

## Oxidative photocatalytic degradation of benzene vapor over TiO<sub>2</sub>

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### Abstract

The variables included in a parametric study of the photocatalytic oxidative degradation (PCO) of benzene in a closed reactor over films of Degussa P-25 TiO<sub>2</sub> under fluorescent black-light radiation centered at 367 nm were: concentrations of benzene, O<sub>2</sub> and water vapor; photons/sec incident on the catalyst; and temperature. Concentrations of benzene and CO<sub>2</sub> were measured. All measurements of photocatalytic behavior were performed with freshly deposited films of P-25 which had been preconditioned by irradiating for 15 h while flowing 80 ml min<sup>-1</sup> of dry air through the reactor. It was found that water vapor promoted the dark-evolution of CO<sub>2</sub> and inhibited the dark-adsorption of benzene by the preconditioned catalyst. Under irradiation, water vapor promoted the formation of CO<sub>2</sub> and the initial removal of benzene. Dark-adsorption of benzene increased linearly with concentration of benzene vapor. The initial rate of photocatalytic removal of benzene was first order in concentration of benzene vapor but the higher the initial concentration of benzene the more the rate of its removal diminished as reaction proceeded. Photocatalytic production of CO<sub>2</sub> lagged far behind removal of benzene. The initial rates of photocatalytic removal of benzene vapor and generation of CO<sub>2</sub> were, respectively, independent of concentration of O<sub>2</sub> from 800 ppmv to 100% and approximately one-third order in O<sub>2</sub>. The initial kinetic orders in number of photons/sec entering the reactor of removal of vaporized benzene and generation of CO<sub>2</sub> over the range (7–42) × 10<sup>-8</sup> Einstein s<sup>-1</sup> were, respectively, 1.85 ± .03 and 1.60 ± .07 in air into which 0.44 mmol of water had been injected and 1.59 ± .07 and 1.41 ± .05 in dry air. Over the range 15–70°C, the rate of removal of benzene did not vary significantly with temperature in the presence or absence of water vapor while the rate of generation of CO<sub>2</sub> varied in a way corresponding, respectively, to E<sub>A</sub> = 3.9 ± 0.4 and 9.4 ± 0.9 kJ mol<sup>-1</sup> in the presence and absence of water vapor. Mechanistic implications of the data are discussed.  
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### 1. Introduction

Interest in oxidative photocatalytic mineralization (conversion to CO<sub>2</sub>) of benzene has been stimulated in recent years by its use as an anti-knock additive in gasoline and its carcinogenicity. Benzene is now an ubiquitous component of gasoline vapor associated with transfer of the fuel and with decontamination (e.g., by air-stripping) of soil polluted by leakage from underground tanks or by spillage.

The literature on oxidative photocatalytic degradation of vaporized benzene is still relatively sparse. Benzene was one of 17 vaporized organic compounds the photocatalytic oxidative degradation (PCO) of which over a film of Degussa P-25 was investigated at room temperature by Lichtin et al. [1]. A total of 1000 ppmv of benzene vapor was reacted in a closed stirred reactor in air containing 3% of water vapor under Pyrex-filtered radiation from a medium-pressure mercury lamp. Under these conditions the photoefficiency, E<sub>p</sub>, of

initial removal of benzene was 0.10 molecule per incident photon absorbable by the catalyst. An investigation by Fu et al. [2] of mineralization of benzene vapor by PCO under BLB fluorescent radiation centered at 350 nm in an annular flow reactor packed with particles of TiO<sub>2</sub> prepared by a sol-gel procedure explored a number of system variables. These included the dependence of the fraction of benzene removed and CO<sub>2</sub> yield on the ratio of catalyst mass to molar flow rate of benzene, reaction temperature, concentrations of water vapor and O<sub>2</sub>, and platinization of the catalyst. Conditions which gave essentially complete mineralization without significant production of intermediates were identified. Vaporized benzene was subjected by Sitkiewitz and Heller [3] to PCO at 30°C in a recirculating flow reactor over films on soda-lime glass slides of TiO<sub>2</sub> which had been prepared by a sol-gel procedure. Pyrex-filtered radiation from a high-pressure mercury lamp was employed. The dependence of the rate of generation of CO<sub>2</sub> on irradiance and on the concentrations of O<sub>2</sub> and water vapor was investigated. Generation of CO<sub>2</sub> was not detectable in the absence of added O<sub>2</sub> or

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water vapor but the rate of formation of CO<sub>2</sub> was independent of the concentrations of both of them in the ranges of 0.6–2.5% water vapor and 21–100% O<sub>2</sub> and varied with the square root of incident irradiance. An investigation by Lichtin et al. [4] of PCO at room temperature of 14 binary mixtures of vaporized organic compounds included the reaction of benzene and *i*-octane in air in an annular flow reactor over a film of Degussa P-25 TiO<sub>2</sub> under irradiation at and near 360 nm. Under these conditions, 54 ppmv of benzene and 900 ppmv of *i*-octane had only minor effects on each others rates of removal up to 100% removal but benzene greatly diminished the rates of formation and decay of acetone, the major intermediate formed from *i*-octane. Jacoby et al. [5], studied PCO of 116–130 ppmv of benzene in air containing 980–1000 ppmv of water vapor in an annular flow reactor at room temperature over a film of P-25 TiO<sub>2</sub> irradiated with black-light with its emission maximum at 356 nm. At steady state, approximately 4% of the benzene was removed and converted almost completely to CO<sub>2</sub> and CO in a ratio of 4:1. These products continued to be evolved after the reactant feed was stopped, presumably due to their slow desorption from the catalyst and to oxidation of adsorbed intermediates. Intermediates extracted from the catalyst with water were identified by HPLC elution times as malonic acid, phenol and benzoquinone and/or hydroquinone. These workers also report that, under their standard conditions, 2.8 times as much benzene was adsorbed on the catalyst under irradiation as in the dark. This appears to be the first published report of significant photoadsorption of a volatile organic compound. Evaluation of adsorption involved determination of the amount of benzene removed from the vapor corrected for its removal by PCO but details of this differential method are not given.

