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Kinetics of the Oxidation of Trichloroethylene in Air via Heterogeneous Photocatalysis

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Trichloroethylene in solution with air is oxidized rapidly in the presence of irradiated titanium dioxide. Dichloroacetyl chloride (DCAC), which is formed as an intermediate during the trichloroethylene reaction, also undergoes photocatalytic oxidation. This paper describes the kinetics of these reactions and how operating conditions influence the observed reaction rates. Annular photocatalytic reactors with thin films of titanium dioxide catalyst were used to make kinetic measurements. Observations of the reaction rate of trichloroethylene were made while varying parameters such as catalyst loading, feed flow rate, feed composition, and ultraviolet light energy. The observed reaction rates are higher by several orders of magnitude than those previously reported in the literature, and an expression for the prediction of rate as a function of reactant partial pres sure is provided. The rate of reaction of the DCAC intermediate is also discussed. Air is shown to be an optimum oxidant, and an optimum humidity is established. The reaction is shown to proceed indefinitely under dry conditions, supporting the existence of a chlorine radical propagated surface reaction.

INTRODUCTION

The photocatalytic oxidation of trichloroethylene (TCE) in contact with irradiated titanium dioxide (TiO_2) results in the formation of dichloroacetyl chloride (DCAC), phosgene ($COCl_2$), carbon monoxide (CO), molecular chlorine (Cl_2), carbon dioxide (CO_2), and hydrogen chloride (HCl) (1). $COCl_2$ is stable in the thin film photocatalytic reactors on the time scale of interest, though it will hydrolyze in the presence of humid air on many heterogeneous surfaces, including TiO_2, via a non-photocatalytic, heterogeneous hydrolysis reaction (1). CO, Cl_2, CO_2, and HCl are unreactive in contact with irradiated TiO_2. DCAC, however, undergoes photocatalytic oxidation. This paper reports observations of the reaction rates of the photocatalytic oxidation of TCE and DCAC and the factors that influence these rates.

METHOD

A schematic drawing of the apparatus used to collect the data reported here has been previously published (2, 3). Detailed descriptions of the experimental apparatus and procedures are available in the literature (3, 4). Sample gases make a single pass through the photocatalytic reactor at flow rates on the order of 10 liter/min. Analysis is performed by an on-line Fourier transform infrared (FTIR) gas analyzer (Nicolet 8220) that directly samples the entire reactor effluent in flow-through mode without splitting or dilution. Representative product spectra have been published (1, 2). Most of the experimental work conducted during the course of this investigation was carried out under a set of standard operating conditions listed in Table 1. Departures from these standard operating conditions are reported explicitly.

Annular photocatalytic reactors coated with Degussa P-25 TiO_2 (≈75% anatase, 50 m^2/g) were used in this investigation. The catalyst is applied to the inside surface of a Pyrex reactor tube via a wash coat technique (1, 3). This coated Pyrex tube forms the outside surface of an annular reactor. A cylindrical light source, typically a fluorescent black light (Sylvania F8T5BLB, 8 W, spectral maximum at 356 nm), forms the inner surface of the annulus. A germicidal lamp (Sylvania G8T5, 8 W, spectral maximum at 254 nm) was also tested. A Blak-Ray J221 long-wave UV-meter (UVP) was used to measure light intensity. Hydraulic diameter is defined as the diameter of the inner annular surface (outside diameter of the lamp) subtracted from the diameter of the outer annular surface (inside diameter of the reactor tube, coated with TiO_2) and is a critical parameter controlling mass transfer and photon flux in the annular reactor. Kinetic measurements were made using a photocatalytic reactor with a hydraulic diameter of 0.9 mm.

A flat reactor was also used in the investigation. It fea-

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TABLE 1

Definition of Standard Operating Conditions

Experimental variable	Standard nominal value
Pressure	67 kPa (500 Torr)
Temperature	294 K
UV source/primary wavelength	Black light/356 nm
UV energy incident	5.3 mW/cm^2
TCE feed partial pressure	6.7 Pa (50 mTorr)
Water vapor feed partial pressure	67 Pa (500 mTorr)
Injector delivery pressure	187 kPa (15 psig)
Sample cylinder pressure (continuous operation)	222 kPa (20 psig)
Initial sample cylinder pressure (batch operation)	1200 kPa (160 psig)
FTIR resolution	2 Wavenumber
Number of scans per spectra	≥32
Solvent	Zero air and UHP N_2

tures a film of TiO_2 applied to the surface of a microscope slide (25 × 75 mm) via the wash coat technique. The coated slide fits into a Teflon housing. A quartz window is placed over the Teflon housing and is sealed. Illumination is provided externally, allowing the UV light intensity to be controlled by varying the proximity of the light source to the catalyst film. Drawings of both the annular and flat plate reactors have been published (3).

RESULTS AND DISCUSSION

Units Expressing Extent of Catalyst

Several sets of units are useful in describing the rate of the oxidation of TCE via heterogeneous photocatalysis. The units used in the proposed kinetic model are μmol/s/m^2-illuminated-catalyst based on the geometric area of the coated Pyrex substrate. Although these units underestimate the total area of catalyst participating in the reaction, significant benefits result from their use. Figure 1 shows that the geometric-area-based rate of destruction of TCE increases with catalyst loading (coating thickness) until all of the UV photons are absorbed. At this point the rate becomes independent of catalyst loading, and coating-to-coating repeatability for rate measurements can be achieved. Therefore, subsequent rate data were taken using UV-opaque catalyst films with catalyst loadings greater than 0.5 mg/cm^2.

