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Changing the Product State Distribution and Kinetics in Photocatalytic Surface Reactions Using Pulsed Laser Irradiation

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Heterogeneous semiconductor photocatalysis has shown promise for the degradation of a number of volatile organic species that pose significant environmental concerns.[1−5] Photocatalytic methods can provide significant advantages over existing hazardous waste treatments such as incineration,[6] physical processes such as adsorption,[7] and bioremediation.[8,9] Studies have shown that complete mineralization is often possible, even for chlorinated species, while capital, fuel, and energy costs for photocatalytic processes can be significantly lower than for comparable thermal treatments.[10] The initial steps involved in photocatalysis that include the excitation of electrons to the conduction band and migration of these electrons and holes to the surface are well-known, although a number of issues pertaining to the complex surface chemistry are not fully understood.

One question we raise is the effect of using different irradiation methods to initiate the surface chemistry. Nearly all of the heterogeneous photocatalytic experiments to date have employed continuous UV lamps, with few exceptions.[11−13] For example, in the case of dichloromethane (CH_2Cl_2) photocatalytic degradation using UV lamps, complete mineralization to HCl, CO_2, and Cl^- occurs in the liquid phase,[14−16] while in the gas phase, the undesirable intermediate phosgene (CCl_2O) is also observed.[17] In this paper, we report our initial results on the photodegradation of CH_2Cl_2 over a TiO_2 photocatalyst, in which we observe dramatic changes in the product distribution that depend on the UV irradiation source. In experiments using a continuous xenon arc lamp, we observe the formation of CCl_2O, HCl, and CO_2 in agreement with previous studies. However, when we use a pulsed 351-nm excimer laser, CCl_2O and HCl are no longer produced, and the kinetics of the CH_2Cl_2 degradation are altered.

Experiments were conducted using a glass reaction cell that provided an orthogonal, crossed beam arrangement for UV excitation and in situ FTIR detection. A catalyst consisting of a 1-cm^2 tungsten mesh coated with 25-nm TiO_2 particles (Degussa P25) was prepared to provide a clean, dry surface on which the photocatalytic degradations could occur. Samples were prepared following methods originally developed by Yates and co-workers in their investigation of chloromethane and trichloroethylene (TCE) photooxidation.[18−20] Briefly, the catalyst was prepared by first spraying a 90% acetone/10% water suspension of TiO_2 particles (100 g/L) onto a tungsten mesh, which was heated electrically to 340−370 K, allowing the liquid to evaporate. The TiO_2-coated sample was calcined in the presence of O_2 at 773 K for 5 h and then mounted into the reaction chamber where it was purged with N_2 gas for 1 h. Finally, the sample was heated electrically at 473 K for 2 h under high vacuum. Pressures in the reaction chamber were maintained at 10^{-5} Torr prior to photodegradation experiments. CH_2Cl_2 (Fisher Scientific Co.) was purified by filtration through an alumina column[20] and by subsequent vapor pressure distillation. Approximately 12 μmol of the reactant and 35 μmol of O_2 were introduced into the IR cell. Either broad band UV, produced by a high-pressure Xe−Hg lamp (Oriel) operating at 350 W with a water cell for IR absorption, or 351-nm light from a Xe−F excimer laser (Lambda Physik Compex) operating at 20 Hz with ca. 26- to 100-mJ, 10-ns pulses, was used to initiate the reactions. FTIR scans were typically obtained every 15 min during the lamp experiments and every 30 min during the laser experiments. Reference FTIR spectra were acquired immediately before introducing reagents into the reaction cell. Additionally, GC/MS analysis of the gas-phase species was performed using an online Varian Saturn 2 ion trap system.

