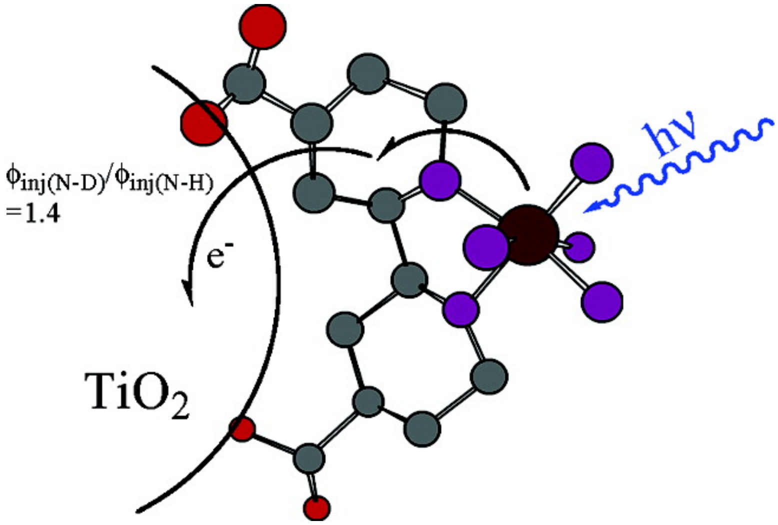
Communication

A Nuclear Isotope Effect for Interfacial Electron Transfer: Excited-State Electron Injection from Ru Ammine Compounds to Nanocrystalline TiO

Feng Liu, and Gerald J. Meyer

J. Am. Chem. Soc., **2005**, 127 (3), 824-825• DOI: 10.1021/ja045266a • Publication Date (Web): 24 December 2004



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Nuclear Isotope Effect for Interfacial Electron Transfer: Excited-State Electron Injection from Ru Ammine Compounds to Nanocrystalline TiO_2

Feng Liu and Gerald J. Meyer*

Departments of Chemistry and of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218

Received August 5, 2004; E-mail: meyer@jhu.edu

There now exists a large body of experimental data that demonstrates ultrafast femtosecond interfacial electron transfer from a molecular excited state to anatase TiO_2 nanoparticles.[1−3] For Ru(II) polypyridyl sensitizers, this finding raises interesting issues regarding which excited state(s) is involved in the injection process, i.e., the Franck−Condon state, singlet, triplet, or vibrationally “hot” singlet or triplet states of either, and which processes compete kinetically with electron injection, i.e., vibrational cooling, intersystem crossing, internal conversion, ligand field state population, or radiative and nonradiative decay.[2] The current thinking appears to be that subpicosecond injection arises from a singlet excited state, while slower injection is from the thermally equilibrated excited state.[3,4] Isotopic substitution studies have been widely employed and have provided valuable insights for Ru photochemistry and photophysics[5] but have received very little attention at semiconductor interfaces.[6] In fact, kinetic isotope effects have not been observed at sensitized interfaces. Here we report the first experimental evidence that nuclear isotopic substitution of molecular sensitizers can indeed be used to control excited-state interfacial electron injection yields.

The compounds of interest are $Ru(NH_3)_4(deeb)(PF_6)_2$, $Ru(en)_2(deeb)(PF_6)_2$, and $Ru(NH_3)_5(eina)(PF_6)_2$, where deeb is 4,4′-$(CO_2CH_2CH_3)_2$-2,2′-bipyridine, en is ethylenediamine, and eina is 4-CO_2Et-pyridine. The synthesis of the ruthenium ammine compounds is very similar to reported procedures for closely related compounds.[7−9] Hydrogen NMR and UV−vis spectra were consistent with the given formulations. Deuteration of the ammine ligands was performed by exchange in 1:1 MeOD/D_2O (containing $\sim 10^{-3}$ M DCl) solution under an argon atmosphere followed by evaporation of the solvent under reduced pressure at room temperature in the dark. The extent of the reaction was monitored by infrared spectroscopy, wherein the N−H stretching modes decreased with a concomitant increase of the N−D stretching intensity.[10] It was found that the N−H stretching bands were essentially gone after four consecutive exchanges in MeOD/D_2O. The asymmetric C=O stretching frequency remained at ~ 1710 cm^{-1} before and after deuteration. Freshly prepared TiO_2 films were soaked in pD 2.5 D_2SO_4/D_2O or pH 2.5 H_2SO_4/H_2O, rinsed with acetonitrile, and dried under vacuum three times prior to attachment of the sensitizers from millimolar acetonitrile solutions. The expected isotopic substitution of the sensitized TiO_2 thin films was verified by ATR-FTIR.

