



PERIYAR GOVT. ARTS COLLEGE , CUDDALORE
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UNIT V

INORGANIC PHOTO CHEMISTRY

The Photochemistry of Transition-Metal Complexes

○ What is the nature of the interaction of light with matter?

- For an effective electronic transition, there must be an interaction between the electric field vector of the light and the electric dipole of the molecule.
- The probability of absorption is expressed by the well-known Beer-Lambert law.

$$A = \epsilon cl = \log \frac{I_0}{I}$$

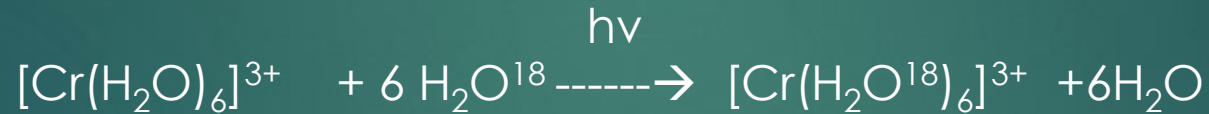
○ Electronic transitions for coordination compounds

- A large variety of electronic transitions are possible for coordination compounds. Two of those which are encountered most frequently, d-d transitions and ligand-to-metal charge transfer transitions (LMCT).
- The efficiency of a particular primary process is quantified by a quantum yield.

$$\phi = \frac{\text{no of molecules undergoing that process}}{\text{no of photons absorbed by the reactant}}$$

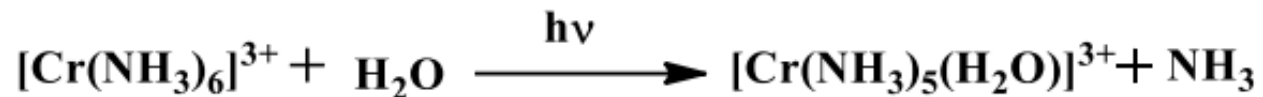
Photoaquation Reactions

- * Ligand field irradiation of chromium(III) complexes leads primarily to substitution reactions.
- * The most common reaction in aqueous solution is photosubstitution of a ligand by water. Photoaquation reactions involving light-induced exchange of water between $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and the solvent. The reaction is followed by using isotopically labeled H_2O^{18} as the solvent, where sequential photosubstitution of the H_2O molecules leads to the formation of $[\text{Cr}(\text{H}_2\text{O}^{18})_6]^{3+}$

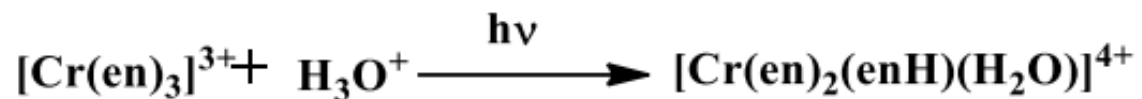


- * The quantum yields at 261, 408, and 574 nm are rather low ($\phi = 0.02$) and wavelength independent. These low quantum yields for the aquation reaction correspond with a mechanism involving labilization of a water ligand in the excited state

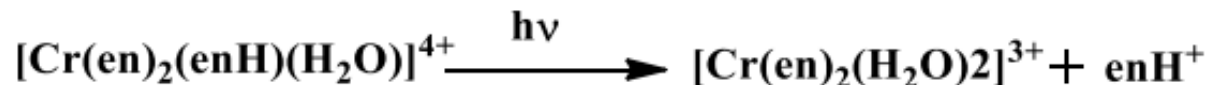
- For other octahedral complexes such as $[\text{Cr}(\text{NH}_3)_6]^{3+}$, the first step in the photoreaction in aqueous solution involves photoaquation of one of the ammonia ligands to give $[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$



- For the corresponding hexacoordinated tris chelated complex $[\text{Cr}(\text{en})_3]^{3+}$, the initial photoreaction leads to substitution at one of the coordination positions to give $[\text{Cr}(\text{en})_2(\text{enH})(\text{H}_2\text{O})]^{4+}$. This photoreaction involves dissociation of one end of a coordinated ethylenediamine, followed by protonation of the nitrogen on the free "hinged" ethylenediamine arm of the chelate.



