

Photocatalytic Dechlorination of Aqueous Carbon Tetrachloride Solutions in TiO₂ Layer Systems: A Chain Reaction Mechanism

Johannes Stark and Joseph Rabani*

Department of Physical Chemistry and the Farkas Center, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received: March 29, 1999; In Final Form: July 5, 1999

Quantum yields of chloride ions exceeding unity are obtained upon illumination of TiO₂ layers in aqueous solutions containing CCl₄ and methanol. The TiO₂ layers were prepared by spin coating using concentrated colloidal solution (prepared by hydrolysis of the propoxide). Absorbed light intensities were 7×10^{-11} to 2×10^{-8} ein cm⁻² s⁻¹. There is only a small, if any, effect of methanol concentration on the Cl⁻ yield in the range 0.2–5 M. Above 5 M, the yield remains nearly constant in the absence of air but decreases in aerated solutions. Only negligible Cl⁻ yield is obtained in the absence of methanol. In the presence of oxygen, the rate of photocatalytic Cl⁻ build up is proportional to the square root of the light intensity, as expected in a chain reaction. A similar study in oxygen-free solutions shows [Cl⁻] leveling off at the higher light intensities. The quantum yield increases with pH in both the presence and absence of oxygen, reaching values $\varphi \approx 7$ at pH 12.2, at the lowest light intensity. In the absence of oxygen, there is no observable effect of CCl₄ concentration on the Cl⁻ yield above 1×10^{-3} M, while the oxygen-containing systems show nearly linear increase of the yield upon increasing [CCl₄]. Thermal catalyzed formation of chloride is observed in the absence of oxygen. In the absence of oxygen, removal of adsorbed hydroxyl radicals, OH[•]_{ads}, by the methanol enables the electrons that have escaped recombination to react with CCl₄, producing chloride ions and CCl₃[•] radicals. This is followed by electron injection to the TiO₂ conduction band and subsequent hydrolysis of the CCl₃⁺ intermediate to carbon dioxide and HCl. A chain reaction mechanism is proposed also for oxygen-containing systems. The CCl₄ – O₂^{•-} adduct is the chain carrier and the termination involves dismutation of O₂^{•-} radical ions.

Introduction

Interest in the detailed mechanism of illuminated TiO₂ reactions arises from the intensive use of aqueous TiO₂ in photocatalytic organic reactions and its application for detoxification of pollutants from wastewaters.^{1–32} Considerable amount of work has been recently carried out on photocatalytic removal of chlorinated methane and other hydrocarbons, both in gas phase^{33–37} and in solution.^{38–51} Thermal catalysis of organic halogens in gas⁵² as well as liquid³⁹ phase has also been reported. These steady-state illumination studies of TiO₂ powders focused on product analysis at high light intensities and long illumination times, attempting to find the conditions for complete mineralization and the role of oxidative and reductive pathways and the role of additives. The use of TiO₂ powders makes it difficult to obtain reliable quantum yields because of light scattering. Accumulation of products complicates the reaction mechanism when competition of the products for the reactive intermediates becomes important.

The present manuscript concerns mechanistic studies on dechlorination of CCl₄. For this purpose we used for the first time TiO₂ layers which are fully transparent in the visible range. Such layers enable accurate determination of product quantum yields from which alternative mechanisms for the photocatalytic

process can be examined. Our study of this system reveals some features that have not been noticed before, such as the relatively efficient chain dechlorination reaction inducing chloride ion yields much greater than unity, and which, surprisingly, takes place also in the presence of oxygen. This chain reaction was not reported before, apparently because it was suppressed at high light intensities used. Our observations enable the separation of the pH effect on $\varphi_{\text{OH}_{\text{ads}}^{\bullet}}$ (the yield of adsorbed hydroxyl radicals) from reactions of OH⁻ ions with reactive intermediates.

Experimental Section

Materials. CCl₄ (Frutarom), methanol (Frutarom), NaOH (Frutarom), HClO₄ (Baker), Na₂HPO₄ (Sigma), NaH₂PO₄ (BDH), Na₂CO₃ (Baker), and NaHCO₃ (Frutarom) were used as received. Phosphate buffer was used to adjust the pH between 7 and 9. Carbonate/bicarbonate was used between pH 9 and 11, while pHs > 11 were adjusted using NaOH. An Orion Ross combination glass electrode was used for pH measurements (± 0.01 pH units at 25 °C).

Layers. TiO₂ colloid solutions were prepared by hydrolysis of titanium isopropoxide (Aldrich).⁵³ Solutions containing 200 g/L (D₃₅₅ of a 1/1000 solution was 0.13) at pH 2.5 (HNO₃) were used for the preparations of thin layers on ITO by successive spin coatings (1 min at 3500 rpm). Unless otherwise will be stated, three coatings were used, yielding a TiO₂ layer

* Author to whom correspondence should be addressed. E-mail: rabani@vms.huji.ac.il.

with optical absorption 0.3 at 355 nm. Layer dimensions were usually $0.9 \times 2.5 \text{ cm}^2$ with a thickness of $1 \pm 0.15 \mu\text{m}$.

Illumination. The excitation light source was a 75 W Xe lamp. The light was filtered by Pyrex glass (2 mm thick, cutting off below 300 nm) and an Oriel 59800 cutoff filter (transmitting below 400 nm). The light intensity was adjusted by appropriate neutral density filters, and was monitored by an OPHIR NOVA 10A-P-SH during illumination to ensure stability of the light. Heating by the IR irradiation was minimized by a water filter (9.5 cm). The illumination area was 1.2 cm^2 .

Reaction Cell. Experiments in air- and oxygen-saturated solutions were carried out in a closed 5 cm^3 cell with Pyrex windows, containing 4 cm^3 of CCl_4 -saturated solution ($5 \times 10^{-3} \text{ M}$) in water. Usually 0.2 M methanol was used as an OH scavenger.

Cells sealed with rubber septum were permeable to oxygen, particularly after puncturing with a needle. Oxygen-free solutions were therefore prepared by injection of 0.7 cm^3 of deaerated 0.65 M CCl_4 in methanol to a syringe containing 100 cm^3 water at the appropriate pH. The water solution was deaerated before addition of CCl_4 /methanol by bubbling with high-purity Ar gas. The CCl_4 /methanol solution was deaerated by shaking in a bottle (sealed with a rubber septum) after replacing the air in the gas phase by Ar. We avoided deaeration of the organic solutions because of the relatively high vapor pressure of CCl_4 . The measured amount of the organic solution was injected to the aqueous solution by means of an argonated small syringe, in the absence of a gas phase. This procedure excluded any detectable amounts of oxygen (confirmed by the lack of oxidation of a reduced methyl viologen solution). The solution (15 cm^3) was transferred to the illumination cell containing the TiO_2 layer fitted with a glass taper joint and a Teflon stopcock through a capillary pipe under a mild stream of argon. The solution was stirred by means of a magnetic stirrer. This method provided an oxygen-free system even after many hours, without significant depletion of CCl_4 by evaporation.

