Driving Force Dependence of Electron Transfer from Electronically Excited $[Ir(COD)(\mu-Me_2pz)]_2$ to Photo-Acid Generators

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ABSTRACT: We report the rates of electron transfer (ET) reactions of electronically excited $[Ir(COD)(\mu-Me_2pz)]_2$ with onium salt photoacid generators (PAGs). The reduction potentials of the PAGs span a large electrochemical window that allows determination of the driving force dependence of the ET reactions. Rate constants of ET from electronically excited $[Ir(COD)(\mu-Me_2pz)]_2$ to onium PAGs are determined by the reaction driving force until the diffusion limit in acetonitrile is reached.

INTRODUCTION

State-of-the-art photolithography utilizes onium salts that decompose to produce strong acids upon exposure to light. The strong acid reacts with acid sensitive functional groups in a polymeric matrix, creating a solubility switch and ultimately producing a lithographic pattern. Such lithographic patterning schemes are important as they are used to manufacture advanced integrated circuits for semiconductor chips.^{1,2} The onium salt photoacid generators (PAGs, Figure 1) used in photolithography have been the subject of much research owing to the ability to tune their properties to the different wavelengths typically used in modern optical lithography (248 and 193 nm). Extreme ultraviolet (EUV) lithography at 13.5 nm has been identified as a leading candidate for next-generation high-resolution patterning technology.³

PAGs have been studied in detail concerning their mechanism(s) to produce acid upon direct photolysis and sensitization.^{4–7} Electron transfer to PAG has been proposed to be one excited-state pathway that leads to the production of acid. This pathway may become more important in EUV lithography, as 13.5 nm light (91.8 eV) is proposed to produce high energy photoelectrons which in turn thermalize upon interaction with various components of a photoresist, including the PAGs.^{8–17} While a correlation has been proposed for the acid generation efficiency to the reduction potential of PAGs,^{10,11} to date, no studies have been conducted to understand which factors determine the rates at which PAGs are reduced. Therefore, we investigated PAG reduction by

employing electronically excited $[Ir(COD)(\mu-Me_2pz)]_2$ (COD = 1,5-cyclooctadiene; Me₂pz = 3,5-dimethylpyrazolyl) as an electron donor (Figure 2). To facilitate comparisons with previous work, our investigations were performed in acetonitrile solution.¹⁸

RESULTS AND DISCUSSION

Absorption and luminescence spectra of $[Ir(COD)(\mu-Me_{3}pz)]_{2}$ are shown in Figure 3. As previously reported, the absorption spectrum reveals an intense peak at $\lambda_{\rm max}$ = 525 nm ($\varepsilon \sim 8.7 \times$ 10^3 M⁻¹ cm⁻¹).^{18,19} This feature is accompanied by a less intense absorption at ~390 nm (ε ~ 1390 M^{-1} cm⁻¹) and a higher energy $\pi - \pi^*$ system (below 250 nm). Upon excitation at 530 nm, the iridium complex luminesces in solution (Figure 3). There are two broad components in the emission spectrum: the less intense feature is at ~575 nm (Stokes shift ~1660 cm⁻¹), and the more prominent component is centered near 705 nm (Stokes shift ~4865 cm⁻¹). Note that the excitation spectra that give rise to both emission features ($\lambda_{em} = 575$ and 705 nm) are virtually identical, confirming that both are attributable to a single molecular species. The 575 nm emission has been assigned to ¹B₂ fluorescence and the 705 nm feature to ${}^{3}B_{2}$ phosphorescence. The quantum efficiencies are 0.0001

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Figure 1. PAG structures. The anion (not shown) is perfluorobutanesulfonate (PFBUS) in all cases.



Figure 2. Structure of $[Ir(COD)(\mu-Me_2pz)]_2$



Figure 3. Room temperature absorption and luminescence spectra of $[Ir(COD)(\mu-Me_2pz)]_2$ in acetonitrile solution.

and 0.0038, respectively (relative to $[Ru(bpy)_3][PF_6]_2$ in $CH_3CN: \Phi_{PL} = 0.062$).²⁰

Cyclic voltammetry of $[Ir(COD)(\mu-Me_2pz)]_2$ in CH₃CN solution has been reported previously.²¹ One-electron oxidation occurs at 0.28 V, and the first one-electron reduction is at -2.51 V vs SCE (saturated calomel electrode).

Combining luminescence data with electrochemical data reveals the reduction potential of the iridium excited state (Figure 4). The (cation/excited state) reduction potential is \sim -1.6 V vs SSCE (saturated standard calomel electrode). Although the methylated complex may not produce enough driving force for reduction of the most negative onium PAG, it provides a good trade-off between reducing power and molecular stability for our work.

