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Heterogeneous Photoassisted Catalysis: Conversions of Perchloroethylene, Dichloroethane, Chloroacetic Acids, and Chlorobenzenes

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The chlorinated hydrocarbons perchloroethylene, dichloroethane, monochloroacetic and dichloroacetic acids, in dilute aqueous solutions, are completely mineralized to HCl and CO_2 by photoassisted heterogeneous catalysis with an aqueous slurry of near-uv illuminated TiO_2. Trichloroacetic acid was dehalogenated at a negligible rate. Rate parameters from the present and our earlier studies indicate that the relative chlorocarbon mineralization rates at the 1 to 50-ppb levels of relevance to water supply contamination appear to be dichloroacetaldehyde $\gg$ trichloroethylene > perchloroethylene > dichloroacetic acid ~ dichloromethane > trichloromethane ~ (1,2)-dichloroethane ~ monochloroacetic acid > tetrachloromethane > trichloroacetic acid. The heterogeneously photocatalyzed conversion of monochlorobenzene in dilute (70–400 ppm) aqueous solutions yields (1) *ortho*- and *para*-chlorophenol, which may subsequently be dechlorinated to yield aromatic oxygenates (*ortho*- and *para*-benzoquinone, and the corresponding hydroquinones), or (2) condensation products such as 4,4′-dichloro-1,1′-biphenyl. No evidence of ring opening was noted. Similar but more complex behavior was noted with a dichlorobenzene.

INTRODUCTION

The discovery of chlorinated hydrocarbons in both natural and drinking waters has focused attention on a potentially serious environmental problem in Europe (*1*) and North America (*2, 3*). The use of chlorine in conventional drinking water disinfection contributes to the formation of chlorinated organics. The toxicity of chlorinated hydrocarbons decreases with decreasing chlorine content (*4*), thus even partial degradation with dehalogenation may be considered partial detoxification. A novel, photocatalytic process for total degradation (mineralization) of dilute (10–100 ppm) aqueous solutions of chloromethanes (*5, 6*) and trichloroethylene (*7, 8*) has been developed in our laboratory. The chlorinated molecular contaminants were converted to environmentally acceptable substances, namely carbon dioxide and hydrogen chloride. Here, we examine the photoassisted catalytic conversions of other molecules which have been detected in water supplies or simulated water chlorination procedures: chlorobenzene and *o*-dichlorobenzene (*o*-DCB) (*8*), perchloroethylene (*9, 11*), chloroacetic acids (*10*), and dichloroethane (*9, 11*).

EXPERIMENTAL

The kinetic studies were made in a batch reactor described previously (*5–7, 12*). A slurry of 0.1 wt% of titanium dioxide in water was recirculated through a quartz annular reactor illuminated by seven commercial black-light fluorescent bulbs (GE BLB – 15 W) arranged parallel to the reactor axis. The catalyst was Fisher certified grade TiO_2, Lot No. 745547, with a surface area of 7 m^2/g, as determined by BET nitrogen adsorption. The predominant (~95%)

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crystalline modification was anatase, as determined by X-ray diffraction.

The black lights emitted predominantly 320–400 nm light, with virtually no emission below 300 or above 500 nm.[1] These lamps present illumination wavelengths sufficient to photoexcite TiO_2 (need $\lambda \leq 360$ nm) while eliminating homogeneous reaction due to $\lambda < 300$ nm.

The total fluid volume was ~635 cm^3; the illuminated volume 300 cm^3. The absorption efficiency of the reactor, defined as (photons absorbed/photons emitted by lamp based on manufacturer's specification) ×100, was approximately 22% (*12*). The liquid/solid slurry was maintained at 28 ± 1°C by circulation through external cooling coils.

The concentration of product chloride ion was determined continuously as before (*5–7, 12*) with a specific chloride ion selective electrode (HNU Systems) in the reactor recycle loop. Product CO_2 formation was confirmed by postreaction helium purging of the reacted fluid, and subsequent passage of the gaseous purge stream through a barium hydroxide solution; barium carbonate precipitate demonstrated CO_2 production (*5–7, 12*).

