

## SEPARATION OF PHOTOREDOX PRODUCTS BY LOCAL POTENTIAL FIELDS\*

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### Summary

Polyelectrolytes, ion exchangers and charged colloids can be used to control the rates of photo-induced chemical reactions. In particular, polyelectrolytes possess several additional features which make them attractive as suitable microassemblies in such systems. These include a well-defined structure whose properties of size, shape, charge density etc. may be modified by conventional synthetic techniques, the possibility of attaching specific molecular chromophores chemically to a polyelectrolyte such that they possess the desired properties (*e.g.* light absorption, redox potential, solubility etc.) and their possible adsorption to colloidal catalysts and electrodes. Special emphasis on charge separation and the inhibition of photochemical back reactions by polyelectrolytes is therefore made.

Charge separation effects are critically reviewed. Large effects on the quantum yields of photochemical electron transfer products are reported. The reactions of zwitterionic quenchers with excited photosensitizers in the presence of polyelectrolytes or charged colloids are also described in which there seems to be a lack of microenvironmental effect on the quantum yields of charge separation. The possible reasons for this are discussed.

In general, back reactions are expected to be inhibited in the presence of polyelectrolytes when one of the reacting species lies in the polymer field and the other is an ion bearing the same charge as the polyion. However, the inhibition effect is usually found to be only of one or two orders of magnitude.

On the basis of pulse radiolytic measurements of the rate of bimolecular reactions of polyelectrolyte radicals, it can be concluded that polyelectrolytes may lead to the inhibition of back reactions by up to five or six orders of magnitude if the two photochemical transient species are bound to different polyelectrolyte molecules carrying the same electric charge. A photochemical system which fulfils the conditions is described,

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\*Paper presented at the Fifth International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan, August 26 - 31, 1984.

and ways in which to apply such systems to the photochemical cleavage of water are discussed.

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## 1. Introduction

The purpose of this paper is to evaluate the possible contribution of microenvironments, particularly polyelectrolytes and charged colloids, to the direct conversion of solar energy into useful chemical energy. We shall restrict our discussion to the photochemical formation of  $H_2$  and  $O_2$  from water, which is the most popular photogeneration process of redox fuels currently under investigation.

A typical conversion and storage system involves the following reactions:



Reaction (1) represents the excitation of a photosensitizer S. The excited state  $S^*$  must possess the appropriate energy and a sufficiently long lifetime to be able to transfer an electron to the acceptor A (or to accept an electron from a donor; these two cases are symmetrical). Reaction (3) and reaction (4) produce  $O_2$  and  $H_2$  respectively, together with the regeneration of the initial reactants S and A, and may require appropriate redox catalysts. The net result is the decomposition of water to  $H_2$  and  $O_2$ , with energy storage of  $57 \text{ kcal mol}^{-1}$ .

It is not possible to store all the energy absorbed in process (1) since reactions (2) - (4) require a certain driving force. Energy storage means the formation of products, the free energy of which is more positive than the free energy of the reactants. Such products must be kinetically stable, *i.e.* an activation energy barrier must exist between the products formed and the initial reactants, and this can be achieved only if part of the absorbed photon energy is "lost" by its conversion to heat. Therefore a partial loss of the absorbed solar energy is inevitable. Since from thermodynamics it is predicted that a spontaneous process proceeds in the direction of lower free energy, there is a danger of losing the excess free energy during any of the intermediate stages by the so-called "back reaction" such as  $S^* \rightarrow S$  followed by



While  $S^* \rightarrow S$  can be suppressed in many systems by using sufficiently high concentrations of A, reaction (5) remains the main obstacle to achieving direct photochemical energy storage with reasonable yields. One of the main ways to effect inhibition or prevention of such reactions is to add an appropriate microenvironment, and the use of some of these microassemblies is the topic of discussion in this paper.

## 2. Use of microassemblies

Chemical reactions may take place either on the surface or within the assembly. The rates and yields of the reactions can vary according to the nature of both the microenvironment and the reactants, and this may be exploited to allow an improvement in the overall efficiency of formation of the photochemical electron transfer products. Both uncharged and charged microenvironments have been investigated in photochemical systems. The uncharged systems include monolayers [1 - 3], microemulsions [4 - 7] and bilayer lipid membranes [8 - 12]. When the products of photochemical electron transfer are separated into two different phases, their rate of back reaction decreases due to the physical barrier which must be overcome. It should be noted, however, that when the initial reactants ( $S^*$  and A) are also separated by means of two phases their overall apparent rate of conversion to photochemical products may be reduced, since this may unfavourably affect the electron transfer yields in the initial step.

Micelles and charged vesicles add an extra phase and at the same time also display a strong electric field in their vicinity. Many groups have investigated photochemical redox reactions in these microenvironmental systems [13 - 26]. An interesting application was reported by Moroi *et al.* [14] who dissolved the photosensitizer methylphenothiazine in lauryl sulphate micelles, where  $Cu^{2+}$  was the counter-ion. The photochemical electron transfer product  $Cu^+$  escaped to the bulk of the solution where it reduced  $Fe(CN)_6^{3-}$ . The back reaction between the two products  $Fe(CN)_6^{4-}$  and the methylphenothiazine cation was drastically inhibited by the micellar electrostatic barrier between the two phases. Another class of microenvironments includes the highly charged assemblies, polyelectrolytes [27 - 36], ion-exchange resins [37 - 40], charged colloids [41 - 43] and charged membranes [44, 45], where the strong electric field is the most important factor affecting the rates and yields of the photochemical reactions. In the following sections we shall confine our discussion to this group of microenvironments, with special emphasis on polyelectrolytes.

