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Production of Hydrogen by Irradiation of Metal Complexes in Aqueous Solutions

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Several systems in which molecular hydrogen is produced by photoreduction of protons in aqueous solutions are discussed. One mononuclear system, $IrCl_6^{2-/3-}$, *is considered in detail. Ultraviolet irradiation of concentrated HCl solutions of* $IrCl_6^{3-}$ *yields* $IrCl_6^{2-}$ *and* H_2. *It is proposed that the reactive excited states are protonated species such as* $HIrCl_6^{2-}$ *that possess Cl → Ir charge transfer character, and that the photoredox mechanism involves initial release of atomic hydrogen. Irradiation of* $IrCl_6^{2-}$ *in aqueous HCl solutions over a broad range of wavelengths results in the formation of* $IrCl_6^{3-}$ *and* Cl_2. *Aqueous HCl is converted to hydrogen and chlorine by coupling the two photoreactions. The possible advantages of using metal cluster complexes to facilitate photochemical hydrogen production are outlined, and related experiments on* $Mo_2X_8^{4-}$ *(X = Cl, Br) and* $Rh_4b_8^{6+}$ *(b = 1,3-diisocyanopropane) are reviewed. Recent experiments have shown that* $Mo_6Cl_{14}^{2-}$ *possesses a long-lived excited state (180 μs in* CH_3CN*; 2eV) that undergoes electron transfer reactions in solutions, and possible extensions of this work aimed at photoreduction of protons are considered.*

Introduction

For several years our research group has been concerned with the photochemistry of transition metal complexes in aqueous solutions. One reaction that we have explored extensively is the photoreduction of protons to molecular hydrogen. Systems that we have investigated include $Mo_2(aq)^{4+}$ [1], $Mo_2(SO_4)_4^{4-}$ [1, 2], $Mo_2X_8^{4-}$ (X = Cl, Br) [1], $Re_2X_8^{2-}$ [3], and $Fe_3(CO)_{11}^{2-}$ [4]. A few highlights of this work will be reviewed here, but our main objective is to present some new results as well as a few thoughts relating to the mechanisms of photoreduction of protons. One mononuclear model system ($IrCl_6^{2-/3-}$) will be treated in some detail, and this will be followed by a discussion of some of our recent work on polynuclear complexes.

Hexachloroiridates

The photochemistry of $IrCl_6^{2-}$ ($E^\circ = 0.867$ V) [5] has been investigated by two groups [6, 7], and Waltz and Adamson have shown [8] that ultraviolet excitation of $IrCl_6^{3-}$ under certain conditions can lead to the formation of $IrCl_6^{2-}$. We felt that there was a good chance that hydrogen could be produced by irradiation of $IrCl_6^{3-}$, so we began a series of experiments aimed at that goal. In parallel with our photochemical studies, we investigated the electronic spectra of the hexachloroiridates.

The ground state of $IrCl_6^{3-}$ is $^1A_{1g}$ $(2t_{2g})^6$. Transitions from $^1A_{1g}$ to *d–d* excited states produce four weak absorption bands in the 650–350 nm region of the spectrum of $IrCl_6^{3-}$ (Fig. 1). The two relatively weak bands observed at 615 ($\epsilon = 7.5$) and 560 nm ($\epsilon = 10$) are attributable to spin-forbidden transitions ($^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$), whereas those at 415 ($\epsilon = 76$) and 356 nm ($\epsilon = 64$) represent spin-allowed excitations ($^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$) [9]. The intense, high energy band at 206 nm (Fig. 1) has been assigned to a spin-allowed $\pi(Cl) \rightarrow 2e_g$ transition [10]. Waltz and Adamson, however, observed [8] that solutions of $IrCl_6^{3-}$ that were irradiated under an atmosphere of N_2O yielded $IrCl_6^{2-}$ and N_2, the products expected from solvated electron formation. Although the quantum yield for N_2 production was

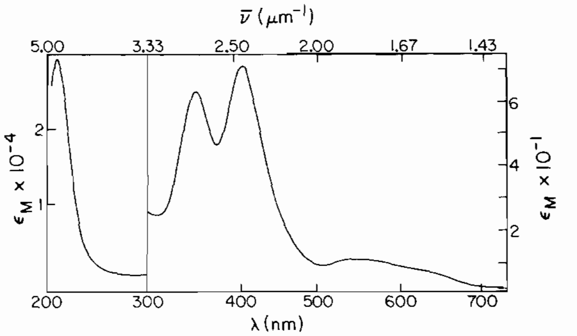

Fig. 1. Electronic absorption spectrum of $IrCl_6^{3-}$ (Na_3IrCl_6) in aqueous solution at 300 K.