The TiO_2 layer was near to the optical window from which the light entered, with the TiO_2 -coated side facing the solution. The layer was preequilibrated with the solution in the dark by vigorous mixing (magnetic stirrer) during 20 min prior to illumination. Mixing continued during illumination.

Measurement of Cl^- . Chloride was measured using a chloride-sensitive electrode (ORION 9617BN) connected to an ORION A720 monitor. Before analysis, the pH was made alkaline, the solution evaporated to dryness, and refilled with 0.02 M NaNO_3 solution. This procedure was used to keep a constant ionic strength and to concentrate the chloride while removing the volatile solutes.

Formaldehyde was analyzed by its reaction (1.5 h at room temperature) with dinitrophenylhydrazine (DNPH). Spectrophotometric measurements were carried out at 360 nm using Kontron's Uvikon 860 spectrophotometer. The reagent was a freshly prepared solution of $5.4 \times 10^{-4} \text{ M}$ DNPH solution in 1 M HCl. We used $\Delta\epsilon_{360}(\text{product} - \text{DNPH}) = 3520 \text{ M}^{-1} \text{ cm}^{-1}$. The absorbance has been found to increase linearly at the $[\text{HCOH}]$ range 2 to $8 \times 10^{-5} \text{ M}$.

Gas chromatography was used for determination of CHCl_3 and CH_2Cl_2 . The gas chromatograph was Hewlett-Packard 5890 series II equipped with a TC detector, HP-1 methyl-silicone $5 \text{ m} \times 0.53 \text{ mm}$ column, HP 3396 integrator, and FID detector. The samples were extracted from the aqueous solution with *p*-xylene (Sigma, HPLC grade).

The amount of absorbed light was determined from the decrease in light intensity observed upon replacing a bare ITO

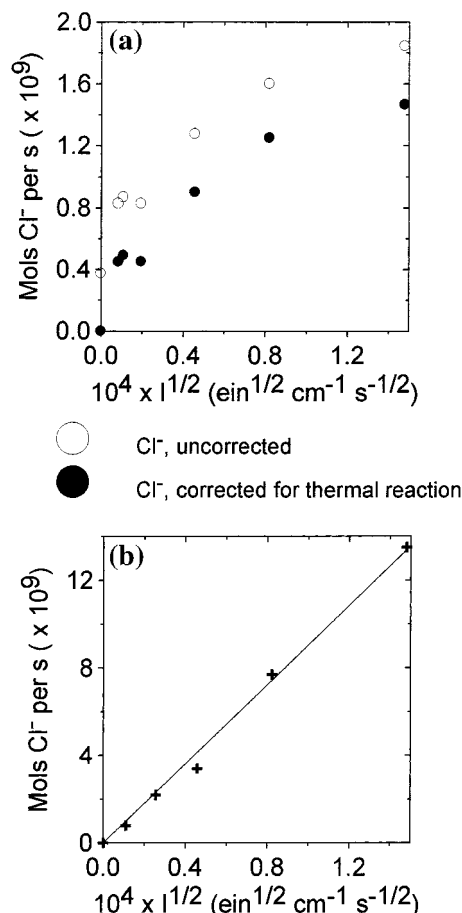


Figure 1. (a) Formation of Cl^- as a function of $I^{1/2}$. Deaerated (Ar) system containing $5 \times 10^{-3} \text{ M}$ CCl_4 and 0.2 M MeOH at pH 12.2. (b) Formation of Cl^- as a function of $I^{1/2}$. Systems containing air, $5 \times 10^{-3} \text{ M}$ CCl_4 , and 0.2 M MeOH at pH 12.2.

glass with one coated with TiO_2 , using the Fe^{3+} oxalate actinometer.⁵⁴

Results

Oxygen-Free Solutions. Illumination of the TiO_2 layer in the presence of air-free solution typically containing $5 \times 10^{-3} \text{ M}$ CCl_4 and 0.2 M methanol induces formation of the chloride ion, the concentration of which increases linearly with the time of illumination. The quantum yield of the chloride ion, ϕ_{Cl^-} , depends only little, if at all, on methanol concentration in the range 0.2–10 M. There is, however, a remarkable effect of light intensity on the rate of chloride formation. This is shown in Figure 1a, where the rate of build up is plotted against the square root of light intensity. Note that under the conditions of Figure 1a, chloride ions are also produced by a dark reaction. We suggest that a chain reaction accounts for the light-induced process, although the rate increases slower than \sqrt{I} and approaches saturation (namely, rate independent of light intensity) above $10^{-8} \text{ ein cm}^{-2} \text{ s}^{-1}$.

The quantum yield of Cl^- does not depend on CCl_4 concentration (7.5×10^{-4} to $5 \times 10^{-3} \text{ M}$). There is, however, a strong effect of pH above 9, both on the photolytic and on the dark processes, as shown in Figure 2. Phosphate buffer (3–30 mM) and carbonate (4–40 mM) have only a small, if any effect on the yield.

Measurements of Chloroform, Methylene Chloride, and Formaldehyde. There are no measurable amounts of either CHCl_3 ($[\text{CHCl}_3]/[\text{Cl}^-] < 0.15$) or CH_2Cl_2 ($[\text{CH}_2\text{Cl}_2]/[\text{Cl}^-] <$

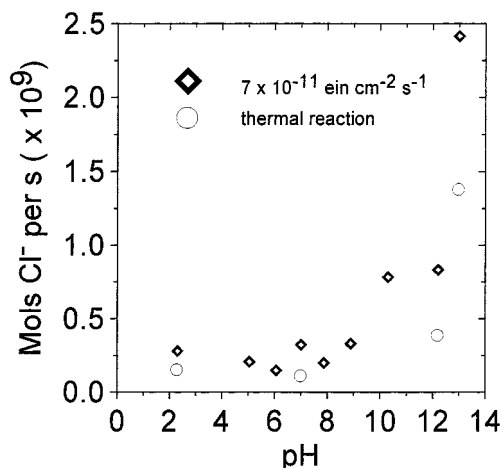


Figure 2. Effect of pH on the rate of Cl^- formation. Deaerated (Ar) system containing 5×10^{-3} M CCl_4 and 0.2 M MeOH at pH 12.2. $I = 7 \times 10^{-11}$ ein $\text{cm}^{-2} \text{s}^{-1}$.

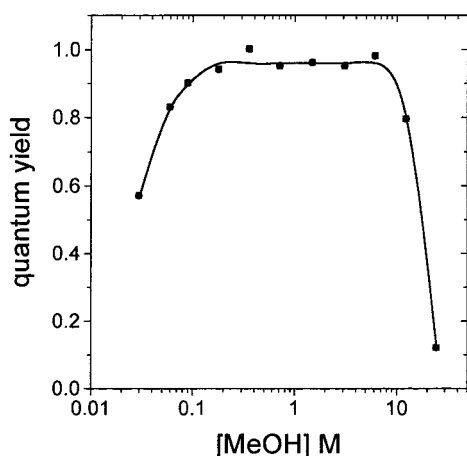


Figure 3. Effect of methanol concentration on the quantum yield of Cl^- . Aerated solutions, 7×10^{-9} ein $\text{cm}^{-2} \text{s}^{-1}$, 5×10^{-3} M CCl_4 at pH 12.2.

