

Appendix F

INTERMEDIATE DETECTION DURING TiO₂ PHOTOCATALYZED AS(III) OXIDATION USING ELECTRON PARAMAGNETIC RESONANCE

F.1 Introduction

Electron paramagnetic resonance (EPR) spectroscopy has been used to examine paramagnetic species in a variety of systems. In this analytical technique, unpaired electrons in a magnetic field absorb microwave energy in amounts equal to the difference between the electrons' spin up and spin down energy levels. The resulting signals can be used to identify paramagnetic species and nearby nuclei.

Many groups have employed EPR spectroscopy to detect reactive oxygen intermediates produced under illumination at the TiO₂ surface. Paramagnetic intermediate species have been detected directly on TiO₂ (Gonzalez-Eliphe et al. 1979; Howe and Gratzel 1987; Wang and Yeh 1991; Anpo et al. 1999; Coronado et al. 2001; Attwood et al. 2003; Yu et al. 2004), but most of these studies were conducted at 77 K or 4 K using dehydrated or partially dehydrated TiO₂. Since the hydration state of the catalyst surface impacts the radical formation mechanisms (Gonzalez-Eliphe et al. 1979), it is not clear that radicals observed under the above conditions would exhibit similar behavior in an aqueous system like that used for As(III) oxidation.

Alternatively, spin trapping agents can be used to scavenge short-lived radicals and form secondary radical species that are stable for significant time periods under ambient conditions. Use of spin trapping agents such as 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), 5-(diethoxyphosphoryl)-5-methyl-1-pyrroline *N*-oxide, and α -phenyl *N*-*tert*-butyl nitrene have allowed researchers to detect reactive oxygen intermediates generated on TiO₂ in aqueous solution (Jaeger and Bard 1979; Keszler et al. 2004; Mrowetz et al. 2004).

Because As(IV) has previously been implicated as an intermediate in homogeneous As(III) oxidation (Daniels 1962) and because a 2-electron transfer at the TiO₂ surface is highly unlikely, we have proposed several possible intermediate pathways for the photocatalyzed oxidation of As(III) to As(V) that involve As(IV) as an intermediate (Chapter 3). However, studies conducted thus far have neither looked for nor found any evidence of As(IV) radicals on the catalyst surface. In addition to the TiO₂ studies targeting oxygen species discussed above, EPR has previously been used to detect As(IV) radicals produced on arsenate-containing solids as a result of X-ray damage (Lin and McDowell 1964; Subramanian et al. 1977). Therefore, the primary goal of this project was to determine if As(IV) generation at the TiO₂ surface during sample illumination could be detected using EPR spectroscopy.

F.2 Materials and Methods

Samples were prepared either in solution or as Degussa P25 powder. Suspensions containing 0.05 g L⁻¹ TiO₂ and 5.0 mM NaNO₃ (Mallinckrodt) were tested in the presence and absence of 50 μ M As(III) (Baker Analyzed, NaAsO₂) and 0.1 M 2-propanol (EMD

OmniSolv). For spin trapping experiments, DMPO (Aldrich) was weighed out in a glove box, sealed, and added to the TiO₂ suspension to achieve 100 mM DMPO immediately prior to EPR sample introduction. For solid powder experiments, As(III) was added to P25 TiO₂ slurry at a concentration of 100 μM As g⁻¹ TiO₂. After rotating in the dark overnight to achieve sorption equilibrium, the TiO₂ powder was recovered by vacuum filtration and dried at 60 °C for 2 hours. Plain P25 was examined with and without desiccation at 60 °C.

Samples were analyzed either at room temperature or at 77 K using a Bruker EMX EPR Spectrometer operated under conditions listed in Table F.1. Spectra were recorded before, during, and after illumination by a 250 W lamp (Schott KL 2500 LCD) connected to the sample tube by a fiber optic cable.

Table F.1. Instrumental conditions for EPR measurements.

