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Photoredox Reactions of Metal Ions for Photochemical Solar Energy Conversion*

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Solar energy conversion to chemical potential energy is thermodynamically feasible by many routes. One possible route is the photochemical reaction of metal ions in water to produce hydrogen and an oxidizer. The photooxidation of several low-valent transition metal ions, including europium(II), vanadium(II), and copper(I) complexes, proceeds in aqueous acidic media according to:

$$M^{n+} + H^+ \xrightarrow{h\nu} M^{(n+1)+} + \tfrac{1}{2}H_2.$$

Quantum yields in 1.0 *M* hydrochloric or perchloric acid at 313 nm are: $\Phi_{Eu(III)} = 0.16$, $\Phi_{V(III)} = 0.15$, and $\Phi_{Cu(II)} = 0.34$. This reaction proceeds in visible light with a minimum of photochemical complications for Eu(II) and Cu(I) salts, and since the oxidation of copper(I) halo-complexes is endergic and hence potentially useful for energy storage, the mechanism of photooxidation has been studied. The product quantum yield is strongly affected by the acidity, irradiation wavelength and H-atom scavengers. Photoredox reactions of a number of metal ions and the requirements for using such in a solar energy scheme are discussed.

Introduction

The quantum conversion of solar radiation possesses several advantages over thermal processes for the utilization of solar energy including the ability to be converted to electrical energy without the intervention of a heat engine. The solar to electrical conversion can be carried out directly by means of photovoltaic or photoelectrochemical devices or alternatively, by photochemical means with the intermediate formation of high energy photoproducts. These photoproducts provide an advantage in that the contained chemical energy can be stored and/or transported prior to on-site conversion to usable energy. Photosynthesis, of course, provides an example of this latter scheme of quantum conversion to high energy photoproducts, storage as biomass, and possible ultimate conversion to thermal or electrical energy.

This paper will outline some attempts at nonbiological photochemical fuel formation, specifically hydrogen formation by photoredox reactions of inorganic ions. The value of hydrogen as a fuel for future consideration has been extensively discussed (*1*) and a means of coupling the efficient formation of such a fuel with a solar energy conversion system has many desirable aspects, not the least of which is the storage of solar energy in a stable form.

A flow diagram for such a process is shown in Fig. 1. The photochemical process is used to generate a charge separation and to form stable, energy-containing photoproducts, which may be stored. In principle these products need not be ionic but are shown as such for simplicity. Energy retrieval, which

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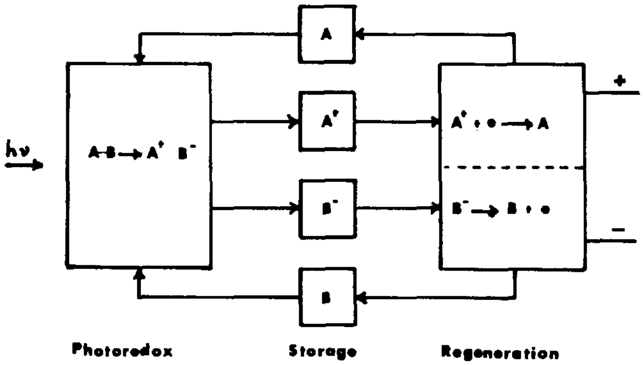


FIG. 1. General schematic of photochemical charge separation, storage of photoproducts, and electrochemical regeneration of reactants.

may be accomplished electrochemically at an inert electrode, regenerates the original reactants.