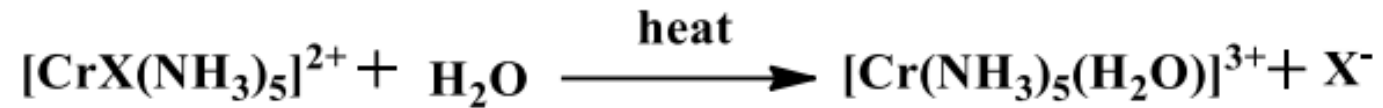
- This "hinging" reaction is then followed by a second photoaquation step to give $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$, a reaction that results in displacement of the monodentate enH ligand by water.



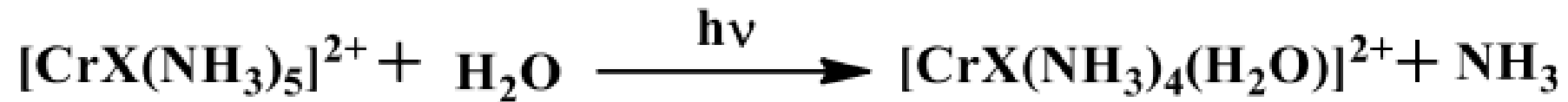
- The quantum yields for the different complexes cover a relatively small numerical range, which is indicative of a similar photoaquation mechanism for all of these different complexes.

Complexes	Quantum Yield
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	0.02
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	0.3
$[\text{Cr}(\text{en})_3]^{3+}$	0.37
$[\text{Cr}(\text{CN})_6]^{3-}$	0.12
$[\text{Cr}(\text{NCS})_6]^{3-}$	0.26
$[\text{Cr}(\text{urea})_6]^{3+}$	0.10
$[\text{Cr}(\text{oxalate})_3]^{3-}$	0.09

- Mixed-ligand complexes of chromium(III) also undergo photoaquation reactions.
- Under thermal conditions, aquation of the halide ion (X⁻) is the preferred pathway.

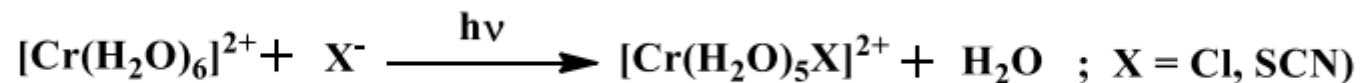


- * Under the influence of light, photoaquation of an ammine ligand is the preferred pathway
- * The stereochemical origin of the labilized NH₃ is trans to the coordinated Cl⁻ as shown by isotope-labeling experiments, although the final reaction product has the cis configuration':



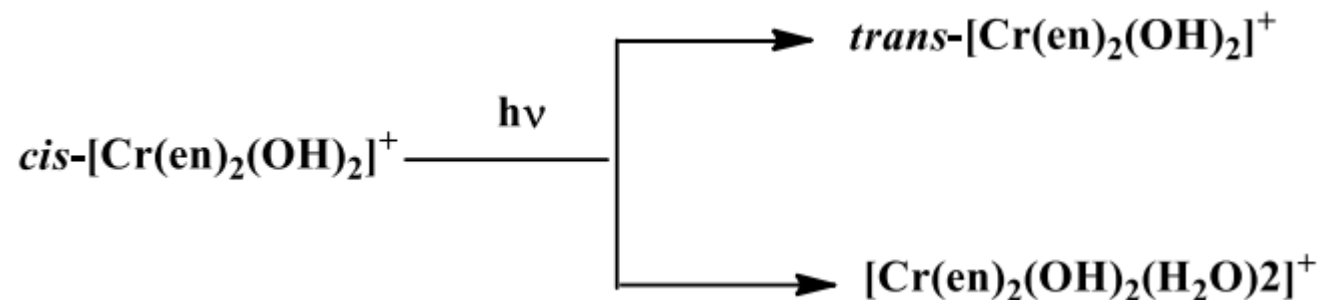
Photoanation Reactions

- Chromium(III) complexes also undergo photoanation reactions. When aqueous solutions of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ are photolyzed in the wavelength range of 400-575 nm in the presence of Cl^- or SCN^- , replacement of a water molecule by the anionic ligand occurs.



* A comparative study of the photoaquation and photoanation reactions has been carried out by photolyzing $[\text{Cr}(\text{NH}_3)_6]^{3+}$ in an aqueous solution containing added chloride ion. Aquation and anation therefore only compete with each other for the vacant coordination position in $[\text{Cr}(\text{NH}_3)_5]^{3+}$ that is formed by the photodissociation of an ammonia molecule.