Mineralization of chloromethanes and trichloroethylene are established as requiring *molecular* oxygen to maintain continuing photocatalytic reaction, i.e., the ultimate oxygen source is not water (*6, 14*). In the present experiments, a small side arm in the recycle loop electrode monitoring cell was left open to the atmosphere. This open recirculation configuration had resulted earlier in 10–15% loss from the slurry solution of the more volatile chloromethanes (*6*); with 10–100 ppm aqueous solutions of perchloroethylene and the chloroacetic acids no such loss occurred, as demonstrated ultimately by ~100% recovery of all chlorine (in reactant) as HCl (see Results).

The chlorinated hydrocarbons were used as received, without further purification: mono- and dichloroacetic acids (Aldrich Chemicals, >99%), trichloroacetic acid (Mallinkrodt Chemicals), mono- and dichlorobenzene (Gallard Schlesinger, ANALAR grade), (1,2-dichloroethane (>99.7%) (Mallinkrodt Chemical, AR grade), and perchloroethylene (>99% Aldrich Chemical).

Analysis of chloromethanes, chloroethane, and chloroethylene, and chloroacetic acids proceeded as described earlier (*6, 7*). For the chlorobenzene experiments, the liquid reaction samples were withdrawn periodically using a 20-ml syringe. Each 20 ml aqueous sample was mixed with 40 ml of anhydrous ethyl ether (Mallinkrodt) and equilibrated. Approximately 8 g of sodium chloride was used to saturate the aqueous phase to enhance the extraction process. Each 20 ml reaction sample was extracted three times. The ether solution was concentrated 10 times by evaporation of solvent, then was analyzed by chromatography with flame ionization detection. To determine the concentrations of the reactant and products in the original water solution withdrawn from the reactor, the distribution of the reactant and products in the final ether and water layer was determined (*15*), and used to calculate aqueous phase concentrations of reacted solutions. Organic reactants and products were confirmed or identified by GC–MS (*15*). The concentrations of reactant and products were determined with a Perkin–Elmer Sigma 1 gas chromatograph on 19% OV 101, 80/100 Supelcoport column.

RESULTS AND DISCUSSION

A. Perchloroethylene, Dichloroethane, and Chloroacetic Acids

Complete conversion of chlorinated hydrocarbons was demonstrated by chlorine balances, e.g., recovery of 98% chlorine as (H)Cl for 67 ppm initial $CHCl_2COOH$ in 3 h, and 102% chlorine as (H)Cl for 46.4 ppm

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[1] General Electric Co., Schenectady, N.Y. The spectral emission from a 15-w lamp is given by the manufacturer as (watts): <300 nm (—), 300–310 nm (0.0038), 310–320 nm (0.0366), 320–340 nm (0.4425), 340–360 nm (0.4425), 340–360 nm (1.046), 360–380 nm (0.6750), 380–400 nm (0.1575), 400–500 nm (0.593).

initial Cl_2CCCl_2 after 1 h 10 min of illumination of circulating slurry (*13*).

The *initial* rates of chloride appearance plotted vs *initial* reactant concentration exhibited a curvature characteristic of a saturable surface (Fig. 1) for mono- and dichloroacetic acid, perchloroethylene, and dichloroethane (*16*). No chlorine release was observed for trichloroacetic acid.

Our previous reports (*5–7*) for other chlorocarbons (CH_2Cl_2, $CHCl_3$, CCl_4, $HClCCCl_2$) found that the initial conversion rates were reasonably described by a simple Langmuir form

$$\text{rate } (t = 0) = \frac{kK[\text{chlorocarbon}]}{1 + K[\text{chlorocarbon}]} \quad (1)$$

as demonstrated most conveniently by the linearity of plots of reciprocal rate vs reciprocal initial concentration

$$\frac{1}{\text{rate}_0} = \frac{1}{kK[\text{chlorocarbon}]_0} + \frac{1}{k} \quad (2)$$

The slope for Eq. (2) is $(kK)^{-1}$ and the intercept = k^{-1}.

