# Trichloroethylene-Promoted Photocatalytic Oxidation of Air Contaminants

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The prospects for photocatalytic purification and treatment of air depend centrally on finding conditions for which the apparent photoefficiency for contaminant disappearance is near or above 100%. We recently demonstrated that destruction of a low photoefficiency contaminant, toluene, by addition of a high photoefficiency compound, trichloroethylene, could raise the toluene photoefficiency to provide 100% conversion in a single pass, fixed bed illuminated catalyst, using a residence time of about 5–6 ms. The present paper establishes the generality of this TCE enhancement of contaminant rate and photoefficiency by examining the photocatalytic oxidation of various common contaminants at $50 \text{ mg/m}^3$ in air, including alcohols, aldehydes, ketones, aromatics, and chloroalkanes using near-UV-illuminated titanium dioxide powder in a flow reactor, in the absence and presence of trichloroethylene (TCE). Compounds exhibiting TCE rate promotion were toluene, ethylbenzene, *m*-xylene, methyl ethyl ketone (MEK), acetaldehyde, butyraldehyde, methyl *tert*-butyl ether (MTBE), methyl acrylate, 1,4-dioxane, and hexane. Rate inhibition by TCE was exhibited for acetone, methylene chloride, chloroform, and 1,1,1-trichloroethane. TCE presence had almost no effect on the benzene and methanol rates. Butanol and vinyl acetate single component conversions were 100% under our standard low flow rate conditions; increasing the flow rate quenched TCE conversion in the presence of butanol, and therefore no TCE enhancement effect could be noted. © 1997 Academic Press

## INTRODUCTION

Recent process economic estimates by Miller and Fox (1) indicate that photocatalytic treatment of lightly contaminated air is commercially attractive only for conversions of high photoefficiency reactants such as trichloroethylene (TCE) or methanol/ethanol. In contrast, air contaminants exhibiting lower apparent photoefficiency (below 20–30%) represented by air contaminated with fuel components (benzene, toluene, xylenes) or paint components (xylenes, odor compounds, etc.) were found to compare less favorably to incinerative and carbon adsorption processing.

Gas–solid photocatalytic oxidation of air contaminants has now been demonstrated for a broad range of contaminant classes. However, the photoefficiency for such

conversions are often mediocre. For example, Berman and Dong (2) reported apparent photoefficiencies of less than 15% for toluene, benzene, isooctane, hexane, and 1,2-dichloroethane and less than 1% for trioxane, carbon tetrachloride, methylene chloride, chloroform, methyl chloroform, and vinyl chloride. Since most candidate contaminants demonstrated to be destroyed by photocatalytic air treatment show low photoefficiencies when fed individually in air, the commercial future of this potential process chemistry depends centrally on finding conditions which raise the apparent photoefficiencies of pertinent contaminants to the order of 100%.

A potential method for improving the photoefficiencies of less reactive contaminants was first indicated by Berman and Dong (2). They noted that "a novel method for the sensitization of photocatalytic heterogeneous reactions" was to add TCE to air contaminated by the compound of interest. In a static photoreactor, these authors found that the time for 90% conversion of iso-octane, methylene chloride, and chloroform could be reduced by one-third to one-half of the original times of 22.5, 550, or 720 s, respectively.

Luo and Ollis (3) demonstrated with toluene that this type of enhancement could lead to 100% conversion in a single pass reactor. Toluene is the most important emission contributor to both ozone formation and noncancer chemical risks in current air emissions in the United States (4). Toluene-only air feeds gave 10–15% conversion at pseudosteady state, whereas for toluene feed levels below about $100 \text{ mg/m}^3$ in the presence of $250–750 \text{ mg/m}^3$ of TCE, total conversion of both compounds was achieved initially during a single pass flow through a thin powder layer reactor with a 5-ms residence time in the illuminated zone.

TCE is not unique in providing reaction rate enhancement. Sauer *et al.* (5) recently demonstrated that two other chlorinated olefins, perchloroethylene (PCE) and trichloropropene (TCP), exhibit very high photoefficiencies for individual conversions, and when each was fed with toluene, the conversion of the latter was raised again to 100%. These two individual chlorocarbons in air display unusually high photoefficiencies during their own photocatalytic oxidation, as does TCE.

Berman and Dong (2) suggested that "the function of the added (TCE) sensitizer is to provide the radicals required

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to initiate chain propagated destruction of the pollutant." We subsequently proposed a specific mechanism involving a new activation path for toluene: that of chain transfer from active chlorine in the chlorocarbon oxidation chain (3).

To explore the generality of this substantial enhancement effect, we have examined whether TCE could enhance the rate of conversion of a broad range of common air pollutants: alcohols, aldehydes, ketones, aromatics, and chloroalkanes. We screened 18 pollutants guided by the EPA priority lists which identify the most important air pollutant contributors to three distinct types of undesirable risks: ozone formation promoters, noncarcinogenic air toxics, and carcinogenic air toxics (4).

From these conversion data, we attempted to discern the dominant mechanism by correlations constructed for three assumed slow step cases (6):

(a) adsorbed pollutant reacts directly with a surface species other than hydroxyl or chlorine radical (e.g., holes $(h^+)$, anion vacancy, etc...),

(b) adsorbed pollutant reacts directly with surface radicals (hydroxyl or chlorine),

(c) incoming pollutant reacts directly with adsorbed (hydroxyl or chlorine) radicals.