Cyclic voltammetry of the onium PAGs reveals irreversibility upon one-electron reduction (Figure 5). The electrochemical irreversibility of all PAGs is maintained based on the scan rate dependence (up to 6 V/s). This indicates that the chemistry ensuing reduction is fast on the electrochemical time scale. The resultant decomposition following electrochemical reduction affords the strong acid required for resist patterning. The four PAGs utilized in this study have the following reductive peak potentials: (1) $E_{pc} = -1.83$; (2) $E_{pc} = -1.50$; (3) $E_{pc} = -1.14$; (4) $E_{pc} = -0.52$ V. All electrochemical values were adjusted to an SSCE reference for comparison with previous work.

Luminescence lifetime quenching of 3 [Ir(COD)(μ -Me₂pz)]₂* by DBI-PFBUS (4) in acetonitrile solution is







Figure 5. Cyclic voltammograms of 1-4 in 0.1 M tetrabutylammonium perchlorate acetonitrile solution.

shown in Figure 6; the quenching rate constant from Stern– Volmer analysis is $6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Dynamic quenching constants of 2.0×10^6 , 4.2×10^8 , and $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ were determined for PAGs 1–3, respectively. Importantly, sulfonium cations have been shown to efficiently quench triplet excited states through triplet-to-triplet energy transfer.²² However, energy transfer is ruled out as a quenching mechanism, as the PAG excited triplets are energetically well above ³[Ir(COD)(μ -Me₂pz)]₂*. Thus, the observed quenching processes are attributable to reduction of the PAGs.

Quenching rate constants vs PAG cathodic peak potentials are plotted in Figure 7. Data in blue circles are from this work; the data in red squares are for reactions with pyridinium acceptors.¹⁸ Notably, the two data sets are in strikingly good agreement: both establish that ET rates at higher driving forces are near the diffusion limit.

CONCLUSIONS AND OUTLOOK

We established that a series of onium PAGs employed in lithographic technologies can be reduced by electronically excited $[Ir(COD)(\mu-Me_2pz)]_2$. ET rate constants are determined by the reaction driving force until the diffusion limit in acetonitrile is reached. Future work will help determine if the rate of PAG reduction is a crucial component in EUV lithography.

EXPERIMENTAL SECTION

 $[Ir(COD)(\mu-Me_2pz)]_2$ was prepared according to a literature method and gave satisfactory analytical data.²³ All chemicals were used directly from the supplier. Nuclear magnetic



Figure 6. Luminescence quenching of 3 [Ir(COD)(μ -Me₂pz)]₂* by 4 (black = 0.00 mM; red = 0.37 mM; blue = 0.46 mM; cyan = 0.88 mM). Inset: Stern–Volmer plot.



Figure 7. Rate constant vs quencher cathodic peak potential (blue circles, this work; red circles, data from refs 18 and 19). Dotted line is the diffusion limit in acetonitrile solution. The $[Ir(COD)(\mu-Me_2pz)]_2^+/^3[Ir(COD)(\mu-Me_2pz)]_2^*$ potential is -1.6 V vs SSCE.

resonance (NMR) spectra for all compounds were obtained either on a 300 or 500 MHz spectrometer. The chemical shifts are reported in δ (ppm) values relative to internal TMS (tetramethylsilane) for ¹H NMR, and the solvent for ¹³C NMR. ¹⁹F NMR chemical sifts are reported in ppm relative to CFCl₃ ($\delta = 0$) and were referenced using C₆F₆ ($\delta = -164.9$) as an external standard. Multiplicities are indicated by s (singlet), d (doublet), m (multiplet). Coupling constants, *J*, are reported in Hertz (Hz).

All onium–PFBUS salts were prepared similarly to that given for 1 (below) using the appropriate onium halide.

TBTPS-PFBUS (1): Tris(4-(*tert*-butyl)phenyl)sulfonium bromide (5.00 g, 9.77 mmol, 1.0 equiv) and potassium perfluorobutanesulfonate (3.64 g, 10.8 mmol, 1.1 equiv) were dissolved in dichloromethane (100 mL) and water (100 mL) and vigorously stirred at room temperature for 18 h. The layers were separated, and the organic phase was washed with water (5 × 50 mL, 250 mL total) and concentrated under reduced pressure to afford the title compound (6.71 g, 85%) as a white solid. ¹H NMR (500 MHz, (CD₃)₂CO) δ : 7.84–7.88 (m, 12H), 1.35 (s, 27H). ¹³C{¹H} NMR cation (500 MHz, (CD₃)₂CO) δ : 158.62, 131.33, 128.93, 122.33, 35.38, 30.52. ¹⁹F NMR (300 MHz, (CD₃)₂CO) δ : -82.28 (3F), -115.66 (2F), -122.45 (2F), -126.86 (2F). HRMS cation (ESI), *m/z* C₃₀H₃₉S (M)⁺ calcd 431.3, obsd 432.0. HRMS anion (ESI), *m/z* C₄F₉O₃S⁻ calcd 299.0, obsd 299.1.