We report here a parametric study of the PCO of benzene in a closed reactor over films of Degussa P-25 TiO<sub>2</sub> under fluorescent black-light radiation centered at 367 nm. Variables included the concentrations of benzene, O<sub>2</sub> and water vapor; temperature; and intensity of radiation incident on the catalyst. Rates of removal of benzene and of generation of CO<sub>2</sub> were measured.

## 2. Experimental

### 2.1. Reagents

TiO<sub>2</sub> was Degussa P-25 (finely divided and, according to Degussa, mostly anatase with some rutile, partly amorphous, and with a surface area of 50 m<sup>2</sup> g<sup>-1</sup>). 'Dry' grade air, grade 2.0 O<sub>2</sub>, N<sub>2</sub> and mixtures thereof, grade 0 Ar and grade 4.0 CO<sub>2</sub> were from WESCO and, according to WESCO, contained no more than 10 ppm of water vapor. The water content of all reaction mixtures designated in this report as dry contained a concentration of water vapor below the 150 ppmv GC detection limit. Benzene was Baker Analyzed HPLC grade. Laboratory deionized water was used for preparation

of solutions, suspensions of catalyst and water vapor. Benzene and water were introduced into the reactor as measured volumes of liquid which completely vaporized before reactions were started. The minimal concentration of O<sub>2</sub>, 800 ppmv, was achieved by enclosing the entire reactor in an air tight glove-bag (an Aldrich two-handed 500 l AtmosBag) and flowing a stream of N<sub>2</sub> through the bag during the duration of the experiment. In addition, the enclosed reactor was purged with flowing N<sub>2</sub> for several hours before benzene was introduced and irradiation started.

### 2.2. Deployment of catalyst

TiO<sub>2</sub> was deployed as a thin (approximately 10 μm thick [1]) film of particles deposited on the interior surface of the reactor. The catalyst coating was prepared by placing a previously sonicated mixture of 5 g of TiO<sub>2</sub> and 20 ml of water in the reaction vessel and manually rotating the vessel horizontally in air two turns. The reaction vessel was then drained vertically and dried by heating with a blow dryer at 100°C for about 2 min. The catalyst film was pretreated before each reaction by irradiating for 15 h with the lamp described below while flowing 80 ml min<sup>-1</sup> of dry air through the reactor. Preliminary experiments had established that this treatment was sufficient to remove adventitious adsorbate with which the catalyst, as supplied, was contaminated and which generated CO<sub>2</sub> upon irradiation in the presence of air. Used catalyst was removed from the reactor after each experiment by scrubbing with a test-tube brush and Alconox solution. A fresh coating of pristine catalyst was applied before the next experiment.

### 2.3. Reactor

The closed batch reactor, adapted from an Ace Glass 7840 unit comprised a 507 ml magnetically stirred cylindrical Pyrex reaction chamber, a 6 W (electrical) Vilbur–Lourmat Tl-6 fluorescent lamp, emission from which was found spectrophotometrically to be centered at 367 nm, enclosed in a cylindrical water-cooled Pyrex well, a port capped with a silicone rubber septum for introduction and removal of reactants or products, a second port used for circulating pretreatment air or other gases and a thermometer well. Measured amounts of liquid benzene were introduced through the sample port. Stirring was continued until dark-adsorption, as measured by GC, reached equilibrium and the reaction was then started by turning on the lamp.

### 2.4. Lamp output

The output of the 6 W 367 nm fluorescent lamp was routinely stabilized by removing it from the reactor, covering it with aluminum foil, turning it on for 10 min and turning it off for 1.5 min before turning it on in the reactor to start a reaction. Output was reduced for studies of dependence on number of photons per unit time entering the reactor by cov-

