reactivity in a series such as $[PorFe(NO)_2]^+$, $[PorFeNO]^+$, PorFeNO, and $[PorFeNO]^-$ provides a unique opportunity to evaluate the effect of changing only the number of electrons in the $[PorFe(NO)_2]^+$ metal–ligand unit. Further crystallographic data will enhance this comparison.

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Registry No. $[(TPP)Fe(NO)_2]ClO_4$, 80964-55-2; (TPP)FeNO, 52674-29-0; (OEP)FeNO, 55917-58-3; $(OEP)FeClO_4$, 50540-30-2.

Time-Resolved Resonance Raman Investigation of Photostimulated Electron Transfer from Amines to *trans*-Stilbene

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The formation of radical ion pairs via photostimulated electron transfer is a process of fundamental importance in photochemistry and photobiology. Fast transient electronic-absorption spectroscopy has been employed to study the formation and dynamics of radical ions;[1] however, the characterization of reactive intermediates from featureless absorption spectra is often less than fully satisfactory. Time-resolved resonance Raman (TR^3) spectroscopy provides a powerful technique for both the characterization of reactive intermediates and the investigation of reaction dynamics.[2] We report preliminary results from our TR^3 investigation of electron transfer from the tertiary amines ethyldiisopropylamine and 1,4-diazabicyclo[2.2.2]octane (Dabco) to the singlet state of *trans*-stilbene. These results provide the first experimental evidence for the formation of the stilbene radical anion via photostimulated electron transfer from an organic electron donor to singlet *trans*-stilbene and serve to elucidate the differences in chemical behavior between trialkylamines and Dabco with singlet stilbene.[3]

Both ethyldiisopropylamine and Dabco quench the fluorescence of singlet *trans*-stilbene with rate constants that exceed the rate of diffusion in acetonitrile solution (2×10^{10} M^{-1} s^{-1}). The measured lifetime of *trans*-stilbene in acetonitrile solution (τ = 50 ps[4]) and the Stern–Volmer quenching constants[3c] for ethyldiisopropylamine (4.9 M^{-1}) and Dabco (8.0 M^{-1}) provide singlet quenching rate constants of 1×10^{11} and 2×10^{11} M^{-1} s^{-1}, respectively. These values may reflect static quenching which results from the high amine concentrations necessary for the observation of quenching of the short-lived stilbene singlet or, perhaps, weak ground-state complexation. Quenching of singlet stilbene by tertiary amines, including ethyldiisopropylamine, results in moderately efficient formation of stilbene–amine adducts and reduced stilbene (eq 1); whereas, quenching by Dabco is not chemically productive.[3c]

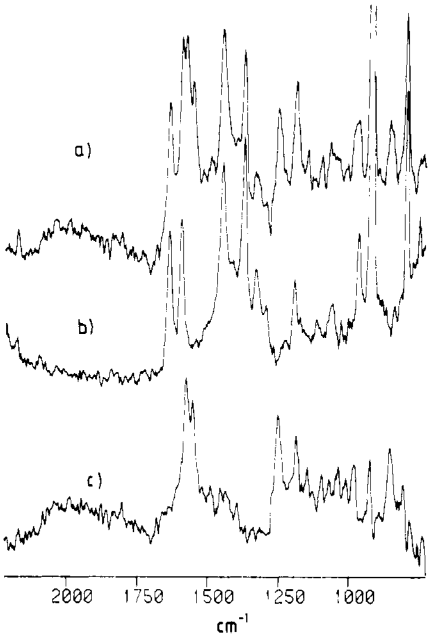

Figure 1. Raman spectrum of *trans*-stilbene (0.01 M) and Dabco (0.5 M) in acetonitrile solution: (a) 40 ns after photolysis pulse; (b) without preceding photolysis pulse; (c) difference spectrum due to the *trans*-stilbene anion radical.

$$\underset{0.01\ \mathrm{M}}{\mathrm{PhCH{=}CHPh}} + \underset{1.0\ \mathrm{M}}{\mathrm{EtN}(i\text{-}\mathrm{Pr})_2} \xrightarrow[\mathrm{MeCN}]{h\nu} \underset{\Phi = 0.11}{\mathrm{PhCH_2CH(Ph)CH(CH_3)N}(i\text{-}\mathrm{Pr})_2} + \underset{\Phi = 0.11}{\mathrm{PhCH_2CH_2Ph}} + \underset{\Phi = 0.034}{\mathrm{PhCH_2CH(Ph)CH(Ph)CH_2Ph}} \quad (1)$$

