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Sensitized Photoreduction of Nitrate in Homogeneous and Micellar Solutions

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Two organic sensitizers (S), *N*-methylphenothiazine and *N,N,N',N'*-tetramethylbenzidine, were found to reduce nitrate ions after excitation to the triplet state. The photoreduction is irreversible and follows the sequence

$$S^T + NO_3^- \rightarrow S^+ + NO_3^{2-}$$
$$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^-$$
$$NO_2 + S \rightarrow S^+ + NO_2^-$$

$$\text{(net)}\quad 2S + NO_3^- + H_2O + \xrightarrow{h\nu} 2S^+ + NO_2^- + 2OH^-$$

For every triplet state produced, two donor molecules are oxidized and one nitrate ion is reduced to nitrite. The reactions were examined in homogeneous (water–ethanol) and micellar solutions. Rate constants for the individual processes were determined by a laser flash photolysis technique, and a detailed account of the energetics of this light energy conversion and storage system is given.

Introduction

Considerable effort has recently been directed toward finding chemical processes that are capable of quantum storage of light energy. These systems have potential importance because they may be utilized for the exploitation of solar radiation to produce a chemical fuel. A major problem has been the inability to preclude energy degradation of the excited state. In the case of a light-activated redox reaction such as formulated in reaction 1, the goal is to prevent the back-reaction between the oxidized donor and the reduced acceptor.

$$D + A \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} D^+ + A^- \qquad (1)$$

Systems that are endergonic in the forward direction frequently backreact at a diffusion-controlled rate in homogeneous solution, leading to rapid thermal dissipation of the light energy. One method whereby inhibition of the undesirable back-transfer of electrons may be achieved is to employ heterogeneous solutions such as micellar or membrane systems.[2,3] Here, ultrathin electrostatic barriers present as charged-phase boundaries make the kinetic control of the electron-transfer events feasible. Another alternative is to search for systems where the unstable intermediates formed in the forward reaction of eq 1 are converted into stable products before recombination can occur. This concept applies, for example, to the reduction of thallic ions[4] and mercuric ions[5] by ruthenium tris(bipyridine). A similar strategy is used in the present study to achieve light-induced reduction of nitrate to nitrite ions by organic sensitizers.

Experimental Section

(i) Materials. *N*-Methylphenothiazine (Aldrich) and *N,N,N',N'*-tetramethylbenzidine (Eastman Kodak) were purified by repeated recrystallization from ethanol. Sodium lauryl sulfate (NaLS) and dodecyltrimethylammonium chloride (DTAC) (Eastman Kodak) were recrystallized several times from ethanol or ethanol–ether mixtures. Deionized water was refluxed over $KMnO_4$ and subsequently distilled twice from a quartz still. All other reagents were at least reagent grade and used as supplied.

(ii) Sample Preparation. The hydrophobic compounds were solubilized in the micellar solutions by stirring the mixtures at 50–60 °C. Samples were deoxygenated by bubbling with highly purified argon.

(iii) Apparatus. The 347-nm light of a frequency-doubled Q-switched ruby laser (JK 2000) delivering a 15-ns pulse of less than 50 mJ of energy initiated the photochemical reactions. Transient species were monitored by fast kinetic spectrophotometry in the 10^{-8}–10^{-1}-s time regime. The experimental arrangement has been described in detail elsewhere.[6]

Results and Discussion

(i) Photoreduction of Nitrate in Water–Ethanol Solution (2:1 v/v). *N*-Methylphenothiazine (MPTH) solutions in a mixture of water and ethanol exhibit the characteristic strong absorption of this sensitizer in the near-UV region with a tail extending into the visible region. Light excitation of MPTH in the solution leads to formation of triplet states with a quantum yield of almost unity. The triplet-state formation was confirmed by laser photolysis experiments which showed the formation of a transient absorption centered around 465 nm, which has been identified as a T_1–T_n transition of MPTH.[7] At high laser intensities, which were avoided in the present study, biphotonic photoionization is noticeable.

A surprising and important effect was observed when laser flash photolysis was carried out on solutions of MPTH to which nitrate was added: the nitrate quenched the triplet state of MPTH. The oscillogram in Figure 1a illustrates the temporal behavior of the MPTH(T_1) absorption at 465 nm. The transient absorption is present immediately after the laser pulse but then decays rapidly according to first-order kinetics.

