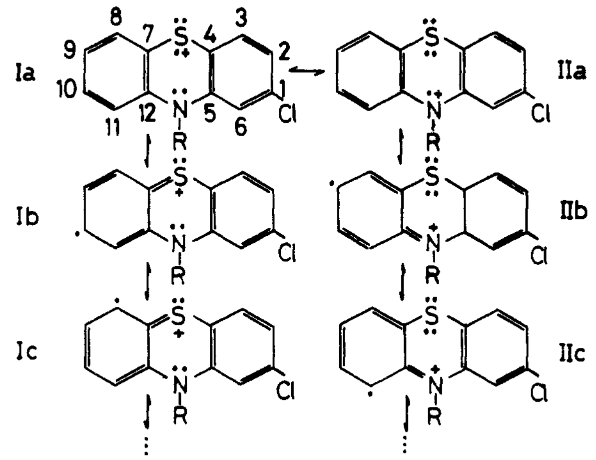
Scheme I



So, the supposed tetrahedral character of the C(13) bonds is not probably rigorous for the radical in solution and, consequently, the values $|\theta_a| \simeq |\theta_b| \simeq 60°$ are only approximated. In any case, the magnetic equivalence observed for the β-protons reflects the symmetric disposition of the side chain at the level of the N(1)-C(13) bond.

The Electronic Effect of the Cl Substituent. The comparison of the EPR parameters of promazine$^+$ (PRMZ$^+$) and CPZ$^+$ (Table V), which differ only in the presence of the Cl atom substituting for H(1), can afford some information about the electronic effect produced by that atom. The g_0 value of PRMZ$^+$ and other N-substituted phenothiazine derivatives in sulfuric solution is close to 2.0052 and similar to the $\langle g \rangle$ value obtained in salt crystals;[12,13] however, although the solid CPZ$^+$ perchlorate salt presents the same $\langle g \rangle$ value, the g_0 value obtained for the radical in solution is somewhat higher. This significant difference indicates that the solvent molecules interact with the CPZ$^+$ molecule in a specific way, changing the unpaired electron spin density distribution, probably through hydrogen bonding with the Cl atom. An increase in the mean g value when the powder is dissolved in diluted sulfuric acid has been also observed in PTAZ$^+$ and interpreted in a similar way.[29] In that case, the solvent interaction was able to produce a g shift similar to that induced by the side chain in the N-substituted derivatives. Here, the Cl atom could act as a different site to produce hydrogen bonding and the observed increase in the mean g value.

The redistribution of charge and spin density of the unpaired electron due to the presence of the Cl atom, when CPZ$^+$ is in solution, is also indicated by the differences in the hfsc of CPZ$^+$ and PRMZ$^+$. The increase of $a_{\mathrm{H}(10)}$ and the decrease of $a_{\mathrm{N}(1)}$, $a_{\mathrm{H}(2,9)}$, and $a_{\mathrm{H}(6,11)}$ can be explained by considering resonant structures I and II of Scheme I. The presence of Cl can induce a shift in favor of structures I in relation to structures II. Thus, the spin density at the sulfur atom, with a spin-orbit coupling constant larger than that of the nitrogen, would increase, explaining the observed small increase of the mean g_0 value. Since this increase is observed only in the sulfuric solution spectra, the charge and spin redistribution may be related to the higher radical-solvent interaction induced by the presence of the Cl substituent. The apparent anomalous behavior of the smaller hfsc, $a_{\mathrm{H}(3,8)}$, can be due to a lack of precision in its evaluation. The decrease of the coupling constant value $a_{\beta\mathrm{H}}$ can be a consequence of the decrease of the π spin density, ρ^{π}_{N}, in N(1). If a hyperconjugative mechanism is accepted for spin transmission from the heterocycle to the side chain, a proportionality between the p[N(1)] character of the molecular orbital containing the unpaired electron and the value of $a_{\beta\mathrm{H}}$ should be expected, and in fact the same value is found for the ratio $a_{\beta\mathrm{H}}/a_{\mathrm{N}}$ in CPZ$^+$ and PRMZ$^+$.

Registry No. CPZ$^+$ClO$_4^-$, 61866-45-3.

---

(29) López Rupérez, F.; Conesa, J. C.; Soria, J., to be published.

