

## LIGHT-INDUCED ELECTRON TRANSFER REACTIONS\*

NORMAN SUTIN

*Chemistry Department, Brookhaven National Laboratory, Upton, N.Y. 11973 (U.S.A.)*

(Received August 18, 1978)

### Summary

The reactions of the luminescent excited states of the polypyridine-ruthenium(II) complexes ( $*\text{RuL}_3^{2+}$ ) with electron acceptors and donors are discussed. These electron transfer reactions convert the excited state into  $\text{RuL}_3^{3+}$  and  $\text{RuL}_3^+$ , respectively. The former ruthenium complex is a more powerful oxidant and the latter is a more powerful reductant than the excited state itself. Some applications of these complexes in the conversion and storage of solar energy are presented. Theoretical models for electron transfer reactions are described and the implications of these models for the quenching and back electron transfer reactions are discussed. It is pointed out that the exploitation of the inverted region may provide a useful means of slowing down back electron transfer reactions.

---

### 1. Introduction

This article is concerned with the photo-induced electron transfer reactions of metal complexes in solution. This is a broad subject and the principles will be illustrated by considering the ground and excited state reactions of the polypyridine-ruthenium complexes. These systems have been extensively studied in recent years, so much so that they could be regarded as the inorganic chemists' answer to the challenge of photosynthesis. Indeed, examination of the current literature shows that work on porphyrin- and polypyridine-related systems are at roughly comparable stages of development, at least so far as their ability to effect the photo-induced decomposition of water is concerned. Since the thermodynamic aspects of photochemical energy conversion have been considered in several publications [1 - 3] these will not be discussed here; instead the kinetic and mechanistic aspects of the problem will be emphasized. In so doing use will be made of theoretical

---

\*Paper presented at the Second International Conference on the Photochemical Conversion and Storage of Solar Energy, Cambridge, August 1978.

models that have been developed for thermal electron transfer reactions in solution, and, based upon these models, some criteria for selecting systems for study will be proposed.

The electron transfer reactions of the excited state of tris(2,2'-bipyridine)ruthenium(II) ( $*\text{Ru}(\text{bpy})_3^{2+}$ ) were first reported by Gafney and Adamson [4] while Creutz and Sutin [5] were the first to point out that the tris(bipyridine)ruthenium complexes might be capable of effecting the decomposition of water induced by visible light. Numerous investigators have contributed to characterizing the properties and reactions of  $*\text{Ru}(\text{bpy})_3^{2+}$  [6 - 23]. These studies have shown that the ground state complex absorbs visible light to form a d-to- $\pi^*$  charge transfer excited state which is relatively long lived (lifetime 0.6  $\mu\text{s}$  in water, Table 1) and which undergoes facile electron transfer reactions:



The formation of the excited state can be viewed as the creation of an electron-hole pair within the complex (eqn. 1). As a consequence the excited molecule is expected to be both a stronger reductant and a stronger oxidant than the ground state molecule by the excitation free energy of 2.1 eV. This is reflected in the reduction potentials shown in Table 2. It should be noted that  $*\text{Ru}(\text{bpy})_3^{2+}$  is not as good a reductant as  $\text{Ru}(\text{bpy})_3^+$  nor as good an oxidant as  $\text{Ru}(\text{bpy})_3^{3+}$ . It is also evident that the excited states of the  $\text{OsL}_3^{2+}$  and  $\text{FeL}_3^{2+}$  complexes tend to be shorter lived than those of the corresponding  $\text{RuL}_3^{2+}$  complexes (Table 1) and that  $*\text{Os}(\text{bpy})_3^{2+}$  is a better reductant and  $\text{Os}(\text{bpy})_3^{3+}$  a poorer oxidant than the ruthenium analogs (Table 2). It has not yet been determined whether the approximately 1 ns long excited state of the  $\text{FeL}_3^{2+}$  complexes is charge transfer or ligand field in character.

Unlike many metal complexes,  $\text{Ru}(\text{bpy})_3^{2+}$  does not readily undergo photochemical loss of ligands. In fact, in the absence of other reagents, this

TABLE 1

Excited state lifetimes for iron(II), ruthenium(II) and osmium(II) polypyridine complexes in water at 25 °C

Ligand L	$\text{FeL}_3^{2+}$ $\tau_0$ (ns) <sup>a</sup>	$\text{RuL}_3^{2+}$ $\tau_0$ (ns) <sup>b</sup>	$\text{OsL}_3^{2+}$ $\tau_0$ (ns) <sup>c</sup>
4,4'-( $\text{CH}_3$ ) <sub>2</sub> bpy	0.76	330	~ 9
bpy	0.81, 0.83 <sup>e</sup>	600	19
1,10-Phenanthroline(phen)	—	920	84
4,7-( $\text{C}_6\text{H}_4\text{SO}_3$ ) <sub>2</sub> phen <sup>2-</sup>	0.43	3860 <sup>d</sup>	—
Terpyridyl(terpy)	2.54	< 5, > 1.2 <sup>f</sup>	—

<sup>a</sup> From ref. 24; <sup>b</sup> from ref. 14; <sup>c</sup> from ref. 7; <sup>d</sup> from ref. 25, with  $\mu = 0.1 \text{ M}$ ; <sup>e</sup> from ref. 26; <sup>f</sup> from ref. 27.

TABLE 2

Formal reduction potentials<sup>a</sup> of iron(II), ruthenium(II) and osmium(II) polypyridine complexes at 25 °C

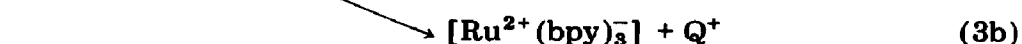
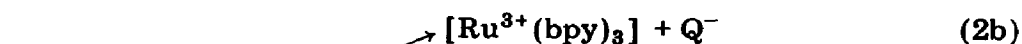
Couple	M = Fe $E^\circ$ (V)	M = Ru $E^\circ$ (V)	M = Os $E^\circ$ (V)
$M(\text{bpy})_3^{3+} + e = M(\text{bpy})_3^{2+}$	+1.05 <sup>b</sup>	+1.26 <sup>b</sup>	+0.82 <sup>c</sup>
$*M(\text{bpy})_3^{2+} + e = M(\text{bpy})_3^+$	-	+0.84 <sup>c,d</sup>	+0.59 <sup>c</sup>
$M(\text{bpy})_3^{3+} + e = *M(\text{bpy})_3^{2+}$	-	-0.84 <sup>b</sup>	-0.96 <sup>b</sup>
$M(\text{bpy})_3^{2+} + e = M(\text{bpy})_3^+$	-1.27 <sup>f</sup>	-1.26 <sup>e</sup>	-1.22 <sup>e</sup>

<sup>a</sup> Potentials against the normal hydrogen electrode. <sup>b</sup> From ref. 14; <sup>c</sup> from ref. 7; <sup>d</sup> from ref. 18; <sup>e</sup> from ref. 28; <sup>f</sup> estimated from ref. 28.

complex undergoes no net photochemical reaction when oxygen-free aqueous solutions at room temperature are irradiated with visible light. The reactions of the excited molecule are therefore restricted primarily to outer sphere electron transfer and to energy transfer processes. It undergoes three types of bimolecular reaction. These are electron loss (eqn. (2)), electron addition (eqn. (3)) and energy transfer (eqn. (4))



In the first reaction (oxidative quenching) the excited state transfers a  $\pi^*$  electron to a suitable substrate while in the second (reductive quenching) an electron is added to the  $d^5$  metal centers of the excited state. The products of these reactions are  $RuL_3^{3+}$  and  $RuL_3^+$ , respectively. The former is a very powerful oxidizing agent and the latter a very powerful reductant (Table 2). The quenching reactions thus convert the excited state into ruthenium species which have longer lifetimes than the excited state and which are more oxidizing (eqn. (2)) or more reducing (eqn. (3)) than the excited state itself. As will be seen, the properties of the quencher are crucial to the efficient use of the energy of the excited molecule. As a consequence of the reaction of the excited complex with a redox quencher the electron and hole produced by photon absorption are separated and become localized on *different* molecules:

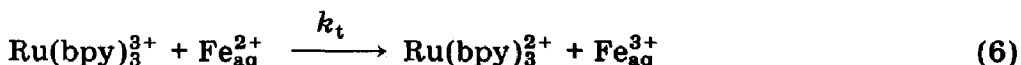
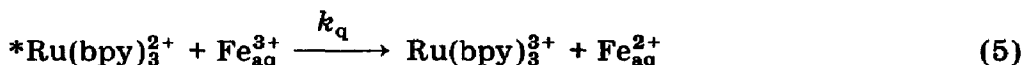


A suitable quencher thus must satisfy several conditions: its reaction with the excited complex must be rapid (since the lifetime of the excited state is short) but not too exothermic (since this will decrease the energy available for storage), and the back reaction of the reduced or oxidized quencher with the oxidized or reduced complex must be relatively slow (so that the electron transfer products can undergo secondary reactions).