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low (0.031), Waltz and Adamson's work raised the possibility that the transition responsible for the 206 nm band is charge transfer to solvent (CTTS) in nature.

Flash photolysis studies of $IrCl_6^{3-}$ in our laboratory showed no transient attributable to e^-(aq); the negative result was not definitive, however, owing to lifetime limitations of the apparatus [3]. At this point we decided to see if the 206 nm band exhibited any of the characteristics normally found [11] for CTTS absorptions, namely, (1) a blue shift of several nanometers when the solvent is changed from H_2O to D_2O; (2) a blue shift when organic solutes and solvents are added; (3) a blue shift upon increasing the ionic strength; and (4) a very slight red shift upon increasing the temperature. None of these shifts was observed in our studies of medium effects on the position of the 206 nm band; thus, a CTTS assignment is inappropriate [3].

In the course of the above study, we noted that the 206 nm band is extremely broad, tailing out considerably toward low energy. Because this large bandwidth suggested the possibility of one or more additional transitions, a spectrum was recorded in rigid solution at 60 K (Fig. 2). The band at 206 nm sharpens and intensifies, but more interesting is the appearance of new features at about 240 and 265 nm.

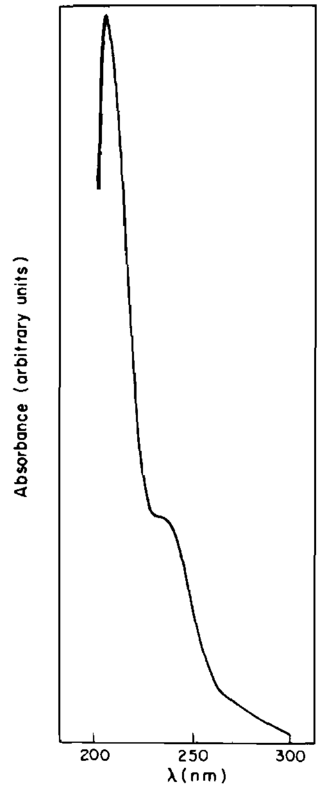

Fig. 2. Electronic absorption spectrum of $IrCl_6^{3-}$ in rigid solution (Na_3IrCl_6 in 50% saturated aqueous LiCl) at 60 K.

These new absorptions are not due to CTTS excitations, as both are present (slightly red-shifted to 250 and 278 nm) in a KCl pellet spectrum of $IrCl_6^{3-}$ at 15 K.

It is reasonable to assign all three bands that are observed below 300 nm in the $IrCl_6^{3-}$ spectrum to Cl → Ir charge transfer transitions. Analogous features in the spectrum of $IrBr_6^{3-}$ are significantly red-shifted, as would be expected. The detailed assignments are somewhat uncertain, but it is likely that the more intense bands (206 and 250 nm) represent fully allowed transitions ($^1A_{1g} \rightarrow {}^1T_{1u}$). The 278 nm band is the lowest energy charge transfer feature that we have resolved, and it may be attributed to a $\pi(Cl) \rightarrow 2e_g$ singlet → triplet transition ($^1A_{1g} \rightarrow {}^3T_{1u}$).