The MPTH(T_1) half-life of about 2 μs under these conditions is much shorter than in NO_3^--free solutions, where $\tau \simeq 80$ μs. The kinetics of the MPTH(T_1) decay are found to be pseudo first order in NO_3^- concentration, and Stern–Volmer analysis yields

$$k_2 = 2.7 \times 10^6\ M^{-1}\ s^{-1}$$

for the biomolecular quenching rate constant. Detailed spectroscopic analysis revealed that the product of the quenching reaction is the *N*-methylphenothiazine cation radical $MPTH^+$. Concomitant with and matching the triplet decay

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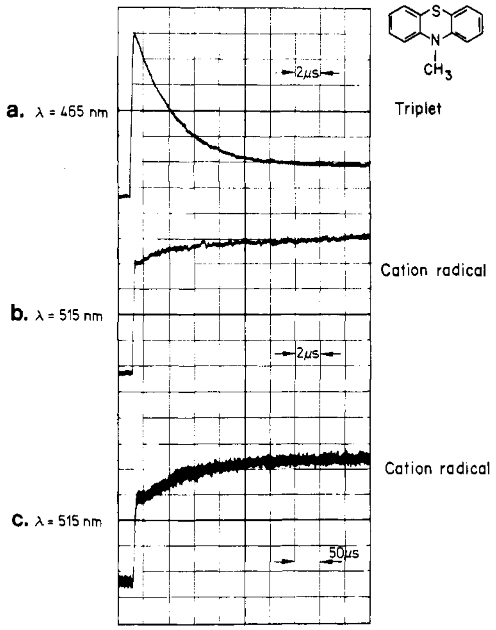

Figure 1. Temporal behavior of 465- and 515-nm absorptions in the laser photolysis of 1.5×10^{-4} M MPTH in 0.1 M $NaNO_3$ in water–ethanol (2:1 v/v) at pH 5.

is the growth of $MPTH^+$ ($\lambda_{max} = 515$ nm), as shown in Figure 1b. The transient spectrum present after completion of the triplet decay is readily identified[7] with that of $MPTH^+$. From this behavior one infers that $MPTH(T_1)$ undergoes oxidative quenching by NO_3^-:

$$MPTH^T + NO_3^- \xrightarrow{k_2} NO_3^{2-} + MPTH^+ \qquad (2)$$

From the known extinction coefficients[7] of $MPTH(T_1)$ and $MPTH^+$, the efficiency of radical ion production from the quenching of triplet states (cage-escape yield) is calculated to be nearly 100%.

An attractive feature of the photoredox process (2) is the instability of NO_3^{2-}, which decomposes in aqueous medium[8] according to

$$NO_3^{2-} + H_2O \xrightarrow{k_3} NO_2 + 2OH^- \qquad (3)$$

The half-life of NO_3^{2-} in alkaline medium is only 12.5 µs, corresponding to a pseudo-first-order rate constant of

$$k_3 = 5.5 \times 10^4 \text{ s}^{-1}$$

The lifetime of NO_3^{2-} is further reduced under acidic conditions[8] and amounts to about 5 µs under the experimental conditions employed in Figure 1. The rapid conversion of NO_3^{2-}, a reducing species, into NO_2, a strongly oxidizing agent, efficiently prevents any thermal back electron transfer in reaction 2. The fate of the NO_2 radical is reduction to nitrite by excess ground-state MPTH:

$$MPTH + NO_2 \xrightarrow{k_4} MPTH^+ + NO_2^- \qquad (4)$$

Reaction 4 manifests itself in Figure 1c as an additional growth of the $MPTH^+$ absorption on a longer time scale following the photoredox process (2). Figure 1c also shows that after completion of this process there are no further changes in the $MPTH^+$ concentration. From the evaluation of the 515-nm growth, one obtains for the rate constant of reaction 4 the value

$$k_4 = 6.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

Table I. Rate Constants (M^{-1} s^{-1}) for Redox Reactions in the Photoinduced Reduction of Nitrate and Nitrogen Dioxide by MPTH

reacns	anionic micelle (NaLS)	cationic micelle (DTAC)	water-ethanol (2:1 v/v)
$MPTH^T + NO_3^- \xrightarrow{k_2} MPTH^+ + NO_3^{2-}$	5.5×10^4	3.5×10^5	2.7×10^6
$MPTH + NO_2 \xrightarrow{k_4} MPTH^+ + NO_2^-$	6.6×10^7	5.1×10^7	6.6×10^7

The overall mechanism of NO_3^- photoreduction may be formulated as

$$2MPTH + NO_3^- + 2H^+ \xrightarrow{h\nu} 2MPTH^+ + NO_2^- + H_2O \qquad (5)$$

Hence , at sufficiently high nitrate concentration, each photon absorbed gives rise to oxidation of two MPTH molecules.

