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Heterogeneous Photocatalysis: Degradation of Dilute Solutions of Dichloromethane (CH_2Cl_2), Chloroform ($CHCl_3$), and Carbon Tetrachloride (CCl_4) with Illuminated TiO_2 Photocatalyst

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In dilute (10–200 ppm) aqueous solutions, the chloromethanes CCl_4, $CHCl_3$, and CH_2Cl_2 are completely mineralized to CO_2 and HCl by the heterogeneous photocatalyst TiO_2. The reaction rates in the absence of accumulated product are described by a simple Langmuir form,

$$\text{rate} = \frac{k \cdot K[\text{chloromethane}]}{1 + K[\text{chloromethane}]}.$$

The relative rate constants are in the approximate ratio of 29 (trichloro-) : 9 (dichloro) : 1 (tetrachloromethane). Chloride ion inhibits the rate of degradation, as do product protons, as shown by experiments with added initial CsCl or HCl.

INTRODUCTION

Heterogeneous photoassisted catalysis has been established by us as effective for complete mineralization (to dissolved CO_2 and HCl) of dilute aqueous solutions of two major light chlorinated hydrocarbon solvents: chloroform ($CHCl_3$) (*1 – 3*) and trichloroethylene (*1, 2, 4*). While waste hydrocarbon liquids or vapors containing these difficult chlorinated components may be treated satisfactorily by high temperature process such as incineration (*5*) or catalytic combustion in the presence of simultaneous hydrocarbon oxidation (*6*), respectively, such high temperature treatments of very dilute halocarbon aqueous solutions are impractical. The present paper extends our results to a comparison with chloroform of the photocatalytic degradation of two other common chloromethanes, namely, dichloromethane (CH_2Cl_2) and carbon tetrachloride (CCl_4). Some experiments with dilute aqueous solutions of methane are indicative of common changes in catalyst surface behavior following activation of CH_x species.

EXPERIMENTAL

The differential conversion, recycle photorector, has been described previously (*1, 3, 4*). The catalyst was Fisher certified grade TiO_2, Lot 773688. All reactants examined were from commercial sources and were used directly, without further purification, in aqueous solutions typically of 10–1000 ppm chlorinated hydrocarbon.

The catalyst loading and illumination were maintained constant at 0.1 wt% TiO_2, and 6.6×10^{-4} Einsteins/min, respectively. The use of black lights as illumination sources ($320 \leq \lambda \leq 400$ nm) allowed avoidance both of homogeneous photodechlorinations (which may occur below 300 nm (*7*)) and of unnecessary visible components, since TiO_2 is appreciably activated only by photons of wavelength $\lambda \leq 350$ nm. The concentration of chloride ions (*8, 9*) was determined continuously as before (*1–4*) with a specific chloride ion electrode placed in the recycle loop. Formation of carbon dioxide product was established from barium carbonate formation when a reacted solution was purged with helium

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which then passed through a barium hydroxide solution.

Two procedures were used to examine the role of molecular oxygen in the overall photocatalytic conversions:

(a) *closed system:* an illuminated TiO_2 solution was purged with helium for 1 hr, at which time purging was stopped, chlorocarbon injected, and the system remained closed to air at all times.

(b) *open system:* no prior helium purging was used to strip O_2 or CO_2 from the starting distilled water charge. The recycle loop gas–liquid separator (gas volume ~ 200 ml) contained air at the start of an experiment.

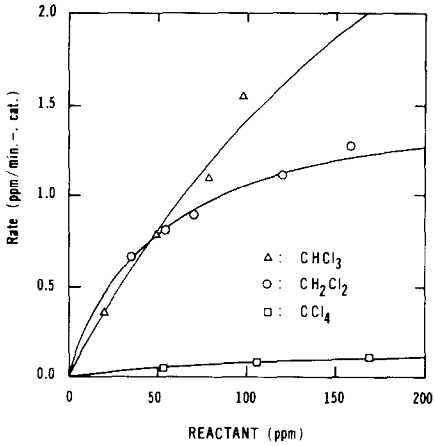

FIG. 1. Initial reaction rate vs initial reactant concentration. *T*, 27–29°C, "open" system, 0.1 wt% TiO_2 catalyst. Reactant: CH_2Cl_2 (○), $CHCl_3$ (△), CCl_4 (□).

RESULTS AND DISCUSSION

In our preceding studies (*1–4*), the conversion of the reactants, chloroform and trichloroethylene, was found to be inhibited by one or more products, namely, chloride ion (Cl^-) and/or protons (H^+). In the present study, therefore, *initial* rate measurements were made between 25 and 200 ppm reactants as a function of the initial reactant concentration. These results are presented in Fig. 1 which compares the three reactants dichloromethane, trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride). The nearly straight line behavior of both trichloromethane and tetrachloromethane signal relatively weak binding (low coverages) at these concentrations, while dichloromethane exhibits a clear surface saturation influence as the initial concentration approaches 200 ppm CH_2Cl_2.

