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PHOTOCHEMICAL REACTIONS CARRIED OUT WITHIN A SILICA GEL MATRIX[†]

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Summary

Silica gel–water systems were constructed and photochemical reactions were studied in these systems via pulse laser methods. Three photoactive probe species, ruthenium tris(bipyridine) ($Ru(bpy)_3^{2+}$), uranylion (UO_2^{2+}) and pyrene butyltrimethyl ammonium bromide, were studied with various anions, cations and neutral quenchers. In the gels the cationic probes $Ru(bpy)_3^{2+}$ and UO_2^{2+} show properties similar to those in porous colloidal silica and unlike those in bulk water. The subsequent reactions of all bound probes with added quenchers are explained in terms of electrostatic interactions of the gel network and the added quenchers.

1. Introduction

The polymerization of sodium silicate to form a gel has been studied for many decades, and a number of different mechanisms have emerged [1 - 5]. The gel can be formed by the addition of acid to sodium silicate or to a colloidal silica solution [6 - 8]. The effects of temperature [9], pH [10, 11], soda-to-silicate ratio [12] and choice of acid [13] have all been investigated. Small-angle X-ray scattering [14] and thermal aging studies have demonstrated that the gel can best be visualized as being made up of discrete particles which come together to form a network, the vacant space being taken up by water.

Numerous photochemical studies have been performed with molecules adsorbed on commercially available silica gel surfaces. Examples include the photophysics of adsorbed pyrene [15 - 17], the study of photoinduced free radicals [18 - 22], surface reactions with gels containing metal ions and metal oxides [23 - 26] and a variety of spectroscopic [27 - 31] and photolytic [32 - 35] investigations. The unique feature of the work to be presented in this paper is that the reactive species are all contained within the gel rather than being adsorbed on the surface.

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

2. Experimental details

Spectroscopic techniques for both absorption and emission, and also for steady state and pulsed laser studies, have been described earlier [36], and only brief details are necessary here.

Absorption spectra were recorded on a Perkin–Elmer 552 spectrophotometer and fluorescence spectra were recorded with a Perkin–Elmer MPF-44B spectrofluorometer. Flash photolysis studies were carried out using a Lambda Physik EMG-100 laser employing nitrogen gas ($\lambda_{ex} = 3371$ Å).

The Nalco silica used for comparison was no. 1115 (pH 10.4; 40 Å radius). All solutions of silica 1115 were run at 20% dilution in doubly distilled deionized water. The porous colloidal silica was prepared according to a published method [37] which produces particles of approximately 1000 Å diameter and a viscosity of 1.06 relative to water when run at 30% dilution.

The ruthenium tris(bipyridine) dichloride was obtained from the G. Frederick Smith Co. Reagent grade uranyl acetate was obtained from J. T. Baker Chemicals. Eastman supplied the N,N-diheptyl-4,4'-bipyridinium dibromide (heptyl viologen, HVI^{2+}). All the other chemicals were of reagent grade or higher purity and were used without further purification.

2.1. Preparation

The silica gel was formed by stirring 20.3 g of $Na_2SiO_3 \cdot 9H_2O$ dissolved in 100 ml of distilled deionized water with acid-charged Dowex 50-X8 cation exchange resin for 20 min. The resin was first converted to the H^+ form with 2 N HCl and was then washed repeatedly with distilled deionized water until a negative test for Cl^- was obtained at 0.001 M $AgNO_3$ for at least 10 min. The resin was suction filtered to remove excess water prior to the addition of the silicate mixture, and the resin was similarly removed at the end of the ion exchange process. The resulting solution had a density of 1.01 g ml^{-1} (pH 7) and was found from a flame test to be free of sodium. Stock solutions were prepared by dissolving appropriate amounts of quenchers in the silica solution if the proper final concentrations required more than 0.1 ml of an aqueous stock solution per 5 ml of silica solution.

The silica solution was placed in methacrylate disposable UV–visible cells, sonicated briefly to remove air bubbles, sealed with Parafilm and allowed to gel.

