compromise between ligand lability (thermal processes) and photochemical processes. Quantum yields and selectivity may improve with the choice of chelates and solvents. It is hoped that, if elemental selectivity is achieved, then such processes as those described here can be employed in photochemical separation processes[4,24] for those lanthanides and actinides with only one stable oxidation state in solution.

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Terence Donohue

Laser Induced Chemistry Group, Laser Physics Branch
Optical Sciences Division, Naval Research Laboratory
*Washington, D.C. 20375*

Applications of Photoinduced Electron-Transfer Reactions: Visible Light Mediated Redox Reactions of Substrates Using Transition Metal Complexes as Catalysts

Sir:

Electron-transfer quenching of excited states has become a well-established phenomenon through numerous investigations.[1-5] These reactions can produce potentially powerful oxidants and reductants; however, the usual consequence is no permanent chemistry since the products rapidly react with each

other in a subsequent electron-transfer step. Recently, it was demonstrated that both quenching and back-electron-transfer processes could be retarded for metal complexes by the incorporation of bulky hydrophobic groups around the periphery of the complex;[6] for reductive quenching of complexes such as RuL_3^{2+*} by certain amines the coupling of reduced back-electron-transfer rates with a rapid reaction of one of the products permits the isolation of the high energy reduced product RuL_3^+.[6] In the present paper we report studies in
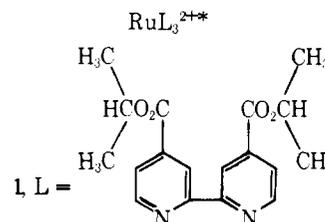
which *oxidative* quenching of excited states of metal complexes such as **1**, $Ru(bpy)_3^{2+}$ (**2**), and metalloporphyrins can be used to accomplish permanent chemical changes. In this case the key to avoiding nonproductive back-reaction is the secondary reaction of a highly reactive oxidized substrate with solvent in a hydrogen-atom transfer generating neutral free radicals which are not highly oxidizing. The cases reported here indicate that both "reagents" generated in the quenching process can be used in carrying out selective reactions with visible light as a reagent and metal complexes in nonaqueous media as catalysts.

It has previously been demonstrated through luminescence quenching experiments and flash photolysis studies that paraquat (PQ^{2+}) (N,N'-dimethyl-4,4'-bipyridine) quenches excited states of **1, 2**, and palladium octaethylporphyrin (**3**) in acetonitrile or butyronitrile by electron transfer as shown:[2,6]

$$MC^{n+*} + PQ^{2+} \rightarrow MC^{(n+1)+} + PQ^+ \qquad (1)$$

Back-electron transfer

$$MC^{(n+1)+} + PQ^+ \rightarrow MC^{n+} + PQ^{2+} \qquad (2)$$
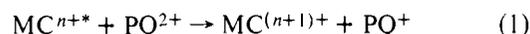
rapidly regenerates the starting materials with rate constants $k = 1.8, 8.1$, and 1.4×10^9 M^{-1} s^{-1} for **1, 2**, and **3**, respectively. Thus the systems of PQ^{2+} and **1, 2**, or **3** in dry acetonitrile have a net photostability. In rather striking contrast we find that addition of small to moderate amounts of several organic materials to solutions containing metal complexes and PQ^{2+} results in net photochemical change. The photoreaction can be conveniently monitored by ESR or by changes in the absorption spectrum as shown in Figure 1 for **1** and PQ^{2+}. In the ESR experiments, irradiation of several samples, carefully dried and degassed with argon, leads to the same results: no paramagnetic species are detectable prior to irradiation, but upon photolysis with visible ($\lambda > 420$ nm) light a rapid generation of a single paramagnetic species is observed. Both the envelope and hyperfine splitting pattern are consistent with the identification of this species as the paraquat radical cation, PQ^+.[7,8] Changes observed in the UV–visible spectra of degassed irradiated solutions (Figure 1) are completely consistent with the ESR results. A rapid formation of PQ^+ (λ_{max} at 605 and 395 nm) is observed, but no net decomposition of **1** occurs. The results appear best described by a sequence in which electron-transfer quenching (eq 1) is followed by oxidation of the added substrate to regenerate **1**