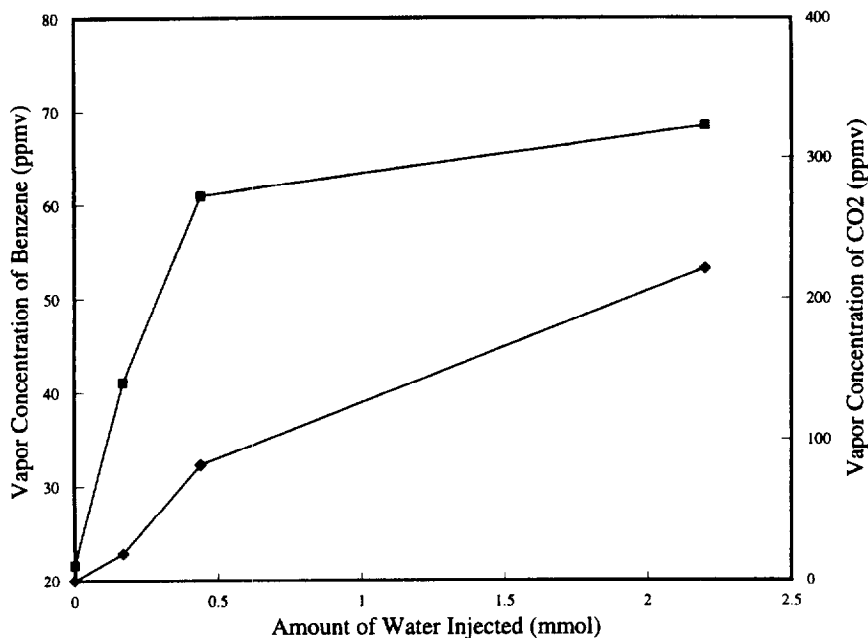


Fig. 1. Dependence of initial dark steady state vapor concentration of benzene, —■—, and CO<sub>2</sub>, —◆—, on concentration of water vapor (2.3 μmol of benzene initially supplied, air).

ering the lamp with one or more sleeves of onion-skin paper,<sup>1</sup> a procedure which was shown spectrophotometrically to not alter the emission spectrum of the lamp. The number of photons entering the reactor per unit time was determined by ferrioxalate actinometry [6].<sup>2</sup>

### 2.5. Analyses of benzene and CO<sub>2</sub>

Benzene was determined by gas chromatography on an HP5890 instrument with FID using a 10 m × 0.53 mm × 1 μm HP-FFAP capillary column. CO<sub>2</sub> was determined by gas chromatography on a Perkin-Elmer Sigma 300 instrument with TCD using a Supelco 80/100 mesh Porapak Q column. The detection limit of CO<sub>2</sub> in this system was 5–8 ppmv. The probable error in the analysis was as much as ±300% at concentrations near the detection limit and declined to about ±10% for concentrations of CO<sub>2</sub> greater than 80 ppmv.

## 3. Results and discussion

### 3.1. Effect of water vapor on sorption of benzene and CO<sub>2</sub>

In a series of experiments, 2.25 μmol of benzene vapor was dark-equilibrated in the presence of varying amounts of water vapor with catalyst film which had been pre-conditioned as described above. As shown in Fig. 1, the equilibrium vapor concentrations of both benzene and CO<sub>2</sub> increased with

increasing concentrations of water vapor. These data show that P-25 films which had been preconditioned by our standard procedure, which reduced CO<sub>2</sub> in dark-equilibrium with them to below detectability, evolved CO<sub>2</sub> when exposed to water vapor in the dark. All or part of this CO<sub>2</sub> may have resulted from hydrolysis of surface carbonate. CO<sub>2</sub> may also have been generated by reaction of water with other surface species which were not removed by the preconditioning process. Presumably, the observed increase in vapor concentration of benzene with increasing concentrations of water vapor resulted from competition for adsorption sites.

### 3.2. Stoichiometry

CO<sub>2</sub> is the only product which was identified and studied. Fig. 2 displays the dependence on the amount of water injected into the reactor of the vapor concentration of CO<sub>2</sub> after 30 min of irradiation relative to 6 times the vapor concentration of benzene equivalent to the amount of benzene injected. Gas phase concentrations of CO<sub>2</sub> were corrected for their dark-equilibrated values. It is seen that water promoted the formation of CO<sub>2</sub>. Fig. 2 also shows the dependence on the amount of injected water of consumption of benzene during 2 min of irradiation. It is seen that water vapor promoted the initial consumption of benzene but that this effect diminished as the concentration of water vapor increased. It may be inferred that water accelerates one or more of the steps through which C<sub>6</sub>H<sub>6</sub> undergoes complete degradation of its carbon skeleton to CO<sub>2</sub>. Alternatively or additionally, water may alter the reaction sequence through which the degradation occurs. Either or both of these possibilities may involve promotion by water of desorption of CO<sub>2</sub> analogous to the observed dark-desorption. Whatever the detailed chem-

<sup>1</sup> A description of this procedure and its validation will be published elsewhere.

<sup>2</sup> See S.L. Murov, I. Carmichael, G.L. Hug (Eds.), Handbook of Photochemistry, 2nd edn., Marcel Dekker, New York, 1993, pp. 299–305.