0.02). Even if chloroform is initially added, it is quickly depleted to below the detectable limit.

Relatively low formaldehyde yields have been measured. At the lowest intensities used, the initial rate of formaldehyde build up increases linearly with illumination time. The quantum yield of formaldehyde decreases upon increasing the light intensity. However, it is considerably lower than the respective yields of chloride formation at any given intensity. Thus, at 7×10^{-11} ein $\text{cm}^{-2} \text{s}^{-1}$ (0.2 M methanol, pH 12.2) we measured $\varphi_{\text{HCHO}} \approx 0.14$,⁵⁵ compared to $\varphi_{\text{Cl}^-} = 5.6$ (corrected 40 and 45% for thermal reaction, respectively). At higher intensities, where "saturation" is observed with respect to chloride build up, the ratio $\varphi_{\text{Cl}^-}/\varphi_{\text{HCHO}}$ decreases to 9.

Results in the Presence of Oxygen. The rate of Cl^- formation increases linearly with $I^{1/2}$ (Figure 1b). Methanol concentration has no effect on φ_{Cl^-} in the range 0.1–6 M. A sharp decrease of φ_{Cl^-} takes place when methanol concentration exceeds 10 M (Figure 3). The effect of oxygen concentration is presented in Figure 4, where a sharp increase from $\varphi_{\text{Cl}^-} = 0.15$ (under Ar) to $\varphi_{\text{Cl}^-} = 1$ at 2.5×10^{-4} to 1.2×10^{-3} M O_2 takes place (Figure 4, 7×10^{-9} ein $\text{cm}^{-2} \text{s}^{-1}$ at pH 12.2). In contrast with the results in air free solutions, where φ_{Cl^-} is nearly independent of $[\text{CCl}_4]$, a nearly linear increase with CCl_4 concentration is observed in the presence of oxygen. The rate of Cl^- formation increases linearly with $[\text{OH}^-]^{1/2}$ over a wide range of pH. This is shown in Figure 5. Deviation occurs at the

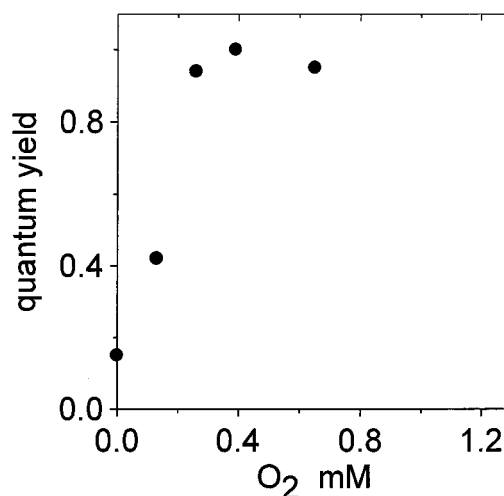


Figure 4. Effect of O_2 concentration on Cl^- formation. 5×10^{-3} M CCl_4 at pH 12.2 containing 0.2 M CH_3OH , $I = 7 \times 10^{-9}$ ein $\text{cm}^{-2} \text{s}^{-1}$.

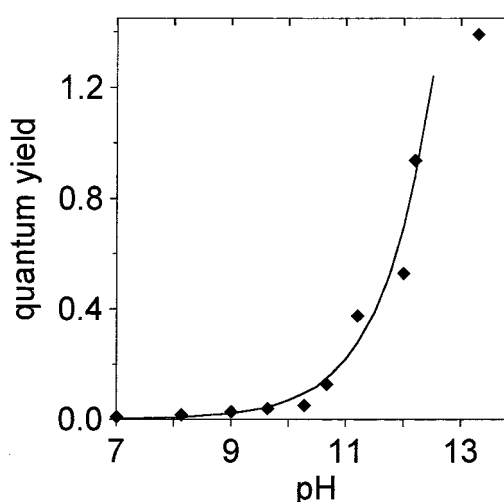


Figure 5. Effect of pH on Cl^- formation. 5×10^{-3} M CCl_4 at pH 12.2 containing 0.2 M CH_3OH , air-saturated, $I = 7 \times 10^{-9}$ ein $\text{cm}^{-2} \text{s}^{-1}$. Solid line: calculated with $K_{18k19} = 85 \text{ M}^{-1} \text{s}^{-1}$.

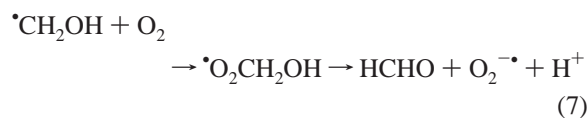
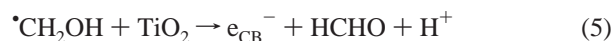
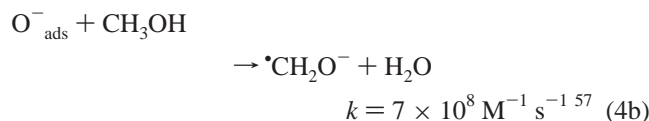
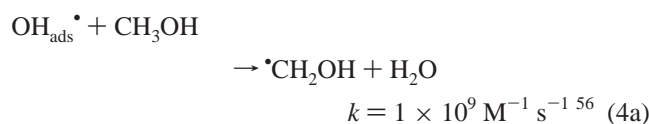
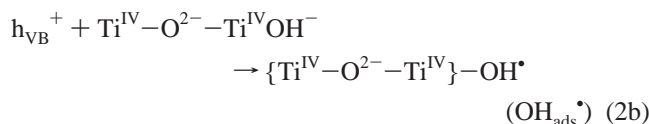
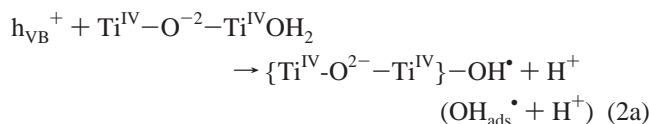
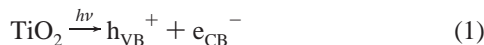
highest pH (apparently because of saturation of the TiO_2 surface) and at pH < 8. No dark reaction takes place in the presence of O_2 .

Build up of formaldehyde, measured at pH 12.2 in CCl_4 saturated solutions containing 0.2 M methanol, is linear with illumination time. The quantum yield of formaldehyde, $\varphi_{\text{HCHO}} = 0.40 \pm 0.08$ (standard deviation), represents an average value for the entire range of light intensities used in this work. The effect of light intensity is relatively small: φ_{HCHO} changes from 0.46 at the lowest to 0.31 at the highest intensity used. The ratio $\varphi_{\text{Cl}^-}/\varphi_{\text{HCHO}}$ however, varies from ≈ 14 at the lowest to 1.7 at the highest intensity. The change of this ratio reflects predominantly the variation of φ_{Cl^-} with light intensity.