## 2. Oxidative quenching

The excited state of  $\text{RuL}_3^{2+}$  can be oxidized by aquo ions (e.g.  $\text{Tl}_{\text{aq}}^{3+}$  [10],  $\text{Fe}_{\text{aq}}^{3+}$  [8, 14],  $\text{Eu}_{\text{aq}}^{3+}$  [14] and  $\text{Cu}_{\text{aq}}^{2+}$  [16]), metal complexes (e.g.  $\text{Ru}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  [4, 8, 9]) or organic molecules (e.g. paraquat ( $\text{N,N}'$ -dimethyl-4,4'-bipyridinium $^{2+}$  ion) and nitroaromatics in acetonitrile [8, 12]). The assignment of an oxidative quenching mechanism to these reactions is based upon the detection of the expected electron transfer products after flash photolysis of the systems or upon free energy or other rate considerations.

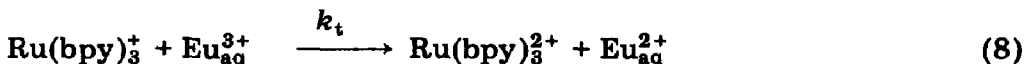
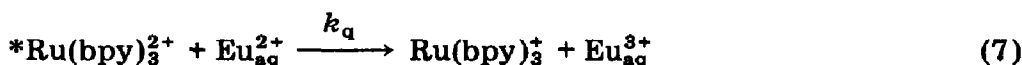
The quenching reactions are generally followed by the back reaction of the primary products to re-form the ground state reactants:



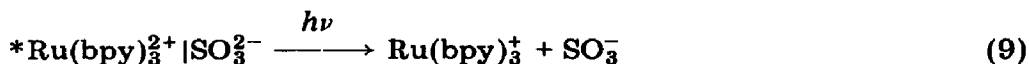
In the example cited, the back reaction is relatively slow ( $k_t = 4.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) compared with the quenching reaction ( $k_q = 2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) [14]. As a consequence, appreciable steady state concentrations of  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Fe}_{\text{aq}}^{2+}$  are attained under continuous photolysis conditions and these can be readily detected by photogalvanic measurements which thus afford another means of characterizing the system [29].

## 3. Reductive quenching

Aquo ions, of which the best characterized is the  $\text{Eu}_{\text{aq}}^{2+}$  system [23], can reduce the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  to  $\text{Ru}(\text{bpy})_3^+$ . The absorbance changes after flash photolysis of solutions containing  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{Eu}_{\text{aq}}^{2+}$  are consistent with the following scheme:

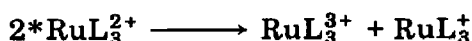


The first reaction is the reduction of the excited state by  $\text{Eu}_{\text{aq}}^{2+}$  ( $k_q = 2.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) and the second is the re-formation of the ground state reactants in the back electron transfer reaction ( $k_t = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ). Other reducing agents that can convert  $^*\text{Ru}(\text{bpy})_3^{2+}$  to  $\text{Ru}(\text{bpy})_3^+$  include metal complexes such as  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  [18], anions such as sulfite and ascorbate [30], and organic amines, for example, N,N-dimethylaniline or triethylamine in acetonitrile [31, 32]. (As in the oxidative case, the assignment of a reductive mechanism in these cases is based upon the detection of the electron transfer products, or, less directly, upon relative rate considerations.) There is good evidence [30] that the reaction of  $\text{Ru}(\text{bpy})_3^{2+}$  with sulfite is a two-photon process with  $\text{Ru}(\text{bpy})_3^+$  being produced by charge transfer absorption within a  $^*\text{Ru}(\text{bpy})_3^{2+}$ -sulfite ion pair:

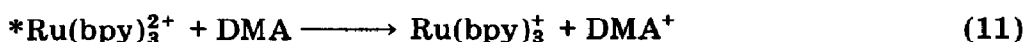
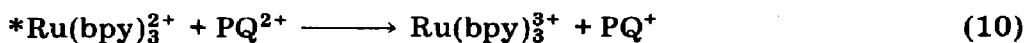


#### 4. Simultaneous formation of $\text{RuL}_3^{3+}$ and $\text{RuL}_3^+$ in quenching reactions

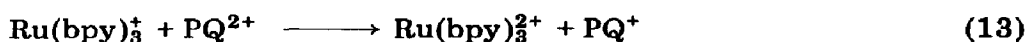
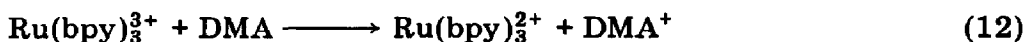
Perhaps the simplest method of generating both  $\text{RuL}_3^{3+}$  and  $\text{RuL}_3^+$  from  $^*\text{RuL}_3^{2+}$  is the disproportionation of two excited molecules according to



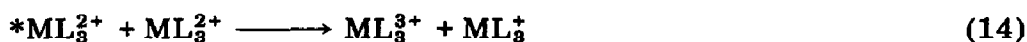
Although the disproportionation is too slow to be detected in solution ( $k < 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [33]), it is promoted on micelles [34]. As pointed out previously [7], the disproportionation may be catalyzed by a pair of redox quenchers such as  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{3+}$ . The reduced form of the couple generates  $\text{Ru}(\text{bpy})_3^+$  from the excited state while the oxidized form generates  $\text{Ru}(\text{bpy})_3^{3+}$ . Since the back electron transfer rates for this pair of quenchers are diffusion controlled, high yields of the disproportionation products would not be obtained. By contrast, relatively high yields can be obtained by irradiating an acetonitrile solution containing both paraquat ( $\text{PQ}^{2+}$ ) and dimethylaniline (DMA) [35]:



These quenching reactions are followed by the back reactions



The reaction of an excited molecule with its parent ground state molecule generally does not proceed spontaneously:



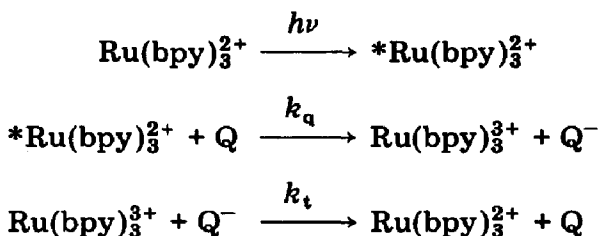
However, this type of reaction can occur if the ground and excited state molecules are different. Thus it has been proposed [7] that a reaction

analogous to reaction (14) could account for the observations of Sprintschnik *et al.* [36, 37]. These authors reported the formation of hydrogen and oxygen from the photodecomposition of water mediated by monolayers of  $\text{RuL}_3^{2+}$  complexes but these observations could not subsequently be reproduced with purified materials [37 - 39]. The presence of  $\text{RuL}_3'^{2+}$  impurities in the original  $\text{RuL}_3^{2+}$  sample could have led to the formation of the +1 and +3 complexes which might have produced hydrogen and oxygen in subsequent reactions.

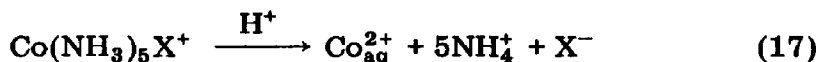
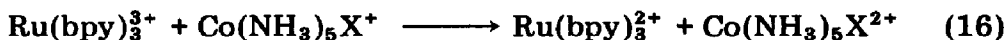
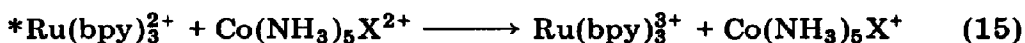
## 5. Photochemical conversion and storage reactions

We have seen that reactions of  $^*\text{Ru}(\text{bpy})_3^{2+}$  with redox quenchers convert the excited state into a powerful oxidant  $\text{Ru}(\text{bpy})_3^{3+}$  or a powerful reductant  $\text{Ru}(\text{bpy})_3^+$  and that the quenching reactions are generally followed by relatively rapid back reactions which re-form the ground state reactants. We next consider ways of competing with these back reactions so that the net conversion of the excitation energy into chemical, electrical or light energy might be accomplished.