In Figure 1, IR spectra are shown, indicating the progress of the photocatalytic oxidation of CH_2Cl_2 in the presence of O_2 using lamp irradiation. Initial FTIR scans 1A and 1D show the characteristic peaks for CH_2Cl_2; 2990, 1276, and twin peaks at 764 and 749 cm^{-1}. Spectra 1B and 1E, collected after 60 min of irradiation, indicate a decrease in the CH_2Cl_2 absorption at 2990 cm^{-1} and an intensity shift within the twin peak structure. Characteristic chloroform ($CHCl_3$) absorption bands were observed at 1219 and 771 cm^{-1}. Additionally, CO_2 and CO bands centered around 2345 and 2166 cm^{-1}, respectively, were observed. Spectra 1C and 1F, taken after 135 min, show the appearance of three new species, CCl_4 at 795 cm^{-1}, CCl_2O with two peaks at 1831 and 849 cm^{-1}, and HCl by a series of peaks 3031 to 2679 cm^{-1}. The observed absorption bands were assigned by comparison with IR standards[21] and literature data for the case of phosgene.[22] Approximately 0.12 μmol of CCl_2O was produced, representing 1% of the total carbon species within the system. GC/MS scans confirmed the presence of all of the above species in runs taken at various times during the experiment.

Figure 2 contains spectra collected during a photocatalytic experiment using the pulsed UV laser source. Spectra 2A and 2D again show the characteristic frequencies of CH_2Cl_2 prior to irradiation. After 270 min of laser irradiation, spectra 2B and 2E follow the trends established by the lamp experiment, with CH_2Cl_2 absorption diminishing as the chloroform, CO_2, and CO bands increase in intensity. However, spectra 2C and 2F, taken after 540 min of irradiation, show marked differences compared to the results obtained with lamp irradiation. Although CCl_4 is observed, no HCl or CCl_2O is apparent in these two spectra. GC/

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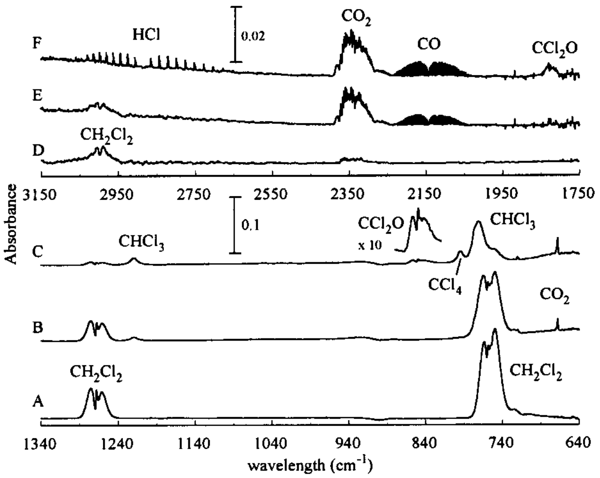

Figure 1. FTIR spectra taken during a typical lamp irradiation experiment. Spectra A−C: 1320 to 650 cm^{-1}; spectra D−F: 3100 to 1750 cm^{-1}. Spectra A and D show the characteristic CH_2Cl_2 absorption peaks before UV irradiation. B and E were collected after 60 min of UV irradiation, C and F after 135 min.

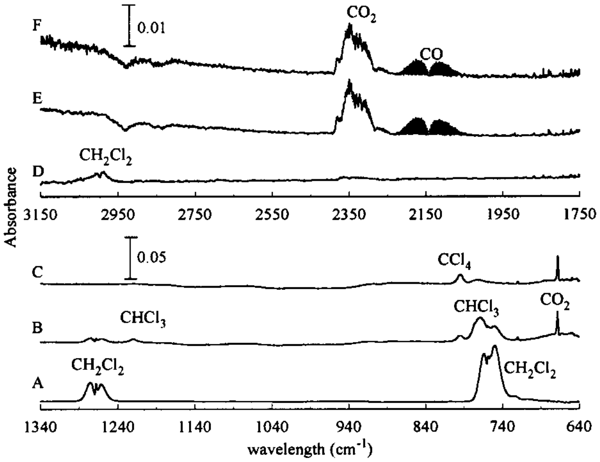

Figure 2. FTIR spectra taken during a laser irradiation experiment. Spectra A−C: 1320 to 650 cm^{-1}; spectra D−F: 3100 to 1750 cm^{-1}. Spectra A and D were collected before irradiation, B and E after 270 min of laser irradiation, C and F after 540 min.

MS scans taken during and after the long irradiation periods confirmed the FTIR observations that no phosgene was produced, to the detection limit of our experiments (roughly 0.2 nmol). There was also no GC/MS evidence for formation of larger C species.