## 3. Effects of polyelectrolytes on rates of chemical reactions

A polyelectrolyte is a polyionic molecule, usually with a high charge density. In some cases there is a charge on every repeating unit. The ability

of polyelectrolytes to affect the rates of chemical reactions is well known [46 - 60]. The enhancement of the reactions between species which possess the same electric charge is attributed to a concentration effect on the reactants. In the presence of the polyelectrolyte, both reactants are confined to the polymer volume so that their effective concentration increases by the ratio  $V_s/V_e$  where  $V_s$  is the total volume of solution and  $V_e$  is the volume of the electric field near the polymer. In fact, the electric field decreases continuously with distance from the polymer and therefore the definition of  $V_e$  is somewhat arbitrary. When very low concentrations of the polymer are used, enhancement of chemical reactions by several orders of magnitude is observed. A well-known example is the reaction between  $\text{Hg}^{2+}$  ions and  $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ , the rate of which was reported to increase by more than five orders of magnitude on addition of poly(vinyl sulphonate) [45]. From the point of view of energy storage, a more important feature of polyelectrolyte solutions is their retardation effect on reactions between ions of opposite charge [52 - 58]. This is attributed to electrostatic attraction of the ion carrying the opposite charge to that of the polymer, together with repulsion of the ion bearing the same charge as that of the polymer. Thus, the reacting ions may be somewhat separated in the solution volume, and their reaction is slowed down. Experiments have demonstrated factors of inhibition of up to two orders of magnitude.

#### 4. Application of polyelectrolytes to photochemical systems

Polyelectrolytes have also been used in photochemical systems [27 - 36, 61]. Enhancement of the rates of quenching reactions by several orders of magnitude was achieved [27 - 29] as a result of concentration effects. In the presence of a sufficient concentration of inert ions, these enhancement effects may be reversed because of an exchange of reacting ions with inert ions [27]. High concentrations of inert ions may completely neutralize the electric field of the polymer, and in this case the reaction will be the same as in the absence of the polymer at the given ionic strength. A reversal effect is also observed on increasing the concentrations of the reacting ions beyond the capacity of the polymer, which was found to range from 25% to 70% coverage [27, 28, 35, 36]. Highly charged counter-ions may also induce cross-linking and precipitation of the polymer [28, 29, 34, 62]. The yields of separated photoredox products and their rates of recombination may also be dramatically affected by the presence of an appropriate polyelectrolyte, as will be shown later.

Two types of interaction between a polymer and a counter-ion have been distinguished [63]. Site binding involves direct contact of the ion with the polymer. A complex (which may be labile or stable) is formed, and this is usually related to a change in the optical absorption spectrum of the ion (*e.g.* as observed in the  $\text{Fe}^{3+}$ -poly(vinyl sulphate) system) [29].

The second type of interaction between a polyelectrolyte and an ion is termed territorial binding, the nature of which is mainly electrostatic. The ions are delocalized in the volume range of the electrostatic forces of the polymer charge. The distribution of the ions in the solution volume has been treated using two models. In the condensation model a certain fraction of the ions are considered to be condensed at the polymer surface [64 - 67]. In another approach a Poisson-Boltzman distribution is assumed [68 - 73]. For strong interactions, *e.g.* when multicharged ions are involved, these two models are expected to lead to similar conclusions.

Polyelectrolytes may therefore potentially be an important tool in controlling the efficiencies of photoredox processes which are related to solar energy storage. Their main value lies in their ability to control the rates of photochemical reactions. However, they also possess other advantages: their structure is usually well defined, they may be relatively easily chemically modified, they can act as supports for colloidal catalysts for  $H_2$  and  $O_2$  generation or can be adsorbed onto other materials (including semiconductor and other electrodes), and they may be used in photoelectrochemical systems. Much information on these and other features of polyelectrolytes (and polymers in general) can be found in two excellent reviews which have recently been published [74, 75].

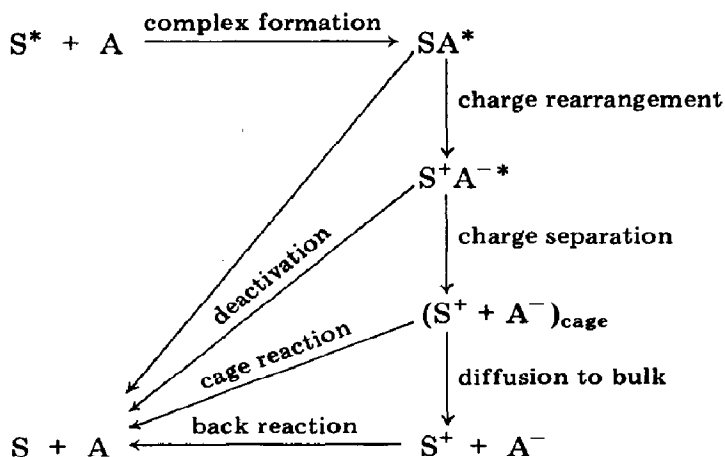
## 5. Photosensitizers and quenchers covalently bonded to polyelectrolytes

Several polymeric photosensitizers [76 - 92] and quenchers [93 - 96] have been used in photochemical systems. Their preparation is relatively simple and is based on the attachment to the photosensitizer, or quencher, of a functional group which is able to polymerize, such as a vinyl group. A polymer is then prepared where the photosensitizer or quencher appears in the repeating group of the polymer. It can also be "diluted" by means of copolymerization [86, 97], and in some cases the site of one photochemically active group in a polyelectrolyte can be fixed [96]. Species containing both quencher and photosensitizer on the same polymer have also been prepared [98].

