

Photoinduced Electron-Transfer Reactions of Metal Complexes in Solution

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Molecular or mechanistic photochemistry has been an area of intense activity and rapid advances for 20 years. Early investigations chiefly with organic systems were extended subsequently into reactions of organometallics and transition-metal complexes.

One of the most important and general processes characterized has been the quenching or generation of an excited state by one-electron transfer reactions. By "quenching" we refer to (usually nonradiative) deactivation of an electronically excited molecule (excited state) by bimolecular interaction with a ground-state molecule (quencher). Among the possible results of such quenching are single electron transfer to or from the excited substrate, excitation energy transfer from excited substrate to quencher, net chemical reaction (in substrate, quencher, or both), and net radiationless decay. As quenching via electron transfer has become well studied, it has been frequently found that the same excited substrate can be quenched by electron donors and acceptors. It is a little ironic that the importance of these reactions was recognized only recently since it was long ago established that in photosynthesis an excited chlorophyll mediates redox reactions which originate in one-electron-transfer reactions of the excited magnesium complex.¹⁻³

In this Account we examine solution-phase one-electron-transfer reactions which originate from excited states of metal complexes. We review both the general properties of these reactions and applications in which net chemical change occurs as a result of a one-electron-transfer quenching event. Most, but not all, of the work discussed involves reactions initiated by excitation of metalloporphyrins or poly(pyridyl)ruthenium(II) complexes. These complexes have strong absorption in the visible region. Most of the chemical reactions discussed can be initiated by selective excitation with relatively low-energy visible light.

Photoinduced Redox Reactions of Porphyrins and Metalloporphyrins

Early studies by Livingstone and co-workers⁴⁻⁷ established that fluorescence of chlorophyll and related compounds can be quenched by electron-deficient aromatic compounds such as quinone and nitro aromatics as well as by potential electron donors. In some cases this could be shown to occur in the excited states as a dynamic process while in other cases ground-state

complex formation^{8,9} is probably responsible for the reduction in fluorescence. Our investigations showed that both excited singlet and triplet states of simple metalloporphyrins could be quenched by electron donors and acceptors.^{10,11} Although frequent correlations between quenching rates and quencher reduction (or oxidation) potential can be obtained,¹²⁻¹⁵ it has been found that quenching here can lead to excited complexes (exciplexes), ion pairs, or free ions depending on the system investigated and the medium polarity. In other studies it was found that excited states of metalloporphyrins can react with certain electron donors to yield ring-reduced products such as chlorins and dihydrochlorins.¹⁶⁻²²

While electron transfer is likely involved in several of these processes, other mechanisms are frequently difficult to exclude. Thus, while a number of these studies clearly indicate net one-electron transfer to give free ions can occur,^{12-15,23} the multiplicity of reaction

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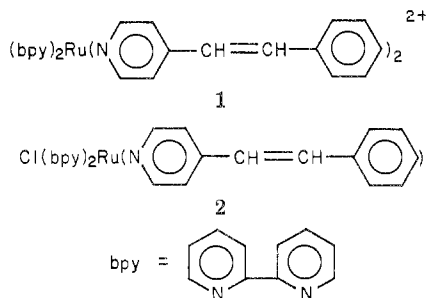
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David G. Whitten was born in Washington, D.C. Both his undergraduate and graduate studies were at the Johns Hopkins University, where he received the Ph.D. degree in 1963. Following postdoctoral work at the Jet Propulsion Laboratory (as a member of the U.S. Army) and with George Hammond at the California Institute of Technology, he moved to the University of North Carolina, where he is now Professor. His research interests include photochemical and thermal reactions in solution and the solid state, catalysis, and the chemistry and properties of organized assemblies, including micelles, vesicles, monolayer films, and supported multilayers.

paths plus the propensity to give permanent photo-products make the porphyrins and their metal complexes something less than ideal substrates for a comprehensive investigation of the specific electron-transfer process.

Light-Induced Electron-Transfer Reactions with Poly(pyridine)ruthenium(II) Complexes

Our interest in the polypyridyl complexes of ruthenium(II), iron(II), osmium(II), and iridium(III) was aroused by the presence of strong electronic transitions of relatively distinct orbital origin in most of the complexes and by reports of strong solution luminescence for some of them.²⁴⁻²⁸ Initial investigations of the photoreactivity of some ruthenium(II) complexes showed strong wavelength effects which could be correlated with the orbital origin of these transitions.^{29,30} In particular, it was found that for the stilbazole complexes 1 and 2 activation of the long-wavelength met-



al-to-ligand charge-transfer ($d \rightarrow \pi^*$) transition led to chemical change best explainable as involving an intermediate resembling an oxidized metal-reduced ligand (radical anion) species.^{29,30} In contrast, shorter wavelength irradiation into the predominantly stilbazole intraligand ($\pi \rightarrow \pi^*$) transition led to photochemistry characteristic of the free stilbazole ligand.