Quantitative interpretation of these curves requires a mechanistic model for adsorption. It is possible that dichloromethane adsorbs as an ion, by reaction with, e.g., a hole (+) at the surface

$$CH_2Cl_2 + \boxplus_s \rightarrow [CH_2Cl_2]_{ads}^+ \qquad (1a)$$

Alternately, our previous study (*1, 3*) with chloroform ($CHCl_3$) strongly suggests a dissociative form of adsorption, since both Cl^- and H^+ appear to contribute to reaction inhibition, and these are likely to influence separately the Brønsted acidity and basicity, respectively, which TiO_2 surfaces are known to possess (*10*). Thus, a different dissociative mode of adsorption could exist as in Eq. (1b):

$$CH_2Cl_2 \rightarrow (H^+)_{ads} + (CHCl_2)_{ads}^- \qquad (1b)$$

where we may expect (H^+) to be on the lattice oxygen, and $(CHCl_2)_{ads}^-$ to be bound to the lattice cation, Ti(IV). In either case, a clear reverse reaction exists, as indicated by Eqs. (2a) and (2b), respectively:

$$[CH_2Cl_2]_{ads}^+ + e^- \text{ (lattice)} \rightarrow CH_2Cl_2\text{(solution)} \qquad (2a)$$

$$(H^+)_{ads} + (CHCl_2)_{ads}^- \rightarrow CH_2Cl_2\text{(solution)} \qquad (2b)$$

The first case (1a, 2a) would lead to a simple Langmuir isotherm behavior, where the steady-state concentration of holes (+) and electrons (e^-) near the lattice surface would depend on the illumination intensity, *I*. Thus, the coverage θ is

$$\theta_{CH_2Cl_2} = \frac{K_{CH_2Cl_2}(I) \cdot [CH_2Cl_2]}{1 + K_{CH_2Cl_2}(I)[CH_2Cl_2]}. \qquad (3a)$$

The dissociative adsorption model provides an equilibrium between the species:

$$CH_2Cl_2 \overset{K_0}{\rightleftarrows} (H^+)_{ads} + (CHCl_2)_{ads}^-$$

As a negligible pH shift is observed on addition of dichloromethane to the solution, the value of $(H^+)_{ads}$ may be expected to remain ~ constant, required by the equilibrium for water dissociation:

$$[H^+][OH] \cong 10^{-14}\,M.$$

Under this reasonable condition, $(H^+)_{ads}$ will be ~ constant, and we will have

$$\theta_{(CHCl_2^-)} \approx \frac{K[CH_2Cl_2]}{1 + K[CH_2Cl_2]}. \quad (3b)$$

Since illumination may produce a steady state rather than "equilibrium" condition, the K above again may be intensity dependent.

If the slow step in the chlorocarbon degradation depends on the first power of the coverage $\theta_{CH_2Cl_2}$ (Eq. (3a)) or $\theta_{(CHCl_2)}$ (Eq. (3b)), then the Langmuir test plot of reciprocal rate vs reciprocal initial concentration should be linear, as indeed is found in Fig. 2 for dichloromethane. The parameters for the rate Eq. (4),

$$\text{rate} = \frac{k_{CH_2Cl_2}K_{CH_2Cl_2}[CH_2Cl_2]}{1 + K_{CH_2Cl_2}[CH_2Cl_2]}. \quad (4)$$

are found from Fig. 3 to be $k_{CH_2Cl_2} = 1.58$ ppm/(min − g · cat) and $K_{CH_2Cl_2} = 2.02 \times 10^{-2}$ ppm^{-1}. The solid curve through the dichloromethane data in Fig. 2 is calculated from these two values.

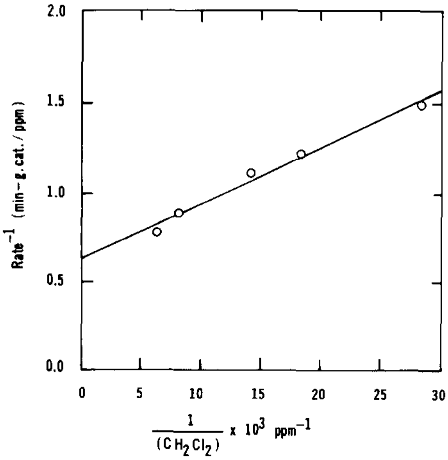

FIG. 2. Reciprocal initial rate vs reciprocal initial concentration: dichloromethane (CH_2Cl_2).