(30) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

Effects of the Polyelectrolyte Poly(vinyl sulfate) on the Photosensitized Electron-Transfer Reactions of Tris(2,2′-bipyridine)ruthenium(II) with a Dipolar Zwitterionic Viologen

Richard E. Sassoon, Ze'ev Aizenshtat, and Joseph Rabani*

Energy Research Center, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

(Received: March 28, 1984; In Final Form: November 14, 1984)

The photosensitized electron-transfer system containing Ru(bpy)$_3^{2+}$ as photosensitizer and *N,N*′-bis(4-sulfonatotolyl)-4,4′-bipyridyldiylium (BSV) as quencher was investigated in aqueous solutions containing the polyelectrolyte poly(vinyl sulfate) (PVS). This is the first system where acceleration of the forward quenching reaction together with considerable retardation of the reaction regenerating the ground-state species occurs on addition of a charged microenvironment. Both the BSV molecule, possessing a large dipole moment, and the Ru(bpy)$_3^{2+}$ cation are concentrated in the polyelectrolyte field and steady-state emission experiments showed that the distribution of BSV in the potential field of PVS may be described by the Poisson-Boltzmann equation. The reaction between BSV and Ru(bpy)$_3^{2+}$ results in an electron transfer, yielding BSV$^{-}\cdot$ and Ru(bpy)$_3^{3+}$ as products. There is evidence for formation of an outer-sphere complex between BSV$^{-}\cdot$ and Ru(bpy)$_3^{3+}$. The yields of electron transfer were hardly affected by the presence of PVS although the rate of the reverse electron-transfer reaction was somewhat reduced. This was attributed to the distribution of charge over the BSV$^{-}\cdot$ radical anion product. The effects of pH, addition of an inert salt, and variation of coverage of the polyelectrolyte were also investigated for the system.

Introduction

The Coulombic interactions of potential fields of polyelectrolytes can be very important in influencing the rates and yields of chemical reactions[1-10] and their effects on photosensitized electron-transfer reactions can greatly enhance the efficiency of conversion of light energy into stored chemical energy.[5-9] The

---

(1) (a) H. Morawetz and J. A. Shafer, *J. Phys. Chem.* **67**, 1293 (1963); (b) H. Morawetz and B. Vogel, *J. Am. Chem. Soc.*, **91**, 563 (1969); (c) H. Morawetz and G. Gordimer, *ibid.*, **92**, 7532 (1970).

(2) I. A. Taha and H. Morawetz, *J. Am. Chem. Soc.*, **93**, 829 (1971).

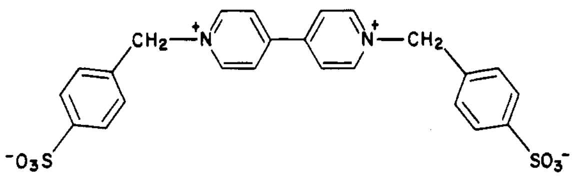
(3) (a) S. Kunugi and N. Ise, *Z. Phys. Chem.* (*Frankfurt Am Main*), **92**, 69 (1974); (b) T. Ishiwatari, T. Maruno, M. Okubo, T. Okubo and N. Ise, *J. Phys. Chem.*, **85**, 47 (1981); (c) N. Ise, T. Okubo, and Y. Yamamura, *ibid.*, **86**, 1694 (1982); (d) T. Okubo, M. Ueda, M. Sugimura, H. Kitano, and N. Ise, *ibid.*, **87**, 1224 (1983); (e) N. Ise and T. Okubo, *Macromolecules*, **11**, 439 (1978); (f) A. Enokida, T. Okubo, and N. Ise, *ibid.*, **13**, 49 (1980).

0022-3654/85/2089-1182$01.50/0

rates of electron-transfer quenching of the lowest emitting charge-transfer state of $Ru(bpy)_3^{2+}$ by Cu^{2+} and Fe^{3+}, for example, may be increased by up to 3 orders of magnitude.[5,6] Furthermore, the yields of photoinduced-electron-transfer products may also be dramatically improved on addition of a polyelectrolyte[7,8] as was observed, for instance, on addition of the positive polyelectrolyte polybrene to the photochemical system containing $Ru(bpy)_2(CN)_2$ as photosensitizer and $Fe(CN)_6^{3-}$ as quencher.[8]

In this investigation a photochemical system is described in which, for the first time, large acceleration of the forward electron-transfer reaction followed by a significant inhibition of the back-electron-transfer reaction is observed on addition of a polyelectrolyte. The study of the behavior of a zwitterionic dipolar molecule in a polyelectrolytic field is also a novel aspect of the investigation to be described. Several zwitterionic photosensitizers[11-13] and quenchers[14-19] have appeared in the literature and zwitterionic viologens such as *N*,*N*′-bis(sulfonatopropyl)-4,4′-bipyridyldiylium and *N*,*N*′-bis(carboxyethyl)-4,4′-bipyridyldiylium have been studied as quenchers in photochemical systems in the presence of micelles,[15-17] vesicles,[17] and charged colloids.[14,15] However, in none of these systems was acceleration of the forward reaction observed although the back-electron-transfer reaction could be inhibited by a factor of up to 200 in the presence of appropriate micelles.[16]

