

## Diffusion-Limited Interfacial Electron Transfer with Large Apparent Driving Forces

Georg M. Hasselmann and Gerald J. Meyer\*

Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

Received: June 23, 1999

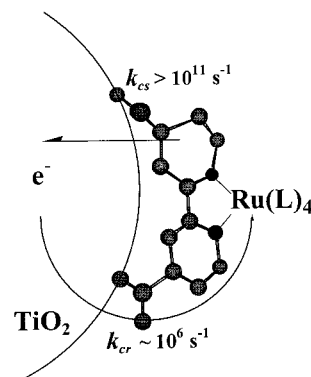
The Re(I) coordination compounds *fac*-Re(deeb)(CO)<sub>3</sub>(X), where deeb is 4,4'-(COOEt)<sub>2</sub>-2,2'-bipyridine and X is I<sup>−</sup>, Br<sup>−</sup>, Cl<sup>−</sup>, or CN<sup>−</sup>, and [*fac*-Re(deeb)(CO)<sub>3</sub>(py)](OTf), where OTf<sup>−</sup> is triflate anion and py is pyridine, have been prepared, characterized, and anchored to nanocrystalline (anatase) TiO<sub>2</sub>. In regenerative solar cells with 0.5 M LiI–0.005 M I<sub>2</sub> acetonitrile electrolyte, the Re(I) compounds convert absorbed photons into electrons efficiently. The rate of interfacial charge separation could not be time resolved,  $k_{cs} > 10^8 \text{ s}^{-1}$ . Thermodynamically favorable recombination of the injected electron in TiO<sub>2</sub> with the oxidized sensitizer requires milliseconds for completion. Charge recombination kinetics have been quantified on a 10<sup>−7</sup>-s and longer time scale and are insensitive to the Re sensitizer employed. The charge recombination kinetics have been contrasted with other sensitized TiO<sub>2</sub> materials and are insensitive to an ~960-mV change in apparent driving force. The results suggest that charge recombination is rate limited by diffusional encounters of the injected electron with the oxidized sensitizer.

## Introduction

Impressive photon-to-current efficiencies realized from colloidal TiO<sub>2</sub> (anatase) films sensitized to visible light with Ru(II) polypyridyl compounds in regenerative photoelectrochemical cells have renewed interest in molecular approaches to solar energy conversion.<sup>1–3</sup> A key to the high solar conversion efficiencies realized with these materials is a remarkable difference in interfacial charge separation and recombination rate constants (Scheme 1). Recent ultrafast absorption studies reveal that charge separation occurs on a femtosecond time scale.<sup>4–7</sup> In contrast, charge recombination occurs on a slower time scale, with average rate constants generally reported to be ~10<sup>6</sup> s<sup>−1</sup> based on a multiexponential analysis of transient optical data.<sup>8–11</sup> Therefore, an ~5 order of magnitude difference in the rates of charge separation and recombination is present at this semiconductor interface. Slow recombination allows iodide, or other electron donors, to efficiently intercept the interfacial charge-separated state before energy-wasting recombination occurs.<sup>2,12</sup>

Explanations for why this fortuitous difference in interfacial rates exists have been discussed in the literature.<sup>2,12,13</sup> Since different molecular orbitals are involved in the charge separation and recombination processes, different rates are expected. For (dπ)<sup>6</sup> polypyridyl compounds, the excited states are metal-to-ligand charge transfer (MLCT), and charge separation occurs from the π\* levels of a diimine ligand while charge recombination occurs to the t<sub>2g</sub> orbitals of the metal. The thermodynamic driving force for these processes is not easily calculated because the nature and energetics of the redox-active state(s) in TiO<sub>2</sub> remain unknown. For single-crystal materials, the conduction band continuum is generally thought to be the electron acceptor,<sup>14</sup> and charge separation is activationless and irreversible due to phonon release as the injected electron thermalizes to the conduction band edge, E<sub>cb</sub>.<sup>15</sup> The temperature<sup>16</sup> and driving force<sup>17,18</sup> dependence for charge recombination in sensitized nanocrystalline TiO<sub>2</sub> materials are reported to be consistent with Marcus kinetic inverted behavior.<sup>2</sup>

