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SOLAR ENERGY STORAGE REACTIONS INVOLVING METAL COMPLEXES

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Abstract – Photochemical properties of transition metal complexes are dis-
cussed as they relate to possible schemes for energy storage. Complexes
of copper(I) with π-acceptor ligands have been used to sensitize isomeri-
zations of organic molecules, and there is room for considerable further
investigation in this area. Electron transfer reactions have been more
intensively studied. These reactions fall into three broad categories:
ionization, oxidative addition/reductive elimination, and excited state
electron transfer. Experiments in the first two categories have generally
led to rather poor storage efficiency and have required ultraviolet light.
But long-lived excited states of coordination compounds can participate in
chemical reactions with high efficiency, and such systems are promising
for solar energy storage. Specific systems of this type that are discussed
in detail involve electron transfer quenching of the lowest emissive
excited states of $Ru(2,2'\text{-bipyridine})_3^{2+}$, $M_2(\text{diisocyanoalkane})_4^{2+}$ (M=Rh,Ir),
and $Mo_6Cl_{14}^{2-}$.

INTRODUCTION

The realization that the world faces shortages of fossil fuels has spurred research into all
types of alternative energy sources. Because it is plentiful and environmentally clean,
solar energy has been the object of a particularly intense research campaign. However, there
are two major drawbacks to its widespread use: sunlight is a dilute form of energy, meaning
that a commercial installation would require large areas of collectors; and energy could only
be produced intermittently by such a plant. The storage of solar energy in chemical form
would help to circumvent the second of these objections. Also, if sunlight could be used to
produce a fuel by a photochemical reaction, dwindling fossil fuel supplies could be replaced
directly. This paper examines recent developments in the field of photochemical energy stor-
age, concentrating on the role of transition metal complexes in causing or promoting these
reactions.

THE SOLAR SPECTRUM AND ENERGY STORAGE REQUIREMENTS

Several authors have discussed [1-3] the factors limiting the performance of a photochemical
energy storage system: First, the chromophore must absorb light of relatively low energy in
order to make use of a significant portion of the solar spectrum. Second, the excited state
formed on absorption of light must undergo subsequent reactions with high probability. And
third, the exothermic reaction of the photochemical products (to give the starting materials
again) must be controllable.

The second and third of these constraints are largely a function of the particular chemical
system chosen for energy storage. But the nature of the solar spectrum imposes fundamental
limits on the efficiency of any photochemical sequence. Most of the energy in sunlight
appears as photons of relatively long wavelength [4]; only a small portion lies in the ultra-
violet region of the spectrum. The maximum possible efficiency η_p of a storage system based
on the reaction

$$X \xrightarrow{\ h\nu\ } X* \tag{1}$$

depends on the threshold wavelength λ_1, the maximum wavelength thermodynamically sufficient
to cause reaction (1); here $\lambda_1 = N^0 hc/\Delta G_1^0$. It is assumed in the derivation of η_p that all
light of $\lambda \leq \lambda_1$ is absorbed, that the quantum yield for formation of X* is 1, and that the
energy of X* is extracted and stored at the optimum rate. The values of η_p obtained for

various threshold wavelengths, using a typical solar spectrum for a sunny day near noon, are given in the Table [1].   Additional considerations, such as intersystem crossing to produce

TABLE   Maximum Efficiencies η_P for Various Threshold Wavelengths λ_1

λ_1/nm	η_P
400	0.04
500	0.14
600	0.22
700	0.28
800	0.31
900	0.32
1000	0.30
1100	0.31
1200	0.29
1300	0.28
1400	0.26

photoactive states, the decay of such states, and energy losses in subsequent thermal reactions of X*, reduce this figure further; Bolton suggests 0.13 as the maximum fraction of total solar energy that could be stored in a chemical system under ideal conditions [1].