The weight of each coating was also recorded so that the value for the rate could be expressed as μmol/s/g-catalyst. These units have been used in the literature, though difficulties are encountered when attempting to determine whether the entire mass of catalyst is illuminated and taking part in the reaction (5). Figure 1 reveals that the weight-based rate increased with a decrease in catalyst loading. More photons are incident upon the average unit of mass of catalyst as the TiO_2 coating becomes thinner (lighter).The lowest loading reported in Fig. 1, about 0.04 mg/cm^2, was achieved with an annular reactor with a thin (≈400 nm), translucent layer of TiO_2 deposited via an ultrasonic nebulization and pyrolysis process developed by Wold (6). This film is very photoactive and achieved the highest rates based on the weight of the catalyst.

In our experiments, the thin films of catalyst used during rate measurements were illuminated by 5.3 mW/cm^2 of UV energy. An estimate of the amount of catalyst taking part in the photocatalytic reaction can be obtained from Fig. 1. The transition to the flat part of the geometric-area-based rate curve coincides with the absorption of all of the UV light. One may interpolate from this curve that at a catalyst loading of 0.3 mg/cm^2, the entire mass of catalyst is participating in the reaction. An estimate of the light penetration depth is obtained by dividing the interpolated catalyst loading by the density of the catalyst film. Upper and lower limits on the density of the catalyst film are estimated as the measured density of the bulk TiO_2 powder (0.09 g/cm^3) and the density of solid TiO_2 assuming a 0.3 void fraction (2.9 g/cm^3). Penetration depths of 30 and 1 μm, respectively, are calculated with the limiting density estimates. These values bracket those reported in the literature (7).

Photons are the most expensive component in the operation of a photocatalytic reactor. Therefore, from an engineering standpoint, the most appropriate units are based upon the total energy input into the reactor. In terms of these units, the reaction rate observed when using a thin-film annular reactor powered by an 8-W fluorescent black light is 0.01 μmol/J. This value can be compared directly with all other types of reactors, regardless of geometry, catalyst configurations, and light source. These units are also useful for comparison with incineration and catalytic combustion waste treatment techniques.

Table 2 compares rates of the oxidation of TCE via heterogeneous photocatalysis from the literature with the maximum rates observed in this investigation. Dibble and Raupp reported a rate based on the weight of the catalyst bed that was lower by more than three orders of magnitude than the rate reported here (5). Their reactor featured a thick bed of catalyst layer illuminated with 0.14 mW/cm^2 of UV energy. When the Dibble and Raupp measurement is converted to the geometric area basis and extrapolated to 5.3 mW/cm^2 via the linear relationship between photon flux and reaction rate described below, the result is within 10% of the value observed during this investigation. This result confirms the utility of the geometric-area-based units for purposes of comparison and scale-up. Yamakazi-Nishida *et al.* (8) used a packed bed reactor and reported

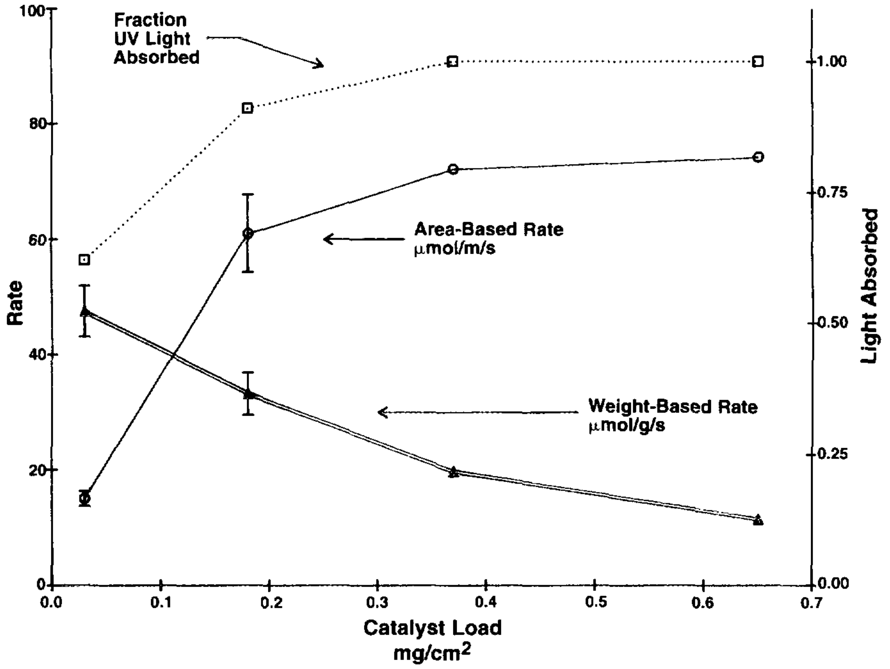

FIG. 1. The rate of the reaction of TCE in air in contact with irradiated TiO_2 on two bases; the geometric area of catalyst film(µmol/m_2/s), and the weight of the catalyst film (µmol/g/s). These rate data are plotted on the left abscissa. The fraction of near-UV photons absorbed by the catalyst film (dotted line) is plotted on the right abscissa. The ordinate is catalyst loading (weight of the catalyst film divided by the area of the catalyst film). The near-UV radiation incident on the catalyst film was 5.3 mw/cm^2. The geometric area of the catalyst film was 9.8 cm^2.