Approaches using this general idea have most commonly involved the attempted photodecomposition of water catalyzed by metal salts in the following way:

fuel formation:

$$H_2O + M^{n+} \xrightarrow{h\nu} \tfrac{1}{2}H_2\uparrow + HO^- + M^{(n+1)+}, \quad \Delta G > 0 \qquad (1a)$$

or

$$H^+ + M^{n+} \xrightarrow{h\nu} \tfrac{1}{2}H_2\uparrow + M^{(n+1)+}; \qquad (1b)$$

oxidizer formation:

$$H_2O + 2M^{(n+1)+} \xrightarrow{h\nu} \tfrac{1}{2}O_2\uparrow + 2H^+ + 2M^{n+} \qquad (2a)$$

or

$$2HO^- + 2M^{(n+1)+} \xrightarrow{h\nu} \tfrac{1}{2}O_2\uparrow + 2M^{n+} + H_2O; \qquad (2b)$$

the net balanced reaction being

$$H_2O \xrightarrow{h\nu} H_2 + \tfrac{1}{2}O_2. \qquad (3)$$

Energy can then be recovered in a fuel cell or by combustion. In actuality, both Eqs. (1) and (2) can be considered as fuel/oxidizer reactions alone, i.e., in Eq. (1) H_2 is the fuel and $M^{(n+1)+}$ is the oxidizer; thus if Eq. (1) is endergic then the reverse reaction should occur spontaneously in a galvanic or fuel cell according to:

$$M^{(n+1)+} + \tfrac{1}{2}H_2 + HO^- \rightarrow M^{n+} \; H_2O, \quad \Delta G < 0. \qquad (4)$$

Net electrical work can be recovered.

Quantum Yields and Conversion Efficiencies

The quantum yield, Φ, in a photochemical reaction is defined as moles of product per Einstein absorbed. Primary photochemical processes can have quantum yields less than 1 because deactivation modes such as collisional stabilization, emission, and back reaction compete with the desired chemical reaction. The energy conversion efficiency of a photochemical solar energy process, Q, is simply energy stored/energy input. With monochromatic radiation of wavelength λ, Q is defined (*2*) as

$$Q_\lambda = 100 \times \frac{\Phi_\lambda \Delta G^0_{298}}{hc/\lambda}, \qquad (5)$$

where Φ is the quantum yield at λ, hc/λ is the energy of an Einstein at wavelength λ, and ΔG^0_{298} is the standard free-energy change for the reaction involved. For a distribution of wavelengths, i.e., white light, an integrated form should be used taking into account the changes in incident radiation intensity, absorbance, and quantum yield with wavelength. The simpler Q does, however, convey a general idea of efficiency over a limited range.

Photochemical System Requirements

The main requirements for a viable photochemical conversion scheme involving quantum conversion, storage, and energy regeneration are:

(1) The photochemical reaction must be endergic, i.e., energy storing with $\Delta H > 0$ for processes involving thermal end use and $\Delta G > 0$ for those involving electrical end use.

(2) The photoproducts should be kinetically stable, i.e., the reverse exergic reaction must be slow in comparison to the photchemical reaction under the photolysis conditions. Separation of the products from the reaction mixture can be a useful means of preventing back reactions.

(3) The action spectrum of the reactants should coincide with the solar irradiance to a maximal extent and the absorbance of the products be minimal in the same range.

(4) The photochemical reaction should have a high quantum yield and the regenerative reaction have a high efficiency of usable energy generation with a minimum of side reactions in both cases.

(5) The components of the system, even if catalytic, should be inexpensive.

Results

Photooxidation of Low-Valent Metal Salts

The general reaction:

$$M^{n+} + H^+ \xrightarrow{h\nu} M^{(n+1)+} + \tfrac{1}{2}H_2 \quad (6)$$

has been observed for a number of metals including many of the first row transition elements as well as the lanthanide elements, cerium and europium, as shown in Table I.

Cerium(III)

The best known solar energy conversion scheme involving the photoredox reactions of metal salts is that proposed by Heidt *et al.* based upon the reactions of cerium salts (*3*). Cerous perchlorate, in acidic aqueous media photooxidizes at 254 nm to a cerium(IV) complex according to

$$Ce(H_2O)_6^{3+} + H^+ \xrightarrow{h\nu} Ce(IV)_{aq} + \tfrac{1}{2}H_2. \quad (7)$$

The resulting Ce(IV) ion is a strong oxidizing agent and either under the influence of light or in the dark will oxidize water:

$$2Ce(IV) + H_2O \xrightarrow[\text{or dark}]{h\nu} 2Ce(III) + 2H^+ + \tfrac{1}{2}O_2. \quad (8)$$

Although the cell potential for the initial photochemical reaction is large, $E_0 = 1.7$ V, $\Delta G^\circ = 164$ kJ/mole, the quantum yield for Eq. (7) is only 1.3×10^{-3} resulting in a Q of 4.5×10^{-2}%. An additional complication arises in that the absorbance spectrum of the Ce(IV) complex formed overlaps appreciably that of the reactants, masking part of the incident radiation from the primary photoreaction. The wavelength response is not appropriate for terrestrial solar applications.