Colloidal catalysts for  $H_2$  and  $O_2$  formation can also be stabilized by polymers [81, 94, 99]. If polyelectrolytes are used as stabilizers, it is possible to construct a system in which the appropriate photochemical product is produced in the polymer field where the catalyst is "waiting" ready to enhance the subsequent reactions. A considerable amount of work has been carried out in recent years on polyelectrolytes adsorbed onto electrodes [77, 83, 84, 100 - 115]. The coating of electrodes with polyelectrolytes opens additional possibilities for employing such polymers in photoelectrochemical processes.

## 6. Charge separation

Charged microenvironments in general and polyelectrolytes in particular may affect the charge separation process in a photoelectron transfer system. Reaction (2) is usually quite a complicated process, involving complex formation followed by charge rearrangement, charge separation and formation of the electron transfer products in the bulk of the solution. The products are first formed in a photochemical cage where no solvent molecules lie between them, and then competition between diffusion from the cage to the bulk of the solution and reversed electron transfer (reaction (5)) in the cage takes place. These processes are summarized in the following reaction scheme:



At each intermediate stage the system may react back to produce the ground state reactants.

In the particular case where  $S^+$  and  $A^-$  are ions with opposite charges (it should be noted that  $S$  and  $A$  may also represent ions) a polyelectrolyte effect on the charge separation step is possible. Such an effect was first reported for  $S \equiv \text{Ru}(\text{bpy})_3^{2+}$  ( $\text{bpy} \equiv 2,2'$ -bipyridine) and  $A \equiv$  iron(III) nitri-lotriacetic acid ( $\text{FeNTA}$ ) or cobalt(III) acetylacetonate using poly(vinyl sulphate) [30]. The quantum yields of the charge separation products in these systems increased from 0.22 to 0.75 and from 0.07 to 0.45 respectively on addition of poly(vinyl sulphate). In contrast, ruthenium(III) acetylacetonate, nitrobenzene and  $\text{O}_2$ , when used as quenchers, produced no charge separation products either in the absence or in the presence of poly(vinyl sulphate) [30]. These results are related to the Marcus equation [116, 117]

$$k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2} \quad (8)$$

where  $k_{ab}$  is the rate constant for the electron transfer reaction,  $K_{ab}$  is the equilibrium constant for that reaction,  $k_{aa}$  and  $k_{bb}$  are the self-exchange rate constants for each of the appropriate redox couples and  $f_{ab}$  is defined as follows:

$$\log f_{ab} = \frac{(\log K_{ab})^2}{4 \log(k_{aa}k_{bb}/z^2)} \quad (9)$$

where  $z$  is the collision frequency (taken as  $10^{11} \text{ M}^{-1} \text{ s}^{-1}$ ). It has been found that whenever the calculated Marcus activation-controlled rate constant for the back reaction was very fast (e.g.  $10^{16} \text{ M}^{-1} \text{ s}^{-1}$  for nitrobenzene) no charge separation products were observed even in the presence of the polyelectrolyte. Product formation apparently can be observed when the Marcus calculated rate constant is of the order of the diffusion-controlled rate. (When the back reaction is much slower, products may be formed with a high quantum yield even in the absence of the polymer.) In the above discussion it is implicitly assumed that the effect of the polyelectrolyte is at the stage of escape from the photochemical cage. This is not necessarily always the case. It is conceivable that the polyelectrolyte may affect the charge rearrangement as well as the charge separation stages. In both cases the polymer field is expected to interact with the intermediates ( $S^+A^{-*}$  or  $S^+ + A^-$ ) so that the free energy decreases for charge separation. The correlation with the Marcus rate constants may still hold in this case.

A strong polyelectrolyte effect was found when  $S \equiv \text{Ru}(\text{bpy})_2(\text{CN})_2$  and  $A \equiv \text{Fe}(\text{CN})_6^{3-}$  [34]. The positive polymer polybrene (repeating unit  $\{(\text{CH}_2)_3\text{N}(\text{CH}_3)_2(\text{CH}_2)_6\text{N}(\text{CH}_3)_2\}^{2+}$ ) induced an increase in the quantum yield for photochemical electron transfer from practically zero to unity. In general, a system should be composed such that the photosensitizer lies on the polymer while the quencher is in the bulk. The reason for this is the short lifetime and low concentrations of the excited photosensitizer. The probability of reaction is very small if all the quencher molecules are taken out from most of the solution volume by the polymer. If the polymer concentration is very low, an excited photosensitizer will not live long enough to diffuse and to meet a polymer molecule. For polybrene an "inverted" system was possible because of the low molecular weight of the polybrene molecule, which corresponds to 11 monomer units only. Therefore the distribution of the quencher was not so significantly affected as to prevent reaction of the excited  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  with the  $\text{Fe}(\text{CN})_6^{3-}$  carried by the polymer.

