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LETTERS TO THE EDITORS

Photocatalytic Oxidation of Chlorobenzene in Aqueous Suspensions of Titanium Dioxide

INTRODUCTION

In a study of the heterogeneous photocatalytic decomposition of some chlorinated hydrocarbons in aqueous slurries of TiO_2, Ollis *et al.* (*1*) reported no evidence of ring opening with monochloro- and dichlorobenzenes or with decomposition products which included *ortho*- and *para*-chlorophenols. This observation is of importance to water purification using UV-illuminated TiO_2 slurries since it shows that under some conditions there may only be partial oxidation. Some partially oxidized compounds, chlorophenols for example, are more toxic or odorous than their parent.

Presumably Ollis *et al.* (*1*) based their report on a failure to observe CO_2. This was surprising since in our laboratories a number of studies have been made of the rates of formation of CO_2 from various aromatic compounds, including monochloro- and dichlorobenzene and the isomeric chlorophenols, in UV-illuminated aqueous suspensions of TiO_2. The rate of CO_2 formation from these compounds was quite significant and not greatly different from other aromatic compounds. Since CO_2 formation is unequivocal evidence for destruction of the aromatic ring, and because of the importance of obtaining total oxidation in water purification, the experiments were repeated with monochlorobenzene, paying particular attention to the total amount of CO_2 formed from the illuminated suspension.

EXPERIMENTAL

Materials. Degussa P25 grade TiO_2 was used; this product is primarily in the anatase form and has a BET surface area of 50 ± 15 m^2 g^{-1} and an average primary particle size of 30 nm. The water used in the preparation of all solutions was obtained from a Millipore Waters Milli-Q water purification system. The chlorobenzene was British Drug Houses laboratory reagent grade. Commonwealth Industrial Gases food grade carbon dioxide was used for calibration of the gas chromatograph (GC).

Apparatus and procedure. Suspensions of TiO_2 were illuminated in a 450-cm^3 photochemical reactor with a centrally located 100-W medium-pressure mercury lamp. The lamp was surrounded by a borosilicate glass sheath through which thermostatically controlled cooling water at 25°C was circulated. The reactor was fitted with gas inlet and outlet ports and an access port for the addition of solutes. The inlet gas was fed into the suspension via a sintered glass disk in the bottom of the reactor. In addition to the agitation by the gas bubbles, the suspension was stirred magnetically. Air in the free space (≈ 50 cm^3) above the suspension was pumped by means of a peristaltic pump through a silica gel trap and an automatic gas sampling valve connected to a Hewlett–Packard Model 5750 gas chromatograph and back to the reactor. The gas chromatograph was fitted with Porapak Q columns and thermal conductivity detectors. Helium was used as the carrier gas. The automatic gas sampling valve was controlled by a Hewlett–Packard Model 3390A reporting integrator which also integrated the areas of the curves on the chromatograms. The GC was calibrated by the addition of known volumes of CO_2 to the photochemical reactor under conditions identical

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to the experiment but without illumination. Variations were observed in the blank CO_2 for different suspensions. Therefore, before each run the gas above the suspension was sampled from the loop at regular intervals during 60 min illumination, to establish the blank. An aqueous solution of chlorobenzene was then added to the suspension to give the required concentration. Sampling, with illumination, was continued for a further 60 min.

RESULTS AND DISCUSSION

In experiments in which the chlorobenzene concentration was initially 10^{-3} *M* (112 ppm) and the weight of TiO_2 was varied, it was established that

(a) in the absence of TiO_2, the rate of CO_2 formation was trivial, and

(b) the maximum rate of CO_2 formation was obtained with a TiO_2 loading of 0.5 g/400 ml but a loading of 0.2 g/400 ml gave a CO_2 formation rate of approximately 94% of this maximum rate.

A TiO_2 loading of 0.2 g/400 ml was therefore used in subsequent experiments.

The results for increasing concentrations of chlorobenzene in 400 ml of suspension are shown in Fig. 1. Each of the data sets have been corrected for the blank. Plateaux were reached with the five lower concentrations at illumination times that increased with increasing concentration. The dashed lines show the theoretical amounts of CO_2 required by

$$C_6H_5Cl + 7O_2 \xrightarrow{TiO_2/h\nu} 6CO_2 + HCl + 2H_2O \quad (1)$$

For chlorobenzene concentrations of 12.5, 25.0, 37.5, 50.0, and 100.0 μM they are, respectively, 0.73, 1.46, 2.19, 2.92, and 5.84 cm^3 at 25°C. Allowing for the addition of constant volumes to facilitate plotting, the experimental plateaux are in good agreement with those calculated for total oxidation according to Eq. (1).