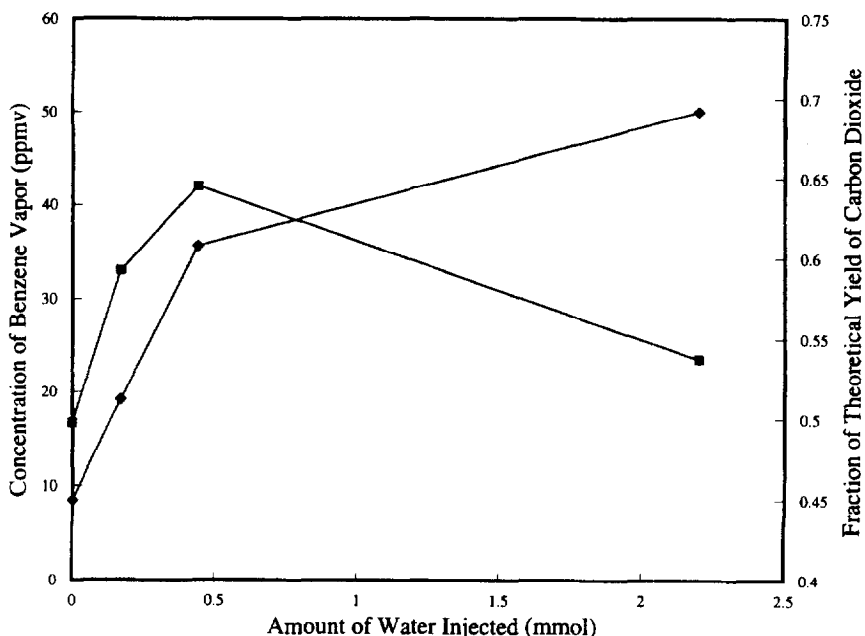


Fig. 2. Dependence on concentration of water vapor of concentration of benzene vapor removed by 2 min of irradiation, —■—, and of yield of  $\text{CO}_2$  after 30 min of irradiation, —◆—, fraction of theoretical yield of  $\text{CO}_2$  = concentration of  $\text{CO}_2$  generated/[6 × concentration of benzene equal to amount initially injected] ( $2.3 \mu\text{mol}$  of benzene initially supplied, air,  $4.2 \times 10^{-7}$  Einstein  $\text{s}^{-1}$ ).

istry through which water promotes the complete conversion of benzene to  $\text{CO}_2$ , high water vapor content is important for practical photocatalytic oxidative mineralization of benzene vapor.

### 3.3. Dependence on benzene concentration of rates of removal of benzene and formation of $\text{CO}_2$

Orienting experiments showed that the dark-equilibrated concentration of benzene vapor in the presence of a constant amount of added water vapor increased linearly (from 82 to 12 000 ppmv) with increase in the amount of (liquid) benzene introduced into the reactor. No liquid benzene was observable over the entire range. Similarly, the amount of benzene measured by difference to be dark-adsorbed on the catalyst increased linearly with increase in the vapor concentration of benzene over the same range. This behavior is consistent with Langmuir adsorption at a distance from saturation. Under irradiation, the initial rate of removal of benzene in the presence of a constant concentration of water vapor and air was first order in concentration of benzene vapor over the above concentration range. Fig. 3 shows that the higher the initial concentration of benzene the more its fractional rate of removal diminished as the reaction proceeded. Presumably, this behavior is due to accumulation of intermediate products on the surface of the catalyst as evidenced by its gradual browning. As shown in Fig. 4, under the indicated conditions, initial (2 min) yields of  $\text{CO}_2$  were very low over the entire range of concentrations of benzene vapor. Fig. 4 also shows yields of  $\text{CO}_2$  after 85 min of irradiation under the latter conditions and after 2 min and 60 min of

irradiation at a higher irradiance. These data indicate inhibition of formation of  $\text{CO}_2$  by benzene and/or one or more intermediate products of its decomposition. Fig. 5 shows the dependence on initial concentration of benzene vapor of fractional consumption of benzene and of molar yields of  $\text{CO}_2$  relative to six times the molar consumption of benzene after 60 min of reaction. These data show that the fractional removal of benzene and its conversion to  $\text{CO}_2$  under the indicated conditions were both essentially complete with initial concentrations of benzene vapor up to about 500 ppmv but declined with further increase in initial concentration of benzene vapor. The relative yield of  $\text{CO}_2$  declined more steeply with increasing initial concentration of benzene than did the fractional removal of benzene.

The observed first order dependence of the initial rate of removal of benzene from the vapor phase on concentration of benzene vapor at concentrations up to 12 000 ppmv is consistent with Langmuir behavior of photoadsorption remote from saturation and conversion of adsorbed benzene which is first order in its surface concentration. The reaction or reactions responsible for removal of benzene is or are apparently inhibited by one or more reaction products, probably intermediates. Inhibition of the reaction or reactions responsible for removal of benzene vapor must be the cause of part of the associated reduction in rate of formation of  $\text{CO}_2$  but the greater decline in conversion to  $\text{CO}_2$  indicates that one or more intermediate steps is or are also inhibited in a similar fashion. It is also possible that benzene itself competes with intermediate products for catalyst sites and thereby functions as an inhibitor of generation of  $\text{CO}_2$ .