## SCHEME 1



In an effort to better understand interfacial charge recombination and its driving force dependence, we have prepared a series of Re(I) bipyridine compounds for TiO<sub>2</sub> sensitization. We report here the preparation, characterization, and photoelectrochemical properties of *fac*-Re(deeb)(CO)<sub>3</sub>(X), where deeb is 4,4'-(CO<sub>2</sub>-Et)<sub>2</sub>-2,2'-bipyridine and X is I<sup>−</sup>, Br<sup>−</sup>, Cl<sup>−</sup>, or CN<sup>−</sup>, and [*fac*-Re(deeb)(CO)<sub>3</sub>(py)](OTf), where OTf<sup>−</sup> is trifluoromethanesulfonate (triflate) anion and py is pyridine. Re(bpy)(CO)<sub>3</sub>X compounds generally absorb light in the blue and ultraviolet regions, so we do not expect efficient sunlight harvesting or solar energy conversion with these sensitizers.<sup>19</sup> However, Re(I) compounds are excellent probes of interfacial electron transfer due to their high stability and interesting geometric and redox properties.<sup>20</sup> The facial geometry about Re(I) likely affords more uniform molecular orientation on TiO<sub>2</sub> than does the commonly utilized *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub> sensitizer.<sup>21</sup> More important for this study is the fact that the Re(II/I) reduction potentials are significantly positive of those from other inorganic sensitizers. In principle, this provides a larger driving force for interfacial charge recombination. Our hope was that the relatively minor ligand substitution changes would not influence the energetics of the injected electron in TiO<sub>2</sub> such that the driving force for charge recombination would be systematically

varied in a known manner with each sensitizer. An important observation from these studies is that the charge recombination kinetics are insensitive to the identity of the sensitizer over an  $\sim 960$ -mV change in apparent driving force on a  $10^{-7}$ -s and longer time scale. The results suggest that recombination is rate limited by diffusional encounters of the injected electrons and oxidized sensitizers.

### Experimental Section

The preparation of nanocrystalline  $\text{TiO}_2$ , the photoelectrochemical measurements, and the spectroscopic measurements have been previously described.<sup>8,26</sup> The transient absorption measurements were performed with 417-nm light excitation, with typical pulse energies of  $1\text{--}2\text{ mJ/cm}^2$ .<sup>8,26</sup>

**Sensitizer Preparation.** *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>, *cis*-Ru(dcb)<sub>2</sub>-(CN)<sub>2</sub>, *cis*-Os(dcb)<sub>2</sub>(CN)<sub>2</sub>, and Ru(dcb)(bpy)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> were available from previous studies.<sup>22,23</sup> The methods for preparation of the Re(I) compounds are given below. We note that the corresponding Re(I) compounds with unsubstituted bipyridine ligands have been long known.<sup>20</sup>

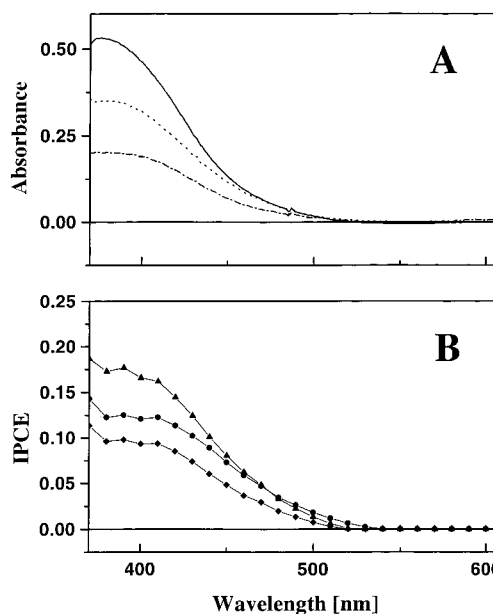
**[Re(CO)<sub>3</sub>(deeb)(py)](OTf).** A 100-mg portion of Re(CO)<sub>3</sub>-(deeb)Cl was stirred with 80 mg of AgOTf (99%, Aldrich) in 200 mL of dichloromethane (99.6%, Aldrich) overnight in the dark. A white solid was filtered, and the filtrate was evaporated to 30 mL. Bright yellow Re(CO)<sub>3</sub>(deeb)OTf precipitated upon the addition of 100 mL of hexane (98.5%, Aldrich). The solid was filtered and refluxed with 1 mL of pyridine (99%, Fisher) in 100 mL of toluene. The desired product was obtained upon reducing the volume of toluene by evaporation and addition of hexanes. Anal. Calcd (found): C, 37.59 (36.95); N, 5.26 (5.11); H, 2.65 (2.67). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 9.38, d, 2 H, H<sub>6</sub>; 8.89, s, 2 H, H<sub>3</sub>; 8.22, m, 4 H, 2', 5; 7.85, tr, 1 H, H<sub>4'</sub>; 7.28, tr, 2 H, 3'; 4.46, q, 4 H, CH<sub>2</sub>; 1.41, tr, 6 H, -CH<sub>3</sub>. IR (KBr, cm<sup>-1</sup>): 2032 (strong), 1940 (strong, broad), 1714 (strong).

