Photoreduction of Thioindigo: Photoinitiated Two-Electron Transfer within a Substrate-Quencher Pair

Kirk S. Schanze, Charles Giannotti,[1] and
David G. Whitten*[2]

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received May 31, 1983

A wide variety of excited states can be quenched by electron donors;[3] usually the quenching event involves one-electron transfer yielding a radical pair.[4] In many systems net two-or-more-electron redox processes are required to produce "permanent" products; thus the radicals formed initially must undergo subsequent reactions such as coupling, disproportionation, or hydrogen abstraction which are typically bimoleuclar.[5] Recent studies have shown that quenching of several excited substrates by tertiary amines such as trialkylamines, reduced nicotinamides, and acridans can produce radical pairs via a sequence of electron transfer-proton transfer which occurs on the picosecond time scale.[6-9] In these cases it is generally assumed that, except for coupling, further reduction of the acceptor occurs primarily by disproportionation of the "semireduced" radical.[4,10,11] However, for a number of these reductants (:DH), the radical product from the electron transfer-proton loss (·D) is strongly reducing such that further reduction of either a ground-state acceptor or reducible radical is possible.[8,12] These reductants can thus function as potential two-electron donors, and it would appear possible that with suitable electron acceptors as reducible substrates net two-electron transfer can occur within a substrate-quencher pair.

In the present paper we report an investigation of the photoreduction of thioindigo (TI) by the aforementioned tertiary amines to form the two-electron reduction product *leuco*-thioindigo (TIH_2), which offers a clear example of this type of reaction. A study by ESR and laser flash photolysis techniques shows that at least two reaction paths operate in the remarkably clean conversion of the photogenerated radical pair, [TIH·, ·DH], to products including a second reduction within the pair, which accounts for the major fraction of the net reduction. Analysis of this reaction suggests that such reactions should occur fairly generally in processes that involve stepwise electron- and proton-transfer reactions but that amount to a photochemical *hydride* transfer.

Photolysis (546 nm) of degassed solutions of TI with tertiary amines, *N*-benzyl-4,4-dihydronicotrinamide (BNAH) and *N*-methylacridan leads to bleaching of the visible absorption band at 540 nm concurrent with the development of a solvent-dependent absorbance at 390-435 nm. Isosbestic points are maintained throughout the irradiation (see Figure 1). Upon admission of air to the photolyzed solutions, quantitative regeneration of the visible absorbance spectrum characteristic of TI occurs. Mass spectral analysis shows that the photoproduct has a molecular weight of 298 g/mol. These results are consistent with the hypothesis that photoreduction of TI by electron donors occurs leading to net two-electron reduction and formation of TIH_2 (eq 1); air oxidation of TIH_2 regenerates TI. Limiting quantum yields are in the range 0.03-0.5.[13]

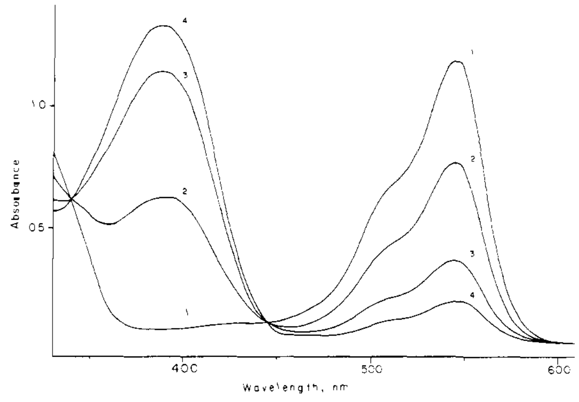
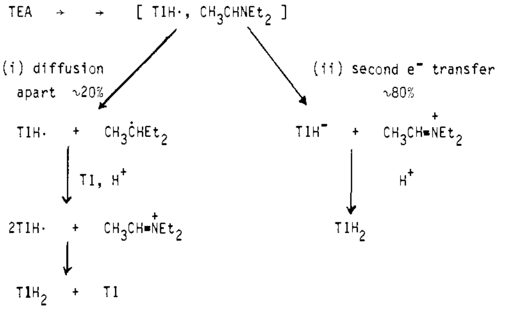
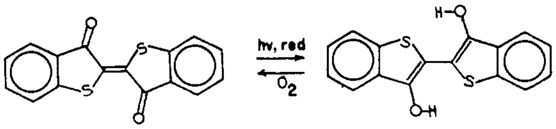


Figure 1. Changes in UV-vis spectrum with photolysis of 5×10^{-5} M TI/0.05 M TEA in benzene at $\lambda > 500$ nm. (1-4) Increasing irradiation times.

Scheme I





(1)

Electrochemical studies by Bard et al.[14] indicate that TI undergoes two reversible one-electron reductions in aprotic solvents; in the presence of proton donors an irreversible two-electron reduction occurs at a potential of -0.4 V (potentials vs. SCE). We have confirmed that this reduction is concurrent with formation of TIH_2. It can be deduced from these experiments that TIH· is readily reduced with a half-wave potential ≥ -0.4 V.