About the time these investigations were under way, a number of reports on quenching phenomena and photoreactivity of the strongly luminescent complex tris(2,2'-bipyridine)ruthenium(II) $[Ru(bpy)_3^{2+}]$ appeared.³¹⁻³⁴ This complex is reasonably stable toward unimolecular photoreactions, and the major consequence of most excited-state quenching was either no permanent reaction or a redox reaction. Our attention was initially drawn to the chemistry of $Ru(bpy)_3^{2+}$ by controversy as to whether quenching occurs via electron transfer as opposed to excitation energy transfer.³³⁻³⁶

Our initial investigations involved quenching and flash spectroscopic studies of $Ru(bpy)_3^{2+}$ with reagents whose reactivity might be expected to differentiate between energy-transfer and electron-transfer quench-

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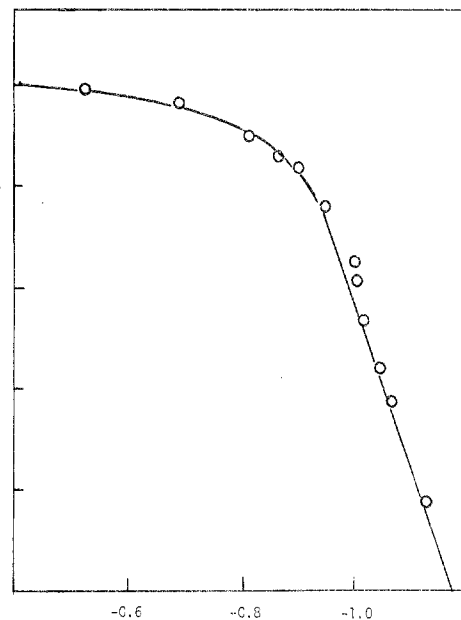
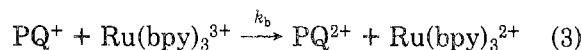
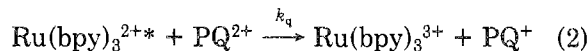
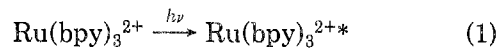


Figure 1. Plot of $\log k_q$ vs. quencher reduction potential, $E_{1/2}(Q/Q^-)$ (volts vs. SCE), $Ru(bpy)_3^{2+}$ as the substrate and nitro aromatics as quenchers in acetonitrile. Extrapolation gives $E_{1/2}(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+}) = -0.81$ V after correcting for the work required to bring the product ions together (see ref 39).

ing paths. Studies with the potential electron acceptor 1,1'-dimethyl-4,4'-bipyridinium dication (paraquat or dimethylviologen) (PQ^{2+}) proved particularly instructive.³⁷ This dication does not absorb in the visible or near-UV, and its lowest excited state (~ 71 kcal/mol) is considerably above that of $Ru(bpy)_3^{2+}$ (~ 50 kcal/mol); thus energy-transfer quenching should be substantially endothermic and extremely slow. In fact, PQ^{2+} was found to quench $Ru(bpy)_3^{2+}$ at rates near the diffusion-controlled limit ($k_q = 2.5 \times 10^9$ M⁻¹ s⁻¹).³⁷ Although no permanent chemical change was observed as a consequence of the quenching, flash photolysis studies show transient bleaching of the absorption corresponding to $Ru(bpy)_3^{2+}$ and a concurrent buildup of absorption in the visible and near-UV corresponding to the product of one-electron reduction of PQ^{2+} .³⁷ The overall steps occurring are given by eq 1-3.



Similar behavior was observed for $Ru(bpy)_3^{2+}$ with other electron acceptors, including the isomerizable dication N,N' -dimethyl-1,2-bis(4-pyridyl)ethylene whose reduction potential (-0.49 V) is nearly the same as that for PQ^{2+} but whose excited triplet is very close to the energy of $Ru(bpy)_3^{2+*}$. Here it could be shown that very little quenching by energy transfer occurs and that the dominant route is electron transfer.^{37,38}

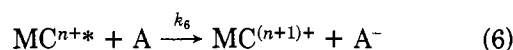
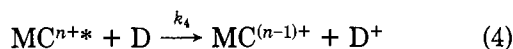
A study of quenching of $Ru(bpy)_3^{2+*}$ by a series of nitro aromatics having variable reduction potentials allowed us to assess kinetically the excited-state reduction potential $E_{1/2}(Ru(bpy)_3^{3+}/Ru(bpy)_3^{2+*})$ as -0.81