Discussion

Absorption of a photon by a TiO_2 nanocrystallite produces an electron–hole pair (process 1). Valence band holes oxidize surface water molecules producing adsorbed hydroxyl radicals, also referred to as "trapped holes" (reactions 2). Process 3 represents trapping of the electrons. In alkaline solutions $\text{OH}_{\text{ads}}^\bullet$ is expected to undergo ionic dissociation, producing $\text{O}^{\bullet-}_{\text{ads}}$. The reactions of both forms of OH^\bullet are known to be qualitatively similar. In the absence of scavengers, efficient electron–hole recombination takes place, involving both mobile and trapped

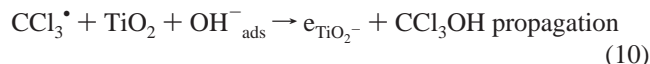
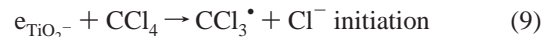
forms of the electrons and the holes. Although both recombination and trapping processes take place in the ps time range, adsorbed reactants are capable competing for electrons and holes. Thus, the hydroxyl radical, OH[•]_{ads}, reacts with scavengers such as methanol by hydrogen abstraction (reactions 4). Reactions 1–4 take place irrespective of the presence of oxygen. Subsequent reactions are affected by oxygen: In the absence of oxygen, the [•]CH₂OH radical is expected either to inject an electron into the TiO₂ conduction band according to reaction 5 or to decay by disproportionation according to reaction 6.



In either case, there is formation of formaldehyde, although the amount is doubled if reaction 5 is the predominant one. Oxygen reacts with both [•]CH₂OH and e_{TiO₂}⁻ according to reactions 7 and 8, respectively, both producing the superoxide radical ion, O₂^{•-}. The rate constant $k_7 = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁸ has been reported for homogeneous aqueous solution. The rate constant $k_8 = 7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ⁵⁹ has been reported for the trapped electron in TiO₂ colloid solution. The peroxy radical intermediate, [•]O₂CH₂OH quickly decomposes to yield the superoxide radical ion and formaldehyde in the presence of a base.⁶⁰ Thus, in the presence of oxygen, the mechanism must involve reactions of O₂^{•-}. This is in contrast to the initial step in the absence of oxygen, involving reduction by the electrons which escape recombination with holes.

Mechanism in the Oxygen-Free Systems. Only negligible yields of chloride are observed in the absence of methanol. This implies that reaction 9 does not compete with electron–hole recombination, namely, CCl₄ reacts only with the electrons that remain after the removal of the OH[•]_{ads} and O^{•-}_{ads} radicals by methanol. The lack of [CCl₄] effect on the rate of Cl⁻ build up

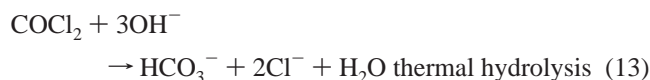
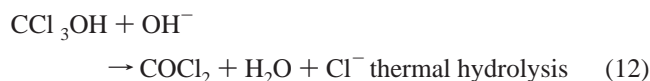
in methanol-containing systems also supports the conclusion that CCl₄ does not compete for the electrons.



The high quantum yields of chloride ions, reaching 6 at the lower intensities used, indicate a chain reaction. We suggest reactions 10 and 11 as the propagation and termination steps, respectively.

Methanol concentration (0.2–12 M) has no measurable effect on the yield of chloride. This indicates that complete scavenging of OH[•]_{ads} (or O^{•-}_{ads}) by the methanol takes place already at the lower concentration,⁶¹ in contrast to the decrease in electron yield reported earlier for [methanol] > 6 M in a pulsed laser study.⁶² The earlier observation has been assigned to electron transfer from methanol to a TiO₂ hole, with subsequent recombination of CH₃OH^{•+} radical ions with conduction band electrons. Under our present conditions, only one electron–hole pair is produced in the same micro-volume, while under the conditions of laser photolysis, recombination is more effective since many pairs are simultaneously produced.

Reaction 10 accounts for the large difference between chloride and formaldehyde yields. This reaction qualitatively explains the strong pH effect on the Cl⁻ yield (Figure 2), although the initiation rate may also increase at elevated pH values. The product of reaction 10, CCl₃OH, decomposes to chloride ions and CO₂ by reactions 12 and 13.⁶³



Alternative Mechanisms—Ar-Saturated Solutions. An alternative mechanism involving hydrogen abstraction by CCl₃[•], so that the chain is carried by reactions 5 and 14 instead of reactions 9 and 10 can be ruled out as the main path of Cl⁻ formation. Such a mechanism predicts the formation of equivalent concentrations of chloride ions, formaldehyde, and chloroform, in contrast to the



observed $\varphi_{\text{HCHO}} \ll \varphi_{\text{Cl}^-}$. It may also be argued that the high yields of chloride reflect high yields of water oxidation at the high pH values, since the driving force for OH⁻ oxidation is larger than that for water oxidation. However, measurements of formaldehyde in oxygen-containing systems, under conditions where $\varphi_{\text{HCHO}} = 2\varphi_{\text{OH}_{\text{ads}}}$ indicate that $\varphi_{\text{OH}_{\text{ads}}}$ is much less affected by pH (in the range 7–12) compared to φ_{Cl^-} . Moreover, without a chain process, the maximum chloride yield can reach $\varphi_{\text{Cl}^-} = 2$, in the unlikely case that both the quantum yield for scavenging of OH[•]_{ads} by methanol and that for electron injection from CH₂OH[•] reach unity.

The conclusion that the chain mechanism involves reaction 10 agrees with the results showing $\varphi_{\text{Cl}^-} \gg \varphi_{\text{HCHO}}$. According to the above reaction scheme, the yields of Cl⁻ and formaldehyde are not directly interrelated because the propagation

reactions 9 and 10 do not involve methanol radicals. On the other hand, if there is no chain formation of Cl^- , the ratio $\varphi_{\text{Cl}^-}/\varphi_{\text{HCHO}}$ is expected to be 2 (in either case, whether $\text{CH}_2\text{OH}^\bullet$ radicals react according to reaction 5 or disappear by disproportionation),⁶⁴ contrary to the observations.