Irradiation (254 nm) of a 12 *M* HCl solution of $IrCl_6^{3-}$ at room temperature results in the disappearance of $IrCl_6^{3-}$ and the appearance of $IrCl_6^{2-}$ (Fig. 3). Hydrogen evolution accompanies the formation of $IrCl_6^{2-}$:

$$H^+ + IrCl_6^{3-} \xrightarrow[12\,M\,HCl]{254\text{ nm}} IrCl_6^{2-} + \frac{1}{2}H_2 \qquad (1)$$

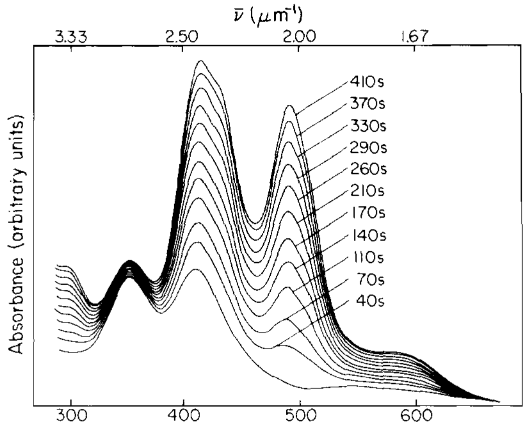

Fig. 3. Electronic spectral changes in a 12 *M* HCl solution originally 6.7 × 10^{-3} *M* in $IrCl_6^{3-}$ on 254 nm irradiation.

Exhaustively photolyzed solutions were Toepler-pumped for hydrogen and $IrCl_6^{2-}$ was analyzed by spectrophotometric methods, confirming the above stoichiometry [3].

The quantum yields for the reaction are extremely sensitive to proton concentration (Fig. 4). At high proton activity, the photoprocess resulting in H_2 production is much more efficient, possibly due to proton association with ground state $IrCl_6^{3-}$. Proton concentration dependence for photoproduction of hydrogen is also seen [12] for $Fe(CN)_6^{4-}$, a case in which the ground state species exists in protonated forms at low pH.

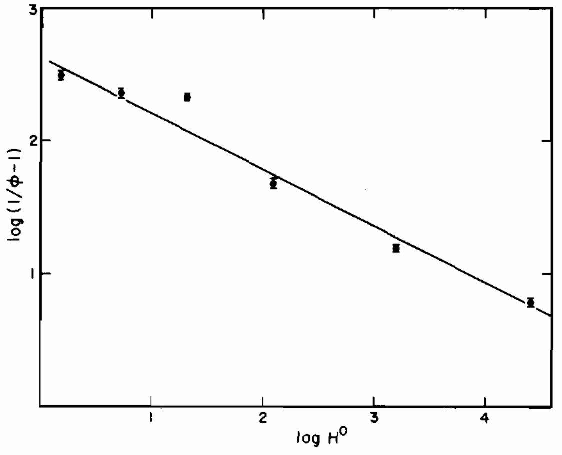

Fig. 4. Stern-Volmer plot based on quantum yields for photooxidation of $IrCl_6^{3-}$ at various proton activities H° (Φ 254 nm) in HCl solutions: 12.0 *M*, 0.28; 9.0 *M*, 0.127, 6.0 *M*, 0.0411; 4.0 *M*, 0.00921; 2.0 *M*, 0.00868, 1.0 *M*, 0.00653).

The quantum yields for formation of $IrCl_6^{2-}$ are also highly wavelength dependent in 12 *M* HCl ($\Phi = 0.28$, 254 nm; $\Phi \sim 10^{-4}$, 313 nm; $\Phi \sim 0$, >366 nm). Our placement of the energies of the Cl → Ir transitions in $IrCl_6^{3-}$ allows a reasonable interpretation of this photochemistry. The fact that the photoreaction proceeds with a relatively high quantum efficiency at 254 nm suggests that one or both of the two lower charge transfer excited states are involved in the mechanism. Direct excitation to either state is possible, and the triplet also could be populated by rapid intersystem crossing from $^1T_{1u}$. Both excited states have Ir(II)–Cl· character, corresponding to the $(2t_{2g})^6(2e_g)^1$ configuration for Ir:

$$[\mathrm{Ir(II)}\text{–}\dot{\mathrm{C}}\mathrm{l}]^*$$

It is likely that $IrCl_6^{3-}$ exists in equilibrium with various protonated species in strongly acidic solutions. We propose that Cl → Ir excited states of such protonated species can dissociate to form $IrCl_6^{2-}$ and hydrogen atoms, according to the following scheme for photoproduction of H_2:

$$H^+ + IrCl_6^{3-} \rightleftharpoons HIrCl_6^{2-} \quad (2)$$

$$HIrCl_6^{2-} \xrightarrow{h\nu} [HIrCl_6^{2-}]^*[^3T_{1u} \text{ or } ^1T_{1u}] \quad (3)$$

$$[HIrCl_6^{2-}]^* \longrightarrow IrCl_6^{2-} + H \quad (4)$$

$$H + H^+ \longrightarrow H_2^+ \quad (5)$$

$$2H \longrightarrow H_2 \quad (6)$$

$$H + HIrCl_6^{2-} \longrightarrow H_2 + IrCl_6^{2-} \quad (7)$$

$$H_2^+ + IrCl_6^{3-} \longrightarrow H_2 + IrCl_6^{2-} \quad (8)$$

The dependences of the overall quantum yields for Ir(IV) production on light intensity and on initial $IrCl_6^{3-}$ concentration can be accommodated satisfactorily by the above scheme [3]. Since we observed no transient absorption attributable to Cl_2^- in flash photolysis studies [3], we believe that the $[\mathrm{Ir(II)}\text{–}\dot{\mathrm{C}}\mathrm{l}]^*$ excited state does not release atomic chlorine at a significant rate.

The rate of photooxidation of $IrCl_6^{3-}$ in these solutions decreases as irradiation is continued, probably due to competitive light absorption by $IrCl_6^{2-}$. The molar extinction coefficients at 254 nm for the two ions are 960 and 7550, respectively.

Hexachloroiridate (IV) is also photosensitive: in separate experiments, solutions of $IrCl_6^{2-}$ in 6 *M* HCl gave $IrCl_6^{3-}$ on irradiation. Quantum yields for formation of $IrCl_6^{3-}$ as a function of irradiation wavelength were as follows: 254 nm, 0.128; 313 nm, 0.107; 366 nm, 0.090; 420 nm, 0.0159; 488 nm, 0.00361. No aquation products were observed in these experiments ($[IrCl_6^{2-}] = 6.7 \times 10^{-4}$ *M*). The rate of $IrCl_6^{2-}$ photoreduction also decreases as irradiation is continued; and $IrCl_6^{2-}$ reappears slowly in the solutions after irradiation is stopped. In this case corrections for inner filter effects and secondary photolysis cannot account for the decrease in reaction rate. We propose that Cl_2 is the oxidant produced on irradiation of $IrCl_6^{2-}$, and that it inhibits further photoreaction by reacting thermally with $IrCl_6^{3-}$ to regenerate $IrCl_6^{2-}$. Two lines of evidence rule against O_2 as the oxidation product: (1) O_2 does not react thermally with $IrCl_6^{3-}$ at rates anywhere near those observed in our studies of the reappearance of $IrCl_6^{2-}$ in the photolyzed solutions, and (2) experiments in $H_2{}^{18}O$-labeled hydrochloric acid gave no evidence for $^{18}O_2$ formation. Finally, the rate of oxidation of $C_2O_4^{2-}$ by $IrCl_6^{2-}$ increases dramatically on irradiation ($\lambda > 300$ nm), a strong indication that Cl_2 is the oxidation product.

Our finding that $IrCl_6^{2-}$ is reduced photochemically to $IrCl_6^{3-}$ in 6 *M* HCl solutions is interesting in view of the results obtained by Moggi and coworkers [7], whose studies on $IrCl_6^{2-}$ were performed in 2 *M* $HClO_4$ solutions with and without added NaCl. They found aquation to be the principal photoreaction in the absence of NaCl, but also observed photoredox chemistry when NaCl was added. Although their experimental conditions differ somewhat from ours, the observation that added Cl^- promotes photoreduction of $IrCl_6^{2-}$ appears common to both studies.