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± 0.02 V.³⁹ A plot (Figure 1) of the electron-transfer quenching constant vs. quencher reduction potential shows clearly the point at which electron-transfer quenching becomes endothermic. Similar plots have been obtained for several other substrate-quencher systems. From the ground-state potential in the same medium, $E_{1/2}(\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}(\text{bpy})_3^{2+}) = +1.29$ V, it can be seen that photoexcitation increases the oxidizing power by 2.10 V, a value very close to the spectroscopic excited-state energy (2.18 V) of $\text{Ru}(\text{bpy})_3^{2+}$.³⁹ In subsequent studies it was found that $\text{Ru}(\text{bpy})_3^{2+}$ could be efficiently quenched by electron donors such as amines and aromatic ethers.⁴⁰⁻⁴⁴ In these investigations a pattern similar to that described by eq 1-3 was observed.

The general picture that has emerged from a large number of investigations is that the excited states of a wide variety of metal complexes, both emissive and nonluminescent, can be quenched by electron donors (eq 4) or electron acceptors (eq 6) in net one-electron-



transfer processes. While these processes can occur with very high rates and efficiencies, they are generally followed by energy-wasting back reactions (eq 5, 7) which also usually occur with high rates and efficiencies such that the frequent result is no net chemical reaction. Much recent work from these and other laboratories has been devoted to finding ways to circumvent back-reactions 5 and 7 such that net useful chemical reaction can be accomplished. The bulk of this Account deals with our efforts to develop applications of these reactions.

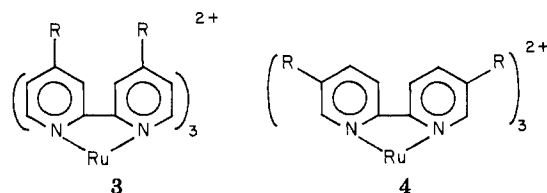
Net Chemical Change via Light-Driven One-Electron-Transfer Reactions

Our basic strategy has been the following: where possible, substrate-quencher systems have been chosen in which structural features reduce the rates of the back-reactions (eq 5 and 7) substantially below the diffusion-controlled limit; further, ways have been devised to remove rapidly one of the initial products formed in reactions 4 and 6 such that the other product either is stored or reacts subsequently in steps leading to permanent chemical changes; finally, since the initial products of the one-electron-transfer reactions are usually reactive radical species, it has been necessary to find ways of marshalling the oxidizing or reducing ability of these one-electron reagents to drive multielectron redox processes producing stable products that

incorporate some of the absorbed light energy.

The possibility that useful chemistry could be derived from systems in which the back-reactions are relatively slow or initial products are diverted has been realized in a number of studies in which photogalvanic responses are the consequence of simple light-induced electron-transfer events.⁴⁵⁻⁴⁸ In an early case, a modest photogalvanic effect was demonstrated to be due solely to slowness of back electron transfer; it concerned the $\text{Ru}(\text{bpy})_3^{2+/3+}$ - $\text{Fe}^{3+/2+}$ system, studied in our laboratories,³⁷ as well as by Sutin and co-workers.⁴⁸ In this system, the rate constant for the back-reaction is unusually low ($k = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) even though the back-reaction is thermodynamically highly favorable ($K = 6.1 \times 10^8$).³⁷ Steady photolysis of one chamber of a two-compartment cell resulted in a sufficient concentration gradient between the dark and illuminated compartments to permit a photogalvanic response.⁴⁸

In other investigations we have found it possible to reduce rate constants for both the quenching processes and back-reactions by incorporating bulky hydrophobic groups into the substrate or quencher.^{49,50} For example, in studies involving a series of ruthenium complexes (3 and 4), it was found that while both quenching by PQ^{2+}



and back-reactions remained highly exothermic for the several complexes used, changing of R from H- to D-OOC- (where D = dihydrocholesterol) reduced k_6 by more than two orders of magnitude and k_7 by nearly one order of magnitude.⁵⁰ In contrast, neutral organic electron acceptors quenched the luminescence of various complexes in the series with rates that were little affected by the structure of R.⁵⁰ This observation, coupled with the finding that the quenching process was attenuated much more sharply than the back-reaction for the $\text{RuL}_3^{2+/3+}$ - $\text{PQ}^{2+/1+}$ system, suggested that an optimum situation would involve the reductive quenching of complexes 3 with neutral electron donors.

