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$\leftarrow {}^1\Sigma_g$, respectively.²⁷ The wavelengths of the laser excitation used in the SERS experiments, 488, 514.5, 647.1, and 676.4 nm, are either at the tail end of or far from the lowest transition ${}^1\Sigma_u \leftarrow {}^1\Sigma_g$, and therefore no RRS is expected with these wavelengths of excitation.

In conclusion, the anodic reactions of Pt in 0.1 M KBr solution resulted in the formation of Br_2 and Br_3^- . SERS was observed

from the adsorbed Br_2 molecularly bound to the Pt electrode surface with the excitation wavelengths 514.5, 647.1, and 676.4 nm. SERS was also observed from Br_3^- coadsorbed on the Pt electrode surface with 488-, 514.5-, 647.1-, and 676.4-nm excitations. We have demonstrated that Pt, although it does not have the proper dielectric functions in the visible region to sustain electromagnetic resonances on surfaces, can still give rise to the SERS effect.

Registry No. Br_2 , 7726-95-6; Br_3^- , 14522-80-6; Pt, 7440-06-4.

(27) P. W. Tasker, *Mol. Phys.*, **33**, 511 (1977).

Flash Photolysis Observation of the Absorption Spectra of Trapped Positive Holes and Electrons in Colloidal TiO_2

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When a TiO_2 sol containing an adsorbed electron scavenger such as platinum or methyl viologen is flashed with a 347-nm laser, an immediate broad absorption with $\lambda_{\text{max}} = 475$ nm is observed. In acid solution the absorption decays within milliseconds. In alkaline solution it decays within microseconds, depending on the OH^- concentration, and OH^- ions are consumed in the process. In the presence of scavengers for positive holes the decay is faster, while oxygen does not have any effect. This absorption spectrum is attributed to excess positive holes trapped at the surface of the colloidal particles. When a TiO_2 sol containing an adsorbed scavenger for positive holes, such as polyvinyl alcohol or thiocyanate, is flashed, a broad absorption with $\lambda_{\text{max}} = 650$ nm is observed. It decays in the presence of electron scavengers. This spectrum is attributed to excess electrons trapped close to the surface of the colloidal particles.

Introduction

Titanium dioxide has, during the past 6 years, been studied as a catalyst of photoreactions. In their pioneering studies Bard and co-workers used TiO_2 suspensions and showed that the chemical reactions were brought about by the electrons and positive holes generated upon illumination with near-UV light.¹ More recently laser flash photolysis studies, in which colloidal TiO_2 was used, were carried out to detect short-lived intermediates.^{2,3} For example, the respective absorptions of Br_2^- and MV^+ were seen in flashed TiO_2 sols containing Br^- anions or MV^{2+} cations ($\text{MV}^{2+} = \text{methylviologen}$; 1,1'-dimethyl-4,4'-bipyridinium ion).

The present study was undertaken to detect the primary intermediates of the chemical reactions, i.e., the oxidizing and reducing species which are formed in TiO_2 itself. It had already been supposed by Bard that the electrons and positive holes are trapped in surface states from which they react with dissolved compounds. It seemed possible that these trapped species had optical absorptions which were detectable by flash photolysis. The optical observation of occupied and unoccupied electronic surface states would enable one to follow the kinetics of heterogeneous reactions at the TiO_2 /solute interface in greater detail.

Our present paper serves also to emphasize the principle according to which photocatalyzed reactions in TiO_2 sols can be achieved with sizable yield only if two scavengers (one for electrons, e^- , and one for positive holes, h^+) are present and at least one of them is adsorbed at the colloidal particles. It is the adsorbed scavenger which determines the yield of the reaction of the non-

adsorbed one. Despite the numerous chemical effects which have been observed with TiO_2 sols or suspensions, this principle does not seem to have been stated precisely.