We will deal here with two general types of energy storage schemes: photoisomerization, in which the endergonic reaction

$$X \rightarrow Y \tag{2}$$

is carried out photochemically and the high-energy product Y is stored; and photoredox, where X*, or a species formed from it, undergoes an electron transfer reaction. The photoredox experiments have been designed almost exclusively with the goal of promoting reactions such as

$$H_2O \rightarrow H_2 + 1/2\ O_2\ . \tag{3}$$

Few photochemical reactions are known for excitation wavelengths above 600 nm; most require ultraviolet light. So the aspiring solar chemist faces two challenges: to maximize the efficiency of the storage reactions, and to extend the useful region of the spectrum as far to the red as possible. Our discussion will center on the recent use of transition metal complexes to attack these two problems.

PHOTOISOMERIZATION

The photoinduced conversion of a molecule to a higher-energy, metastable isomer, as illustrated by reaction (2) above, suggests an attractive system for solar energy storage. Ideally, X should be highly photosensitive and Y inert; and a catalyst should be available for rapid conversion of Y to X when the stored energy is to be extracted again.

In practice the choice of substrates has been largely restricted to organic molecules [5], where energy differences and activation energies for isomerization are generally large. Perhaps the most-studied example is the system norbornadiene(NBD) - quadricyclane(Q), where ΔG_4^0 is 110 kJ mol^{-1} [6]:

$$\tag{4}$$

Although λ_4 here is 1080 nm, suggesting that good solar energy storage efficiencies might be achievable, norbornadiene is transparent well into the ultraviolet. Based on an estimate of 300 kJ mol^{-1} for the lowest triplet state of NBD [7], conventional triplet sensitization might allow use of longer wavelengths. Both organic chromophores [8] and, more recently, Cu(I) complexes [9-12] have been employed as sensitizers. Even in these systems, however, ultraviolet light is necessary to achieve reaction (4).

The evolution of heat from high-energy materials such as quadricyclane is less difficult. Some transition metal complexes are excellent catalysts for the conversion of Q to NBD [13, 14].

Two problems seem particularly acute in this type of solar energy scheme: the short wave-lengths required for the photochemical steps, and side products produced in the thermal reaction. Research with other copper(I) complexes [15] as sensitizers is addressing the first question, and a paper by Samuel [16] analyzes the problem of side products and the tolerances for a viable photoisomerization system.

PHOTOREDOX PROCESSES

Photoisomerization reactions offer a simple scheme for energy storage, but the stored energy can only be released again in the form of heat. Isomers are generally relatively close in energy and therefore have low energy storage capacity. Metastable molecules produced by redox reactions, however, are often called fuels because their combustion is so highly exothermic. Energy storage in photosynthetic organisms operates exclusively by photoredox mechanisms, and by-products of these reactions, the fossil fuels, are our most convenient and useful energy sources today. Energy storage in the form of a compact fuel [such as hydrogen, eq. (3)] would reduce transportation problems and make the stored energy available in many forms [17]. An artificial chemical system could in principle improve on natural photosynthesizers: although the energy storage process in plants has an efficiency of 6 to 8% [2], much of the stored energy is then used in metabolism. We discuss here three general ways in which transition-metal complexes have been used in photoredox reactions.

Photoionization

This type of scheme may be discussed with reference to the water-splitting reaction. We may use a metal complex, represented by M, to sensitize reaction (3) in two steps:

$$M + H^+ \rightarrow M^+ + 1/2 \; H_2 \tag{5}$$

$$M^+ + 1/2 \; H_2O \rightarrow M + 1/4 \; O_2 + H^+ \tag{6}$$

Several metal ions, for example Mn(IV) [18] and Co(III) [19], are known to carry out reaction (6). Thus a catalytic cycle would be complete if corresponding reduced metal complexes could be made to photoreduce H^+ to H_2.

Low-valent metal complexes often exhibit intense metal to ligand charge transfer (MLCT) or charge transfer to solvent (CTTS) absorption bands. The use of far-ultraviolet light to cause reaction (5) is illustrated by work with Fe^{2+} in aqueous solution [20,21]. Similar experiments with europium(II) also gave hydrogen under 366 nm irradiation [22]; but in this case reaction (5) is exergonic. Certain copper(I) complexes also have been irradiated in the ultraviolet to induce photoionization, simultaneously producing H_2 [23,24].