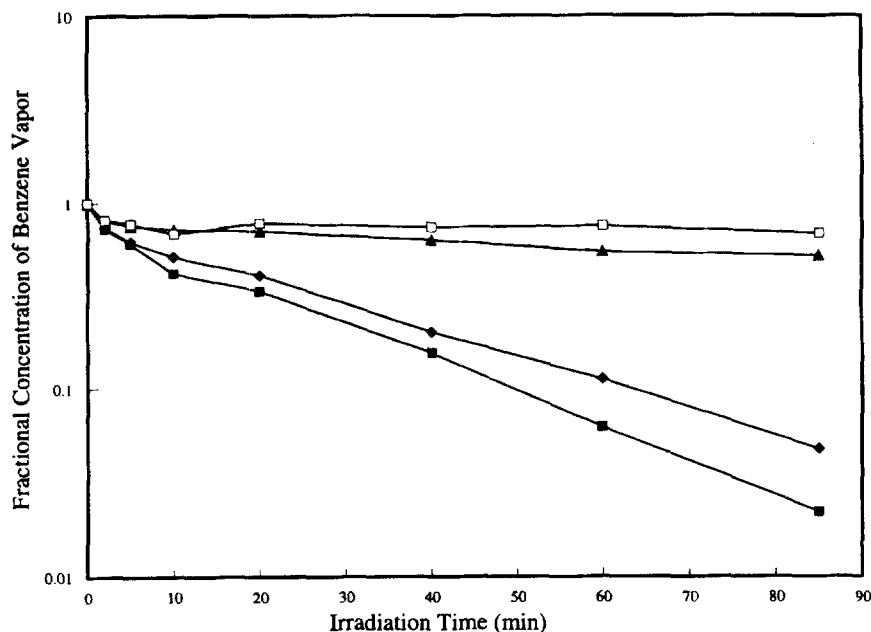


Fig. 3. Dependence of variation of rate of removal of benzene vapor with time of irradiation on initial concentration of benzene vapor: 82 ppmv, —■—; 168 ppmv, —◆—; 1545 ppmv, —▲—; 12,411 ppmv, —□—; (0.44 mmol of water initially supplied, air,  $1.4 \times 10^{-7}$  Einstein  $s^{-1}$ ).

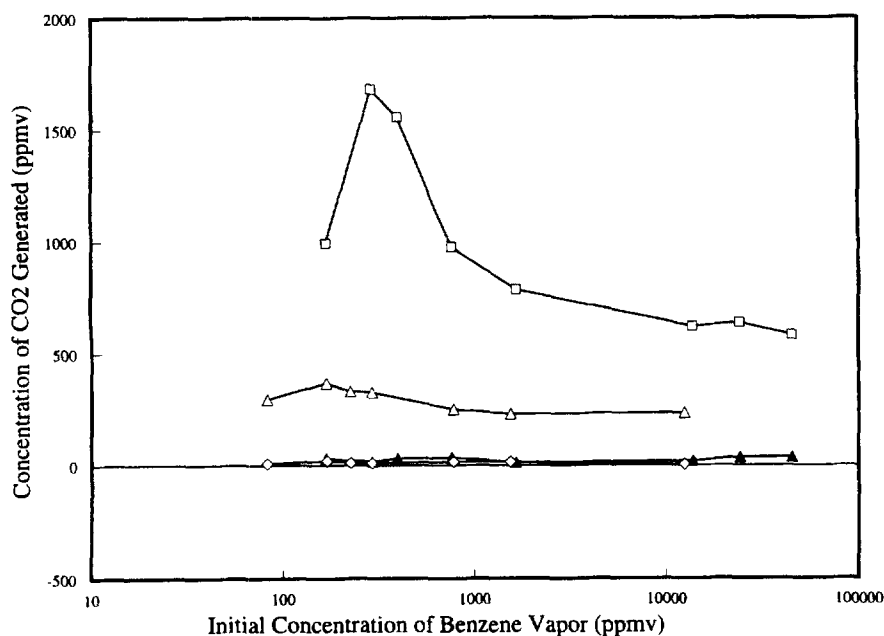


Fig. 4. Dependence on initial concentration of benzene vapor of formation of  $CO_2$  by irradiation for 2 min with  $1.4 \times 10^{-7}$  Einstein  $s^{-1}$ , —◇—; for 85 min with  $1.4 \times 10^{-7}$  Einstein  $s^{-1}$ , —△—; for 2 min with  $4.2 \times 10^{-7}$  Einstein  $s^{-1}$ , —▲—; and for 60 min with  $4.2 \times 10^{-7}$  Einstein  $s^{-1}$ , —□—; (0.44 mmol of water initially supplied, air).

### 3.4. Dependence on concentration of $O_2$ of rates of removal of benzene and formation of $CO_2$

As seen in Fig. 6, variation of the supplied concentration of  $O_2$  from 800 ppmv to 100 vol.% had an insignificant effect on the initial rate of removal of benzene in the absence of added water and, except for the reaction in the presence of only 800 ppmv of  $O_2$ , very little effect on the rate of its removal up to consumption of 95% of the benzene. With the initial concentration of  $O_2$  only 800 ppmv the rate of removal

of benzene vapor became much slower than with the higher concentrations of  $O_2$  after about 50% of the initially supplied benzene had been removed. Similar results were obtained for 1–100 vol.%  $O_2$  under the same conditions but with 0.4 mmol of water added. As shown in Fig. 7, the rate of formation of  $CO_2$  increased significantly with increasing concentration of  $O_2$  in the absence of added water, corresponding to a formal order in  $O_2$  of  $0.33 \pm 0.05$ . Similar results corresponding to a formal order of  $0.36 \pm 0.06$  in  $O_2$  were obtained in the presence of 0.4 mmol of added water.  $CO_2$  was not detectable in the