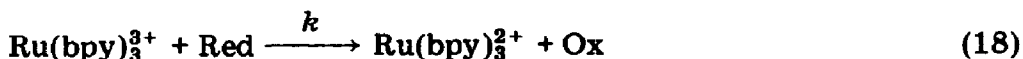
The back reaction in the oxidation quenching sequence



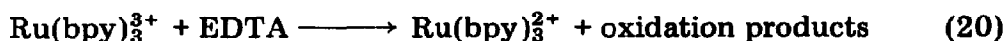
can be suppressed if either  $\text{Ru}(\text{bpy})_3^{3+}$  or  $\text{Q}^-$  can be scavenged very rapidly. The removal of  $\text{Q}^-$  occurs in the reaction of  $^*\text{Ru}(\text{bpy})_3^{2+}$  [4, 9] (or, better yet, of  $^*\text{Os}(\text{bpy})_3^{2+}$  [40]) with halopentamminecobalt(III) complexes  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  where the aquation of  $\text{Co}(\text{NH}_3)_5\text{X}^+$  is competitive with its oxidation by  $\text{Ru}(\text{bpy})_3^{3+}$ :



When  $\text{O}_2$ -Ti(IV) is used as a quencher,  $\text{Ru}(\text{bpy})_3^{3+}$  also accumulates in the system [41], possibly as a result of Ti(IV) combining with the  $\text{O}_2^-$  produced in the quenching reaction. In these systems the back reaction is prevented when the photoproduced reductant is removed. By contrast, removal of  $\text{Ru}(\text{bpy})_3^{3+}$  (the oxidized photoproduct) can be accomplished by the addition of a reducing agent:

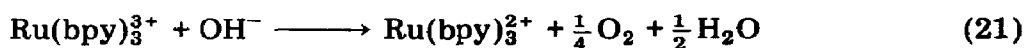


For aqueous media, reductants which react rapidly with  $\text{Ru}(\text{bpy})_3^{3+}$  and which do not rapidly quench the excited state include sulfite ( $k = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [30], ascorbate ( $k \geq 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , estimated from data in ref. 42), ethylenediaminetetraacetic acid (EDTA) ( $k = 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , pH 8.2 [50] and triethanolamine (TEA) ( $k = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [43]). Relatively high concentrations of the paraquat radical cation have been generated in aqueous solution using this approach [44]. When a solution containing  $\text{Ru}(\text{bpy})_3^{3+}$ , paraquat and EDTA is irradiated, the  $\text{Ru}(\text{bpy})_3^{3+}$  formed in the oxidation of the excited state by paraquat ( $\text{PQ}^{2+}$ ) is reduced to  $\text{Ru}(\text{bpy})_3^{2+}$  by EDTA:

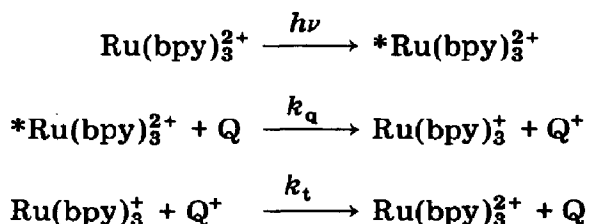


This occurs even when the EDTA and the paraquat are separated by a vesicle wall [45]. In acetonitrile  $\text{PQ}^+$  can be generated by reducing  $\text{RuL}_3^{3+}$  complexes with triphenylamine [46], pyridine, 2,6-lutidine, N,N-dimethylformamide or water [47]. Interest in systems of this type derives from the fact that the paraquat radical cation is capable of generating  $\text{H}_2$  in the presence of a catalyst, such as hydrogenase [48] or platinum [49].

Since  $\text{Ru}(\text{bpy})_3^{3+}$  is a very strong oxidizing agent it is not surprising that it reacts rapidly with a large variety of reductants. A particularly remarkable reaction of  $\text{Ru}(\text{bpy})_3^{3+}$  is its ability to oxidize hydroxide ion to  $\text{O}_2$  (eqn. (21)), a process which could find important application in the catalyzed photodecomposition of water [5]:

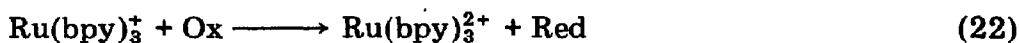


In an analogous manner, the back reaction in the reductive quenching sequence

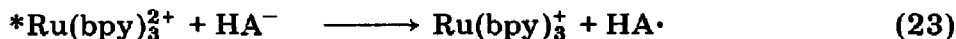


can be suppressed if either  $\text{RuL}_3^+$  or  $\text{Q}^+$  can be scavenged very rapidly. When  $\text{Q} =$  triethylamine and  $\text{RuL}_3^{2+}$  is an ester of the 4,4'-dicarboxylic acid derivative of  $\text{Ru}(\text{bpy})_3^{2+}$  the back reaction is sufficiently slow (presumably because of electrostatic effects and the shielding of the ruthenium center by the hydrophobic groups) for the radical cation to undergo secondary reactions either with the solvent or with the unreacted quencher [32]. As a consequence of these reactions,  $\text{RuL}_3^+$  can be generated in high yield in acetonitrile. This

system thus provides an example of the suppression of the back reaction by the removal of  $Q^+$ . Since  $\text{Ru}(\text{bpy})_3^+$  is a powerful reducing agent the back reaction can also be suppressed by the addition of a relatively mild oxidant:

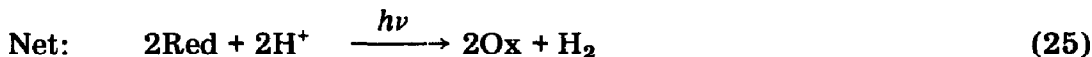
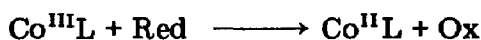
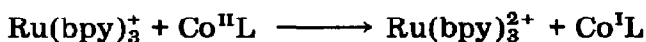
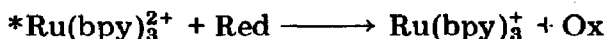
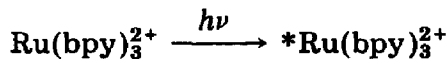


One example of this is the irradiation of a solution containing  $\text{Ru}(\text{bpy})_3^{2+}$ , ascorbate and  $\text{Os}(\text{NH}_3)_5\text{X}^{2+}$  [50]:



The net result of reactions (23) and (24) is the light-driven reduction of  $\text{Os}(\text{NH}_3)_5\text{X}^{2+}$  by ascorbate. Analogous results are obtained when  $\text{Ox} = \text{Rh}(\text{bpy})_2\text{Cl}_2^+$  [43] or  $\text{CoL}(\text{H}_2\text{O})_2^{2+}$  ( $\text{L} = \text{Me}_6[14]4,11\text{-diene N}_4$ ) [51]. The reduced forms of these oxidants may form hydrides which might decompose to form  $\text{H}_2$  under suitable conditions. With this end in view these systems are currently under active investigation [25, 51]. Preliminary results indicate that  $\text{H}_2$  is indeed produced when a solution containing  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{CoL}(\text{H}_2\text{O})_2^{2+}$  and either ascorbate or  $\text{Eu}_{\text{aq}}^{2+}$  is irradiated with visible light. The following reductive quenching sequence can account for these observations:

### Scheme I

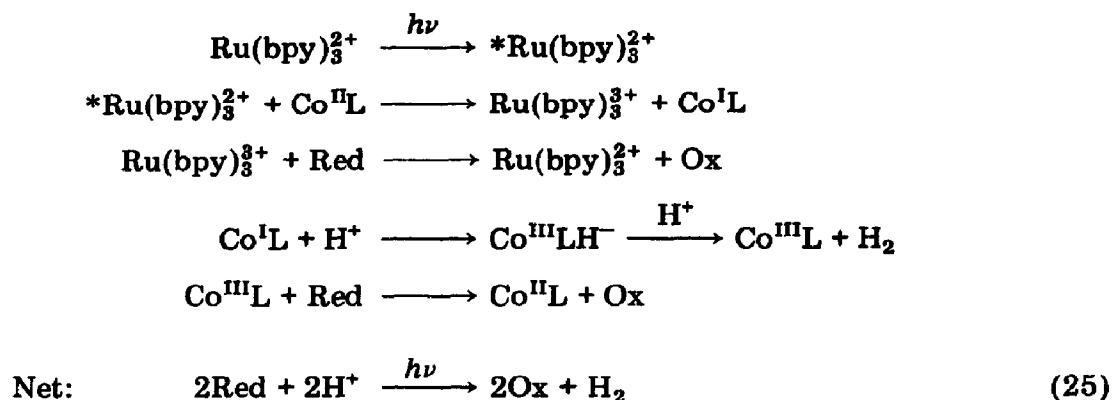


Although the net reaction (eqn. (25)) is not uphill when  $\text{Red} = \text{Eu}_{\text{aq}}^{2+}$ , it is when  $\text{Red} = \text{ascorbate}$  [51]. Scheme I with  $\text{Eu}_{\text{aq}}^{2+}$  as the reductant is thus an example of a photo-assisted reaction (in this instance the assistance is by visible light; the reaction of  $\text{Eu}_{\text{aq}}^{2+}$  with acid can also be promoted by the direct excitation of  $\text{Eu}_{\text{aq}}^{2+}$  with ultraviolet light [52]). By contrast, Scheme I with  $\text{Red} = \text{ascorbate}$  is an example of an energy storage reaction.