Our studies with complexes such as 3 and 4 (R = $(\text{CH}_3)_3\text{CHO}_2\text{C}$ - (3a and 4a) and other carboxy ester derivatives) and trialkylamines such as triethylamine and diisopropylethylamine have demonstrated that in several cases the combination of a slow back-reaction with a rapid reaction of one of the initial products, in this case the amine radical cation, can lead to relatively efficient formation of the reduced complex RuL_3^+ as a "permanent" product.⁴⁹⁻⁵¹ Thus irradiation of 3a in

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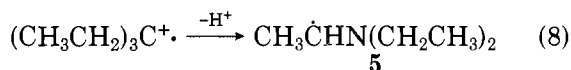
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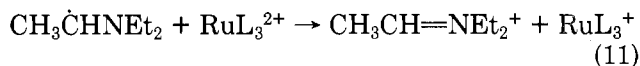
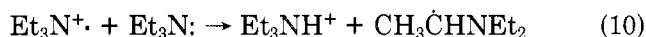
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the presence of triethylamine leads to quenching but no detectable back-reaction; instead the reduced complex RuL_3^+ accumulates in high efficiency ($\phi = 0.4$ in acetonitrile with lower efficiencies in less polar organic solvents) and can be readily detected by its characteristic visible and ESR spectra.⁴⁹⁻⁵² The fact that only a single permanent paramagnetic product accumulates indicates that the trialkylamine radical cation formed in the initial electron-transfer step is consumed by the subsequent reaction.⁵² Study of the reaction by photochemical ESR techniques has indicated that the initially formed radical cation must undergo proton loss to generate the neutral radical **5** (eq 8). This radical



is detected as an intermediate by formation of its adduct with nitrosodurene and other spin traps.^{52,53}

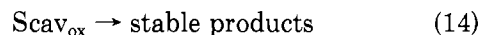
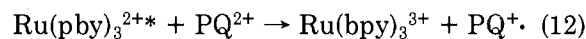
The overall sequence of reactions that occurs in this system is given in eq 9-11. The crucial step in ob-



taining net chemical reaction in high efficiency is reaction 10 in which a strongly oxidizing initial product—the amine cation radical—is converted into a good reductant, neutral radical **5**. This would allow a potential quantum efficiency of 2 for reduction of the metal complex in what (in the absence of light) is a moderately endothermic reaction. The reason somewhat lower efficiencies have so far been obtained is not completely clear. However, it appears that the major reduction in overall efficiency is due to net radiationless decay in the quenching step (eq 9) owing to back-reaction in the geminate pair in competition with free ion formation.

Net chemical reactions can be obtained from complexes **3** and **4** by reductive or oxidative quenching to form highly reactive products in electron-transfer steps. On the other hand, reactions which normally are followed by rapid back electron transfer from the otherwise "stable" products frequently can be driven to yield net chemical change by addition of scavengers to remove one of the products. A number of investigations have involved oxidative quenching of $\text{Ru}(\text{bpy})_3^{2+*}$ or excited dyes by PQ^{2+} in the presence of oxidizable substrates such as thiols, amines, amides, and organic oxygen compounds.⁵⁴⁻⁶² In these systems the reaction

sequence generally involves quenching by electron transfer (eq 12) followed by regeneration of the starting



metal complex or dye through reduction by the scavenger. Thus the scavenger is consumed and the reduced form of the oxidant, in this case the radical cation, PQ^+ , accumulates.⁵⁴ For a net reaction to occur it is necessary for the oxidized scavenger rapidly to convert to nonoxidizing products; otherwise the oxidized scavenger will simply oxidize PQ^+ , so that a "relay" reaction occurs, ultimately regenerating the ground states of the starting materials.⁶³

We have examined several cases in which oxidizable scavengers that do not participate in the excited-state quenching step are added to solutions of $\text{Ru}(\text{bpy})_3^{2+}$ and PQ^{2+} , using spin traps as well as product analysis to determine the fate of the primary product of scavenger oxidation. In several cases the major products and trapped radicals detected are those derived by hydrogen atom abstraction from the solvent.⁵⁴ Thus reaction 15



must be a major route; once again a powerful oxidant is converted to a nonoxidizing product so as to allow the relatively strong reductant PQ^+ to survive. There are clearly numerous possibilities for extending this type of reaction with other systems.

Coupling of Light-Driven One-Electron Reactions to Multielectron Redox Conversions through Heterogeneous Catalysts

An area of considerable interest is the interfacing of light-driven electron-transfer reactions to multiple-electron equivalent redox processes. Among a number of techniques that have been attempted and developed for accomplishing this,⁶⁴⁻⁷¹ many of the most successful have involved the use of colloidal or heterogeneous catalysts.^{57-61,64,71-73} Investigations in a number of laboratories have demonstrated that initial products, such as reduced metal complexes, PQ^+ , and other reduced organic substances, can be used with catalysts

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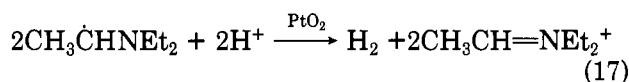
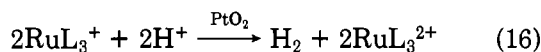
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such as PtO₂ (Adams catalyst), RuO₂, and various colloidal species to promote reduction of water to hydrogen.^{57-61,73} In other studies it has been found that various oxidized species produced by visible light induced electron-transfer reactions can be used with some of the same catalyst systems to mediate rapid and efficient water oxidation to give oxygen.