The solution gels at room temperature in about 8 h, but samples were kept for a further 2 days before being subjected to quenching studies since no aging effects (changes in the probe lifetime or quenching rate) could be observed for gel systems after that time.

2.2. Spectral studies

The emission spectrum of ruthenium tris(bipyridine) ($Ru(bpy)_3^{2+}$) is essentially the same in the gel as in water. It is pertinent to note that it is blue shifted on the Nalco 1115 colloidal silica particles. 4-(1-pyrenyl)butyl-

TABLE 1

Half-lives of probes in various media

Medium	Half-life (ns) of $Ru(bpy)_3^{2+}$	Half-life (ns) of PN+	Half-life (μs) of UO_2^{2+}
Water	415	101	10.1
Silica 1115	495	98	440
Porous silica	2110	—	129
Gel, air	628	88	101
Gel, oxygen free	795	100	—

trimethyl ammonium bromide (PN+) has an identical emission spectrum in water, in silica 1115 and in the gel. UO_2^{2+} in the gel has a spectrum intermediate between that in water and that in silica 1115.

Analysis of the lifetime of excited molecules in various media confirms that the gel structure offers an environment with characteristics between those of an aqueous homogeneous medium and a colloidal silica solution (Table 1).

PN+ is photochemically destroyed inside porous colloidal silica, but in degassed water or Nalco silica solutions it has an excited state half-life of about 100 ns. If the gel is formed in the presence of air, (PN+)* has a half-life that is somewhat shorter (only 88 ns) owing to quenching by dissolved oxygen. A gel formed under a pure nitrogen atmosphere (oxygen free) or one formed under a vacuum with PN+ inside gives the normal 100 ns (PN+)* half-life. Subsequent exposure to air for several days induces a virtually negligible decrease in the lifetime, indicating only a very gradual oxygen penetration. Similarly, if $Ru(bpy)_3^{2+}$ is present in a gel formed under oxygen-free conditions, its excited state half-life is 795 ns rather than 628 ns as obtained if the gel is formed in air. The 795 ns half-life is shorter than that of $Ru(bpy)_3^{2+}$ in porous colloidal silica but longer than that in any of the other media. $(UO_2^{2+})^*$ is unaffected by oxygen and has a half-life in the gel which is very similar to that in porous colloidal silica.

2.3. Fluorescence depolarization

Fluorescence depolarization has been used to examine the mobility of a probe molecule in a variety of environments in order to study, for instance, the fluidity of micellar interiors [38, 39], the structure of vesicles [40] and the interior of cellophane [41]. The degree of polarization P is given by [42]

$$P = \frac{I_{v,v} - I_{v,h}(I_{h,v}/I_{h,h})}{I_{v,v} + I_{v,h}(I_{h,v}/I_{h,h})}$$

where $I_{v,v}$ and $I_{h,h}$ represent the emission intensity measured at the parallel positions of the polarizing filters, $I_{v,h}$ and $I_{h,v}$ denote the emission intensity measured at the crossed positions of the polarizing filters, the first subscript denotes the orientation of the electric field vector for the excitation slit and

the second subscript denotes that for the emission slit (v and h represent vertical and horizontal orientations respectively).

The Perrin equation [43] describes the depolarization of the fluorescence in terms of the local probe viscosity:

$$\frac{1/P - 1/3}{1/P_0 - 1/3} = 1 + \frac{kT\tau}{\eta V}$$

where k is the Boltzmann gas constant, T is the Kelvin temperature, τ is the natural lifetime of the probe's excited state and V is its effective volume. P_0 is the degree of polarization measured in an extremely viscous medium.

The results for $Ru(bpy)_3^{2+}$, PN+ and UO_2^{2+} are shown in Table 2. In all three cases, the gel structure seems to restrict the motion of the bound probes significantly.

The degree of polarization in the gel is 0.0956 for $Ru(bpy)_3^{2+}$, 0.0838 for UO_2^{2+} and 0.0308 for PN+. By way of contrast, the degree of polarization is only 0.0176 for pyrene sulfonic acid in the gel compared with 0.00122 in water. This indicates that the three cationic probes are bound to the silica network but that the negatively charged pyrene sulfonic acid is located more towards the water phase. The amount of light scatter from the gels is very small and leads to corrections of less than 4% in the data.

