

ELECTROCHEMISTRY IN LIQUID SO₂. PHOTOHOLE EMISSION FROM A PLATINUM ELECTRODE

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Photoemission of holes from a platinum electrode into liquid sulfur dioxide was investigated by determining the photocurrent produced by both Ar ion and rhodamine 6G dye laser illumination (611.3 to 457.9 nm). A plot of photocurrent versus potential obeyed the five-halves law and yielded threshold potentials that linearly correlated with excitation energy. Holes are injected from a photoexcited Pt electrode into an SO₂/tetra-*n*-butyl ammonium PF₆⁻ electrolyte solution with a threshold potential of 3.74 V versus AgREF that corresponds to an energy level of -9.1 ± 0.1 eV versus vacuum. This level is 0.4 eV beyond the estimated level for reversible electrochemical oxidation of solvent.

1. Introduction

We report here studies of photohole injection into liquid SO₂/tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆) solution from a Pt surface under visible illumination. The study examines the wavelength dependency of this process and correlates the threshold potentials for photohole injection to electronic energy levels in SO₂. The photoemission of electrons from metallic electrodes into aqueous and non-aqueous solutions has been the subject of many investigations [1–4]. These have been useful in elucidating the electronic energy levels of solvents. There have been fewer studies of hole photoemission (resulting in anodic photocurrents). Gerischer and co-workers [5–10] have studied the anodic photocurrents that result upon illumination (at wavelengths of 340–730 nm) of a gold electrode in contact with aqueous solutions. Clear evidence of photohole emission and a *pH*-independent threshold energy level at -9.1 eV, ascribed to the valence band edge of liquid H₂O, was found [7]. These measurements in aqueous solutions at positive potentials are hampered by the formation of oxide layers on metal surfaces (e.g., Au₂O₃ on Au), that can behave as *n*-type semiconductors and produce anodic photocurrents that are large compared to those for direct photohole emission from the metal.

Liquid SO₂, which has been used as a solvent for electrochemical studies [11–14], has several advantages in photohole emission experiments. The very positive anodic oxidation limit of a Pt electrode in SO₂/TBAPF₆ (equivalent to ≈ 4 V versus aqueous SCE) [13] provides a large positive potential range for investigation. Moreover, there is no evidence for oxide formation on Pt in this solvent system.

2 Experimental

The general experimental procedures along with solvent purification and handling techniques have been reported previously [11]. Anhydrous grade sulfur dioxide (99.99%) was obtained from Matheson Gas Products, Inc., Houston, TX. The supporting electrolyte, tetra-*n*-butyl ammonium hexafluorophosphate (TBAPF₆), prepared as previously described [13], was recrystallized three times from ethyl acetate/ether and vacuum-dried at 110°C for 48 h. The electrochemical cell and transparent quartz dewar have been reported previously [15]. The platinum disk working electrode (projected area 0.032 cm²) was polished prior to use with a 0.3 μm alumina slurry. All potentials were referenced to a Ag quasi-reference electrode (AgREF), of a type previously described [13], which was in con-

tact with the solution through an asbestos fiber sealed in glass. The counter electrode, Pt gauze (1 cm²), was inserted directly into the solution. The resistance of a 0.1 M SO₂/TBAPF₆ solution (measured between the working and counter electrodes) with a conductivity bridge (Industrial Instruments, Inc.) was 6.1 kΩ. Since the measured photocurrents were, at most, of the order of 100 nA, the uncompensated IR drops were less than 1 mV.

Electrochemical measurements were carried out with a Princeton Applied Research (PAR) model 173 potentiostat and a PAR 175 universal programmer. Current-potential curves were recorded on a Houston Instruments model 2000 X-Y recorder (Houston Instruments, Austin, TX). The light sources were an Ar-ion laser (Spectra Physics, model 171-01) and dye laser (Spectra Physics, model 375) with rhodamine 6G. The dye was irradiated with the Ar line at 541.5 nm. The light beams from these were chopped at 47 Hz with a PAR model 192 variable frequency chopper and the resulting currents synchronously detected with a PAR 5204 lock-in amplifier.

3 Results and discussion

A cyclic voltammogram of a Pt electrode in SO₂/0.1 M TBAPF₆ at -40°C is given in fig. 1a. No appreciable anodic faradaic current (i_e , < 30 μA/cm²) flows until ≈ 2.8 V versus AgREF, where solvent oxidation begins [13]. No reduction wave is seen upon scan reversal, indicating that the product of solvent oxidation (or the "solvated hole") is not stable. Typical photocurrent (i_p) versus potential (V) curves for irradiation with chopped laser light of several wavelengths are given in figs. 1c-1e. These i_p - V curves were reproducible on repeated scans over this potential region. Note that the photocurrent onset shifts to less positive potentials as the photocurrent excitation energy increases from 2.03 to 2.70 eV. The i_p - V behavior for excitations of 2.27, 2.41, 2.50 and 2.54 eV, not shown in fig. 2, were similar to those given. Note that it was not necessary to add a hole scavenger, since the rate of reaction of the "free hole" with solvent and the subsequent decomposition reaction are probably sufficiently rapid to prevent return of all holes to the electrode. Similar scavenging of holes by solvent is found in aqueous solutions [5-7].