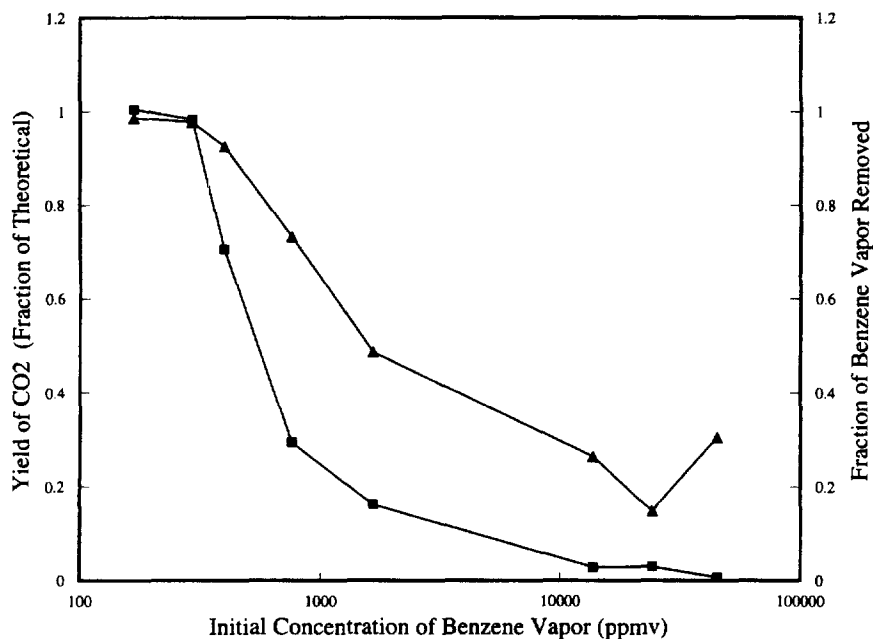


Fig. 5. Dependence on initial concentration of benzene vapor of CO<sub>2</sub> yield, —■—, and fractional consumption of benzene, —▲—, after 60 min of reaction (0.44 mmol of water initially supplied, air,  $4.2 \times 10^{-7}$  Einstein s<sup>-1</sup>).

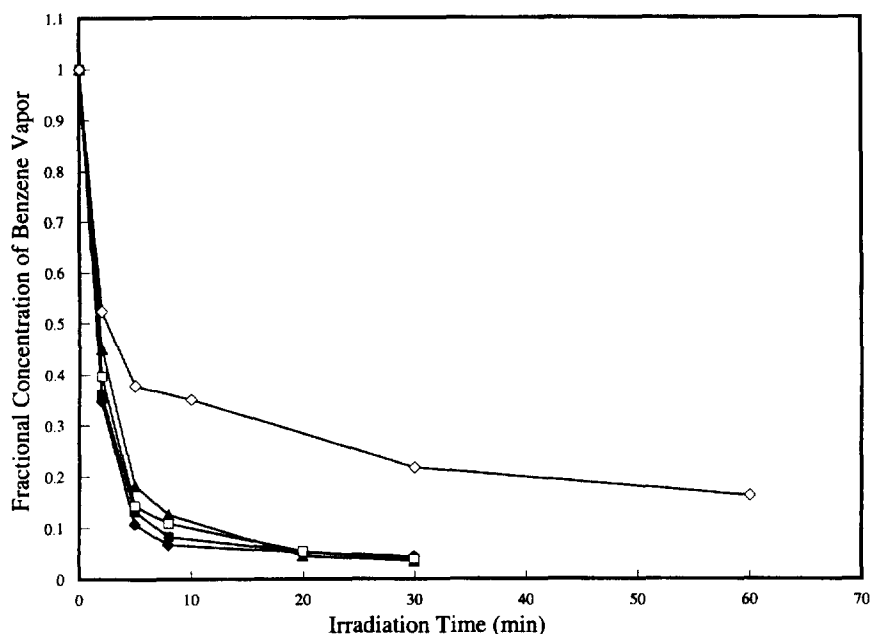


Fig. 6. Dependence of rate of removal of benzene vapor on concentration of O<sub>2</sub> in absence of added water vapor: —◇—, 800 ppmv of O<sub>2</sub>; —■—, 1 vol.% O<sub>2</sub>; —◆—, 5 vol.% O<sub>2</sub>; —▲—, 20 vol.% O<sub>2</sub>; —□—, 100 vol.% O<sub>2</sub>; (no added water, 4.5 μmol of benzene initially supplied,  $4.2 \times 10^{-7}$  Einstein s<sup>-1</sup>).

absence of water vapor when the initial concentration of O<sub>2</sub> was 800 ppmv.

Since the initial rate of removal of benzene is (in the absence of added water vapor) virtually independent of the concentration of O<sub>2</sub> from 800 ppmv to 100%, it is tempting to conclude that O<sub>2</sub> is not involved in determining the rate of removal of benzene. However, the deceleration of removal of benzene as the reaction proceeds when the initial concentration of O<sub>2</sub> is only 800 ppmv relative to the O<sub>2</sub>-independent behavior observed with 1–100 vol.% O<sub>2</sub> suggests a rate-

determining role for O<sub>2</sub> which is saturated by less than 800 ppmv. As O<sub>2</sub> is consumed by its reaction with benzene, the concentration of O<sub>2</sub> apparently drops below the amount required for saturation. Possibly, the process which is saturated is the capture by adsorbed O<sub>2</sub> of conduction-band electrons to generate O<sub>2</sub><sup>-</sup> [7] or equivalent species. O<sub>2</sub> is apparently involved in one or more of the reaction steps involved in the complete degradation of benzene to CO<sub>2</sub>. The observed fractional order in O<sub>2</sub> is consistent with a multistep process.