It is known that the aromatic ring is hydroxylated when aromatic compounds in aqueous suspensions of TiO_2 are illuminated with near-UV light (*2*). However, in 1980 Bard *et al.* (*3*) reported that benzene yields CO_2, and more recently Barbeni *et al.* (*4*) noted that 4-chlorophenol is completely degraded to CO_2 and HCl in UV-illuminated aqueous suspensions of TiO_2. Therefore, even if the degradation of chlorobenzene proceeds exclusively via the formation of chlorophenol, CO_2 and HCl are the expected final products. However, there is a possibility that concurrent reactions occur which lead to the formation of CO_2 directly from chlorobenzene as well as via chlorophenol formation. Hashimoto *et al.* (*5*) discuss the possibility of concurrent reactions occurring with CO_2 formation directly from benzene and via intermediate phenol formation. Regardless of the rela-

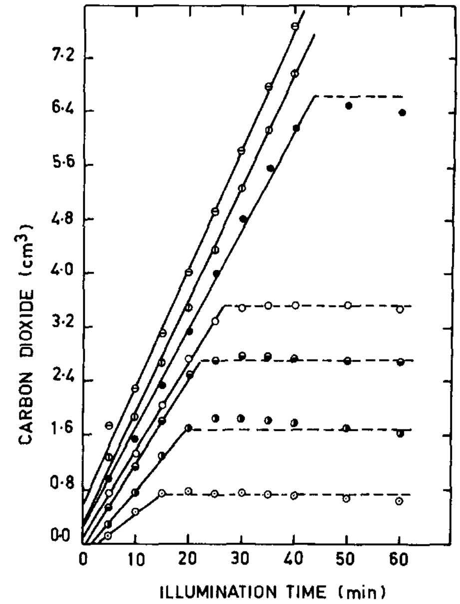

FIG. 1. Carbon dioxide yields for 400 ml aqueous TiO_2 suspensions containing different concentrations of chlorobenzene. TiO_2 (0.2 g) 100-W medium-pressure mercury lamp, 25°C. Each suspension was illuminated for 60 min before the chlorobenzene was added to correct for background CO_2. To facilitate plotting, the following constant amounts of CO_2 were added: (⊙) 1.40 ppm, +0.0; (◑) 2.81 ppm, +0.20; (◒) 4.22 ppm, +0.40; (○) 5.62 ppm, +0.60; (●) 11.25 ppm, +0.80; (⦶) 28.1 ppm, +0.80; (⊖) 56.2 ppm, +1.60.

tive extent of competing reaction pathways the present results show that (a) CO_2 is formed when chlorobenzene in aqueous TiO_2 suspensions is illuminated with UV light, and (b) essentially all the chlorobenzene is converted to CO_2 when the chlorobenzene is present at concentrations of 10^{-4} M (11.2 ppm) and less.

In their experiments, Ollis *et al.* (*1*) used Fischer certified grade TiO_2, with a BET surface area of 7 m^2 g^{-1} and ≈95% anatase. The surface area of their sample was considerably smaller than that of the Degussa P25 TiO_2. Since the photocatalytic reactions take place at the surface of the TiO_2, an enhanced rate of reaction for the larger surface area TiO_2 was expected. The disagreement, however, is not with the magnitude of the reaction rate but with the observation of total oxidation in one case against partial oxidation in the other.

The initial rates of formation of CO_2 at the different chlorobenzene concentrations are shown by the straight lines in Fig. 1 and were calculated by the method of least squares. The experimental points are reasonably linear up to the plateaux. The relationship between the rate of CO_2 formation and the chlorobenzene concentration is Langmuirian (Fig. 2). The line drawn through the experimental points in Fig. 2 was obtained by the method of least squares assuming the expression

$$R(CO_2) = k_1k_2[\phi Cl]/(1 + k_1[\phi Cl]), \quad (2)$$

where $R(CO_2)$ is the rate of CO_2 formation in parts per million per minute, and $[\phi Cl]$ is the chlorobenzene concentration in parts per million.

The parameters k_1 and k_2 were found to be 0.41 ± 0.04 ppm^{-1} and 0.85 ± 0.24 ppm min^{-1}, respectively. Assuming the reaction stoichiometry given by Eq. (1), the rate of destruction of chlorobenzene in ppm min^{-1} in reactions giving CO_2, $R(-\phi Cl)$, will be given by

$$R(-Cl) = 0.058[\phi Cl]/(1 + 0.41[\phi Cl]). \quad (3)$$

It is concluded that there are significant differences in the photoreactions initiated by different grades of TiO_2 although these may be in primarily the same crystalline form. Degussa P25 TiO_2 is capable of total oxidation of chlorobenzene whereas Fischer certified grade TiO_2 appears to be capable of partial oxidation only. Therefore, Degussa P25 TiO_2 is a superior catalyst for the photodestruction of organic impurities in water. Less active forms of TiO_2 may be used to advantage in photocatalyzed syntheses where partial oxidation is required.

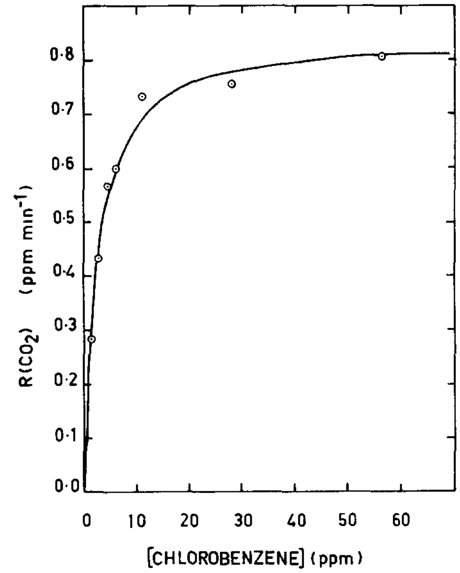

FIG. 2. Rate of carbon dioxide formation versus chlorobenzene concentration. UV-illuminated suspensions of TiO_2, 0.2 g/400 ml, 100-W medium-pressure mercury lamp, 25°C. Rates were calculated from the least squares determined slopes of Fig. 1.

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