TABLE 2

Highest Observed Reaction Rates

Reference	µmol / s-m² catalyst (geometric area)	µmol / s-g catalyst	µmol / j
This investigation	84[a]	47[b]	0.01[a]
Dibble and Raupp (5)[c]	2	7.5×10^{-3}	1×10^{-4}
Yamazaki-Nishida et al. (8)[d]	NA	2.6×10^{-1}	0.14
Kutsuna et al. (9)[e]	1.6	1.3×10^{-2}	5.6×10^{-5}

[a] Feed contained 187 mTorr TCE and 744 mTorr water vapor; UV flux = 5.3 mW/cm^2 from an 8-W bulb.

[b] Feed contained 54 mTorr TCE and 298 mTorr water vapor; UV flux = 5.3 mW/cm^2 from an 8-W bulb.

[c] Feed contained 158 Torr TCE and 7.1 Torr water vapor; UV flux = 0.14 mW/cm^2 from a 4-W bulb.

[d] Data from a packed bed reactor; feed composition not reported; UV flux = 5.4 mW/cm^2 from four 4-W bulbs.

[e] Rate estimated from model parameters for 76 mTorr TCE in dry feed; UV flux reported as a rate constant of 0.046 min^{-1} for photodissociation of NO_2 under N_2 from five 60-W bulbs.

a high reaction rate, on an energy basis, relative to the thin film configuration.

Reaction Regimes

The annular photocatalytic reactors used in this investigation have negligible intraparticle transport resistance due to their two-dimensional thin-film catalyst configuration and the further limitation of light penetration depth. Consequently, only a bulk-transport-controlled regime and a surface-reaction-controlled regime exist (10). Figure 2 is a plot of the observed rate of destruction of TCE and the conversion of TCE as a function of the average linear velocity of the reactant stream. More than 50 separate measurements were used in constructing this figure and the tabulated data are available in the literature (3). As the rate of flow increases, the reaction rate becomes independent of the fluid velocity and the reactor is free of mass transport limitations. The high fluid velocity also leads to a low TCE conversion. This lack of transport limitations and low conversion establish the flow region above 700 cm/s as the proper experimental space in which to apply the differential method to measure the rate of the surface reaction. All subsequent rate data are taken under these conditions. At lower velocities, where the conversion of

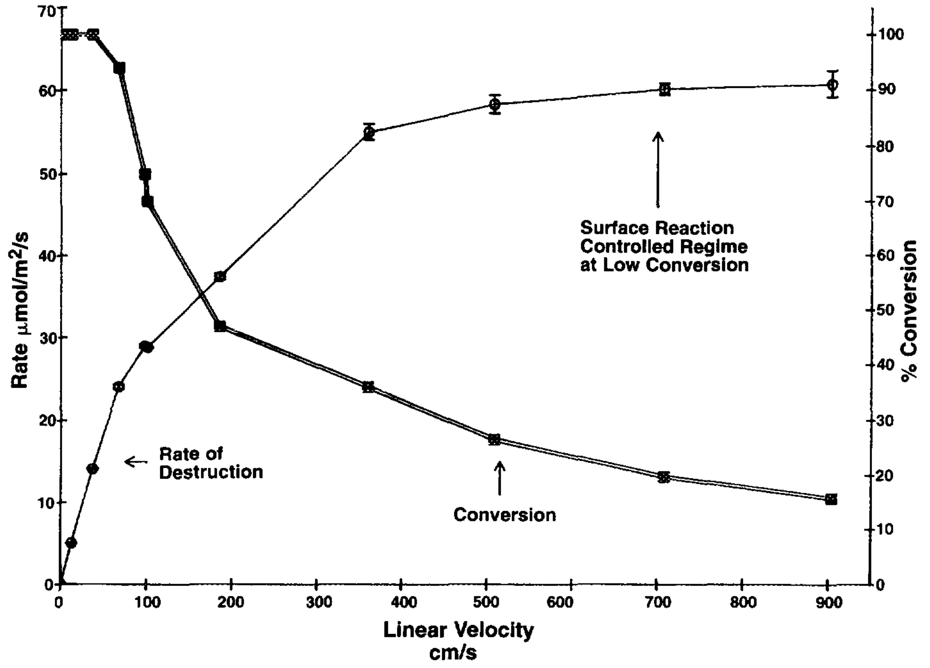

FIG. 2. Experimental space appropriate for differential analysis of reaction rate of the photocatalytic oxidation of TCE in air in contact with irradiated TiO_2. Reaction rate data are plotted on the left abscissa. TCE conversion data are plotted on the right abscissa. The ordinate is average linear flow velocity.

TCE is high, the integrated form of the Langmuir–Hinshelwood rate expression developed below closely predicts the observed conversion as a function of residence time. This indicates that the surface-reaction-controlled regime extends to lower fluid velocities, but the TCE conversions are high and the assumptions implicit in differential analysis are not valid.

Reactant and Intermediate Partial Pressure Dependence

It has been established that the reaction proceeds through a DCAC intermediate (1). A direct oxidation pathway has also been proposed based on the fact that the oxidation of a feed mixture of DCAC in air produces a different proportion of products than that observed during the oxidation of TCE (1, 3). These pathways are

$$2\,\mathrm{TCE} + \mathrm{O_2}\ \underbrace{\xrightarrow{r_1} 2\,\mathrm{DCAC} \xrightarrow{r_2}}_{r_3}\ \mathrm{Products}, \qquad [1]$$

where r_1 is the rate of formation of DCAC from TCE, r_2 is the rate of conversion of DCAC into products, and r_3 is the rate of direct oxidation of TCE to products. The same products, $COCl_2$, CO_2, CO, HCl, and Cl_2, are formed by both the reactant and the intermediate. They are stable in the thin-film photocatalytic reactor on the time scale of interest (1). The remainder of this paper will document efforts to experimentally measure $(r_1 + r_3)$ and r_2 under a variety of conditions.