The absorption spectra of the deuterated compounds anchored to TiO_2, abbreviated $[Ru(ND_3)_4(deeb)]/TiO_2$, $[Ru(en\text{-}D_4)_2(deeb)]/TiO_2$, and $[Ru(ND_3)_5(eina)]/TiO_2$, showed metal-to-ligand charge-transfer (MLCT) bands in the visible region, Figure 1 and Table 1. The absorption spectra did not change significantly when the ammine ligands were deuterated. A quasi-reversible Ru(III/II) reduction potential was observed that shifted 10−15 mV when deuterated.[11] All compounds were found to be nonemissive in fluid solution and on TiO_2 or ZrO_2 surfaces with excited-state lifetimes <10 ns.

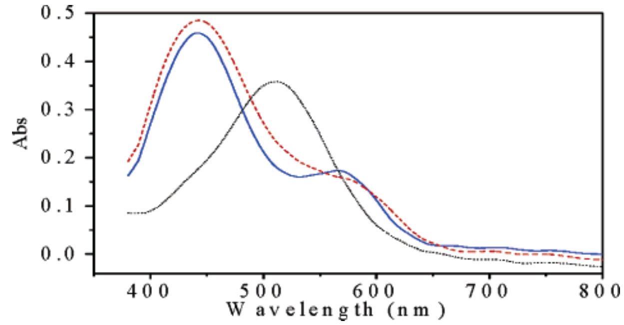


Figure 1. Absorption spectra of representative $[Ru(ND_3)_4(deeb)]/TiO_2$ (- - -), $[Ru(en\text{-}D_4)_2(deeb)]/TiO_2$ (—), and $[Ru(ND_3)_5(eina)]/TiO_2$ (···) samples under one atmosphere of argon.

Table 1. Absorption, Electrochemistry, and Electron Injection Yields of Natural Isotopic and Deuterated Compounds Anchored to TiO_2[a]

sensitizer	λ_{abs} (nm)	$E_{1/2}(Ru^{III/II})$ (mV)[b]	ϕ_{inj} (417 nm)[c]	ϕ_{inj} (532 nm)[c]
$[Ru(NH_3)_4(deeb)]^{2+}$	440, 575	575	0.19 ± 0.01	0.10 ± 0.01
$[Ru(ND_3)_4(deeb)]^{2+}$	443, 580	585	0.28 ± 0.02	0.13 ± 0.01
$[Ru(en)_2(deeb)]^{2+}$	438, 568	726	0.31 ± 0.04	0.24 ± 0.02
$[Ru(en\text{-}D_4)_2(deeb)]^{2+}$	440, 568	713	0.39 ± 0.02	0.33 ± 0.03
$[Ru(NH_3)_5(eina)]^{2+}$	515	247	0.14 ± 0.01	0.09 ± 0.01
$[Ru(ND_3)_5(eina)]^{2+}$	511	233	0.20 ± 0.02	0.13 ± 0.01

[a] Injection yields were measured spectroscopically at room temperature under one atmosphere of argon. The experimental error represents standard deviations from multiple samples. [b] The $Ru^{III/II}$ reduction potential measured by cyclic voltammetry in 0.1 M tetra-butylammonium perchlorate acetonitrile electrolyte. All potentials were measured vs a Ag/AgCl reference electrode. [c] Excitation with 417 and 532.5 nm light.

Pulsed light excitation of $[Ru(NH_3)_4(deeb)]/TiO_2$ in an argon atmosphere yielded an absorption spectrum consistent with the formation of the oxidized dye and an injected electron, Figure 2.

