Photocatalytic Dechlorination of Air Free Aqueous Carbon Tetrachloride Solutions in TiO₂ Layer Systems. A Chain Reaction Mechanism

By Johannes Stark and Joseph Rabani*

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

(Received August 3, 1998; accepted December 10, 1998)

Quantum yields of chloride ions exceeding unity are observed upon illumination of TiO₂ layers in aqueous solutions containing CCl₄ and methanol. The layers were produced by spin coating of TiO₂ (prepared by hydrolysis of the propoxide) from concentrated colloid solutions. Absorbed light intensities ranged from 7×10^{-11} to 3×10^{-8} ein cm⁻² s⁻¹. No effect of alcohol concentration on the yield is observed in the range 0.01-12 M. A negligible yield of chloride ion is obtained in the absence of methanol. Pre-equilibration of the layer with the CCl₄ solution proved necessary for maximization of the yields of photo-dechlorination. The rate of build up of the chloride ions increases nearly linearly with the square root of the light intensity at the lowest intensities which were employed. At the lowest intensity, the quantum yield φ (corrected for dark reaction) increases from ≈ 1 in the pH range 2–6 to $\varphi > 6$ at pH 12.2. There is no observable effect of CCl₄ concentration above 1 mM.

The high quantum yields and the roughly square root dependence on light intensity (at very low intensities) indicate that a chain reaction takes place.

Introduction

Interest in the detailed mechanism of illuminated TiO_2 reactions arises from the intensive use of aqueous TiO_2 in photocatalytic organic reactions and its application for detoxification of pollutants from waste waters [1-19]. The primary step in the reaction mechanism is the photo-generation of pairs of electrons and holes according to reaction 1. Trapping of the electrons (reaction 2) and holes (reaction 3) occurs within less than 30 ps [20-25].

$$TiO_2 \xrightarrow{h\nu} h_{VB}^+ + e_{CB}^-$$
(1)

$$e_{CB}^{-} \longrightarrow e_{tr}^{-}$$
 (2)

* Corresponding author.

$$h_{VB}^{+} \longrightarrow h_{u}^{+}$$
 (3)

In the absence of scavengers, recombination of electrons and holes takes place (reactions 4-6).

$$e_{CB} + h_{VB}^+ \longrightarrow TiO_2$$
 (4)

$$e_{tr} + h_{VB}^{+} \longrightarrow TiO_2$$
 (5)

$$e_{tr} + h_{tr}^{+} \longrightarrow TiO_2$$
 (6)

The trapped positive hole, h_{tr}^+ , has been assumed to be a surface bound OH radical, produced by oxidation of surface water or OH ions (reaction 7a or 7b respectively).

$$h_{VB}^{+} + Ti^{IV} - O^{-2} - Ti^{IV} O H_{2} \rightarrow \{Ti^{IV} - O^{-2} - Ti^{IV}\} - OH^{\cdot} (OH_{ads}) + H^{+}$$
(7a)

$$h_{VB}^{+} + Ti^{IV} - O^{-2} - Ti^{IV} O H^{-} \rightarrow O H_{ads}^{-}$$
(7b)

Considerable amount of work has been recently focused on photocatalytic removal of chlorinated methane and other hydrocarbons, both in gas phase [26-28] and in solution [29-39]. Thermal catalysis of organic halogens in gas [40] as well as liquid [30] phase has also been reported. The present manuscript concerns mechanistic studies on dechlorination of CCl₄ induced by photolysis of TiO₂ layers in the absence of oxygen.

Experimental

Formaldehyde was analyzed by its reaction with dinitrophenylhydrazine (DNPH). Chloride was measured by a chloride sensitive electrode (ORION 9617BN), connected to an ORION A720 monitor. TiO₂ colloidal solution was prepared by hydrolysis of titanium isopropoxide (Aldrich) according to the reported procedure [41]. Preparation of thin layers on ITO was carried out by successive spin coatings, yielding TiO₂ layers with optical absorption 0.3 at 355 nm and thickness $(1\pm0.15) \mu m$.