Iron (II)

Photooxidation of ferrous salts (*4*, *5*) takes place with a much greater efficiency (Q =

TABLE I

METAL ION PHOTOOXIDATION REACTIONS

$M^{n+} + H^+ \xrightarrow{h\nu} M^{(n+1)+} + \tfrac{1}{2}H_2$

Couple	E_0, (V)	λ (nm)	Φ_{ox}	Ref.
Ce^{III}/Ce^{IV}	−1.7	254	1.3×10^{-3} (1 M $HClO_4$)	(*3*)
Fe^{II}/Fe^{III}	−0.77	254	0.15 (0.15 M H_2SO_4)	(*4*, *5*)
Cu^{I}/Cu^{II}	−0.45	275	0.65 (1 M HCl)	(*6*)
V^{II}/V^{III}	+0.25	313	0.15 (1 M HCl)	(*7*)
Cr^{II}/Cr^{III}	+ 0.41	254	0.3 (1 M HCl)	(*8*)
Eu^{II}/Eu^{III}	+0.43	365	0.14 (1 M $HClO_4$)	(*9*)

2.3%) due primarily to the much greater quantum yield, $\Phi_{254} = 0.15$ in $0.15\,M\,H_2SO_4$ solutions. The applicability of iron salts is limited by both lack of overlap with the solar irradiance and a very powerful masking effect of the ferric ion. Indeed the highly absorbing qualities of the ferric ion, as its bromo-complex $FeBr_4^-$, have been utilized in a photoreduction of Fe(III) to Fe(II) with the formation of bromine (*10*) ($\Phi 1.5 \times 10^{-2}$, Q_{436} 0.3%)

$$(Fe^{3+}Br^-) \xrightarrow{h\nu} Fe^{2+} + \tfrac{1}{2}Br_2. \qquad (9)$$

Copper(I)

Chloro- or bromocomplexes of Cu(I) are photochemically oxidized to Cu(II) with the simultaneous reduction of hydrogen ions to hydrogen gas (*6*). The reaction, where *L* is a chloro or bromo ligand,

$$Cu(I)L_n^{1-n} + H^+ \xrightarrow{h\nu} Cu(II)L_n^{2-n} + \tfrac{1}{2}H_{2(g)} \qquad (10)$$

is promoted by light at the ultraviolet end of the solar spectrum ($\lambda < 320$ nm) with a sizeable quantum yield. The reaction has been carried out in the laboratory as well as in sunlight. The standard Gibbs free energy is positive for the process and since hydrogen gas is evolved from the system allowing for storage and energy recovery in an electrochemical cell, this reaction is capable of converting and storing solar energy.

The irradiation of 0.01 *M* aqueous solutions of CuCl and CuBr is carried out in HCl and HBr, respectively, of varying H^+ and halide concentration. In the case of CuCl in HCl, $[H^+]$ was varied from 10^{-7} to 5 *M*, and $[Cl^-]$, from 1 to 5 *M*, in mixtures of HCl with NaCl or $HClO_4$ as needed. Nearly optimum quantum yields are obtained when $[H^+] = [Cl^-] = 1\,M$. That the stoichiometry is as shown in Eq. (10) was verified by the quantitative determination of Cu(II) species spectrophotometrically and by the detection of $H_{2(g)}$ qualitatively by mass spectrometry, and quantitatively by volume. Quantum yields and efficiencies at several wavelengths are listed in Table II.