A bleach of the MLCT absorption bands was observed with a weak positive absorption feature at wavelengths greater than 650 nm. Similar features were also obtained in the transient absorption spectrum for $[Ru(en)_2(deeb)]/TiO_2$. The transient absorption spectrum for the deuterated compounds on the TiO_2 was identical to that of the natural isotopic compounds on surface. The appearance of this state could not be time resolved, indicating that injection occurred on a subnanosecond time scale. The quantum yields for injection were determined by comparative actinometry as previously described, Table 1.[12] The injection yields, ϕ_{inj}, approximately doubled when the excitation wavelength was changed from 532.5 to 417 nm. The injection yields were also found to increase by ∼ 30−50% when the ammine ligands were deuterated and they were independent of the incident irradiance from 1.5 to 10 mJ/pulse. Ground-state absorption measurements before and after the laser excitation experiments revealed negligible sensitizer decomposition at the surface. Control experiments with $[Ru(bpy)_2(deeb)]/TiO_2$

10.1021/ja045266a CCC: $30.25

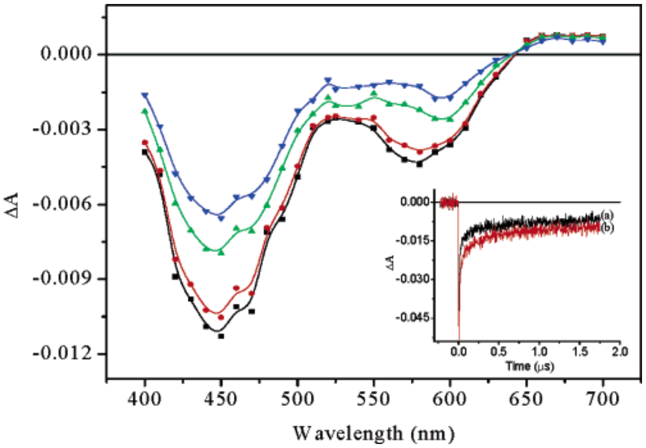


Figure 2. Absorption difference spectra observed after 532.5 nm laser excitation (~10 mJ/pulse, 8−10 ns fwhm) of [Ru(NH_3)$_4$(deeb)]/TiO_2 under Ar at room temperature. The spectra are shown at delay times of 0 ns (■), 20 ns (●), 200 ns (▲), and 1 microsecond (▼). (Inset) Single wavelength transients monitored at 450 nm for [Ru(NH_3)$_4$(deeb)]/TiO_2 (a) and [Ru(ND_3)$_4$(deeb)]/TiO_2 (b).

demonstrated that deuteration of the TiO_2 surface alone did not influence the injection yields. Interestingly, the rate for recombination of the injected electron with the oxidized sensitizer was unaffected by deuteration or the excitation wavelength and required milliseconds for completion.

Increased injection yields with higher energy excitation have previously been observed for other sensitized TiO_2 materials and are consistent with injection from "hot" excited states.[3,13] The appearance of a kinetic isotope effect has not been previously reported and implies that the injection rate constants are competitive with vibrational relaxation and/or intersystem crossing. Early studies of Ru ammine compounds focused on the role of ligand field excited states in photochemical ligand loss[14] and weak MLCT emission has only recently been reported at low temperature.[15] At 77 K, it was also found that ammine perdeuteration increased the MLCT lifetime by about a factor of ~2−3, depending on the number of ammine ligands.[15] These studies implicated high-frequency N−H (or N−D) modes as important nonradiative decay pathways, and it is likely that something similar is occurring at these semiconductor interfaces at room temperature. Excited-state electron injection and nonradiative rate constants are competitive, and the heavier isotope slows nonradiative decay, resulting in higher injection yields.[16] Clearly more studies, particularly on short time scales, are needed to fully understand the mechanistic details of interfacial electron transfer in these systems.

In conclusion, for the first time a kinetic isotope effect has been measured for excited-state electron injection into TiO_2 nanocrystallites, with an empirical deuterium isotope effect of $\phi_{\mathrm{inj(N-D)}}/\phi_{\mathrm{inj(N-H)}} = 1.3-1.5$. This finding indicates that energy conversion and interfacial electron transfer can be controlled by nuclear substitution. There exists, in fact, very little experimental data for kinetic isotope effects at *any* semiconductor interface,[6] and this report shows that the effects can be quite significant as is expected theoretically.[17] These interfacial isotope effects are clearly kinetic in origin and likely emanate from changes in the nonradiative decay rate constants. Significantly, isotopic substitution increases the quantum yield for excited-state electron injection without increasing the rate constant for charge recombination.

Acknowledgment. We are grateful to the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy for grant support (DE-FG02-96ER14662).