A deaerated acetonitrile solution of *trans*-stilbene (0.01 M) and Dabco (0.5 M) is irradiated at 337 nm with a pulsed nitrogen laser (1 mJ/pulse) at 298 K. After a time delay of Δt ns, the solution is irradiated at 484 nm with an excimer laser pumped dye laser (1 mJ/pulse). The Raman scattered light is spectrally resolved by a double-grating spectrograph (2 cm^{-1} resolution). After amplification in a gated image intensifier, the Raman spectra are recorded by means of an optical multichannel analyzer and stored in a computer for further data handling.[5] Improvement in signal to noise ratio is achieved by sampling over approximately 500 excite–probe cycles. The Raman spectra obtained without and with photolysis (Δt = 40 ns) are shown in Figure 1. Similar but more intense spectra are obtained for solutions of *trans*-stilbene (0.01 M) and ethyldiisopropylamine (1.0 M). Amine concentrations were selected to provide ca. 80% quenching of singlet *trans*-stilbene by both amines. The difference spectra shown in Figure 2 for singlet stilbene and ethyldiisopropylamine (Δt = 100 ns, 500 ns, and 2.5 μs) demonstrate the absence of persistent Raman-active species. The frequencies and relative intensities of the prominent peaks in the difference spectra (Figures 1c and 2a; 1577, 1553, 1251, 1180, 979, 848, 625 cm^{-1}) correlate well with those previously reported by Takahashi and Maeda[6] and by Dosser et al.[7] for the anion radical of *trans*-stilbene.[8]

The time dependence of the stilbene anion radical signal intensity was determined by comparing the intensity of the

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(1) Mataga, N.; Ottolonghi, M. "Molecular Association"; Foster, R., Ed.; Academic Press: London, 1979; Vol. 2, Chapter 1.

(2) For significant examples and leading references see: (a) Hub, W.; Schneider, S.; Dörr, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 323–324. (b) Atkinson, G. H.; Dosser, L. R. *J. Chem. Phys.* **1980**, *72*, 2195–2197. (c) Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1981**, *103*, 2495–2496. (d) Dallinger, R. F.; Farquharson, S.; Woodruff, W. H.; Rogers, M. A. J. *Ibid.* **1981**, *103*, 7433–7440.

(3) (a) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152–158. (b) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977**, *99*, 7991–7996. (c) Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Org. Chem.* **1981**, *46*, 1077–1082.

(4) Peters, K. S., private communication.

(5) For a description of the apparatus see: Dörr, F.; Hub, W.; Schneider, S. *J. Mol. Struct.* **1980**, *60*, 233–238.

(6) Takahashi, C.; Maeda, S. *Chem. Phys. Lett.* **1974**, *28*, 22–26.

(7) Dosser, L. R.; Pallix, J. B.; Atkinson, G. H.; Wang, H. C.; Levin, G.; Szwarc, M. *Chem. Phys. Lett.* **1979**, *62*, 555–561.

(8) The absence of peaks assignable to amine cation radicals is due to the lower (resonant) Raman scattering cross section of such species compared to the *trans*-stilbene anion radical. For the Raman spectrum of the Dabco cation radical see: Ernstbrunner, E. E.; Girling, R. B.; Grossman, W. E. L.; Hester, R. E. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 501–508.

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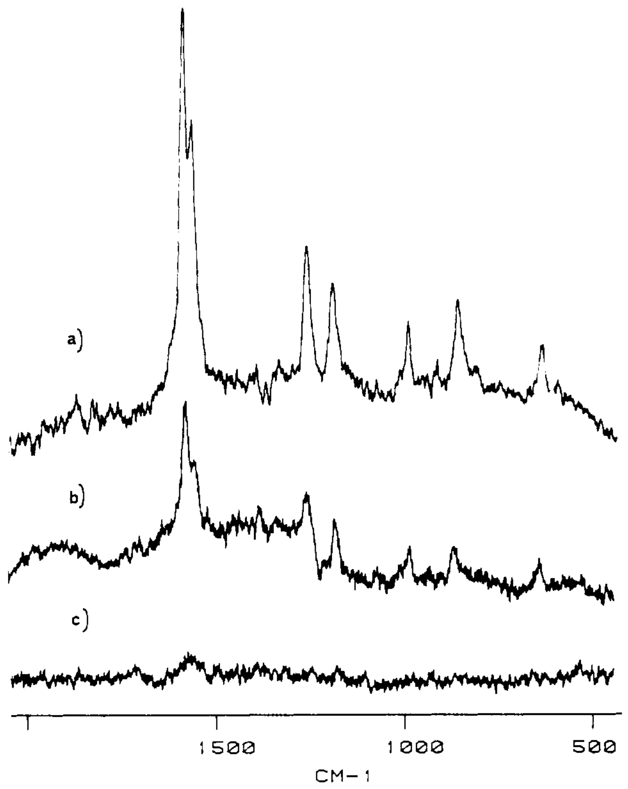