TABLE II

QUANTUM YIELDS AND ENERGY CONVERSION EFFICIENCIES FOR PHOTOOXIDATION OF Cu(I) IN 1 *M* HCl OR HBr

	HCl		HBr	
λ, (nm)	$\Phi_{Cu(II)}$	*Q* (%)	$\Phi_{Cu(II)}$	*Q* (%)
275	0.65	6.5	0.31	3.1
280	0.65	6.6	0.23	2.3
301	0.44	4.9	0.15	1.6
313	0.34	3.9	0.08	0.9

The Cu(I) complexes in the solutions described here have a considerably higher absorbance than the photoproducts, as is shown by the absorption spectra, in HCl, of the Cu(I) reactants and Cu(II) products in Fig. 2. An even larger difference in absorption was

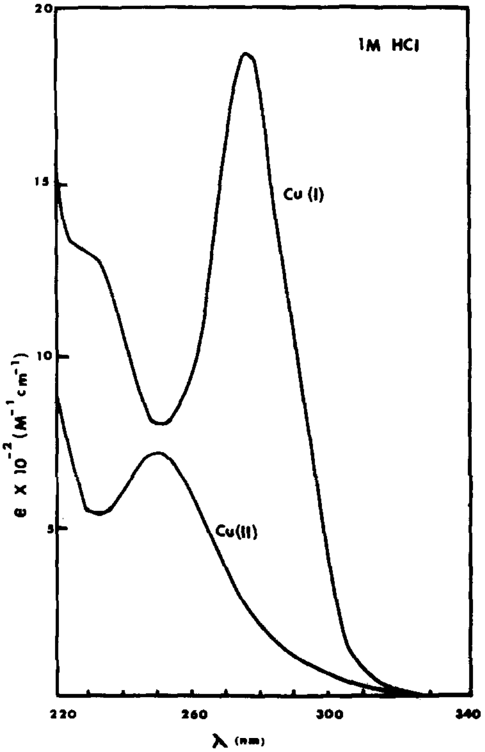


FIG. 2. Absorption spectra of Cu(I) reactants and Cu(II) products in 1 *M* HCl.

noted for the bromocomplexes of Cu(I) and (II) in 1 *M* HBr. Therefore the Cu(II) species cause very little internal masking and the rate of H_2 formation appears to be nearly zero order till at least 90% completion, which is expected under conditions of total light absorption by reactants and constant incident light intensity.

The Cu(I) species in the reactant system are undoubtedly a mixture of polyhalo-copper ions. A recent study by Sugasaka and Fujii (*11*) shows that $CuCl_2^-$ and $CuCl_3^{2-}$ are the complexes present in chloride ion solutions of CuCl and that the absorption band at 275 nm is due to the $CuCl_3^{2-}$ species only. Since the highest quantum yields correspond to this spectral region, $CuCl_3^{2-}$ is concluded to be the primary, if not sole, photoactive species.

From the values of known thermodynamic quantities (*12*) the value of $\Delta G°$ for the reaction

$$CuCl_3^{2-} + H^+ \rightarrow CuCl_3^{1-} + \tfrac{1}{2}H_{2(g)} \qquad (11)$$

is calculated to be +43.5 kJ/mole. The energy conversion efficiency calculated by Eq. (5) at 275 nm is then 6.56%.

Although terrestrial sunlight is nearly devoid of light at 275 nm, the reaction does, nevertheless, occur in sunlight due to the fact that the absorbance of the Cu(I) species overlaps the ultraviolet end of the solar spectrum, from 290 to about 320 nm. Illumination of an icewater-cooled CuCl solution in 1 *M* HCl, with sunlight concentrated by a parabolic reflector having an effective light-gathering area of 490 cm², went to completion in 18 min, as compared to 10 min for a run with a 200 W mercury lamp. This run occurred on a clear day, March 31, 1976, at 1100 hours solar time in Las Cruces, New Mexico, which has a latitude of 32°N and an altitude of 1500 m. If this were scaled up, the effective energy-capturing ability of this system is about 56 kW/mile². While this is admittedly a rather small energy output, all the optimum conditions for the process have yet to be determined. In particular, the effects of temperature, ionic strength, and copper concentration are being studied in more detail. In addition, other complexes of copper(I) and other metallic ions are being explored with the goal of shifting the wavelengths of photoactivity more into the visible region of the solar spectrum.