Parameter	Value
Microwave frequency	9.8 GHz
Microwave power	12.7 mW
Modulation frequency	100 kHz
Modulation amplitude	2.0 G
Number of scans	10
Central field	3490 G
Sweep width	100 G
Time constant	10.24 ms
Receiver gain	7.1×10^3

F.2 Results and Discussion

A summary of the samples tested and resulting signals, if any, is given in Table F.2. Most sample conditions yielded no radical signal, but signals were detected for dried P25 powder at 77 K (Fig. F.1) and for a P25 suspension with DMPO analyzed at room temperature (Fig. F.2).

Paramagnetic species are typically identified by their g -factors and hyperfine splitting constants (a values). The g -factor is a proportionality constant equal to

$$g = h\nu / \mu_B B_0, \quad (\text{F.1})$$

where h is Plank's constant, ν is the frequency of the microwave radiation, μ_B is the Bohr magneton, and B_0 is the applied magnetic field. The hyperfine splitting constants represent the distance between multiplet peaks. Although these parameters have been previously reported for As(IV), $\text{O}_2^{\cdot-}$, and $\cdot\text{OH}$, they are affected by spin trapping agents, the presence and type of TiO_2 , solvent, and solution (Jaeger and Bard 1979). Therefore, the radical responsible for the signals in Figures F.1 and F.2 cannot be unequivocally identified without further experiments, but its signal is most consistent with that of $\text{O}_2^{\cdot-}$.

Table F.2. Summary of samples tested and resulting signals.

Sample	Temperature	Results
P25 powder, desiccated at 60 °C overnight	77 K	g values: 2.1296, 2.1099, 2.0968, 2.0941, 2.0843
0.05 g L ⁻¹ P25 + 0.005 M NaNO ₃ + 100 mM DMPO	295 K	g values: 2.0614, 2.0526, 2.0438, 2.0351; a values: 14.88, 15, and 14.9
P25 powder + As(III), dried for 2 hours at 60 °C	77 K	No signal
P25 powder, not previously desiccated	77 K	No signal
0.05 g L ⁻¹ TiO ₂ + 5 mM NaNO ₃ + 50 μM As(III)	77 K	No signal
0.05 g L ⁻¹ TiO ₂ + 5 mM NaNO ₃ + 0.1 M 2-propanol	77 K	No signal
0.05 g L ⁻¹ TiO ₂ + 5 mM NaNO ₃	295 K	No signal
0.05 g L ⁻¹ TiO ₂ + 5 mM NaNO ₃ + 50 μM As(III)	295 K	No signal

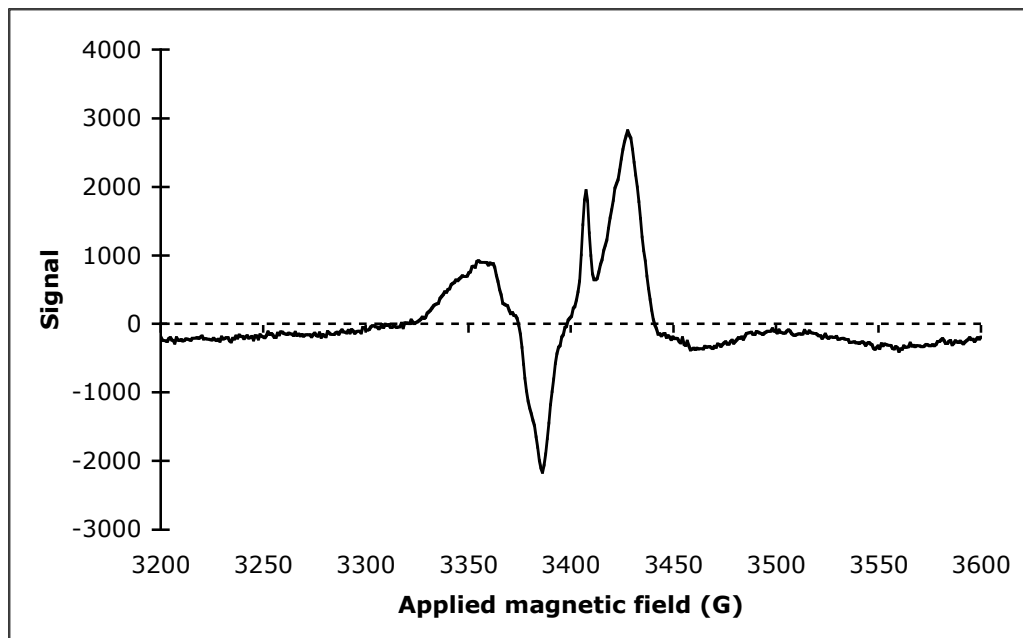


Figure F.1. EPR spectra for P25 powder analyzed at 77 K under illumination. The dark background signal is subtracted from the illuminated signal.