TPS-PFBUS (2): ¹H NMR (500 MHz, $(CD_3)_2CO$) δ : 7.89– 7.96 (m, 9H), 7.83 (t, J = 8 Hz, 6H). ¹³C{¹H} NMR cation (500 MHz, $(CD_3)_2CO$) δ : 134.95, 131.87, 131.62, 125.27. ¹⁹F NMR (300 MHz, $(CD_3)_2CO$) δ : -82.36 (3F), -115.70 (2F), -122.53 (2F), -126.90 (2F). HRMS cation (ESI), m/z $C_{30}H_{39}S$ (M)⁺ calcd 263.1, obsd 263.4. HRMS anion (ESI), m/z $C_4F_9O_3S^-$ calcd 299.0, obsd 299.1.

DTBPI-PFBUS (3): ¹H NMR (500 MHz, $(CD_3)_2CO$) δ : 8.27 (d, J = 8 Hz, 4H), 7.61 (d, J = 8 Hz, 4H), 1.30 (s, 18H). ¹³C{¹H} NMR cation (500 MHz, $(CD_3)_2CO$) δ : 156.51, 135.74, 129.59, 110.97, 35.15, 30.57. ¹⁹F NMR (300 MHz, $(CD_3)_2CO$) δ : -82.32 (3F), -115.79 (2F), -122.53 (2F), -126.94 (2F). HRMS cation (ESI), $m/z C_{30}H_{39}S$ (M)⁺ calcd 393.1, obsd 393.7. HRMS anion (ESI), $m/z C_4F_9O_3S^-$ calcd 299.0, obsd 299.1.

DBI-PFBUS (4): ¹H NMR (500 MHz, $(CD_3)_2CO$) δ : 8.35 (dd, J = 1, 8 Hz, 2H), 8.30 (d, J = 8 Hz, 2H), 7.84 (t, J = 8 Hz, 2H), 7.69 (dt, J = 1, 8 Hz, 2H). ¹³C{¹H} NMR cation (500 MHz, $(CD_3)_2CO$) δ : 142.40, 131.57, 131.37, 131.17, 127.43, 121.10. ¹⁹F NMR (300 MHz, $(CD_3)_2CO$) δ : -82.36 (3F), -115.48 (2F), -122.49 (2F), -126.94. HRMS cation (ESI), $m/z C_{30}H_{39}S$ (M)⁺ calcd 279.0, obsd 279.2. HRMS anion (ESI), $m/z C_4F_9O_3S^-$ calcd 299.0, obsd 299.1.

Photochemistry. UV-visible absorption measurements employed a Cary 50 UV-vis spectrophotometer with 1 cm path length quartz cuvettes. Steady-state and time-resolved spectroscopic data were collected in the Beckman Institute Laser Resource Center (California Institute of Technology). Emission and excitation spectra were recorded on a Jobin Yvon Spec Fluorolog-3-11. Sample excitation was achieved via a xenon arc lamp with wavelength selection provided by a monochromator. Right angle luminescence was sorted using a monochromator and detected with a Hamamatsu photomultiplier tube (PMT) with photon counting (PMT model R928P).

For time-resolved measurements, laser excitation was provided by 8 ns pulses from a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) operating at 10 Hz. The third harmonic was used to pump an optical parametric oscillator (OPO, Spectra-Physics Quanta-Ray MOPO-700) tunable in the visible region to provide laser pulses at 525 nm. Scattered excitation light was rejected by suitable long pass and short pass filters, and luminescence wavelengths were selected for detection by a double monochromator (Instruments SA DH-10) with 1 mm slits. Light was detected with a PMT (Hamamatsu R928). The PMT current was amplified and recorded with a GageScope transient digitizer. Data were averaged over approximately 100 shots. All instruments and electronics in these systems were controlled by software written in LabVIEW (National Instruments). Data manipulation was performed with either MATLAB R2012a or MATLAB R2013a (Mathworks, Inc.).

Electrochemistry. Cyclic voltammograms were collected in a one compartment cell with a Pt working electrode (BASi, MF-2013), Pt wire auxiliary electrode (BASi, MW-4130), and Ag/AgCl reference electrode (BASi, MF-2052). Tetrabutyl ammonium perchlorate (0.1 M, >99%, Sigma-Aldrich) in acetonitrile (HPLC grade, Sigma-Aldrich) solution was the electrolyte for all electrochemical experiments. Caution! Perchlorate salts are potentially explosive and should be handled with care.

Prior to each experiment, the Pt working electrode was thoroughly cleaned and polished with an alumina slurry, rinsed with distilled water, and dried. The electrolyte solution was checked for contamination of electrochemically active species by conducting a cyclic voltammetry experiment prior to addition of the PAG analyte, sweeping across an electrochemical potential window of 0 to -2.0 V vs Ag/AgCl. Upon confirming a clean electrolyte solution, the selected PAG was dissolved in the electrolyte solution ($\sim 10^{-3}$ M PAG concentration) followed by N₂ purging for 5–10 min prior to electrochemical measurements. Three successive cyclic voltammograms were collected for each PAG for determination of cathodic peak potentials. The scan rate for each potential sweep was 0.1 V s⁻¹ with a step size of 0.01 V. No *iR*-compensation was applied.

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Notes

The authors declare no competing financial interest.

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