Data from Fig. 1 as well as data for dichloroethane (*16*) are plotted according to Eq. (2) in Fig. 2. The rate constant k and equilibrium binding constant K for each reactant, calculated from Fig. 2 using Eq. (2), are summarized in Table 1, along with corresponding data from our previous studies of trichloroethylene (*7, 12*) and chloromethanes (*5, 6, 13*).

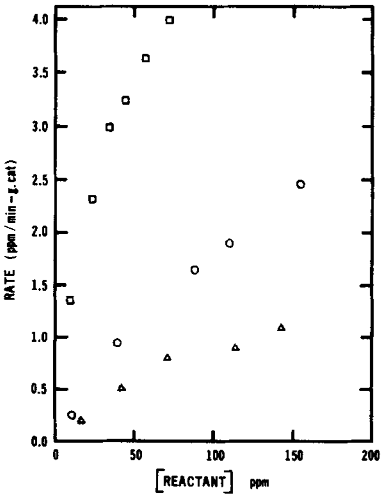

FIG. 1. Initial rate vs initial reactant concentration. (□) Perchloroethylene, (○) dichloroacetic acid, (△) monochloroacetic acid.

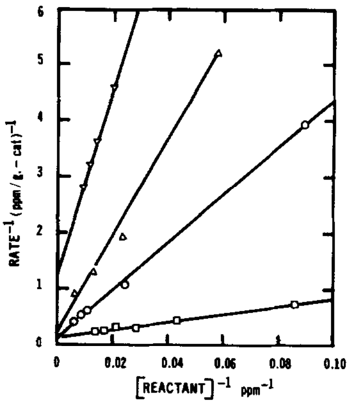

FIG. 2. Reciprocal initial rate vs reciprocal initial concentration. (□) Perchloroethylene, (○) dichloroacetic acid, (△) monochloroacetic acid, (▽) dichloroethane.

As with early chlorocarbons studied, inhibition by product (H)Cl appeared. Again, use of a single site inhibition model (without specification of the actual inhibiting entity) of a simple Langmuir form (Eq. (3))

$$\text{rate} = \frac{kK[\text{chlorocarbon}]}{1 + K[\text{chlorocarbon}] + K_{Cl}[Cl^-]} \quad (3)$$

provides an evaluation of K_{Cl} by plotting reciprocal initial rate vs measured $[Cl^-]$ at fixed initial chlorocarbon levels,

TABLE 1

Langmuir Rate Parameters for Chlorocarbon Mineralization

Reactant	k (ppm/min − g · cat.)	K (ppm^{-1})	Reference
CH_2Cl_2	1.6	0.02	(*6*)
$CHCl_3$	4.4	0.003	(*5*)
CCl_4	0.18	0.005	(*6*)
$Cl_2C{=}CClH$	830.0	0.01	(*7*)
$Cl_2C{=}CCl_2$	6.8	0.021	(Present)
$H_2ClCCClH_2$	1.1	0.011	(*16*)
Cl_2CCHO	4.4×10^2	0.25	(*7*)
$H_2ClCCOOH$	5.5	0.0021	(Present)
HCl_2CCOOH	8.5	0.0028	(Present)
Cl_3CCOOH	~0	—	(Present)

$$\frac{1}{\text{rate}} = \frac{1 + K[\text{chlorocarbon}]}{kK[\text{chlorocarbon}]} + \frac{K_{\text{Cl}}}{kK[\text{chlorocarbon}]}[\text{Cl}^-]. \quad (4)$$

Figure 3 demonstrates the linear character of such inhibition plots for perchloroethylene and dichloroacetic acid. The apparent inhibitor binding constant, K_{Cl}, is found to be 0.021 and 0.0074 ppm^{-1} with PCE and the chlorinated acid, respectively. These values may be compared with our earlier corresponding inhibitor findings of $K_{\text{Cl}} = 0.005$ (trichloroethylene) (*7*) and 1.8×10^{-2} ppm^{-1} (trichloromethane) (*5*). As we noted previously (*5–7*), both H^+ and Cl^- *may* function as inhibitors on the TiO_2 surface. A better rate form for inhibitor influences must await clearer mechanistic studies of reactant activation.