The precise catalytic species involved in these processes remains unknown or under investigation in most cases.⁷³ In our investigations, we have attempted to find systems in which water reduction or oxidation can be efficiently mediated in a mechanistically simple process. We have succeeded in finding two systems in which heterogeneous catalysis can be coupled with reductive quenching of metal complex excited states to give efficient reduction of water. One of these is the reductive quenching of **3a** by amines such as triethylamine, which was described above, as it occurs in aprotic solvents such as acetonitrile. When **3a** is irradiated in aqueous acetonitrile with triethylamine, there is no buildup of the reduced metal complex although a steady buildup of acetaldehyde (from hydrolysis of the imine cation produced in eq 12) and the trapping of radical **5** indicate that net chemical change stemming from electron transfer is occurring.⁵³

When reduced **3a** is treated with water there is rapid regeneration of the dication but no efficient production of molecular hydrogen. In contrast, when **3a** is irradiated in aqueous acetonitrile containing triethylamine and a small amount of PtO₂, the metal complex is photostable and there is a steady evolution of hydrogen gas.⁷⁴ The reaction is catalytic in the metal complex; turnover numbers of 300 mol of H₂/mol of complex have been obtained for samples in which the hydrogen collects above the solution.⁷⁴ Since the hydrogen is in part subsequently consumed, presumably through catalyzed hydrogenation of unsaturated byproducts such as acetaldehyde, much higher turnovers should be obtainable if the hydrogen were removed. The quantum efficiencies obtained are in the range 0.3-0.4 and experiments with D₂O established that the hydrogen comes from water.⁷⁴

From knowledge of the reaction in the absence of catalyst and water, and the present results, the mechanism for the hydrogen generation appears to comprise eq 9-11, 16, and 17. **5** is a powerful enough reducing



agent to reduce protons to hydrogen in the presence of an appropriate catalyst.^{75,76} Whether RuL₃⁺ reacts first with protons, yielding RuL₃H²⁺, or with the catalyst directly in eq 16 is uncertain since we find evidence that RuL₃⁺ can react rapidly with either protons or catalyst in the absence of the other.⁷⁴

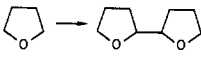
The characteristics of this rather simple system are probably related to those of others in which similar catalysts have been used to generate hydrogen from

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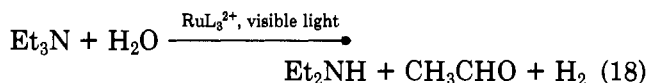
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Table I
Estimated^a Enthalpies of Reaction for Oxidation of Organic Substrates via Hydrogen Evolution

generalized reactions	
$\text{Z-H} \xrightarrow[\text{reduceable metal complex}]{\text{visible light } h\nu} \text{Z-Z (or Z}_{\text{Ox}}) + \text{H}_2$	
reaction	ΔH , kcal/mol
Et ₂ NH → EtN=CHCH ₃ + H ₂	17
EtOH → CH ₃ CHO + H ₂	8
	13
C ₆ H ₅ CH ₃ → C ₆ H ₅ CH=CH ₂ + H ₂	13
CH ₃ CH ₃ → CH ₂ =CH ₂ + H ₂	~33
CH ₂ =CH ₂ → CH≡CH + H ₂	

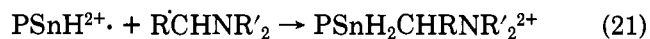
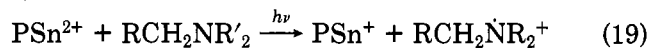
^a Bond energies used to determine ΔH values: K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948); J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 1962, p 32.

light-driven electron-transfer processes.^{57,58} The attractive features of the present system are its high efficiency, its simplicity in principle, and its convenience in practice. The overall reaction is of course not water splitting but water reduction with simultaneous oxidation of triethylamine (or other tertiary amine) (eq 18).



Thermochemical data^{77,78} indicate the overall reaction to be moderately endothermic ($\Delta H \approx 14$ kcal/mol). The overall efficiency of energy conversion at the threshold excitation (540 nm for **3a**) is 10-12% with the quantum yields obtained in these initial investigations.