$$MC^{(n+1)+} + \text{substrate} \rightarrow MC^{n+} + \text{substrate}^+ \qquad (3)$$
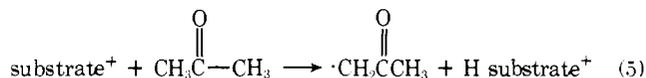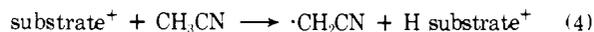
in competition with back electron transfer (eq 2). Substrates which have been found thus far to react under irradiation of **1** leading to a build up of PQ^+ include pyridine, 2,6-lutidine, N,N-dimethylformamide, triethylamine, and water.[9] Since
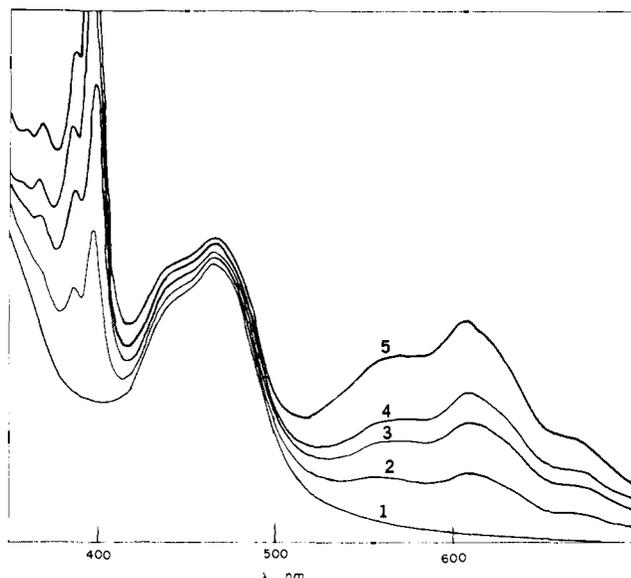
Figure 1. Spectral changes occuring in the visible-near-UV on irradiation of an acetonitrile–2,6-lutidine (2:1) mixture containing PQ^{2+} and **1** with visible light. Curve 1: sample prior to irradiation. Curves 2–5 are from the same sample after progressive irradiations.

1 is not altered in the overall reaction, it seems likely that the initial oxidation in eq 3 involves electron transfer from the substrate to RuL_3^{3+}. That reaction of these substrates with oxidized **1** should occur is not in itself surprising. The potential for the $RuL_3^{3+/2+}$ couple is 1.59 V[6] indicating that the RuL_3^{3+} should be a powerful oxidant. All of these substrates have anodic limits for electrochemistry at values of 1.6 V or lower.[10,11] Not surprisingly, acetonitrile and acetic acid which have anodic limits of 2.4 and 2.0 V, respectively, are unreactive.[10] However, what is remarkable is the fact that the combination of rapid reaction of $MC^{(n+1)+}$ with the substrate and subsequent rapid reaction of oxidized substrate to form stable products can compete with reaction of PQ^+ with these oxidants. As a measure of the overall effectiveness of these processes, an initial quantum yield of 0.07 for the production of PQ^+ is obtained for a solution containing 5×10^{-4} M **1** and 0.04 M PQ^{2+} M PQ^{2+} with 33% 2,6-lutidine in acetonitrile; for **2** a value of 2% is obtained under the same reaction conditions. With these concentrations quenching of **1*** and **2*** by PQ^{2+} is complete[12] and the measured values give an indication of the extent to which eq 3 and ensuing reactions compete with processes regenerating PQ^{2+}. Even higher quantum efficiencies (0.4 with **1** and 0.17 with **2**) have been obtained for more reactive aliphatic amines such as triethylamine[6] under concentrations where the excited state is not quenched by the amine. In a sealed degassed solution of acetonitrile–2,6-lutidine, the PQ^+ formed is relatively stable in the dark showing only a 1–2% decrease over 24 h as measured spectrophotometrically. For N,N-dimethylformamide, triethylamine, and pyridine, the PQ^+ formed in the reaction also decays only slowly on standing; however, addition of oxygen or other potential oxidants readily regenerates PQ^{2+} (vide infra). Both palladium octaethylporphyrin (**3**) and platinum tetraphenylporphyrin show qualitatively similar behavior on irradiation in the presence of PQ^{2+} and 2,6-lutidine in acetonitrile; however, for both metalloporphyrins somewhat lower efficiencies of PQ^+ buildup are indicated.
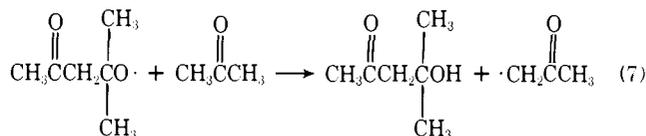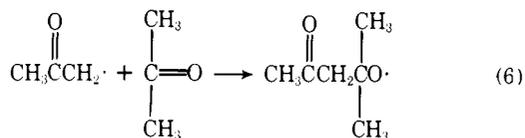
Since the only lasting paramagnetic product detectable by ESR under initial or prolonged irradiation is PQ^+, the radical cations formed in eq 3 must undergo rapid subsequent reactions. With the substrates studied to date and nitriles or acetone as solvents the major reaction of substrate$^+$ subsequent to eq 3 appears to by hydrogen-atom abstraction from the solvent