- An associative mechanism involving a heptacoordinate has also been proposed to explain the stereochemical specificity in the photoaquation of substituted ammine complexes,
- Photoaquation can also be accompanied by isomerization of the metal complex. An example is found in the photochemistry of $\text{cis}-[\text{Cr}(\text{en})_2(\text{OH})_2]^+$ where both photoisomerization to $\text{trans}-[\text{Cr}(\text{en})_2(\text{OH})_2]^+$ and photoaquation to $[\text{Cr}(\text{en})_2(\text{OH})_2(\text{H}_2\text{O})_2]^+$ are observed.



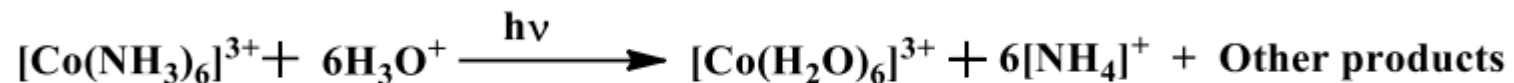
Photosubstitution and Photoredox Reactions

- The major photochemical pathway for cobalt(III) complexes in solution is substitution

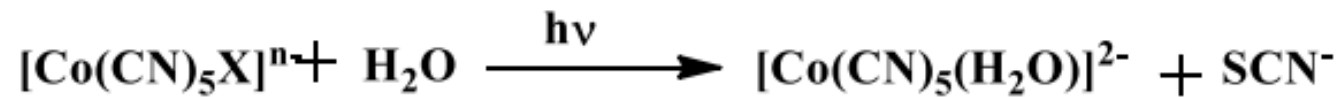


- This difference can be explained on the basis of the excited states of the two sets of complexes. Thus, while the lowest excited state of the hexacyano complexes have triplet character, that of the hexaammine complex has quintet character
- Irradiation at 254 nm into the charge transfer band of the cobalt(III) complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ results in photoredox reactions to give cobalt(II) complexes.

The overall reaction is



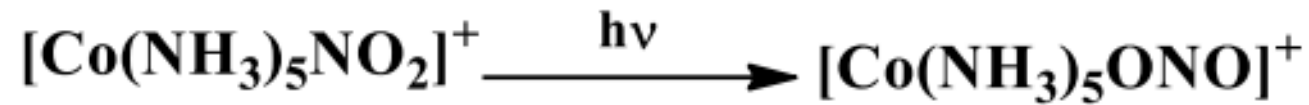
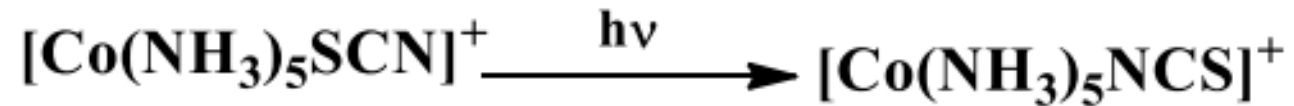
- Photolysis of the mixed-ligand complex ions $[\text{Co}(\text{CN})_5\text{X}]^{n-}$ [where, X is CN^- , N_3^- , Br^- , OH^- ($n = 3$) and H_2O ($n = 2$)] in the presence of thiocyanate ion gives primarily the aquation product $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$, along with the linkage isomers of the thiocyanate substitution product.



Photoisomerization Reactions

- Irradiation of $\text{cis-}[\text{CoCl}_2(\text{en})_2]^+$ in methanol solution into the first charge transfer band results in isomerization to $\text{trans-}[\text{CoCl}_2(\text{en})_2]^+$.
- Isomerization of cobalt(III) complexes has been explained on the basis of the angular overlap model. This model is based on the assumption that the photosubstitution in the complex $[\text{MA}_4\text{XY}]$ occurs by loss of Y in the lowest triplet state.

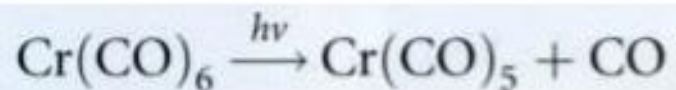
- Photo induced linkage isomerization of cobalt(III) ammine complexes has also been observed when one of the ligands is ambidentate.



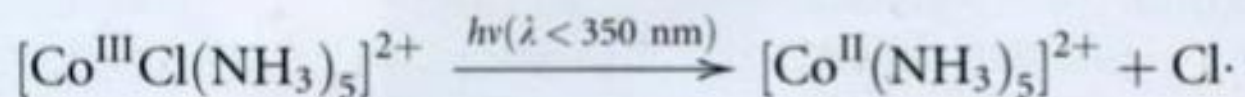
- These photoisomerization reactions are believed to proceed via a pathway where irradiation leads to a thermally equilibrated LMCT excited state. In this excited state, the complex dissociates to give the radical pair.

