

Chloride-catalyzed oxidation of phenol in pulsed-laser irradiation titanium dioxide sols

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Abstract. The kinetics of photolysis of phenol in presence of two kinds of TiO₂ colloid in acid aqueous solution medium was studied by transient absorption spectroscopy. The absorbance and quantum yield of the phenoxyl radicals is strongly influenced by the chloride ions. The process of laser flash photolysis of phenol in the presence of chloride has been discussed.

Keywords. Photolysis of phenol; phenoxyl radical; TiO₂ colloid system.

1. Introduction

Photocatalysis by semiconductor particles in liquid systems is an area of great interest because of its applications in solar energy utilization and waste treatment. From the latter point of view, irradiation of titanium dioxide suspensions in water containing phenol appears to be a promising approach (Okamoto *et al* 1985). The present work was undertaken with the aim of studying the primary steps of phenol oxidation in aqueous TiO₂ systems. Since it is difficult to study spectral and kinetic properties of transients in suspensions, transparent sols of TiO₂ were used. Oxidation processes proceed by the intermediates of photogenerated holes and/or OH radicals at the semiconductor/liquid interface. In the case of phenol in acid aqueous medium, phenoxyl radicals are expected as observable transients in both cases, since OH adducts to phenol rapidly convert to phenoxyl (Land and Ebert 1967). In the following, we present a study of the production of phenoxyl radicals in laser-pulse-irradiated TiO₂ sols in acid medium. The influence of the mode of production of the sol and of the acid used to acidify it was investigated. Analysis of the dependence of phenoxyl yield on laser pulse energy was performed in order to get information about the mechanism of the oxidation process.

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2. Experimental

2.1 Preparation of sols

Sols of different compositions were prepared in the following ways:

- (1) From TiCl_4 by the method of Moser and Graetzel (1982);
- (2) From Ti(IV)-tetrakispropylate (Ti-TIP) following the method of Bahnemann *et al* (1984) but using HNO_3 instead of HCl ;
- (3) The final pH was adjusted using either HCl or HClO_4 .

2.2 Properties of sols

The structure of the particles was anatase (at least partially) as determined from X-ray crystallography. Optical absorption displayed a sharp edge with onset around 385 nm characteristic for TiO_2 . The solutions used for irradiation contained 3.2 g/l TiO_2 in the case of the sol from TiCl_4 and 1.6 g/l TiO_2 in the case of the sol from Ti-TIP. The sol from TiCl_4 further contained 0.006 mol/l Cl^- .

2.3 Transient spectroscopy

An Nd:YAG laser (QUANTA-RAY DCR-1) with a pulse length of 10 ns at 355 nm was used for irradiation of the samples. A set-up with controlled irradiation geometry allowed determination of quantum yields (Grabner *et al* 1990). Transient spectra and kinetics were recorded by means of a transient digitizer. Averages over 64 or 256 individual shots were taken which allowed the detection of absorbances as low as 3×10^{-4} .

3. Results and discussion

Spectra A, B and C in figure 1 display the characteristic absorption bands of the phenoxyl radical (Land and Ebert 1967). The absorbances are different depending on the type of sol and on the acid used to adjust the pH. With the sol from Ti-TIP, phenoxyl is found only if HCl is added. It is difficult to judge if some phenoxyl absorption is present in spectrum D, but in any case the yield would be much lower than in the other cases. Comparison of spectra C and D suggests that the presence of Cl^- is necessary for the oxidation of phenol. Spectrum B seems to represent a special case raising the following question: in what respect are the sols from TiCl_4 and from Ti-TIP different as far as phenol oxidation is concerned?

Figure 2 again shows the large differences in phenoxyl absorption between the different systems investigated. Analysis of decay kinetics yields a second-order reaction with $2k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ (Schuler and Buzzard 1976) (data taken from curve A). This value is in good agreement with that known from bimolecular reaction of phenoxyl radicals in homogeneous aqueous solution (Khudyakov and Kuz'min 1984).