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 cut-off filter (transmitting below 400 nm). The light intensity was adjusted by appropriate neutral density filters. Heating by the IR irradiation was minimized by a water filter (9.5 cm). The illumination area was 1.2 cm^2 . 0.2 M methanol was used as an OH scavenger. During photolysis, as well as within 20 minutes prior to photolysis the solution was stirred by a magnetic stirrer. Fe³⁺ oxalate was used for actinometry [42].

φ (Cl ^{**})	φ (HCOH)'	$Cl^- \times 10^{10}$ mol s ⁻¹	HCHO \times 10 ¹⁰ mol s ⁻¹	$I \times 10^{8}$ ein cm ⁻² s ⁻¹
_	_	3.8	0.008	0 (blank)
0.06	0.007	12.2	1.5	2.2
0.185	0.017	12.2	1.1	0.67
0.34	0.016	7.2	0.31	0.21
0.04	0.02	1.6	0.36	0.21 ²
1.6	0.05	6.1	0.19	0.038
6.7	0.17	4.7	0.12	0.007

 Table 1. Rates and quantum yields of HCOH and Cl formation at pH 12.2. 3.2 cm³ solutions. Results corrected for dark formation.

 $^{\prime}$ Initial yields (in the range where [HCHO] increases linearly with illumination time).

 $^{2}_{2}$ 3×10⁻² M H₂PO₄⁻/HPO₄⁻ buffer, pH 7.

Results and discussion

Illumination of the TiO₂ layer in the presence of air free solution containing typically 5×10^{-3} M CCl₄ and 0.2 M methanol induces formation of chloride ions and formaldehyde. The quantum yields are independent on [methanol] (>0.2 M) and [CCl₄] ($7.5 \times 10^{-4} - 5 \times 10^{-3}$ M), although the rates of building up depend on light intensity as shown in Table 1. Chloride ions, and to lesser extent formaldehyde are produced also in the dark. Although the mechanism of the dark reactions has not been studied, the results of Table 1 have been corrected for the dark reaction by subtraction, the magnitude of which is shown in the first line of Table 1. A remarkable increase in the rate of chloride build up is observed at pH > 9: at 2×10^{-9} ein cm⁻² s⁻¹, the rate of chloride ion formation (mol s⁻¹) increases from 1×10^{-10} at pH 7 to 3×10^{-10} (pH 8.8), 7.5×10^{-10} (pH 12.2) and 2.2×10^{-9} (pH 13).

The rate of formaldehyde formation is always much lower than the respective rate of chloride. Both rates show deviations from linear dependency on $I^{1/2}$, approaching constant values at relatively high intensities.

Mechanism

We suggest that chloride ions are produced by a chain reaction mechanism. Reaction (8) removes adsorbed OH' radicals, OH_{ads}^{*} and leaves electrons available for the slow reduction of CCl_4 (reaction 9). This reduction initiates a chain process, propagated by reaction (11) and terminated by (12). Reactions (13) and (14) produce additional chloride ions. Reaction (11) accounts for the large difference between chloride and formaldehyde yields, because this propagation reaction does not involve methanol. This reaction qualitatively explains also the strong pH effect on Cl^- build up. The "saturation" of Cl⁻ formation rate at elevated intensities is attributed to the slow rate of reaction (9), resulting with build up of electrons which compete for the TiO₂ holes. This competition is expected to affect the yield of HCHO too. The nearly linear increase of the rate of formaldehyde build up with I^{1/2} at low intensities may suggest that formaldehyde is also produced by a chain process. If this is so, the large difference between the yields of chloride and formaldehyde would indicate that the two chain processes take place in parallel, e.g. reaction (10) and (15) account for the propagation of formaldehyde formation, producing equivalent concentrations of chloride ions, formaldehyde and chloroform. Such chain process cannot be a major path for Cl⁻ formation since the experiments show that $\varphi_{HCHO} \ll \varphi_{Cl}$. However, competition between reaction (4), (5) and (7) may also account for the observation in view of the relatively high steady state concentration of the electrons.