Product inhibition of chloroform conversion was noted earlier (*1, 3*). A simple competitive inhibition term in chloride ion appears to suffice here for dichloromethane when various Cl^- concentrations are introduced as CsCl:

$$\text{rate} = \frac{k_{CH_2Cl_2}K_{CH_2Cl_2} \cdot [CH_2Cl_2]}{1 + K_{CH_2Cl_2}[CH_2Cl_2] + K_{Cl}[Cl^-]} \quad (5a)$$

thus

$$\frac{1}{\text{rate}} = \frac{1}{k_{CH_2Cl_2}K_{CH_2Cl_2}[CH_2Cl_2]} (1 + K_{CH_2Cl_2}[CH_2Cl_2] + K_{Cl}[Cl^-]. \quad (5b)$$

The corresponding data plot of inverse rate vs $[Cl^-]$ as CsCl (Fig. 3) at constant reactant concentration ($(CH_2Cl_2)_0 = 61.5$ ppm) is satisfactorily represented by a straight line. The inhibition binding constant is $K_{Cl^-} = 1.56 \times 10^{-2}$ ppm^{-1}, a value about 3 times that determined previously

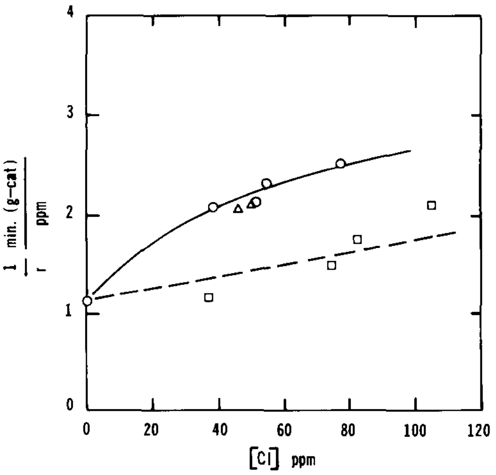

FIG. 3. Reciprocal initial rate vs chloride ion initial concentration at constant reactant level (dichloromethane = 61.5 ppm). (Catalyst batch #1 (○): Cl^- added as HCl. Catalyst batch #2: Cl^- added as HCl (△) or as CsCl (□).)

(*4*) for inhibition of TCE conversions ($\sim 5 \times 10^{-3}$ ppm^{-1}).

The data for Cl as HCl show a more rapid decline of rate (increased reciprocal rate, Fig. 3) with the first addition of HCl, followed by a linear behavior of reciprocal rate vs Cl^- concentration. This behavior provides indirect confirmation of our suggestion of a dissociative adsorption of dichloromethane (Eq. (1b)), since H^+ from HCl would be a competitive inhibitor to H^+ from CH_2Cl_2. However, a model that rationalizes the rapid rate decline at smaller HCl values and a linear variation of inverse rate with HCl at larger HCl levels is not yet evident.

The chloroform kinetics of Fig. 1 show very little curvature; the curve shown corresponds to ($K_{CHCl_3} = 3.7 \times 10^{-3}$ ppm^{-1}, $k_{CHCl_3} = 5.2$ ppm/(min · g-cat)). Similarly, the carbon tetrachloride data are reasonably described with $k_{CCl_4} = 0.18$ ppm/(min · g-cat) and $K_{CCl_4} = 8.9 \times 10^{-3}$ ppm^{-1}.

The kinetic and thermodynamic constants evaluated from Figs. 1–3 are summarized in Table 1. Within the accuracy of the data, chloroform and carbon tetrachloride bind with approximately equal strength, whereas dichloromethane binds more strongly. The order of specific reactivity is seen from the k_R values to be $CHCl_3 > CH_2Cl_2 \gg CCl_4$. The strength of CH_2Cl_2 binding is such, however, that at concentrations below 50 ppm reactant, the absolute rate of reaction (Fig. 1), reflecting the product (k_RK_R), is greater for dichloromethane than for chloroform.

The concentrations of halocarbons at which drinking water criteria are concerned are in the range of 10–100 parts per *billion.* For trihalomethanes in particular ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$), the *total* trihalomethane level allowed for community water sytems serving 10,000 or more people in the USA is 100 μg/liter, i.e., approximately 100 parts per billion (0.1 parts per million). For these concentrations of interest in public water supplies, the data of Fig. 1, and the parameter values of Table 1 indicate that all three reactants would behave as pseudo-first-order systems. Their relative reactivities under these conditions are seen from the product (k_RK_R) (fourth column, Table 1) to be

$$\text{dichloromethane} > \text{trichloromethane} \gg \text{carbon tetrachloride.}$$

TABLE 1

Parameter Values for Chloromethane Conversions

Reactant	k_R $\left(\frac{\text{ppm}}{\text{min-g} \cdot \text{cat.}}\right)$	K_R (ppm^{-1})	k_RK_R (min-g · cat.)$^{-1}$	K_{Cl} (ppm^{-1})
CH_2Cl_2	1.6	2.0×10^{-2}	3.2×10^{-2}	1.56×10^{-2}
$CHCl_3$	5.2	3.7×10^{-3}	1.94×10^{-2}	$(5 \times 10^{-3})^a$
CCl_4	0.18	8.9×10^{-3}	$.16 \times 10^{-2}$	

[a] Ref. (*3*).