In figure 3, at the pulse end, a broad absorption with $\lambda_{\text{max}} < 350 \text{ nm}$ is found which transforms into the phenoxyl spectrum at longer times. The short-time decay of the broad band is first-order with a rate of $2.3 \times 10^5 \text{ s}^{-1}$ giving a rate constant with

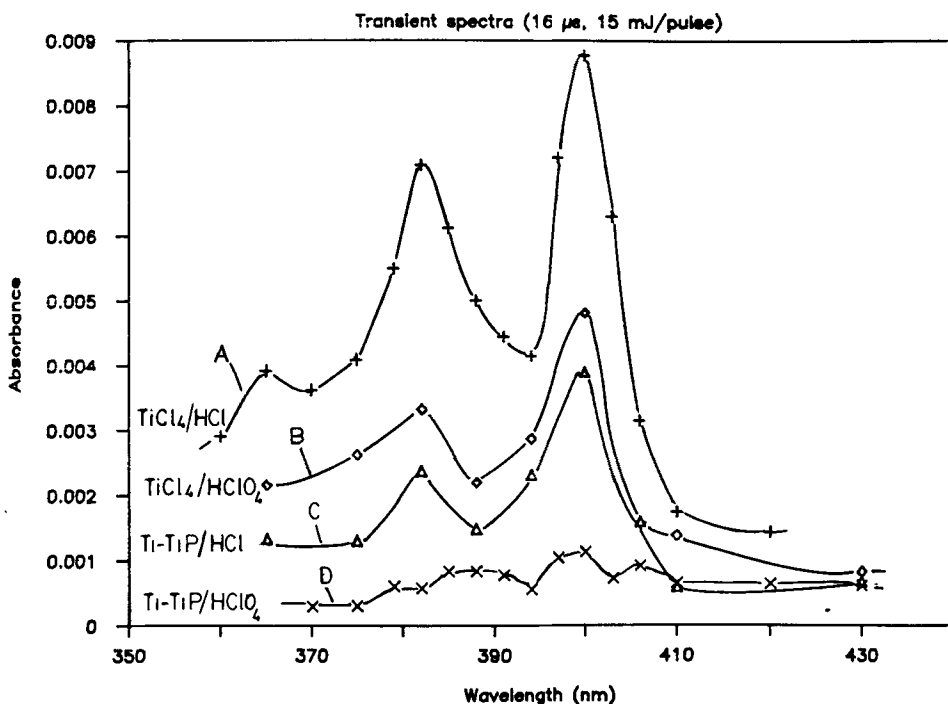


Figure 1. Spectra of transients obtained 16 μ s after the pulse (15 mJ) in the following systems: (A) Sol from TiCl_4 , pH 1 (adjusted with HCl), 0.01 M phenol; (B) Same as A, but pH adjusted with HClO_4 ; (C) Sol from Ti-TiP, pH 1 (adjusted with HCl), 0.01 M phenol; (D) Same as C, but pH adjusted with HClO_4 .

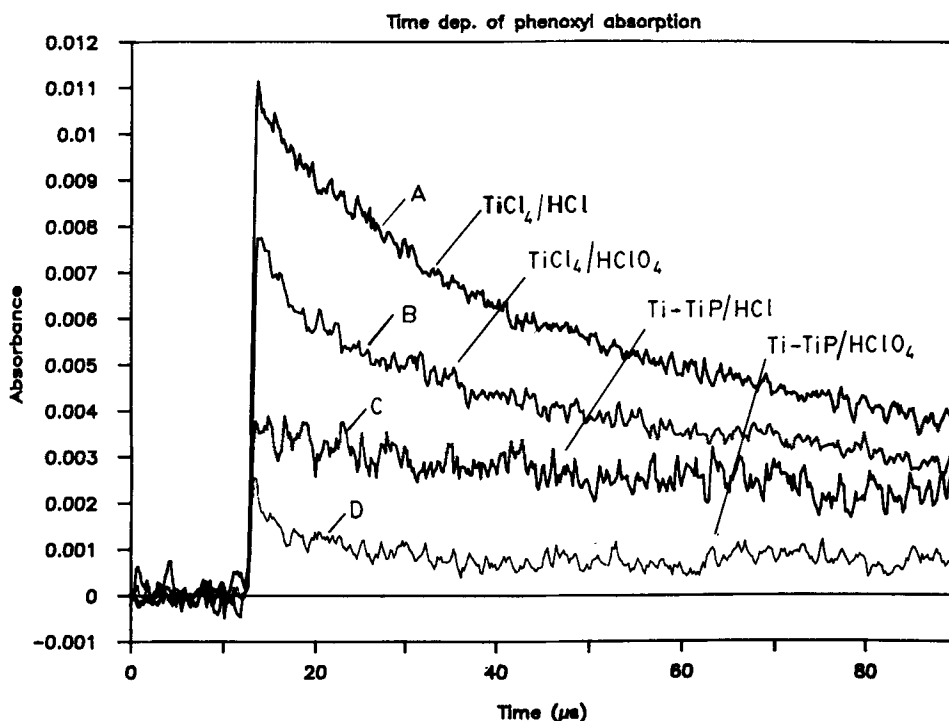


Figure 2. Time course of absorbance at 400 nm (maximum of phenoxyl absorption) at 12 mJ/pulse. Systems are as in figure 1.