**Re(CO)<sub>3</sub>(deeb)Br.** A 200-mg (0.4924 mmol) portion of Re(CO)<sub>5</sub>Br (Aldrich) and 183 mg of deeb were refluxed in 100 mL of toluene for 3 h. The mixture was cooled to room temperature, and Re(CO)<sub>3</sub>(deeb)Br precipitated as a bright orange solid. Anal. Calcd (found): C, 35.08 (34.82); H, 2.48 (2.51); N, 4.31 (4.40). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 1.45, tr, 6 H, -CH<sub>3</sub>; 4.44, q, 4 H, -CH<sub>2</sub>-; 8.07, d, 2 H, H<sub>5</sub>; 8.95, s, 2 H, H<sub>3</sub>; 9.21, d, 2 H, H<sub>6</sub>.

**Re(CO)<sub>3</sub>(deeb)Cl.** A 200-mg (0.5529 mmol) portion of Re(CO)<sub>5</sub>Cl (Aldrich) and 183 mg of deeb were refluxed in 100 mL of toluene for 3 h. The mixture was cooled to room temperature, and Re(CO)<sub>3</sub>(deeb)Cl precipitated as a bright orange solid. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 1.45, tr, 6 H, -CH<sub>3</sub>; 4.45, q, 4 H, -CH<sub>2</sub>-; 8.06, d, 2 H, H<sub>5</sub>; 8.92, s, 2 H, H<sub>3</sub>; 9.18, d, 2 H, H<sub>6</sub>. Re(CO)<sub>3</sub>(dcH<sub>2</sub>b)Cl was obtained by stirring 50 mg of Re(CO)<sub>3</sub>(deeb)Cl in 20 mL of pH 9 water for 1 h. Upon addition of HCl, the free acid precipitated out of solution. Anal. Calcd (found): C, 35.01 (34.94); H, 1.56 (1.79); N, 5.44 (5.35).

**Re(CO)<sub>3</sub>(dcb)CN.** This compound was available from previous studies.<sup>22</sup>

**Re(CO)<sub>3</sub>(deeb)I.** A 100-mg portion of Re(CO)<sub>3</sub>(deeb)Cl was stirred with 80 mg of AgOTf in 200 mL of dichloromethane overnight in the dark. A white solid precipitate was filtered, and the filtrate was evaporated to 30 mL. Bright yellow Re(CO)<sub>3</sub>(deeb)OTf precipitated upon the addition of 100 mL of *n*-hexane. The solid was filtered and refluxed with 400 mg of NaI in 100 mL of toluene. NaOTf and excess NaI were removed by filtration, and the desired product was obtained upon reducing the volume of toluene by evaporation and addition of *n*-hexane. Anal. Calcd (found): C, 32.72 (32.64); H, 2.31 (2.32);



**Figure 1.** (A) Absorption spectra of Re(CO)<sub>3</sub>(deeb)Cl (—), Re(CO)<sub>3</sub>-(deeb)Br (···), and Re(CO)<sub>3</sub>(deeb)I (---) anchored to TiO<sub>2</sub> in neat acetonitrile. An underivatized nanocrystalline film in acetonitrile was employed as the reference. (B) Photoaction spectrum of Re(CO)<sub>3</sub>(deeb)Cl (▲), Re(CO)<sub>3</sub>(deeb)Br (◆), and Re(CO)<sub>3</sub>(deeb)I (●) anchored to TiO<sub>2</sub>. The spectra were obtained in 0.5 M LiI–0.05 M I<sub>2</sub> in ACN. The IPCE is the incident photon-to-current efficiency.

N, 4.02 (3.92). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  = 1.44, tr, 6 H, -CH<sub>3</sub>; 4.48, q, 4 H, -CH<sub>2</sub>-; 8.04, d, 2 H, H<sub>5</sub>; 8.96, s, 2 H, H<sub>3</sub>; 9.25, d, 2 H, H<sub>6</sub>.