Systems of special interest contain zwitterionic quenchers, in particular, viologen derivatives. These include  $N,N'$ -bis(carboxymethyl)-4,4'-bipyridinium (CMB) [118],  $N,N'$ -bis(3-sulphonatopropyl)-4,4'-bipyridinium (SPB) [41, 42, 82, 91, 92, 118 - 121],  $N,N'$ -bis(3-sulphonatopropyl)-2,2'-bipyridinium (DQS) [43],  $N,N'$ -bis(2-sulphonatoethyl)-4,4'-bipyridinium (BSEP) [122] and  $N,N'$ -bis(4-sulphonatotoloyl)-4,4'-bipyridinium (BSV) [35, 36].

CMB was used in micellar solutions [118] whereas SPB was used in micellar [118, 119, 121], polyelectrolyte [82, 91, 92] and  $\text{SiO}_2$  colloidal solutions [41, 42, 119, 120]. DQS was used in colloidal  $\text{SiO}_2$  solutions [43], BSEP was employed in water (no microenvironment) [122] and BSV was studied in polyelectrolyte solutions (poly(vinyl sulphate)) [35, 36].

Except for the BSV system, the rate of quenching was only slightly affected by the presence of the microenvironment. Table 1 summarizes the effects of adding various microenvironments on the charge separation in zwitterionic quencher systems. Similar results are found for zwitterionic quencher systems containing polyelectrolyte-bound photosensitizers [82, 91, 92]. Micelles seem to act more specifically than polyelectrolytes and charged colloids. Sodium dodecylsulphate micelles cause a decrease (by a factor of about 2) in the quantum yield for charge separation when the quencher is CMB or SPB. This is contrary to the effect observed in non-zwitterionic systems which have been described above and can be accounted for if there are hydrophobic interactions [82, 86, 87, 91, 92, 97] between the micelles and the quencher which oppose the separation of the products. The effect of sodium tetradecyldioxyethylenesulphate ( $C_{14}(\text{OEG})_2\text{SO}_4^- \text{Na}^+$ ) micelles on the  $\text{Ru}(\text{bpy})_3^{2+}$ -SPB system is similar. However, when bis(2,2'-bipyridyl)-(4,4'-dinonadecyl-2,2'-bipyridyl)ruthenium ( $\text{Ru}(\text{bpy})_3 \cdot 2\text{C}_{19}^{2+}$ ) is used as a photosensitizer instead of  $\text{Ru}(\text{bpy})_3^{2+}$  the quantum yield for electron transfer to SPB seems to increase somewhat, and this effect seems to be specific to the system containing the  $C_{14}(\text{OEG})_2\text{SO}_4^-$  micelle and  $\text{Ru}(\text{bpy})_3 \cdot 2\text{C}_{19}^{2+}$ . When the environment is the  $\text{SiO}_2$  colloid the quantum yield for charge separation increases compared with the appropriate values in the absence of the colloid. The increase is by about 60% for SPB (calculated from the appropriate laser flash photolysis data assuming that the examples chosen for representation are at the same flash intensity). The effect is more dramatic with DQS, where the yield increases from 0 to 0.15 on addition of  $\text{SiO}_2$ . The effect of a polyelectrolyte on the zwitterionic system  $\text{Ru}(\text{bpy})_3^{2+}$ -BSV is unique, however, and is described below.

In several photochemical systems [30, 34, 124] it has been found that a reaction involving an ion and a neutral molecule is about 40% slower in the presence of a polymer with a charge contrary to that of the ion. This is because of the much lower rate of diffusion of the ion, which is restricted to the polymer field. However, the BSV molecule, despite its formal zero charge, quenches  $\text{Ru}(\text{bpy})_3^{2+}$  up to 40 times faster when poly(vinyl sulphate) is present. Such an effect was not observed in any other system. This is explained by the large dipole moment which is attributed to the BSV, as demonstrated in Fig. 1. The BSV dipoles are oriented in the polymer field so that the positive charges are close to the polymer, and thus the net effect is attraction. After the transfer of an electron to produce  $\text{BSV}^-$ , the molecule will possess three negative charges and two positive charges. Since the orientation remains such that the positive charges are nearer the polymer, there is practically no effect of increased yield of charge separation products as is observed in several photochemical electron transfers involving simple neutral compounds [30, 34].

Although SPB does not seem to possess a dipole moment (no significant enhancement of the rate of quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by the  $\text{SiO}_2$  colloid was observed), it is conceivable that during the reaction with the  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer in the  $\text{SiO}_2$  field a temporary dipole is induced



TABLE 1

Quantum yields and reaction rate constants in various photochemical systems containing zwitterionic quenchers: effect of micro-environments