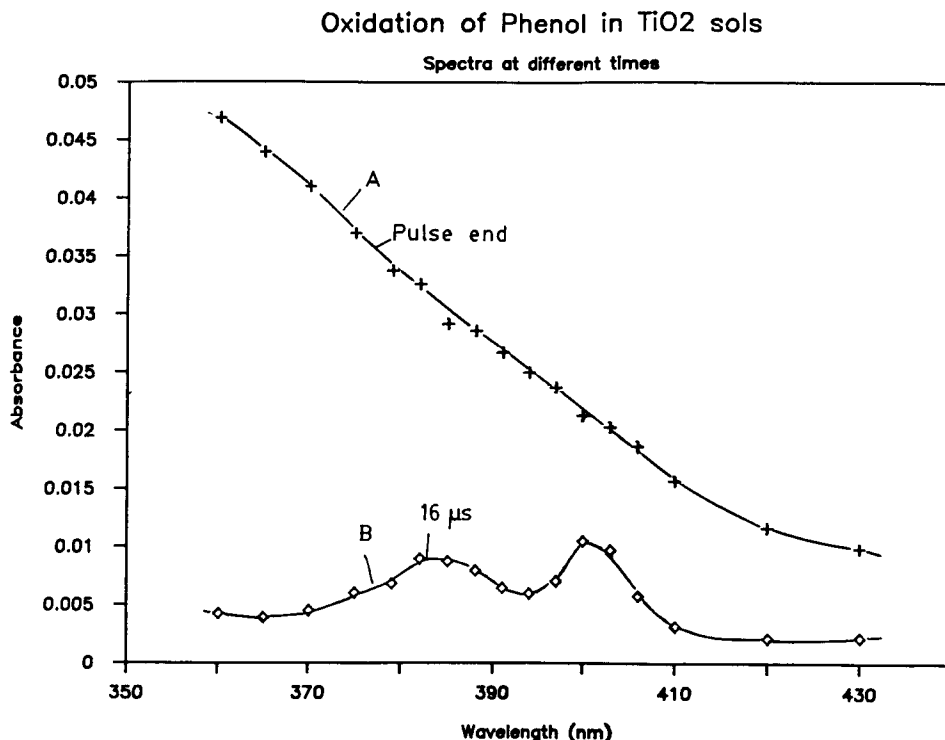
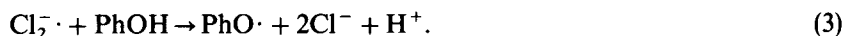


Figure 3. Spectra of transients at pulse end (A) and $16 \mu\text{s}$ after the pulse (B) obtained from TiCl_4 -sol, pH 0.3 (HCl), containing $5 \times 10^{-4} \text{ M}$ phenol.

phenol of $4.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Analysis of absorbance at the pulse end allows assignment of the spectrum to Cl_2^- radicals which are the precursors of phenoxyl radicals owing to the reaction sequence:



Hole oxidation of halide ions is documented in the literature (Moser and Graetzel 1982).

A result similar to that shown in figure 3 was also obtained when HClO_4 was used to adjust the pH, showing the Cl_2^- are always formed prior to phenoxyl radicals.

Figure 4 clearly shows different behaviour for the systems studied. Saturation is obtained for system C, but much less for systems A and B although these are not linear either.

From figure 5, results at low pulse energies show that system B is linear whereas system C shows saturation.

A quantum yield for phenoxyl production of 0.0057 can be deduced from system B using $\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$ (Schuler and Buzzard 1976).

Figure 5 clearly shows that phenol oxidation processes are different in systems B (sol from TiCl_4 , acidified with HClO_4) and C (sol from Ti-TIP, acidified with HCl).