The photosensitizer used in this study was $Ru(bpy)_3^{2+}$,[20,21] while the quencher was the dibenzylsulfonate viologen *N*,*N*′-bis(4-sulfonatotolyl)-4,4′-bipyridyldiylium (BSV) with the following structure:



The polyelectrolyte added to the photochemical system was poly(vinyl sulfate) (PVS) which has been used in several previous studies involving photoredox systems in polyelectrolytic environments.[5-7] It can attract both the positive $Ru(bpy)_3^{2+}$ ion and the dipolar BSV molecule into its electrostatic field. Preliminary results of this system have been described already in the literature.[9]

Experimental Section

The dibenzylsulfonate viologen *N*,*N*′-bis(4-sulfonatotolyl)-4-4′-bipyridyldiylium (BSV) was synthesized according to the four-stage procedure given below.

α-Bromotoluene-4-sulfonyl chloride (A) was prepared according to the literature method.[22] Methyl α-bromotoluene-4-sulfonate (B) was prepared by adding 15 g of a 25% NaOH solution dropwise to a magnetically stirred solution of 25 g of A in 25 mL of methanol. The temperature of the solution was maintained at 25 °C and stirred for a further hour. The product was then filtered off, washed with water and with a 4% sodium carbonate solution, and then again with water. It was finally dried over 98% H_2SO_4 in a vacuum desiccator for 24 h to give 16.2 g of product.

$[BSV(Me)_2]^{2+}\ (Br^-)_2$ (C) was produced by refluxing 14.8 g of B and 4 g of 4,4′-bipyridine in 70 mL of CCl_4 for 2 h under an argon atmosphere. The solvent was evaporated off and the ester was recrystallized twice from water to yield 7.8 g of product.

BSV (D) was prepared by refluxing a mixture of 4 g of LiBr and 6.4 g of C in 120 mL of DMF under an argon atmosphere for 16 h. The solvent was evaporated off and the crude product was dissolved in boiling water and treated with activated charcoal. Two recrystallizations from water followed by drying in vacuo over 98% H_2SO_4 gave 1.8 g of product. Anal. Calcd for $C_{10}H_8N_2(C_7H_6SO_3)_2{\cdot}H_2O$: C, 56.03; H, 4.28; N, 5.48; S, 12.13. Found: C, 56.26; H, 4.46; N, 5.70; S, 12.13.

BSV was stored in the dark under an inert atmosphere and fresh stock solutions were prepared on the day experiments were carried out. $Ru(bpy)_3Cl_2{\cdot}6H_2O$ was obtained from K and K Fine Chemicals and recrystallized once from water. Its concentration was determined spectrophotometrically by using a value of $\epsilon_{\max}^{452\text{nm}} = 14400\ M^{-1}\ cm^{-1}$. Poly(vinyl sulfate) (PVS) obtained from Sigma Chemical Co. was purified by recrystallization from methanol as previously described in the literature.[6] A 0.66% stock solution of the potassium salt of the PVS polymer (molecular weight $\simeq$ 250000) equivalent to a concentration of 4×10^{-2} M in monomer units or 2.6×10^{-5} M in polymer units was prepared. Unless otherwise stated, all concentrations of PVS are given in terms of monomer units. All other materials were of analytical reagent grade and were used without further purification. Water was distilled and passed through a Millipore water purification system. The pH of the solutions was adjusted when necessary by addition of either $HClO_4$ or NaOH and unless otherwise noted all solutions were deaerated by bubbling with either purified argon or helium gases before use.

All experiments were carried out at a temperature of 24 ± 2 °C. Absorption spectra were recorded on a Bausch and Lomb Spectronic 2000 spectrophotometer and quenching of the emission of the lowest excited state of $Ru(bpy)_3^{2+}$ by BSV was measured on a Perkin-Elmer MPF-4 fluorescence spectrometer. Excitation was carried out at 450 nm and the emission was measured at 605 nm. Laser flash photolysis experiments were carried out on a Model DL-200 Molectron tunable dye laser (450 μJ, 10 ns) pumped by a Molectron UV 14 pulsed N_2 laser (4.0 mJ, 10 ns). The optical setup and the detection system have already been described.[9,23] Unless otherwise stated, the number of photons deposited in a 1-cm cell per laser pulse was 1.5×10^{16} photons/cm^3 as measured by a $Ru(bpy)_3^{2+}/Fe^{3+}$ actinometer solution and all the results obtained by laser flash photolysis were averaged over the signals from 64 pulses. Furthermore, unless noted to the contrary the wavelength of excitation was 457 nm, the concentrations of $Ru(bpy)_3^{2+}$ and BSV were 3.5×10^{-5} and 3×10^{-4} M, respectively, and the pH of solution was in the range 5–7. Pulse radiolysis experiments were carried out by using a Varian V7715B linear accelerator whose experimental setup has been described previously[24] and steady-state γ-irradiation of solutions was carried out by using a Radiation Machinery Corp. cesium-137 γ-source.