Microenvironment	Acceptor	Photosensitizer	Quantum yield of redox products	Quenching rate constants ( $M^{-1} s^{-1}$ )	Rate constants of back reactions ( $M^{-1} s^{-1}$ )
Sodium dodecylsulphate micelles	CMB	$Ru(bpy)_3^{2+}$	$\approx 0.2^a$		$6.5 \times 10^9$
	CMB	$Ru(bpy)_3^{2+}$	$\approx 0.09^a$		$9.5 \times 10^8$
	SPB	$Ru(bpy)_3^{2+}$	$\approx 0.2^a$	$1.3 \times 10^9$	$7.8 \times 10^9$
Sodium dodecylsulphate micelles	SPB	$Ru(bpy)_3^{2+}$	$\approx 0.1^a$		$(8 \cdot 9) \times 10^8$
	SPB	$Ru(bpy)_3^{2+}$	$\approx 0.1^a$		$1.7 \times 10^8$
$C_{14}(OEG)_2 SO_4^-$ micelles	SPB	$Ru(bpy)_3 \cdot 2C_{10}^{2+}$	$\approx 0.25^a$		$4 \times 10^7$
	SPB	$Ru(bpy)_3^{2+}$	$A^b$	$1.5 \times 10^9$	$7.9 \times 10^9^c$
$SiO_2$ colloids	SPB	$Ru(bpy)_3^{2+}$	$1.6A^b$	$1.5 \times 10^9$	$5.7 \times 10^7^d$
	DQS	$Ru(bpy)_3^{2+}$	0	$5.9 \times 10^8$	$10^9 \cdot 10^{10e}$
$SiO_2$ colloids	DQS	$Ru(bpy)_3^{2+}$	$0.15^a$	$4 \times 10^8$	$1 \times 10^7^c$
	BSV	$Ru(bpy)_3^{2+}$	$0.12 - 0.15^f$	$1.4 \times 10^9$	$B^f$
Poly(vinyl sulphate)	BSV	$Ru(bpy)_3^{2+}$	$0.10 - 0.15^f$	Up to $5.2 \times 10^{10}$	$\approx 0.1B^f$

<sup>a</sup> Values are based on a quantum yield for methylviologen cation radical  $MV^+$  formation equal to 0.2 in the  $Ru(bpy)_3^{2+}$ - $MV^{2+}$  system.

<sup>b</sup> Relative quantum yields; from ref. 41, Fig. 3, it follows that the quantum yields of net separated electron transfer products are the same both in the absence and in the presence of  $SiO_2$ .

<sup>c</sup> pH 9.8.

<sup>d</sup> In the presence of  $Fe(CN)_6^{3-}$  [123] or anthraquinone sulphonates [42] the regeneration of ground state  $Ru(bpy)_3^{2+}$  could be inhibited by a factor ranging from 25 to 1000 on addition of  $SiO_2$  colloid.

<sup>e</sup> Estimated on the basis of similar systems.

<sup>f</sup> Relative quantum yields; there is evidence for a complex between the photochemical electron transfer products and hence the values of the quantum yields are not certain. The time profile of the back reaction yielded a rate law between first and second order, and lifetimes rather than rate constants are reported. The first lifetime of the decay of the electron transfer products was nearly one order of magnitude longer in the presence of polyelectrolyte than it was in homogeneous solution.

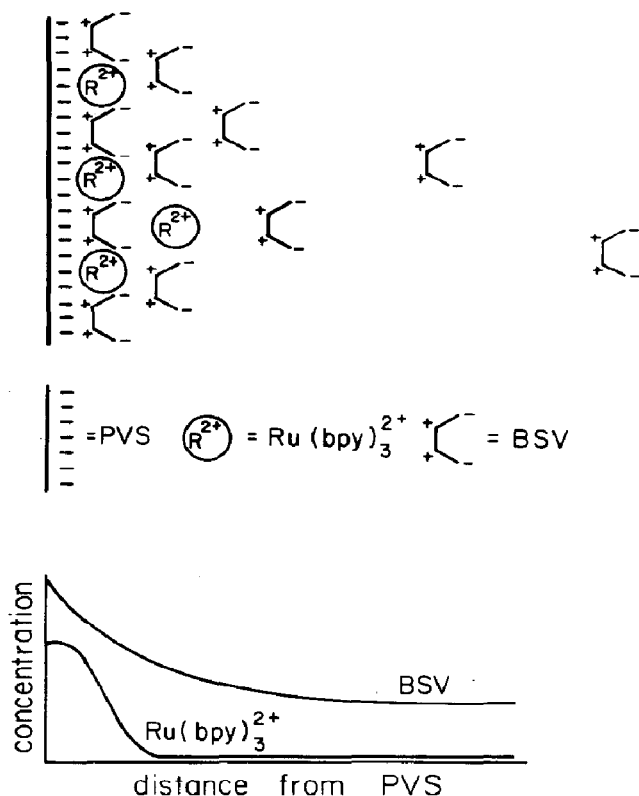


Fig. 1. A schematic representation of the distribution of  $\text{Ru}(\text{bpy})_3^{2+}$  cations and BSV molecules away from the PVS polyanion. The doubly positively charged  $\text{Ru}(\text{bpy})_3^{2+}$  species are much more strongly bound to the negatively charged polyelectrolyte than are the dipolar zwitterionic BSV molecules.

so that, similar to BSV, no increase in quantum yield is observed. DQS shows an increase in quantum yield from 0 to 0.15. The DQS has a trans configuration [43] which has only a small dipole moment, if any. This configuration is not expected to be affected by the field of the polymer, and therefore DQS is expected to behave like a simple uncharged molecule.

## 7. The back reaction

The strong effect of polyelectrolytes on the quantum yields of charge separation products is not followed by a similar effect on the back reaction. Usually, a retardation effect of not more than one order of magnitude is observed. For cobalt(III) acetylacetonate and FeNTA [30] the back reaction was attributed to side reactions, involving the free ligand in the case of the cobalt complex (the cobalt(II) complex which is produced by the reduction of the cobalt(III) compound quickly decomposes) and protonation of the  $\text{FeNTA}^-$  product with the formation of  $\text{FeNTAH}$  in the case of the iron complex, followed by a fast reaction with  $\text{Ru}(\text{bpy})_3^{3+}$ , which is

unaffected by the polymer charge. However, even when  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  are used with polybrene as the microenvironment a true back reaction was observed between  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Ru}(\text{bpy})_2(\text{CN})_2^+$  with a reaction rate constant of  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in the presence of polybrene. This value is close to the diffusion-controlled limit so that no significant inhibition could possibly take place. Similarly, in the  $\text{Ru}(\text{bpy})_3^{2+}$ -BSV system [35, 36] a factor of inhibition of only about one order of magnitude is observed. The  $\text{SiO}_2$  colloid seems to be more effective in inhibiting the back reaction. Inhibition by factors of  $10^2 - 10^3$  have been reported (see Table 1, footnote e). The micelles (Table 1) inhibit the back reactions by about one order of magnitude, which is similar to the effect of the polyelectrolytes.