A reasonable scheme for the photoreduction of $IrCl_6^{2-}$ features electron transfer to a charge transfer excited state from a chloride ion, as follows:

$$IrCl_6^{2-} \xrightarrow{h\nu} [\mathrm{Ir(III)Cl_5}\text{–}\dot{\mathrm{C}}\mathrm{l}]^{2-*} \xrightarrow{Cl^-} IrCl_6^{3-} + Cl \quad (9)$$

$$2\mathrm{Cl} \longrightarrow \mathrm{Cl_2} \tag{10}$$

$$\mathrm{Cl} + \mathrm{Cl^-} \longrightarrow \mathrm{Cl_2^-} \tag{11}$$

$$\mathrm{Cl_2} + \mathrm{IrCl_6^{3-}} \longrightarrow \mathrm{IrCl_6^{2-}} + \mathrm{Cl_2^-} \tag{12}$$

$$\mathrm{IrCl_6^{3-}} + \mathrm{Cl_2^-} \longrightarrow \mathrm{IrCl_6^{2-}} + 2\mathrm{Cl^-} \tag{13}$$

Prolonged 254 nm irradiation of $\mathrm{IrCl_6^{2-}}$ in 6 *M* HCl produces relatively high concentrations of $\mathrm{IrCl_6^{3-}}$, and the reduced species undergoes secondary photolysis to yield $\mathrm{IrCl_6^{2-}}$ and H_2 (the latter product was identified by mass spectral measurements) [3]. In this medium the hexachloroiridates photocatalyze proton reduction and chloride oxidation:

$$\mathrm{H^+} + \mathrm{Cl^-} \xrightarrow[\mathrm{IrCl_6^{2-/3-}}]{254\ \mathrm{nm}\ (6\,M\ \mathrm{HCl})} \frac{1}{2}\mathrm{H_2} + \frac{1}{2}\mathrm{Cl_2} \tag{14}$$

Conversion of aqueous HCl to hydrogen and chlorine stores a substantial amount of chemical energy, and if the reaction could be driven by lower energy photons it would be an attractive chemical system for the storage of solar photon energy.

From the results we have obtained form $\mathrm{IrCl_6^{2-/3-}}$, it is reasonable to suggest that the related $\mathrm{IrBr_6^{2-/3-}}$ couple will photocatalyze the conversion of hydrogen bromide to hydrogen and bromine. Because corresponding X → Ir charge transfer transitions fall at lower energy in $\mathrm{IrBr_6^{2-/3-}}$ than in $\mathrm{IrCl_6^{2-/3-}}$, it is probable that hydrogen can be produced by irradiation of $\mathrm{IrBr_6^{3-}}$ well above 254 nm. Intense bands attributable to allowed Br → Ir ($^1A_{1g} \rightarrow {}^1T_{1u}$) transitions peak at 243 and 272 nm in the $\mathrm{IrBr_6^{3-}}$ absorption spectrum [3], so the lowest energy spin-forbidden charge transfer transition ($^1A_{1g} \rightarrow {}^3T_{1u}$) probably falls in the 300 nm region. Studies of the photochemical behavior of the hexabromoiridates in aqueous HBr solutions are underway.

Polynuclear Complexes

Much of our research in inorganic photochemistry has involved polynuclear complexes. Not only do such complexes offer low-lying excited states, they also may have available sites at the cluster surface to facilitate the multi-electron transfer steps needed to produce molecular hydrogen. It is reasonable to consider, for example, the possibility of photochemical hydrogen production by direct reaction of an excited metal cluster complex (M_n^*; n ⩾ 2) with protons:

$$\mathrm{M_n^*} + 2\mathrm{H^+} \longrightarrow \mathrm{M_n^{2+}} + \mathrm{H_2} \tag{15}$$

An important step might involve the reaction of M_n^* and H^+ to form an unstable hydride, which would then break down in aqueous solution to give H_2:

$$\mathrm{M_n^*} + \mathrm{H^+} \longrightarrow \mathrm{M_nH^+} \tag{16}$$

$$\mathrm{M_nH^+} + \mathrm{H^+} \longrightarrow \mathrm{M_n^{2+}} + \mathrm{H_2} \tag{17}$$

Association of one or two protons with a metal cluster in its ground state could provide a facile pathway for photoproduction of hydrogen:

$$\mathrm{M_n} + \mathrm{H^+} \rightleftharpoons \mathrm{M_nH^+} \tag{20}$$

$$\mathrm{M_nH^+} \xrightarrow{h\nu} \mathrm{M_nH^{+*}} \tag{21}$$

$$\mathrm{M_nH^{+*}} + \mathrm{H^+} \longrightarrow \mathrm{M_n^{2+}} + \mathrm{H_2} \tag{22}$$

$$\mathrm{M_n} + 2\mathrm{H^+} \rightleftharpoons \mathrm{M_nH_2^{2+}} \tag{23}$$

$$\mathrm{M_nH_2^{2+}} \xrightarrow{h\nu} \mathrm{M_n^{2+}} + \mathrm{H_2} \tag{24}$$

Reductive elimination of H_2 occurs upon ultraviolet excitation of certain mononuclear metal hydrides [13], and it might be possible to achieve the related reaction (24) from low-lying excited states of protonated metal clusters.

Experiments by Mann and Lewis in 1977 on a binuclear rhodium complex containing 1,3-diisocyanopropane(b) bridging groups revealed what we thought at first [14] was an example of the scheme encompassed by (20)–(22):

$$\mathrm{Rh_2b_4^{2+}} \xrightarrow[12\,M\ \mathrm{HCl}]{546\ \mathrm{nm}} \mathrm{Rh_2b_4Cl_2^{2+}} + \mathrm{H_2} \tag{25}$$

Later work by Sigal, however, demonstrated that the reaction proceeds as follows [15]:

$$2\mathrm{Rh_2b_4^{2+}} \xrightarrow{12\,M\ \mathrm{HCl}} \mathrm{Rh_4b_8Cl_2^{4+}} + \mathrm{H_2} \tag{26}$$

$$\mathrm{Rh_4b_8Cl_2^{4+}} \xrightarrow[12\,M\ \mathrm{HCl}]{546\ \mathrm{nm}} 2\mathrm{Rh_2b_4Cl_2^{2+}} + \mathrm{H_2} \tag{27}$$

The photochemical step is in fact the conversion of the tetranuclear complex, $\mathrm{Rh_4b_8Cl_2^{4+}}$, to $\mathrm{Rh_2b_4Cl_2^{2+}}$ and H_2. Various lines of evidence suggest that the precursor to H_2 is generated by net heterolytic cleavage of the tetranuclear species (probably by a complicated pathway) [15]:

$$\mathrm{Rh_4b_8Cl_2^{4+}} \xrightarrow[12\,M\ \mathrm{HCl}]{546\ \mathrm{nm}} \mathrm{Rh_2b_4^{2+}} + \mathrm{Rh_2b_4Cl_2^{2+}} \tag{28}$$

$$\mathrm{Rh_2b_4^{2+}} \xrightarrow{12\,M\ \mathrm{HCl}} \tfrac{1}{2}\mathrm{Rh_4b_8Cl_2^{4+}} + \tfrac{1}{2}\mathrm{H_2} \tag{29}$$

The photochemistry of this system is related more to reaction (15) than to (20)–(22), with the important modification that the binuclear reductant is photogenerated from a larger cluster, rather than being an excited state with the same degree of aggregation as the ground state. The mechanism of reaction (29) is not known, but it probably involves oxidative addition of H^+ to $Rh_2b_4^{2+}$ (30), followed either by reaction of the unstable hydride with another proton (31), or by direct elimination of H_2 from a tetranuclear dihydride intermediate (33):

$$Rh_2b_4^{2+} + H^+ \xrightarrow{12\,M\,\mathrm{HCl}} Rh_2b_4H^{3+} \qquad (30)$$

$$Rh_2b_4H^{3+} + H^+ \xrightarrow{12\,M\,\mathrm{HCl}} Rh_2b_4^{4+} + H_2 \qquad (31)$$

$$Rh_2b_4^{2+} + Rh_2b_4^{4+} \xrightarrow{12\,M\,\mathrm{HCl}} Rh_4b_8Cl_2^{4+} \qquad (32)$$

$$2Rh_2b_4H^{3+} \longrightarrow [Rh_4b_8H_2]^{6+} \xrightarrow{12\,M\,\mathrm{HCl}} Rh_4b_8Cl_2^{4+} + H_2 \qquad (33)$$

Thus the system that could have been an example of scheme (20)–(22) is in reality a complicated special case. If we continue to pursue schemes (20)–(22) and (23)–(24), then we must pick clusters whose redox potentials are somewhat more positive than $Rh_2b_4^{2+}$, and ones that are not likely to fall into an intermediate 'oligomeric trap' ($Rh_4b_8Cl_2^{4+}$) after one-electron oxidation.