Prompt and delayed reactions

Key point: Reactions of electronically excited species are classified as prompt or delayed.



and the scission of Co—Cl bonds:



Both processes occur in less than 10 ps and hence are called **prompt reactions**.

Transitions in metal-metal bonded systems

Key points: Population of a metal–metal antibonding orbital can sometimes initiate photodissociation; such excited states have been shown to initiate multielectron redox photochemistry.

d-d and charge-transfer reactions

Key point: A useful first approximation is to associate photosubstitution and photoisomerization with $d-d$ transitions and photoredox reactions with charge-transfer transitions, but the rule is not absolute.

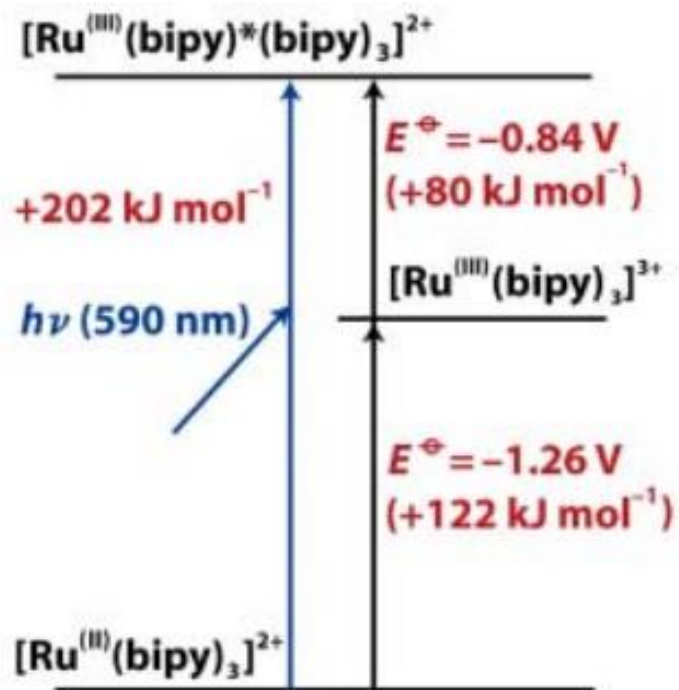


Fig. 20.23 The photoexcitation of $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{2+}$ can be treated as if the excited state is a Ru^{III} cation complexed to a radical anion of the ligand.

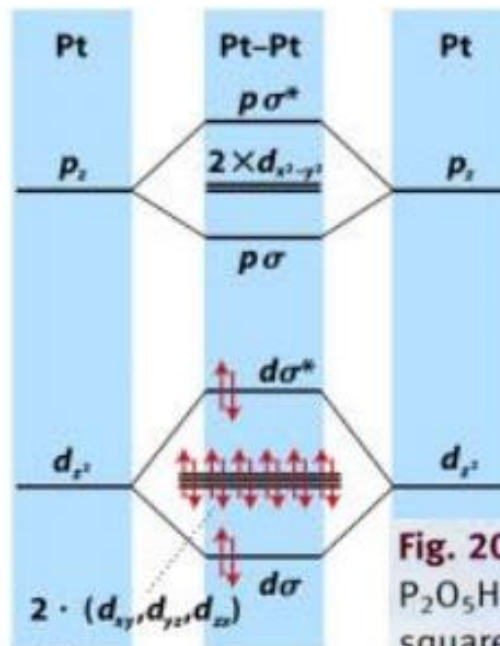


Figure 20.24
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by S. L. Friess, P. W. Atkins, T. L. Cottrell, J. F. Keenan, W. T. Miller, and

Fig. 20.24 The dinuclear complex $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]^{4-}$ consists of two face-to-face square-planar complexes held together by a bridging pyrophosphito ligand. The metal p_z and d_{z^2} orbitals interact along the Pt–Pt axis. The other p and d orbitals are considered to be nonbonding. Photoexcitation results in an electron in the antibonding σ^* orbital moving into the bonding σ orbital.