Fluorescence quenching of TI by tertiary amines[15,16] and BNAH occurs at the diffusion-controlled rate; K_{sv} for quenching of TI by triethylamine (TEA) is 110 ± 3 M^{-1} in benzene. Quantum yields for TI disappearance as a function of [TEA] have been measured for photolysis at 546 nm in degassed benzene; a linear double-reciprocal plot has an intercept/slope ratio of 94 ± 10 M^{-1}. Reasonable agreement with K_{sv} obtained by fluorescence quenching implies that the photoreduction occurs as a result of quenching of $^1TI^*$. This result is in accord with experiments which show that only donors with low oxidation potentials ($E_{ox} < 0.5$ V) quench $^3TI^*$.[15] (The electron donors used in our experiments have $E_{ox} > 0.5$ V.)[17,18]

Laser flash photolysis has been carried out to monitor the dynamics of the photoreduction on the nanosecond-microsecond

---

(1) C. N. R. S., Institut de Chimie des Substances Naturelles, Gif sur Yvette, France.

(2) Address correspondence to this author at: Department of Chemistry, University of Rochester, River Station, Rochester, NY 14627.

(3) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Lawrence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321. (c) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.

(4) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(5) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 10.

(6) Peters, K. S.; Freilich, S. C.; Schaeffer, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 5701.

(7) Peters, K. S.; Schaeffer, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 7566.

(8) Peters, K. S.; Simon, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 6403.

(9) Peters, K. S.; Pang, E.; Rudzki, J. *J. Am. Chem. Soc.* **1982**, *104*, 5535.

(10) Roth, H. D. In "Chemistry Induced Magnetic Polarization"; Muus, L. T., Atkins, P. W., McLaughlin, K. A., Pedersen, J. B., Eds.; Reidel: Dordrecht, The Netherlands, 1977; Chapter 4.

(11) Hore, P. J.; Volbeda, A.; Dijkstra, K.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 6262.

(12) Monserrat, K.; Foreman, T. K.; Grätzel, M.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 6667.

(13) For photoreduction of TI by TEA, the limiting quantum yield increases with increase in solvent polarity.

(14) Yeh, L. R.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1976**, *70*, 157; **1977**, *81*, 319.

(15) Memming, R.; Kobs, K. *Chem. Phys. Lett.* **1981**, *80*, 475.

(16) Memming, R.; Kobs, K. *J. Phys. Chem.* **1981**, *85*, 2771.

(17) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.

(18) Martens, F. M.; Verhoeven, J. W.; Gase, R. A.; Pandit, U. K.; De-Boer, Th. J. *Tetrahedron* **1978**, *34*, 443.

0002-7863/83/1505-6326$01.50/0

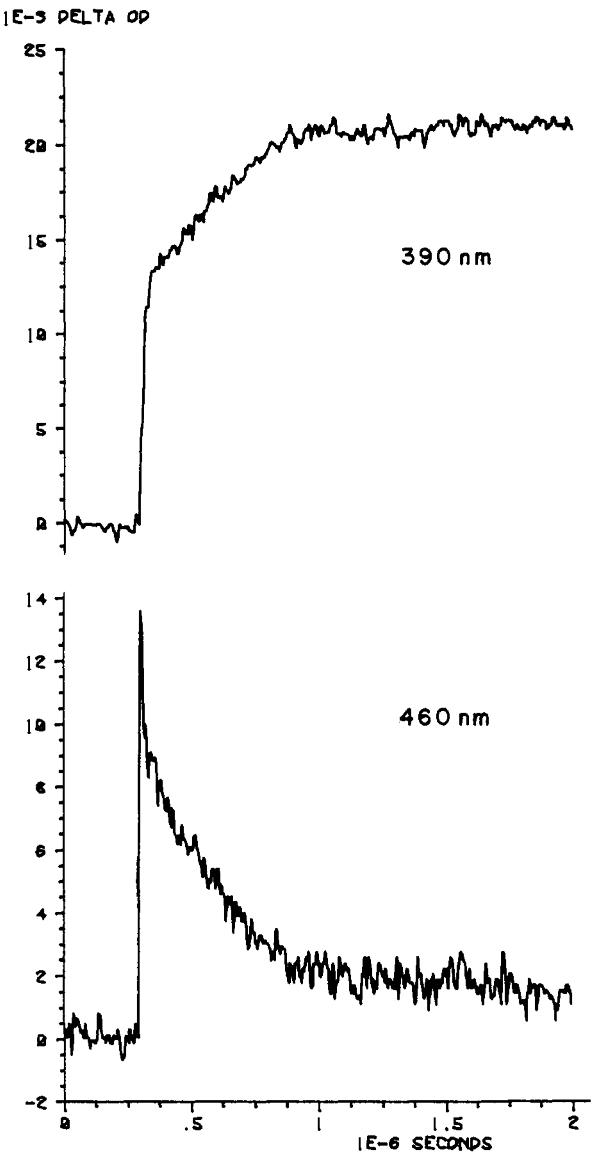


Figure 2. Transient absorbance monitored at 390 (upper trace) and 460 nm (lower trace) for 5 × 10^{-5}M TI/1.0 M TEA in benzene, 532-nm laser excitation.

