

MECHANISMS OF PHOTOCHEMICAL REACTIONS OF TRANSITION METAL COMPLEXES: EXCITED STATE ELECTRON TRANSFER AND ORGANOMETALLIC PHOTOCHEMISTRY

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1. Introduction

Inorganic photochemistry is a field that once focused on the substitution and redox chemistry of Werner complexes in aqueous media [1]. Now, the field includes significant contributions involving many classes of compounds involving many different types of one-electron excited states (see for example ref. 2 for a series of papers on the state of the art in inorganic photochemistry). In this retrospective view I shall focus on two areas of the field where remarkable progress has been made and where much can be expected in the future: excited state electron transfer and organometallic photochemistry.

2. Electron transfer to and from photoexcited metal complexes

The fact that a photoexcited molecule can be a more potent oxidant and a more potent reductant than the ground state can, in principle, be exploited to effect the conversion of light to chemical and/or electrical energy. No additional evidence beyond the knowledge that natural photosynthesis works is needed to establish that photochemical energy conversion is a practical possibility. For inorganic photochemists a 1972 report by Gafney and Adamson [3] on $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} \equiv 2,2'$ -bipyridine) can be regarded as the initial stimulation for an enormous thrust in research of excited state electron transfer reactions of metal complexes. Much of the research has been carried out with the hope of being able to sensitize the oxidation and reduction of H_2O to effect the generation of fuel (H_2 and O_2) from H_2O and sunlight. The research has involved some of the most active groups in inorganic photochemistry and many reviews have appeared from these groups in recent years [4 - 9].

The research of excited state electron transfer of metal complexes has involved not only $\text{Ru}(\text{bpy})_3^{2+}$ and related osmium species, but also complexes having metal-metal bonds such as $\text{Re}_2\text{Cl}_8^{2-}$ [10] and

$\text{Ph}_3\text{SnRe}(\text{CO})_3(1,10'\text{-phenanthroline})$ ($\text{Ph} \equiv \text{phenyl}$) [11], as well as high nuclearity systems such as $\text{Mo}_6\text{Cl}_{14}^{2-}$ [12]. A feature that these systems have in common is that the lowest excited state is relatively long lived and generally emissive in fluid solution at room temperature. The long lifetime is essential to the ability to quench efficiently the excited species in a bimolecular reaction:

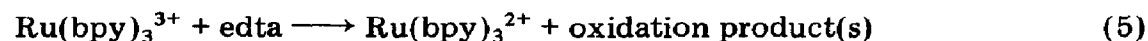
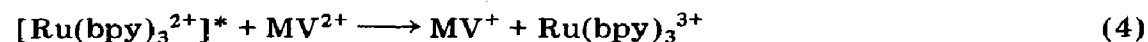


The discovery of a large number of long-lived photoexcited transition metal complexes in the past dozen years has been crucial to the development of the present understanding of the various excited state processes in general and, in particular, has allowed the detailed investigation of bimolecular electron transfer reactions.

Studies of the electron transfer quenching of excited metal complexes have revealed a great deal about the properties of the metal complexes, but there has been only limited success in sensitizing the sustained formation of high energy redox products such as H_2 and O_2 from H_2O . Generally, the excited complexes are only one-electron transfer reagents, while the desired products require more than one electron per molecule formed. The basic difficulty stems from the fact that the ultimate formation of energy-rich redox products involves a primary one-electron step as in eqn. (1a) or eqn. (1b). The primary products $\text{M}^+ + \text{Q}_1^-$ or $\text{M}^- + \text{Q}_2^+$ are thermodynamically unstable *as desired* but, unfortunately, the primary products are generally labile and react rapidly according to



So-called back reactions of this kind degrade optical energy to heat. There are many schemes where a sacrificial reagent such as ethylenediaminetetraacetic acid (edta) allows the generation of H_2 as in



In this scheme MV^{2+} is N,N' -dimethyl-4,4'-bipyridinium and the catalyst can be a suspension of platinum of high surface area. In this complicated, but now familiar, scheme the edta is irreversibly oxidized by the primary photo-generated oxidant $\text{Ru}(\text{bpy})_3^{3+}$ to regenerate $\text{Ru}(\text{bpy})_3^{2+}$, precluding back

reaction with the reductant MV^+ that can be used to generate H_2 via a catalyzed process (eqn. (6)). Unfortunately, H_2 generation occurs at the expense of edta. In such a case it is not even evident that the net sensitized reaction is an overall up-hill process.