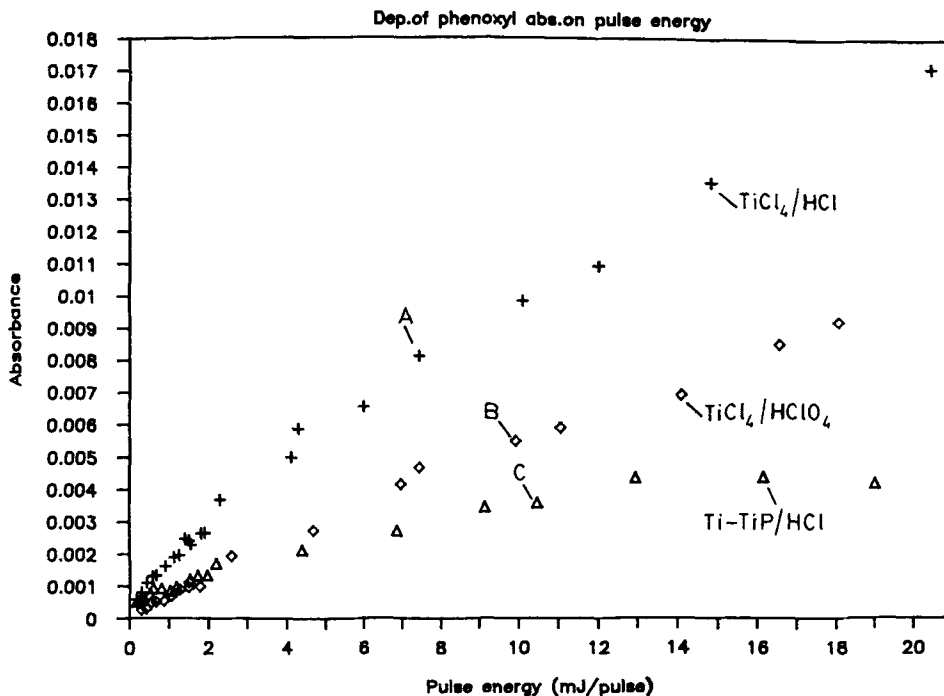


Figure 4. Dependence of absorbance on laser pulse intensity monitored at 400 nm 0.5 μ s after pulse end for the following systems containing 0.01 M phenol: (A) Sol from TiCl₄, pH 1 (HCl); (B) Sol from TiCl₄, pH 1 (HClO₄); (C) Sol from Ti-TiP, pH 1 (HCl).

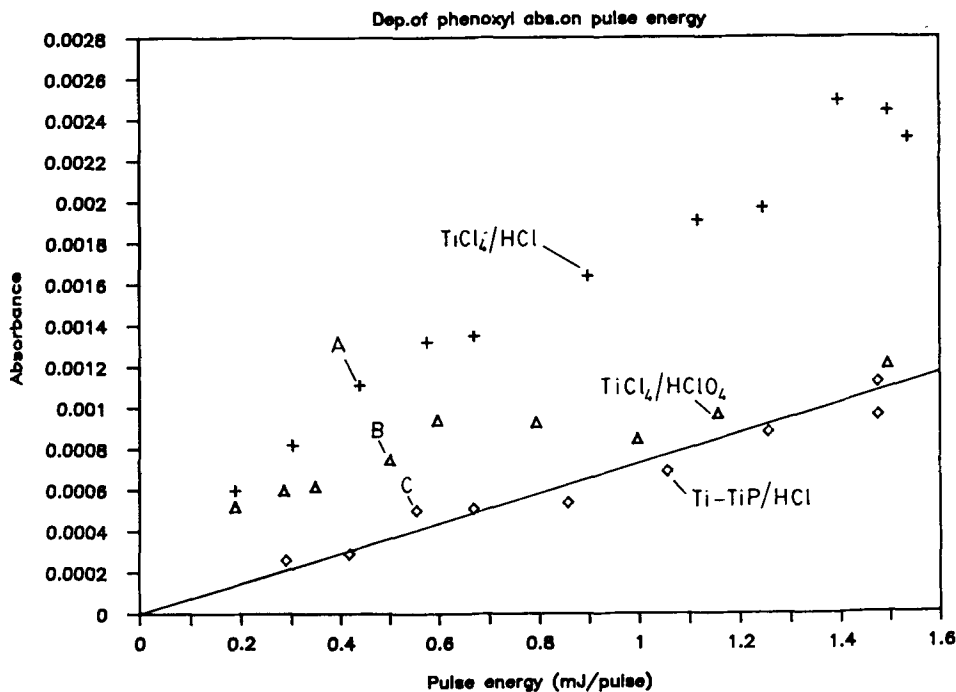


Figure 5. Same as figure 4, but low pulse energy region only.