The effect of light intensity on the rate of formaldehyde formation may reflect the slowness of reaction 9. Thus, as the light intensity is increased, the yield of formaldehyde decreases from $\varphi_{\text{HCHO}} = 0.14$ (at 7×10^{-11} ein $\text{cm}^{-2} \text{s}^{-1}$) to < 0.01 (at 2×10^{-8} ein $\text{cm}^{-2} \text{s}^{-1}$). In the same range of light intensities φ_{Cl^-} varies from 5.6 to 0.05. The proposed interpretation predicts a larger intensity effect on the chloride yield compared to the effect on φ_{HCHO} . The decrease of the latter is attributed to enhanced electron-hole recombination resulting from higher steady-state concentrations of trapped electrons. The trapped electrons react with holes before they are converted to adsorbed hydroxyl radicals. This affects φ_{HCHO} since the methanol reacts only with holes which are trapped at the surface as $\text{OH}^\bullet_{\text{ads}}$, reaction 4 being the only source of formaldehyde. The chloride yield, on the other hand, is affected both by the decrease of $\varphi_{\text{OH}^\bullet}$ and by the enhanced rate of the termination reaction 11 at the higher light intensities. Note that formation of the bi-radical $:\text{CCl}_2$ by a two-electron reduction of CCl_4 has been proposed^{64,67} in oxygen-free systems containing CCl_4 . Accumulation of trapped electrons at high light intensities may favor formation of $:\text{CCl}_2$. Recombination of the bi-radical produces tetrachloroethylene, although hydrolysis to CO and Cl^- is also possible. In either case, if $:\text{CCl}_2$ is produced, it must suppress the chain initiation step because its formation must be at the expense of CCl_3^\bullet . For each $:\text{CCl}_2$ bi-radical which might have disappeared by recombination, 2 Cl^- ions and one HCHO molecule would have been produced. On the other hand, for each $:\text{CCl}_2$ bi-radical which would have disappeared by hydrolysis, 4 Cl^- ions and one HCHO molecule would have been produced. These ratios of $[\text{Cl}^-]/[\text{HCHO}]$ are considerably lower than the experimental ratios. Thus, a ratio 8.6 was measured at the highest light intensity. Lower intensities favor even higher ratios. In conclusion, formation of $:\text{CCl}_2$ is not ruled out at the higher intensities which were used, although it is not a major precursor of Cl^- ions under our conditions (perhaps with the exception of the highest intensity used).

Kinetic Constants—Air-Free Systems. The rate of chain propagation is given by $d[\text{Cl}^-]/dt = 4k_{10}[\text{OH}^\bullet_{\text{ads}}][\text{CCl}_3^\bullet]$. The factor “4” is introduced to account for additional chloride formation by reactions 12 and 13. Thus, the initiation reaction produces one chloride ion for each electron that reacted with CCl_4 , while each propagation cycle produces three additional chloride ions.

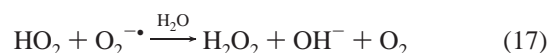
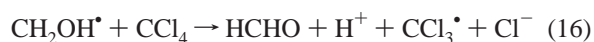
If the layer can be considered as closely packed spherical TiO_2 molecules, only 1/3 of the illuminated volume (1.2 cm^2 area and 1μ thickness) is available for the aqueous solution of reactants and intermediates. The stable reaction products are carried away outside the layer first by diffusion to the open surface and then by convection resulting from the vigorous stirring of the solution which is outside the layer. Reactions involving species that are produced at the TiO_2 or are strongly adsorbed to its surface such as $\text{OH}^\bullet_{\text{ads}}$, eTiO_2^- , OH^-_{ads} may involve both adsorbed reactants and molecules reaching the surface from the bulk. Adsorption of reactants may affect the overall rate of the chain reaction; however, in the absence of quantitative information we find it convenient to use the homogeneous bulk concentrations of reactants such as OH^- and CCl_4 . The proposed mechanism, assuming steady-state concentration for CCl_3^\bullet radicals, leads to the propagation rate equation

$d[\text{Cl}^-]/dt = 4k_{10}[\text{OH}^-](\varphi I/2k_{11})^{1/2}$, where I stands for the absorbed light intensity (ein $\text{dm}^{-3} \text{s}^{-1}$), φ is the quantum yield for electrons escaping recombination with holes (namely, the quantum yield for the initiation reaction), k_{10} (s^{-1}) and k_{11} ($\text{M}^{-1} \text{s}^{-1}$) are the rate constants for reactions 10 and 11, respectively.

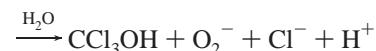
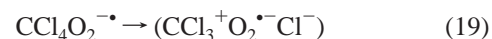
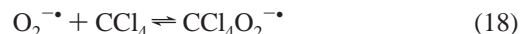
The initial slope of Figure 1a is $(2 \times 10^{-9})/(8 \times 10^{-5}) = 2.5 \times 10^{-5} \text{ mol cm s}^{-1/2} \text{ ein}^{-1/2}$, or 0.13 in units of $\text{M s}^{-1/2} \text{ ein}^{-1/2} \text{ dm}^{3/2}$. The value for k_{11} in aqueous solution is $3.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$.⁶⁵ Taking average $\varphi = 0.1$ for the lowest intensities at pH 12.2, $k_{10} = 2 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$. Since $[\text{CCl}_3^\bullet]_{\text{ss}} = (\varphi I/2k_{12})^{1/2} = 2.3 \times 10^{-5} I^{1/2}$, at the highest intensity $[\text{CCl}_3^\bullet]_{\text{ss}} = 1.3 \times 10^{-5} \text{ M}$, yielding a calculated half-life time of the termination step $\approx 100 \mu\text{s}$. Using a typical diffusion coefficient of $3 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, the average distance which a free CCl_3^\bullet radical diffuses during the half-life time is about a quarter of the layer thickness. This distance may be smaller if a considerable fraction of the CCl_3^\bullet radicals is adsorbed to the TiO_2 surface. Such adsorption would of course affect the derivation of the kinetic parameters.

The mechanism presented above predicts linear dependency of the propagation rate on $[\text{OH}^-]$. Indeed, the yield of chloride ions increases sharply in alkaline solutions. However, due to inaccuracy introduced by the substantial contribution of thermal formation of chloride ions no quantitative comparison between experimental and calculated pH effect was attempted.

Oxygen-Containing Systems. Oxygen reacts with all three reducing intermediates, $\text{CH}_2\text{OH}^\bullet$, eTiO_2^- , and CCl_3^\bullet according to reactions 7, 8, and 15, respectively. Reaction 15, however, can be



ignored since reaction 9 which produces the CCl_3^\bullet radical is expected to be suppressed by reaction 8. Formation of CCl_3^\bullet by reaction 16 is also unlikely since $k_{16} < 10^6 \text{ M}^{-1} \text{s}^{-1}$.⁶⁶ Under homogeneous conditions, at pH 5–13 (no TiO_2), the $\text{O}_2^{\bullet-}$ radical ion disproportionates according to reaction 17 with HO_2^\bullet , $k_{17} = 9.7 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$. HO_2^\bullet is known to be a weak acid, $pK_{\text{HO}_2} = 4.8$.⁶⁷



We propose that a chain process producing Cl^- ions is initiated by the relatively rapid equilibrium reaction 18, followed by the propagation process (reaction 19). Reaction 17 terminates the chain. The $\text{O}_2^{\bullet-}$ radical ion has been reported to react with CCl_4 in aprotic media,⁶⁸ and has also been suggested as an active intermediate in oxidation of organic substrates.⁶⁹ In the aqueous media equilibrium, reaction 18 is expected to be strongly shifted to the left so that $[\text{CCl}_4\text{O}_2^{\bullet-}] \ll [\text{O}_2^{\bullet-}]$. According to this mechanism, the yield of Cl^- ions does not depend on the competition between reactions 5 and 7 since both reactions eventually produce the $\text{O}_2^{\bullet-}$ radical ion. The intermediate CCl_3OH is hydrolyzed according to reactions 12 and 13, producing three additional chloride ions and carbon dioxide. Note that reaction 17 produces hydrogen peroxide; however, no H_2O_2 was

observed in alkaline solutions, and only insignificant amounts were measured in neutral solutions. Control experiments show that under our conditions hydrogen peroxide is decomposed at the TiO₂ surface by a photocatalytic process. These results suggest that adsorbed H₂O₂ molecules produced by reaction 17 yield additional OH• radicals according to the Haber–Weiss reaction 20.