Figure 3 shows the DCAC carbon atom product fraction as a function of TCE feed partial pressure. This curve documents that during the photocatalytic oxidation of TCE up to 85% of the carbon atoms from reacted TCE molecules are measured as DCAC molecules in the product mixture. This implies that $r_1 \gg r_3$ and a measurement of $(r_1 + r_3)$ provides a reasonable estimate of r_1. TCE rate data $(r_1 + r_3 \approx r_1)$ and DCAC rate data (r_2) are also shown in Fig. 3 as functions of reactant feed partial pressure.

The differential experiments that generated the TCE rate data were run in a photochemical reactor with a 0.9-mm hydraulic diameter and a 7-mg catalyst coating covering 10 cm^2 of Pyrex substrate. It was operated with a flow of 8.8 liter/min (at 22°C and 500 Torr), establishing an average residence time of 3 ms. The catalyst film was irradiated with 5.3 mW/cm^2 of UV light and the TCE/air feed had a water vapor partial pressure of about 750 mTorr. The DCAC rate measurements came from a similar reactor with a longer catalyst film (covering 25 cm^2 and weighing 13 mg) and operated at the same flow rate. This allowed an 8-ms average residence time for the DCAC/air feed, which contained approximately 900 mTorr of moisture. The TCE rate data comprise

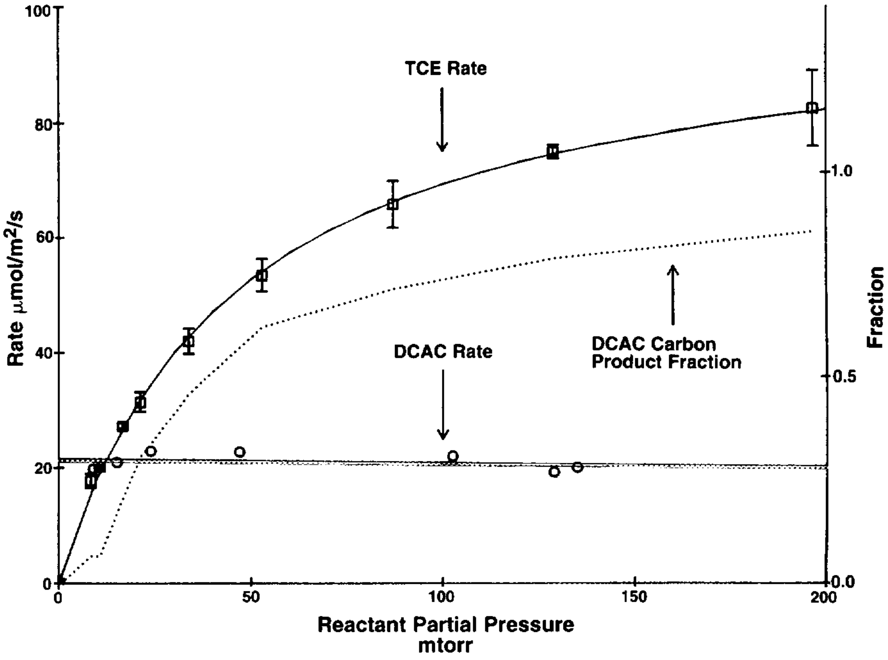

FIG. 3. The rates of reaction of TCE in air and DCAC in air are plotted on the left abscissa. The product carbon atom fraction of DCAC produced during the TCE reaction (dotted line) is plotted against the right abscissa. The ordinate is reactant partial pressure.

36 separate measurements and the tabulated data are available in the literature (3). The curve through the TCE rate data was generated from the Langmuir–Hinshelwood correlation:

$$r = \frac{kP}{(1/K_A) + P}. \qquad [2]$$

Though agreement between the model predictions and the data is not compelling mechanistic evidence, the form of Eq. [2] describes a pseudo-first-order reaction where the reactant is molecularly adsorbed, and products and intermediates are weakly or noncompetitively adsorbed. The rate of the reaction, r, has units μmol/s/m^2-illuminated-catalyst based on the geometric area of the coated Pyrex substrate, and k is the surface reaction rate constant. The light intensity was held constant so irradiation parameters (photon flux and photoefficiency) are implicit in k. The effect of photon flux and photon energy on the rate of the reaction is discussed below. K_A is the adsorption equilibrium constant, and P is the partial pressure of TCE. The values for k and K_A, generated by fitting the model to the data for TCE, are 101 μmol/s/m^2 and 0.022 mTorr^{-1}, respectively.

The DCAC rate data comprise 23 separate measurements and the tabulated data are available in the literature (3). The reaction rate of DCAC is insensitive to reactant feed partial pressure in the range of experimentation. The least-squares line fit to the data had a slope of 0.006, implying a zero-order rate law ($r = k$). The rate constant has a value of 22.5 μmol/s/m^2; irradiation parameters are incorporated in this constant as above. A zero-order rate expression in this concentration range is not unexpected, as DCAC adsorbs strongly relative to TCE (11).

Since DCAC is being created and destroyed in the reacting TCE system, the rates of these reactions must be considered simultaneously; the effect of the presence of the intermediate on the reaction rate of the reactant, and vice versa. As shown by the dotted line in Fig. 3, the proportion of DCAC in the product mixture from the photocatalytic oxidation of TCE increases with the partial pressure of TCE in the feed. DCAC builds up as the reaction rate of TCE increases. Therefore, TCE molecules successfully compete with DCAC molecules for available oxidative species on the catalyst surface.