TABLE 2

Degree of polarization

Medium	Polarization	Viscosity relative to water
Ru(bpy)$_3$$^{2+}$		
Water	0.00513	1
0.5 M NaLS	0.00736	1.57
20% silica 1115	0.0798	26.0
30% porous silica	0.0211	19.4
Silica gel	0.0956	47.0
50% ethylene glycol (50% water at 77 K)	0.191	
PN+		
Water	3.85×10^{-4}	
20% silica 1115	0.020	
Silica gel	0.0308	
50% ethylene glycol (50% water at 77 K)	0.0182	
UO$_2$$^{2+}$		
Water	-1.68×10^{-4}	
20% silica 1115	0.0426	
Porous silica	0.0421	
Silica gel	0.0838	
Tetrahydrofuran	0.0111	

NaLS, sodium lauryl sulfate.

3. Quenching studies

The probes $Ru(bpy)_3^{2+}$, PN+ and UO_2^{2+} all bind to colloidal silica particles where the negatively charged silica surface profoundly affects the approach of quenching species to the bound excited probe molecules. The pseudo-first-order quenching rate constants for a variety of species in various media are listed in Tables 3 - 5 for reactions with excited $Ru(bpy)_3^{2+}$, PN+ and UO_2^{2+} respectively. The data show that the gel structure offers less electrostatic repulsion to the approach of negative quenchers ($Fe(CN)_6^{3-}$, $NO_2-CH_2-CH_2-COO^-$, I^-, Br^- and CNS^-) than do silica 1115 colloidal particles. The network offers hindrance to unbound neutral quenchers such as nitrobenzene and nitromethane. Ethanol, however, can hydrogen bond to the silica network [44] where it is in close proximity to the bound uranyl ion, so that reaction rate enhancement is observed in the gel compared with in water. This is not the case for colloidal silica. At high pH, such as with the 20% silica 1115 pH 10 solutions, the bulky hydrated Na^+ counter ion inhibits hydrogen bonding from alcohols or polyethers to the silica particle. The silica colloids, in addition to not binding ethanol, offer steric hindrance to the quencher as it attempts to react with $(UO_2^{2+})^*$, decreasing the reaction rate compared with that in water. Quenching with ethanol has been described earlier [45] and is known to involve hydrogen atom transfer [46]

$$(UO_2^{2+})^* + CH_3CH_2OH \longrightarrow UO_2^+ + CH_2\overset{.}{C}HOH + H^+$$
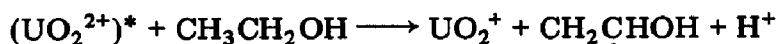
whereas the reaction between the excited uranyl ion and the anions listed occurs by electron transfer [47]. Positive quenchers such as Cu^{2+}, Tl^+ and HVI^{2+} react even more slowly with $Ru(bpy)_3^{2+}$ or PN+ in the gel system than in colloidal silica, which may indicate that the gel structure affords significantly greater silica surface area than is available in the colloidal system and the reactants are spaced further apart.

If the sodium salt of pyrene sulfonic acid is contained in the gel it would not be expected to bind to the negatively charged silica surface. The quenching rate constant of pyrene sulfonic acid with nitromethane in the gel is 3.4×10^9 l mol^{-1} s^{-1} compared with 6.3×10^9 l mol^{-1} s^{-1} in water indicat-

TABLE 3

Ruthenium tris(bipyridine) quenching rate constants k_q (λ_{em} = 610 nm)

	k_q (l mol^{-1} s^{-1}) in the following media			
	Water	0.05 M NaLS	20% silica 1115	Gel
Nitrobenzene	3×10^9	1×10^9	7.6×10^8	2.8×10^8
$Fe(CN)_6^{3-}$	3.8×10^{10}	$<10^7$	1.0×10^8	1.1×10^9
Cu^{2+}	5.3×10^7	1.8×10^8	1.6×10^7 (pH 3.2; r = 200 Å; Nalco silica 1034-A)	5.2×10^6
HVI^{2+}	7.4×10^8	8.75×10^8	3.4×10^8	2×10^8