The subsequent fast reactions 4 and 7 result with the formation of O₂•⁻ and HCHO. Thus, the overall net effect is destruction of H₂O₂ and doubling the yield of HCHO so that $\varphi_{\text{HCHO}} = 2\varphi_{\text{OH}^\bullet}$. The steady-state concentration of O₂•⁻ radical ions and hence the chain length and Cl⁻ yield are not affected by reaction 20. H₂O₂ may also compete for e_{TiO₂}•⁻, although it is not likely in view of the much higher concentration of oxygen. The yields of both HCHO and Cl⁻, however, are independent of the detailed mechanism by which H₂O₂ is reduced.

The observed yields of chloride ions are much higher than the respective yields of formaldehyde, indicating that a chain reaction involving hydrogen abstraction from methanol by radicals such as CCl₃O₂• cannot be important.

Kormann, Bahnemann and Hoffmann⁷⁰ proposed that recombination of OH•_{ads} induces $I^{1/2}$ dependency of the build up of chloride ions in the TiO₂–chloroform system at high light intensities. The effect of intensity on $\varphi_{\text{OH}^\bullet}$ will be discussed later (see section on formaldehyde yield).

Kinetic Constants—Oxygenated Systems. The rate of build up of chloride ion is given by eq 21

$$d[\text{Cl}^-]/dt = 4K_{18}k_{19}(K_{\text{HO}_2}[\text{OH}^-]\varphi_{\text{OH}^\bullet}/(k_{17}K_w))^{1/2}[\text{CCl}_4]I^{1/2} \quad (21)$$

where $\varphi_{\text{OH}^\bullet}$ stands for the quantum yield of the adsorbed OH• radicals. [OH⁻] and [CCl₄] are constant at a given pH and CCl₄ concentration, provided that the diffusion of these species from the bulk is sufficiently fast to compensate for their depletion inside the layer during photolysis. The concentrations on the TiO₂ surface may differ from those in the bulk due to adsorption. However, in the absence of specific data concerning adsorption, we assumed homogeneous distribution of transients inside the layer and used the bulk concentrations of hydroxide ions and CCl₄. Diffusion of the intermediates CCl₄O₂•⁻ and O₂•⁻ to the bulk was ignored. The proposed mechanism accounts for the observed linear increase of Cl⁻ formation rate with $I^{1/2}$ (Figure 1b), [CCl₄], and [OH⁻]^{1/2} (the latter in the pH range 9–12, Figure 5). Although not clearly seen in Figure 5, the observed yields at pH < 9 are 2–3 times higher than the calculated ones. Under these conditions, the rate of termination is relatively high, and the chain reaction is highly suppressed. A different mechanism (unnoticed at the higher pH values because of the longer chains) may produce additional Cl⁻ ions. In addition, as discussed before, the initiation yield may increase with pH as a result of increased $\varphi_{\text{OH}^\bullet}$. At pH 13.2 the observed chloride yield falls below that predicted by eq 21. This is probably related to saturation of the TiO₂ surface by OH⁻ ions which is apparently approached at this pH.

We have not observed Cl⁻ formation upon reaction of an alkaline solution containing CCl₄ with KO₂ in the absence of TiO₂. KO₂ is ionized in water yielding O₂•⁻ radical ions. Consequently, TiO₂ has a double role: photosensitization of the process and activation of the reactive intermediates.

The slope of Figure 1b is $9.0 \times 10^{-5} \text{ mol cm s}^{-1/2} \text{ ein}^{-1/2}$, or $0.41 \text{ M s}^{-1/2} \text{ ein}^{-1/2} \text{ dm}^{3/2}$. This slope is equal to $4K_{18}k_{19}$ –

$(K_{\text{HO}_2}[\text{OH}^-]\varphi_{\text{OH}^\bullet}/(k_{17}K_w))^{1/2}[\text{CCl}_4]$. Inserting the values $K_w = 10^{-14}$, $K_{\text{HO}_2} = 1.6 \times 10^{-5} \text{ M}$, $k_{17} = 9.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $[\text{OH}^-] = 0.016 \text{ M}$, $[\text{CCl}_4] = 0.005 \text{ M}$ and $\varphi_{\text{OH}^\bullet} = 0.2$ (see next section) yields $K_{18}k_{19} = (90 \pm 15) \text{ M}^{-1} \text{ s}^{-1}$.

Formaldehyde Yield. In the presence of oxygen at pH 12.2, $\varphi_{\text{OH}^\bullet} = 1/2\varphi_{\text{HCHO}} = 0.2$. This relatively high yield represents an average value for the entire intensity range studied in the present work, although the experimental results show a systematic decrease from 0.46 to 0.31. This behavior is similar to that reported by Sun and Bolton⁶¹ for the methanol system in CCl₄-free aerated suspensions of TiO₂ powder, although their yields are much lower. From Figure 5,⁶¹ $\varphi_{\text{OH}^\bullet} = 0.060\text{--}1.4 \times 10^2 I^{1/2}$, showing a comparable (33%) decrease of $\varphi_{\text{OH}^\bullet}$ to that reported here. The relatively small intensity effect is expected as oxygen removes the electrons (reaction 8) and prevents the build up of a high steady-state electron concentration which is required for enhanced recombination with holes. The relatively small change of $\varphi_{\text{OH}^\bullet}$ does not introduce an observable deviation from the linear relationship between the rate of chloride formation and $I^{1/2}$ (Figure 1b). Note that the rate of Cl⁻ buildup is expected to increase with $\varphi_{\text{OH}^\bullet}^{1/2}$, and therefore, the effect of light intensity on the yield of OH• is much smaller than its effect on the termination reaction. $K_{18}k_{19} = 90 \text{ M}^{-1} \text{ s}^{-1}$ fits well with the pH effect (line in Figure 5). This indicates that $\varphi_{\text{OH}^\bullet}$ does not change much with pH in our system.

The situation is different in the absence of oxygen. Since electrons react relatively slowly with CCl₄, the build up of sufficiently high local steady-state electron concentrations which are sufficient to compete with reaction 4 is feasible. Under such conditions, the yield of OH• and consequently the yields of formaldehyde and chloride show strong dependency on light intensity, such as shown in Figure 1a. Note that unlike the oxygenated systems, φ_{HCHO} does not reflect directly on $\varphi_{\text{OH}^\bullet}$ because the fate of •CH₂OH is not clear as it depends on the relative rates of reactions 5 and 6.

Alternative Mechanisms. Although the proposed mechanism agrees very well with the results, we have considered several alternative mechanisms.