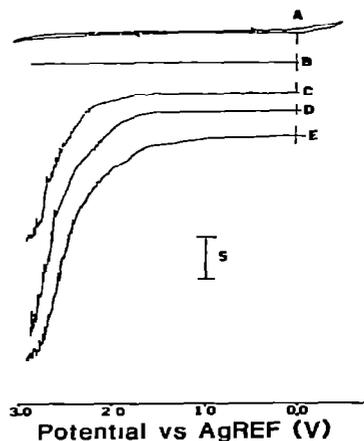


Fig. 1. Current-potential curves for Pt electrode in liquid SO₂, 0.1 M TBAPF₆. (a) Cyclic voltammogram, $S = 10 \mu\text{A}$. (b) Potential scan with lock-in amplification in the absence of illumination. Photocurrent under light modulation, 47 Hz, with lock-in detection, for photon energy $h\nu$ (eV) and photon flux ϕ_p (photons s⁻¹ cm⁻²): (c) $h\nu = 2.03$, $\phi_p = 1.5 \times 10^{17}$, $S = 12.5$ nA; (d) $h\nu = 2.61$, $\phi_p = 6.9 \times 10^{16}$, $S = 5$ nA; (e) $h\nu = 2.71$, $\phi_p = 7.2 \times 10^{16}$, $S = 10$ nA.

To obtain the threshold potential, plots of $i_p^{0.4}$ versus V , according to the equation of Brodsky and Gurevich [1,3] have been used

$$i = C (h\nu - h\nu_0 - eV)^{5/2}, \quad (1)$$

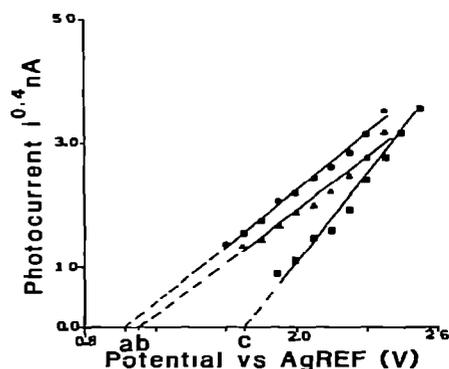


Fig. 2. Photocurrent ($i^{0.4}$) versus potential, for SO₂, 0.1 M TBAPF₆. Threshold potentials (E_{th}) are shown for different photoexcitation energies: (a) $E_{th} = 1.03$ V, $h\nu = 2.71$ eV; (b) $E_{th} = 1.13$ V, $h\nu = 2.61$ eV; (c) $E_{th} = 1.71$ V, $h\nu = 2.03$ eV.

Table 1
photoexcitation energies and threshold potentials for photohole injection process in liquid SO_2

Laser dye	Excitation energy (eV)	Photon flux (photons $\text{s}^{-1} \text{cm}^{-2}$) $\times 10^{16}$	Threshold potential (V versus AgREF)
dye	2.03	15	1.72
dye	2.27	11	1.47
argon	2.41	7.8	1.30
argon	2.50	7.5	1.21
argon	2.54	7.4	1.20
argon	2.61	6.9	1.13
argon	2.71	7.2	1.03

where ν is the frequency of the excitation source, ν_0 is the threshold frequency at $V = 0$ versus the reference electrode, and C is a proportionality constant. The Fowler relation ($i_p^{0.5}$ versus V) [16] has also been used; this yields similar values of threshold potential with our data.

The threshold potentials, obtained by a least-squares treatment of the data, are given in table 1. The slopes of the lines in fig. 2 are slightly different because of differences in the photon flux at the different wavelengths (6.9×10^{16} to 1.5×10^{17} photons $\text{s}^{-1} \text{cm}^{-2}$).

A plot of threshold potential versus excitation energy (fig. 3) has a slope of 1.00 ± 0.02 in line with theoretical expectations and often found for photoelectron

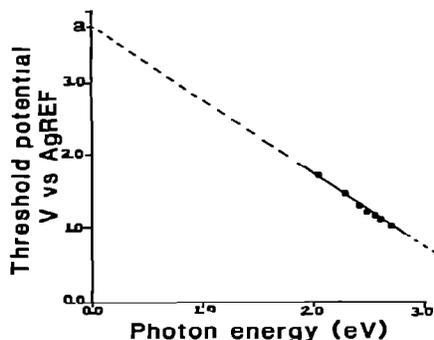


Fig. 3 Threshold potential (V) versus photoexcitation energy (eV), for TBAPF₆ in liquid SO_2 . Intercept, a , is taken as the valence band edge of liquid SO_2 , 3.74 V versus AgREF.