A similar study was undertaken with tetramethylbenzidine (TMB) as a sensitizer. Here we find the analogous rate parameters for the reduction of NO_3^- (eq 2) and NO_2 (eq 4) to be

$$k_2 = 7.3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} \qquad k_4 = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

As in the case of MPTH, the efficiency of electron transfer from TMB triplets to nitrate, as well as from TMB to NO_2, was found to be close to unity.

(ii) Photoreduction of Nitrate in Aqueous Micellar Solutions. The photoactive species used in the present study are sparingly soluble in water. To carry out investigations in a homogeneous aqueous system, it was necessary to employ a less polar cosolvent, such as ethanol. Alternatively, it was also possible to solubilize the organic donor in organized assemblies such as NaLS and DTAC micelles. The peculiarity of the situation encountered with such systems lies in the fact that the reactants are present in two different phases. The apolar interior of the micelles is the site of the photoactive electron donor, while the nitrate ions are located in the surrounding aqueous medium. Whenever electrons are transferred from donor molecules to acceptor ions, they must be transported across the charged interface separating the two phases.

Kinetic data obtained from laser photolysis experiments of aqueous solutions containing micelles of DTAC and NaLS are summarized in Table I together with the results from water–ethanol solutions. As can be understood from simple electrostatic considerations, the rate of reaction 2 is retarded considerably by anionic micelles. The negative surface potential of NaLS micelles at the ionic strength employed ($\mu \simeq 0.1$ M $\simeq [NaNO_3]$) amounts to about 75 mV,[9] which is sufficiently negative to inhibit the approach of NO_3^- ions to the charged surface of the micelle. On the other hand, electrostatic as well as hydrophobic interactions lead to a high local concentration of nitrate in the double-layer region of alkyltrimethylammonium halide micelles.[10] Therefore, cationic aggregates should exhibit a catalytic effect on reaction 2. Inspection of Table I reveals, however, that the value of k_2 for DTAC, though markedly higher than for the NaLS solution, remains below the k_2 value for water–ethanol. This behavior may be rationalized in terms of reaction energetics, which are discussed in the subsequent section.

Contrary to the nitrate situation, the rate of reaction of NO_2 with MPTH is independent of the surface charge of the micelle. As observed earlier,[11] the reactions of neutral radicals

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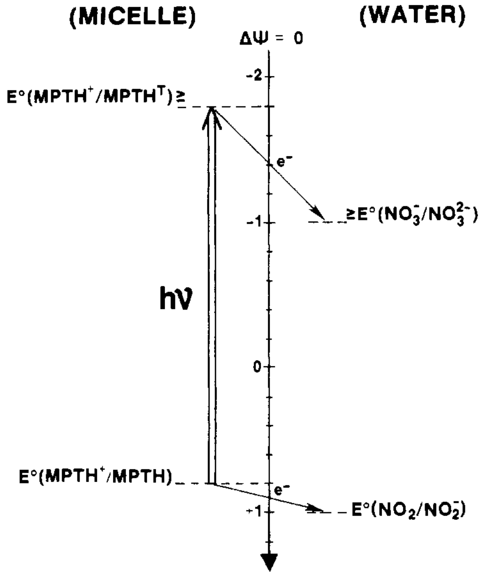

Figure 2. Redox potentials of the four redox couples involved in the photoreduction of nitrate to nitrite.

in ionic micellar solutions can be understood on the basis of homogeneous kinetics. Thus, the rate constants of reaction 2 are approximately the same in both homogeneous and micellar solutions. Apparently, there is a low activation barrier for the migration of NO_2 across the water-lipid interface of the micelle.