The better correlations obtained were (a) in the absence of chlorine and (b) or (c) in the presence of chlorine; these correlation results appear in Figs. 1a–1c.

As the latter correlations support participation of chlorine radical in a slow step, the present paper compares gas phase chlorine mechanisms of oxidation vs pollutant structure to further test the data consistency regarding chlorine radical participation and discusses current nonhydroxyl possibilities in the absence of chlorine. As we have recently argued that photocatalyst deactivation is a common phenomenon (7), we note also evidence of deactivation in the presence as well as absence of chlorine. The pace of deactivation depends strongly on reactant structure as well as chlorine presence.

## EXPERIMENTAL

The photocatalyzed degradation of trace levels of organic compounds in air was carried out using near-UV-illuminated titanium dioxide (anatase) powder in a flow reactor, designed previously (8) to study the photocatalytic oxidation kinetics of acetone, 1-butanol, formaldehyde, and *m*-xylene and also used for our previous chlorine enhancement work (3, 5).

The Degussa P25 TiO$_2$ catalyst was characterized by the manufacturer as having a primary particle diameter of 30 nm, a surface area of 50 m$^2$/g, and a crystal structure of mostly anatase. The particles were spherical and nonporous, with stated purity of >99.5% TiO$_2$. Stated impurities included Al$_2$O$_3$ (<0.3%), HCl (<0.3%), SiO$_2$ (<0.2%),

and Fe$_2$O$_3$ (<0.01%). This catalyst was used as supplied, without pretreatment. The model contaminants hexane and chloroform were of HPLC grade, the acetaldehyde of reagent grade, and the acetone and methanol of certified grade, all supplied by Fisher. The methyl *tert*-butyl ether, 2-butanone, and 1-butanol used were of HPLC grade, and 1,1,1-trichloroethane, butyraldehyde, vinyl acetate, methyl acrylate, and trichloroethylene were above 99% purity and were supplied by Aldrich. The pressurized gases (air, helium, hydrogen) were scientific grade, supplied by a local vendor.

A 100-W black light (UVP) lamp provided vertical near-UV illumination at 300–400 nm. All experiments were performed at 22–24°C.

### Description of a Typical Run

The contaminant feed gas reservoir was alternately evacuated and refilled to 1 atm at least three times with scientific grade air in order to remove any contaminants from previous runs. Suitable amounts of liquid contaminant and deionized water (for humidification) are injected into the reservoir sample port. To aid vaporization, a heat gun warms up the reservoir lightly for about 30 min. Following complete vaporization of both liquid injections, the reservoir is filled with additional air up to a final pressure of 2 atm. This pressure is sufficient to provide the desired reactor gas flow rates over a full day. An air stream directly from the air tank and a gas mixture stream from the lightly pressurized reservoir are mixed continuously and passed through mass flow sensors and controllers which communicate with the mass-flow controller unit (Linde FM4574). A broad range of contaminant feed concentrations can be examined for flow reactor studies by variation of the two stream rates. During reaction, the flow mixture passes downward through the illuminated catalyst layer of the photoreactor. The photoexcitation light source is placed 1 cm above the reactor window, about 9 cm above the catalyst bed. Two lateral ports allow capture of sample aliquots of either the feed or the product stream. All vapor samples are analyzed by gas chromatography (Perkin-Elmer Sigma 1) operating with a flame ionization detector (FID). An SS Alltech column is used with 0.1% AT-1000 on 80/100 carbograph packaging.