OH _{ads} +CH ₃ OH	\rightarrow CH ₂ OH + H ₂ O	$k = 1 \times 10^9 M^{-1} s^{-1}$ [43]	(8)
O _{ads} ⁺ +CH ₃ OH	\rightarrow CH ₂ O ⁻⁺ +H ₂ O	$k = 7 \times 10^8 M^{-1} s^{-1} [44]$	
$e_{TiO_2}^- + CCl_4$	\rightarrow CCl ₃ ⁻ +Cl ⁻	Initiation	(9)
CH ₂ OH [•] +TiO ₂	$\rightarrow e_{CB}^{-}$	Doubling electron yield	(10)
$CCl_3^++TiO_2^++OH_{ads}^-$	$\rightarrow e_{CB}^- + CCl_3OH$	Propagation	(11)
2 CCl_3	$\rightarrow C_2 Cl_6$	Termination	(12)
CCl ₃ OH+OH ⁻	\rightarrow CCl ₂ O+H ₂ O+Cl ⁻	Thermal hydrolysis	(13)
$CCl_2O+3 OH^-$	\rightarrow HCO ₃ ⁻ +2 Cl ⁻ +H ₂ O	Thermal hydrolysis	(14)
$CCl_3 + CH_3OH$	\rightarrow CHCl ₃ + CH ₂ OH [•]		(15)

Acknowledgment

This work was supported by the Joint Israel-German Research Project MOS/BMBF. We wish to thank Dr. D. W. Bahnemann and Prof. Robert Schiller for most useful discussions.

References

- 1. B. Kraeulter and A. J. Bard, J. Am. Chem. Soc. 100 (1978) 2239, 5985.
- 2. M. Fujihira, Y. Satoh and T. Osa, Nature 293 (1981) 206.
- 3. D. F. Ollis, C.-Y. Hsiao, L. Budiman and C.-L. Lee, J. Catal. 88 (1984) 89.
- 4. R. W. Matthews, J. Phys. Chem. 91 (1987) 3328.
- 5. R. W. Matthews, J. Catal. 111 (1988) 264.
- 6. H. Al-Ekabi, N. Serpone, E. Pelizzetti, C. Minero, M. A. Fox and R. B. Draper, Langmuir 5 (1989) 250.
- 7. C. S. Turchi and D. F. Ollis, J. Catal. 122 (1990) 178.
- K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka and A. Itaya, Bull. Chem. Soc. Jpn. 58 (1985) 2015.