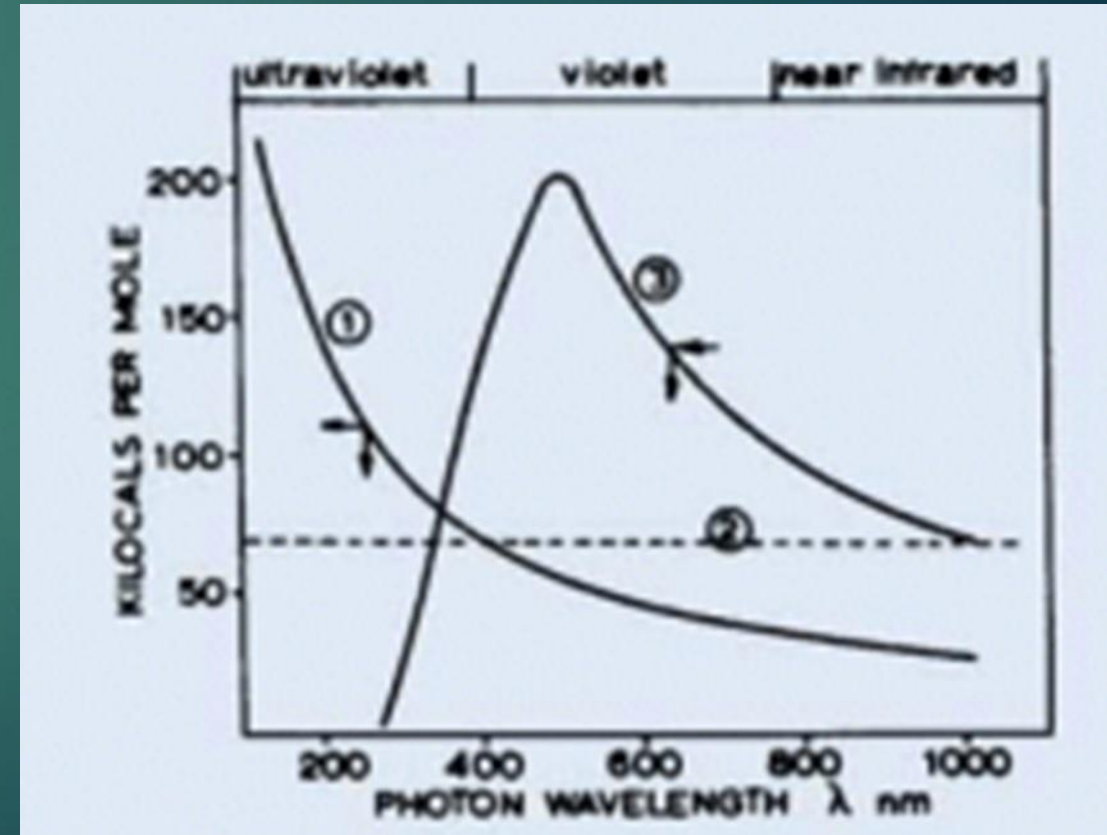
Solar Energy Conversion Using Platinum Group Metal Co-ordination Complexes

Co-ordination complexes of ruthenium and rhodium have been shown to have potential applications in solar energy conversion. When illuminated with visible light on a laboratory scale these complexes catalyse photolysis reactions or exhibit photogalvanic effects to produce hydrogen or electricity.

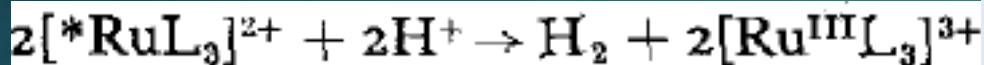
co-ordination complexes of ruthenium and rhodium in the photogeneration of hydrogen gas or electricity. Electrically generated power needs to be stored for use

Ruthenium Complexes for the Photolysis of Water

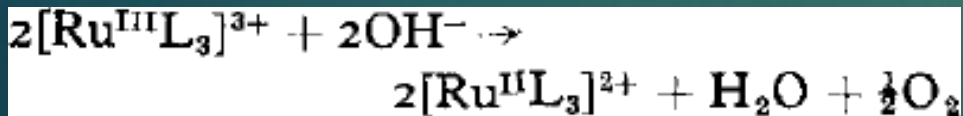
The cleavage of water into gaseous hydrogen and oxygen requires approximately 70 kcal/mol Light quanta in the visible region of the electromagnetic spectrum (400 to 700 nm) have low energies, [Figure 1](#), and therefore to achieve water photolysis in this region a step-wise process involving more than one photon is necessary. Moreover, since water is transparent to visible light a photo-catalyst is required to absorb the incident light and transfer its energy to water molecules *via* redox reactions.