TABLE 4

4-(1-Pyrenyl)butyltrimethyl ammonium bromide quenching rate constants k_q (λ_{em} = 375 nm)

	k_q (1 mol^{-1} s^{-1}) in the following media			
	Water	0.05 M NaLS	20% silica 1115	Gel
CH_3NO_2	3.8×10^9	2.6×10^9	1.1×10^9	1.3×10^9
Tl^+	3.2×10^9	1.7×10^{10}	1.6×10^{10}	5.8×10^8
Cu^{2+}	1.9×10^9	1.8×10^9	5.4×10^8 (pH 3.2; r = 200 Å; Nalco silica 1034-A)	7.8×10^7
3-nitropropionic acid	6.7×10^9	$< 10^7$	2.0×10^8	7.2×10^8

TABLE 5

Uranyl ion quenching rate constants k_q (λ_{em} = 520 nm)

|	k_q (1 mol^{-1} s^{-1}) in the following media		
	Water	20% silica 1115	Gel
I^-	4.8×10^9	2.4×10^6	1.7×10^8
Br^-	2.8×10^8	2.5×10^4	2.8×10^7
CNS^-	2.2×10^9	3.7×10^5	1.8×10^8
Ethanol	2.8×10^5	1.3×10^3 (dynamic)	
	5.05×10^5	3.5×10^3 (steady state)	1.05×10^6

ing little influence of the gel structure. The probe PN+ is bound to the gel but is also able to stick out and away from the silica network as it is bound via a butyl chain to the gel structure. The rate constants for the quenching of PN+ by nitromethane are similar in water and in the gel. Caution must be taken in interpreting the nitromethane data because some nitromethane may evaporate through the Parafilm seal as the gel is formed. The rate constants of nitromethane in the gel, then, must be at least as fast as those recorded in Table 4 but could be faster. The quenching for the Ru(bpy)$_3{}^{2+}$ and PN+ systems were all pseudo first order, following Stern—Volmer kinetics and having exponential first-order decays with complete agreement between the steady state and pulsed laser studies which indicated that the quenching was purely dynamic in nature.

Only (UO$_2{}^{2+}$)* exhibits essentially a simple first-order decay in the gel; nevertheless as soon as quenching species were added the decays became complex and needed to be fitted by the sum of the two-exponentials

$$F(t) = F_0\{A \exp(-k_1 t) + (1 - A) \exp(-k_2 t)\}$$

where $F(t)$ is the emission intensity as a function of time, F_0 is the emission intensity immediately following the laser pulse, A is the partition coefficient ($0 \leqslant A \leqslant 1$) between the two excited state environments, and k_1 and k_2 are the two different decay rates encountered. By comparing the ratio A_0/A of the areas under the decay curve with the ratio I_0/I of the steady state emission intensities at the peak maximum, the quenching process was found to be exclusively dynamic in nature for the gel system for quenching with UO_2^{2+} as well. Adjusting the ionic strength of the medium with sodium acetate had no effect on the multi-exponential nature of the decay.

It appears that UO_2^{2+} can bind to the SiO^- units of the silica lattice in two ways: (1) through simple electrostatic (ionic) bonding of UO_2^{2+} to the negatively charged surface, and (2) through silica displacement of water from the inner coordination sphere of the UO_2^{2+}:

$$[UO_2(H_2O)_6]^{2+} + HO\!\!-\!\!Si\!\!\lessgtr \longrightarrow [UO_2(H_2O)_5(HO\!\!-\!\!Si\!\!\lessgtr)]^{2+} + H_2O$$
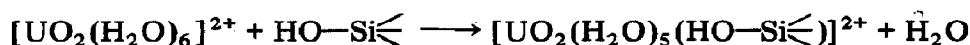
The six equational H_2O ligands only slightly perturb the spectral properties of the UO_2^{2+} [48], so that replacement of an H_2O by an SiOH unit should have little effect on the excited state lifetime. Water exchange on UO_2^{2+} is known [49] to be about 10^5 s^{-1} at 3 °C, and a comparable rate of exchange with the silica is reasonable at room temperature. Ligand substitution, however, would require the UO_2^{2+} to be in closer contact with the colloidal network when binding in this form rather than in a simple ionic association that does not disturb the uranium inner coordination sphere. The closer the UO_2^{2+} is to the negatively charged silica surface, though, the more difficult it is for reactions by anionic quenchers to occur. A table of the kinetic parameters (Table 6) for UO_2^{2+} quenching by Br$^-$ indicates that, although the UO_2^{2+} undergoes reactions when bound in either form, one type of situation is about ten times more susceptible to anionic attack than the other. Furthermore, significant interconversion from the less vulnerable to the more vulnerable form takes place on the microsecond time scale of the reaction, as indicated by the fact that the α coefficient steadily increases, *i.e.* if no interconversion took place within the excited state uranyl lifetime,

TABLE 6

Kinetic parameters for the quenching of uranyl ion in silica gel with NaBr

[Q] (M)	k_1 (l mol^{-1} s^{-1})	k_2 (l mol^{-1} s^{-1})	A
0	7.27×10^4	6.82×10^3	0.0688
2×10^{-4}	1.01×10^5	1.69×10^4	0.203
4×10^{-4}	1.47×10^5	2.16×10^4	0.376
6×10^{-4}	1.72×10^5	2.28×10^4	0.447
8×10^{-4}	2.00×10^5	2.28×10^4	0.524
0.001	1.92×10^5	2.25×10^4	0.579

$F = F_0\{A \exp(-k_1 t) + (1 - A) \exp(-k_2 t)\}$.

then α would simply represent the static partition coefficient of the UO_2^{2+} between the two bound forms (environments). Increasing quencher concentrations would subsequently only affect k_1 and k_2, but this is not the case. α steadily increases, so that a significantly larger fraction of the reaction occurs through the faster pathway as the less reactive form of the UO_2^{2+} is converted to the more vulnerable one. The two different bonding modes with interconversion from one to the other readily account for these kinetic effects.

3.1. Transient absorption

Pulsed laser studies of the system give rise to short-lived intermediates. The transient absorption spectrum of 1×10^{-4} M PN+ in silica gel is shown in Fig. 1. The spectrum consists of a single band centered at approximately 445 nm. The decay profile (Fig. 2) indicates that the absorption is due to the $(PN+)^+$ radical cation. Just as for silica 1115, no hydrated electrons could be observed. The electron is apparently taken up in the silica network. Figure 3 shows the decay of $(PN+)^T$ against the $(PN+)^+$ radical cation background.

The transient absorption spectrum of 0.0015 M UO_2^{2+} in silica (Fig. 4) displays one peak immediately after the laser pulse, with little variation at later periods of observation. In aqueous solutions the transient spectrum has two peaks, but only one is observed with colloidal silica [39]. As expected, the spectrum of excited UO_2^{2+} in the gel structure is comparable with that in colloidal silica. At the high concentrations required to observe the absorption of the transient species, uranyl ground state—excited state interactions considerably shorten the excited state lifetime (from 101 μs at 2×10^{-4} M to about 40 μs at 0.0015 M).

The excitation spectrum of 2×10^{-4} M uranyl acetate in the gel is shown in Fig. 5 and can be directly compared with the spectra of the same species in water or on silica 1115 which are also shown in Fig. 5. The spectra are similar; the differences probably indicate modification of the uranyl species in these media. The exact nature of the modification is not known
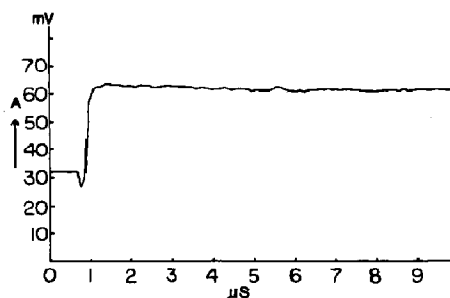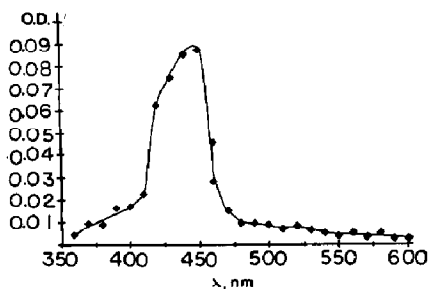

Fig. 1. Absorption spectrum of short-lived intermediates of 1×10^{-4} M PN+ 750 ns after the laser pulse.