Supporting Information Available: Table of *t*-test results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Tachibana, Y.; Moser, J. E.; Grätzel, M.; Klug, D. R.; Durrant, J. *J. Phys. Chem. B* **1996**, *100*, 20056. (b) Hannappel, T.; Burfeindt, B.; Storck, W.; Willig, F. *J. Phys. Chem. B* **1997**, *101*, 6799. (c) Heimer, T. A.; Heilweil, E. J. *J. Phys. Chem. B* **1997**, *101*, 10990. (d) Ellingson, R. J.; Asbury, J. B.; Ferrere, S.; Ghosh, H. N.; Sprague, J. R.; Lian, T.; Nozik, *J. Phys. Chem. B* **1997**, *101*, 6455. (e) Turner, G. M.; Beard, M. C.; Schmuttenmaer, C. A. *J. Phys. Chem. B* **2003**, *106*, 11716. (f) Piotrowiak, P.; Galoppini, E.; Wei, Q.; Meyer, G. J.; Wiewior, P. *J. Am. Chem. Soc.* **2003**, *125*, 5278.
(2) McCusker, J. K. *Acc. Chem. Res.* **2003**, *36*, 876.
(3) (a) Benko, G.; Kallioinen, J.; Korppi-Tommola, J. E. I.; Yartsev, A. P.; Sundström, V. *J. Am. Chem. Soc.* **2002**, *124*, 489. (b) Benko, G.; Myllyperko, P.; Pan, J.; Yartsev, A. P.; Sundström, V. *J. Am. Chem. Soc.* **2003**, *125*, 1118.
(4) Bhasikuttan, A. C.; Suzuki, M.; Nakashima, S.; Okada, T. *J. Am. Chem. Soc.* **2002**, *124*, 8398.
(5) Browne, W. R.; Vos, J. G. *Coord. Chem. Rev.* **2001**, *219−221*, 761.
(6) Nakabayashi, S.; Itoh, K.; Fujishima, A.; Honda, K. *J. Phys. Chem.* **1983**, *87*, 5301.
(7) Lavallee, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583.
(8) (a) Broomhead, J. A.; Kane-Maguire, L. A. P. *J. Chem. Soc.* **1967**, 546. (b) Witschy, J. K.; Beattie, J. K. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 969. (c) Mahoney, D. F.; Beattie, J. K. *Inorg. Chem.* **1973**, *11*, 2561.
(9) Liu, F.; Meyer, G. J. Manuscript in preparation.
(10) (a) Staufer, M.; Neyman, K. M.; Jakob, P.; Nasluzov, V. A.; Menzel, D.; Rösch, N. *Surf. Sci.* **1996**, *369*, 300. (b) Meyer, T. J.; Taube, H. *Inorg. Chem.* **1968**, *7*, 2369.
(11) Weaver, M. J.; Nettles, S. M. *Inorg. Chem.* **1980**, *19*, 1641.
(12) Bergeron, B. V.; Kelly, C. A.; Meyer, G. J. *Langmuir* **2003**, *19*, 8389.
(13) (a) Ferrere, S.; Gregg, B. A. *J. Am. Chem. Soc.* **1998**, *120*, 843. (b) Moser, J. E.; Grätzel, M. *Chimia* **1998**, *52*, 160. (c) Islam, A.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Murata, S.; Takahashi, Y.; Sugihara, H.; Arakawa, H. *Chem. Lett.* **2000**, 490. (d) Liu, F.; Meyer, G. J. *Inorg. Chem.* **2003**, *42*, 7351.
(14) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213. (b) Durante, V. A.; Ford, P. C. *Inorg. Chem.* **1979**, *18*, 588. (c) Carlos, R. M.; Neumann, M. G.; Tfouni, E. *Inorg. Chem.* **1996**, *35*, 2229.
(15) Xie, P.; Chen, Y.-J.; Endicott, J. F.; Uddin, M. J.; Seneviratne, D.; McNamara, P. G. *Inorg. Chem.* **2003**, *17*, 5040.
(16) (a) Freed, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272. (b) Maruszewski, K.; Bajdor, K.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1995**, *99*, 6286.
(17) (a) Ramakrishna, S.; Willig, F.; May, V. *J. Chem. Phys.* **2001**, *115*, 2743. (b) Ramakrishna, S.; Willig, F.; May, V.; Knorr, A. *J. Phys. Chem. B* **2003**, *107*, 607.

JA045266A