Experimental Section

Preparation of the Colloids. Colloidal TiO_2 was prepared by the dropwise addition of titanium tetraisopropoxide dissolved in propanol-2 to hydrochloric acid solution of pH 1.5. The final concentrations of TiO_2 and propanol-2 were 1.5×10^{-2} and 1.2 M, respectively. This mixture was stirred overnight until it was virtually clear. After vacuum evaporation of the solvent a soluble white powder of TiO_2 remained. The final solution was made by dissolving 500 mg of this powder in 1 L of water. This solution had a pH of 3. Alkaline TiO_2 solutions were made by fast addition of the estimated amount of 0.1 M NaOH to the vigorously stirred acid solution. All these solutions were optically transparent and showed the steep increase in absorption below 380 nm which is typical for colloidal TiO_2 .³ The absorbance at the laser wavelength of 347 nm was 50%.

Colloidal platinum was prepared by reducing a 3×10^{-4} M H_2PtCl_6 solution with 1.7×10^{-3} M sodium citrate (1 h and 100 °C). Excess ions were removed with Amberlite MB1 ion-exchange resin until a specific conductivity of 3–5 $\mu\text{S}\cdot\text{cm}^{-1}$ was reached. This colloidal platinum solution was added to the above acid TiO_2 solution in the ratio of 1:15. The solvent was then evaporated under vacuum and a brown powder obtained. This powder was redissolved to obtain the final solution of Pt-covered TiO_2 , the pH of which was adjusted as described above.

Apparatus. The flash photolysis experiments were carried out with a frequency-doubled JK ruby laser ($\lambda = 347.1$ nm; 15-ns pulse width). The changes in optical absorption and conductivity were measured. The solution was passed continuously through a quartz cell, which was equipped with two sets of glassy carbon electrodes. The technical details of the optical detection system

(1) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 7729. Bard, A. J. *Science* **1980**, *207*, 139. Izumi, I.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1981**, *85*, 218. Ward, M. D.; Bard, A. J. *Ibid.* **1982**, *86*, 3599.

(2) Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 241.

(3) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977.

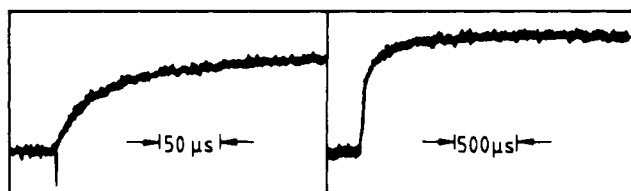


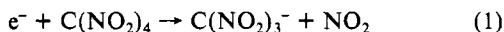
Figure 1. Buildup of the absorption of $C(NO_2)_3^-$ measured at 365 nm after the laser flash at two time scales.

and the ac conductivity setup have been described elsewhere.⁴ A laser flash produces a large number of charge carriers in one colloidal particle. It was found that the quantum yields at larger laser doses were very small; in order to prevent the charge carriers from recombining rather low laser doses had to be applied. The data from 16 to 64 flashes were digitized and transferred to a PDP11/40 computer by a Tektronix 7612 D programmable digitizer and a Camac interface. The laser dose and photocurrent were automatically recorded for each flash. The digitized signals were analyzed on-line with a Tektronix 4010 interactive graphic display. The base line (without laser pulse on) was subtracted each time; decay and buildup kinetics were analyzed with computer programs described elsewhere.^{4c}

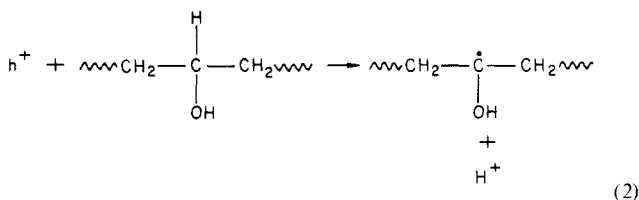
Dosimetry had to be carried out for both the optical absorption and conductivity measurements. For this purpose, a dosimeter was developed which allowed one to calibrate both measurements at one time. The details of this dosimeter will be described elsewhere. It contained 2×10^{-3} M benzophenone (as absorbing substance) and 5×10^{-4} M tetranitromethane in a 3:1 water-propanol-2 mixture at pH 3. Permanent increases in absorption at 350 nm due to the formation of the nitroform anion, $\epsilon = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, and in conductivity due to H^+ and the nitroform anion ($\Delta\kappa = 360 \text{ S}\cdot\text{cm}^2$) are produced in this dosimeter, the quantum yield of these products being 1.12 at 347.1 nm. This quantum yield is independent of the presence of air. The laser doses employed were in the range of 2×10^{-6} to 2×10^{-5} mol of photons absorbed in 1 L of solution.