The photoionization of strongly metal-metal bonded species has been studied in our laboratory [25]. Under 254 nm irradiation, quadruply-bonded $d^4 - d^4$ systems are oxidized by H^+ to mixed-valence $d^3 - d^4$ species or to dinuclear $d^3 - d^3$ complexes. One-electron oxidized products were identified for $Mo_2(SO_4)_4^{4-}$ [26,27] and $Re_2Cl_8^{2-}$ [28]; $Mo_2(aq)^{4+}$ ultimately underwent two-electron oxidation [27].

Recent results indicate that hexachloroiridate(III) could be used in a photochemical energy storage cycle. Waltz and Adamson were the first to observe photoionization of $IrCl_6^{3-}$, trapping the ejected electron with N_2O [29]. The irradiation (254 nm) of $IrCl_6^{3-}$ in dilute acid solution produces, among other products, hexachloroiridate(IV) and hydrogen [28]:

$$H^+ + IrCl_6^{3-} \rightarrow IrCl_6^{2-} + 1/2 \; H_2 \tag{7}$$

Here the standard electrode potential for the $IrCl_6^{2-/3-}$ couple, 0.867 V [30], suggests that a substantial amount of energy has been stored in reaction (7). Details of this photoreaction and of possible side reactions (including aquation) are now being studied.

Another type of photoionization process, this time involving the transfer of electrons to a metal atom by LMCT excitation, has been examined by Yamase and co-workers [31,32]. Near-ultraviolet light reduces alkylammonium isopolymolybdates(VI) to persistent mixed-valence Mo(V)-Mo(VI) complexes and unidentified oxidation products both in the solid state and in solution [31]. The mixed-valence complexes (blue in solution) were also found to be photosensitive, and a galvanic cell containing the blue ion in the anode compartment and a

platinum wire in the cathode compartment produced hydrogen when irradiated [32]. Questions of stoichiometry and quantum yield remain unresolved, but the system is potentially quite interesting.

Photoassisted oxidative addition and reductive elimination

These are common processes for organometallic compounds and offer possibilities for photochemical energy storage. They may be illustrated respectively by the forward and reverse directions of the following reaction:

$$M + X{-}Y \rightleftarrows X{-}M{-}Y \tag{8}$$

The oxidation state of the metal atom is formally increased by two on the addition of XY. These reactions are best known for square planar complexes M. Where XY is a halogen the concept is intuitively appealing; but where the process involves an alkyl halide or a protic acid (e. g., HCl, CH_3NO_2, or $PhC{\equiv}CH$) the term oxidation seems less appropriate. To the extent that the oxidative-addition product H-M-Y has hydridic character, reaction with a second molecule of acid may be proposed:

$$H{-}M{-}Y + HY \rightarrow Y{-}M{-}Y + H_2 \tag{9}$$

Reaction (9) could then be followed by reductive elimination of Y-Y, regenerating the square planar starting material and catalyzing the overall reaction

$$2HY \rightarrow H_2 + Y_2 \tag{10}$$

For the hydrogen halides HCl and HBr reaction (10) is highly endergonic, and this scheme would be a useful one for energy storage.

There are few photochemical studies of simple oxidative addition and reductive elimination. Dihydro complexes of cobalt(III) [33] and iridium(III) [34] have been shown to eliminate hydrogen on ultraviolet irradiation, but no efforts have been made to incorporate these reactions into a catalytic cycle.

More encouraging results have been obtained with polynuclear complexes. Solutions of $Mo_2X_8^{4-}$ (X=Cl,Br) underwent oxidative addition of HX from aqueous solution when exposed to 254 nm light [27]. The $Mo_2X_8H^{3-}$ [not an oxidative-addition product in the sense of reaction (8), but at least one in which H^+ has formally been reduced and Mo(II) oxidized] then decomposed, giving H_2 and a dinuclear Mo(III) species.

Geoffroy has reviewed [35] the photochemistry of metal hydride complexes, and finds the dissociation of H from monohydro complexes to be rare. A more common photoprocess is the dissociation of other ligands [e. g., carbon monoxide from $HCo(CO)_4$]. One compound that produces H_2 photochemically is $HIr(PF_3)_4$, giving the dinuclear species $Ir_2(PF_3)_8$ (an overall bimolecular reductive elimination) [36]. It was claimed that the dinuclear Ir product could be converted back to $HIr(PF_3)_4$ on reaction with water, but the details of the chemistry of this system have not been reported.