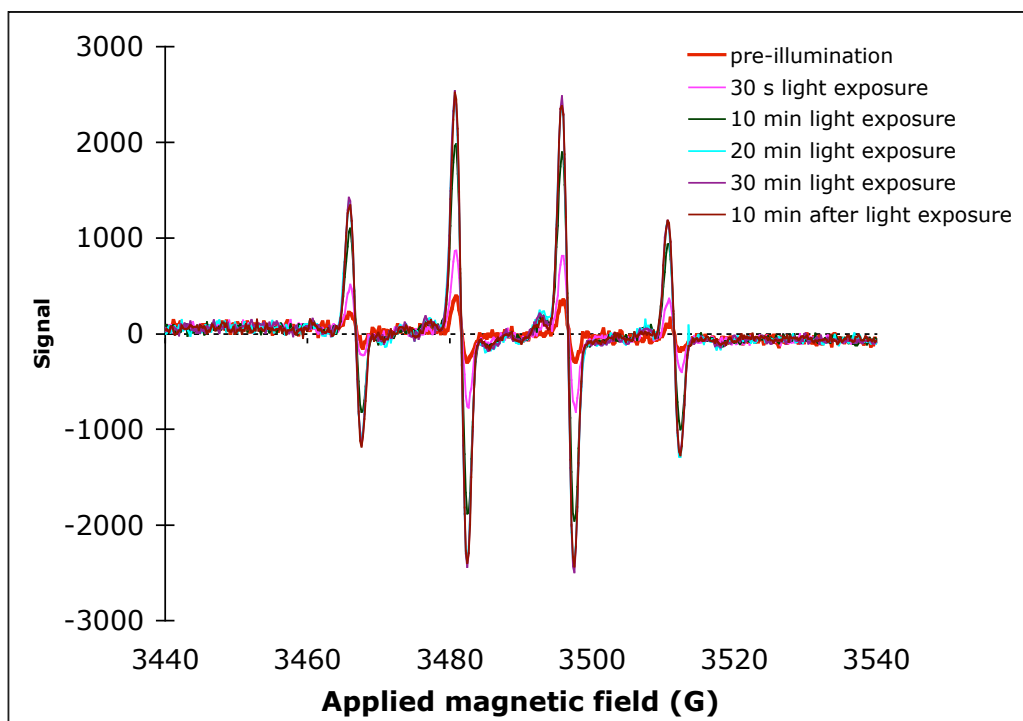


Figure F.2. EPR spectra over different periods of illumination. Conditions: 0.05 g L^{-1} TiO_2 , 5 mM NaNO_3 , 100 mM DMPO .

When DMPO is present in solution, the radical signal increases over the first 20 min of irradiation and stays constant thereafter (Fig. F.2). Loss of signal was not seen even 10 min after the exposure to irradiation ceased, indicating that the DMPO adduct is stable over relatively long time periods.

No signal suggesting the presence of As(IV) radical was detected. Moreover, the detection of only one radical species, rather than at least two signals corresponding to the species known to be present on TiO₂ during illumination (O₂^{•-} and [•]OH), indicates that the current method is not sufficient to detect all radicals in the system. This failure to detect As(IV) or other radicals could be due to these radicals' short lifetimes and small steady-state concentrations. This shortcoming could be addressed by using an EPR spectrometer capable of making more rapid measurements, but such an instrument was not available at this institution. Certain adjustments to reaction conditions using the current EPR instrument may also have resulted in additional signal, but this was deemed unlikely. Consequently, this project was dropped.