Results and Discussion

Excess Electrons. Figure 1 shows the optical changes which were observed upon the flashing of a TiO_2 solution containing 8×10^{-4} M tetranitromethane and 5×10^{-3} M polyvinyl alcohol. Tetranitromethane is a well-known electron scavenger which reacts according to



The nitroform anion $C(NO_2)_3^-$ is stable and can be readily detected by its strong absorption at 350 nm.⁵ The absorption is built-up in two steps, the respective half-lives being 29 and 215 μs . In the absence of polyvinyl alcohol, no absorption signals were observed. Polyvinyl alcohol is often used as a stabilizer for colloids. We attribute its promoting action of the reduction of tetranitromethane to the scavenging of positive holes



An equal number of electrons is therefore prevented from recombining with holes. In the presence of other adsorbed scavengers for h^+ such as thiocyanate anions, only the first step of the absorption of $C(NO_2)_3^-$ was observed. This step is attributed to the reaction of excess electrons (eq 1). The second step is attributed

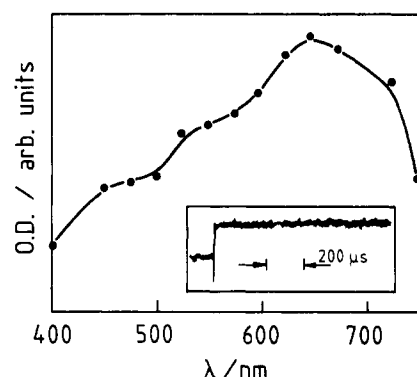
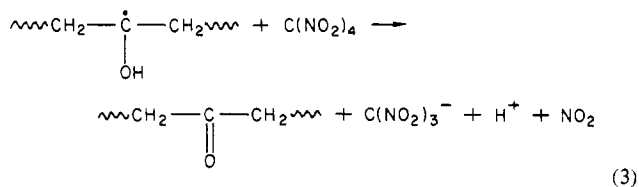


Figure 2. Optical absorption of a 5×10^{-3} M polyvinyl alcohol containing TiO_2 sol immediately after the flash and the time profile of the absorption at 625 nm (inset).



Figure 3. Time profile of the 392-nm absorption (a) and the conductivity (b) of a TiO_2 sol containing 5×10^{-5} M methyl viologen, pH 10.

to the reduction of tetranitromethane by the macroradicals which were formed in the scavenging of positive holes (eq 2):⁶



With increasing tetranitromethane concentration both steps became faster. The fact that reaction 1 took place *after* the laser flash shows that the excess electrons on TiO_2 were long-lived. Similar observations have recently been made by Grätzel and co-workers³ who used methyl viologen as an electron scavenger in the presence of polyvinyl alcohol. Methylviologen is also reduced in two steps. This has apparently been missed by Grätzel et al.

When a TiO_2 sol containing only polyvinyl alcohol as additive was flashed, an absorption was present immediately which did not disappear in the time range of observation of several milliseconds. Figure 2 shows the absorption spectrum. It is attributed to long-lived reducing intermediates from the photolysis of TiO_2 . In the presence of oxygen or other electron scavengers, this absorption decayed after the flash. Long-lived electrons have already been observed in experiments where electrons were transferred to the colloidal TiO_2 particles from radiolytically generated organic radicals.² The lifetime as well as the shape of the absorption spectrum of these long-lived electrons depend strongly on how the colloid was prepared. The electrons are probably trapped close to the surface. Their spectrum resembles the blue absorption which is known for the hydrate of Ti_2O_3 .