time scale.[19] Time-resolved difference spectra resulting from 532-nm laser excitation of degassed solutions of TI with 1.0 M TEA in benzene show immediately after the laser pulse (10–20 ns) a broad absorbance that extends from 360 to 500 nm. After 500 ns the difference spectrum evolves to a more resolved absorbance centered at 390 nm extending to 450 nm. This spectrum persists out to the maximum time delays obtainable (50–100 μs); notable is the fact that this spectrum is similar to that of TIH_2 (see Figure 1). Time evolution of the absorbance at 390 and 460 nm is shown in Figure 2. At 460 nm a transient absorbance is noted; the transient decays to 20% of the initial value with a first-order rate constant $k = 3.6 \times 10^6$ s^{-1} (τ = 280 ns) and remains constant out to long times. At 390 nm an initial step is noted with the laser pulse followed by a grow in concurrent with the above decay. We attribute the 460-nm transient to the species TIH· as first a radical pair [TIH·, ·D] and subsequently the free radical. The 390-nm absorbance appears due to both TIH· and TIH_2, but primarily to the latter at long times.

The laser flash experiments suggest that two pathways exist for formation of TIH_2 from the radical pair formed via photoinduced electron transfer–proton transfer. These paths are outlined in Scheme I. The residual absorbance at 460 nm can be attributed to free radicals, TIH·, that form TIH_2 via disproportionation. The presence of this path is supported by ESR studies which confirm the generation of a single radical with a hyperfine spectrum attributable to TIH·.[21,22] However the bulk of the product formed in benzene is generated too rapidly to occur via this second-order process. The relatively rapid reaction of TIH· from the radical pair that competes with free radical formation is evidently a second electron transfer occuring within the radical pair (hence first order with $k = 3 \times 10^6$ s^{-1}), as outlined in Scheme I. This path provides a two-electron reduction or net *hydride transfer* from the tertiary amine to TI before the radicals diffuse apart.[22]

While the present reaction is noteworthy in that it involves a single photon initiated net two electron transfer, it should be anticipated to be possible or even general for a variety of appropriately matched donors and acceptors where an intervening proton transfer can occur. The long lifetime for the radical pair in the present case (or relatively slow rate for the second electron transfer) suggests that the pair should be a triplet and that intersystem crossing has occurred subsequent to or concurrent with the electron-transfer quenching.[23] It is reasonable to anticipate that the lifetime of the radical pair and relative importance of the paths in Scheme I should vary with solvent polarity and viscosity. We are currently examining this for the above and a number of related reactions.

Acknowledgment. We are grateful to the U. S. Department of Energy (Contract DE-AS05-81ER10815.A000) for support of this research.

Registry No. Thioindigo, 522-75-8; *N*-benzyl-1,4-dihydronicotinamide, 952-92-1; *N*-methylacridan, 4217-54-3.

---

(19) Laser flash photolysis apparatus as described in ref 20, except a pulsed monitoring lamp was used.

(20) Winkle, J. R.; Worsham, P. R.; Schanze, K. S.; Whitten, D. G. *J. Am. Chem. Soc.*, in press.

(21) Solutions of TI with tertiary amines, hydroquinone, and phenol during photolysis show a single ESR signal (5 line, g_{iso} = 2.0040 ± 0.0001, a_s = 15.40 ± 0.01 G) attributed to TIH.

(22) Studies suggest that $CH_3\dot{C}NEt_2$ has sufficient potential to reduce TI and TIH·.[12]

(23) Further experiments (e.g., CIDNP) to provide evidence that the radical pair is indeed a triplet are planned. Alternatively, the stability of TIH· may account for the radical pair lifetime.

Two Novel Examples of Hydroxylation of Aromatic Rings in Coordination Chemistry

Pinaki Bandyopadhyay,[1a] Debkumar Bandyopadhyay,[1a]
Animesh Chakravorty,*[1a] F. Albert Cotton,*[1b]
Larry R. Falvello,[1b] and Scott Han[1b]

Department of Inorganic Chemistry
Indian Association for the Cultivation of Science
Calcutta 700032, India
Department of Chemistry
and Laboratory for Molecular Structure and Bonding
Texas A&M University
College Station, Texas 77843

Received June 3, 1983

The hydroxylation of an aromatic ring, i.e., ArH → ArOH, is an important process in chemistry and biology.[2] We report here two novel examples of this reaction, each occurring in a coordination complex in which the aryl group is part of an arylazo

---

(1) (a) Indian Association for the Cultivation of Science. (b) Texas A&M University.

(2) Hayaishi, O., Ed., "Molecular Mechanisms of Oxygen Activation"; Academic Press: New York, 1974.