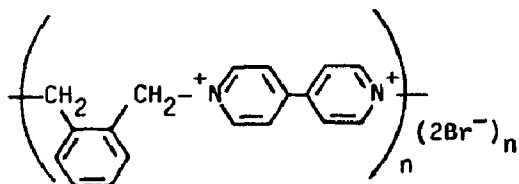
## 8. Viologen polymers

The lack of strong inhibition in the polyelectrolyte systems calls for the consideration of two effects. Firstly, the binding of an ion by the polyelectrolyte field may involve a dynamic equilibrium, particularly if it is territorial binding, and it is possible that a fraction of the ions with a charge opposite to that of the polymer are in the bulk at any given time. If, for example, 10% of the ions are in the bulk, they may participate in the back reactions and the result would be an apparent rate constant which is one order of magnitude smaller than the rate constant for the same reaction when all species are in the bulk. As will be seen later, this possibility can be ruled out, and it is possible to show that the back reactions under conditions of low coverage of the polymer involve bound ions. Secondly, the fact that the polymer charge is partially neutralized at the specific site of the counter-ion at a given time must be considered, *e.g.*  $\text{Fe}(\text{CN})_6^{4-}$  in the field of polybrene [34] neutralizes four charges (out of an average total of 22). Therefore the oxidizing species approaching the  $\text{Fe}(\text{CN})_6^{4-}$  may be inhibited less than expected on the basis of the full charge of the polymer. Polymeric quenchers such as polyviologens, where the viologen chromophore is covalently bonded to the polymer chain, therefore possess the double advantage that the viologen unit is not able to diffuse into the bulk of solution and that it carries the positive charge of the polyelectrolyte so that there is no partial neutralization. Hence, no quenching reversal phenomena can occur in which the viologen unit is displaced into the bulk of other charged species.

Several polyviologens have been used as electron acceptors [93, 94, 96]. It has been generally observed that the quenching of the neutral photosensitizer  $\text{Ru}(\text{bpy})_2(\text{CN})_2$  [96] is 2 - 4 times slower than the analogous reaction with methylviologen. Moreover, when only one viologen molecule is covalently bonded to a positive polymer, there is only a small, if any, effect of the position of the viologen moiety on the rate of quenching. Practically the same rate is observed when the viologen moiety is at the end of the polymer chain or in the middle. The quantum yield of back reaction

between the photochemical electron transfer products,  $\text{Ru}(\text{bpy})_2(\text{CN})_2^+$  and the reduced positive viologen polymer shows a striking similarity to the results obtained from systems containing methylviologen as quencher. Thus, the quantum yield for photochemical electron transfer ranges from 0.06 to 0.13 for six different viologen polymers compared with 0.09 for methylviologen. The rate constant for back reaction (which was found to be second order) ranges from  $2.3 \times 10^9$  to  $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (with methylviologen the rate constant is  $9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ). Since a reaction with a polymer is expected to be about 50% slower due to the lower diffusion rate of the polymer, the contribution of the polymer field to the inhibition of the back reaction seems to be surprisingly small. (It should be noted that the comparison is with methylviologen and not with the monomer, about which no data are available. However, the qualitative feature of this discussion appears to hold in any case, since the actual reaction rate constants are sufficiently close to the diffusion limit and no large inhibition could have taken place.) It might be argued that viologen polymers are conducting [93, 94, 125 - 127] and therefore that the back reaction with  $\text{Ru}(\text{bpy})_2(\text{CN})_2^+$  may take place at any part of the polymer, not necessarily at the site where the photochemical electron transfer took place. This would increase the cross section for the reactions and hence compensate for the retardation effect of the electric field. However, two of the six polymers tested [96] are evidently non-conducting as they have just one viologen group per positive polymer.

An investigation of photochemical systems containing  $\text{Ru}(\text{bpy})_3^{2+}$  and various polyviologens has also been undertaken [93, 94, 96]. The trends found in these systems are similar to those reported for  $\text{Ru}(\text{bpy})_2(\text{CN})_2$ ; in particular, there is no great retardation effect on the rates of quenching and the back reactions. The quantum yields for electron transfer are also similar to the corresponding methylviologen systems, namely in the range 0.063 - 0.16 (compared with about 0.20 for methylviologen). The rate of back reaction is usually inhibited by up to a factor of 2.5 only, and in two cases it is even enhanced [93, 96]. An exception to this is the poly *o*-xylylviologen, which has the following repeating unit:



This gives a quenching rate constant of  $5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  with the  $\text{Ru}(\text{bpy})_3^{2+}$  photosensitizer (*cf.* that for methylviologen ( $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ )), a quantum yield for photoreduction of 0.57 (the highest value for all the tested viologens) and a rate constant for back reaction of  $9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (*cf.* that for methylviologen ( $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )).