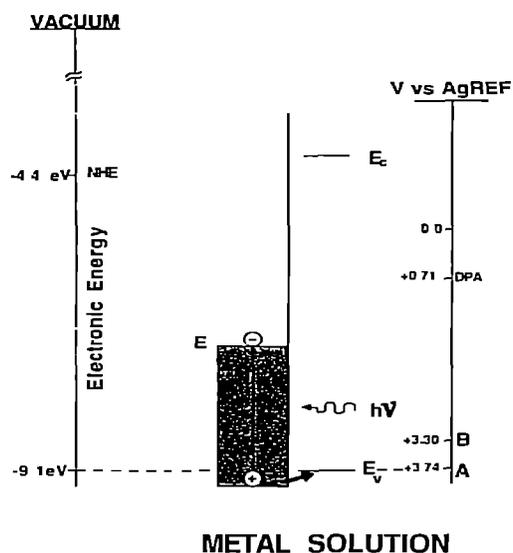


Fig. 4 Photohole injection process at Pt electrode liquid SO_2 , 0.1 M TBAPF₆ solution. E is the electrode Fermi level, E_v is the energy of the valence band edge, E_c is the energy of the conduction band edge, and $h\nu$ is the energy of the excitation source. The energy level for hole injection is shown on a potential scale (A versus AgREF) and on an absolute scale (versus vacuum) B is the calculated energy of the solvated hole.

emission studies. The intercept with the potential axis, extrapolating to zero excitation energy is 3.74 ± 0.03 V versus AgREF.

A diagram of the photohole injection process at a Pt electrode SO_2 /0.1 M TBAPF₆ solution interface is shown in fig. 4. The energy for hole injection, corresponding to a threshold potential of 3.74 ± 0.03 V versus AgREF, can be related to a vacuum electronic energy level by referencing the AgREF to the 9-10-diphenyl anthracene^{0/+} (DPA) couple with the usual assumption that the potential of this couple is independent of solvent [11,17]. The redox potential of this couple was 0.71 V versus AgREF in this study for 0.1 M TBAPF₆ in liquid SO_2 and is 1.35 V versus aqueous SCE [18]. If we assume the same value in water and take the energy level of the NHE to be -4.40 eV versus vacuum [19], the energy calculated for the hole-accepting level (or valence band edge of SO_2) is -9.1 ± 0.1 eV versus vacuum. This value is smaller than the ionization potential (IP) of SO_2 in the gas phase,

12.32 ± 0.01 eV [20], because some interaction of the emitted hole with solvent and supporting electrolyte ions will lower the energy needed for formation of the unrelaxed SO_2^+ species. An estimate of the extent of this interaction can be obtained by plotting IP versus the redox potential of the same species in the solvent of interest. Plots of this sort have been reported previously [21–24] and have been shown to follow a relation

$$V_{\text{redox}} = A(\text{IP}) + B, \quad (2)$$

where A is near unity. A plot of IP versus V_{redox} was prepared for several couples in SO_2 (species, IP, V_{redox} versus AgREF): phenothiazine, 7.26 eV, 0.32; thianthrene, 7.92 eV, 0.82; DPA, 7.10 eV, 0.71; ferrocene, 6.86 eV, 0.08. Because of the limited available IP data for those couples that have been previously studied in SO_2 , and because these couples are close in V_{redox} values, a line of slope (A) 1.0 was assumed. However, even on this basis, the gas-phase IP would predict a potential corresponding to the production of thermalized SO_2^+ , 5.5 V versus AgREF, i.e. at ≈ 1.8 V more positive than the observed threshold. This suggests that liquid SO_2 involves significant interactions between the SO_2 molecules to produce a valence band in the solvent at least 1.8 eV above the solvated isolated molecule level.

We can also compare this level with that for the background oxidation of solvent. Irreversible oxidation occurs at ≈ 3.0 V versus AgREF. Since the SO_2^+ that is formed reacts rapidly, probably by extracting an F^- from the PF_6^- , the actual reversible potential for solvent oxidation occurs at more positive values. If the reaction of SO_2^+ with PF_6^- occurs near the diffusion-controlled limit, the reversible potential would be ≈ 0.3 V more positive than the background oxidation, i.e. at ≈ 3.3 V versus AgREF or -8.7 eV versus vacuum. This would imply that the "dry hole" injected at -9.1 eV solvates to the extent of ≈ 0.4 eV.

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