One cluster system that offers an opportunity to demonstrate (20)–(22) or (23)–(24) has an octahedral (d^4) core, as for example in $Mo_6Cl_{14}^{2-}$. We have shown that this species can be oxidized to $Mo_6Cl_{14}^-$ by electron transfer quenching of $Mo_6Cl_{14}^{2-*}$ (180 μs in CH_3CN; 2eV) by various acceptors (Fig. 5) [16] and experiments in strong acid solutions aimed at direct hydrogen generation are underway. The two-electron oxidized state (Mo_6Cl_{14}) should be extremely unstable in this system, and may not be accessible. However, there is a chance at extremely high [Cl^-] that some stabilization could come from anion binding ($Mo_6Cl_{15}^-$), allowing the following photochemistry to take place:

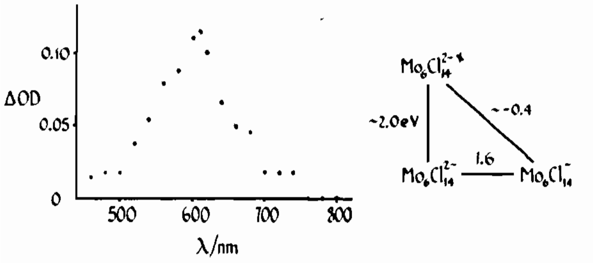

Fig. 5. Transient difference spectrum 80 μs after flash irradiation of a solution of methylviologen (MV^{2+}) and $Mo_6Cl_{14}^{2-}$ ($(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN, 300 K). The absorption system near 600 nm is attributable to MV^+. A modified Latimer diagram including $Mo_6Cl_{14}^{2-}$, $Mo_6Cl_{14}^-$, and $Mo_6Cl_{14}^{2-*}$ appears on the right-hand side (electrode potentials, V *vs.* SCE in CH_3CN solution).

$$Mo_6Cl_{14}^{2-} + H^+ \underset{}{\overset{12\,M\,\mathrm{HCl}}{\rightleftarrows}} Mo_6Cl_{14}H^- \qquad (34)$$

$$Mo_6Cl_{14}H^- \xrightarrow{h\nu} Mo_6Cl_{14}H^{-*} \qquad (35)$$

$$Mo_6Cl_{14}H^{-*} + H^+ \xrightarrow{(Cl^-)} Mo_6Cl_{15}^- + H_2 \qquad (36)$$

$$Mo_6Cl_{15}^- + Mo_6Cl_{14}^{2-} \longrightarrow 2Mo_6Cl_{14}^- + Cl^- \qquad (37)$$

The overall reaction would be:

$$2Mo_6Cl_{14}^{2-} + 2H^+ \xrightarrow{h\nu} 2Mo_6Cl_{14}^- + H_2 \qquad (38)$$

The redox potential of the octahedral $(d^4)_6$ core cluster can be tuned in at least three ways. Fine tuning can be done by substitution of Cl^- in $Mo_6Cl_{14}^{2-}$ by other ligands (*e.g.*, Br^-). More dramatic electronic perturbations may be achieved by changing Mo(II) to W(II) in the core, and asymmetry may be built in by isoelectronic substitutions such as Nb(I) for Mo(II).