Reaction pathways. For perchloroethylene and the reactive chloroacetic acids ($Cl_2HCCOOH$, ClH_2CCOOH), no reaction intermediates were noted, only the appearance of final products HCl and CO_2. Thus, a mechanistic discussion is necessarily hypothetical.

(a) Perchloroethylene. Our previous study of the chloroolefin trichloroethylene (TCE) conversion noted the appearance of dichloroacetaldehyde (DCA, Cl_2HCCHO), which was in turn mineralized to HCl and CO_2 (*7*). This intermediate lead us to propose the sequence involving hydroxyl radical attack of TCE

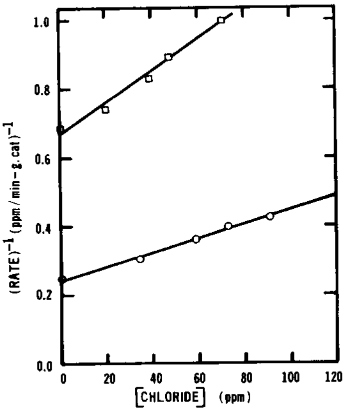

FIG. 3. Inhibition by HCl. Inverse initial rate vs initial chloride (as HCl) concentration. (○) Perchloroethylene $[(Cl_2C{=}CCl_2)_0 = 69.6 \text{ ppm}]$ (□) dichloroacetic acid $[(Cl_2HCCOOH)_0 = 67 \text{ ppm}]$.

$$OH^- + (h^+)_{\text{lattice}} \rightarrow \cdot OH \quad (5a)$$

$$Cl_2C{=}CClH_{\text{sol'n}} \rightarrow [Cl_2C{=}CClH]_{\text{ads}} \quad (5b)$$

$$[Cl_2C{=}CClH]_{\text{ads}} + \cdot OH \rightarrow [Cl_2C{=}CHOH]_{\text{ads}} + \cdot Cl \quad (5c)$$

$$[Cl_2C{=}CHOH]_{\text{ads}} \rightarrow [Cl_2HCCHO]_{\text{ads}} \quad (5d)$$

$$[Cl_2HCCHO]_{\text{ads}} \rightarrow \underset{\text{(DCA)}}{Cl_2HCCHO} \quad (5e)$$

$$\cdot Cl + e^-_{\text{lattice}} \rightarrow Cl^-. \quad (5f)$$

(The generation of hydroxyl radicals from illuminated TiO_2 in water has been established (*17*) (Reaction (5a).)

Homogeneous gas phase reactions of perchloroethylene with hydroxyl radicals yields dichloroacetyl chloride (*18*):

$$Cl_2C{=}CCl_2 + \cdot OH \rightarrow \underset{\text{(DCAC)}}{Cl_2HCCOCl} + \cdot Cl.$$

We observed no DCAC or any other intermediate in our perchloroethylene study (sensitivity ~2–3 ppm). However, the intermediate DCA in our TCE degradation study (*7*) was established as being very strongly adsorbed: the binding constant of DCA is large, $K = 0.25$ ppm^{-1}, and its rate constant is second only to that for trichloroethylene (Table 1). It is not unreasonable that a related, strongly adsorbed intermediate may be formed on the surface in PCE conversions, and that it is rapidly converted to HCl and CO_2. Other homogeneous phase pathways involving molecular oxygen or hydrogen peroxide attack of PCE have noted intermediates including trichloroacetyl chloride or phosgene (*19*). The latter would be unstable in water, hydrolyzing rapidly. The former would imply no chlorine release, in contrast to our data demonstrating immediate dechlorination.