A fresh 25-mg sample of TiO$_2$ is spread uniformly over the surface of the porous fritted glass plate at the start of each run, providing a 0.5 mm thick TiO$_2$ powder layer and the same TiO$_2$ surface area for each run. The initial inlet concentration is measured. Then, we allow a "dark" period during which the contaminated air feed passes through the bed without illumination until the outlet concentration equals the inlet. This pretreatment is required because both the catalyst and the fritted glass have considerable surface areas. Consequently, an appreciable time, varying with each pollutant from minutes to hours, is needed to reach
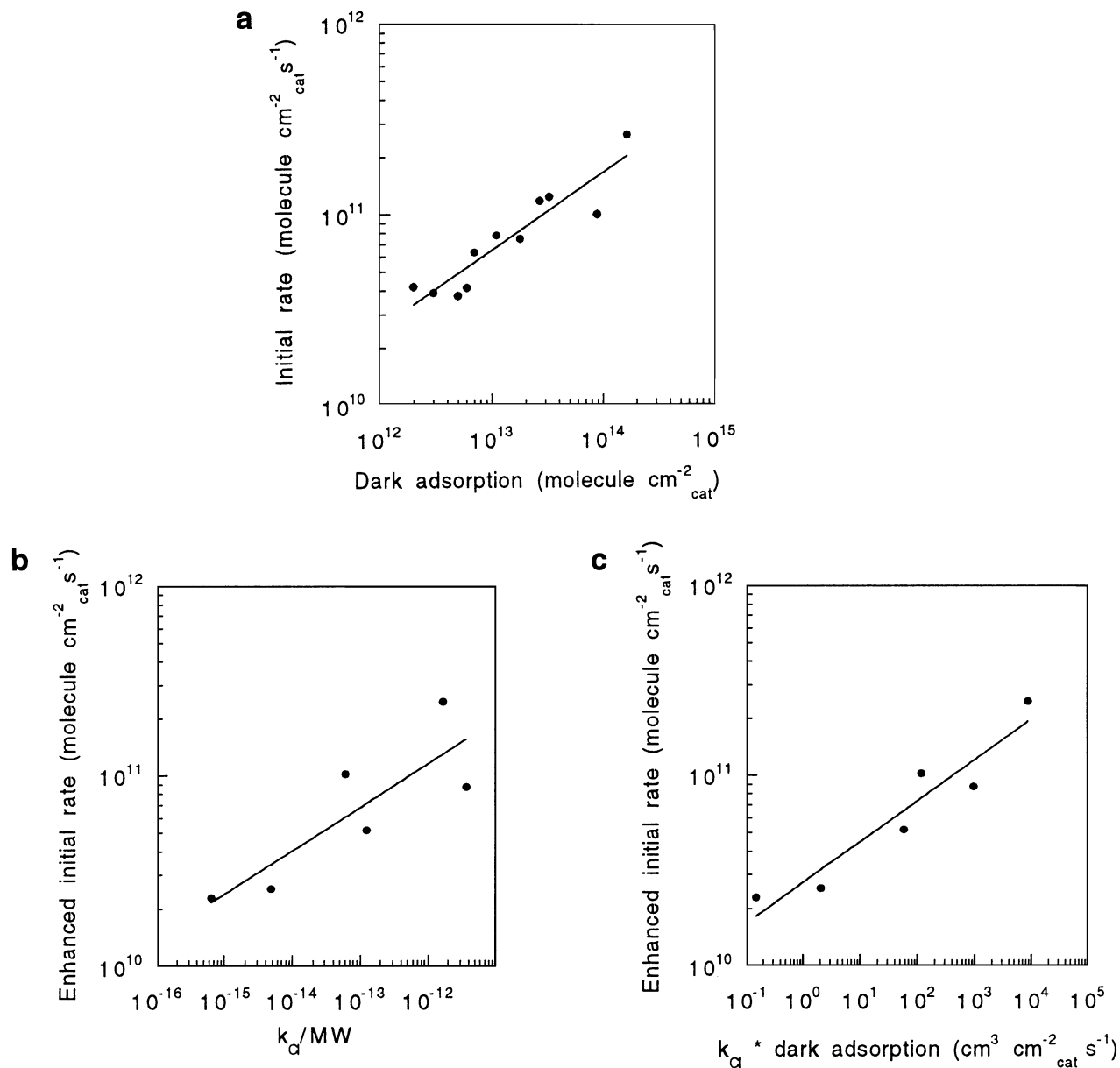
**FIG. 1.** (a) Initial rate in the absence of TCE for each compound vs dark adsorption. (b) Enhanced initial rate (TCE added) vs literature second order chlorine rate constants divided by pollutant molecular weight. (c) Enhanced initial rate (TCE added) vs the product of second order chlorine rate constant time the dark adsorption.

gas–solid dark equilibrium. When that condition is achieved, the light is turned on and gas samples are taken every 5 to 30 min. The irradiation is maintained for 4–6 h. For our screening study, a total gas flow rate of 0.82 cm³/s is used composed of 0.56 cm³/s of pure air mixed with 0.26 cm³/s contaminated reservoir flow.

### RESULTS

*Experimental Conditions*

Relative humidity, 7% (1000 mg $H_2O/m^3$)
Mass of $TiO_2$, 25 mg

Apparent $TiO_2$ bed thickness, 0.5 mm ($TiO_2$ apparent compacted density, 0.150 g cm⁻³; $TiO_2$ density, 3.8 g cm⁻³)
Actual bed thickness, 21 $\mu$m
Illuminated thickness range, 2–60 $\mu$m (9)
Residence time range, 0.2–6.3 ms

For each of the 18 compounds screened for possible photocatalytic initial rate enhancement by TCE, two transient experiments were run: degradation of the pollutant (50 mg/m³) in air in (i) the absence and (ii) the presence of TCE (290 mg/m³).

For both experiments, we measured or noted pollutant conversion vs time in absence of TCE, catalyst deactivation

and any change of color, and intermediates detected by flame ionization. For the second experiments, we also determined TCE conversion vs time in the presence of the pollutant.