This kind of process makes an almost ideal solar energy converter since the products, a gas and an aqueous solution, separate spontaneously, preventing back reactions, and are quite stable by themselves, thus allowing for indefinite storage and later use during sunless periods. The recovery of the stored chemical energy could be attained by recombination of $H_{2(g)}$ and the Cu(II) species in an electrochemical cell, which would regenerate the photochemical reactants as described in Fig. 1. The reactor would consist of a hydrogen anode (similar to one used in a hydrogen–oxygen fuel cell) and an inert cathode on which the Cu(II) complex is reduced to Cu(I). Alternative cycles involving other electrochemical reactions can also be envisioned.

Titanium (III)

The charge-transfer shoulder of $Ti(H_2O)_6^{3+}$ extends to 290 nm (*13*) and although both the cell potential (E_0Ti(III)/Ti(IV) = −0.1 V), and overlap with the solar spectrum are small this ion could serve as another example in an energy conversion scheme. Additionally, the Ti(IV) species formed in this reaction have little absorption in this range avoiding the problem of masking by photoproducts.

The irradiation of solutions of pure $TiCl_3$ in 1 *M* HCl does not proceed with any detectable rate of hydrogen formation ($\Phi < 10^{-2}$) within the limits of our experimental procedure. However, in the presence of trace amounts of copper salts the reaction proceeds (*14*) smoothly with the stoichiometry

$$\text{Ti(III)} + H^+ \xrightarrow[\text{Cu salts}]{h\nu} \text{Ti(IV)} + \tfrac{1}{2}H_2. \qquad (12)$$

Spectrophotometric studies indicate that the copper is present as $CuCl_3^{2-}$, whose photooxidation is discussed above.

In view of these results we suggest that the photooxidation of Ti(III) may occur in the following manner:

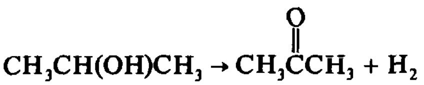
$$\mathrm{Cu(I)} \xrightarrow{h\nu} \mathrm{Cu(I)}^{*}, \qquad (13)$$

$$\mathrm{Cu(I)}^{*} + \mathrm{H}^{+} \rightarrow \mathrm{Cu(II)} + \tfrac{1}{2}\mathrm{H}_2, \qquad (14)$$

$$\mathrm{Cu(II)} + \mathrm{Ti(III)} \rightarrow \mathrm{Cu(I)} + \mathrm{Ti(IV)}. \qquad (15)$$

The photochemistry is that of Cu(I), the Ti(III) acting mainly as a nonabsorbing reducing agent to recycle the copper.

This photocatalysis by Cu(I) can, in principle, be used to drive other nonspontaneous, nonphotoactive reactions and we have extended this photocatalysis to the decomposition of isopropanol to acetone and hydrogen ($\Delta G°$ = 6.7 kJ/mole). Photolysis of 0.02 M Cu(I) in 0.5 M HCl containing 0.5 M isopropanol produces hydrogen and acetone and quickly achieves a plateau rate of hydrogen evolution. The reaction ceases when the isopropanol is consumed. However, the efficiency of conversion is low since the net reaction,



$$\mathrm{CH_3CH(OH)CH_3} \rightarrow \mathrm{CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3} + \mathrm{H_2} \qquad (16)$$

has such a low $\Delta G°$.

Discussion

Dependence upon Acidity

A strong relationship exists between solution acidity and the quantum yield of hydrogen formation. Reactions are generally carried out below pH 3 and in solutions containing concentrations of acid up to 6 M. Half-order dependence of quantum yield on hydronium concentration has been noted for ferrous (*5*), europous (*9*), vanadous (*7*), and cuprous (*6*) salts in HCl or $\mathrm{HClO_4}$. This dependence is generally of the form

$$\Phi_{\mathrm{H_2}} = a + b[\mathrm{H}^{+}]^{1/2} \qquad (17)$$

as shown in Fig. 3 for Cu(I) photolysis and is best explained by the Noyes model for secondary recombination (*15*).