Reaction 19 may involve the formation of the CCl₃O₂• radical instead of CCl₃OH + O₂•⁻. Equation 21 can be derived on the basis of this mechanism if the formation of CCl₃O₂• is followed by spontaneous dissociation to CCl₃• + O₂•⁻ or by reaction of the peroxy radical with water or hydroxide ions producing CCl₃OH + O₂•⁻, provided that the reaction with OH⁻ is not rate determining. A different result is obtained in the case that the CCl₃O₂• radical lives long enough to recombine to a tetroxide. The tetroxide is expected to decompose and produce molecular oxygen and two CCl₃O• radicals,⁷¹ the latter abstract hydrogen from methanol, with the formation of CCl₃OH and •CH₂OH. This kind of chain propagation produces Cl⁻ ions and HCHO at a ratio 4:1. Although the linear dependencies of the rate of Cl⁻ build up on $I^{1/2}$, [CCl₄], and [OH⁻]^{1/2} are predicted by this mechanism, the maximum calculated ratio of [Cl⁻]/[HCHO] is much lower than the experimental ratio 14.3 reached at $1.2 \times 10^{-10} \text{ ein cm}^{-2} \text{ s}^{-1}$.

Involvement of hydroxide ions instead of water molecules in reaction 19 can be ruled out. Such mechanism is expected to show much stronger dependency of φ_{Cl^-} on pH than actually observed, because this mechanism predicts both linear increase of the propagation rate with [OH⁻] and a parallel decrease of the termination rate with increasing [OH⁻]^{1/2}.

Termination of the chain by recombination of CCl₃O₂• radicals can be ruled out because of two reasons. First, such termination is not expected to show the observed pH effect,

which in this case must be attributed to enhancement of the propagation rate at elevated pH. This would require to invoke reaction of OH^- with $\text{CCl}_4\text{O}_2^{\bullet-}$ at the propagation rate-determining step. The kinetics of such a mechanism yields linear dependency of the Cl^- formation rate on $[\text{OH}^-]$, in contrast to the experimental results. In addition, it is difficult to see how $\text{CCl}_3\text{O}_2^{\bullet}$ recombination terminates the chain without releasing three Cl^- ions which would predict that $[\text{Cl}^-]/[\text{HCHO}] > 8$, while experiments at the highest light intensity (pH 12.2) show a ratio < 2 .

Conclusions

Efficient dechlorination takes place upon UV photolysis of TiO_2 nanocrystallite layers in contact with aqueous solutions containing both CCl_4 and methanol. Quantum yields much higher than one are reported here for the first time, suggesting an efficient chain reaction in both the presence and absence of oxygen. The work has been focused on chloride ion build up in CCl_4 -methanol aqueous systems. Earlier works on photocatalytic dehalogenation of organic compounds show considerably lower product yields than in the present work.^{41–48} The difference arises from the use of higher pH values and relatively low light intensities in the present work. The preparation method of the TiO_2 and its use in the form of a layer may also have contributed to the length of the chain.

In oxygen-free systems, the mechanism involves initiation by electron reduction of CCl_4 followed by electron injection from the $\bullet\text{CCl}_3$ radical to the TiO_2 layer. Termination of the chain takes place by $\bullet\text{CCl}_3$ recombination. The $\text{CCl}_4\text{O}_2^{\bullet-}$ adduct initiates the chain in the presence of O_2 . The proposed mechanism is in agreement with the effects of pH, intensity, and $[\text{CCl}_4]$.

This study indicates that the yield of $\bullet\text{OH}$ changes only little with light intensity and pH, and is considerably higher than previously reported for TiO_2 powder.⁶¹ Further work is in progress on the yields in CCl_4 -free systems.

Acknowledgment. We acknowledge the support of the Israel–German Research Program MOS/BMBF. We thank Dr. D. W. Bahnemann, Dr. Sara Goldstein, Prof. Robert Schiller, and Prof. Clemens von Sonntag for most useful discussions.