The $Ru(bpy)_3^{3+}$ formed in the quenching step (eqn. (4)) is a sufficiently potent oxidant that H_2O could be oxidized to O_2 , but this four-electron process, like H_2 evolution, requires catalysis. A catalyst system that will allow the use of H_2O as the only sacrificial reagent in the photosensitized formation of H_2 and O_2 has not yet been devised. The photosynthetic system uses CO_2 and H_2O as sacrificial reagents to effect formation of reduced carbon compounds and O_2 . A key to the efficiency of the photosynthetic system is likely to be the structured arrangement of the components of the photosynthetic apparatus that cannot be imitated by homogeneously dissolved complexes. The natural apparatus is arranged such that back reaction of early high energy redox products is inhibited. Transition metal complexes that efficiently absorb light and undergo electron transfer processes to give energetic redox products exist. However, effective inhibition of the back reaction has not been achieved with molecular-based systems. This problem is of paramount significance and is the key to success in photochemical energy conversion. Future work will probably be directed toward interfacial systems where some success has already been realized, as at semiconductor-liquid electrolyte interfaces [13].

While the practical objective of energy conversion has not yet been realized, the area of excited state electron transfer will remain active in order to continue the establishment of the basic properties of excited states. Additional application areas may include imaging systems and stoichiometric synthesis, both of which may prove easier to achieve than large-scale energy conversion systems. In many situations it will be necessary to synthesize organized assemblies, in order to achieve desired results; this will be especially important to achieve efficient photochemical energy conversion.

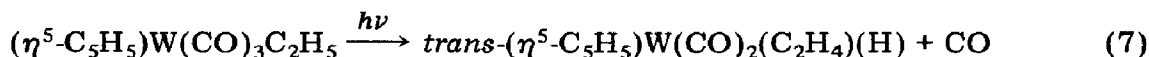
3. Organometallic photochemistry

Organometallic complexes have been the object of intense study in several major research groups. Much of the work has been carried out with the underlying objective of synthesizing new catalysts and reactive intermediates. The photoinduced reductive elimination of H_2 from dihydrides and polyhydrides to generate coordinatively unsaturated species (typically 16-electron complexes) has been established as a major photoreaction class [14]. Additionally, metal-metal bond cleavage has been established as a general photoreaction class for complexes having two-electron metal-metal bonds [15], *e.g.* $Mn_2(CO)_{10}$, to give 17-electron radicals and more recently 15-electron radicals from Pd-Pd cleavage in $Pd_2(CNR)_6^{2+}$ [16]. However, as for many classical Werner complexes [1], ligand photosubstitution of organometallic complexes, and especially of metal carbonyls, has been the

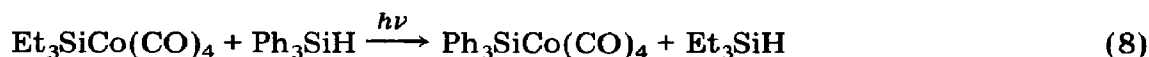
most active area of organometallic photochemistry [17]. For organometallic complexes, however, the photosubstitution chemistry is being extended to the study of high nuclearity clusters such as $H_4Ru_4(CO)_{12}$ [18]. Two of the dominant themes in organometallic photochemistry that will continue to thrive are low temperature photochemistry and catalysis.