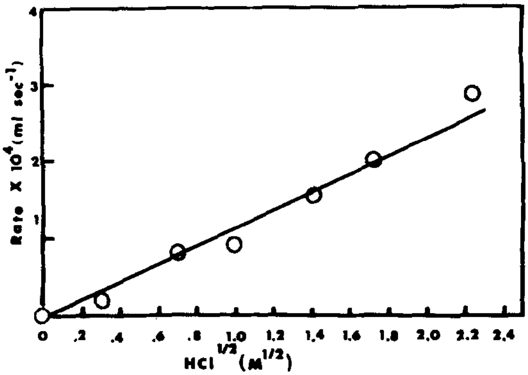


FIG. 3. Hydrogen evolution vs square root of HCl concentration for photolysis of 0.01 M solutions of CuCl at $\mu = 5$.

Geminate Pair Mechanism

A pair of reactive fragments initially produced in the primary photoprocess may undergo recombination while still in the solvent cage in which they were formed, i.e., primary recombination; or they may undergo diffusive displacements and recombine as a result of a reencounter, secondary recombination. The theoretical treatment by Noyes of the effect of scavengers on the secondary recombination process gives the result that secondary recombination should decrease as a function of the square root of scavenger, H^{+}, concentration and this effect should be operative at relatively low (10^{-2} M) concentrations of scavenger.

Thus, a possible mechanism for hydrogen formation would be as follows:

$$M^{2+} \xrightarrow{h\nu} M^{2+*}, \qquad (18)$$

$$[M^{2+}]^{*} \rightarrow M^{2+}, \qquad (19$$
deactivation;

$$[M^{2+}]^{*} + \mathrm{H_2O} \rightarrow \overline{[M\mathrm{OH\ H}]^{2+}}, \qquad (20)$$
geminate pair formation;

$$\overline{[M\mathrm{OH\ H}]^{2+}} \rightarrow M^{2+} + \mathrm{H_2O}, \qquad (21)$$
primary recombination;

$$\overline{[M\mathrm{OH\ H}]^{2+}} + S \rightarrow M\mathrm{OH}^{2+} + S\mathrm{H}, \qquad (22)$$
scavenging of primary pair;

$$\overline{[M\mathrm{OH\ H}]^{2+}} \rightarrow \overline{M\mathrm{OH}^{2+}} + \overline{\mathrm{H}}, \qquad (23)$$
diffusion to secondary pair;

$$\overline{M\mathrm{OH}^{2+}} + \overline{\mathrm{H}} \rightarrow M^{2+} + \mathrm{H_2O}, \qquad (24)$$

secondary recombination;

$$\overline{M\mathrm{OH}^{2+}} + \overline{\mathrm{H}} + S \rightarrow M\mathrm{OH}^{2+} + S\mathrm{H}, \qquad (25)$$

scavenging a separated pair;

$$S\mathrm{H} \rightarrow \text{products}. \qquad (26)$$

For the situation in which $\mathrm{H^+}$ is the scavenger, S,

$$\mathrm{H} + \mathrm{H^+} \rightarrow \mathrm{H_2^+}, \qquad (27)$$

$$\mathrm{H_2^+} + M^{2+} \rightarrow \mathrm{H_2} + M^{3+}, \qquad (28)$$

or

$$M^{2+} + \mathrm{H} \rightarrow M\mathrm{H}^{2+}, \qquad (29)$$

$$M\mathrm{H}^{2+} + \mathrm{H^+} \rightarrow \mathrm{H_2} + M^{3+}, \qquad (30)$$

the formation of $\mathrm{H_2^+}$ and its reduction by another equivalent of metal as required by the stoichiometry leads to the observed product formation.