(b) (1,2)-Dichloroethane (*16*). An intermediate chlorocarbon, which appeared and subsequently disappeared, was identified by GC–MS as vinyl chloride ($CH_2{=}CHCl$). A possible route to this monochlorinated olefin is given in

$$OH^- + h^+_{\text{lattice}} \rightarrow \cdot OH \qquad (6a)$$

$$[H_2ClCCClH_2]_{\text{ads}} + \cdot OH \rightarrow [H_2ClCCH_2OH]_{\text{ads}} + Cl\cdot \qquad (6b)$$

$$[H_2ClCCH_2OH]_{\text{ads}} \rightarrow \underset{(VC)}{H_2C{=}CHCl} + H_2O \qquad (6c)$$

$$Cl\cdot + e^-_{\text{lattice}} \rightarrow Cl^- \qquad (6d)$$

$$2.5O_2 + [H_2C{=}CHCl]_{\text{ads}} \rightarrow 2CO_2 + HCl + H_2O. \qquad (6e)$$

This sequence is the chlorocarbon analog to that proposed previously for gas/solid photocatalytic oxidation of the hydrocarbon isobutane (*20, 21*):

$$\underset{\substack{\text{(saturated}\\ \text{reactant)}}}{\text{isobutane}} \xrightarrow{+\cdot OH} \underset{\substack{\text{(strongly}\\ \text{adsorbed}\\ \text{intermediate)}}}{\text{isobutanol}} \xrightarrow{-H_2O}$$

$$\underset{\substack{\text{(olefinic}\\ \text{intermediate)}}}{\text{isobutene}} \xrightarrow{+O_2} \underset{\substack{\text{(final products .}\\ \text{of olefin scission)}}}{\text{acetone} + CO_2}$$

(c) Chloroacetic acids. Under nearly anaerobic conditions, acetic acid is photocatalytically decarboxylated to methane (and trace ethane) and CO_2 (*22–24*). In the presence of dissolved oxygen corresponding to atmospheric equilibration, no methane is collected during acetic acid conversion (*24*), implying complete oxidation to CO_2:

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O. \qquad (7)$$

A similar aerobic decarboxylation of dichloroacetic acid in the presence of oxygen would produce CO_2 and a phosgene-like moiety, which would hydrolyze instantly:

$$Cl_2HCCOOH + O_2 \rightarrow 2CO_2 + 2HCl. \qquad (8)$$

The monochloroacetic acid also yielded no observed organic intermediates

$$ClH_2CCOOH + \tfrac{3}{2}O_2 \rightarrow 2CO_2 + H_2O + HCl. \qquad (9)$$

B. Chlorinated Benzenes

Disappearance of monochlorobenzene was observed in the simultaneous presence of TiO_2 and illumination. With catalyst alone, it did not react; short time homogeneous photochemical conversions were negligible (*15*).

Illumination of a water/TiO_2 slurry containing 70 ppm chlorobenzene first showed oxidation of the reactant to *p*- and *o*-chlorophenol (Fig. 4), followed by dechlorination of the chlorophenols to yield *o*- and *p*-benzoquinones and the corresponding hydroquinones and/or catechols.

Higher initial chlorobenzene level (130 ppm) produced *o*- and *p*-chlorophenols and hydroquinones again, but benzoquinones were not detected. We established (*15*) by separate experiments that (i) the oxidation of a hydroquinone solution to a benzoquinone solution could proceed by homogeneous photochemistry with 300 < λ < 400 nm, or more quickly by photoassisted TiO_2 catalysis. However, the presence of chlorobenzene clearly inhibited hydroquinone ox-

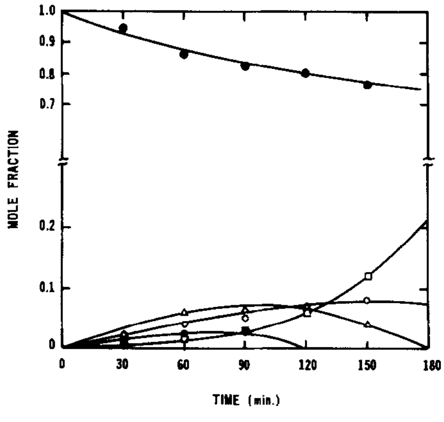

FIG. 4. Monochlorobenzene conversion vs time: (●) Chlorobenzene, (△) *o*-chlorophenol, (○) *p*-chlorophenol, (■) hydroquinone, and catechol, (□) *o*- and *p*-benzoquinone.

idation: the conversion of 20 ppm hydroquinone became immeasurably slow at 100 ppm chlorobenzene.