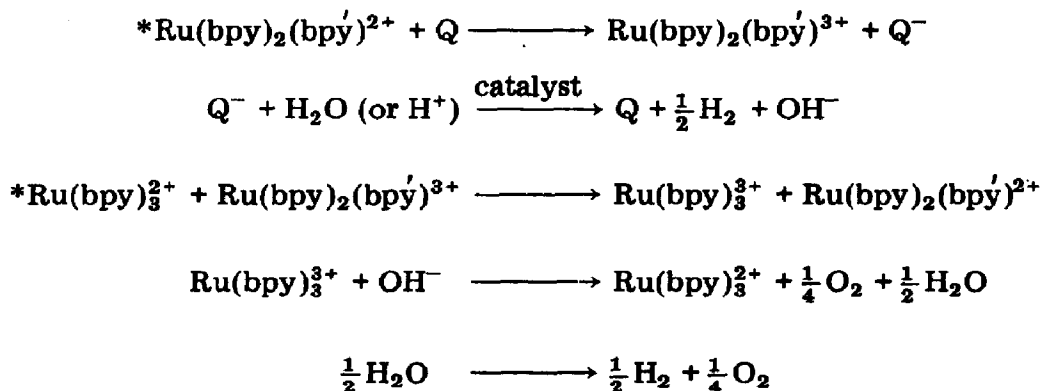
By changing the relative concentrations of  $\text{Red}$  and  $\text{Co}^{\text{II}}\text{L}$  it is, in principle, possible to arrive at the same net reaction (eqn. (25)) by an oxidative quenching sequence. This is shown in the following scheme:



## Scheme II



However, Scheme II will not work for the particular system considered since  $\text{Co}^{\text{II}}\text{L}$  does not quench the excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  ( $k_q \leq 6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  [51]). As we have seen (Table 2),  ${}^*\text{Ru}(\text{bpy})_3^{2+}$  is a poorer reductant than  $\text{Ru}(\text{bpy})_3^+$  and  ${}^*\text{Ru}(\text{bpy})_3^{2+}$  therefore generally reacts more slowly with a given oxidant than does  $\text{Ru}(\text{bpy})_3^+$  ( $k = 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of  $\text{Ru}(\text{bpy})_3^+$  with  $\text{Co}^{\text{II}}\text{L}$  [51]). Nor is the situation improved by the shorter natural lifetime of  ${}^*\text{Ru}(\text{bpy})_3^{2+}$  or the more rapid back reaction expected for the primary quenching products in Scheme II (but see below). Scheme II does, however, have one advantage over Scheme I, namely, the powerful oxidant  $\text{Ru}(\text{bpy})_3^{3+}$  is generated as an intermediate in Scheme II. This affords the possibility of using milder reductants in Scheme II and, in particular, if  $\text{Red} = \text{OH}^-$ , of making the net reaction the photo-induced decomposition of water into  $\text{H}_2$  and  $\text{O}_2$  [5]. This might be accomplished in a cell of the following type. In one compartment is placed a solution containing the oxidative quencher ( $\text{Q} = \text{Co}^{\text{II}}\text{L}$ ,  $\text{PQ}^{2+}$  or  $\text{Rh}^{\text{III}}(\text{bpy})_3^{3+}$  (see later)) and any catalyst that may be required for the evolution of hydrogen. This compartment is separated from a  $\text{Ru}(\text{bpy})_3^{2+}$  solution at  $\text{pH} \approx 9$  [5] by a membrane containing a membrane-soluble  $\text{Ru}(\text{bpy})_2(\text{bpy}')^{2+}$  derivative (*cf.* ref. 45). Upon illumination the following reactions could occur



It has been reported [53] that  $H_2$  is produced when a mixture of a rhodium-bipyridine complex ( $Rh(bpy)_3^{3+}$  or  $Rh(bpy)_2(H_2O)_2^{3+}$ ), TEA/TEAH<sup>+</sup> and chloroplatinate are irradiated with visible light. Evidence was presented that the formation of  $H_2$  occurs via a rhodium(III) hydride ( $Rh(bpy)_2H(H_2O)^{2+}$ ) which is decomposed by the colloidal platinum formed in the photochemical decomposition of the chloroplatinate. Since TEA/TEAH<sup>+</sup> does not quench  $*Ru(bpy)_3^{2+}$  but  $Rh(bpy)_3^{3+}$  quenches  $*Ru(bpy)_3^{3+}$  at a close-to-diffusion controlled rate [43], a mechanism involving the formation of  $Ru(bpy)_3^+$  can be ruled out. This suggests that the reaction proceeds via an oxidative quenching pathway or, perhaps, by an energy transfer mechanism. Evidence for a pathway involving oxidative quenching comes from the fact that  $Ru(bpy)_3^{3+}$  and  $Rh(bpy)_3^{3+}$  are produced in the 530 nm flash photolysis of mixtures of  $Ru(bpy)_3^{2+}$  and  $Rh(bpy)_3^{3+}$  either in the presence or absence of TEA/TEAH<sup>+</sup> [25, 43]. The  $Rh(bpy)_3^{3+}$  presumably undergoes very rapid ligand loss to produce  $Rh(bpy)_2^{2+}$  which then disproportionates to form  $Rh(bpy)_2^+$  and  $Rh(bpy)_2(H_2O)_2^{3+}$  [25, 43].

The various hydrogen-generating systems that have been discussed are summarized in Table 3. For the sake of completeness, Table 3 also includes a non-sensitized system. It will be of interest to learn how the optimum quantum yields for  $H_2$  formation for the sensitized systems compare with those that can be obtained by direct photolysis of colored metal complexes.

Before concluding this section some other applications of photochemically generated  $RuL_3^{3+}$  and  $RuL_3^+$  should be noted. The use of the  $Ru(bpy)_3^{2+}/Fe_a^{3+}$  system in a photogalvanic cell has already been mentioned [29]. A somewhat different application involves the use of a cell consisting of an n-type  $TiO_2$  electrode connected to a platinum electrode [55]. In this cell the  $Ru(bpy)_3^{2+}$  acts as a sensitizer. The excited state injects an electron into the conduction band of the  $TiO_2$  electrode; this electron flows through the external circuit to the platinum electrode where hydrogen is produced.

TABLE 3

Summary of  $Ru(bpy)_3^{2+}$ -sensitized systems that produce hydrogen with visible light

Quencher	Reductant	Oxidant	Catalyst	Reference
PQ <sup>2+</sup>	EDTA	-	Pt	45
PQ <sup>2+</sup> <sup>a</sup>	EDTA	-	Hydrogenase	44
$Rh(bpy)_3^{3+}$ or $Rh(bpy)_2(H_2O)_2^{3+}$	TEA	-	Pt	43, 49
Eu <sup>2+</sup> or ascorbate	-	CoL(H <sub>2</sub> O) <sub>2</sub> <sup>2+</sup> <sup>b</sup>	-	47
$[(Rh)_2(bridge)_4H]^{3+}$ <sup>c</sup>	-	-	-	54

<sup>a</sup>The sensitizer is proflavin not  $Ru(bpy)_3^{2+}$ . <sup>b</sup>L = Me<sub>6</sub>[14]4,11-diene N<sub>4</sub>. <sup>c</sup>Not a sensitized reaction but the direct photolysis of the rhodium(I) dimer; bridge = 1,3-diisocyanopropane.

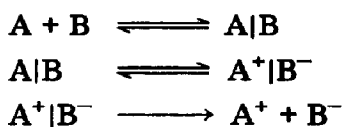
In another application,  $\text{Ru}(\text{bpy})_3^{2+}$  is oxidized by holes generated photochemically in the valence band of an  $\text{MoS}_2$  electrode [56]. The formation of oxygen then occurs by hydroxide reduction of  $\text{Ru}(\text{bpy})_3^{3+}$  rather than by the oxidation of hydroxide at the electrode surface. As a consequence the oxidation of the sulfur atoms at the electrode surface to sulfate is inhibited.

The excited state of  $\text{Ru}(\text{bpy})_3^{2+}$  can be generated in the reduction of  $\text{Ru}(\text{bpy})_3^{3+}$  by  $\text{Ru}(\text{bpy})_3^+$  [57], sodium borohydride [58],  $e_{\text{aq}}^-$  [59], hydrazine [60], EDTA [61] or hydroxide ion [60]. This chemiluminescent reaction can be used to provide a dramatic demonstration of the formation of  $\text{Ru}(\text{bpy})_3^{3+}$  in, for example, the reaction of  $^*\text{Ru}(\text{bpy})_3^{2+}$  with  $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$  complexes. Irradiation of  $\text{Ru}(\text{bpy})_3^{2+}$  solutions containing  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$  produces  $\text{Ru}(\text{bpy})_3^{3+}$  according to reaction (15). Injection of the irradiated solution into excess  $\text{NaOH}$ -EDTA yields a bright flash of luminescence from the radiative decay of the  $^*\text{Ru}(\text{bpy})_3^{2+}$  produced in the reduction of  $\text{Ru}(\text{bpy})_3^{3+}$ .

