see Table I).

The high photoefficiencies observed in fluorocarbon solvents have more in common with the efficiencies reported in the gas-phase photooxidation of TCE by Nimlos et al. [14] than with the results in aqueous solution. The gas-phase photooxidation was postulated to occur by a radical chain reaction involving Cl radicals. The chain-carrying steps suggested by these authors involve addition of a chlorine atom to TCE to produce an alkyl radical that reacts with oxygen. In a series of steps, dichloroacetyl chloride and a chlorine radical are formed, and the latter continues the chain reaction. A similar reaction pathway may be occurring in fluorocarbon solvents, and a search for radicals as well as detailed kinetic and photoefficiency measurements are in progress. The main reactions can be expressed as

$$CHClCCl_2 + OH\cdot \text{------------>} \cdot OHCHClCCl_2 \qquad (3)$$

$$\cdot OHCHClCCl_2 \text{--------------->} Cl\cdot + \text{products} \qquad (4)$$

$$CHClCCl_2 + Cl\cdot \text{------------->} CHCl_2CCl_2\cdot \qquad (5)$$

$$CHCl_2CCl_2\cdot + O_2 \text{----------->} CHCl_2CCl_2O_2\cdot \qquad (6)$$

$$2CHCl_2CCl_2O_2\cdot \text{------------>} 2CHCl_2COCl + 2Cl\cdot + O_2 \qquad (7)$$

The photoefficiency experiments emphasize two points: (a) a higher photoefficiency for TCE photooxidation can be attained in fluorocarbon than in aqueous suspension; (b) radical-chain mechanism is possibly involved in the TCE photooxidation in fluorocarbon media. Photooxidation of TCE in a single fluorocarbon phase (no deliberately added H_2O) with suspended TiO_2 shows an increase in apparent photoefficiency by more than a factor of 3 and supports the conclusion that major photodegradation reaction takes place in the fluorocarbon phase.

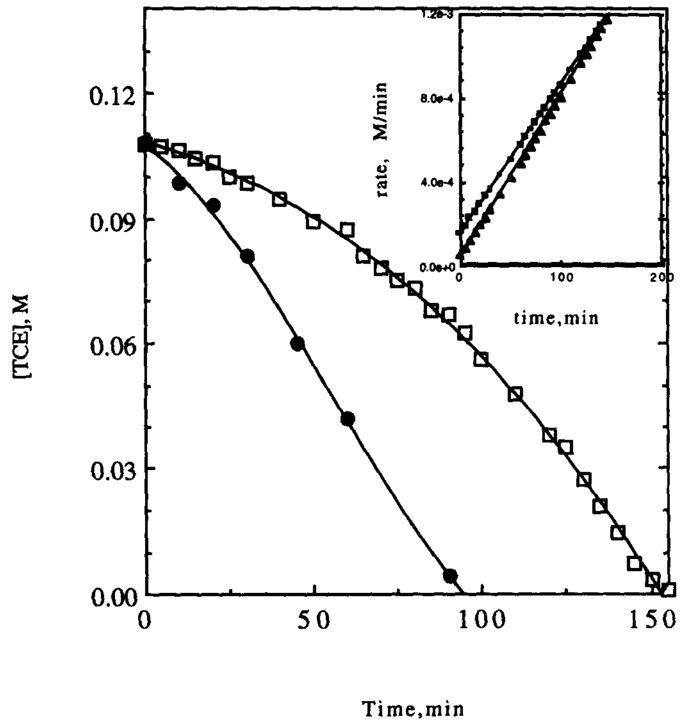

Figure 2. The kinetics of TCE photodegradation in 9 mL pre-illuminated Galden®, 1 mL water (open squares) or 1 mL 1 M HCl aqueous solution (solid circles) and 10 mg TiO_2. The inset plots the reaction rates in Galden®/water (M/min) as a function of time uncorrected (open squares) or after correction for evaporation losses (open triangles). Reaction rates were obtained from the slopes of the concentration-time plot.