---

[4] R. Fernandez-Prini, E. Baumgartner, and D. Turyn, *J. Chem. Soc., Faraday Trans. 1*, **74**, 1196 (1978).

[5] (a) D. Meisel and M. S. Matheson, *J. Am. Chem. Soc.*, **99**, 6577 (1977); (b) C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Phys. Chem.* **83**, 257 (1979).

[6] D. Meisel, J. Rabani, D. Meyerstein, and M. S. Matheson, *J. Phys. Chem.*, **82**, 985 (1978).

[7] D. Meyerstein, J. Rabani, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, **82**, 1879 (1978).

[8] R. E. Sassoon and J. Rabani, *J. Phys. Chem.*, **84**, 1319 (1980).

[9] R. E. Sassoon and J. Rabani, *Isr. J. Chem.*, **22**, 138 (1982).

[10] N. J. Turro and T. Okubo, *J. Phys. Chem.*, **86**, 1535 (1982).

[11] J. N. Demas, E. W. Harris, and R. P. McBride, *J. Am. Chem. Soc.*, **99**, 3547 (1977).

[12] O. Johansen, A. Launikonis, A. W.-H. Mau, and W. H. F. Sasse, *Aust. J. Chem.*, **33**, 1643 (1980).

[13] I. Willner and Y. Degani, *J. Chem. Soc., Chem. Commun.*, 1249 (1982).

[14] I. Willner, J.-M. Yang, C. Laane, J. W. Otvos, and M. Calvin, *J. Phys. Chem.*, **85**, 3277 (1981).

[15] C. Laane, I. Willner, J. W. Otvos, and M. Calvin, *Proc. Natl. Acad. Sci. U.S.A.*, **78**, 5928 (1981).

[16] P. A. Brugger, M. Grätzel, T. Guarr, and G. McLendon, *J. Phys. Chem.*, **86**, 944 (1982).

[17] T. Nagamura, T. Kurihara, T. Matsuo, M. Sumitani, and K. Yoshihara, *J. Phys. Chem.*, **86**, 4368 (1982).

[18] Y. Itoh, Y. Morishima, and S. Nozakura, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 167 (1983).

[19] Y. Degani and I. Willner, *J. Chem. Soc., Chem. Commun.*, 710 (1983).

[20] J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971).

[21] C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci., U.S.A.*, **72**, 2858 (1975).

[22] S.-C. Wong, G. D. J. Green, and E. Shaw, *J. Med. Chem.*, **21**, 456 (1978).

[23] D. Lougnot, G. Dolan, and C. R. Goldschmidt, *J. Phys. E*, **12**, 1051 (1979).

[24] R. E. Sassoon, Ph.D. Thesis, Hebrew University of Jerusalem, Jerusalem, Israel, Dec 1983.

Results and Discussion

Spectral Measurements on BSV and Its Reduced Radical Anion. The optical absorption spectrum of BSV contains a peak in the near-ultraviolet at $\lambda_{max} = 260$ nm ($\epsilon_{max} = 23300$ M^{-1} cm^{-1}).

The BSV$^{-}\cdot$ radical anion was produced by irradiation from the cesium-137 γ-source of a deaerated solution of BSV containing 1% v/v (0.131 M) 2-propanol and 1% v/v (0.137 M) acetone with a G value of 6.2.[25] No evidence for a slow reaction between H_2O_2 and BSV$^{-}\cdot$ was found unlike in the analogous case of methylviologen.[26] The BSV$^{-}\cdot$ species undergoes dimerization according to equilibrium 1 such that, at high doses from the γ-source, the

$$2BSV^{-}\cdot \rightleftharpoons (BSV^{-}\cdot)_2 \tag{1}$$

presence of (BSV$^{-}\cdot$)$_2$ dimer becomes appreciable, where the appearance of the peak at around 560 nm suggests dimer formation. Thus, in order to obtain the true absorption spectrum of BSV$^{-}\cdot$ monomer, a deaerated 2-propanol/acetone aqueous solution of 3×10^{-4} M was subjected to various doses of γ-irradiation and the absorption spectra of the products were recorded. By extrapolation of the value D/cl to zero concentration of radical species, where D is the optical density of the solution at wavelength λ after irradiation, c is the total concentration of radical species produced, and l is the optical path length, one then obtains the true extinction coefficient of the monomer radical species at that wavelength. The visible absorption spectrum of BSV$^{-}\cdot$ monomer was found to contain two peaks at 602 nm ($\epsilon_{max} = 11300$ M^{-1} cm^{-1}) and at 724 nm ($\epsilon_{max} = 2400$ M^{-1} cm^{-1}) while there is a trough in the spectrum at around 460 nm. The equilibrium constant for equilibrium 1 was estimated to be around 8000 M^{-1}, which is considerably higher than the value of about 500 M^{-1} obtained for the methylviologen cation radical.[27]