### Reactivity and Enhancement of Molecular Structure

*Aromatics.* For the aromatics tested the reaction rate is, in increasing order: benzene, toluene, ethylbenzene, and *m*-xylene. The conversion rate for each aromatic except benzene is substantially enhanced by the presence of TCE. Toluene, ethylbenzene, and *m*-xylene have similar structures (methyl and ethyl groups attached to the ring) and also exhibit similar profiles of conversion vs time (example given for ethylbenzene in Fig. 2). In these three cases, deactivation is evident for conversion of the pollutants in the presence or absence of TCE, as well as for the conversion of TCE itself in the presence of pollutant. With benzene (Fig. 3), however, the TCE conversion vs time is always 100% for the nearly 5-h run, and enhancement is barely noticeable (10% improvement only for the first few minutes). The data in Fig. 2 have not reached steady state; the conversion vs time is still dropping slowly due to TiO$_2$ deactivation. Consequently, all TCE enhancement tests involved comparisons of the maximum initial reaction rate at early times, before any deactivation becomes important. No gas phase intermediates were detected for any aromatic case. After photochemical degradation of toluene, ethylbenzene, and *m*-xylene as either single components or in mixed feeds with TCE, the partially deactivated catalyst was light brown, whereas no color change was seen with benzene.
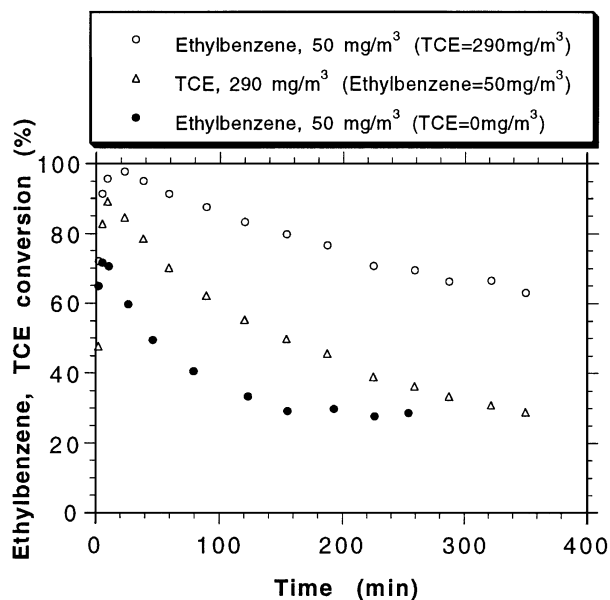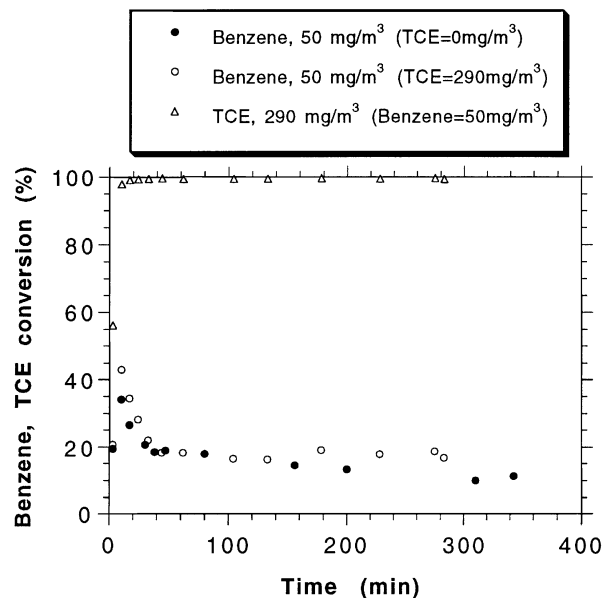


**FIG. 3.** Conversion vs time for benzene and TCE (single feed and cofeed).

*Aldehydes.* The conversions of both acetaldehyde and butyraldehyde (Fig. 4) are very high (near 97–98%). These conversions in the presence of TCE are brought up to 100%. The conversion of TCE, however, is depressed to 90%. No deactivation or change of TiO$_2$ color is noted.

*Alcohols.* 1-Butanol (Fig. 5) reacts similarly to butyraldehyde. Methanol conversion is lower then 1-butanol, and its rate is depressed by the addition of TCE. TCE
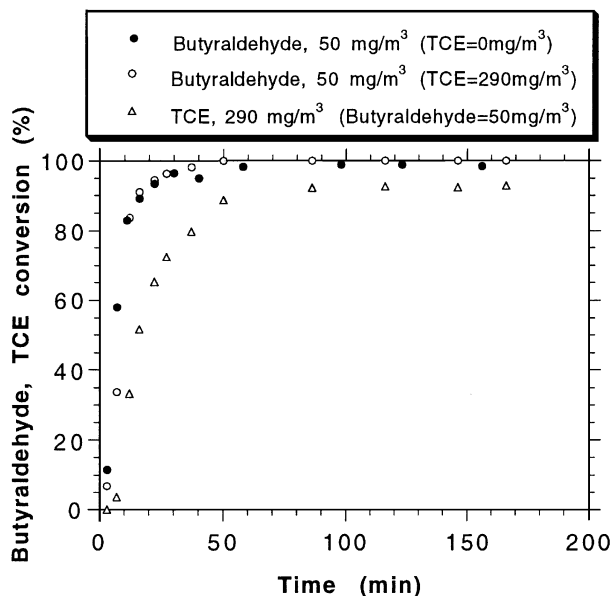


**FIG. 2.** Conversion vs time for ethylbenzene and TCE (single feed and cofeed).



**FIG. 4.** Conversion vs time for butyraldehyde and TCE (single feed and cofeed).

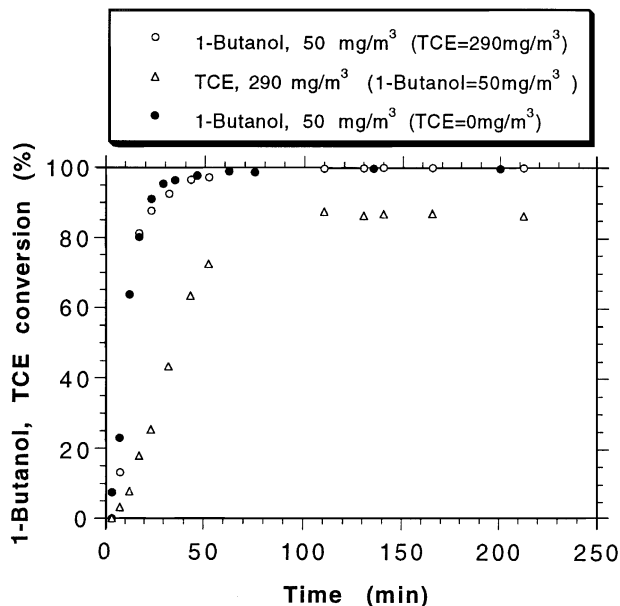**FIG. 5.** Conversion vs time for 1-butanol and TCE (single feed and cofeed).