Excess Positive Holes. In the experiments of Figure 3, a TiO_2 sol at pH 10, where the colloidal particles are negatively charged, was used. This solution did not contain any added scavenger for positive holes. Methyl viologen, MV^{2+} , which is adsorbed at the colloidal particles in alkaline solution, served as electron scavenger. The absorption of the radical cation $MV^{\cdot+}$ was present imme-

(4) (a) Asmus, K.-D. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 417. (b) Kelm, M.; Lilie, J.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882. (c) Shinohara, N.; Lilie, J.; Simic, M. G. *Inorg. Chem.* **1977**, *16*, 2809.

(5) Asmus, K.-D.; Henglein, A.; Ebert, M.; Keene, J. P. *Ber. Bunsenges. Phys. Chem.* **1964**, *68*, 657.

(6) This reaction was shown to occur by a pulse radiolysis experiment. The solution contained N_2O (2.5×10^{-2} M), tetranitromethane (1×10^{-4} M), and polyvinyl alcohol (2.5×10^{-2} M). The primary species of water were rapidly converted into $\cdot OH$ radicals that attacked the polymer to produce macroradicals. The absorption of $C(NO_2)_3^-$ was built-up after the pulse corresponding to a rate constant for reaction 3 of $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. It was also observed that 33% of the $\cdot OH$ radicals attacked the polymer at the methylene group, the resulting macroradical not being able to contribute to the reduction of tetranitromethane.

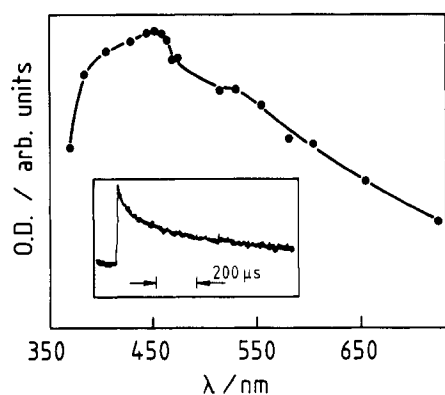


Figure 4. Optical absorption of a TiO_2 sol containing deposited colloidal platinum immediately after the flash and the time profile of the absorption at 472 nm (inset).

diately after the laser flash. The conductivity of the solution decreased with a half-life of $8.5 \mu\text{s}$. With increasing OH^- concentration this time became shorter. The decrease in conductivity is attributed to the oxidation of OH^- by positive holes, i.e., to the first step of the evolution of oxygen or hydrogen peroxide at the TiO_2 particle. The fact that this reaction took place *after* the laser flash is taken as an indication for the existence of a long-lived oxidizing intermediate in the photolysis of TiO_2 . The decrease in conductivity was not observed in the absence of methyl viologen. The amount of $\text{MV}^{\cdot+}$ formed corresponded to the amount of OH^- consumed. At low laser doses the quantum yield of the $\text{MV}^{\cdot+}$ formation or OH^- consumption was 0.35. At larger doses it decreased as the $\text{h}^+ + \text{e}^-$ recombination competed more successfully with the $\text{e}^- + \text{MV}^{2+}$ scavenging reaction.

Figure 4 shows the results of experiments for the detection of the optical absorption of the oxidizing intermediate. In order to assure a long lifetime, an acid solution was used. MV^{2+} could not be used as electron scavenger as the colloidal particles were

positively charged and did not adsorb this cation. It has already been recognized by Bard and co-workers that platinum deposited on TiO_2 particles acts as a scavenger for electrons. In fact, the Pt-containing TiO_2 sol had an absorption immediately after the laser flash which ranged over a wide portion of the visible spectrum. In the absence of Pt, this absorption did not occur. It can be seen from Figure 4 that the maximum of the absorption was at 475 nm and that the signal slowly faded away. The decay curve could not be fitted by one or two exponentials which indicates that processes with a wide spectrum of lifetimes contributed to the decay. Oxygen did not influence the decay. In the presence of scavengers for positive holes which were not strongly adsorbed, such as propanol-2, the spectrum immediately after the flash had the same intensity but the absorption decayed faster. In the presence of an adsorbed h^+ scavenger such as thiocyanate, the intensity of the spectrum immediately after the flash was decreased and the subsequent decay was also faster.