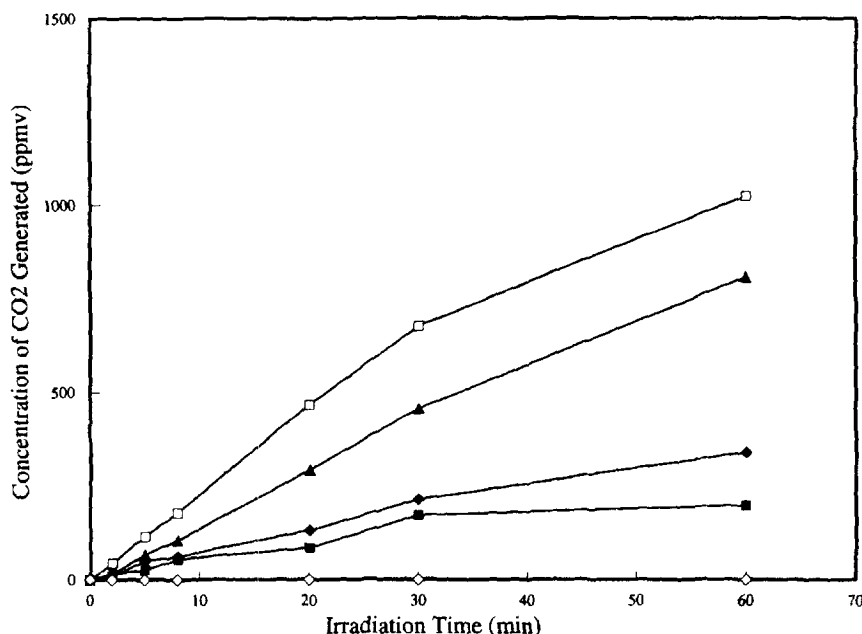


Fig. 7. Dependence of rate of generation of  $\text{CO}_2$  on concentration of  $\text{O}_2$  in absence of added water vapor:  $\diamond$ —, 800 ppmv of  $\text{O}_2$ ;  $\blacksquare$ —, 1 vol.%  $\text{O}_2$ ;  $\blacklozenge$ —, 5 vol.%  $\text{O}_2$ ;  $\blacktriangle$ —, 20 vol.%  $\text{O}_2$ ;  $\square$ —, 100 vol.%  $\text{O}_2$ ; (no added water,  $4.5 \mu\text{mol}$  of benzene initially supplied,  $4.2 \times 10^{-7}$  Einstein  $\text{s}^{-1}$ ).

### 3.5. Dependence of rates of removal of benzene and formation of $\text{CO}_2$ on number of photons entering the reactor per unit time

First order rate constants for removal of 60% of benzene vapor were determined at three different values of the number of photons per unit time entering the reactor in the presence and absence of added water vapor. Rates of formation of  $\text{CO}_2$  were also measured over the same range of conditions and reaction times. Fig. 8 is a log–log plot of rate constants for removal of benzene and rates of formation of  $\text{CO}_2$  vs. Einstein  $\text{s}^{-1}$  entering the reactor in the presence of 0.44 mmol of added water. Since the area of the catalyst film was kept constant and essentially all the photons entering the reactor impinged on the film, the slopes of the plots shown in Fig. 8 equal  $O_i$ , the order in irradiance of, respectively, removal of benzene vapor and formation of  $\text{CO}_2$ . The values of  $O_i$  for reaction in dry air were determined in the same way. The resulting values of  $O_i$  are assembled in Table 1. The dependence on irradiance of the photoefficiency of removal of benzene,  $E_p$ , is presented in Table 2.

The data indicate that, under the conditions employed, the initial rate of removal of benzene is controlled by a process involving an average of between 1.5 and 2 photons per molecule removed. These results can be rationalized by assuming that the fastest process responsible for removal of benzene is initiated by the cooperative action of two photon-produced charge carriers while a slower parallel reaction is initiated by a single charge carrier. Presumably, the initiating charge carriers are sufficiently deeply trapped at the surface of the catalyst [8] to allow time for them to react with adsorbed benzene. This interpretation implies that the fraction of initially-formed charge carriers which are so trapped is essen-

Table 1  
Kinetic order in irradiance,  $O_i$

Process	mmol of water injected	$O_i$
Removal of benzene <sup>a</sup>	0.44	$1.85 \pm 0.03$
	none	$1.59 \pm 0.07$
Formation of $\text{CO}_2$ <sup>b</sup>	0.44	$1.60 \pm 0.07$
	none	$1.41 \pm 0.05$

<sup>a</sup>First order rate constants, first 60% of reaction.

<sup>b</sup>Initial rates, first 60% of reaction.