### Results

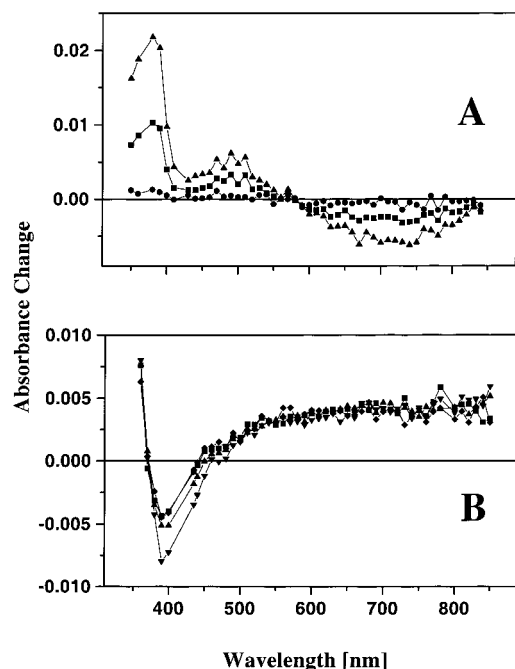
The Re(I) compounds have MLCT absorption maximum between 375 and 430 nm and photoluminesce in the visible region with single-exponential lifetimes in argon-purged acetonitrile.<sup>19</sup> Quasi-reversible voltammetry is observed in acetonitrile electrolyte for the oxidation of these compounds at a glassy carbon working electrode.<sup>24</sup> The voltammetry is termed quasi-reversible since the oxidation peak is 70–90% larger than the reduction peak at scan rates of 50–200 mV/s for all the compounds except Re(deeb)(CO)<sub>3</sub>I, which displayed no reduction wave after oxidation.

The excited-state reduction potentials were calculated from eq 1, where  $\Delta G_{\text{es}}$  is the free energy stored in the thermally equilibrated MLCT excited state, estimated by extrapolation of the corrected PL spectra. The spectroscopic and electrochemical properties are summarized in Table 1.

$$E_{1/2}(\text{Re}^{\text{II}*}) = E_{1/2}(\text{Re}^{\text{II}}) - \Delta G_{\text{es}} \quad (1)$$

Sensitizer attachment to nanocrystalline TiO<sub>2</sub> films occurs after soaking in  $\sim 10$  mM acetonitrile solutions of the compounds. The films take on the yellow color of the sensitizers. The MLCT maximum is partially masked by the fundamental absorption of TiO<sub>2</sub>, and only the long-wavelength absorption tail is clearly observed (Figure 1). The photoaction spectrum of these sensitizers, compared to that of a nascent TiO<sub>2</sub> film, reveals that the Re(I) compounds sensitize TiO<sub>2</sub> beyond 500 nm (Figure 1). The incident photon-to-current efficiency (IPCE) is low in the visible region due to the expected poor light absorption of the sensitizers at these wavelengths.

Excited-state absorption difference spectra, uncorrected for photoluminescence, of Re(deeb)(CO)<sub>3</sub>Cl in neat acetonitrile are



**Figure 2.** (A) Absorption difference spectra, uncorrected for photoluminescence, recorded after 417-nm excitation (1–2 mJ/pulse,  $T = 25\text{ }^{\circ}\text{C}$ ) of *fac*- $\text{Re}(\text{CO})_3(\text{deeb})\text{Cl}$  in 1.0 M  $\text{LiClO}_4$  acetonitrile solution. The spectra were acquired 0 ( $\blacktriangle$ ), 30 ( $\blacksquare$ ), and 70 ( $\bullet$ ) ns after the laser pulse. (B) Absorption difference spectra recorded after 417-nm excitation (1–2 mJ/pulse,  $T = 25\text{ }^{\circ}\text{C}$ ) of *fac*- $\text{Re}(\text{CO})_3(\text{deeb})\text{Cl}/\text{TiO}_2$  in 1.0 M  $\text{LiClO}_4$  acetonitrile solution. The spectra were acquired at 10 ( $\blacktriangledown$ ), 50 ( $\blacktriangle$ ), 200 ( $\blacksquare$ ), and 500 ( $\blacklozenge$ ) ns after the laser pulse, respectively.