Irradiation of the tris(2,2'-bipyridyl)ruthenium(II) cation, $[\text{Ru}(\text{bipy})_3]^{2+}$, with visible light results in the promotion of an electron from a molecular orbital of mainly metal character to one of mainly ligand character, [Figure 2](#). This charge transfer excited state can act as both an electron donor or electron acceptor and examination of the reduction potential for this energy-rich species indicates that it should reduce water, as protons, to hydrogen over a wide pH range. While this is a thermodynamically favourable reaction, in practice no reduction is observed and the continuing luminescence of the complex in aqueous solution suggests that the reduction reaction is too slow to compete with excited state decay. The reduction may also be inhibited by back electron transfer processes which regenerate the starting materials. If the reduction reaction

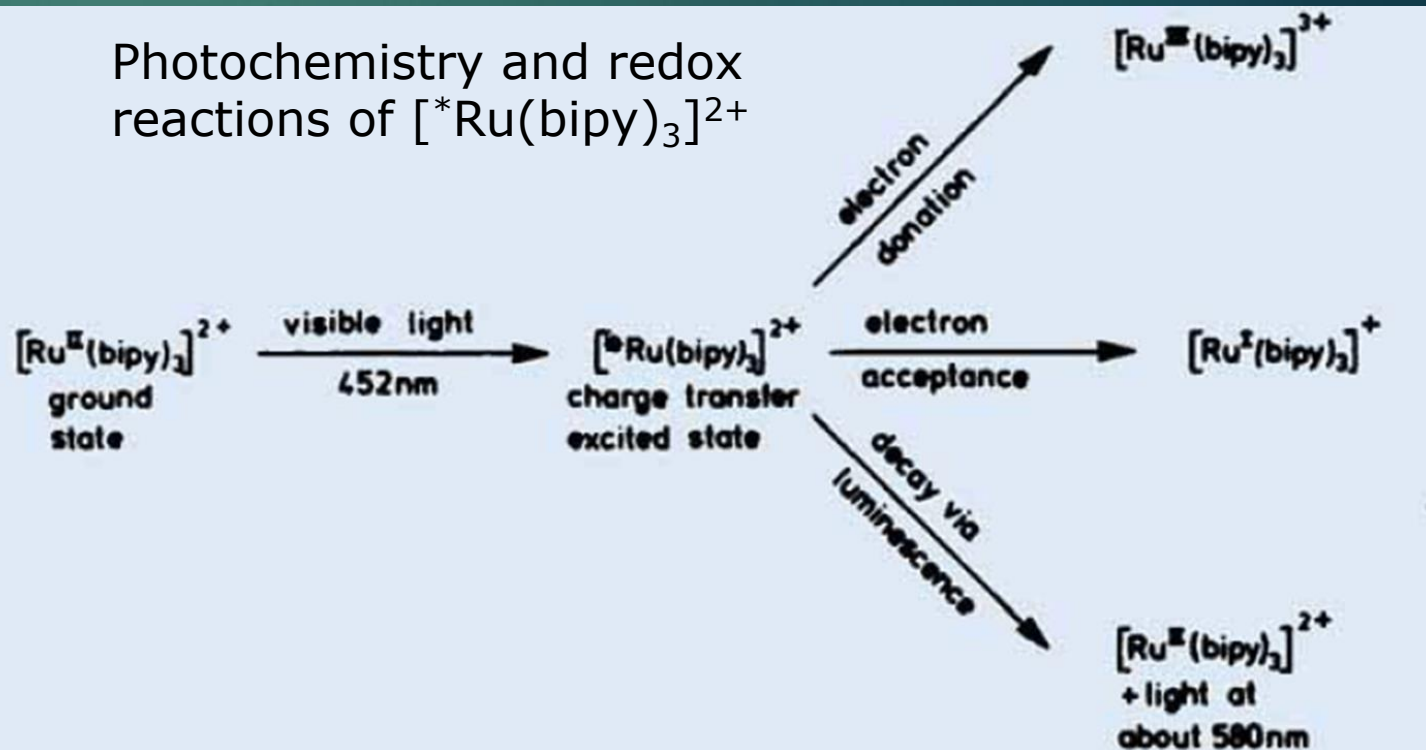


where $[\text{*RuL}_3]^{2+}$ is the excited state of the complex, could be achieved, then the previously reported oxidation of hydroxide ion



could occur. This would produce oxygen and regenerate the original ruthenium complex. The overall reaction would thus be the cyclic catalytic photolysis of water.