A series of long exposure laser experiments (up to 14 h) was conducted to examine whether the laser would require longer reaction times for CCl_2O production. Again, no CCl_2O was produced according to the FTIR and GC/MS data acquired during the runs, even after these spectra showed the complete degradation of CH_2Cl_2. In separate experiments, a sample of CCl_2O could only be partially degraded after laser exposure for 2 h in the presence of TiO_2 and O_2. These experiments suggest that CCl_2O is not a degradation intermediate or product when 351-nm pulsed laser light is used.

In Figure 3 kinetic plots comparing the laser and lamp irradiation experiments provide further evidence that the nature of the excitation can affect the surface chemistry. In Figure 3, a kinetic plot of CH_2Cl_2 photodegradation using the UV lamp is shown, indicating a constant rate of degradation of CH_2Cl_2. In a previous study, Yates observed similar linear kinetics for the photocatalytic oxidation of TCE,[20] which has been ascribed to a rate-determining step of electron transfer from TiO_2 to adsorbed O_2.[23] However, when using the 351-nm pulsed laser, the time dependence of the degradation is exponential, indicating first-order kinetic behavior. These results suggest that alternative mechanisms may be responsible for the degradation.

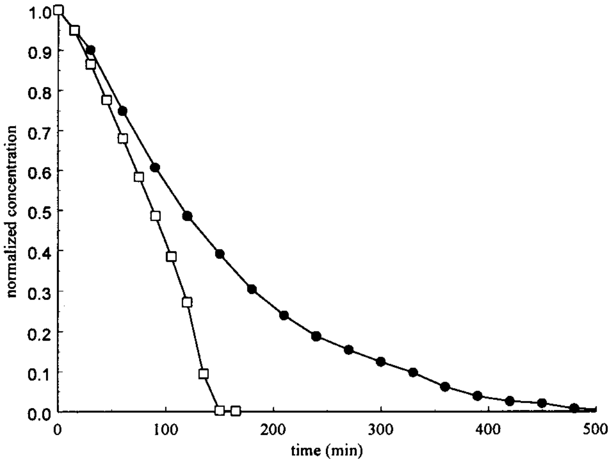

Figure 3. Kinetic plots showing the time dependence of the CH_2Cl_2 degradation during lamp and laser experiments. Lamp data (open squares) follow a linear dependence while the laser data (filled circles) indicate an exponential time dependence.

Additional experiments were carried out to determine the effect of O_2 and laser power on the degradation. In agreement with previous studies,[19,20,24−26] O_2 was required as a coreagent to observe CH_2Cl_2 degradation during lamp irradiation. However, the product distribution resulting from laser irradiation was no different whether O_2 was present or absent in the reaction cell. Control experiments did show, however, that the TiO_2 surface was necessary for degradation to proceed, suggesting that the photons provided by the laser may create a new pathway for the degradation of the CH_2Cl_2 at the surface which does not require O_2. We have ruled out the possibility of laser photodamage in experiments involving laser exposure followed by lamp degradation. The resulting products and kinetics were unchanged in comparison to those of experiments using the lamp only. Varying the laser power did affect the relative concentrations of CO and $CHCl_3$ produced, with CO being favored over $CHCl_3$ at the higher laser powers; however, phosgene and HCl were never observed in any of the laser experiments.

Bandwidth-limited experiments using the lamp were conducted and showed that the phosgene production could be significantly reduced (by a factor of 3) using a 350-nm long-pass filter and even eliminated by further limiting the shorter wavelengths of light. These results indicate a wavelength dependence in the product distribution. However, the photodegradation of methylene chloride still required the presence of O_2, indicating that the initial mechanism for methylene chloride degradation was unchanged.

We believe these experiments provide evidence for selective photocatalytic degradation on TiO_2 semiconductor surfaces. Further work is underway to ascertain the origin of the aforementioned observations, including, for example, the possibility of 2-e reduction.[27,28] In this case carbene formation (CCl_2) in the laser experiments seems unlikely at this time due to their propensity to form phosgene by reaction with OH[29] or multicarbon species, which were not observed. The ability to provide selective degradation may be important for developing new methodologies for destroying hazardous volatile organic compounds.

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