These observations are explained if one attributes the spectrum in Figure 4 to positive holes which are trapped close to the surface of the colloidal particles. The broad absorption spectrum in the visible may be caused by electronic transitions from the valence band to the O^- trap or from the trap into the conduction band. As trapped holes can now be readily detected by their optical absorption, they may be dealt with as are the intermediates in flash photolysis of homogeneous solutions, i.e., the specific rates of reaction with added solutes can be determined. Experiments of this type will be described in detail elsewhere.⁷

Acknowledgment. The authors gratefully acknowledge the assistance by Mrs. M. Gunkel in the preparation of the colloids.

Registry No. $\text{C}(\text{NO}_2)_3^-$, 20143-63-9; MV^{2+} , 4685-14-7; TiO_2 , 13463-67-7; platinum, 7440-06-4; tetranitromethane, 509-14-8; polyvinyl alcohol (homopolymer), 9002-89-5; methyl viologen, 1910-42-5; thiocyanate anion, 302-04-5.

(7) Bahnmann, D.; Henglein, A.; Spanhel, L. *Discuss. Faraday Soc.*, in press.

Eyring Activation Barriers for the Anomalous Dielectric Relaxations of Diphenyl Ether Type Molecules

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Several symmetrically substituted diaryl ethers have been studied in a polystyrene matrix and bis(4-nitrophenyl) ether also in glassy *o*-terphenyl by dielectric absorption techniques in the frequency range $10\text{--}10^5$ Hz over temperatures of 77–323 K. Bis(4-cyanophenyl) ether in polystyrene was also examined at many temperatures in the frequency range $10^4\text{--}10^7$ Hz. In the polystyrene matrix both the molecular and intramolecular relaxation processes were detected for diphenyl ether and bis(4-nitrophenyl) ether. An intramolecular relaxation process was detected for most of the aromatic ethers, and the associated Eyring enthalpy of activation is $\sim 10 \text{ kJ mol}^{-1}$, which is similar to that observed for some alkyl aryl ethers in the same media. The present work establishes that the energy barrier for rotation around the C–O bonds in symmetrically substituted diphenyl ethers is very low and that intramolecular motion would be expected to occur quite readily about these bonds.

Introduction

Fischer¹ first observed the anomalous dielectric behavior of diphenyl ether in nonpolar solvents at microwave frequencies. The mean relaxation time of 2.8 ps at 296 K was much too short when compared with a rigid molecule of a similar size and shape such as 2-hydroxyphenyl phenyl ether, which has a relaxation time of ~ 20 ps under similar conditions.²

Very short relaxation times have also been observed for symmetrically substituted ethers such as bis(4-bromophenyl) ether ($\tau_{293} = 8.7$ ps in Nujol),³ bis(4-nitrophenyl) ether ($\tau_{293} = 12.5$ ps in benzene),⁴ and dibenzyl ether ($\tau_{293} = 18$ ps in benzene).⁵ (See Figure 1 for molecular structures.) Diaryl sulfides and

(1) E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).

(2) W. Maier, *Arch. Sci.*, **12**, 20 (1959).

(3) W. P. Purcell and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 1063 (1961).

(4) R. D. Nelson, Jr., and C. P. Smyth, *J. Phys. Chem.*, **69**, 1006 (1965).

(5) J. E. Anderson and C. P. Smyth, *J. Chem. Phys.*, **42**, 473 (1965).