shown in Figure 2a, after pulsed, 417-nm excitation. The time-resolved absorption difference spectra after pulsed excitation of  $\text{Re}(\text{deeb})(\text{CO})_3\text{Cl}/\text{TiO}_2$  in 1.0 M  $\text{LiClO}_4$  are shown in Figure 2b. Control experiments demonstrate that no absorption transients are observed with unsensitized  $\text{TiO}_2$  films under these conditions. At short delay times, some luminescence and features from the surface-bound  $\text{Re}(\text{I})$  MLCT excited state are observed that decay within 50 ns under these conditions. Therefore, on  $>50$ -ns time scale, the absorption difference spectrum is reasonably assigned to an interfacial charge-separated state,  $[\text{Re}^{\text{II}}(\text{deeb})(\text{CO})_3\text{Cl}^+/\text{TiO}_2(\text{e}^-)]$ . The rate of charge separation could not be time resolved with our instrumentation,  $k_{\text{cs}} > 10^8\text{ s}^{-1}$ .

In previous studies, interfacial electron-transfer kinetics were monitored at ground-excited-state isosbestic wavelengths to ensure that the excited state did not contribute to absorption transients assigned to the interfacial charge-separated state.<sup>8</sup> In the present study, the relatively weak absorbance of the  $\text{Re}(\text{I})$  compounds at the 417-nm excitation wavelength led to small absorption changes at all wavelengths investigated (Figure 2). Monitoring at 820 nm on  $10^{-7}$ -s and longer time scale allowed all of the interfacial charge-separated pairs to be characterized at the same wavelength.

The charge recombination kinetics could not be fit to a first-order model (Figure 3). A sum of three or four first-order rate constants were required in order to fit the entire data set. Alternatively, a sum of two second-order equal concentration processes (bi-second-order) described the data, eq 2, where  $\Delta A_0$

$$\Delta A = \frac{\Delta A_0 - \Delta A_2}{1 + (k_1/\Delta\epsilon)t(\Delta A_0 - \Delta A_2)} + \frac{\Delta A_2}{1 + (k_2/\Delta\epsilon)t(\Delta A_2)} \quad (2)$$

is the initial amplitude (equal to the sum of the contributions from the fast and slow components),  $k_1$  is the second-order rate