Energetic Considerations. In Figure 2 are presented standard potentials of the individual redox systems participating in the photochemical conversion of nitrate into nitrite. An upper limit for the one-electron reduction potential of nitrate has been determined as −1 V.[12] The value for the redox couple NO_2/NO_2^- is derived from the equation

$$E^\circ(NO_2/NO_2^-) = -4.4 + EA(NO_2) = 1\ V \quad (6)$$

where $EA(NO_2)$ designates the electron affinity of nitrogen dioxide in water, for which a value of 5.4 eV has been given.[13] The term −4.4 in the equation converts the absolute potential into the standard reduction potential of the redox system. The E° value for MPTH is assumed to be equal to that of unsubstituted phenothiazine in acetonitrile solution (=0.8 V). Note that in the micellar systems this parameter is influenced by the interfacial-potential difference:

$$E^\circ_{\text{micelle}} = E^\circ_{\text{water}} + (\psi_{\text{micelle}} - \psi_{\text{water}}) \quad (7)$$

The redox potential of the MPTH-triplet state was calculated from the relation

$$E^\circ(MPTH^+/MPTH^T) \geq E^\circ(MPTH^+/MPTH) - \Delta E_T \geq -1.8\ V$$

where ΔE_T is 2.6 V. This represents only an upper limit because energy losses arising from changes in entropy and geometrical configuration during the $T_0 \rightarrow S_0$ transition have been neglected in the derivation of this formula.[14] The direction of electron flow associated with reactions 2 and 4 is also indicated in Figure 2. The reduction of NO_2 is accompanied by a relatively small decrease in free energy (ca. 0.2 eV). In such a case, the Marcus theory predicts a rate of reaction considerably below the diffusion-controlled limit, as indeed is observed. Conversely, from inspection of Figure 2, the decrease of free energy in reaction 2 appears to be substantial. This impression may, however, be deceptive since the redox potential of NO_3^-/NO_3^{2-} may be more negative than −1 V,[13] as discussed above. Moreover, the kinetic impediment in the NO_3^- reduction is likely to be a large reorganization energy associated with the change from the planar NO_3^- to a bent configuration in NO_3^{2-}. Equation 7 expresses the influence of micellar charge on the energetics of the electron-transfer reactions. Clearly, in the case where MPTH is incorporated into cationic aggregates, the redox potentials of MPTH and $MPTH^T$ are shifted to more positive values, making both species weaker reductants. This may explain why the rate of electron transfer from excited MPTH to NO_3^- in DTAC micelles remains below that observed in water-ethanol solution.

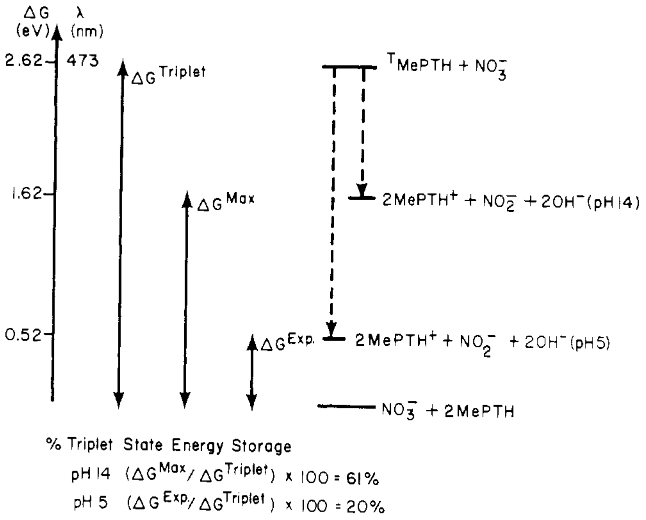

Figure 3. Thermodynamic considerations of light energy storage in the *N*-methylphenothiazine-nitrate system.

The fraction of triplet excitation energy converted into chemical energy during the photoreduction of nitrate to nitrite under standard conditions is

$$f = \Delta G^\circ / \Delta E_T \quad (8)$$

where ΔG° designates the Gibbs free energy change associated with eq 7. The free energy change may be expressed in terms of redox potentials:

$$\Delta G^\circ = 2[E^\circ(MPTH^+/MPTH) - E^\circ(NO_3^-/NO_2^-)] \quad (9)$$

The nitrate potential depends on the pH of the solution according to

$$E^\circ(NO_3^-/NO_2^-) = 0.01 + 0.059(14 - pH) \quad (10)$$

At low pH values (pH <0.61) ΔG° is negative, implying that no light energy conversion is possible under standard conditions. The situation improves markedly as the pH of the medium increases. For example, in pH 5 solutions, in which most of our experiments were carried out, *f* attains a value of 20%. Figure 3 illustrates this situation schematically.