Table 2  
Dependence of  $E_p$  on irradiance

No. of photons per second entering reactor $10^{-8}$ Einstein $\text{s}^{-1}$	$E_p$ molecules of benzene removed per incident photon
7.0	0.0072
14.	0.0095
42.	0.023

<sup>a</sup>In air into which 0.44 mmol of water was injected; based on first 60% of reaction.

tially constant over the measured sixfold increase in irradiance values. That this fraction is small, can be inferred from the values of  $E_p$ , 0.0072–0.023 molecules of benzene removed per incident photon, which are presented in Table 2. (We have shown in a prior report [1] that a film of P-25 similar to those used in the work reported here absorbed about 70% of 367 nm radiation.) An alternative explanation [9] of  $1 < O_i < 2$  is that the fraction of charge carriers which are deeply trapped diminishes with increasing irradiance. The data do not indicate whether the two cooperating trapped

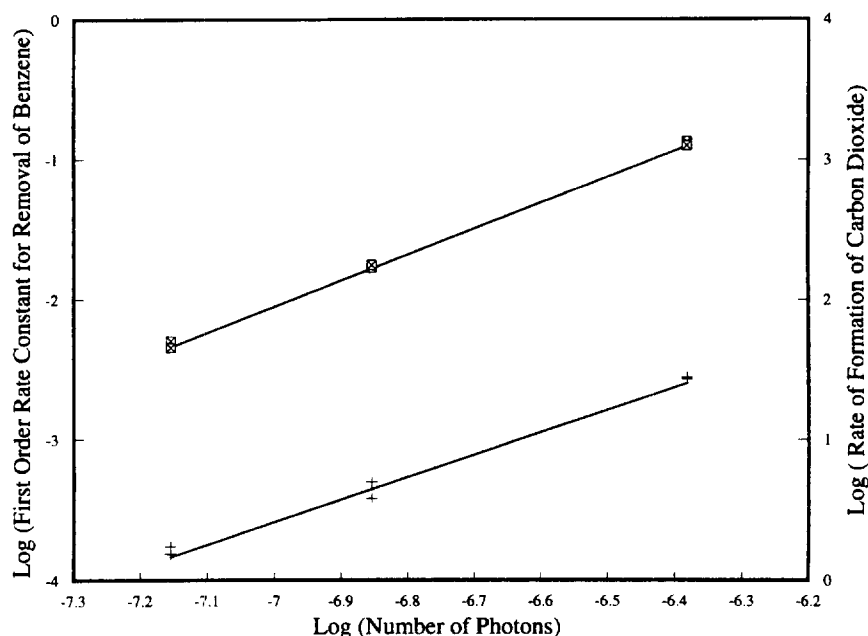


Fig. 8. Dependence on log (number of photons) of log (first order rate constant for removal of benzene vapor) and log (rate of formation of carbon dioxide), (6.8  $\mu\text{mol}$  of benzene and 0.44 mmol water initially supplied, air). —  $\square$  —, rate constant for removal of benzene vapor; —  $+$  —, rate of formation of  $\text{CO}_2$ .

charge carriers are derived from conduction band electrons or valence band holes or from both primary species. The well known nucleophilic reactivity of benzene militates against reaction by electrons trapped as reducing species but is consistent with reaction of electrons trapped as  $\text{O}_2^{\cdot -}$ . The higher order observed in the presence of a high concentration of water vapor is consistent with increased surface concentration of  $\text{OH}^\cdot$  (deeply trapped holes) derived from valence band holes. Our values of  $O_1$  for formation of  $\text{CO}_2$  fit the same pattern as those of  $O_1$  for removal of benzene. Formation of  $\text{CO}_2$  is a multistep reaction the principal rate-determining step of which also appears to involve two photo-derived species. Sitkiewitz and Heller [3] report  $O_1 = 0.5$  for the production of  $\text{CO}_2$  by PCO of benzene over  $\text{TiO}_2$  in air containing 0.6 or 2.5% of water vapor. Their use of irradiance values ranging from approximately 100 to 7500 times our highest irradiance may be responsible for the large difference. In addition, their catalyst, radiation source, mode of deployment of the catalyst and reactor differed widely from our reaction conditions. Choi and Hoffmann [9] have observed that  $O_1$  for the production of  $\text{CCl}_2$  in PCO of  $\text{CCl}_4$  in slurries of P-25  $\text{TiO}_2$  in aqueous  $\text{CH}_3\text{CN}$  declines from 2 to 1 and ultimately to 0.5 with increasing irradiance. Their reaction and conditions are too different from ours to justify detailed comparison.

### 3.6. Dependence on temperature of rates of removal of benzene and formation of $\text{CO}_2$

The rate of removal of benzene did not vary significantly with temperature from 15–70°C in the presence of 0.44 mmol of injected water and in the absence of added water. The small increases observed in the rate of formation of  $\text{CO}_2$  with increasing temperature from 15–70°C corresponded to an

Arrhenius activation energy,  $E_A$ , of  $9.4 \pm 0.9 \text{ kJ mol}^{-1}$  in the absence of added water and to  $3.9 \pm 0.4 \text{ kJ mol}^{-1}$  in the presence of 0.44 mmol of injected water. The negligible variation with temperature of the rate of removal of benzene is consistent with a rate-determining photo process. The small activation energies of formation of  $\text{CO}_2$  are consistent with the rate of this multistep process being influenced by one or more thermal reactions. That  $E_A$  is smaller in the presence of added water vapor than in its absence is consistent with the observed promotion by water of formation of  $\text{CO}_2$  (see Fig. 2).

### Acknowledgements

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