Figure 4 shows the reaction rates of TCE and DCAC measured for influent solutions of TCE in air, DCAC in air, and mixtures of TCE and DCAC in air. The rate of the DCAC reaction is determined from inlet and outlet concentrations of DCAC, taking into account the amount of DCAC produced in the TCE reaction (estimated from the product fraction curve in Fig. 3). The presence of TCE even in relatively low gas-phase concentrations inhibits the rate of the DCAC reaction, but not the converse. The reaction rate of TCE is independent of DCAC partial pressure despite the fact that DCAC adsorbs more

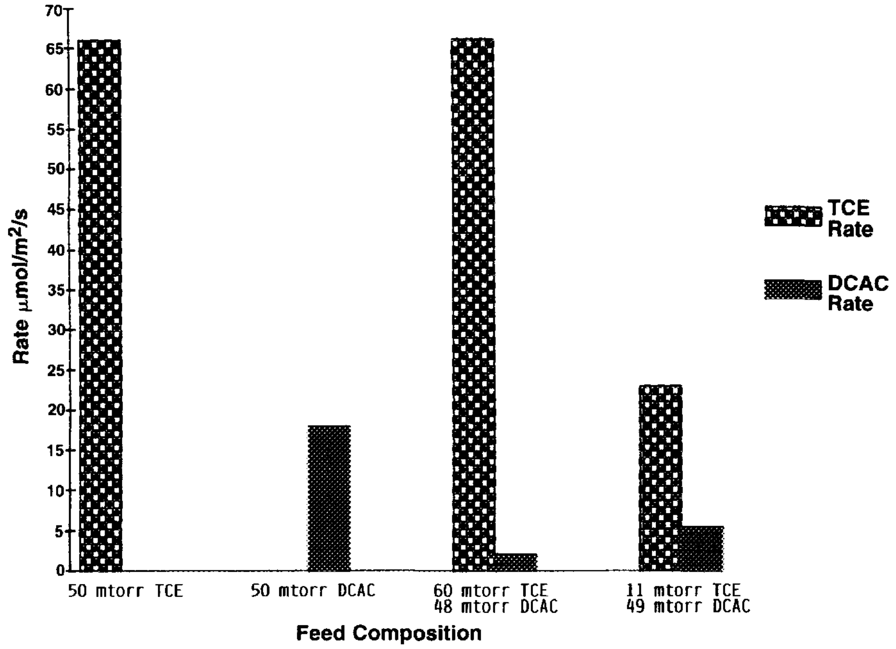

FIG. 4. TCE destruction rate as a function of feed composition: single component TCE feed, single component DCAC feed, and dual component feeds with TCE and DCAC.

strongly. One may conclude from this observation that the two species do not compete for the same adsorption sites.

Water Vapor Partial Pressure Dependence

The relationship between TCE destruction rate and water vapor partial pressure is complex. Figure 5 is a three-dimensional response surface for reaction rate versus water vapor partial pressure and elapsed time. The feed contained a nominal TCE partial pressure of 60 mTorr and the reactor operated with a 4-ms residence time. Examination of this figure reveals that a solution of TCE in dry air provides the highest initial reaction rate, but this rate decreases rapidly during the first hour of operation. A water vapor partial pressure between 500 and 1000 mTorr provides the highest sustainable rate and is, therefore, the optimum humidity range. The initial rate of DCAC destruction is relatively insensitive to water vapor partial pressure (3). This is consistent with expectations, as DCAC adsorbs strongly and may displace water molecules from the catalyst surface while TCE is blocked from active sites by adsorbed water.

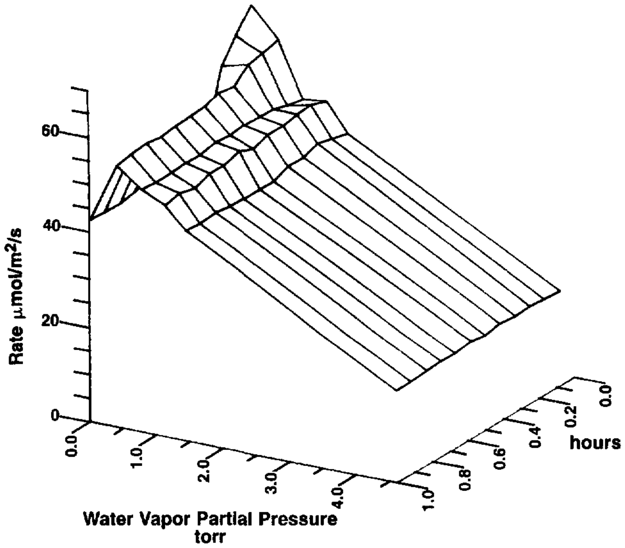

FIG. 5. TCE destruction rate as a function of water vapor partial pressure and elapsed time.