The above-described effects can be qualitatively explained by specific hydrophobic interactions [86, 87, 96] between the 2,2'-bypyridine ligands

of the ruthenium complex and the 4,4'-bipyridine groups of the polyviologens. These interactions have an opposite effect to the electric repulsion of the polymer field. If this is so, perhaps better results can be obtained using other photosensitizer-acceptor (or donor) couples where the electrostatic repulsion is predominant. We have already discussed the relatively small (one order of magnitude) inhibition of the back reaction when the reacting species possess a single charge (such as  $\text{Ru}(\text{bpy})_2(\text{CN})_2^+$  reacting with  $\text{Fe}(\text{CN})_6^{4-}$  in the polybrene field [34]). The attempt to observe greater inhibition with the trivalent ion  $\text{Ru}(\text{bpy})_3^{3+}$  was unsuccessful, at least in the viologen polymer systems, apparently because of hydrophobic interactions. Will the three-valent ions be more effective in other systems? More work is still required to answer this question.

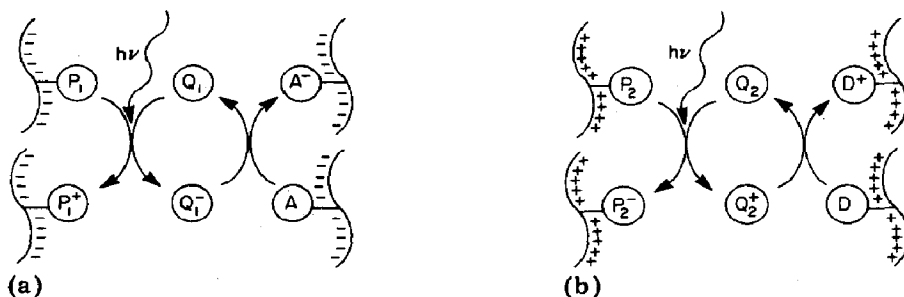
## 9. Ion exchangers

Ion exchangers are expected to act similarly to polyelectrolytes [37 - 40] as they have very similar features except for their insolubility in water. Many ion exchangers swell with large amounts of water and produce a resin-water system sufficiently transparent for emission and pulsed laser measurements, so that comparisons of the behaviour of photoredox systems and polyelectrolyte solutions can be made. So far, only a limited amount of work has been performed. Indeed, in some respects the results are similar to those obtained for the polyelectrolyte systems. Thus, the reaction rate constants for the ionic species  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  with  $\text{Ru}(\text{bpy})_3^{2+}$  adsorbed onto Sephadex SP-C 50 are comparable with those observed in a negative polyelectrolyte, when corrections for the volume effect are made. Quenching rate constants for neutral quenchers are consistently slower in the ion exchanger systems (by factors of 1.5 - 3.5) compared with a factor of about 2 for most polyelectrolyte systems. The results are too scanty for general conclusions, but no dramatic inhibition is observed for the back reaction of the negative acceptor ion with the positive species adsorbed onto the ion exchanger. There is also no strong effect on the quantum yield for charge separation. In conclusion, the ion exchangers probably behave similarly but considerably less effectively than polyelectrolytes.

## 10. Two-polymer systems

It may be concluded from the above discussion that factors of inhibition of the rate of back reaction in photoredox systems of only about one to two orders of magnitude have been achieved on addition of an appropriate polyelectrolyte.

A very large inhibition effect could possibly be obtained in a given polyelectrolyte system when the two back-reacting ions are bound to two different polyelectrolyte molecules, as is shown schematically in Fig. 2.



**Fig. 2. Photosensitized electron transfer systems containing two polyelectrolytes. (a)** The photosensitizer  $P_1$  bound to a negative polyelectrolyte transfers an electron to a neutral quencher  $Q_1$  to produce  $Q_1^-$  which is repelled by the negative polyelectrolyte field and may then transfer its additional negative charge to an acceptor molecule bound to a second negative polyelectrolyte. (The back reaction between the oxidized photosensitizer and the reduced acceptor is drastically retarded as a result of their covalent attachment to negative polyelectrolytes.) **(b)** An analogous system with electron transfer finally yielding a reduced photosensitizer  $P_2^-$  and an oxidized donor species  $D^+$  on separate positive polyelectrolytes.

In this case the rate of back reaction will be retarded both by the high electrostatic repulsive forces between the two polyions and by the relatively low rates of diffusion of the polymer molecules. Separation of the two final photoelectron transfer products on different polyelectrolytes is probably most easily achieved by their covalent attachment to the polyions, since this will remove the possibility of fast back reaction via an escape of ions into the bulk of the solution or via a reaction between two ions lying on the same polymer molecule. A mediator compound is necessary to transfer the electron either from the polymer-bound photosensitizer to the polymer-bound acceptor (Fig. 2(a)) or from the polymer-bound donor to the polymer-bound photosensitizer (Fig. 2(b)). It should be noted that in both cases the low retardation effects of the polyions on the relay compound are also exploited to obtain the overall transfer of charge from one polymer to another.

A simple model for such a system was tested using the technique of pulse radiolysis [62].  $N_2O$ -saturated solutions of polybrene were pulse irradiated and under these conditions about 90% of the primary free radicals produced from the water by the ionizing radiation are in the form of OH radicals. The OH radical abstracts a hydrogen atom from the polybrene and yields a polybrene radical which can only react in a dimerization reaction with another polybrene radical. The rate constant for the second-order decay of the polybrene radical was found to be  $2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . This is about five orders of magnitude slower than the diffusion-controlled rate of decay which is observed for low-molecular-weight free radicals. Of the five orders of magnitude, we estimate that one or two are a result of the lower diffusion rate and three or four result from the electrostatic effect of the polymer field. As the free radicals are produced on the polymer, this system closely simulates the ideal photochemical system described above.