We have recently extended our investigations to some rather different metal complexes including some of the porphyrins studied earlier. In particular we find that irradiation of tin(IV) porphyrins in the presence of amines, water, and PtO₂ leads to hydrogen evolution.⁷⁹ For this system the overall reaction obtained in the absence of catalyst involves primarily reductive addition of the amine to the porphyrin macrocycle to yield substituted chlorin (reduced porphyrin) products.²² The mechanism appears to involve electron transfer from amine to porphyrin followed by proton transfer (eq 19-21) and coupling of the radicals. Irradiation of



the system in the presence of catalyst produces less of the chlorin product, suggesting that the catalyst intercepts one or both of the species produced in eq 20. Labeling experiments have not yet been completed, but the overall reaction is probably similar to the net reaction (eq 18) occurring with the ruthenium complex. Although quantum yields, turnover numbers, and precise mechanistic details have not been determined, there

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are significant indications that catalyzed reactions leading to net multielectron equivalent redox reactions of water and other substrates may be quite general and not at all restricted to exotic heavy metal complexes.

Considering only processes leading to hydrogen evolution, we believe that a number of organic substrates could be oxidized in mechanistically related processes. Table I gives an estimation of reaction endothermicities for a few simple organic compounds which might furnish hydrogen by a net process involving electron abstraction and subsequent proton reduction. All of these reactions except the loss of hydrogen from alkanes seem within reach for metal complexes or dyes absorbing in the visible region, given the wide variety of redox/excited-state energy properties potentially accessible through chemical "tuning" via changes in metal, ligand, or charge. However, it is clear that only modest amounts of energy would be stored in these reactions, except in the last case, and further that the reagents used to generate hydrogen are not all abundant or inexpensive. Thus while it is certainly possible that reactions such as these could be useful on a limited scale or in a system in which the organic reagents could be recycled, it appears that broad applications based on light-driven electron-transfer reactions will be best achieved with systems in which any organic reagents used also function as catalysts.

One approach to accomplishing chemical change or energy storage suggested by a number of investigations is to couple individual light-driven redox reactions in which water is respectively oxidized and reduced. In this way it should be possible for the reagent consumed in the reduction step to be regenerated in the oxidation step, and vice versa. Several reactions involving excited-state oxidation of metal complexes such as $\text{Ru}(\text{bpy})_3^{2+}$ or other RuL_3^{2+} complexes as well as metalloporphyrins generate oxidants which are certainly powerful enough to oxidize water.^{51,52,54,72,73,80,81} Several studies indicate that these oxidized species react slowly in the absence of catalyst or rapidly with catalysts to oxidize water to molecular oxygen. The major problem then appears to be to find a number of "half-reactions" leading to efficient oxygen evolution. It will also be necessary to devise successful interfacing so that two appropriate half-reactions can be coupled so as to produce hydrogen and oxygen efficiently at separate sites. A number of groups, including our own, are currently working toward these objectives. It seems likely that the near future will see the development of several successful systems.⁸²

An alternative to the use of heterogeneous catalysis is the coupling of water reduction or oxidation to a light-driven electron-transfer process in a photoelectrochemical cell. Recent experiments indicate that a variety of electron-transfer quenching phenomena can be coupled with hydrogen or oxygen production concurrent with the generation of a modest photocurrent.⁸³⁻⁸⁵

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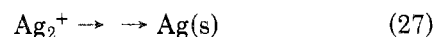
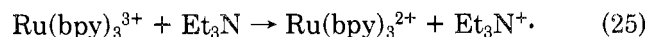
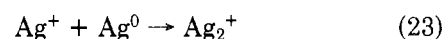
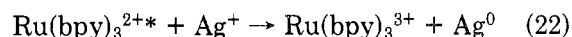
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Other Applications of Photoinduced Electron-Transfer Reactions: Metal Ion Reduction

There are numerous potential applications of light-induced electron-transfer reactions entirely unrelated to energy storage. A system we have very recently investigated is the solution-phase reduction of Ag^+ by $\text{Ru}(\text{bpy})_3^{2+}$.⁸⁶ Examination of polarographic data suggests that Ag^+ might be a good substrate for $\text{Ru}(\text{bpy})_3^{2+}$ since its half-wave reduction potential is in the range +0.4–0.8 V⁸⁷ where rapid and efficient reduction via reaction 8 is normally observed. However, these potentials link the cation and metallic solid; when the reduction is carried out in dilute homogeneous solution, the initial species generated should be a dispersed atomic silver of higher energy and most likely quite different reactivity than the bulk metal. In fact, we find that Ag^+ does quench the luminescence of irradiated $\text{Ru}(\text{bpy})_3^{2+}$ in both aqueous and acetonitrile solution. The quenching constants are much lower than the diffusion-controlled limits expected for an exothermic reduction, and no net reaction is observed in the absence of additional reagents.⁸⁶

Flash photolysis of solutions containing $\text{Ru}(\text{bpy})_3^{2+}$ and Ag^+ does lead to a transient spectrum consistent with oxidation of the metal complex and reduction of Ag^+ to Ag^0 . A rapid back-reaction depletes the transients, indicating that the reduced silver species formed is extremely reactive. Silver ion has previously been reduced via pulse radiolysis;⁸⁸⁻⁹⁰ in these studies it was found that rapid reaction of the initially formed reduced silver species with Ag^+ to give Ag_2^+ dominates all other processes. Consequently the reaction sequence obtained in the present experiment is most likely that given by eq 22–24. When scavengers such as triethylamine are



used to intercept the oxidized ruthenium complex (eq 25, 26), a buildup of metallic silver occurs (eq 27).