**FIG. 7.** Conversion vs time for methyl acrylate and TCE (single feed and cofeed).

conversion is depressed by 10–15% in the presence of either alcohol. No deactivation or change of color of TiO₂ is noted over the nearly 4-h run.

*Ketones.* The individual conversions of acetone (Fig. 6) and 2-butanone are the lowest of the oxygenates examined. TCE addition enhances the 2-butanone (MEK) rate, but depresses acetone conversion at the apparent steady state. TCE conversion is depressed by 15% in the presence of 2-butanone and by only 2% in the presence of acetone.
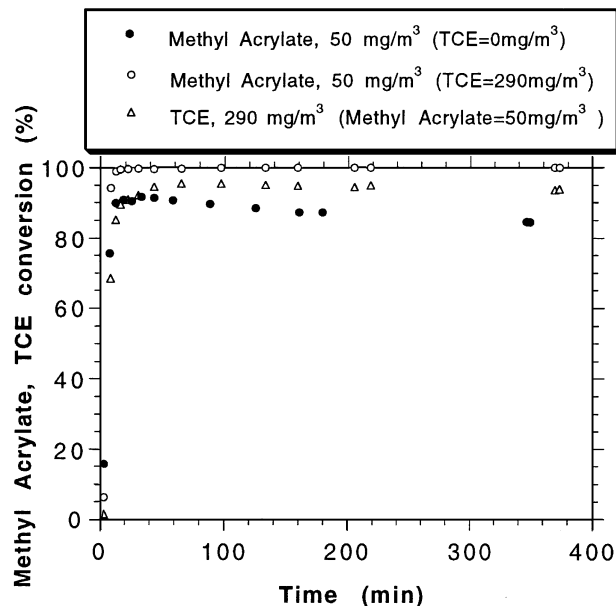


**FIG. 6.** Conversion vs time for acetone and TCE (single feed and cofeed).

*Other oxygenates.* The individual conversions of three other oxygenated compounds (MTBE, methyl acrylate (Fig. 7), and 1,4 dioxane) are high (>92%) and are enhanced by the presence of TCE. TCE conversion was again lowered by 7 to 15% in the presence of these oxygenates. For the final oxygenate examined, vinyl acetate, the single component conversion was 100% under reference conditions, so TCE enhancement was not testable.

*Chloroalkanes.* Chloroalkanes are quite stable relative to aromatics, chloroolefins, and oxygenates. The individual conversions of the three chloroalkanes tested (chloroform, methylene chloride, and 1,1,1-trichloroethane) were low to very low (15% at most at steady state), and their conversions were depressed by TCE presence (methylene chloride is shown as an example in Fig. 8), whereas TCE conversion remained at 100% and exhibited no deactivation.

### Increasing Flow Rate in Order to Lower Conversion

We increased the flow rate from 0.83 to 3 cm³/s in order to produce lower conversion per pass but presumably leave the active center concentrations relatively constant due to a constant illumination and feed concentration. At this higher flow rate, we reexamined 2-butanone, butyraldehyde, 1-butanol, and MTBE, each alone and in the presence of TCE. We chose these four compounds because their conversions measured previously at lower flow rate, alone and in the presence of TCE, were higher than 90% (thus enhancement could not easily be discerned) and because their second order gas rate constant values ($k_{Cl}$) are known.

The conversion of each individual pollutant, MTBE, 2-butanone, 1-butanol, and butyraldehyde, now fell in the
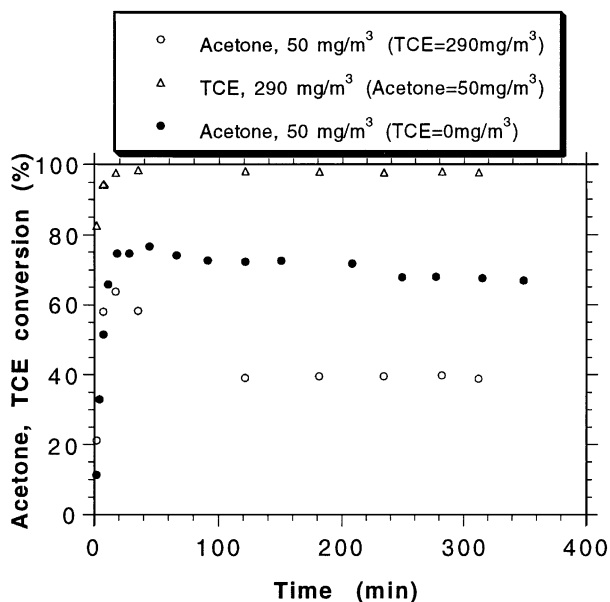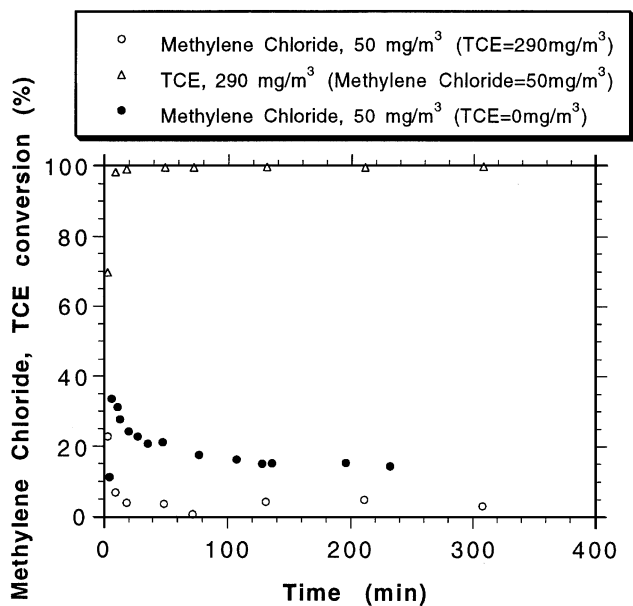
**FIG. 8.** Conversion vs time for methylene chloride and TCE (single feed and cofeed).