**TABLE 1: Photophysical and Electrochemical Properties of  $\text{Re}(\text{I})$  Sensitizers**

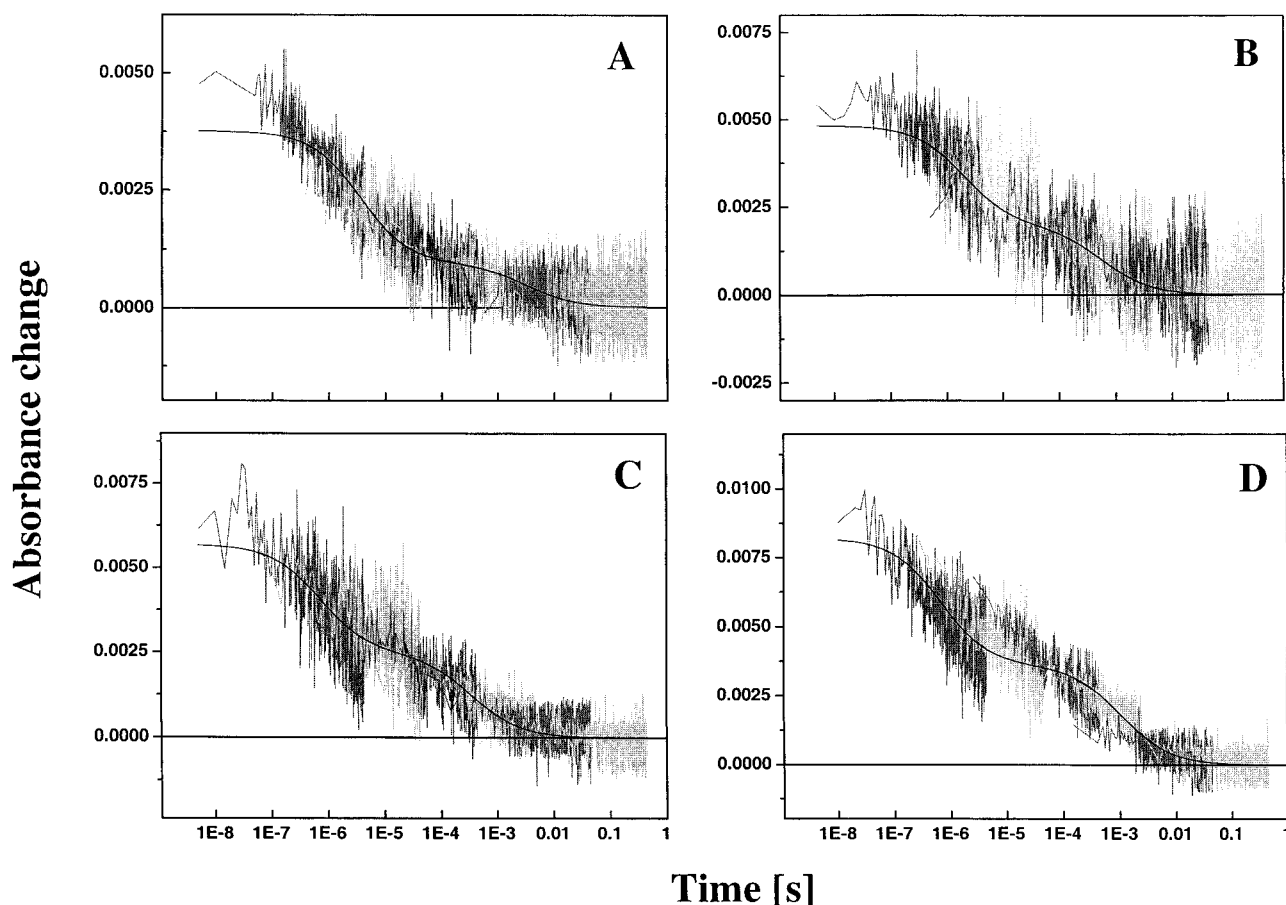
sensitizer <sup>a</sup>	$E_{1/2}$ (V)		$\lambda_{\text{MLCT}}^{\text{abs}}$ (nm) <sup>d</sup>	$\lambda_{\text{MLCT}}^{\text{PL}}$ (nm) <sup>e</sup>	$\phi^f$	$\tau$ (ns) <sup>g</sup>
	$\text{Re}^{\text{II/I}}$ <sup>b</sup>	$\text{Re}^{\text{II/I}}$ <sup>c</sup>				
$\text{Re}(\text{CO})_3(\text{deeb})(\text{py})^+$	1.81	−0.5	380	630	0.080	75
$\text{Re}(\text{CO})_3(\text{dcb})\text{CN}$	$>1.5^h$	−0.9	375	638	0.10	110
$\text{Re}(\text{CO})_3(\text{deeb})\text{Cl}$	1.44	−0.7	412	721	0.013	20
$\text{Re}(\text{CO})_3(\text{deeb})\text{Br}$	1.40	−1.0	413	700	0.030	30
$\text{Re}(\text{CO})_3(\text{deeb})\text{I}$	1.37 <sup>i</sup>	−0.8	432	715	0.040	32

<sup>a</sup> The coordination compound specified, where deeb is 4,4'-( $\text{CO}_2\text{Et}$ )<sub>2</sub>-2,2'-bipyridine, dcb is 4,4'-( $\text{CO}_2\text{H}$ )<sub>2</sub>-2,2'-bipyridine, and py is pyridine. All measurements were performed at room temperature. <sup>b</sup> The  $\text{Re}(\text{II/I})$  potential measured by cyclic voltammetry at 200 mV/s in 1.0 M tetrabutylammonium hexafluorophosphate acetonitrile solution. All potentials are versus the SCE reference. <sup>c</sup> The  $\text{Re}(\text{II/I})$  excited-state reduction potentials estimated with eq 1. <sup>d</sup> The MLCT absorption maximum in acetonitrile solution,  $\pm 1$  nm. <sup>e</sup> The corrected MLCT photoluminescence maximum in acetonitrile solution,  $\pm 4$  nm. <sup>f</sup> The quantum yield for photoluminescence measured by the optically dilute technique<sup>33</sup> using  $\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Et-Py})^+$  as a standard.<sup>34</sup> <sup>g</sup> The excited-state lifetime measured in argon saturated acetonitrile solution,  $\pm 5\%$ . <sup>h</sup> Measured previously in methanol electrolyte, ref 22. <sup>i</sup> The oxidation was irreversible, and only the oxidation potential is given.

constant for the fast component,  $\Delta A_2$  is the amplitude of the slow component,  $k_2$  is the second-order rate constant of the slow component, and  $\epsilon$  is the extinction coefficient.<sup>25</sup> We cannot rule out the possibility that a distribution of second-order rate constants underlies the observed transients. Equation 2 is preferred to multiexponential fits of the data because the rate constants abstracted from second-order analysis are less sensitive to the initial concentration of interfacial charge-separated states formed as a result of different irradiances, electron injection quantum yields, or ground-state absorption. Fits to eq 2 are superimposed on the data shown in Figure 3.<sup>25</sup> The poor fits at short times may be due to some contributions from excited states, so we have restricted the analysis to times longer than  $10^{-7}$  s.