## 6. Theoretical considerations

We have seen that the excited states of  $\text{RuL}_3^{2+}$ ,  $\text{OsL}_3^{2+}$  (and  $\text{CrL}_3^{3+}$ ) complexes undergo facile electron transfer. We next consider some of the factors determining electron transfer rates.

Bimolecular electron transfer reactions proceed in three steps. In the first step the separated reactants come together to form a precursor complex. No bonds are made or broken in forming the precursor complex



in outer sphere reactions. Reorganization of the precursor complex to form the activated complex occurs in the second step. In this step the inner coordination shells of the reactants and the polarization of the surrounding medium adjust to the configuration appropriate to the activated complex. This reorganization is required by the Franck-Condon principle. The actual electron transfer may ( $\kappa < 1$ ), and usually does ( $\kappa = 1$ ), take place during the latter stages of the reorganization of the precursor complex. The dissociation of the successor complex (formed by electron transfer within the precursor complex) occurs in the third step. In terms of this mechanism the rate constant for electron transfer is given by

$$k = K_0 k_{\text{et}} \quad (26)$$

$$k_{\text{et}} = \kappa \frac{kT}{h} \exp\left(-\frac{\Delta G_\lambda^\ddagger}{RT}\right) \quad (27)$$

where  $K_0$  is the equilibrium constant for the formation of the precursor complex from the separated reactants,  $k_{et}$  is the first order rate constant for electron transfer within the precursor complex,  $\kappa$  is the probability of electron transfer within the activated complex and  $\Delta G_{\ddagger}^{\ddagger}$  is the free energy required to reorganize the precursor complex prior to the electron transfer.

The free energy of activation can be broken down into two contributions: an intrinsic contribution and a thermodynamic contribution [62, 63]. The intrinsic contribution to the activation barrier is the energy required to reorganize the inner and outer coordination shells of the reactants prior to electron transfer when the standard free energy change for the reaction is zero. The intrinsic barrier can be obtained from the rates of electron transfer reactions in which the reactants and products are either identical (exchange reactions) or differ only slightly (for example, by only minor modifications of the ligands).

TABLE 4

Rate constants for electron exchange of ground and excited states of metal complexes at 25 °C

Reaction	$k$ ( $M^{-1} s^{-1}$ )	Reference
$Cr_{aq}^{2+} + Cr_{aq}^{3+}$	$< 10^{-5}$	64
$Eu_{aq}^{2+} + Eu_{aq}^{3+}$	$< 2 \times 10^{-4}$	65
$V_{aq}^{2+} + V_{aq}^{3+}$	$1 \times 10^{-2}$	66
$Fe_{aq}^{2+} + Fe_{aq}^{3+}$	4.0	67
$Ru(NH_3)_6^{2+} + Ru(NH_3)_6^{3+}$	$4.3 \times 10^3$	68
$Cr(bpy)_3^{2+} + Cr(bpy)_3^{3+}$	$\approx 2 \times 10^9$	69 <sup>a</sup>
$Cr(bpy)_3^{2+} + *Cr(bpy)_3^{3+}$	$\approx 1 \times 10^8$	69
$Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+}$	$2 \times 10^9$ <sup>b</sup>	70
$Ru(bpy)_3^{3+} + *Ru(bpy)_3^{2+}$	$> 1 \times 10^8$	7
$Ru(bpy)_3^{\ddagger} + Ru(bpy)_3^{2+}$	$> 1 \times 10^8$	14
$*Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+}$	$\approx 1 \times 10^8$	7

<sup>a</sup> See footnote 48 of ref. 69. <sup>b</sup> The value reported ( $1.2 \times 10^9 M^{-1} s^{-1}$ ) has been corrected for diffusion control using  $1/k_{act} = 1/k_{obs} - 1/k_{diff}$  with  $k_{diff} = 3 \times 10^9 M^{-1} s^{-1}$ .

Rate constants for a number of electron exchange reactions are presented in Table 4. It will be seen that, although the electron transfers all involve reactants of charges 2+ and 3+, the rate constants span some sixteen orders of magnitude. As discussed elsewhere [71, 72] the origin of the rate variations lies primarily in the differences in the inner and outer sphere

reorganization energies for the different pairs of reactants. For our purposes the relatively slow exchange rates of the aquo ion systems and the very rapid exchange rates of the excited polypyridine systems are of particular interest: the very rapid electron exchange rates of the excited polypyridine complexes make them ideal as electron donors or acceptors in quenching reactions, while the slow exchange rates of the aquo ions favor slow back electron transfer. (Note the very rapid exchange rate of the  $\text{Cr}(\text{bpy})_3^{2+} + {}^*\text{Cr}(\text{bpy})_3^{3+}$  couple; rapid electron transfer is not restricted to charge transfer excited states [11, 69, 73, 74].) Moreover, in reactions of the ground and excited state polypyridine complexes with aquo ions the largest contribution to the intrinsic barrier will come from the aquo ion couple. This is discussed further below.

When the reactants and products of the electron transfer reaction are no longer identical it becomes necessary to consider the effect of the thermodynamic changes in the reaction on the electron transfer rate. This is most conveniently done in terms of the Marcus cross relations [75 - 78]. These equations relate the kinetic parameters for a reaction accompanied by a net chemical change (a cross reaction) to the kinetic parameters for the component exchange reactions:

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} \quad (28)$$

$$\log f_{12}^* = \frac{(\log K_{12})^2}{4 \log(k_{11} k_{22} / Z^2)} \quad (29)$$

$$\Delta G_{12}^* = \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{\Delta G_{12}^\circ}{2} (1 + \alpha) \quad (30)$$

$$\Delta S_{12}^* = \left( \frac{\Delta S_{11}^*}{2} + \frac{\Delta S_{22}^*}{2} \right) (1 - 4\alpha^2) + \frac{\Delta S_{12}^\circ}{2} (1 + 2\alpha) \quad (31)$$

$$\Delta H_{12}^* = \left( \frac{\Delta H_{11}^*}{2} + \frac{\Delta H_{22}^*}{2} \right) (1 - 4\alpha^2) + \frac{\Delta H_{12}^\circ}{2} (1 + 2\alpha) \quad (32)$$

$$\alpha = \frac{\Delta G_{12}^\circ}{4(\Delta G_{11}^* + \Delta G_{22}^*)}$$

The subscript 12 refers to the cross reaction and the subscripts 11 and 22 to the exchange reactions.

As an example of an electron transfer reaction in which the reactants and products are very different we shall consider the oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by  $\text{Ru}(\text{bpy})_3^{3+}$ :



This reaction illustrates many of the features that are important in asymmetric electron transfer reactions. The activation entropies and enthalpies for the

oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by  $\text{Ru}(\text{bpy})_3^{3+}$  are  $-33 \text{ cal deg}^{-1} \text{ mol}^{-1}$  and  $-0.3 \text{ kcal mol}^{-1}$ , respectively [79]. Note that the activation entropy is very negative and that the activation enthalpy is slightly negative; because of the latter the rates actually *decrease* with increasing temperature. This behavior can be rationalized in terms of the above equations. Substitution of the relevant parameters for the  $\text{Fe}_{\text{aq}}^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$  reaction into eqns. (31) and (32) gives  $\Delta S_{12}^\ddagger = -29 \text{ cal deg}^{-1} \text{ mol}^{-1}$  and  $\Delta H_{12}^\ddagger = -2.9 \text{ kcal mol}^{-1}$ , in good agreement with the observed values [78]. This calculation shows that there is nothing special about the oxidation of  $\text{Fe}_{\text{aq}}^{2+}$  by  $\text{Ru}(\text{bpy})_3^{3+}$ : the unusual activation parameters for the electron transfer reaction derive from its atypical thermodynamic parameters ( $\Delta S_{12}^\circ = -43 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ,  $\Delta H_{12}^\circ = -27 \text{ kcal mol}^{-1}$ ). The origin of these unusual thermodynamic parameters is as follows. The value of  $(S_{2+}^\circ - S_{3+}^\circ)$  is essentially zero for the bipyridine complexes since the relatively large bipyridine ligands effectively shield the surrounding medium from the effect of the charge on the central metal ion. In contrast,  $(S_{2+}^\circ - S_{3+}^\circ)$  is large and positive for the  $\text{Fe}_{\text{aq}}^{2+,3+}$  couple. As a consequence the standard entropy change for the  $\text{Fe}_{\text{aq}}^{2+}$ - $\text{Ru}(\text{bpy})_3^{3+}$  reaction is very negative. Since  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  and  $\Delta G_{12}^\circ \ll 0$  it follows that  $\Delta H_{12}^\circ$  must also be very negative. As a consequence  $\Delta H_{12}^\ddagger$  is negative. (A statistical mechanical interpretation of the negative activation enthalpy is given elsewhere [78].) Similar considerations obtain whenever the differences in the standard entropies of the oxidized and reduced forms ( $S_{\text{red}}^\circ - S_{\text{ox}}^\circ$ ) for the two couples are very different, as also occurs, for example, in the thionine- $\text{Fe}_{\text{aq}}^{3+}$  system.