range 40–80% instead of the earlier reported 90+% for a flow rate of 0.83 cm$^3$/s. It is therefore possible to determine enhancement or inhibition of these pollutants in the presence of TCE. The conversion of MTBE and 2-butanone is noticeably enhanced (by over 20%) by the presence of TCE, whereas the conversion of *n*-butanol and butyraldehyde is unchanged by the presence of TCE at this higher flow rate.

Figure 9 presents the conversion of TCE in the presence of each of 4 pollutants vs the pollutant dark adsorption.
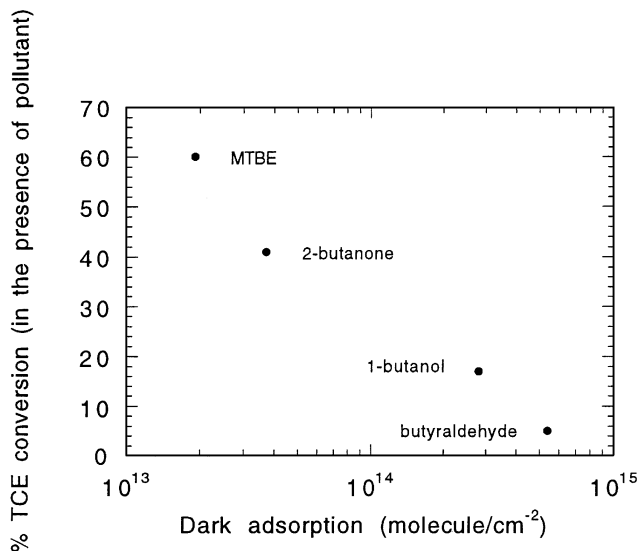


**FIG. 9.** TCE conversion in the presence of pollutant vs pollutant dark adsorption.

Assuming there are 5e+14 adsorption sites/cm$^2$ of TiO$_2$, the pollutant coverages range from 4 to 100%. The TCE conversion rate, known to be very fast when fed alone, is here greatly inhibited. This results show that once the TiO$_2$ surface is covered with adsorbed pollutant, TCE has difficulty displacing it and being degraded. If TCE is degraded only slowly, few Cl· radicals are produced, and no or little enhancement via our presumed chain transfer would be observed as found for 1-butanol and butyraldehyde. However, for a pollutant dark coverage of less than 10%, TCE is still degraded at a rate sufficient to demonstrate chlorine enhancement, as seen for the MTBE and 2-butanone results.

In our earlier toluene–TCE study, enhancement was found only for toluene ≤90 mg/m$^3$ when TCE was fixed at 226 mg/m$^3$. Above this value, toluene rate fell sharply to the toluene only values, and TCE conversion dropped to zero. This result suggested a kinetic and/or thermodynamic influence:

(i) kinetic: excess toluene consumed chlorine radicals and shut down the TCE oxidation;

(ii) thermodynamic: excess toluene covered available surface sites and thereby prevented TCE adsorption.

Data from the present study (Fig. 9) indicates that as the (dark) coverage of pollutant on the surface increases, the TCE conversion decreases sharply, and chlorine rate enhancement falls also. This coupling between higher pollutant levels and diminished or extinguished chlorine promotion appears to be general. Further tests are needed to assign the importance of reactant quenching of TCE rate (kinetic) vs reactant coverage (thermodynamic) influences in diminishing the chlorine enhancement effect.

### Effect of Hexane Addition on Toluene Photocatalytic Oxidation

Gasoline-contaminated soil can be remediated by air or steam stripping to produce an air or air/water vapor stream containing not only BTEX compounds (benzene, toluene, ethylbenzene, and xylenes) but also C$_5$–C$_8$ aliphatics as Gratson *et al.* (10) indicate.

Toluene conversion was noted earlier here and in Ref. (3) to be enhanced by TCE addition. To explore how an aliphatic contaminant presence would affect the photocatalytic oxidation of toluene, we performed experiments including air fed with toluene (T), hexane (H), and/or TCE in the following combinations: T, T/TCE, T/H, T/H/TCE, H, and H/TCE (Table 1).

Hexane conversion is enhanced by TCE addition. The presence of hexane does not substantially slow toluene disappearance (compare rows 1 and 3 of Table 1), and enhancement of toluene conversion by TCE still occurs even in the presence of hexane (compare row 5 to row 2 data). These encouraging results indicate that the

presence of aliphatic compounds in BTEX contaminated air streams does not eliminate the chlorine enhancement of BTEX photocatalytic oxidation, and that these stable saturated hydrocarbons are themselves susceptible to such enhancement.