These results demonstrate the potential of using light-driven electron-transfer reactions to generate potentially useful and interesting reactive species under mild conditions. The technique should be adaptable to preparing a number of reactive atomic species and should complement other methods.⁹¹⁻⁹⁴ Since the

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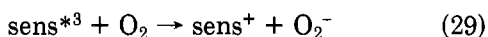
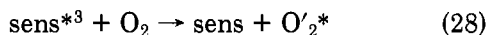
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techniques used are gentle, it should be possible to add a number of potential reactants to intercept the atomic species without affecting the generation steps. In the present case the measured rate constants provide an estimate of the true potential for reduction of silver ion in solution; the value obtained indicates the bulk metal is more stable than the reduced soluble species by 31–44 kcal/mol.⁸⁶

Photooxygenations via Electron Transfer: Superoxide Generation and Reaction

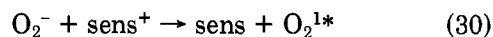
A final example of the generality of light-induced electron-transfer reactions of metal complexes concerns photooxidations involving molecular oxygen. Although several mechanisms for these photooxidations have been suggested or demonstrated, the most general and widely accepted is that involving triplet sensitization of the production of excited singlet oxygen.^{95,96} Singlet oxygen has been shown to have characteristic reactions with a number of different types of substrates. It is frequently assumed that processes involving "sensitization" of molecular oxygen by excited states (usually triplets) of dyes or metal complexes involve exclusively energy transfer (eq 28). Recently a number



of investigations have established or suggested the availability of alternate paths for net photooxygenation reactions.^{97–100} In some of these studies, electron-transfer deactivation of the excited sensitizer by an added donor or acceptor was shown to dominate energy transfer to oxygen.⁹⁹ In these cases electron transfer to oxygen from a radical ion generated in the quenching process has been implicated as the major route for oxygen activation. Thus, net oxidation occurs via nucleophilic attack of superoxide anion on a radical cation; the products are often identical with those obtained in reactions in which singlet oxygen is almost certainly the reactive intermediate.⁹⁹

Other recent investigations have indicated that direct quenching of "sensitizer" triplets by electron transfer to oxygen (eq 29) can be competitive with energy transfer for Rose Bengal and other popular sensitizers.¹⁰⁰ These studies, together with other investigations of competition between energy-transfer and electron-transfer quenching of excited states,^{38,101} suggest that the whole area of photooxygenation and related phenomena such as photodynamic action may be considerably more complicated than previously thought. From examination of the energetics of reactions 28 and

29 for a number of frequently used "sensitizers", it becomes clear that in many cases both reactions are energetically favorable. Even for those cases in which reaction 28 is more highly favored than reaction 29, net occurrence of reaction 28 may involve superoxide formation and subsequent electron-transfer "chemical luminescence" via eq 30. Prominent sensitizers for



which this energetic situation occurs include several free-base porphyrins and metalloporphyrins as well as some other metal complexes such as $\text{Ru}(\text{bpy})_3^{2+}$.

We have recently examined quenching and sensitization processes for a number of these complexes using photochemical ESR techniques.¹⁰² In these studies we used spin traps which form characteristic adducts with superoxide ion¹⁰³ to test its formation and possible intermediacy in photooxidation reactions. Preliminary studies indicate that easily trappable amounts of superoxide are generated by irradiation of $\text{Ru}(\text{bpy})_3^{2+}$, hematoporphyrin IX, and other free-base porphyrins, and several metalloporphyrins including Pd(II), Pt(II), and Zn(II) complexes in a range of aprotic solvents including pyridine and acetonitrile.¹⁰² Because our studies have not yet been made quantitative, we cannot at this time state the efficiency of superoxide production.

However, for the metalloporphyrins we have been able to determine the role of superoxide ion in some solution-phase photooxidations. As pointed out above, on energetic grounds superoxide could be an intermediate in metalloporphyrin-induced photooxidations via the consecutive occurrence of reactions 29 and 30. However this appears not to occur in the cases examined thus far. Protic solvents such as water or methanol rapidly promote superoxide decomposition via protonation and disproportionation of the $\text{HOO}\cdot$ radical.^{104,105} We find that addition of moderate amounts of methanol or water to solutions containing metal complex, oxygen, and spin traps causes drastic reduction of the signal due to the product of superoxide trapping.¹⁰² However, comparison of the photooxidation yields produced by irradiation of similar solutions containing the singlet oxygen acceptor 1,3-diphenylisobenzofuran, but no spin trap, shows no effect due to addition of the protic reagent. Further studies in aprotic solvents indicate that the yield of trapped superoxide ion is virtually unaffected by addition of singlet oxygen quenchers such as 1,4-diazabicyclooctane (Dabco).