The effect of the thermodynamics on the reaction rate is perhaps most readily visualized in terms of potential energy surfaces. This is shown in Fig. 1 in which the potential energies of the close-contact reactants (left-hand

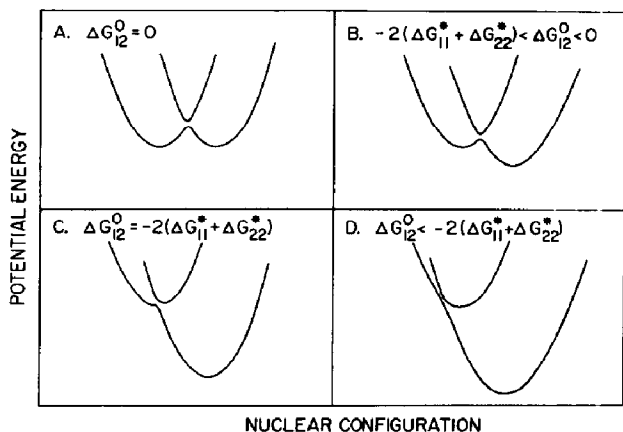


Fig. 1. Profile of the potential energy surface of the reactants (left-hand curve) and the products (right-hand curve) of an electron transfer reaction *vs.* the nuclear configuration of all the atoms in the system for different values of the standard free energy change for the reaction: A, exchange reaction ( $\Delta G_{12}^\circ = 0$ ); B, "normal" electron transfer reaction; C, diffusion-controlled electron transfer reaction; D, "inverted" electron transfer reaction.

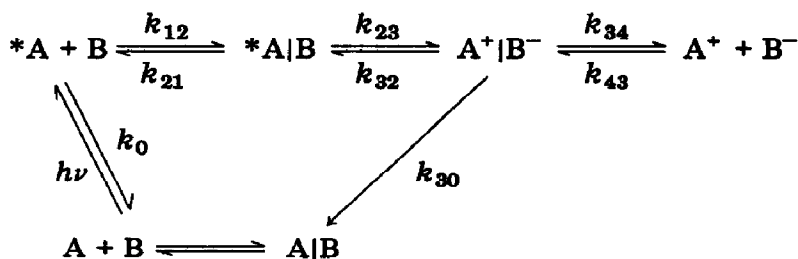
parabola) and close-contact products (right-hand parabola) are plotted as a function of nuclear configuration for various values of  $\Delta G_{12}^{\circ}$ . The distance from the minimum of the reactant curve to the intersection region is a measure of the activation energy for the reaction. Figure 1(A) is for an exchange reaction for which  $\Delta G_{12}^{\circ} = 0$ . The curves are identical and are simply displaced horizontally. The case of a typical cross reaction with a net chemical change is shown in Fig. 1(B). It will be seen that the activation energy is lowered as a consequence of the net free energy change for the reaction. Figure 1(C) is for a diffusion controlled reaction; this occurs when  $\Delta G_{12}^{\circ} = -2(\Delta G_{11}^* + \Delta G_{22}^*)$ . When  $\Delta G_{12}^{\circ} < -2(\Delta G_{11}^* + \Delta G_{22}^*)$  the intersection of the two parabolas occurs on the left-hand side of the reactant parabola (Fig. 1(D)). This is the so-called inverted region where the rate constants are predicted to *decrease* with increasing driving force for the reaction [77, 78]. Although nuclear tunneling effects are expected to diminish the magnitude of this rate decrease, tunneling is not expected to eliminate it entirely since the nuclear tunneling distance increases with the exothermicity of the reaction [33, 78, 80].

The rates of a number of very exothermic electron transfer reactions are indeed slower than expected. These reactions include the oxidation of  $*\text{RuL}_3^{2+}$  by  $\text{ML}_3^{3+}$  complexes [33], the disproportionation of  $*\text{Ru}(\text{bpy})_3^{2+}$  [33], the reaction of  $e_{\text{aq}}^-$  with  $\text{Ru}(\text{bpy})_3^{3+}$  [81] and the reaction of  $e_{\text{aq}}^-$  with electron acceptors in micelles [82]. Although the relatively slow rates of these reactions provide some experimental support for the inverted region predictions, the rate decreases are, in general, smaller than those calculated from the semiclassical model. This could be due to the nuclear tunneling effects mentioned above. Finally, it should be noted that a rate decrease with increasing driving force in the inverted region is also expected on the basis of the energy gap law of radiationless transition theory [69, 80].

## 7. Implications of the electron-transfer models

The efficient conversion and storage of light energy requires that the quenching reactions be rapid and the back reactions slow. Some of the important quenching and back reaction steps in a detailed electron transfer quenching scheme are shown in the following scheme [83, 84]:

Scheme III



Use of the steady state approximation for the concentrations of  $^*A|B$  and  $A^+|B^-$  leads to the following expression for the quenching rate constant:

$$k_q = \left( 1 + \frac{k_{21}}{k_{23}} + \frac{k_{21}k_{32}}{k_{23}(k_{30} + k_{34})} \right)^{-1} k_{12} \quad (34)$$

Various limiting forms of eqn. (34) have been considered [12]. For our purpose we shall assume that  $k_{30} + k_{34} \gg k_{32}$ ; in other words, we shall assume that the reverse of the quenching step can be neglected (neglect of  $k_{32}$  is, in general, not justified if the quenching is endothermic). With the above assumption the expression for  $k_q$  reduces to

$$k_q = \frac{k_{12}k_{23}}{k_{21} + k_{23}} \quad (35)$$

If the quenching reaction is not diffusion controlled then  $k_{21} \gg k_{23}$  and  $k_q$  is given by

$$k_q = \frac{k_{12}k_{23}}{k_{21}} \quad (36)$$

In an entirely analogous manner, the rate constant for the back electron transfer reaction is given by the following equation (provided, as before, that  $k_{30} + k_{34} \gg k_{32}$ ):

$$k_t = \frac{k_{30}k_{43}}{k_{30} + k_{34}} \quad (37)$$

If the back electron transfer reaction is not diffusion controlled then  $k_{34} \gg k_{30}$  and  $k_t$  is given by

$$k_t = \frac{k_{30}k_{43}}{k_{34}} \quad (38)$$

Finally, since  $k_{12} \approx k_{43}$  and  $k_{21} \approx k_{34}$  it follows that the ratio  $k_q/k_t$  is given by

$$\frac{k_q}{k_t} = \frac{k_{23}}{k_{30}} \quad (39)$$

provided that neither  $k_q$  nor  $k_t$  is diffusion controlled and the reverse of the quenching step can be neglected. The ratio  $k_{23}/k_{30}$  should be high if efficient quenching and a high yield of separated electron transfer products are desired. It also follows from eqn. (37) that  $Y$ , the yield of separated electron transfer products, is given by



$$\begin{aligned}
 Y &= \frac{k_{34}}{k_{30} + k_{34}} \\
 &= 1 - \frac{k_t}{k_{diff}}
 \end{aligned}
 \tag{40}$$

where  $k_{diff} = k_{43}$  is the diffusion controlled rate constant for the back electron transfer. Similarly, the fraction of back electron transfer is given by

$$1 - Y = \frac{k_t}{k_{diff}}
 \tag{41}$$

We have seen that the rate of an electron transfer reaction responds differently to driving force or exchange rate changes depending upon whether the intersection of the potential energy surfaces for the reaction occurs in the normal or in the inverted region. We have also discussed the general condition for normal or inverted behavior. In applying these ideas to electron transfer within the encounter pairs of Scheme 1, it is necessary to consider three potential energy surfaces. One surface describes  $*A|B$ , another describes  $A^+|B^-$  and the third describes  $A|B$ . Thus we need to consider two intersections each of which can be normal or inverted. Consequently we distinguish four situations.

### 6.1. Class I: both the quenching and back reactions are normal

In this case  $\Delta G_q^\circ > -2(*\Delta G_{11}^* + \Delta G_{22}^*)$  and  $\Delta G_t^\circ > -2(\Delta G_{11}^* + \Delta G_{22}^*)$  where  $*\Delta G_{11}^*$  is the free energy of activation for the excited state exchange reaction. The intersections of the potential energy surfaces of  $*A|B$ ,  $A^+|B^-$  and  $A|B$  are as in Fig. 2 and the rates of both the quenching and the back reactions will increase with increasing driving force for the reactions. Moreover, since the excitation free energy is equal to the sum of the free energy changes for the quenching and back reactions,

$$*\Delta G = \Delta G_q^\circ + \Delta G_t^\circ
 \tag{42}$$

increasing the exothermicity of the quenching reaction to increase its rate will also decrease the rate of the back reaction by decreasing its exothermicity. Unfortunately, increasing the exothermicity of the quenching reaction also decreases the fraction of the light energy available for storage, thereby decreasing the efficiency of the overall process.