Experiments have also been carried out on a photochemical system containing the compounds possessing the structural formulae given in Fig. 3. The rate constant for the back reaction between the reduced polymer-bound photosensitizer, the  $\text{Ru}(\text{bpy})_3^{2+}$  derivative and the oxidized polymer-bound donor  $N,N,N',N'$ -tetramethyl-*p*-phenylenediamine derivative was measured to be  $1.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  in aqueous solution [128], which is indeed more than five orders of magnitude slower than the rate constant ( $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) for the back reaction between the monomeric species measured in acetonitrile solution [129]. Much more work is now in progress in our laboratory on the construction of an appropriate photochemical system where the seemingly great disadvantage of the polyelectrolytes, namely their low ability to retard reactions with ions of the same charge, is exploited in a two-polyelectrolyte system to achieve inhibition of photochemical back reactions by orders of magnitude considerably higher than any other microenvironment. Here, we take advantage of a unique feature of the polyelectrolytes: the possibility of modifying them permanently by relatively simple synthetic procedures and hence of engineering molecules which will allow the formation of relatively long-lasting photochemical electron transfer products.

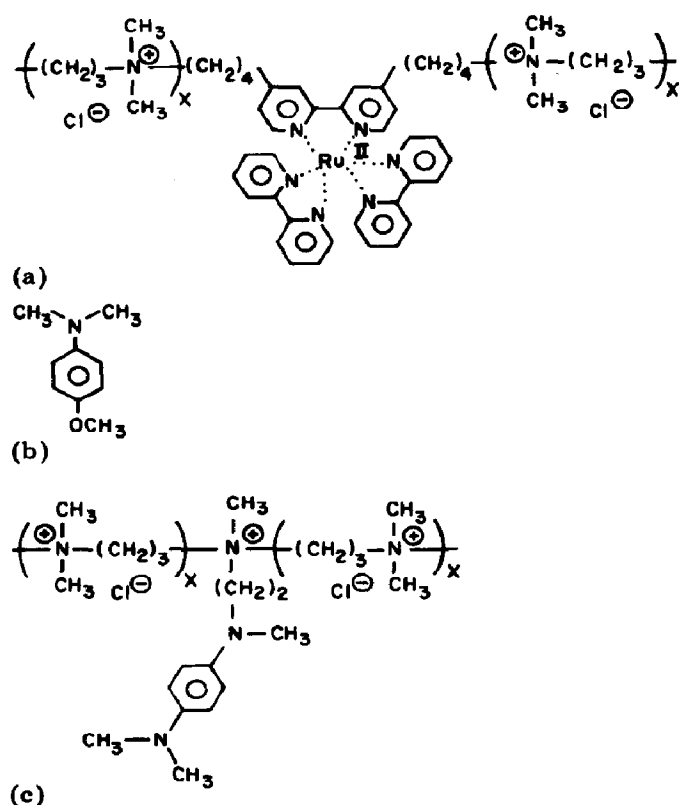


Fig. 3. Structural formulae of compounds used in a two-polyelectrolyte photochemical system: (a)  $\text{P}_2$ ; (b)  $\text{Q}_2$ ; (c)  $\text{D}$ .

## 11. Assessment

There are still many basic problems to be solved concerning the role of polyelectrolytes and other microenvironments in photochemical redox systems. Although we feel now that the qualitative features of polyelectrolytes are well understood, their exact behaviour cannot as yet be predicted. We still do not know the role of charge density, the minimum size of polyion required for it to behave as a polyelectrolyte and the importance of the complex problem of hydrophobic interactions in determining the ability of polyelectrolytes to affect the rates and yields of reactions. In addition, we do not know, when the back reactions involve simple ions, to what extent they can be inhibited and how to predict the effect of the valency of the ions. How does the polymer affect the quantum yields of the electron transfer products? Is it an effect on the charge rearrangement of the activation complex or does it assist in the charge separation stage or, alternatively, with the destruction of the photochemical cage? Even simple comparison studies using different microenvironments with the same photosensitizers and quenchers are still preliminary.

## 12. How to proceed

The possibility of achieving inhibition of back electron transfer by up to about five orders of magnitude seems to be well established. Under steady state illumination, this means that the initial electron transfer products of a redox photochemical system will probably live for many seconds or even minutes. Redox catalysts [130 - 134] may prove useful for further conversion of the energy temporarily stored in the form of the primary redox products to the more stable  $H_2$  and  $O_2$ . Although several years ago it seemed as if a combination of colloidal redox catalysts with a donor-acceptor system might produce reasonably high yields of both  $H_2$  and  $O_2$  [135, 136], more refined work [137 - 144] shows that while catalysed  $H_2$  formation can be easily achieved [137 - 141] the catalysed evolution of  $O_2$  is much less efficient and considerably more complicated [142 - 144]. In particular, the question of whether  $H_2$  and  $O_2$  can be produced simultaneously in the same volume of a solution requires, in our judgment, additional work. Polyelectrolytes can be used as carriers for appropriate colloidal catalysts and can also be adsorbed onto electrodes, and thus the redox potential difference of the photochemical products formed at the polymer can be utilized to electrolyse water in a separate compartment.

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