## Deactivation and Intermediates Observed

Table 2 summarizes observations concerning the presence or absence of deactivation and intermediates during these screening experiments. For all aromatics, two chloroalkanes, and hexane, a substantial $TiO_2$ deactivation is noted, whereas only 2 (acetone, methyl acrylate) of the 10 oxygenates tested caused appreciable catalyst activity loss. Different results can be observed at higher concentrations. For example Péral and Ollis (8) reported $TiO_2$ deactivation for 1-butanol at a feed concentration of 260 mg/m$^3$. Only photooxidation of the branched aromatics (toluene, ethyl benzene, and m-xylene) as either single components or in mixed feeds with TCE led to a brown $TiO_2$.

Intermediates are reported for butyraldehyde, 2-butanone, 1-butanol, and MTBE. For butyraldehyde, and 2-butanone, the same intermediate was detected in mixed feeds with TCE. This intermediate has not been identified, but has a high residence time in the GC column. During the first 40 min or pre-steady state, the 1-butanol, single compound exit concentration slowly decreased to zero, and two intermediate product peaks were present; one was butyraldehyde and the second one is a butyraldehyde oxidation product. Both intermediates disappeared when 1-butanol conversion reached 100%. The same two intermediates were also present when 1-butanol was run in air in the presence of TCE and also disappear once 1-butanol conversion reached 100% (after about 40 min of reaction). Three unidentified intermediates were detected during MTBE photooxidation.

### TABLE 1

**Hexane Effect on Toluene Photocatalytic Oxidation and Enhancement by TCE**

| Inlet | | | % Conversion of A in the presence of B | |
|---|---|---|---|---|
| Toluene, 50 mg/m$^3$ (13.3 ppm) | Hexane, 50 mg/m$^3$ (10.6 ppm) | TCE, 290 mg/m$^3$ (53.9 ppm) | From (highest) | To (at 270 min) |
| A | | | 76 | 12 |
| A | | B | 97 | 36 |
| A | B | | 69 | 13 |
| B | A | | 23 | 3 |
| A | B | B | 95 | 41 |
| B | A | B | 68 | 13 |
| | A | | 62 | 50 |
| | A | B | 81 | 75 |

### TABLE 2

**Results for Each of the 18 Compound Screened**

| Family | Name | Detected intermediates (no TCE/TCE) | Deactivation/color change (no TCE) | Deactivation/color change (TCE) |
|---|---|---|---|---|
| Aromatics | Benzene | No/No | Yes/No | Yes/No |
| | Toulene | No/No | Yes/Yes | Yes/Yes |
| | Ethylbenzene | No/No | Yes/Yes | Yes/Yes |
| | m-Xylene | No/No | Yes/Yes | Yes/Yes |
| Ketones | Acetone | No/No | Yes/No | Yes/No |
| | 2-Butanone | No/Yes | Slight/No | Slight/No |
| Aldehydes | Acetaldehyde | No/No | No/No | No/No |
| | Butyraldehyde | Yes/Yes | No/No | No/No |
| Alcohols | Methanol | No/No | No/No | No/No |
| | 1-Butanol | Yes/Yes | No/No | No/No |
| Other oxygenates | Methyl-tert-Butyl-Ether | Yes/Yes | Slight/No | Slight/No |
| | Methyl acrylate | No/No | Yes/No | No/No |
| | Vinyl acetate | No/No | No/No | No/No |
| | 1,4 Dioxane | No/No | No/No | No/No |
| Alkanes | Hexane | No/No | Yes/No | Slight/No |
| Chloroalkanes | Methylene chloride | No/No | Yes/No | Yes/No |
| | Chloroform | No/No | Yes/No | Yes/No |
| | 1,1,1-trichloro-ethane | No/No | No/No | No/No |
| Chlorinated hydrocarbon | TCE | No | No/No | |

*Note.* Column 1, if intermediates were detected in the absence of TCE/ in the presence of TCE; column 2, if $TiO_2$, deactivation/color change, was noted in the absence of TCE; column 3, if $TiO_2$, deactivation/color change, was noted in the presence of TCE.

### DISCUSSION

Previous gas–solid photocatalysis literature on individual pollutants has ascribed oxidation destruction to pollutant attack by hydroxyl radicals (11, 12), holes (13), photoproduced dioxygen anions (14), or oxygen vacancies (15). Our study ((6) and Fig. 1a) with 18 compounds in the absence of TCE indicates that reaction with a nonhydroxyl active center is most likely. A more fundamental correlation to be attempted would be that of surface second order rate constant for hole or anion vacancy attack vs rate under standard conditions. As such surface second order rate constants are not yet available, we must await this test.

The correlations in Figs. 1b and 1c indicate that chlorine radical attack *is* involved in the likely slow step with TCE present, and in the following discussion we review aspects of chlorine radical oxidation reactions as a function of reactant molecular structure to establish further consistency with the chlorine radical argument.

Catalyst deactivation does occur, but at rates which depend upon both pollutant structure and chlorine (TCE)

presence or absence. A final section discusses the relation of deactivation to chlorine.