Photochemistry and redox reactions of $[\text{*Ru}(\text{bipy})_3]^{2+}$



In 1976 Whitten reported the catalytic photocleavage of water by ruthenium complexes containing bipyridyl ligands bearing long chain organic substituents

Probable impurities associated with the ruthenium complexes initially reported to photocleave water

The free radicals $\text{H}\cdot$ and $\cdot\text{OH}$ are likely intermediates in the catalytic photocleavage reported by Whitten and for the reaction to proceed both the recombination of these radicals to form water:



and back electron transfer reactions of the type must be inhibited.



Photogalvanic Cells Containing Ruthenium Complex Electrolytes

Illumination of dilute aqueous solutions of many redox couples leads to a change in the potential of the couple. Photogalvanic cells based upon this principle

the excited state of $[\text{Ru}(\text{bipy})_3]^{2+}$ can function as both an electron donor or electron acceptor, and photogalvanic cells in which the complex functions in either of these modes have been described recently.

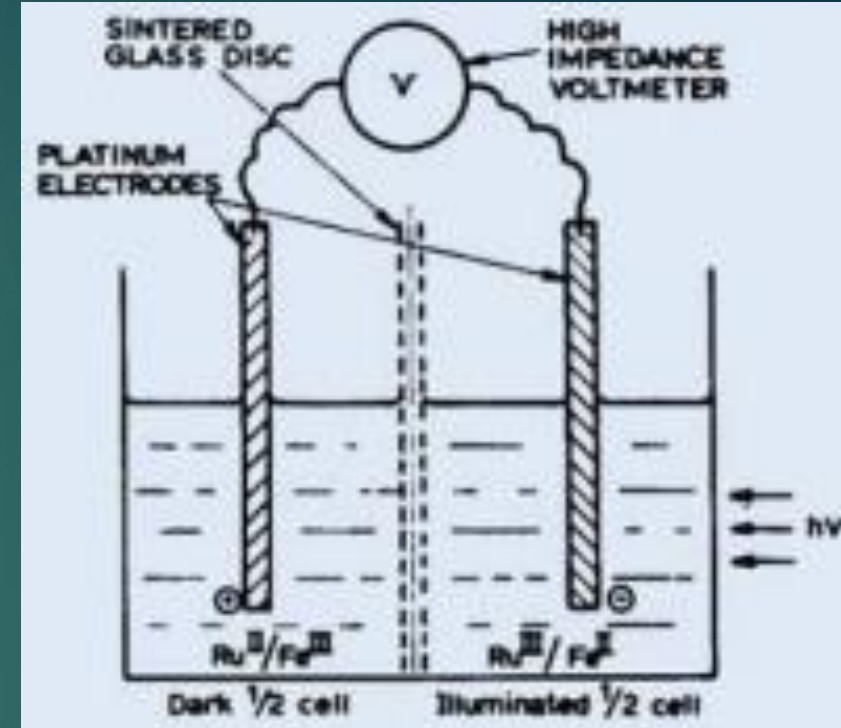
complex acting as an electron donor two half-cells both containing $[\text{Ru}(\text{bipy})_3]^{2+}$, Fe^{3+} and H_3O^+ are connected through an external circuit with one half-cell illuminated while the other is kept dark. In the illuminated half-cell photo-induced electron transfer generates $[\text{Ru}(\text{bipy})_3]^{3+}$ and Fe^{2+} :



A photogalvanic cell containing $[\text{Ru}(\text{bipy})_3]^{2+}$, Fe^{3+} and H_3O^+ in which the ruthenium complex functions as an electron donor

The changed composition of the illuminated half-cell results in a change in its potential relative to the dark half-cell and electrons flow through the external circuit in the direction determined by the dominant couple, from the dark to the illuminated half-cell.

The reversibility of the cell is ensured by mass transfer of Fe^{2+} to the dark half-cell where it reacts with anodically produced $[\text{Ru}^{\text{III}}(\text{bipy})_3]^{3+}$ to regenerate $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{2+}$ and Fe^{3+} .