The present study was carried out with sensitizers that absorb mainly UV light, but nitrate reduction may be feasible using chromophores such as ruthenium tris(bipyridyl) derivatives or narrow-band-gap semiconductors that absorb strongly in the visible region. The attractiveness of such photoconversion systems lies in the irreversibility of the first electron-transfer step in the NO_3^- reduction. The recovery of nitrate from nitrite would have to occur by electrochemical means, while redox catalysts could be employed to produce oxygen from water and the oxidized sensitizer via

$$4S^+ + 2H_2O \rightarrow O_2 + 4S + 4H^+$$

The advantage of such a light-driven galvanic cell is that NO_2^-

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is stable and does not backreact and thus the production of electricity is not restricted to only the illumination period.

A concluding remark relates to the light-induced reduction of nitrate in a biological environment. It is well-known that photosynthetic organisms, in particular, higher plants, can use nitrate instead of carbon dioxide as an electron acceptor. These organisms reduce nitrate to ammonia with chlorophyll as the sensitizer. The present system accomplishes a first step in mimicking this important photobiological reaction.

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Registry No. Nitrate, 14797-55-8; water, 7732-18-5; ethanol, 64-17-5; *N*-methylphenothiazine, 1207-72-3; *N,N,N',N'*-tetramethylbenzidine, 366-29-0; nitrite, 14797-65-0; NaLS, 151-21-3; DTAC, 112-00-5.

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Ab Initio MO Calculations for Hexacyano Complexes

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Ab initio LCAO SCF MO calculations were carried out on the hexacyano complexes $[M(CN)_6]^{3-}$ (M = Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$. The core orbital energies and valence shell ionization potentials are discussed in comparison with XPS results. The maps of the electron-density changes in the formation of coordination bonds are presented. These maps indicate σ donation and π back-donation that are greater in the cobalt(III) than in the chromium(III) complex. A more extensive back-donation is seen in the iron(II) complex. The mechanisms of these interactions are elucidated.

Introduction

Cyanide complex salts have long been known as typical coordination compounds of transition-metal ions having various symmetries, O_h, D_{4h}, T_d, and $D_{\infty h}$. The complexes have been the subject of extensive experimental studies in relation to the electronic structures in the ground and excited states.[2a]

In particular, octahedral complexes are of fundamental importance in the investigations of the coordination chemistry. The absorption spectra of these complexes have been reported by Alexander and Gray.[2b] They discussed the changes of the relative energies of the metal and ligand orbitals and pointed out the importance of the back-donation on the basis of charge-transfer spectra. Jones[3] and Griffith et al.[4] have reported the force constants of metal–carbon and carbon–nitrogen bonds and discussed the natures of the σ and π bondings. The X-ray photoelectron spectra (XPS) have been studied to investigate directly the valence orbital levels of the cyanide complexes by Calabrase et al.,[5] Prins et al.,[6] and Vannerberg.[7] Vannerberg[7] and Sano et al.[8] have reported XPS studies on the core binding energies of cyano ligands and discussed the relation between their shifts and the change in the charge distribution throughout a series of cyano complexes.

On the other hand, theoretical approaches to the electronic structure of the octahedral cyanide complexes have been carried out in terms of the Wolfsberg–Helmholz method by Kida et al.[9] and Alexander and Gray[2b] and the MS–Xα method by Larsson et al.[10,11] The iron cyanide complexes were also studied in terms of the CNDO method[12] and the MS–Xα method.[13,14]

Alexander and Gray[2b] have shown may important aspects of the electronic structures of cyano complexes. However, the detailed electronic structure, orbital interaction, charge distribution, etc. are not shown. Larsson[11] has studied the atomic charges of cyano complexes and showed the extent of σ donation and π back-donation.

We have already reported the electronic structure of $[Co(CN)_6]^{3-}$ obtained by the Hartree–Fock method.[15] In previous papers, we used electron density maps to demonstrate σ donation and π back-donation occurring on the coordination of cyanide ions to a cobalt ion and to show a significant relaxation on the ionization of a d electron. The mechanism of coordinate-bond formation was discussed in terms of interactions between the metal and ligand orbitals. Furthermore, we have also reported the DV–Xα MO calculations of a series of hexacyano complexes, $[M(CN)_6]^{3-}$ (M = Cr, Mn, Fe, and Co) and $[Fe(CN)_6]^{4-}$.[16]

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