Recently, infrared and nmr evidence has been obtained for HY adducts of iridium(I) bridging-isocyanide complexes [Y = Cl, $CH(CN)_2$] [37]. Adducts such as these were originally thought to be present in the blue solutions made by adding $Rh_2b_4^{2+}$ (b = 1,3-diisocyanopropane) to aqueous acid [38]; this would have provided a close analogy to the halogen oxidation products described earlier [39]. Studies of the blue Rh species have been conducted using flash kinetic spectroscopy [40,41], redox titrimetry [42], and X-ray crystallography [43]. These have established that $Rh_2b_4^{2+}$ is oxidized in acidic solution to give a tetranuclear $Rh_4b_8^{6+}$ ion. Thus the evolution of hydrogen from solutions of $Rh_4b_8^{6+}$ is not a photochemical reaction of a metal hydride. In aqueous sulfuric acid, where hydrogen is not produced, the primary photoprocess is homolytic cleavage to two $Rh_2b_4^{3+}$ radicals [40,41]:

$$Rh_4b_8^{6+*} \rightarrow 2Rh_2b_4^{3+} \tag{11}$$

The radicals may in turn be trapped by oxidation, for example, with Fe^{3+}:

$$Rh_2b_4^{3+} + Fe^{3+} \rightarrow Rh_2b_4^{4+} + Fe^{2+} \tag{12}$$

Experiments conducted in hydrochloric acid solution demonstrate that redox reactions occur even in the absence of added oxidants [41,44,45]. Whereas a complete analysis of the kinetics has not been possible, it is reasonable to propose that heterolytic cleavage, or photodisproportionation, also occurs [42]:

$$Rh_4b_8^{6+*} \rightarrow Rh_2b_4^{2+} + Rh_2b_4^{4+} \quad . \tag{13}$$

$Rh_2b_4^{2+}$ has not been observed directly under these conditions, but the product of its reaction with $Rh_4b_8^{6+}$, the hexanuclear $Rh_6b_{12}^{8+}$, does appear. Upon reduction of $Rh_4b_8^{6+}$ with Cr^{2+} in aqueous sulfuric acid solutions, Sigal observed [42] a number of $Rh_4b_8^{6+}/Rh_2b_4^{2+}$ adducts as follows:

$$Rh_2b_4^{2+} + Rh_4b_8^{6+} \rightleftharpoons Rh_6b_{12}^{8+} \tag{14}$$
$$\lambda_{max} = 540nm \quad\quad 550nm \quad\quad 780nm$$

$$2Rh_6b_{12}^{8+} \rightleftharpoons Rh_{12}b_{24}^{16+} \tag{15}$$
$$1300nm$$

$$Rh_2b_4^{2+} + Rh_6b_{12}^{8+} \rightleftharpoons Rh_8b_{16}^{10+} \tag{16}$$
$$960nm$$

Direct reaction of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) with $Rh_4b_8^{6+}$ in aqueous sulfuric acid solution gave analogous polynuclear rhodium cations [46].

We had hoped [47] that oxidative addition and related electron transfer reactions could be promoted photochemically, as a means of energy storage, in complexes with low-lying MLCT excited states. Photooxidation of six-coordinate isocyanide complexes of Cr, Mo, and W has indeed been observed in chlorocarbon solvents [48], but experiments more directly related to energy storage have not been successful.

Reactions of long-lived excited states

Transition metal complexes have been known for many years whose excited states are sufficiently long-lived to participate in bimolecular reactions. Reactions of molecular excited states, including primarily energy and electron transfer, are well known for organic molecules but have only recently been examined in metal complexes. Balzani and co-workers have published two excellent reviews on the subject, emphasizing energy [49] and electron transfer [50].