References and Notes

- Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 2239, 5985.
- Fujihira, M.; Satoh, Y.; Osa, T. *Nature* **1981**, *293*, 206.
- Ollis, D. F.; Hsiao, C.-Y.; Budiman, L.; Lee, C.-L. *J. Catal.* **1984**, *88*, 89.
- Matthews, R. W. *J. Phys. Chem.* **1987**, *91*, 3328.
- Matthews, R. W. *J. Catal.* **1988**, *111*, 264.
- Al-Ekabi, H.; Serpone, N.; Pelizzetti, E.; Minero, C.; Fox, M. A.; Draper, R. B. *Langmuir* **1989**, *5*, 250.
- Turchi, C. S.; Ollis, D. F. *J. Catal.* **1990**, *122*, 178.
- Okamoto, K.; Yamamoto, Y.; Tanak, H.; Tanaka, M.; Itaya, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2015.
- Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69.
- Turchi, C. S.; Ollis, D. F. *J. Catal.* **1989**, *119*, 483.
- Minero, C.; Aliberti, C.; Pelizzetti, E.; Terzian, R.; Serpone, N. *Langmuir* **1991**, *7*, 928.
- Peterson, M. W.; Nozik, A. J. *J. Phys. Chem.* **1991**, *95*, 221.
- Milles, G.; Hoffman, M. R. *Environ. Sci. Technol.* **1993**, *27*, 1681.
- Bahnemann, D.; Bockelmann, D.; Goslich, R. *Solar Energy Mater.* **1991**, *24*, 564.
- Hilgendorff, M.; Hilgendorff, M.; Bahnemann, D. W. *J. Adv. Oxid. Technol.* **1996**, *1*, 35.
- Pelizzetti, E.; Schiavello, M. *Photochemical Conversion and Storage of Solar Energy*; Kluwer Academic Publishers: Dordrecht, 1991.
- Fujishima, A. *IPS-11, Book of Abstracts*; Krishnan, V., Ed.; 1996, p 11.
- Heller, A.; Nair, M.; Davidson, L.; Luo, Z.; Schwitzgebel, J.; Norrell, J.; Brock, J. R.; Lindquist, S.-E.; Ekerdt, J. G. *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier Science Publishers B. V.: Amsterdam, The Netherlands, 1993; Vol. 3, pp 139–153.
- Bahnemann, D. W.; Cunningham, J.; Fox, M. A.; Pelizzetti, E.; Pichat, P.; Serpone, N. *Aquatic and Surface Photochemistry*; Helz, G. R., Zepp, R. G., Crosby, D. G., Eds.; CRC Press: Boca Raton, FL, 1994; pp 261–316.
- Martin, S. T.; Herrmann, H.; Hoffmann, M. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3323.
- Tanaka, K.; Hisanga, T.; Rivera, A. P. *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier Science Publishers B. V.: Amsterdam, The Netherlands, 1993; Vol. 3, pp 169–178.
- Martin, S. T.; Herrmann, H.; Choi, W.; Hoffmann, M. R. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3315.
- Bekbolet, M.; Lindner, M.; Weichgrebe, D.; Bahnemann, D. W. *Solar Energy* **1996**, *56* (5), 455–469.
- Li, X. Z.; Zhang, M.; Chua, H. *Water Sci. Tech.* **1996**, *33* (3), 111–118.
- Ray, A. K.; Catal. *Today* **1998**, *44* (1–4), 357–368.
- Anheden, M.; Goswami, D. Y.; Svedberg, G. *J. Solar Energy Engin. Trans. ASME* **1996**, *118* (1), 2–8.
- Hasegawa, K.; Kanbara, T.; Kagaya, S. *Denki Kagaku* **1998**, *66* (6), 625–634.
- Chen, T. F.; Doong, R. A.; Lei, W. G. *Water Sci. Tech.* **1998**, *37* (8), 187–194.
- Ohko, Y.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. B* **1998**, *102* (15), 2699–2704.
- Inel, Y.; Okte, A. N. *Chemosphere* **1998**, *36* (14), 2969–2975.
- Chen, D. W.; Ray, A. K. *Water Res.* **1998**, *32* (11), 3223–3234.
- Hager, S.; Bauer, R. *Chemosphere* **1999**, *38* (7), 1549–1559.
- Hung, C. H.; Marinas, B. J. *Environ. Sci. Technol.* **1997**, *31*, 562.
- Read, H. W.; Fu, X. Z.; Clark, L. A.; Anderson, M. A.; Jarosch, T. *J. Soil Contamin.* **1996**, *5*, 187–202.
- Lichtin, N. N.; Avudaithai, M.; Berman, E.; Grayfer, A. *Solar Energy* **1996**, *56*, 377.
- Wang, K. H.; Tsai, H. H.; Hsieh, Y. H. *Chemosphere* **1998**, *36* (13), 2763–2773.
- Wang, K. H.; Hsieh, Y. H. *Environ. Intern.* **1998**, *24* (3), 267.
- Yamazaki-Nishida, S.; Fu, X. Z.; Anderson, M. A.; Hori, K. *J. Photochem. Photobiol., A Chem.* **1996**, *97*, 175.
- Spangenberg, D.; Moller, U.; Kleinermanns, K. *Chemosphere* **1996**, *33*, 43.
- Martin, C. A.; Baltanas, M. A.; Cassano, A. E. *Environ. Sci. Tech.* **1996**, *30*, 2355.
- Crittenden, J. C.; Liu, J. B.; Hand, D. W.; Perram, D. L. *Water Res.* **1997**, *31*, 429.
- Choi, W. Y.; Hoffmann, M. R. *Environ. Sci. Tech.* **1997**, *31*, 89.
- Wang, C. C.; Zhang, Z. B.; Ying, J. Y. *Nanostruct. Mater.* **1997**, *9*, 583.
- Calza, P.; Minero, C.; Pelizzetti, E. *Environ. Sci. Tech.* **1997**, *31*, 2198.
- Calza, P.; Minero, C.; Pelizzetti, E. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3765.
- Tajima, M.; Niwa, M.; Fujii, Y.; Koinuma, Y.; Aizawa, R.; Kushiya, S.; Kobayashi, S.; Mizuno, K.; Ohuchi, H. *Appl. Catal. Environ. B* **1996**, *9*, 167.
- Choi, W. Y.; Hoffmann, M. R. *J. Phys. Chem.* **1996**, *100*, 2161.
- Choi, W. Y.; Hoffmann, M. R. *Environ. Sci. Technol.* **1995**, *29*, 1646.
- Rideh, L.; Wehrer, A.; Ronze, D.; Zoulalian, A. *Catal. Today* **1999**, *48* (1–4), 357–362.
- Mills, A.; Wang, J. S. *J. Photochem. Photobiol. Chem.* **1998**, *118* (1), 53–63.
- Ku, Y.; Leu, R. M.; Lee, K. C. *Water Res.* **1996**, *30* (11), 2569–2578.
- Bond, G. C.; Rosac, F. *Catal. Lett.* **1996**, *39*, 261.
- Nazeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Mueller, E.; Liska, P.; Vlachopoulos, N.; Graetzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390.
- Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. Ser. A* **1956**, *235*, 518.
- Stark, J.; Rabani, J. *Z. Physik. Chem.*, in press.
- (a) Adams, G. E.; Boag, J. W.; Currant, J.; Michael, B. D. *Pulse Radiolysis*; Ebert, Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: New York, 1965; pp 131–143. (b) Adams, G. E.; Boag, J. W.; Michael, B. D. *Trans. Faraday Soc.* **1965**, *61*, 1417–1424.

- (57) (a) Wander, R.; Gall, B. L.; Dorfman, L. M. *J. Phys. Chem.* **1970**, *74*, 1819–1821. (b) Gall, B. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1969**, *91*, 2199–2204.
- (58) Adams, G. E.; Willson, R. L. *Trans. Faraday Soc.* **1969**, *65*, 2981–2987.
- (59) Bahnemann, D. W.; Hilgendorff, M.; Memming, R. J. *J. Phys. Chem.* **1997**, *101*, 4265.
- (60) (a) Rabani, J.; Klug-Roth, D.; Henglein, A. *J. Phys. Chem.* **1974**, *78*, 2089–2093. (b) Bothe, E.; Behrens, G.; Schulte-Frohlinde, D. *Z. Naturforsch., Teil B* **1977**, *32B*, 886–889.
- (61) Sun, L.; Bolton, J. R. *J. Phys. Chem.* **1996**, *100*, 4127.
- (62) Rabani, J.; Yamashita, K.; Ushida, K.; Stark, J.; Kira, A. *J. Phys. Chem.* **1998**, *B102*, 1689.
- (63) Mertens, R.; von Sonntag, C.; Lind, J.; Merenyi, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1259.
- (64) Wang, W.-F.; Schuchmann, M. N.; Bachler, V.; Schuchmann, H.-P.; von Sonntag, C. *J. Phys. Chem.* **1996**, *100*, 15843–15847.
- (65) (a) Lesigne, B.; Gilles, L.; Woods, R. J. *Can. J. Chem.* **1974**, *52*, 1135–1139. *J. Phys. Chem.* **1969**, *73*, 3794–3800. (b) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1977**, *81*, 99–104.
- (66) Koester, R.; Asmus, K.-D. *Z. Naturforsch.* **1971**, *26b*, 1104–1108.
- (67) (a) Rabani, J.; Nielsen, S. O. *J. Phys. Chem.* **1969**, *73*, 3736–3744; (b) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1985**, *14*, 1041–100; (c) Behar, D.; Czapski, G.; Rabani, J.; Dorfman, L. M.; Schwarz, H. A. *J. Phys. Chem.* **1970**, *74*, 3209–3213.
- (68) Roberts, J. L.; Sawyer, D. T. *J. Am. Chem. Soc.* **1981**, *103*, 712–714.
- (69) Cermenati, L.; Pichat, P.; Guillard, C.; Albini, A. *J. Phys. Chem. B* **1997**, *101*, 2650–2658.
- (70) Kormann, C.; Bahnemann, D. W.; Hoffmann, M. R. *Environ. Sci. Technol.* **1991**, *25*, 494–500.
- (71) Von Sonntag, C.; Schuchmann, H. P. In *Peroxyl Radicals*; Alfassi, Z., Chichester, Z. B., Eds.; Wiley: New York, 1997; pp 173–234.