- 9. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, Chem. Rev. 95 (1995) 69.
- 10. C. S. Turchi and D. F. Ollis, J. Catal. 119 (1989) 483.
- 11. C. Minero, C. Aliberti, E. Pelizzetti, R. Terzian and N. Serpone, Langmuir 7 (1991) 928.
- 12. M. W. Peterson and A. J. Nozik, J. Phys. Chem. 95 (1991) 221.
- 13. G. Mills and M. R. Hoffman, Environ. Sci. Technol. 27 (1993) 1681.
- 14. D. Bahnemann, D. Bockelmann and R. Goslich, Solar Energy Materials 24 (1991) 564.
- M. Hilgendorff, M. Hilgendorf and D. W. Bahnemann, J. Adv. Oxid. Technol. 1 (1996) 35.
- 16. E. Pelizzetti and M. Schiavello, Photochemical Conversion and Storage of Solar Energy; Kluer Academic Publishers, Dordrecht 1991.
- 17. A. Fujishima, IPS-11, Book of Abstracts, Ed. V. Krishnan, 1996, pp. 11.
- A. Heller, M. Nair, L. Davidson, Z. Luo, J. Schwitzgebel, J. Norrell, J. R. Brock, S.-E. Lindquist and J. G. Ekerdt, in *Photocatalytic Purification and Treatment of Water* and Air, D. F. Ollis and H. Al-Ekabi (eds.), Elsevier Science Publishers B.V Amsterdam, The Netherlands Vol. 3 (1993) 139-53.
- D. W. Bahnemann, J. Cunningham, M. A. Fox, E. Pelizzetti, P. Pichat and N. Serpone, Aquatic and Surface Photochemistry, G. R. Helz, R. G. Zepp and D. G. Crosby (eds.), CRC Press, Inc., Boca Raton, FL (1994) 261-316.
- 20. R. F. Howe and M. Graetzel, J. Phys. Chem. 89 (1985) 4495.
- G. Rothenberger, J. Moser, M. Graetzel, N. Serpone and D. K. Sharma, J. Am. Chem. Soc. 107 (1985) 8054.
- 22. N. Serpone, D. Lawless, R. Khairutdinov and E. Pelizzetti, J. Phys. Chem. 99 (1995) 16655.
- 23. A. J. Nozik and R. Memming, J. Phys. Chem. 100 (1996) 13061.
- D. E. Skinner, D. P. Colombo, J. J. Cavaleri and R. M. Bowman, J. Phys. Chem. 99 (1995) 7853.
- 25. D. P. Colombo and R. M. Bowman, J. Phys. Chem. 100 (1996) 18445.
- 26. C. H. Hung and B. J. Marinas, Environ. Sci. Technol. 31 (1997) 562.
- H. W. Read, X. Z. Fu, L. A. Clark, M. A. Anderson and T. Jarosch, J. Soil Contamin. 5 (1996) 187-202.
- N. N. Lichtin, M. Avudaithai, E. Berman and A. Grayfer, Solar Energy 56 (1996) 377.
- S. Yamazaki-Nishida, X. Z. Fu, M. A. Anderson and K. Hori, J. Photochem. Photobiol. A Chem. 97 (1996) 175.
- 30. D. Spangenberg, U. Moller and K. Kleinermanns, Chemosphere 33 (1996) 43.
- 31. C. A. Martin, M. A. Baltanas and A. E. Cassano, Environ. Sci. Tech. 30 (1996) 2355.
- 32. J. C. Crittenden, J. B. Liu, D. W. Hand and D. L. Perram, Water Res. 31 (1997) 429.
- 33. W. Y. Choi and M. R. Hoffmann, Environ. Sci. Tech. 31 (1997) 89.
- 34. C. C. Wang, Z. B. Zhang and J. Y. Ying, Nanostructured Materials 9 (1997) 583.
- 35. P. Calza, C. Minero and E. Pelizzetti, Environ. Sci. Tech. 31 (1997) 2198.
- 36. P. Calza, C. Minero and E. Pelizzetti, J. Chem. Soc. Faraday Trans. 93 (1997) 3765.
- M. Tajima, M. Niwa, Y. Fujii, Y. Koinuma, R. Aizawa, S. Kushiyama, S. Kobayahi, K. Mizuno and H. Ohuchi, Appl. Cat. Environ. B 9 (1996) 167.
- 38. W. Y. Choi and M. R. Hoffmann, J. Phys. Chem. 100 (1996) 2161.
- 39. W. Y. Choi and M. R. Hoffmann, Environ. Sci. Tech. 29 (1995) 1646.
- 40. G. C. Bond and F. Rosac, Catalysis Lett. 39 (1996) 261.
- 41. M. K. Nazeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos and M. Graetzel, J. Am. Chem. Soc. 115 (1993) 6382-90.
- 42. C. G. Hatchard and C. A. Parker, Proc. Roy. Soc. Ser. A 235 (1956) 518.

- (a) G. E. Adams, J. W. Boag, J. Currant and B. D. Michael, Pulse Radiolysis, Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H. (eds.), Academic Press, New York (1965) 131-43. (b) G. E. Adams, J. W. Boag and B. D. Michael, Trans. Faraday Soc. 61 (1965) 1417-24.
- 44. (a) R. Wander, B. L. Gall and L. M. Dorfman, J. Phys. Chem. 74 (1970) 1819-21.
 (b) B. L. Gall and L. M. Dorfman, J. Am. Chem. Soc. 91 (1969) 2199-204.