It is evident from eqn. (30) that there is another way of modifying the rate of an electron transfer reaction besides changing its driving force and that is by changing the intrinsic barrier for the reaction. In practice this is most effectively done by changing the quencher since, as we have seen, the polypyridine couples have very rapid electron exchange rates and thus their reorganization energies make only a very small contribution to the intrinsic barrier. (Changing the quencher will, in general, also change the driving force for the electron transfer.) Increasing the exchange rate of the quencher will

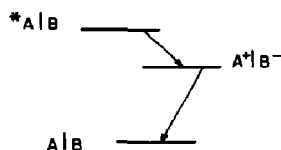
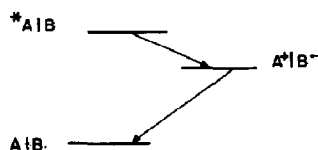
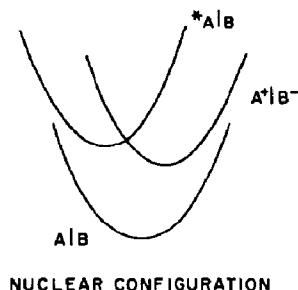
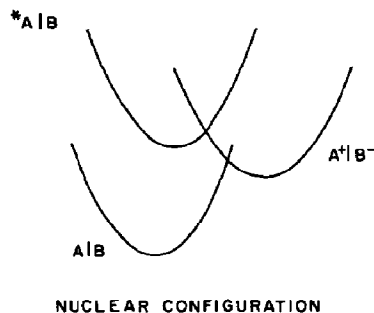


Fig. 2. Profile of the potential energy surfaces for a normal quenching reaction and a normal back electron transfer reaction.

Fig. 3. Profile of the potential energy surfaces for a normal quenching reaction and an inverted back electron transfer reaction.

increase the horizontal displacement of the minima of the  $A|B$  and  $A^+|B^-$  parabolas, effectively increasing the barrier for the back (and quenching) reactions. This is probably the main reason why high yields of electron transfer products are found when aquo ions are used as quenchers: because of the relatively slow exchange rates of the aquo ions the back reactions tend to be slow despite the favorable driving force for the back electron transfer. Although the quenching reactions will also tend to be slow, the rate of the quenching reaction can be increased by increasing the concentration of the quencher. Thus by a judicious combination of driving force and exchange rates a quenching reaction with modest exothermicity can be coupled with a slow back reaction.

### 6.2. Class II: the quenching reaction is normal but the back reaction is inverted

This case is illustrated in Fig. 3. For this case,  $\Delta G_q^\circ > -2(*\Delta G_{11}^* + \Delta G_{22}^*)$  and  $\Delta G_t^\circ < -2(\Delta G_{11}^* + \Delta G_{22}^*)$ . Under these conditions increasing the exothermicity of the quenching reaction (to increase the quenching rate) will increase the rate of the back reaction (by decreasing the energy gap). However, as in the previous case (and indeed for all the cases considered here) increasing the exothermicity of the quenching reaction will decrease the fraction of the excitation energy that is available for storage.

We next consider the effect on the reaction rates of changing the intrinsic barrier. Increasing  $\Delta G_{22}^*$  in this system (for example, by using an

aquo ion as the quencher) will decrease the rate of the quenching reaction but will *increase* the rate of the back reaction by decreasing the nuclear tunneling distance from the  $A^+|B^-$  to the  $A|B$  potential energy surface (Fig. 3).

**6.3. Class III: the quenching reaction is inverted but the back reaction is normal**

For this case,  $\Delta G_q^\circ < -2(*\Delta G_{11}^* + \Delta G_{22}^*)$  and  $\Delta G_t^\circ > -2(\Delta G_{11}^* + \Delta G_{22}^*)$ . This situation will obtain if the quenching reaction is very exothermic, a condition which favors a slow back (and quenching) reaction but which is very inefficient for energy storage. Increasing the displacement of the  $A^+|B^-$  and  $A|B$  parabolas (by increasing  $\Delta G_{22}^*$ ) will increase the quenching rate but decrease the rate of the back reaction.

**6.4. Class IV: both the quenching and back reactions are inverted**

In this case,  $\Delta G_q^\circ < -2(*\Delta G_{11}^* + \Delta G_{22}^*)$  and  $\Delta G_t^\circ < -2(\Delta G_{11}^* + \Delta G_{22}^*)$ . This case is illustrated in Fig. 4. In many respects this and Class II represent the optimum situation for energy storage: these cases can combine a small exothermicity of the quenching reaction (and consequently a relatively efficient storage of the excitation energy) with a slow back reaction rate.

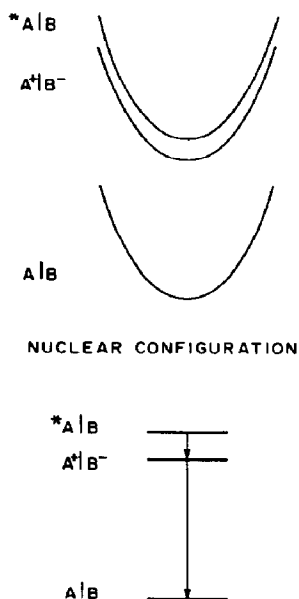


Fig. 4. Profile of the potential energy surfaces for an inverted quenching reaction and an inverted back electron transfer reaction.

## 8. Applications

Most of the systems that we have discussed fall into Class I. Both the quenching and the back reactions have normal free energy dependences and

the back reaction rates are controlled by using a quencher with a slow exchange rate, such as an aquo ion, or a quencher which undergoes a net two-electron change (for example, paraquat or ascorbate) and where the one-electron transfer product either has a different configuration from the quencher, in other words a slow exchange rate (the paraquat radical cation), or undergoes disproportionation which can compete with the back reaction (the ascorbate radical). The effect of the exothermicity of the reaction on the back reaction rate is illustrated by the  $\text{Fe}_{\text{aq}}^{3+}$  [14] and  $\text{Cu}_{\text{aq}}^{2+}$  [16] quenching data. The steady state concentrations of  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Fe}_{\text{aq}}^{2+}$  show the predicted correlation with the standard free energy change for the back reaction. (Note that because of the negative  $\Delta H^\ddagger$  for the reaction of  $\text{Ru}(\text{bpy})_3^{3+}$  with  $\text{Fe}_{\text{aq}}^{2+}$ , the rate of the back reaction will decrease and the steady state concentration of  $\text{Ru}(\text{bpy})_3^{3+}$  and  $\text{Fe}_{\text{aq}}^{2+}$  will increase with increasing temperature). Similarly, the fraction of back electron transfer occurring in the  $\text{Cu}_{\text{aq}}^{2+}$  quenching reaction is given by eqn. (41) and shows the normal dependence on the exothermicity of the back reaction [16].

As mentioned above, if there is a rate decrease in the inverted region, then Class II and IV systems offer the most promise for the conversion and storage of solar energy. To reach the inverted region the donor and quencher should both feature very rapid exchange rates and the driving force for the back reaction should be large. An example of Class II behavior could be the  $^*\text{RuL}_3^{2+} - \text{CoL}(\text{H}_2\text{O})_2^{2+}$  system: the quenching reaction is not very exothermic and could lie in the normal region; by contrast, there is some evidence that the back reaction of  $\text{RuL}_3^{3+}$  and  $\text{CoL}(\text{H}_2\text{O})_2^+$  lies in the inverted region (see Table III of ref. 85). If this result is substantiated, then it suggests that very reactive cobalt(I) species could be generated in quenching reactions for which the back reactions are very exothermic but which nevertheless proceed at rates that are slower than diffusion controlled. The use of the inverted region to control back reaction rates appears promising and clearly merits further study.

## Acknowledgments

The author wishes to acknowledge helpful discussions with Drs. C. Creutz, G. M. Brown and B. Brunshwig. This research was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

## References

- 1 V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and M. Gleria, *Science*, 189 (1975) 852.
- 2 J. R. Bolton, *J. Solid State Chem.*, 22 (1977) 3.
- 3 J. R. Bolton, *Science*, in the press.
- 4 H. D. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, 94 (1972) 8238.
- 5 C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, 72 (1975) 2858.