While investigation on the precise efficiencies of the two processes is currently in progress, it appears that for the several systems examined thus far in solution singlet oxygen (eq 28) and superoxide (29) are formed by competitive paths, by interaction of the metal complex excited state with triplet dioxygen, and that free superoxide ion is not an intermediate en route to singlet oxygen (or vice versa). Since both reactions occur for several different "sensitizers", it will be important to determine the effect of sensitizer structure, environ-

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ment, and other parameters on the competition in future investigations.

Prospects

It seems clear that the near future will see many new applications of light-induced electron-transfer processes, along some of the lines indicated in the present Account as well as in new areas. The interfacing of what are basically single electron-transfer processes to achieve multielectron conversions will doubtless be the focus of many studies. Obvious possibilities for accomplishing this include the construction of specialized complexes containing more than one reactive center and the combination of reagents in molecular assemblies perhaps analogous to the chloroplast or similar functional biological systems. While much attention is currently directed toward possible energy applications of light-induced electron-transfer reactions, other applications

including synthesis should not be neglected. Certainly in common with other photochemical reactions, reactor design for efficient use of light and for moderate- to large-scale conversion of reagents remains a major problem and challenge.

I thank my co-workers, present and former, who obtained the results discussed and made valuable contributions interpreting them and planning subsequent experiments: I. G. Lopp, P. D. Wildes, the late J. C. Yau, R. W. Hendren, J. K. Roy, F. A. Carroll, P. P. Zarnegar, C. R. Bock, A. R. Gutierrez, R. C. Young, P. J. DeLaive, J. A. Mercer-Smith, R. H. Schmehl, T. K. Foreman, and G. S. Cox. Extremely stimulating collaborations and discussions over a long period with Professor T. J. Meyer of this Department and Dr. C. Giannotti of the CNRS, Gif-sur-Yvette, France, have also played major roles in the research described in this account. Finally, the financial support provided by the National Science Foundation, National Institutes of Health, Army Research Office, Alfred P. Sloan Foundation, and North Atlantic Treaty Organization is also gratefully acknowledged.

Raman Optical Activity: A New Probe of Stereochemistry and Magnetic Structure

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The introduction of visible lasers in the early 1960s engendered a flourishing renaissance in Raman spectroscopy.¹ The great virtue of Raman spectroscopy is that it uses a visible light source and analyzes visible scattered light: the inelastically scattered visible photon carries information in the form of a loss or gain of a quantum of energy corresponding to a molecular transition which may be translational, rotational, vibrational, or electronic. Visible radiation can be manipulated and detected with ease, and recent advances in optical and electronic technology have made possible many new and exotic Raman experiments. A case in point is the study of vibrational optical activity by measuring a small difference in the intensity of Raman-scattered light from chiral molecules and molecules in magnetic fields, using right and left circularly polarized incident light.

It has been appreciated for some time that the measurement of natural optical activity associated with molecular vibrations could provide a wealth of new stereochemical information. But only in the last few years have vibrational optical activity spectra been obtained by using both infrared and Raman techniques. The significance of vibrational optical activity becomes apparent when it is compared with conventional elec-

tronic optical activity in the form of optical rotatory dispersion (ORD) and circular dichroism (CD) of visible and near-ultraviolet radiation.² These conventional techniques have proved most valuable in stereochemistry, but since the electronic transition frequencies of most structural units in a molecule occur in inaccessible regions of the far ultraviolet, they are restricted to probing chromophores and their immediate intramolecular environments. On the other hand, a vibrational spectrum contains bands from most parts of a molecule, so the measurement of some form of vibrational optical activity should provide much more information.

The obvious method of measuring vibrational optical activity is by extending ORD and CD into the infrared. But there is a fundamental physical difficulty inherent in this approach: optical activity observables are proportional to the frequency of the *exciting* radiation, and infrared frequencies are orders of magnitude smaller than visible frequencies. This snag is side-stepped using Raman optical activity because the Raman effect provides complete vibrational spectra using *visible* exciting light. At the moment there is a striking complementarity between the infrared and Raman approaches to natural vibrational optical activity.³ Infrared CD cannot penetrate much below about 2000 cm⁻¹, and although Raman optical activity covers the complete vibrational spectrum, it is best below about 2000 cm⁻¹. Thus infrared CD is best for studying fundamental

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