It has been reported that the TiO_2 catalyst quickly and irreversibly deactivates under dry conditions (5, 12). Experiments with a dry feed conducted during this investigation did not confirm these findings. Zero-grade air (<1 ppm moisture) was passed through molecular sieve absorbent pellets to ensure a dry solvent stream. Downstream of the absorbent cartridge, a syringe pump injected TCE into the gas feed. The resultant mixture had a nominal TCE partial pressure of 130 mTorr as it entered a photocatalytic reactor with a hydraulic diameter of 0.9 mm. The reactor was operated for more than 9 h. Figure 6 illustrates that the rate dropped off significantly for the first 2 h before leveling off at a value of about half the initial rate. Further experiments have been run (with zero-grade air but without the absorbent cartridge) continuously for up to 17 h and the results were identical. DCAC and perchloroethylene

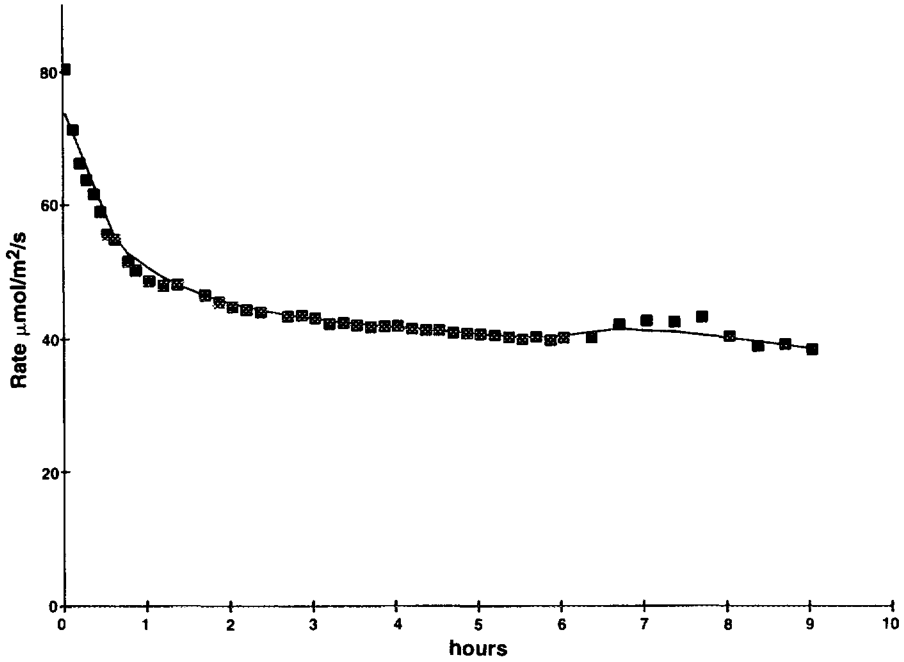

FIG. 6. TCE destruction rate as a function of elapsed time at zero humidity.

(PERC) also exhibited similar behavior in dry feed experiments up to 200 h in duration.

These data contradict the findings of the previous investigators and are surprising. Moisture-derived hydroxyl radicals are a widely postulated oxidative species in gas–solid heterogeneous photocatalysis, and one would expect the eventual depletion of adsorbed water to stop the reaction. Water preadsorbed on the catalyst surface is not a probable explanation as the TiO_2 catalyzed the destruction of about 50 times its weight in TCE during the 9-h run. These observations may be interpreted in terms of a reaction pathway involving moisture-derived hydroxyl radicals contributing to the reaction rate during the first 2 h of the run. After the adsorbed water has been consumed, a steady state involving other reaction pathways is attained. A discussion of reaction pathways for the photocatalytic oxidation of TCE has been published (1). The catalyst regains full activity after exposure to humidity, an observation consistent with this interpretation.

Surface-Bound Oxidants

The reaction proceeds indefinitely at zero humidity; therefore, moisture-derived hydroxyl radicals are not the only active oxidative species. The nature of these additional surface-bound oxidants must be considered. When nitrogen (N_2) is used as the solvent for TCE no reaction occurs, although some investigators have reported the formation of chloroform under these conditions (9). Likewise, a mixture of TCE and water vapor in N_2 is unreactive. Thus, it is apparent that molecular oxygen (O_2) is necessary during the photocatalytic oxidation of TCE. The formation on the irradiated TiO_2 surface of superoxide ions (13) and oxygen adatoms (14) has been discussed in the literature. These species may be responsible for the persistent activity of the catalyst under dry conditions.

Air is the most convenient source of O_2 for the gas–solid heterogeneous photocatalysis of TCE. Air provides oxygen in excess relative to any feed likely to be encountered in a remediation context. The kinetic expression for TCE, therefore, is written as pseudo-zero-order with respect to oxygen, but the dependence of rate on oxygen partial pressure bears investigation. It is desirable to determine whether an optimum oxygen concentration exists, i.e., whether the rate of TCE destruction is higher for oxygen-lean or oxygen-rich solvents relative to air. Figure 7 is a plot of data measuring the rate of destruction of TCE (55 mTorr nominal partial pressure) as a function of oxygen partial pressure. The reaction reaches the maximum rate at an oxygen partial pressure of about 25 Torr and is unchanged up to 105 Torr. Therefore, air is an optimum oxidant, and oxygen does not compete for the same adsorption sites as TCE.

Chlorine (Cl) also plays a part in the photocatalytic oxidation of TCE. Nimlos *et al.* have proposed a chain reaction mechanism involving Cl atoms in the propagation step (2), and the presence of Cl atoms in the reactant molecules accelerates the reaction rate. This is illustrated