In the absence of an efficient quencher, such as Fe^{3+} , the excited state ruthenium complex can function as an electron acceptor towards a gold electrode. The reactions occurring in this cell are:

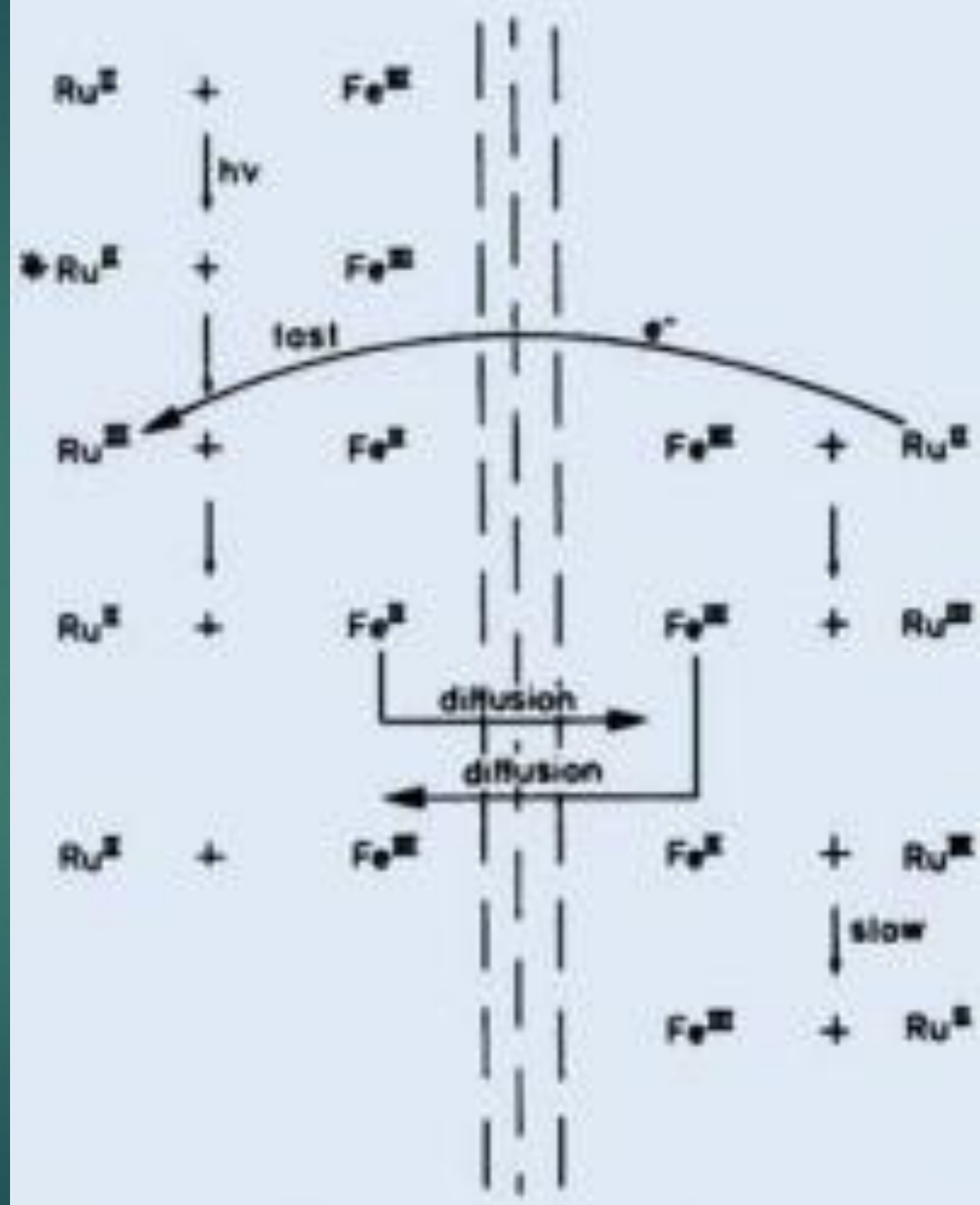


at the illuminated cathode



at the dark anode.

A photocell based on $[\text{Ru}(\text{bipy})_3]^{2+}$ which contains a metal electrode and an n-type semiconductor electrode immersed in a solution of the complex buffered at pH 9 and connected *via* an external circuit. It was proposed that illumination at the semiconductor electrode would produce $[\text{Ru}^{\text{I}}(\text{bipy})_3]^{2+}$ which, under favourable conditions, would inject an electron into the conduction band of this electrode leaving $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{3+}$ which could then oxidise hydroxide ions to oxygen as previously described.



The electron at the semiconductor electrode would flow through the external circuit to reduce water or hydrogen ions at the metal electrode to dihydrogen:

