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Cobalt(III) Sepulchrate: A New Relay for Water Splitting Photochemical Cycles

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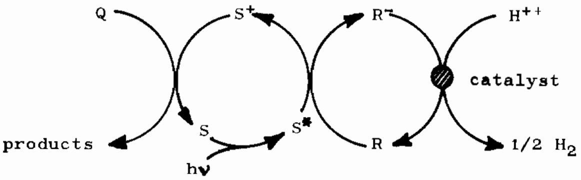
Most of the currently studied systems for the photochemical conversion of solar energy are based on photoredox water splitting cycles (Scheme I), which make use of an electron mediator, usually called a *relay* [1, 2]. The role of the relay (R) is to accept an electron from the excited sensitizer (S*) and to use it in the catalyzed reduction of water to hydrogen. For study purposes, the oxidized sensitizer (S^+) is often prevented from reacting with the reduced relay (R^-) by scavenging with some 'sacrificial' agent (Q), although the ultimate goal remains that of closing the cycle with water oxidation. Many types of molecules have been proposed and tested as sensitizers in cycles of this type [1–4]. By contrast, the available choice of relay species is by now very limited, with methylviologen (1,1′-dimethyl, 4,4′-bipyridinium cation) being by far the most popular [1–4].



Scheme 1

Actually, an ideal relay should satisfy the following rather stringent set of conditions: (i) it must undergo reversible reduction at a reasonable, negative standard potential (practically, $-0.8 < E^\circ < -0.2$ V); (ii) it should have good kinetic factors for outer-sphere electron transfer reactions (*i.e.*, high self-exchange rate); (iii) it should be intrinsically inert both thermally and photochemically (at least in the visible region); (iv) it should not be susceptible to degradation in the reaction conditions of the cycle, notably under hydrogenation conditions. The reasons for the use of methylviologen lie in its satisfactory fulfillment of conditions (i) to (iii). However, the aromatic nucleus of methylviologen is quite inclined to hydrogenation [5]. In fact, its degradation is considered to be the main reason for the progressive loss in efficiency of hydrogen production with time of irradiation.

If new relay systems have to be examined, the following considerations should be borne in mind. Organic molecules do not seem to be good candidates since saturated compounds are not likely to be reducible at reasonable potentials, and unsaturated ones are susceptible to hydrogenation. As far as inorganic substances are concerned, the presence of transition metals seems to be necessary in order to keep the reduction potentials within reasonable limits. On the other hand, inorganic or fully saturated organic ligands should be preferred to unsaturated ones (*e.g.* polypyridines). Along these lines, a number of metal aquo ions (*e.g.*, Eu^{3+}_{aq}, $V(H_2O)_6^{3+}$) and amine-type metal complexes (*e.g.*, $Co(en)_3^{3+}$) could be considered as candidates. Unfortunately, most of these species exhibit low self-exchange rates [6, 7], as the result of high intrinsic barriers and/or non-adiabaticity. Moreover, their reduced forms are often labile, giving rise to irreversible redox behavior. Thus, most of these simple fully inorganic species are not likely to satisfy conditions (i) and (ii), and cannot be considered as viable solutions to the relay problem.

Some years ago, Sargeson [8] synthesized the prototype of a very interesting class of complexes containing the sexadentate polyamine sepulchrate ligand and encapsulated metal ions, namely Co(sepulchrate)$^{3+}$. This complex exhibits the following remarkable properties [8]: (i) it undergoes *reversible* reduction at −0.54 V *vs.* SCE; (ii) the reduced Co(II) complex is appreciably *inert* both with respect to ligand substitution and to metal exchange; (iii) the self-exchange electron transfer rate is relatively *high* ($5.1\ M^{-1}\ s^{-1}$, at $\mu = 0.2\ M$).

These features of Co(sep)$^{3+}$ sharply contrast with the behavior of 'normal' Co(III) complexes (*e.g.*, for $Co(en)_3^{3+}$ the reduction occurs irreversibly at −0.45 V *vs.* SCE, the self-exchange rate constant is $3.4 \times 10^{-5}\ M^{-1}\ s^{-1}$ at $\mu = 0.2\ M$, and the Co(II) product is extremely labile) [9]. Although the reasons of these effects of the 'cage' structure of the ligand are still far from being completely understood [9], the above properties make Co(sep)$^{3+}$ a very

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attractive candidate for use as a relay. We report here some preliminary results obtained with this system.

In aqueous solution, Co(sep)$^{3+}$ quenches the excited state of tris(bipyridine)ruthenium(II), Ru(bpy)$_3^{2+}$. The quenching occurs by electron transfer, as shown by transient reversible bleaching of the Ru(bpy)$_3^{2+}$ absorption in laser flash photolysis experiments. The bimolecular quenching constant, 3.6×10^8 M^{-1} s^{-1} in 1 M H_2SO_4, is larger than the corresponding one for Co(en)$_3^{3+}$ (6.2×10^7 M^{-1} s^{-1} under the same conditions), in spite of the more negative reduction potential of Co(sep)$^{3+}$. This is no doubt due to the high self-exchange rate of the sepulchrate complex.

On the basis of these results, Co(sep)$^{3+}$ has been used as a relay in a sacrificial cycle of the type shown in Scheme I, using Ru(bpy)$_3^{2+}$ as sensitizer, EDTA as sacrificial scavenger, and colloidal platinum as catalyst. Immediate hydrogen evolution was observed upon exposure to light, comparable in efficiency to that observed with the same cycle using methylviologen as relay. Experiments are in progress to monitor the evolution of hydrogen over long irradiation periods, in order to check if Co(sep)$^{3+}$ gives, as expected, more sustained hydrogen production than methylviologen.

In conclusion, we consider Co(sep)$^{3+}$ to be a very promising relay for water-splitting cycles. This new relay is inexpensive and probably resistant to degradation under hydrogenation conditions.

Acknowledgement

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