Dechlorination was a relatively slow reaction, as indicated by Fig. 4, showing about 7% dechlorination at 2 h of reaction. Direct measurement of chloride ion released into solution (as HCl) also indicated about 5% conversion at 2 h.

Biphenyl products were noted after longer times. In runs analyzed after 6 and 10 h, heavy products including 4,4′-dichloro-1,1′-biphenyl and 4,5′-dichloro-1,1′-biphenyl were observed (identification via GC–MS analysis and comparison of product peak MS fragmentation pattern with MS library spectra) (*14*). These products suggest a slow, homogeneous pathway, paralleling catalysis, which activates the initial reactant.

The initial rate of disappearance of monochlorobenzene was measured as a function of reactant level. The results indicate a first-order region below 22–33 ppm, and an approach to saturation above 330 ppm.

Initial rate data for monochlorobenzene are plotted as inverse initial rate versus inverse Cl–benzene concentration in Fig. 5. The relation is linear, as predicted by Eq. (4). The value of $k_{\text{Cl-benzene}}$ determined from Fig. 5 is 0.44 ppm/min-g · cat. and the calculated value of $K_{\text{Cl-benzene}}$ is 1.05×10^{-2} ppm^{-1}. Thus, monochlorobenzene has a relatively small rate constant and binding constant, as seen by comparing these values with those of other chlorinated hydrocarbons (Table 1).

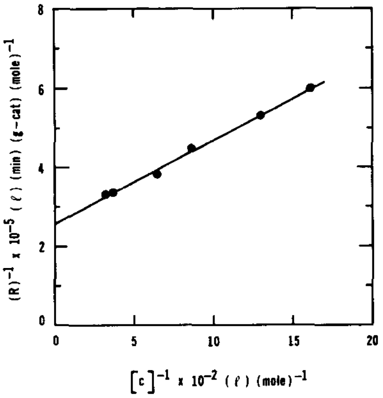

FIG. 5. Monochlorobenzene: reciprocal initial rate vs reciprocal initial concentration.

o-Dichlorobenzene. Photoassisted heterogeneous catalysis of *o*-dichlorobenzene was observed. Initial major products of *o*-dichlorobenzene degradation were identified by GC–MS as *o*-chlorophenol, 2,3-dichlorophenol, and 3,4-dichlorophenol. Thus, partial oxidation of the chloroaromatic again precedes subsequent, slower dechlorination reactions. Multiple products including biphenyl derivatives were noted for longer times of reaction.

Mechanism. Slow homogeneous decomposition in sunlight of aqueous *p*-chlorophenol (*25*) has been observed by Wong and Crosby. Their proposed decomposition scheme considers a photonucleophilic substitution of hydroxide ion for a chlorine on the photoexcited aromatic ring. They ruled out hydroxyl radical attack because the rate was independent of oxygen pressure (implying no hydrogen peroxide involvement) and decreased (but did not stop) with decreasing pH.

In heterogeneous photocatalysis, the near-uv photoexcites the TiO_2, producing an excited surface (TiO_2^*) which may react with adsorbed species. The production of hydroxyl radicals by illuminated TiO_2 has been demonstrated (*17*). Very little dechlorination was observed in photoassisted catalytic degradation of chlorobenzene. Direct dechlorination from chlorobenzene does not seem to occur due to the lack of evidence for any benzene in the solution. Thus, the dechlorination apparently results from the conversion of chlorophenol to hydroquinone or catechol.