It should be noted that no significant difference in the absorption spectrum of either the monomer or the dimer species or in the value of the equilibrium constant for equilibrium 1 was found when BSV$^{-}\cdot$ was generated in the presence of 4×10^{-3} M PVS. This indicates that most if not all the reduced BSV is present in the bulk of solution and is not bound to the polyion. It should also be noted that the absorption spectrum of BSV was unaffected by the pH of solution in the pH range 2–10 although at highly alkaline pH decomposition of the compound to an aldehyde and the BSV$^{-}\cdot$ radical occurs, as has been observed with other viologen species.[28]

Pulse Radiolytic Measurements on the System. BSV$^{-}\cdot$ was generated from arrgon-saturated aqueous solutions of 1×10^{-4} and 2×10^{-4} M BSV containing 1% v/v 2-propanol and 1% v/v acetone, by pulse irradiation from the accelerator. The initial absorption signal obtained immediately after irradiation with a 1-μs pulse of electrons was measured at various wavelengths in the range 420–650 nm. The absorption spectrum obtained for the BSV$^{-}\cdot$ species agreed at every wavelength within 10% with the spectrum recorded by using the steady-state γ-irradiation technique.

The hydrated electron reacts directly with BSV according to eq 2 and measurements of the decay of the absorption signal of

$$BSV + e_{aq}^{-} \rightarrow BSV^{-}\cdot \tag{2}$$

the electron in deaerated BSV solutions containing *tert*-butyl alcohol at pH 10 gave $k_2 = (4 \pm 1) \times 10^{10}$ M^{-1} s^{-1}, a value similar to that for methylviologen.[25] This value was unaffected by the presence of PVS in the concentration range $(1–26) \times 10^{-5}$ M ([BSV] = 1×10^{-5} M). The lack of effect of PVS on the rate of reaction between e_{aq}^{-} and BSV indicates that most of the BSV does not lie on the polymer molecule. It will be shown later that BSV is indeed attracted to the PVS field and may reach concentrations much greater than in the bulk of solution but since the volume of the solution in which the PVS polyion can affect due to its electrostatic field is only a tiny fraction of the total volume of solution at the concentrations of PVS used, the major fraction of BSV will be in the bulk of solution where the rate of its reaction with e_{aq}^{-} is unaffected.

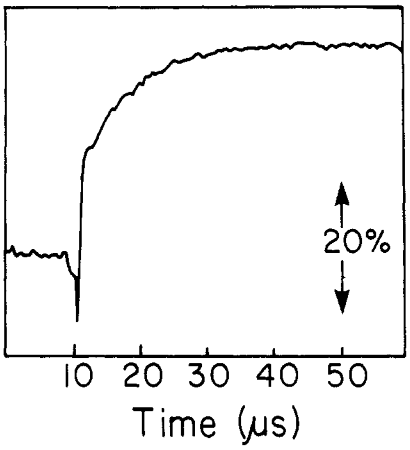


Figure 1. Buildup of absorption signal at 590 nm following pulse irradiation of an argon-saturated solution of 6.6×10^{-5} M Ru(bpy)$_3^{2+}$, 2×10^{-5} M BSV, and 0.01 M *tert*-butyl alcohol at pH 10. The initial signal is due to the absorption of Ru(bpy)$_3^{+}$ and BSV$^{-}\cdot$ formed via reactions 2 and 3 while the slower buildup in absorption represents the additional formation of BSV$^{-}\cdot$ which occurs due to reaction 4. Overall concentration of reduced species produced = 1.8×10^{-6} M.

The hydrated electron also reacts with Ru(bpy)$_3^{2+}$ according to reaction 3 and the rate constant for this reaction has been

$$Ru(bpy)_3^{2+} + e_{aq}^{-} \rightarrow Ru(bpy)_3^{+} \tag{3}$$

measured to be 6×10^{10} M^{-1} s^{-1}.[29] A decrease in this rate constant has been reported in the presence of PVS[30] and was confirmed in this investigation where k_3 was measured to be $(3.5 \pm 0.7) \times 10^{9}$ M^{-1} s^{-1} in 4×10^{-3} M PVS solution. This decrease is clearly due to the repulsive forces exerted on the electron by the negatively charged field binding the Ru(bpy)$_3^{2+}$ ion.[30]