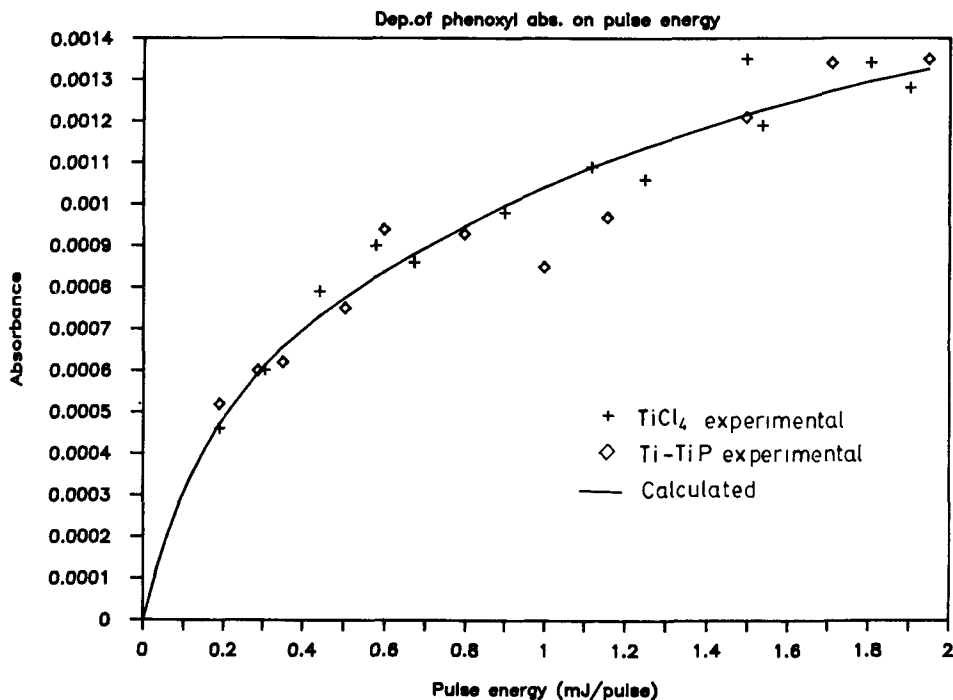


Figure 6. Dependence of absorbance at 400 nm on laser pulse energy: ◇ Sol from Ti-TiP, pH 1 (HCl); + Sol from TiCl₄, pH 1, values obtained in HClO₄ deduced from those in HCl (i.e., difference of systems A and B in figure 5).

A possible interpretation: If we admit that only Cl⁻ that are adsorbed on the particle surface can be oxidized, we could assume that two types of Cl⁻ adsorption mechanisms operate.

- (1) Adsorption of Cl⁻ from added HCl (system C). The form of the pulse energy dependence indicates that oxidation of these Cl⁻ proceeds with higher quantum yield because the slope of adsorbance vs pulse energy is higher in the initial part of the curve. On the other hand, saturation indicates that the amount of Cl⁻ adsorbed is low enough to give a depletion effect at higher pulse energies.
- (2) Adsorption of Cl⁻ stemming from the production of the sol from TiCl₄. Alternatively, there may also exist Ti-Cl bonds as suggested by Davidson *et al* (1984). The quantum yield of oxidation is lower in that case, but the amount of oxidizable species is higher as shown by the lack of saturation.

If this interpretation is correct, system A (sol from TiCl₄, acidified with HCl) should just be the sum of systems B and C as far as phenol oxidation is concerned. Figure 6 shows a test of this conjecture.

Figure 6 shows that the values obtained correspond to the same function within experimental error, confirming the conjecture of two different sources of phenoxyl radicals. Figure 6 also shows the result of a numerical simulation based on a one-photon process producing phenoxyl radicals by the sequence of reactions 1, 2 and 3. If we assume that low amount of Cl⁻ adsorbed is responsible for the saturation effect, the simulation yields values for the quantum yield of phenoxyl formation and the concentration *C* of adsorbed Cl⁻. The result is $\phi = 0.032$ and $c = 1.65 \times 10^{-6}$ Mol/l.

4. Conclusions

- (i) Oxidation of phenoxyl in pulsed-laser-irradiated TiO₂ sols is observed only when adsorbed Cl⁻ (or Ti-Cl bonds) are present.
- (ii) Two different sources of Cl₂⁻, and thus of phenoxyl radicals, are identified, differing in oxidation quantum yields and amount of oxidizable species:
 - (1) adsorbed Cl⁻ stemming from added HCl;
 - (2) adsorbed Cl⁻ (or Ti-Cl bonds) stemming from sol production if TiCl₄ is used as starting material.
- (iii) The quantum yield is lower, but the amount of oxidizable species is higher in the second case.
- (iv) The analysis of the dependence of the yield of photocatalytically produced species on laser pulse energy seems to provide experimental access to the determination of the amount of species adsorbed on the surface of semiconductor particles.

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