$$substrate^+ + CH_3CN \longrightarrow \cdot CH_2CN + H\ substrate^+ \quad (4)$$

$$substrate^+ + CH_3\overset{\overset{\textstyle O}{\|}}{C}-CH_3 \longrightarrow \cdot CH_2\overset{\overset{\textstyle O}{\|}}{C}CH_3 + H\ substrate^+ \quad (5)$$

(eq 4 or 5). This has been indicated as the chief reaction occurring in anodic oxidation of amines in nonaqueous systems.[13-15] We have obtained evidence for reactions 4 and 5 both by spin trapping experiments and product studies. Thus irradiation of **1** or **3** and 2,6-lutidine in acetonitrile containing the spin trap nitrosodurene leads to the detection of radical **4** by ESR. The corresponding radical from isobutyronitrile as

4
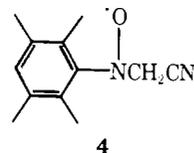
solvent has also been trapped with the nitrosodurene under the same conditions. Irradiation of **1**, PQ^{2+}, and 2,6-lutidine in acetone leads to $PQ^+\cdot$ and to formation of diacetone alcohol and mesityl oxide as the major organic products. These products presumably arise from addition of the radical from acetone (eq 5) to acetone (eq 6, 7) since, at 366 nm, photolysis of n-butyl benzoin ether in acetone leads to the same products plus benzaldehyde in good yield.[16]

$$CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_2\cdot + \underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}=O \longrightarrow CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_2\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}O\cdot \quad (6)$$

$$CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_2\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}O\cdot + CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{\textstyle O}{\|}}{C}CH_2\underset{\underset{\textstyle CH_3}{|}}{\overset{\overset{\textstyle CH_3}{|}}{C}}OH + \cdot CH_2\overset{\overset{\textstyle O}{\|}}{C}CH_3 \quad (7)$$

The viologen radical cation, $PQ^+\cdot$, produced as the other "permanent" product in these experiments, is itself a potentially useful reagent which has been found to react with protons using enzymic[20] or platinum[21] catalysts to generate molecular hydrogen and PQ^{2+}. The results observed in our study appear to be related to other recently reported investigations in which irradiation of visible light absorbing reagents in the presence of PQ^{2+} leads to a buildup of the PQ^+ radical.[20,22] However, in these systems the chemical reactions accompanying PQ^+ formation have not as yet been determined. In our studies we find that quencher oxidants other than PQ^{2+} can be used; both diquat (1,1′-ethylene-2,2′-dipyridylium) and 1,1′-ethylene-4,5-phenanthrolinium give the corresponding radical cations detectable by ESR and their electronic spectra on irradiation with **2** in acetonitrile–2,6-lutidine. These oxidants are unreactive with **1** under the same conditions used for **2**. This result is reasonable as is the lower reactivity of oxidized **2** with different substrates due to the 0.3-V difference in the RuL_3^{3+2+} couple for the two complexes.[6]

The overall sequence of reactions demonstrated by these experiments is remarkable for several reasons. Although it has previously been demonstrated that photoinduced redox reactions can generate high energy reagents as transient species,[1-4,23] the present results indicate that these reagents can be intercepted by selecting appropriate conditions in what appears to be a fairly general process. For example the utilization of **1** with visible light generates a usable reagent, RuL_3^{3+}, in neutral, nonaqueous media which is as potent an oxidant as Ce(IV) in nitric acid.[24] By appropriate choice of solvent-substrate combinations a variety of free-radical re-

actions or redox processes should be possible. The properties of the metal complex, quencher, and substrate should be widely tunable to achieve reagents of varying strength, solubility, and selectivity; the possibilities here are indicated by the rather pronounced differences in redox potential, solubility, and reactivity observed between **1** and **2** by a rather small modification of the ligand. Experiments are underway to determine the scope and products formed with other substrates and solvents.