A variation on the main theme has been explored briefly in our laboratory. As it deserves a closer look in future work, we close by outlining the strategy involved. The required ingredient in this photochemistry is a relatively long-lived metal cluster excited state, one that can engage in bimolecular electron transfer quenching in solution. Quenching by a donor should produce a reactive cluster species, which under appropriate conditions (again high [H^+] may be required) could generate H_2 faster than the bimolecular one-electron transfer back reaction:

$$M_n^* + D \longrightarrow M_n^- + D^+ \qquad (39)$$

$$M_n^- + 2H^+ \longrightarrow M_n^+ + H_2 \qquad (40)$$

$$M_n^+ + D \longrightarrow M_n + D^+ \qquad (41)$$

The net result would be the following conversion:

$$2D + 2H^+ \xrightarrow[M_n]{h\nu} 2D^+ + H_2 \qquad (42)$$

Clearly, further variations can be explored in strong acid solutions, starting with M_nH^{+*} or $M_nH_2^{2+*}$, and these could be more successful in competition with the back reaction.

Milder's study of the $^3A_{2u}$ excited state of $Rh_2b_4^{2+}$ demonstrates [17] that reaction (39) can be achieved with a relatively poor electron donor (TMPD, tetramethylphenylenediamine):

$$Rh_2b_4^{2+*}(^3A_{2u}{:}8.5\mu s;\ 1.7eV) + \mathrm{TMPD} \xrightarrow{CH_3OH} Rh_2b_4^+ + \mathrm{TMPD}^+ \qquad (43)$$

Because the back electron transfer reaction ($Rh_2b_4^+$ and $TMPD^+$) is diffusion-limited ($k \sim 10^9\ M^{-1}\ s^{-1}$), the rate of reduction of protons by $Rh_2b_4^+$ must exceed $10^3\ s^{-1}$ to achieve any significant degree of hydrogen production. In recent experiments we have shown that $Rh_2b_4^+$ does not reduce protons in neutral aqueous solution at rates anywhere near those needed, and only back electron transfer is observed [18]. It seems reasonable to suggest that again there could be an advantage in attempting such photochemical hydrogen production in strong acid solutions with clusters of higher reduction potentials. Experiments along these lines are planned.

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References

1 W. C. Trogler, G. L. Geoffroy, D. K. Erwin and H. B. Gray, *J. Am. Chem. Soc., 100,* 1160 (1978).
2 D. K. Erwin, C. L. Geoffroy, H. B. Gray, G. S. Hammond, E. I. Solomon, W. C. Trogler and A. A. Zagars, *J. Am. Chem. Soc., 99,* 3620 (1977).
3 P. K. Eidem and H. B. Gray, to be submitted for publication.
4 D. R. Tyler and H. B. Gray, *J. Am. Chem. Soc., 103,* 1683 (1981).
5 R. N. Goldberg and L. G. Hepler, *Chem. Rev., 68,* 229 (1968).
6 T. P. Sleight and C. R. Hare, *Inorg. Nucl. Chem. Lett., 4,* 165 (1968).
7 L. Moggi, G. Varani, M. F. Manfrin and V. Balzani, *Inorg. Chim. Acta, 4,* 335 (1970).
8 W. L. Waltz and A. W. Adamson, *J. Phys. Chem., 73,* 4250 (1969).
9 C. K. Jφrgensen, *Acta Chem. Scand., 10,* 500 (1956).
10 C. K. Jφrgensen, *Mol. Phys., 2,* 309 (1959).
11 M. J. Blandamer and M. F. Fox, *Chem. Rev., 70,* 59 (1970).
12 P. L. Airey and F. S. Dainton, *Proc. Roy. Soc. A, 291,* 340 (1966).
13 A. W. Maverick and H. B. Gray, *Pure Appl. Chem., 52,* 2339 (1980).
14 K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond and H. B. Gray, *J. Am. Chem. Soc., 99,* 5525 (1977).
15 I. S. Sigal, K. R. Mann and H. B. Gray, *J. Am. Chem. Soc., 102,* 7252 (1980).
16 A. W. Maverick and H. B. Gray, *J. Am. Chem. Soc., 103,* 1298 (1981).
17 S. J. Milder, H. B. Gray, R. A. Goldbeck and D. S. Kliger, *J. Am. Chem. Soc., 102,* 6761 (1980).
18 A. W. Maverick, unpublished results (1979–80).