On irradiating a 0.01 M *tert*-butyl alcohol solution of Ru(bpy)$_3^{2+}$ in the presence of BSV, one may follow the production of BSV$^{-}\cdot$ at 590 nm ($\epsilon^{590}_{BSV^{-}\cdot} = 10400$ M^{-1} cm^{-1}) where Ru(bpy)$_3^{+}$ has a much lower absorption ($\epsilon^{590}_{Ru(bpy)_3^{+}} = 2000$ M^{-1} cm^{-1}).[31] An example of the time profile observed is shown in Figure 1. The initial signal observed immediately after the pulse is due to the production of BSV$^{-}\cdot$ and Ru(bpy)$_3^{+}$ via reactions 2 and 3. This is followed by a further buildup of the absorption signal due to reaction 4. The rate constant for reaction 4 was determined to

$$Ru(bpy)_3^{+} + BSV \rightarrow Ru(bpy)_3^{2+} + BSV^{-}\cdot \tag{4}$$

be $(5.7 \pm 1.2) \times 10^{9}$ M^{-1} s^{-1}. In the presence of PVS no accurate determination of this rate constant could be made, since significant amounts of Ru(bpy)$_3^{+}$ could not be produced in the presence of BSV. It may be concluded from these results that the ultimate fate of any Ru(bpy)$_3^{+}$ formed in a photochemical system with BSV, by a biphotonic or other effect, is its oxidation to Ru(bpy)$_3^{2+}$ with simultaneous production of BSV$^{-}\cdot$.

Quenching of the Emission of Ru(bpy)$_3^{2+*}$ by BSV. Quenching of the lowest excited emitting state of Ru(bpy)$_3^{2+}$ by BSV occurs by an electron-transfer process.

$$Ru(bpy)_3^{2+*} + BSV \rightarrow \text{electron-transfer products} \tag{5}$$

---

[25] D. Meisel, W. A. Mulac, and M. S. Matheson, *J. Phys. Chem.*, **85**, 179 (1981).

[26] (a) J. S. Bellin, R. Alexander, and R. D. Mahoney, *Photochem. Photobiol.* **17**, 17 (1973); (b) G. Levey, A. L. Rieger, and J. O. Edwards, *J. Org. Chem.*, **46**, 1255 (1981); (c) G. Levey and T. W. Ebbesen, *J. Phys. Chem.*, **87**, 829 (1983).

[27] (a) A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin Trans. 2*, 1787 (1977); (b) A. G. Evans, J. C. Evans, and M. W. Baker, *J. Am. Chem. Soc.*, **99**, 5882, (1977).

[28] A. H. Corwin, R. R. Arellano, and A. B. Chivvis, *Biochim. Biophys. Acta*, **162**, 533 (1968).

[29] D. Meisel, M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **81**, 1449 (1977).

[30] C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Phys. Chem.*, **81**, 1805 (1977).

[31] Q. G. Mulazzani, S. Emmi, P. G. Fuochi, M. Z. Hoffman, and M. Venturi, *J. Am. Chem. Soc.*, **100**, 981 (1978).

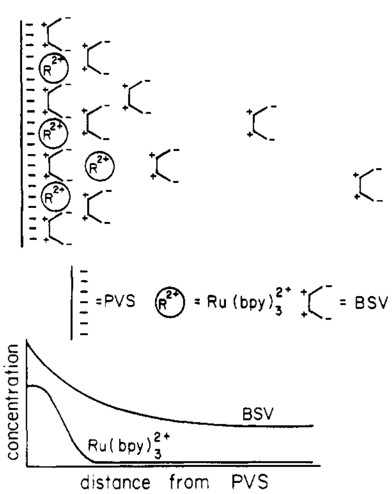


Figure 2. Schematic representation of the distribution of Ru(bpy)$_3^{2+}$ cations and BSV molecules away from the PVS polyion. The doubly positively charged Ru(bpy)$_3^{2+}$ species are much more tightly bound to the negatively charged polyelectrolyte than are the dipolar zwitterionic BSV molecules.

Electronic energy transfer in the primary photochemical step can be ruled out since the energies of the lowest triplet states of many viologen salts are around 70 kcal/mol,[32,33] as compared to the lower value of 49 kcal/mol for Ru(bpy)$_3^{2+*}$.[34]

In the absence of polyelectrolyte, Stern–Volmer plots yielded $k_5 = (1.4 \pm 0.3) \times 10^9$ M^{-1} s^{-1},[9] based on a value of the lifetime of Ru(bpy)$_3^{2+*}$ equal to 0.60 μs. This rate constant is virtually the same as the value of 1.37×10^9 M^{-1} s^{-1} obtained for benzylviologen[33,35] and was found to be unaffected by the pH of solution in the pH range 2–10, although it was affected by the ionic strength of solution. k_5 was found to increase by a factor of about 1.5 on raising the concentration of inert salt (NaClO$_4$) from 0.001 to 0.1 M, suggesting that the effective charge of BSV is not zero. Similar ionic strength effects have been observed for quenching of the emission of the dipolar photosensitizer Ru(bpy)$_2$(bpy(COO$^-$)$_2$) by methylviologen[36] and such ionic strength effects probably indicate the presence of a large dipole moment in the BSV molecule.