An excited state M* of a metal complex M may undergo oxidation or reduction on reaction with an electron acceptor A or donor D, respectively:

$$M* + A \rightarrow M^+ + A^- \tag{17}$$

$$M* + D \rightarrow M^- + D^+ \tag{18}$$

A reaction of the former type (17) was first observed by Gafney and Adamson in 1972 [51]. Many other examples of both (17) and (18) have confirmed that M* is thermodynamically both a better oxidant and a better reductant than M, which is readily understood in terms of simple molecular orbital descriptions of electronic structure. Endergonic redox reactions of metal complexes may therefore be made exergonic by using M* instead of M.

Basic processes. Reactions (17) and (18) may be applied readily to an energy storage scheme. For example, if the system is to produce hydrogen, the reactions

$$A^- + H^+ \rightarrow A + 1/2\ H_2 \quad\quad \text{or} \tag{19}$$

$$M^- + H^+ \rightarrow M + 1/2\ H_2 \tag{20}$$

may be used. Products D^+ or M^+ might then produce an oxidant (such as O_2) in other steps. A major obstacle to achievement of energy storage is that the products of reactions (17) and (18) tend to react with each other again, converting the stored energy to heat:
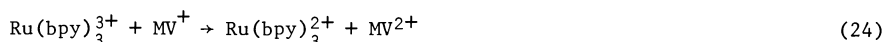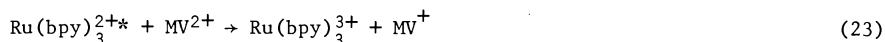
$$M^+ + A^- \rightarrow M + A \tag{21}$$

$$M^- + D^+ \rightarrow M + D \qquad\qquad (22)$$

In Gafney and Adamson's work [51], M was $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and A was $Co(NH_3)_5Br^{2+}$. Here the A^- complex [presumably $Co(NH_3)_5Br^+$] decomposed rapidly in aqueous solution, giving $Co(OH_2)_6^{2+}$. Thus substantial concentrations of $Ru(bpy)_3^{3+}$ could accumulate without interference from (21).

Since these early experiments efforts to use excited state redox reactions in energy storage have most often used $Ru(bpy)_3^{2+}$ as photoreceptor [$\tau(Ru(bpy)_3^{2+*})$ = 0.62 μs in aqueous solution] [49]. Whitten has reviewed recent progress in this area [52].

Lehn and Sauvage used [53,54] a rhodium(III) complex as electron acceptor and triethanolamine to reduce the $Ru(bpy)_3^{3+}$ produced in reaction (17). By far the most popular reagent for oxidative quenching of $Ru(bpy)_3^{2+*}$ has been methylviologen (1,1'-dimethyl-4,4'-bipyridinium, or "paraquat"; abbreviated here as MV^{2+}):

$$Ru(bpy)_3^{2+*} + MV^{2+} \rightarrow Ru(bpy)_3^{3+} + MV^+ \qquad\qquad (23)$$

$$Ru(bpy)_3^{3+} + MV^+ \rightarrow Ru(bpy)_3^{2+} + MV^{2+} \qquad\qquad (24)$$

The rate constants k_{23} and k_{24} are respectively 2.4 x 10^9 [55] and 8.1 x 10^9 $M^{-1}s^{-1}$ [56], so that either $Ru(bpy)_3^{3+}$ or MV^+ must be efficiently scavenged to prevent reaction (24). Amines such as EDTA have been shown to reduce $Ru(bpy)_3^{3+}$, leading ultimately to degradation of EDTA into inert products. Matsuo and co-workers showed that this MV^{2+}-based system could be used as a homogeneous photoreductant [57,58].

Whitten and co-workers have investigated [59] the reductive quenching of $Ru(bpy)_3^{2+}$ and its derivatives by amines. The rate of back electron transfer (22) could be drastically reduced by using substituted bipyridines as ligands, so much so that M^- persisted in solution for days at room temperature.