Oxygen Influences

During the course of dehalogenations, the observed rate of reaction depended clearly on the presence of oxygen in the system. This effect may be due to several influences:

(i) Oxygen is required stoichiometrically for complete mineralization of dichloro- and trichloromethanes. No permanent gases such as CO or H_2 have been detected in these studies. The typical course of reaction produces only CO_2 (noted by barium carbonate precipitate when a helium purge gas is bubbled through a reacted halocarbon solution and then through a $Ba(OH)_2$ trap). These observations are consistent with the following simple stoichiometries:

(a) *dichloromethane*

$$CH_2Cl_2 + O_2 \rightarrow 2HCl + CO_2 \quad (6a)$$

(b) *trichloromethane*

$$CHCl_3 + H_2O + \tfrac{1}{2}O_2 \rightarrow 3HCl + CO_2 \quad (6b)$$

(c) *tetrachloromethane*

$$CCl_4 + 2H_2O \rightarrow 4HCl + CO_2 \quad (6c)$$

Thus, only CCl_4 can be converted to observed products without a clear requirement for oxygen participation.

(ii) The observed *rate* of reaction, as judged either by disappearance of reactant or by appearance of product, is slower in systems well purged at the outset, indicating the participation of molecular oxygen in a kinetically important step.

(iii) In the "closed" system described in the experimental section, operation of the photoreactor under these low oxyen tension conditions with dichloromethane or dibromomethane resulted in a clear color change of the solid (surface) from white to a strong purple. This same color change could be effected by continuous purging of a chlorine-free illuminated TiO_2 suspension with pure methane. In all three cases (dichloromethane, dibromomethane, methane), the color change was quickly reversed when oxygen was admitted to the system. We ascribe this purple color to the accumulation of major amounts of a reduced carbon species on the surface. This species may well be a carbene radical (*11*). The commonality to all three reactants in the absence of oxygen suggests that an alkyl–titanium complex involving (CH_2) and Ti(IV) or Ti(III) is responsible. The absence of this color under "open" reaction conditions suggests that the final step to remove C from the surface as CO_2 is not a particularly slow step. [Indeed, carbon dioxide is produced from formate and oxalate ions, even in *deaerated* suspensions of uv-illuminated zinc oxide, a semiconductor with photocatalytic behavior similar to TiO_2 (*12*). The $\cdot CO_2^-$ and $\cdot OH$ radicals were observed by spin-trapping and ESR detection of the trapped adduct. Those authors suggest CO_2 formation by reaction of $\cdot CO_2^-$ with another hole, i.e.,

$$HCOO^- + \cdot OH \rightarrow HOH + \cdot CO_2^- \quad (7a)$$

or

$$h^+ + HCOO^- \rightarrow H^+ + \cdot CO_2^- \quad (7b)$$

and

$$h^+ + \cdot CO_2^- \rightarrow CO_2 \quad (8a)$$

or

$$\cdot OH + \cdot CO_2^- \rightarrow HCO_3^- \quad (8b)]$$

CONCLUSION

In the concentration range 10–200 ppm, the three chlorocarbons CH_2Cl_2, $CHCl_3$, and CCl_4 are completely mineralized to CO_2 and HCl. The reaction rates in the absence of accumulated product are described by a simple Langmuir form. The relative binding constants, K_R, are dichloro- > tetrachloro- ≈ trichloromethane. The specific reactivities, k_R, are in the approximate ratio of 29 (trichloro-) : 9 (dichloro) : 1 (tetrachloro-). At the parts per billion level of interest in drinking water standards, the product $k_R K_R$ represents the effective first-order rate constant under these conditions, and has the relative ratio of 20 (dichloromethane) : 12 (trichloromethane) : 1.0 (tetrachloromethane).

The dichloromethane conversion is product inhibited, probably by chloride (Cl^-) and/or protons (H^+), as noted previously (*3*) with chloroform conversions and with trichloroethylene conversions. The larger apparent inhibition constant (based on chloride alone) for dichloromethane and trichloromethane (as well as dichloroacetaldehyde (*4*)) compared with trichloroethylene is consistent with (H^+) inhibition, as well as chloride ion, for those reactants such as CH_2Cl_2 and $CHCl_3$ which appear to require two sites (acid/base) for initial activation by the catalyst.

The relative ease of mineralization of these otherwise relatively stable and biologically recalcitrant molecules with heterogeneous photocatalysis at ambient conditions suggests that an appreciable process potential may exist for removal of trace deleterious molecules from water supplies. The assessment of this potential will require economic and catalyst lifetime studies, both of which are now underway in our laboratories.

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