The rate of quenching of Ru(bpy)$_3^{2+*}$ by BSV is greatly enhanced by the presence of PVS in solution[9] and Figure 2 gives a schematic representation of how we believe the Ru(bpy)$_3^{2+}$ ions and the BSV molecules are distributed away from the polyelectrolyte. The Ru(bpy)$_3^{2+}$ ions are concentrated close to the PVS polyion to a much greater degree than the BSV molecules since the Ru(bpy)$_3^{2+}$ ions possess a double positive charge as compared to the relatively small dipole of the BSV species.

The two main theories which are at present accepted to explain the distribution of counterions away from a polyelectrolyte involve either the idea of counterion condensation at the polyelectrolyte surface[37,38] or the use of the Poisson–Boltzmann equation to describe their distribution.[39–44]

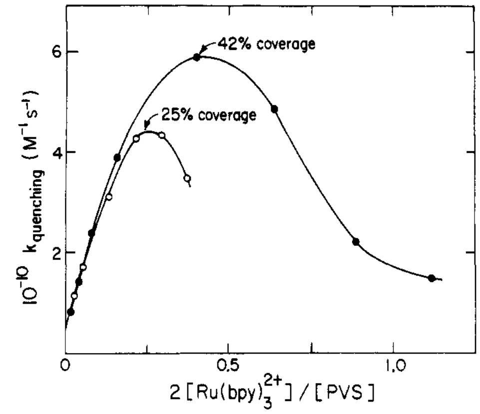


Figure 3. Second-order rate constant for quenching of Ru(bpy)$_3^{2+*}$ by BSV as a function of coverage of PVS by Ru(bpy)$_3^{2+}$. [Ru(bpy)$_3^{2+}$] = 4×10^{-5} M. (a) [BSV] = 3×10^{-4} M (○); (b) [BSV] = 1×10^{-4} M (●). Quenching reversal occurs at higher coverages of PVS at the lower BSV concentration.

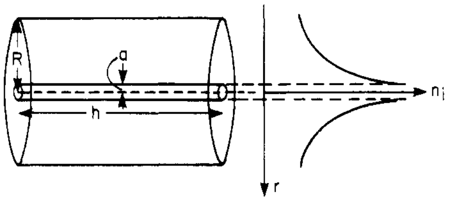


Figure 4. Poisson–Boltzmann distribution of counterions around a polyelectrolyte. The polyion is described as a long cylindrical rod of radius a and length h stretched in a cylinder of radius R which represents the total free volume per polyion.

In the field of photoinduced quenching reactions the consequences of the counterion condensation theory have been used to explain, for example, the increase in the rate of quenching of Ru(bpy)$_3^{2+*}$ by Fe^{3+} and Cu^{2+} on addition of PVS[5,6] and the phenomenon of quenching reversal seen at high coverages of the polyelectrolyte.[2,5] In these studies the photosensitizer and quencher ions were bound in a small polyelectrolyte volume and, when the appropriate volume correction was made, reasonable agreement was obtained between the experimental and predicted results. In the case of quenching by copper ions, as the coverage of polyelectrolyte is increased, displacement of Ru(bpy)$_3^{2+}$ ions into the bulk of solution occurs, where the quenching process is relatively inefficient. Thus, as the PVS concentration is reduced, the rate of quenching increases as more effective concentration of photosensitizer and quencher occurs, then passes through a maximum, and finally decreases as the Ru(bpy)$_3^{2+}$ is released into the bulk.

The phenomenon of quenching reversal is also observed in this work, as may be observed in Figure 3, which describes how the second-order quenching rate constant varies with coverage of PVS by Ru(bpy)$_3^{2+}$ ions. As the PVS concentration is reduced, the quenching rate constant increases to a maximum because of concentration of Ru(bpy)$_3^{2+*}$ ions in the polyelectrolyte field and then decreases as the Ru(bpy)$_3^{2+*}$ is released into the bulk of solution where relatively inefficient quenching takes place. Note that as the concentration of BSV is increased, the maximum quenching rate constant becomes smaller and the position of this maximum moves to lower coverages of PVS by Ru(bpy)$_3^{2+}$. This is because the BSV zwitterionic molecules are also concentrated in the polyelectrolyte field and although they have no overall effect of neutralizing the negative charges of the PVS polyion they effectively disperse the negative charge of the polyelectrolyte in a greater volume. The ability of the polymer to condense the Ru(bpy)$_3^{2+}$ ions and consequently to accelerate the quenching reaction is therefore reduced. It should be noted that in the case of quenching of Ru(bpy)$_3^{2+*}$ by Cu^{2+} the quenching reversal phenomenon occurs above approximately 65% neutralization of the negative sites of the PVS polyion (i.e., at much higher coverages of the polyelectrolyte). We belive that this indicates that there is still a high local concentration of BSV in the polyelectrolyte