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Patricia J. DeLaive, Charles Giannotti,* David G. Whitten*

Department of Chemistry, University of North Carolina Chapel Hill, North Carolina 27514, and Institut de Chimie des Substances Naturelles, C.N.R.S. 91190 Gif-sur-Yvette, France
Received December 5, 1977

Deracemization by Enantioselective Protonation. A New Method for the Enantiomeric Enrichment of α-Amino Acids

Sir:

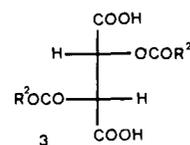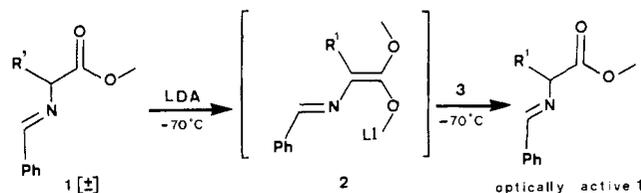Optically active α-amino acids are generally obtained by separation of peptide hydrolysates, resolution of synthetic racemates, asymmetric synthesis,[1] or, less frequently, by spontaneous crystallization of one chiral form with an optically active acid.[2] We report a new method for the enantiomeric enrichment of α-amino acids, based on the principle of deracemization by enantioselective protonation, a technique essentially applied to carbonyl compounds.[3] The protonation of enolates **2** of racemic Schiff base esters **1** by an optically active acid **3** gives the optically active Schiff base **1** with enantiomeric ratio as high as 81:19 (62% ee).
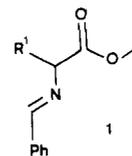
1a, R¹ = Ph
b, R¹ = PhCH₂
c, R¹ = 3-indolylmethyl
d, R¹ = *i*-Pr

The Schiff base methyl esters **1** are readily available in two steps from the corresponding α-amino acids in almost quantitative yields.[4] They are converted by lithium diisopropylamide to the corresponding anions **2**, according to reported procedure.[5] We have treated anions **2** by various (2R,3R)-diacyltartaric acids **3**;[6] the products of the reaction are optically active Schiff base esters **1** (Table I). Hydrolysis of the Schiff base esters **1** to the corresponding amino ester or amino acid can easily be effected without racemization and with good yields.[5] The acids **3** can easily be retrieved after protonation with an excellent yield and with conservation of enantiomeric purity.

3a, R² = *t*-Bu   **3f,** R² = Ph(CH₂)₂
b, R² = *t*-BuCH₂   **g,** R² = (CH₃)₂CBr
c, R² = *t*-Bu(CH₂)₂   **h,** R² = cyclohexyl
d, R² = Ph   **i,** R² = β-styryl
e, R² = PhCH₂   **j,** R² = 1-adamantyl

In a typical experiment, 0.885 g of (±)-methyl *N*-benzylidenephenylglycinate (**1a**, 3.5 mmol) in 6 mL of dry tetrahydrofuran was added under nitrogen at −70 °C to lithium diisopropylamide (5 mmol) prepared from 3.12 mL of a solution of *n*-butyllithium (1.6 M in hexane (5 mmol)) and 0.5 g of diisopropylamine (5 mmol) in 15 mL of dry tetrahydrofuran. After 5 min, protonation was carried out at −70 °C by addition of a solution of 3.18 g of dipivaloyltartaric acid (**3a,** 10 mmol) ([α]²⁵_D −24.1° (*c* 2, dioxane)) in 10 mL of dry tetrahydrofuran. The reaction was continued at −70 °C during a period of 15 min. The homogeneous reaction mixture was allowed to warm to room temperature; the solution was washed once with 10% aqueous sodium bicarbonate and with water. A usual workup gave the crude product, which was recrystallized in hexane (85% yield, [α]²⁵_D −41.9° (CHCl₃), *S* configuration). The diacyltartaric acid **3a** was obtained from the aqueous layer