The kinetics of the photodegradation of TCE in the fluorocarbon system exhibit some interesting differences in comparison with the kinetics reported in aqueous solution [12,13]. Figure 2 is a plot of the concentration of TCE in fluorocarbon vs. time, showing an increase in reaction rate with reaction time throughout most of the reaction (inset). This behavior contrasts markedly with the kinetics of TCE photooxidation in aqueous systems reported by Glaze et al. [12], in which a steady decrease in reaction rate with reaction time was observed. Pre-illumination of the solvent in the presence of TiO_2 only slightly increased the initial rate, indicating that the slow initial reaction can not be attributed to impurities in the system. Rather, the concentration-time dependence is suggestive of self-catalysis, a radical chain reaction, or a contribution from both pathways. Preliminary results indeed indicate the self-catalysis characteristics of the reaction. For example, high concentrations of HCl, which is a reaction product, in the aqueous phase enhance the rate of TCE photodegradation (Fig. 2). The rate enhancement can not be attributed to either pH or chloride alone, since experiments with either NaCl or HNO_3 showed that both promoted the TCE photodegradation, but not as much as HCl. In an unbuffered solution, the system pH drops sharply at the initial stage of the reaction and decreases slowly thereafter. The pH change does not parallel that of reaction rate. Self-catalysis alone can not explain the reaction kinetics, although its presence is qualitatively evident. On the other hand, the very high apparent photoefficiency may be indicative of a radical chain reaction. It seems likely that both self-catalysis and radical chain reaction mechanisms operate in this particular photooxidation of TCE. Detailed kinetic analysis is complicated and is under investigation.

The photooxidation of toluene was briefly investigated to see if the high photoefficiency observed in fluorocarbons extends to reactants other than TCE. The solubilities of toluene in Galden® and perfluorooctane were found to be 280 mM and 330 mM, respectively. Compared to the photooxidation of TCE, the reaction of toluene in Galden® was a much simpler process. Figure 3 shows that the photooxidation of 1% toluene obeys a simple first-order rate law. The apparent photoefficiency (see Table I) reflects the high concentration of reactant and the higher concentration of oxygen available in the fluorocarbon. A number of minor reaction intermediates were produced during the reaction, but they have not been identified or quantified. The degradation of toluene suggests that other organic molecules may also be photocatalytically oxidized in a fluorocarbon medium. The absence of autocatalytic behavior for toluene, as observed for TCE, indicates that the consumption of reactive impurities in the fluorocarbon solvent, if any, had no effect on the observed reaction kinetics.

TCE exhibits a high partition coefficient between fluorocarbon solvents and water, and we have taken advantage of this property to demonstrate that TCE can be transferred from an

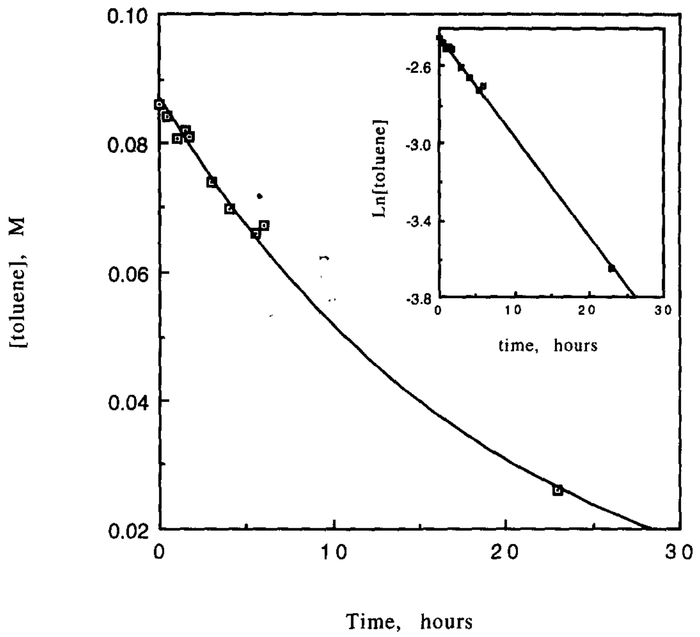

Figure 3. The kinetics of the photodegradation of 1% toluene (v/v) in Galden® with the other conditions the same as shown in Figure 1 showing the concentration of toluene vs time. The linearity of the plot in the inset indicates that the decay is a first-order process.

aqueous solution to a fluorocarbon by membrane-assisted solvent extraction. By using a 5 cm^2, 25 mm thick sheet of hydrophobic, microporous polypropylene (Hoechst Celanese Celgard 2500) as the membrane, we have shown that 3-4 mM TCE in water may be almost quantitatively extracted into an equal volume of fluorocarbon solvent Galden® (aqueous TCE concentration reached below 0.1 mM in 60 min in a single stage). Decreasing the fluorocarbon/water volume ratio to 1/50, TCE from the same aqueous solution was not only extracted but also concentrated into the fluorocarbon Galden® to a concentration of more than 60 mM. It should be noted that the single-stage flat sheet membrane extraction experiments serve to demonstrate the principle and utilization of a hollow fiber membrane module with countercurrent contacting will greatly increase the extraction efficiency [15]. Thus, in principle, the combination of membrane-assisted solvent extraction with TiO_2 catalyzed photooxidation in a fluorocarbon solvent represents the basis for a novel two-stage process for removing and destroying organic contaminants from water. Work is in progress to test a continuously operating reactor based on separation of TCE from water and photodegradation in a fluorocarbon medium.

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