Representative absorption transients assigned to charge recombination are shown in Figure 3, all obtained with 417-nm light excitation (1–2 mJ/cm<sup>2</sup>) and monitoring at 820 nm. The two  $\text{Re}(\text{I})$  sensitizers shown were chosen because they display a large difference in  $\text{Re}(\text{II/I})$  potentials and hence apparent driving force,  $\sim 410$  mV. The *cis*- $\text{Ru}(\text{dcb})_2(\text{NCS})_2$  is shown because it is the most efficient sensitizer reported and it provides the lowest driving force for charge recombination. The  $\text{Ru}(\text{III/II})$  reduction potential in acetonitrile is reported to be 0.85 V vs SCE for *cis*- $\text{Ru}(\text{dcb})_2(\text{NCS})_2$ . Therefore, the apparent driving force for charge recombination spans 960 mV from  $\text{Re}(\text{deeb})(\text{CO})_3(\text{py})^+$  to *cis*- $\text{Ru}(\text{dcb})_2(\text{NCS})_2$ . The *cis*- $\text{Os}(\text{dcb})_2(\text{CN})_2$  sensitizer shown provides a comparison with recombination to the  $t_{2g}$  orbitals of  $\text{Os}(\text{III})$ . The transients are, within experimental error, the same for the data shown, for the other  $\text{Re}(\text{I})$  sensitizers in Table 1, and for *cis*- $\text{Ru}(\text{dcb})_2(\text{CN})_2$  or  $\text{Ru}(\text{dcb})(\text{bpy})_2^{2+}$  measured under the same conditions of light irradiance, electrolyte solution, and  $\text{TiO}_2$  material. The two observed rate constants were  $k_1 = (4 \pm 3) \times 10^8\text{ s}^{-1}$  and  $k_2 = (7 \pm 5) \times 10^5\text{ s}^{-1}$ , where the errors represent a standard deviation for all the sensitizers measured. Conversion of the observed rate constants to units of  $\text{M}^{-1}\text{ s}^{-1}$  is difficult because of unknown extinction coefficients and the ill-defined path length of the mesoporous films. The amplitudes of the two components varied from sample-to-sample; however, the faster component was typically 60–80% of the decay. We note that the standard deviations, particularly of the slow component, would be larger if sensitized  $\text{TiO}_2$  materials prepared from different batches of  $\text{TiO}_2$  under slightly different experimental





**Figure 3.** Time-resolved absorption transients monitored at 820 nm in 1.0 M LiClO<sub>4</sub> acetonitrile solution after 417-nm excitation (1–2 mJ/pulse,  $T = 25\text{ }^{\circ}\text{C}$ ) of the following sensitizers anchored to nanocrystalline TiO<sub>2</sub>: (A) *fac*-Re(CO)<sub>3</sub>(deeb)(pyr)(OTf), (B) *fac*-Re(CO)<sub>3</sub>(deeb)Br, (C) *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>, and (D) *cis*-Os(dcb)<sub>2</sub>(CN)<sub>2</sub>. Superimposed on the spectra are fits to a bi-second-order equal-concentration kinetic model, eq 2, with  $k_1 = (4 \pm 3) \times 10^8\text{ s}^{-1}$  and  $k_2 = (7 \pm 5) \times 10^5\text{ s}^{-1}$ . The data represent an average of 30–50 transients at each time interval.

conditions were included. The origin of the substrate dependence on interfacial charge recombination will be treated elsewhere, since the goal of this study was to keep the materials conditions the same and vary only the molecular sensitizer.