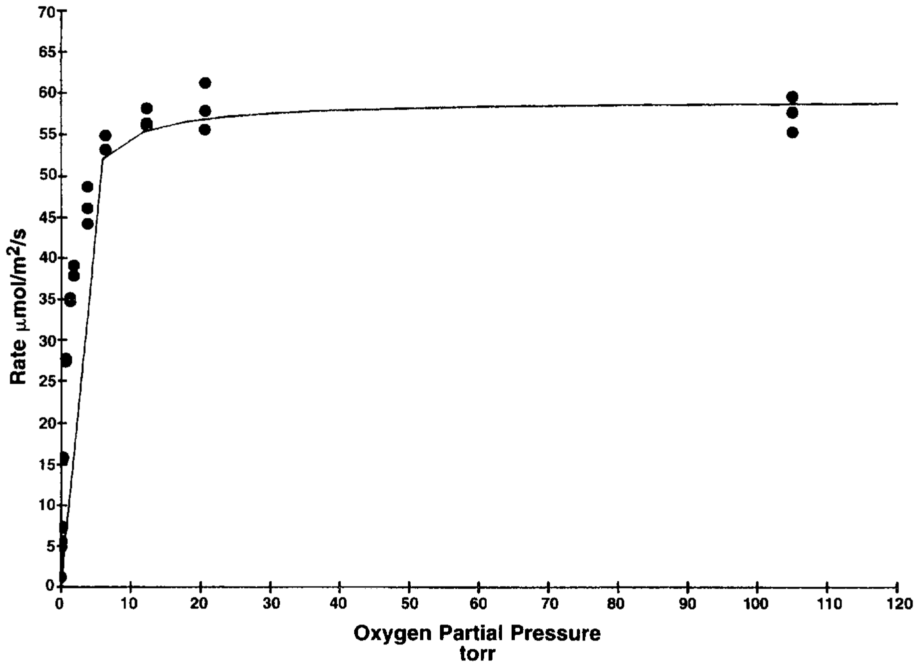

FIG. 7. TCE destruction rate as a function of oxygen partial pressure.

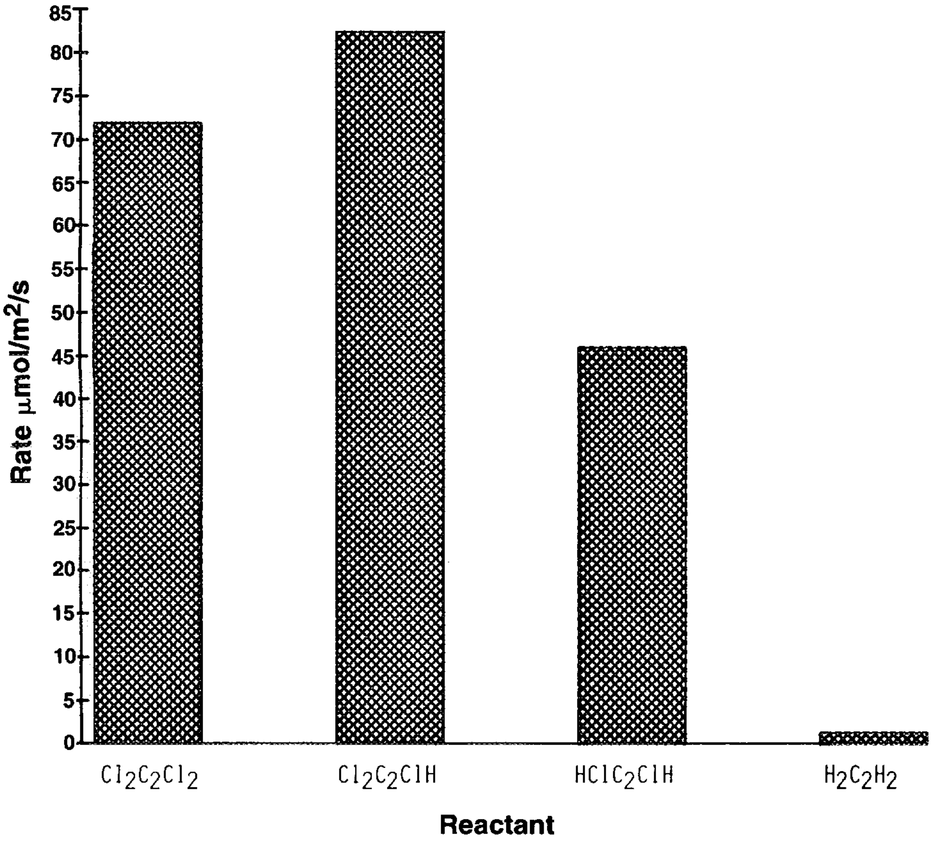

FIG. 8. Initial photocatalytic reaction rates for ethylenes as a function of chlorine substitution.

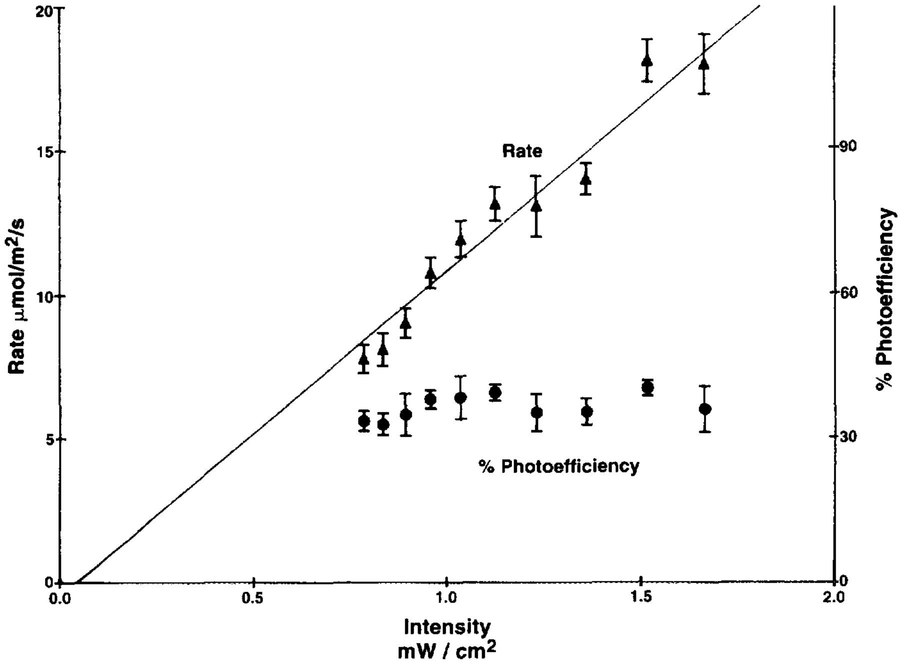

FIG. 9. TCE destruction rate and photoefficiency as a function of UV irradiation intensity.