The products of the excited state reaction may also be separated physically. Matsuo *et al.* showed [60] that the yield of electron transfer products in the reductive quenching of a $Ru(bpy)_3^{2+}$ derivative by N,N-dimethylaniline (DMA) was increased by incorporating the Ru complex into a cationic micelle. Presumably the high positive charge of the Ru(I)-containing micelle inhibits back electron transfer to DMA^+. The opposite strategy was followed by Brugger and Grätzel, who used 1-methyl-1'-tetradecyl-4,4'-bipyridinium ($C_{14}MV^{2+}$)
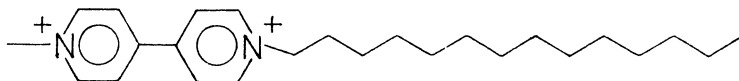

as electron acceptor in the presence of cationic micelles [61]. $C_{14}MV^{2+}$ itself was unaffected by the micelles; but its one-electron reduction product was sufficiently hydrophobic to be taken up, and was thereby isolated from $Ru(bpy)_3^{3+}$. The back electron transfer rate constant was decreased by some two orders of magnitude in this way.

<u>Utilization in Energy Storage</u>. The use of the strongly reducing and oxidizing properties of molecular excited states to split water into H_2 and O_2 is attractive, not only because H_2 is a convenient fuel but also because gaseous oxidation and reduction products can be removed easily from the irradiated solution. Research into photochemical water decomposition has concentrated most heavily on the sensitized reduction of protons to hydrogen; but success has been reported recently in photooxidizing water to O_2 as well.

The principal problem in generation of hydrogen is that two electrons are needed for each molecule. Direct two-electron transfer processes are rare; the only alternative appears to be the generation of radical intermediates. Such radicals are often unstable to disproportionation or other reactions, and so their generation invites energy-wasting processes.

1. $Ru(bpy)_3^{2+}$ as sensitizer

Sutin and co-workers first sensitized the homogeneous evolution of hydrogen from weakly acidic solutions [62]. Their experimental strategy was to initiate a two-electron reaction by the transfer of a single electron. Having established that $Ru(bpy)_3^{2+}$ could be reduced efficiently by Eu^{2+}, they added a macrocyclic Co(II) complex and observed the following reactions:

$$Ru(bpy)_3^+ + Co(II) \rightarrow Ru(bpy)_3^{2+} + Co(I) \qquad\qquad (25)$$

$$Co(I) + 2H^+ \rightarrow Co(III) + H_2 \tag{26}$$
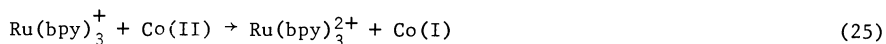
The Co(III) complex was then reduced to Co(II) again by a second Eu^{2+} ion. Similar experiments with ascorbic acid, which also quenches $Ru(bpy)_3^{2+*}$ reductively, also led to hydrogen production, but with substantially lower efficiency. Whereas the reduction of protons by Eu^{2+} is exergonic ($E^0 = 0.43$ V) under their conditions, that by ascorbic acid is not ($E \sim -0.4$ V).

The $Ru(bpy)_3^{2+}$-sensitized oxidation of water to O_2 by $Co(NH_3)_5Cl^{2+}$ has also been claimed [63], but this has yet to be incorporated into a full cycle for the decomposition of water.

The remainder of the experiments in the sensitized reduction of water have used heterogeneous catalysts, particularly colloidal noble metals and noble metal oxides. These materials catalyze the reduction of H^+ to H_2 (perhaps *via* adsorbed H atoms) by one-electron reductants. Catalysis by platinum black of the redox equilibrium

$$2MV^+ + 2H^+ \rightleftharpoons 2MV^{2+} + H_2 \tag{27}$$

has been known since 1934 [64]. A platinum catalyst has been used [65] by Kagan and co-workers to generate H_2 from the MV^+ produced by oxidative quenching of $Ru(bpy)_3^{2+*}$. A similar mechanism, but using a Rh bipyridine complex as electron relay, is presumably involved in the system studied by Lehn and Sauvage [53,54]. And in DeLaive and Whitten's work [66], Adams' catalyst (PtO_2) allowed $Ru(bpy)_3^+$ to reduce protons to hydrogen. All of the experiments in which amines (including EDTA) are the electron donors have in common the following overall reaction:

$$RCH_2NR'R'' + H_2O \rightarrow RCHO + HNR'R'' + H_2 \tag{28}$$
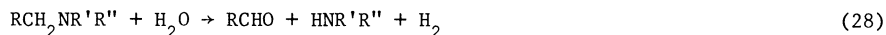
In the case of triethylamine, for example, reaction (28) is endothermic by *ca.* 58 kJ mol^{-1} [66]. Under optimum conditions DeLaive and Whitten were able to obtain 37% hydrogen yield, *i.e.*, every 100 photons absorbed led to the formation of 37 molecules of H_2. A system based on this reaction could, if all photons with $\lambda \leq 500$ nm were absorbed and converted to H_2 with the same efficiency, achieve storage of *ca.* 2% of available solar energy.

The experiments described above have involved the reduction of water by a mild reductant. The report by Kalyanasundaram and Grätzel of simultaneous production of hydrogen and oxygen from water, using a two-catalyst system, therefore represents a major advance [67]. Methylviologen was the oxidative quencher for $Ru(bpy)_3^{2+}$ in their experiments, and H_2 was produced from MV^+ at a Pt catalyst in the usual manner. But $Ru(bpy)_3^{3+}$ is also capable of oxidizing water to O_2 [E^0 for $Ru(bpy)_3^{3+/2+}$ is 1.26 V] [68]. They achieved this by adding RuO_2 as a second heterogeneous catalyst.

2. Other complexes as sensitizers

The tris(bipyridine) complexes of ruthenium offer a number of advantages in photoredox experiments. The excited states are long-lived and of high energy, and readily undergo electron transfer reactions; the complexes are substitution-inert in all three readily accessible oxidation states; and the corresponding Ru(I) and Ru(III) species are powerful reducing and oxidizing agents, respectively. Not all photoredox energy storage schemes involve $Ru(bpy)_3^{2+}$, however; many other complexes have been examined with solar energy storage applications in mind.

Other polypyridine complexes
The properties of other conventional low-spin d^6 polypyridine complexes are closely analogous to those of $Ru(bpy)_3^{2+}$ (see, for example, refs. 68 and 69) and will not be discussed here. Recently, Watts and co-workers have examined the novel iridium(III) complex $(bpy)_2Ir(bpy)-(OH_2)^{3+}$, in which one of the bpy ligands is monodentate and a water molecule occupies the sixth coordination site [70,71]. They find its excited state some ten times longer-lived than that of $Ru(bpy)_3^{2+}$, and are now exploring its redox photochemistry.

Chromium(III) complexes have long been popular subjects for photochemical studies. Lifetimes exceeding 50 μs are known for the ^2E excited states of a number of Cr(III) complexes. Electron transfer to $Cr(bpy)_3^{3+*}$ from $Fe(OH_2)_6^{2+}$ and $Ru(bpy)_3^{2+}$ was demonstrated by flash kinetic spectroscopy in 1976 [72]. In the latter case $Cr(bpy)_3^{2+}$ and $Ru(bpy)_3^{3+}$ were produced by reaction both of $Ru(bpy)_3^{2+*}$ with $Cr(bpy)_3^{3+}$ and of $Cr(bpy)_3^{3+*}$ with $Ru(bpy)_3^{2+}$. Systems in which $Cr(bpy)_3^{2+}$, produced by reductive quenching of $Cr(bpy)_3^{3+*}$, is used to reduce H^+ to H_2 are now being examined [73]. The chemical reductant $Cr(bpy)_3^{2+}$ is unfortunately somewhat substitution-labile in aqueous solution; this interferes with efficient catalysis, as the aquated species are photoinert. However, chromium could be favored in an industrial process

over ruthenium for economic reasons even if it were less durable. The photooxidation of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) by cobalt(III) complexes, while it proceeds with rather low efficiency [74], is of interest because the Cu(I) complex may be irradiated in the 450-500 nm range.