A nonzero intercept (Eq. (17) $a \neq 0$) may be due to diffusion of the secondary pair into the bulk solution, Eq. (31), or coordinated water on the metal ion interfering with primary recombination, Eq. (32).

A third process not involving geminate pairs at all, the direct decomposition to oxidized metal ion and H atom in the bulk, Eq. (33), would also be scavenger concentration independent:

$$\overline{M\mathrm{OH}^{2+}} + \overline{\mathrm{H}} \rightarrow M\mathrm{OH}^{2+} + \mathrm{H_{bulk}}, \qquad (31)$$

$$\overline{[(\mathrm{H_2O})_m M\mathrm{OH\ H}]^{2+}} \rightarrow (\mathrm{H_2O})_{m-1} M(\mathrm{OH})_2^+ + \mathrm{H_2^+}, \qquad (32)$$

$$[M(\mathrm{H_2O})_m^{2+}]^* \rightarrow M\mathrm{OH}\ (\mathrm{H_2O})_{m-1}^{2+} + \mathrm{H_{bulk}}. \qquad (33)$$

The Noyes model for geminate recombinations suggests that primary pairs can be captured only if the scavenger is extremely reactive and/or present in very high concentrations. Coordinated water is present in very high local concentration around the metal ion and although water is a poor scavenger compared to hydronium, the local concentration effect may become important at low hydronium concentrations.

The addition of a neutral scavenger, isopropanol, in the photolysis of Eu(II), affects the rate of reaction slightly (*9*) and acts as a scavenger for H atoms as shown by the greater than stoichiometric yield of $\mathrm{H_2}$, based on Eu(II), due to the recycling of Eu(III) and Eu(II) as shown in Eqs. (34), (35):

$$\mathrm{H} + (\mathrm{CH_3})_2\mathrm{CH{-}OH} \rightarrow (\mathrm{CH_3})_2\mathrm{COH} + \mathrm{H_2}, \qquad (34)$$

$$(\mathrm{CH_3})_2\mathrm{COH} + \mathrm{Eu^{3+}} \rightarrow (\mathrm{CH_3})_2\mathrm{C{=}O} + \mathrm{Eu^{2+}} + \mathrm{H^+}. \qquad (35)$$

Some comment may be made on the formulation of the primary geminate pair, Eq. (20). We have shown this pair as the hydroxo-complex of the oxidized metal ion paired with a H atom. An operationally equivalent formulation would be the oxidized aquo-ion paired to an electron:

$$\overline{M_{\mathrm{ox}}\mathrm{OH}}\ \overline{\mathrm{H}} \leftrightarrow \overline{M_{\mathrm{ox}}\mathrm{OH_2}}\ \overline{\mathrm{e}}.$$

The photooxidation of $\mathrm{Fe(CN)_6^{4-}}$ (*16*) actually produces solvated electrons in the bulk solution which can be detected spectroscopically or intercepted chemically with electron traps such as $\mathrm{N_2O}$ or acetone. The photooxidation of ions listed in Table I does not generally show this behavior. Europous ion does not give spectroscopically detectable concentrations of solvated electrons (*17*), nor is the photooxidation quantum yield affected by acetone (*9*), a well-known solvated electron trap (*18*). Acetone likewise has no effect in the photooxidation of Cu(I) complexes. If the $\overline{M_{\mathrm{ox}}}$ $\overline{\mathrm{e}}$ formulation is a better representation, then there must be an appreciable difference in reactivity of caged vs solvated electrons. Similarly the greater quantum yield for the photooxidation of the anionic complex $\mathrm{CuCl_3^{2-}}$ as compared to the cationic complexes may be related to the charge on the geminate pair, the highest quantum yield for proton scavenging corresponding to the pair with least positive charge: Ce(+3), $\Phi = 10^{-3}$; Ti(+3), $\Phi \cong 0$; Fe, Cr, V, Eu(+2), $\Phi \cong 0.2$; Cu(−2), $\Phi = 0.65$; $Fe(CN)_6^{4-}$ (−4), $\Phi_{e_{aq}} = 0.66$.

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