in Fig. 8, which compares the initial rates of Cl-substituted ethylenes. PERC and TCE react significantly faster than 1,2-dichloroethylene, and ethylene reacts much more slowly than the chlorinated species. Two additional observations point to Cl-propagated oxidation; DCAC is observed in the product mixture from the photocatalytic oxidation of 1,2-dichloroethylene and Cl_2 has been detected during the photocatalytic oxidation of TCE (2). Recent experimentation has also established the formation of Cl_2 during the photocatalytic oxidation of PERC (15).

Light Dependence

Photocatalytic reactors operate in two regimes with respect to light intensity: a first-order regime where the electron hole pairs are consumed more rapidly by chemical reactions than by recombination, and a half-order regime where the recombination rate dominates (16). The operating regime of the thin film photocatalytic reactors was determined experimentally.

The fluorescent black light was used to externally illuminate a flat plate reactor to determine the effect of radiation intensity. Photon flux was controlled by varying the proximity of the lamp to the catalyst surface. Figure 9 illustrates the results of these experiments. The single line is a linear fit to the data. In this light intensity and concentration range (nominal 60-mTorr TCE partial pressure), the photocatalytic reactor operates in the linear regime.

Also plotted in Fig. 9 are points showing photoefficiency as a function of UV intensity. These data correspond to the right-hand ordinate. Photoefficiency is defined as the ratio of the number of molecules of TCE converted to the number of incident photons of sufficient energy. This is a conservative definition, as no allowance is made for photons transmitted or scattered by the catalyst film and changes in oxidation states of greater than one between reactant and products are not accounted for.

The photoefficiency does not vary significantly with UV intensity. This is consistent with expectations in the linear regime, as photons are efficiently harvested, and the recombination of holes and electrons is not a dominant process. For a photoreactor operating in the half-order range, photoefficiency would decrease with increasing intensity.

The values for the photoefficiency shown in Fig. 9 are between 30 and 40% and the maximum value observed in this investigation was 53%. Photoefficiencies greater than unity have been observed at high TCE concentrations (17), and values of up to 4000% have been reported (18). This suggests a chain reaction mechanism. The propagation steps must occur on the surface since evidence suggests gas-phase chemistry is not important (1).

Another factor that might have an impact on the rate of TCE destruction is the wavelength of the UV light. It has been previously reported that variations in photon energy in excess of the band gap of TiO_2 do not effect the product mixture from a photocatalytic reactor (1). An 8-W, low-pressure mercury arc germicidal lamp with a primary spectral output at 254 nm was employed to ascertain the effect of higher energy photons on reaction rate. An increase in reaction rate of about 20% was observed. The rate increase was caused by higher photon flux, rather than by the increase in the energy of individual photons. Germicidal lamps are about 25% more efficient than fluorescent black lights in producing photons with wavelengths less than 385 nm on a per watt basis (19). Thus, the use of the more efficient lamp in a photocatalytic reactor operating in the linear intensity regime leads to the observed increase in rate, as predicted by the rate versus intensity curve shown in Fig. 9. One may conclude that variations in photon energy in excess of the band gap of TiO_2 do not affect the rate of the photocatalytic reaction.

CONCLUSIONS

Several sets of units are useful in describing the rate of a heterogeneous photocatalytic reaction. The rate expressed in units of μmol/s/m^2-illuminated-catalyst based on the geometric area of the coated Pyrex substrate provides coating-to-coating repeatability in the thin-film reactors and can be used to compare rates from different laboratories. The units μmol/J are useful from an engineering standpoint, as they can be used to compare rates from reactors with different catalyst configurations and light sources.

Under conditions appropriate for differential kinetic analysis, a Langmuir–Hinshelwood rate expression was developed. This equation closely predicts the reaction rate of TCE as a function of inlet TCE partial pressure. The rate of photocatalytic oxidation of the intermediate, DCAC, was determined to be independent of DCAC inlet partial pressure in the regime investigated. The presence of TCE inhibits the reaction of DCAC, but not the converse. This indicates that TCE successfully competes with DCAC for available oxidative species, and TCE and DCAC do not compete for the same adsorption sites.

A water vapor partial pressure between 500 and 1000 mTorr provides the highest sustainable rate for the TCE reaction. The reaction proceeds indefinitely, at a reduced rate, under dry conditions. The significance of this observation relative to the involvement of hydroxyl radicals in the oxidative chemistry is not clear, but other oxidative species are involved. Molecular oxygen is a reactant during the photocatalytic oxidation of TCE and air is an optimum oxidant, as O_2 does not compete with TCE for the same adsorption sites. Chlorine is also available to play a part in the photocatalytic oxidation of TCE and the experimental evidence supports the existence of a Cl-propagated chain reaction occurring on the surface. The photocatalytic reactors used in this investigation operated in the linear range with respect to light intensity, and variations in photon energy in excess of the band gap of TiO_2 do not affect the rate of the photocatalytic reaction.

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