Fig. 2. Absorption decay profile of 1×10^{-4} M PN+ in silica gel (decay of the radical cation $(PN+)^+$): absorption wavelength, 450 nm; $I_0 = 349$ mV.
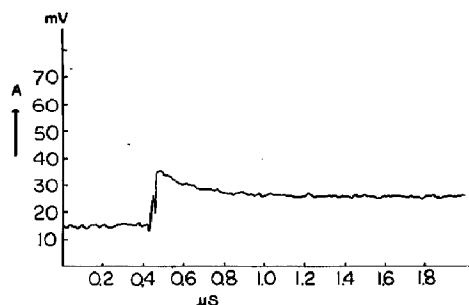
Fig. 3. Absorption decay profile of 1×10^{-4} M PN+ in silica gel (decay of triplet state $(PN+)^T$): absorption wavelength, 475 nm; $I_0 = 491$ mV.
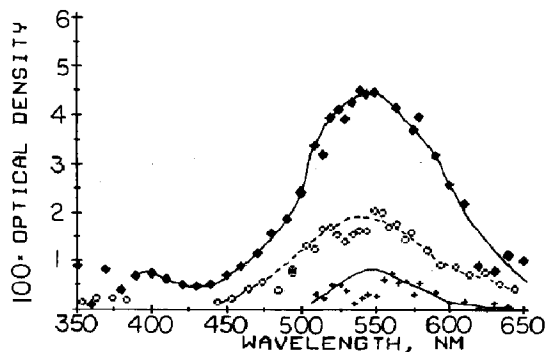
Fig. 4. Transient absorption spectrum of 0.0015 M uranyl acetate in silica gel: ◆, end of the laser pulse absorption; □, 26.4 μs after the pulse; +, 55.7 μs after the pulse.
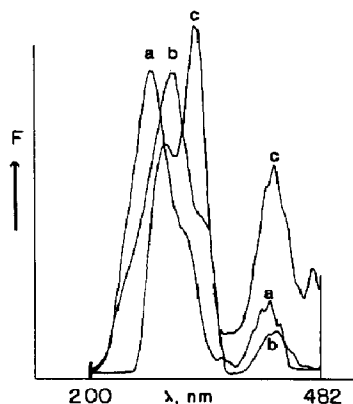

Fig. 5. Excitation spectra obtained by monitoring the emission at 505 nm and scanning the excitation wavelength: curve a, 1×10^{-4} M uranyl acetate in silica 1115; curve b, 1×10^{-4} M uranyl acetate in water; curve c, 2×10^{-4} M uranyl acetate in silica gel. F is the emission intensity in arbitrary units. The instrument gain was adjusted between samples because the emission from UO_2^{2+} is much greater with the colloidal silica than with water.

precisely but could be connected with varying degrees of hydrolysis in the various media, which is common behavior for UO_2^{2+}.

4. Conclusion

The silica gel structure offers a unique medium for carrying out photochemical reactions. The motion of various species is generally slower in the gel than in water. $Ru(bpy)_3^{2+}$ and UO_2^{2+} exhibit luminescence properties very different from those obtained in water, but these properties are similar to those observed with porous colloidal silica. The reactions of excited

cationic species bound to the anionic gel network, with various charged and neutral additives, are readily explicable in terms of electrostatic attractive or repulsive forces between the gel network and the quenching species. Unbound species experience little hindrance due to the gel structure and exhibit kinetic properties that are typical of the species in bulk water. The gel network–water system provides a non-reactive heterogeneous medium for studying various photochemical reactions. The gels themselves are very stable, are easily prepared and can be used to study virtually any water-soluble species.

Acknowledgments

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