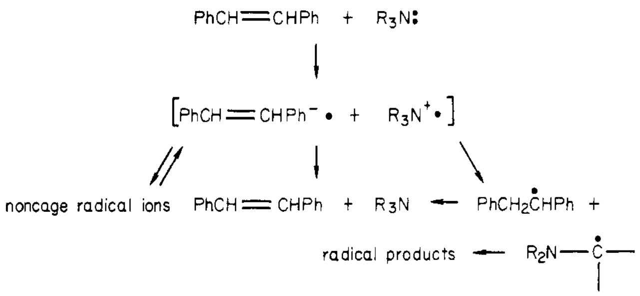
Figure 2. Raman difference spectra of *trans*-stilbene (0.01 M) and ethyldiisopropylamine (1.0 M) in acetonitrile solution at time delays of (a) 100 ns, (b) 500 ns, (c) 2.5 μs.

1577/1553 cm^{-1} peaks in the difference spectra with the intensity of the solvent bands around 1400 cm^{-1} at various time delays. This procedure normalizes the transient intensity for each measurement in the series to equal laser intensity. The data obtained obey a second-order rate law and provide a decay time for the stilbene anion radical Raman signal of ca. 300 ns with both amines. The signal intensity is a function (inter alia) of the radical ion concentration and its resonance Raman scattering cross section. Thus the signal decay time may not equal the anion radical lifetime. We estimate that the quantum yield for stilbene anion radical is ≤ 0.1, based on the equally good compensation of the bands from *trans*-stilbene and the solvent in the TR^3 spectra.

On the basis of previous chemical investigations, the mechanism of product formation upon reaction of singlet stilbene and tertiary amines (eq 1) was proposed to proceed via initial one-electron transfer to generate a stilbene anion radical–amine cation radical pair followed by proton transfer to yield a free-radical pair.[3] Radical pair combination and disproportionation completes the mechanism for product formation (Scheme I). The observation of the stilbene anion radical by TR^3 spectroscopy provides the first direct evidence for electron-transfer quenching of singlet *trans*-stilbene by tertiary amines. Since geminate (in cage) radical ion pairs are known to react or diffuse apart within several nanoseconds of their formation,[9] the stilbene anion radicals observed in the present investigation must arise from diffusion of the initially formed radical ion pair. Both the observed lifetime and second-order decay of the stilbene anion radical are indicative of homogeneous (out of cage) recombination with an amine cation radical as the exclusive decay pathway for the stilbene anion radical.[10]

The observation of stilbene anion radical formation with both ethyldiisopropylamine and Dabco supports an electron-transfer mechanism for quenching of singlet *trans*-stilbene by both amines.

Scheme I



The absence of stilbene–Dabco adduct formation might be due to the high kinetic stability of the Dabco cation radical or more rapid decay of the radical ion pair for Dabco vs. tertiary monoamines.[11] There are reports that singlet quenching by Dabco results in more rapid nonradiative decay to the ground state and/or intersystem crossing to the triplet state than is the case for quenching by tertiary monoamines.[12] Intersystem crossing of *trans*-stilbene exciplexes is known to yield triplet stilbene which undergoes isomerization to yield *cis*-stilbene.[13] On the basis of the measured quantum yields for *cis*-stilbene formation, intersystem crossing is found to be the predominant decay pathway for the radical ion pairs formed from singlet *trans*-stilbene with either Dabco or ethyldiisopropylamine. Thus rapid nonradiative decay cannot account for the inefficient formation of a stilbene–Dabco adduct. The dynamics of singlet stilbene–amine interactions are under continued investigation in our laboratories.[14]

Registry No. Dabco, 280-57-9; ethyldiisopropylamine, 7087-68-5; *trans*-stilbene, 103-30-0; *trans*-stilbene anion radical, 34473-61-5.

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[14] Travel expenses for this project were provided by Nato Research Grant 1911. Support of the work at Northwestern by the National Science Foundation (CHE-8026020) is gratefully acknowledged.

Catalytic Multiple Template-Directed Steroid Chlorinations

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We have described[1-5] several examples of template-directed chlorinations using the radical-relay mechanism. In this process a chlorinating agent delivers a chlorine atom to a template, which then relays it to the hydrogen atom of an attached substrate. The geometrical relationship between the template atom and the substrate determines which hydrogen is actually attacked. The result of this process is that the template is serving only a catalytic function and is regenerated, so that for instance it can be removed from the product chemically and reisolated. Of course a more interesting process would be one in which the regenerated template were in a position to attack additional substrate molecules, leading to true turnover catalysis. We report a first approximation to this situation, in which a single template is attached to three substrate molecules. As hoped, the reaction with this system indeed functionalizes all three substrates, as the template successively

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