The application of low temperature matrix photochemistry techniques to organometallic complexes has proven fruitful in characterizing photogenerated intermediates and in establishing mechanisms of photochemical reactions at room temperature. Early experiments concerned the study of $M(CO)_6$ by Sheline and coworkers [19]. In the early 1970s Turner and coworkers made significant contributions showing that a large number of mononuclear metal carbonyls $XYM(CO)_n$ lose CO to give coordinatively unsaturated, typically 16-electron, complexes $XYM(CO)_{n-1}$ that can be spectroscopically characterized in rigid matrices [20]. Many additional reports have followed that directly establish the nature of the intermediates in room temperature photoreactions (see for example ref. 21). Recent attention has turned to dinuclear [22], trinuclear [23] and tetranuclear [18] clusters with the first examples of the photogeneration of coordinative unsaturation in higher nuclearity clusters. These results are of possible consequence because of the belief that clusters may serve as models for heterogeneous metallic catalysts.

The combination of low temperature photolysis followed by warm-up can lead to direct observation of the elementary steps in a room temperature photoreaction. A simple example is to warm a photogenerated 16-electron species in the presence of a two-electron donor ligand to observe the generation of a net photosubstitution product. The unimolecular reaction represented by



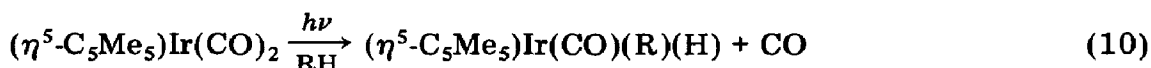
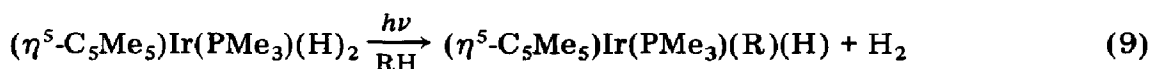
has been shown [24] to proceed via primary loss of CO to give a 16-electron species that can be detected at 77 K. The 16-electron species gives the final product thermally on warming to 196 K with a half-life $t_{1/2} \approx 10$ s. Such chemistry can also be monitored when the organometallic species is anchored to a surface [25]. The exciting prospect for surface-bound molecules is that it may be possible to generate active sites selectively on surfaces and to study interfacial reactions with molecular specificity. In a more complex situation, the bimolecular photochemistry represented by



(Et \equiv ethyl) has been shown [26] to proceed via (i) photochemical loss of CO, (ii) thermal oxidative addition of Ph_3SiH , (iii) thermal reductive elimination of Et_3SiH and (iv) thermal uptake of CO. Each of the intermediates has been observed spectroscopically. Such systems establish that relatively complex photoreaction mechanisms can be established. It is likely that the

methodology can be used to establish the viability of catalytic cycles. The essential is that there be a thermally inert, but photolabile, precursor to each proposed intermediate. A start has been made in the observation of all intermediates in the $\text{Fe}(\text{CO})_5$ -photocatalyzed isomerization of alkenes [27], and in catalyzed reactions of alkynes using carbene complexes [28].

Concerning catalysis, it is worth noting the application of organometallic photochemistry in the discovery of the first examples of addition of simple alkanes, RH , to discrete metal complexes [29, 30] ($\text{Me} \equiv \text{methyl}$):



These reactions proceed, presumably, via primary loss of H_2 and CO respectively to give very active 16-electron species. These systems may provide the basis for photochemical functionalization of alkanes.

The future of organometallic photochemistry is bright. New detailed understanding of electronic structure of complexes having unusual geometrical structures will lead to new photochemistry in that new intermediates can be generated from the common ligand extrusion or metal-metal bond cleavage reactions. Additionally, the application of fast kinetic techniques, especially those employing molecular specific diagnostics, in this area will prove very fruitful in unravelling mechanisms of stoichiometric and catalytic reactions. A conscious effort to discover new photoreactions will probably be very fruitful inasmuch as there are major classes of organometallic complexes that have not been systematically investigated.

Acknowledgments

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