A proposed pathway for chlorobenzene conversion appears in Fig. 6. The chloro groups are moderate deactivating groups and *ortho*/*para* directors (*26*) for ring modification. Thus, electrophilic hydroxyl radical substitution on chlorobenzene at *ortho* and *para* positions of the benzene ring is

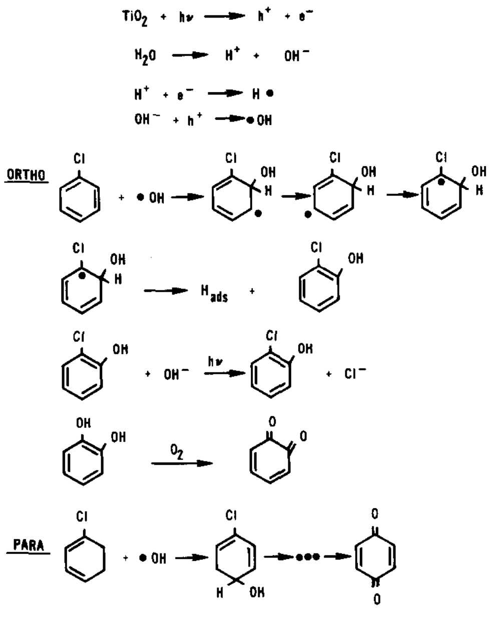

FIG. 6. Proposed conversion schemes for monochlorobenzenes.

expected, producing *o*- and *p*-chlorophenol (Fig. 6). Further substitution of hydroxyl ion removes chloride ion to yield hydroquinone and catechol. (From the mass spectrum of one of our product peaks with mass spectra data, it appears that hydroquinone and catechol were both present in the product mixture.)

A polyphenol such as hydroquinone is easily oxidized to benzoquinone (*27, 31*). We noted earlier that oxidation of hydroquinone can proceed in either a homogeneous or a heterogeneous reaction with black-light illumination.

C. Potential Application to Water Decontaminations

Chloromethanes and chloroethylenes are of concern in drinking water supplies above even very low concentration, e.g., 5–50 ppb (*28*). Thus, use of heterogeneous photocatalysis to reduce the concentration of small chlorocarbons and chlorinated carboxylic acids to such dilute levels as 1–5 ppb would occur in a kinetic regime which, from Table 1, would be first-order in all reactants shown. The simple rate form, Eq. (1), becomes Eq. (10) at these very low concentrations (assuming the surface to be truly Langmurian):

$$\text{rate} \approx kK[\text{chlorocarbon}] \qquad (10)$$

Table 1 indicates that the relative reactivities at low concentrations, characterized by the parameter product kK, is given by the sequences (phosgene hydrolyzes homogeneously, is most reactive)

$$(\mathrm{Cl_2CO})(\text{phosgene}) \gg \text{DCA} \gg \text{TCE} > \text{PCE} > \mathrm{Cl_2HCCOOH} \sim \mathrm{CH_2Cl_2} > \mathrm{CHCl_3} \sim \mathrm{H_2ClCClH_2} \sim \mathrm{ClH_2CCOOH} > \mathrm{CCl_4} > \mathrm{Cl_3CCOOH}.$$

Thus, the strongly bound chloroaldehyde(s) are predicted to be least stable, followed by chloroolefins. Saturated molecules are more stable, with increasing chlorination generally stabilizing both chloromethanes and chloroacetic acids (monochloroacetic acid is the apparent exception). These data indicate that water supplies that are contaminated by the industrial solvent TCE or the dry-cleaning agent PCE could be candidates for a novel water purification process with heterogeneous photocatalysis using near-uv illuminated TiO_2. On the other hand, the chloromethanes (especially $CHCl_3$) produced during conventional chlorination of water supplies (*29, 30*), as well as chloroacetic acids (noted in water chlorination of model humic acid compounds (*9*)) will be more difficult candidates. The mono- and dichlorinated benzenes, which have been noted as water contaminants (*8*) are not suitably treated via this photocatalyst since dechlorination is very slow, intermediates include the bitter chlorophenols, and complete mineralization does not result.

CONCLUSION

Dilute aqueous solutions of dichloroethane, perchloroethylene, and mono- and dichloroacetic acids are completely mineralized by near-uv illuminated TiO_2 slurries.

Trichloroacetic acid is unreactive. Mono- and dichlorobenzenes are not mineralized, but converted to other ring chlorooxygenates and ring oxygenates, as well as some chlorinated biphenyls. Heterogeneous photocatalysis may have strongest potential for removal of chloroolefins and chloroaldehydes from contaminated water supplies.

ACKNOWLEDGMENT

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