Metalloporphyrins

Two research groups have reported that zinc porphyrin complexes sensitize the reduction of H^+ to H_2 by EDTA in the presence of a Pt catalyst. The Zn-based sensitizer is relatively efficient for excitation wavelengths above 500 nm and is more durable and more active than $Ru(bpy)_3^{2+}$ under similar conditions [75]. Kalyanasundaram and Grätzel found several additional features of interest in their experiments [76]: The reaction apparently proceeds by both reductive(EDTA) and oxidative(MV^{2+}) quenching of the metalloporphyrin excited state. Large variations in the quenching rates were observed on changing from anionic to cationic substituents in the porphyrin ring. And the system can be made to produce hydrogen without MV^{2+}.

Other complexes

We have also turned our attention to the redox chemistry of excited states. The intensely phosphorescent triplet excited states of two dinuclear rhodium(I) isocyanide complexes have long lifetimes in acetonitrile solution [77]. The $^3A_{2u}$ lifetimes of $Rh_2b_4^{2+}$ and $Rh_2(TMB)_4^{2+}$ are respectively 8.5 µs and 25 ns at room temperature. The $Rh_2b_4^{2+}$ excited state energy was estimated at 1.7 eV by energy transfer experiments, and electron transfer quenching studies were conducted for both it and $Rh_2(TMB)_4^{2+}$ using reductive and oxidative quenchers. Characteristic absorption maxima for reduced (Rh_2^+) and oxidized (Rh_2^{3+}) species were identified from transient difference spectra.

We hope to make use of the excited state properties in two ways. First, since the Rh_2^+ species are also known to be powerful reductants [78], we envision a cycle in which Rh_2^+ could be produced by reductive quenching and then function as a two-electron donor:

$$Rh_2^+ + 2H^+ \rightarrow Rh_2^{3+} + H_2 \tag{29}$$

Such a system would be similar to that of Sutin *et al.* [62] except that the chromophore would also participate directly in proton reduction. So far we have observed only back electron transfer to regenerate Rh_2^{2+} (22). Second, the oxidative quenching system also offers advantages, especially for $Rh_2b_4^{2+}$. In the reaction system

$$Rh_2b_4^{2+*} + MV^{2+} \rightarrow Rh_2b_4^{3+} + MV^+ \tag{30}$$

$$Rh_2b_4^{3+} + MV^+ \rightarrow Rh_2b_4^{2+} + MV^{2+} \tag{31}$$

k_{30} is probably larger than k_{31}; in addition, reaction (11) might allow competitive removal of $Rh_2b_4^{3+}$. Both of these factors should improve the chances of efficient production of MV^+. The adaptation of this system to hydrogen-producing reactions is now under investigation.

Photoredox behavior has also been observed for two other types of complexes. The phosphorescence of $Ir_2(TMB)_4^{2+}$ is quenched by N,N,N',N'-tetramethyl-p-phenylenediamine(TMPD) with reduction of the iridium complex [37]. The Ir system, with a strong absorption at 625 nm, extends the photoredox response for these isocyanide complexes into the red region of the visible spectrum. Solutions of the molybdenum(II) cluster species $Mo_6Cl_{14}^{2-}$ are also luminescent [79]. Here oxidative quenching occurs in acetonitrile solution with electron acceptors such as MV^{2+}, and the $Mo_6Cl_{14}^-$ ion produced is an extremely strong oxidant ($E_\frac{1}{2} \sim$ 1.6 V *vs.* SCE in CH_3CN).

PROSPECTS

Much of the theoretical groundwork concerning electron transfer in molecular ground and excited states has now been laid. Many of the results described here suggest that a relatively efficient system for photochemical energy storage should be achievable. It seems that several areas in particular would benefit from more intense study. Systems capable of multi-electron transfer are not common, and an effort should be made to design them and incorporate them into photochemical studies. Such experiments might also lead to new catalysts for gas evolution. In this regard we would do well to examine species such as $Co(CN)_5^{3-}$, which is already known [80,81] to catalyze gas-solution redox equilibria. Experiments with photo-induced oxygen evolution [82] might also be useful in this respect. But an almost totally unexplored area is the redox photochemistry of small molecules other than water. Whereas such reactions (*e.g.*, N_2H_4/NH_3; $C_2O_4^{2-}/CO_2$) might ultimately have applications in energy storage, they could also be adapted to the photochemical promotion of other simple reactions.

The future of photoredox chemistry is, so to speak, bright!

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