- 6 T. J. Meyer, *Israel J. Chem.*, 15 (1977) 200.
- 7 N. Sutin and C. Creutz, *Adv. Chem. Ser.*, 168 (1978) 1.
- 8 C. R. Bock, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 96 (1974) 4710.
- 9 G. Navon and N. Sutin, *Inorg. Chem.*, 13 (1974) 2159.
- 10 G. S. Laurence and V. Balzani, *Inorg. Chem.*, 13 (1974) 2976.
- 11 F. Boletta, M. Maestri, L. Moggi and V. Balzani, *Chem. Commun.*, (1975) 901.
- 12 C. R. Bock, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 97 (1975) 2909.
- 13 A. Juris, M. T. Gandolfi, M. F. Manfrin and V. Balzani, *J. Am. Chem. Soc.*, 98 (1976) 1047.
- 14 C.-T. Lin, W. Böttcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 98 (1976) 6536.
- 15 J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, 98 (1976) 4853.
- 16 M. A. Hoselton, C.-T. Lin, H. A. Schwarz and N. Sutin, *J. Am. Chem. Soc.*, 100 (1978) 2383.
- 17 D. Meisel, M. S. Matheson, W. A. Mulac and J. Rabani, *J. Phys. Chem.*, 81 (1977) 1449.
- 18 C. Creutz and N. Sutin, *Inorg. Chem.*, 15 (1976) 496.
- 19 C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 98 (1976) 6384.
- 20 H. E. Toma and C. Creutz, *Inorg. Chem.*, 16 (1977) 545.
- 21 C. P. Anderson, D. J. Salmon, T. J. Meyer and R. C. Young, *J. Am. Chem. Soc.*, 99 (1977) 1980.
- 22 J. N. Demas, E. W. Harris and R. P. McBride, *J. Am. Chem. Soc.*, 99 (1977) 3547.
- 23 C. Creutz, *Inorg. Chem.*, 17 (1978) 1046.
- 24 C. Creutz, T. Netzel, N. Sutin and M. Okumura, to be published.
- 25 G. M. Brown, M. Chou, N. Sutin and C. Creutz, unpublished observations.
- 26 A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley and M. W. Windsor, *Chem. Phys. Lett.*, 37 (1976) 199.
- 27 R. C. Young, J. K. Nagle, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 100 (1978) 4773.
- 28 T. Saji and S. Aoyagui, *J. Electroanal. Chem.*, 58 (1975) 401.
- 29 C.-T. Lin and N. Sutin, *J. Phys. Chem.*, 80 (1976) 77.
- 30 C. Creutz, N. Sutin and B. Brunshwig, to be published.
- 31 C. P. Anderson, T. J. Meyer, D. J. Salmon and R. C. Young, *J. Am. Chem. Soc.*, 99 (1977) 1980.
- 32 P. J. DeLaive, J. T. Lee, H. W. Sprintschnik, H. Abruna, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 99 (1977) 7094.
- 33 C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 99 (1977) 241.
- 34 U. Lachish, M. Ottolenghi and J. Rabani, *J. Am. Chem. Soc.*, 99 (1977) 8062.
- 35 J. K. Nagle, R. C. Young and T. J. Meyer, *Inorg. Chem.*, 16 (1977) 3366.
- 36 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 98 (1976) 2337.
- 37 G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch and D. G. Whitten, *J. Am. Chem. Soc.*, 99 (1977) 4947.
- 38 S. J. Valenty and G. L. Gaines, Jr., *J. Am. Chem. Soc.*, 99 (1977) 1285.
- 39 K.-P. Seefeld, D. Mobius and H. Kuhn, *Helv. Chim. Acta*, 60 (1977) 2608.
- 40 E. Finkenbergh, P. Fisher, S.-M. Y. Huang and H. D. Gafney, *J. Am. Chem. Soc.*, 82 (1978) 526.
- 41 B. Brunshwig, unpublished observations.
- 42 E. Pelizzetti, E. Mentasti and E. Premauro, *Inorg. Chem.*, 17 (1978) 1181.
- 43 G. M. Brown and N. Sutin, work in progress.
- 44 K. Takuma, M. Kajiwara and T. Matsuo, *Chem. Lett.*, (1977) 1199.
- 45 W. E. Ford, J. M. Otvos and M. Calvin, in the press.
- 46 R. C. Young, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, 97 (1975) 4781.
- 47 P. J. DeLaive, C. Giannotti and D. G. Whitten, *J. Am. Chem. Soc.*, in the press.
- 48 M. S. Chan, C. A. Evans, S. Markiewicz, R. Sparks and J. R. Bolton, *Abstracts, First*

- International Conference on the Photochemical Conversion and Storage of Solar Energy, London, Canada, August 1976, p. E7.  
A. A. Krasnovskii, V. V. Nikandrov, G. P. Brin, I. N. Gogotov and V. P. Oschenkov, Dokl. Akad. Nauk SSSR, 225 (1975) 711.
- 49 A. Moradpour, E. Amouyal, P. Keller and H. Kagan, Abstracts, Second International Conference on the Photochemical Conversion and Storage of Solar Energy, Cambridge, England, August 1978, p. 31.
- 50 M. Chou and C. Creutz, work in progress.
- 51 G. M. Brown, B. Brunschwigg, C. Creutz, J. F. Endicott and N. Sutin, to be published.
- 52 D. D. Davis, K. L. Stevenson and G. K. King, Inorg. Chem., 16 (1977) 670; P. R. Ryaston, Solar Energy, 19 (1977) 445; M. Brandys and G. Stein, J. Phys. Chem., 82 (1978) 852.
- 53 J.-M. Lehn and J.-P. Sauvage, Nouveau Journal de Chimie, 1 (1977) 449.
- 54 K. R. Mann, N. S. Lewis, V. M. Miskowski, D. K. Erwin, G. S. Hammond and H. B. Gray, J. Am. Chem. Soc., 99 (1977) 5525.
- 55 W. D. K. Clark and N. Sutin, J. Am. Chem. Soc., 99 (1977) 4676.
- 56 H. Tributsch, Z. Naturforsch., 321 (1977) 972.
- 57 N. E. Tokel-Takvoryan, R. E. Hemingway and A. J. Bard, J. Am. Chem. Soc., 95 (1973) 6582.
- 58 H. D. Gafney and A. W. Adamson, J. Chem. Ed., 52 (1975) 480.
- 59 J. E. Martin, E. J. Hart, A. W. Adamson, H. D. Gafney and J. Halpern, J. Am. Chem. Soc., 94 (1972) 9238.
- 60 F. E. Lytle and D. M. Hercules, Photochem. Photobiol., 13 (1971) 123.
- 61 C. Creutz, unpublished observations.
- 62 R. A. Marcus, J. Phys. Chem., 72 (1968) 891.
- 63 N. Sutin, Acc. Chem. Res., 1 (1968) 225.
- 64 A. Anderson and N. A. Bonner, J. Am. Chem. Soc., 76 (1954) 3826.
- 65 D. J. Meier and C. S. Garner, J. Phys. Chem., 56 (1952) 853.
- 66 K. V. Krishnamurty and A. C. Wahl, J. Am. Chem. Soc., 80 (1958) 5921.
- 67 J. Silverman and R. W. Dodson, J. Phys. Chem., 56 (1952) 846.
- 68 T. J. Meyer and H. Taube, Inorg. Chem., 7 (1968) 2369.
- 69 B. Brunschwigg and N. Sutin, J. Am. Chem. Soc., in press.
- 70 R. C. Young, F. R. Keene and T. J. Meyer, J. Am. Chem. Soc., 99 (1977) 2468.
- 71 N. Sutin, in B. Chance (ed.), Tunneling in Biological Systems, Academic Press, New York, N. Y., in the press.
- 72 N. Sutin, in G. L. Eichhorn (ed.), Bioinorganic Chemistry, Vol. 2, Elsevier, New York, 1973, Chap. 19, p. 611.
- 73 N. A. P. Kane-Maquire and C. H. Langford, Chem. Commun., (1973) 351.
- 74 C. H. Langford and C. P. J. Vuik, J. Am. Chem. Soc., 98 (1976) 5409.
- 75 R. A. Marcus, J. Chem. Phys., 24 (1956) 966.
- 76 R. A. Marcus, Discuss. Faraday Soc., 29 (1960) 21.
- 77 R. A. Marcus, Ann. Rev. Phys. Chem., 15 (1966) 155.
- 78 R. A. Marcus and N. Sutin, Inorg. Chem., 14 (1975) 213.
- 79 J. N. Braddock and T. J. Meyer, J. Am. Chem. Soc., 95 (1973) 3158.
- 80 R. A. Marcus, in B. Chance (ed.), Tunneling in Biological Systems, Academic Press, New York, in the press.
- 81 C. D. Jonah, M. S. Matheson and D. Meisel, J. Am. Chem. Soc., 100 (1978) 1449.
- 82 A. J. Frank, M. Gratzel, A. Henglein and E. Janata, Ber. Bunsenges. Phys. Chem., 80 (1976) 547.
- 83 D. Rehm and A. Weller, Ber. Bunsenges. Phys. Chem., 73 (1969) 834.
- 84 D. Rehm and A. Weller, Israel J. Chem., 8 (1970) 259.
- 85 A. M. Tait, M. Z. Hoffman and E. Hayon, J. Am. Chem. Soc., 98 (1976) 86.