### Enhancement and Molecular Structure

*Aromatics.* Wallington *et al.* (16) noted larger rates differences between reaction of atomic chlorine with benzene vs toluene, and found that the reactivities of the three xylene isomers are essentially indistinguishable and twice that of toluene. They therefore suggested that reaction of chlorine atoms with the substituted aromatics proceeds exclusively through hydrogen abstraction from the alkyl groups to make benzyl radicals, in sharp contrast with hydroxyl radical selectivity. This result is consistent with our experimental data since benzene is not enhanced by TCE (and thus chlorine addition), whereas the three substituted aromatics (toluene, ethylbenzene, and *m*-xylene) all exhibit substantial rate enhancement.

Deactivation of $TiO_2$ vs time is observed for the conversion of the aromatic pollutant in the presence and in the absence of TCE, and for the conversion of TCE itself in the presence of toluene (Fig. 2). After toluene degradation, Luo and Ollis (3) found, by mass spectrum analysis of a methanol extraction from used $TiO_2$ catalyst, the major adsorbed intermediate to be benzoic acid, which they believed is the benzaldehyde oxidation product. The obvious inability to form benzoic acid during photocatalytic degradation of a mixture of benzene and TCE in air would explain why the catalyst does not deactivate (100% TCE conversion). Also this result is consistent with the catalysts' change of color (Table 2) observed after reaction with toluene, ethylbenzene, and *m*-xylene, fed alone or with TCE, but not following reaction with benzene or benzene and TCE.

*Aldehydes.* For homogeneous photochemical oxidation in the presence of chlorine atoms, Niki *et al.* (17) argued the following chain propagation reactions to occur:

$$Cl\cdot + CH_3CHO \rightarrow CH_3CO\cdot + HCl$$
$$CH_3CO\cdot + Cl_2 \rightarrow CH_3CClO + Cl\cdot.$$
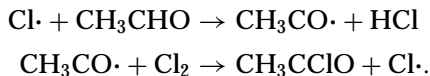
Our experimental results do not test rate enhancement in the case of the aldehydes at low flow rate because of their inherent high reactivity in the absence of TCE. Butyraldehyde was tested at higher flow rate and rate enhancement was not found, perhaps due to high butyraldehyde coverage (see earlier flow rate discussion).

*Alcohols.* The reactant attack by Cl atoms in homogeneous photochemical oxidation appears to occur exclusively at the C−H bonds (12). This mechanism of enhancement has yet to be demonstrated for alcohols here, in as much as a high dark coverage may have been sufficient to block most TCE from the surface and greatly depress TCE conversion (from 80 to 17%) and thus chlorine atom generation as well.

*Ketones.* Our experimental data indicate a low photocatalytic reactivity of acetone and butanone relative to alcohols and aldehydes.

The addition of TCE inhibits the conversion of acetone, which contains only $\alpha$-carbon hydrogens, while the rate of 2-butanone is enhanced by TCE.

*Alkanes.* At much higher hydrocarbon pressures (hydrocarbon 30%, oxygen 20%, and a carrier gas 50%) both normal and branched alkanes, from ethane to octane, are photo-oxidized at room temperature into ketones and aldehydes at a selectivity of 50–80% on the surface of $TiO_2$ (18). In our experiment, the conversion of hexane is comparable to those for aromatics, and no intermediates were detected for our 50 mg/m$^3$ feed concentration.

*Chloroalkanes.* Analogous to the alkanes, chlorine radical reactions with gaseous chloroalkanes proceed via H atom abstraction:

$$Cl\cdot + CH_3Cl \rightarrow HCl + \cdot CH_2Cl.$$
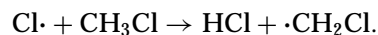
None of the chloroalkane rates are enhanced by TCE addition, consistent with the very low second order chlorine/chloroalkane rate constants (almost four orders of magnitude smaller than for oxygenates) (19).

### SUMMARY

- All photocatalyzed degradation rates of branched aromatics are enhanced by TCE addition; benzene rate enhancement is negligible. A combination of chlorine radical preferential attack on side chain vs aromatic ring and of a low benzene vs branched aromatic surface coverage are believed to contribute to the strong difference in reactivities.

- Among the oxygenates, TCE enhancement is demonstrated for 2-butanone, MTBE, methyl acrylate, and 1,4-dioxane. Acetone and methanol conversions are partially inhibited. Vinyl acetate, 1-butanol, acetaldehyde, and butyraldehyde are sufficiently reactive to give nearly 100% conversion as single component feeds, so TCE enhancement is not tested seriously under our standard 50 mg/m$^3$ feed condition. Acetaldehyde conversion at 150 mg/m$^3$ is only partial, and does exhibit TCE enhancement.

- Increasing the flow rate to 3 cm$^3$/s diminished TCE conversion substantially for contaminants with high dark coverages (butanol or butyraldehyde) and no TCE enhancement could be measured.

- All chloroalkane degradation rates are inhibited by TCE.

- Hexane's conversion is enhanced by TCE addition. Mixtures of hexane and toluene, and presumably of other related alkane/aromatic compounds, also exhibit enhanced rates upon TCE addition. Thus, the chlorine promotion effect operates with mixtures as well as individual contaminants.

• Comparison of our photocatalytic data with literature homogeneous photochemical oxidation indicates that a chlorine atom initiation of attack provides a reasonable rationale for the TCE enhancement effect.

• Further experiments are needed to reveal the enhancement, if any, for other alcohols, ketones, and aldehydes.

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