## Discussion

The key result is that the kinetics for charge recombination from TiO<sub>2</sub> to the oxidized sensitizer are independent of the identity of the oxidized sensitizer on a 100-ns and longer time scale. This indicates an insensitivity not only to an  $\sim 960\text{-mV}$  change in apparent driving force but also to molecular geometry, the nature of the metal (Re, Ru, or Os), and the number of carboxylic acid groups present on the sensitizer (2 or 4). Remarkably, we have found that the recombination kinetics are more sensitive to the materials processing conditions and sample history than to the identity of the sensitizer.

The insensitivity of interfacial kinetics to the sensitizer employed may indicate that the donor level(s) in TiO<sub>2</sub> shift with the formal reduction potential of the sensitizer in such a way that the actual Gibbs free energy change for charge recombination is a constant.<sup>27</sup> While this may be the case, it does not explain why recombination appears to be slow. Our observations indicate that charge recombination is slow, not because of inherently slow rate constants but because the reaction follows second-order equal concentration kinetics. If efficient separation of the geminate interfacial charge-separated pair occurs, then the kinetics for charge recombination should follow second-order equal concentration kinetics. It has, in fact, been shown

that, when the electron concentration is increased with an applied potential, the charge recombination rate increases.<sup>11a</sup>

Our speculation is that charge recombination is rate limited by diffusional encounters of the injected electrons and the oxidized sensitizers. The diffusion may involve the injected electron, the oxidized sensitizer, or both. Diffusion of electrons in TiO<sub>2</sub> gives rise to slow photocurrent responses in these materials.<sup>28</sup> It is generally agreed that photocurrent responses are due to trapping/detrapping of the injected electrons as they diffuse through the material. Our work has shown that the photocurrent rise time displays a power law dependence on light intensity, with an exponent of approximately  $-0.7$ . These data can be simulated by assuming that the diffusion constant is second-order in the concentration of trapped electrons.<sup>28b</sup> Intermolecular electron transfer between surface-bound molecular complexes has also been observed.<sup>8c,29</sup> Diffusion of both the electron and the oxidized sensitizer, therefore, has precedence and provides an appealing explanation for why charge separation is so much faster than charge recombination in these materials. Charge separation occurs to state(s) proximate to the excited sensitizer, while charge recombination requires that the injected electron and oxidized dye approach each other by a diffusional process. It is interesting to note that initial attempts to observe Marcus kinetic inverted behavior in solution were also frustrated by diffusion-limited encounters of the donor and acceptor.<sup>30</sup>

This finding has an important implication in studies of alternative inorganic sensitizers for regenerative photoelectro-

chemical cells.<sup>2</sup> It is often found that some molecular sensitizers convert light into electricity more efficiently than others under the same experimental conditions of semiconductor material, electrolyte, wavelength of light, temperature, etc.<sup>26,31</sup> It is straightforward to determine the fraction of light absorbed by the sensitized material at any given wavelength. However, it is difficult to rationalize the molecular origin of different *absorbed* photon-to-current efficiencies with photoelectrochemical measurements alone. If the results described here can be generalized to the operational solar cell, then a lower photocurrent efficiency is *not* due to more rapid charge recombination for a given sensitizer but must reflect differences in interfacial charge separation yields and/or donor oxidation efficiencies.

## Conclusions

A series of structurally related Re(I) compounds are found to sensitize TiO<sub>2</sub> to visible light. The Re MLCT excited states inject electrons into TiO<sub>2</sub> with rate constants that could not be time resolved in this study,  $k_{cs} > 10^8 \text{ s}^{-1}$ . Charge recombination transients were quantified by a bi-second-order kinetic model that yields rate constants independent of the Re sensitizer employed. Furthermore, a comparison with *cis*-Ru(dcb)<sub>2</sub>(NCS)<sub>2</sub>, which is one of the most efficient sensitizers known, and other inorganic sensitizers displays charge recombination kinetics that are indistinguishable from those of the Re sensitizers. Therefore, with an ~960-mV change in apparent driving force, there is no evidence of Marcus kinetic inverted behavior for this important interfacial electron-transfer process. Charge recombination is also insensitive to the sensitizer molecular geometry, the identity of the metal (Re, Ru, or Os), and the number of carboxylic acid groups (2 or 4). The results suggest that charge recombination is rate limited by diffusional encounters of the injected electron and oxidized sensitizer. Evaluation of the driving force dependence for interfacial charge transfer across molecular-semiconductor interfaces continues to be an important experimental goal.<sup>32</sup>

**Acknowledgment.** The Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, is gratefully acknowledged for research support. G.M.H. thanks the Link foundation for an Energy Fellowship.

## References and Notes

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