---

(32) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972).
(33) (a) E. Amouyal, B. Zidler, P. Keller, and A. Moradpour, *Chem. Phys. Lett.*, **74**, 314 (1980); (b) E. Amouyal and B. Zidler, *Isr. J. Chem.*, **22**, 117 (1982).
(34) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
(35) K. Takuma, Y. Shuto, and T. Matsuo, *Chem. Lett.*, 983 (1978).
(36) G. L. Gaines, *J. Phys. Chem.*, **83**, 3089 (1979).
(37) G. S. Manning, *Acc. Chem. Res.*, **12**, 443 (1979).
(38) G. S. Manning, *J. Chem. Phys.*, **51**, 924, 934 (1969).
(39) R. M. Fuoss, A. Katchalsky, and S. Lifson, *Proc. Natl. Acad. Sci. U.S.A.*, **37**, 579 (1951).
(40) T. Alfrey, P. W. Berg, and H. Morawetz, *J. Polym. Sci.*, **7**, 543 (1951).
(41) M. Fixman, *J. Chem. Phys.*, **70**, 4995 (1979).
(42) M. Ishikawa, *Macromolecules*, **12**, 498 (1979).
(43) M. Ishikawa, *J. Phys. Chem.*, **83**, 1576 (1979).
(44) G. Weisbuch and M. Gueron, *J. Phys. Chem.*, **85**, 517 (1981).
(45) Deleted in proof.
(46) Deleted in proof.

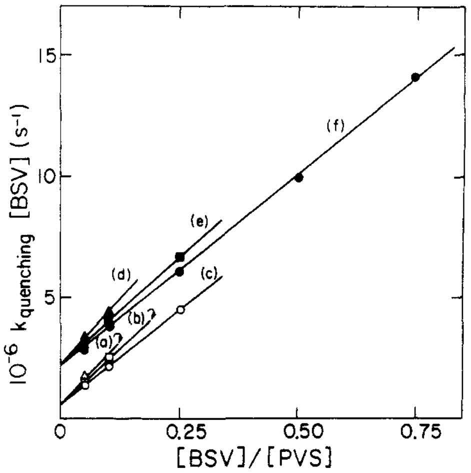


Figure 5. Plots of the pseudo-first-order quenching rate constants, uncorrected for the concentration of BSV, as a function of [BSV]/[PVS] at constant coverage of PVS by doubly positively charged ions. [$Ru(bpy)_3^{2+}$] = 4 × 10^{-5} M. The appropriate concentration of inert $Ba(ClO_4)_2$ was added in order to obtain the required coverage. (i) [BSV] = 1 × 10^{-4} M, total fraction of negative charges of PVS neutralized by doubly positively charged cations equals (a) 0.05 (△), (b) 0.12 (□), and (c) 0.20 (○). (ii) [BSV] = 3 × 10^{-4} M, total fraction of negative charges of PVS neutralized by doubly positively charged cations equals (d) 0.05 ▲), (e) 0.12 (■), and (f) 0.20 (●).

volume reducing the effectiveness of PVS.

Since BSV possesses no overall charge but only a dipole moment, its alignment in the polyelectrolyte field is more difficult to interpret quantitatively according to the counterion condensation theory. From the position of maximum quenching in Figure 3, the overall coverage by $Ru(bpy)_3^{2+}$ and BSV of polymer charge at which quenching reversal occurs may be estimated to be about 65% assuming the dipole moment to be equivalent to about 0.4 of a formal positive charge. This is approximately the same degree of neutralization of the negative sites of PVS by dipositive ions at which quenching reversal occurs in the $Ru(bpy)_3^{2+}/Cu^{2+}$ photochemical system.[5] However, volume-corrected quenching rate constants cannot easily be calculated since only a small fraction of the BSV zwitterions may be bound to the polyelectrolyte.

The distribution of the BSV molecules from the polyelectrolyte can, however, be described probably more accurately by a Poisson–Boltzmann type of equation (Figure 4). Using the model of Fuoss et al.[39] and Alfrey et al.[40] one may represent the polyion by a long cylindrical rod of radius a and length h with ν charges uniformly distributed on its surface. The polyion is stretched along the axis of a cylinder of radius R which represents the total volume of solution per polyion. Solution of such an equation leads to an expression for the concentration of ions of type i at any distance r away from the polyelectrolyte given by

$$n_i(r) = n_i(R) \exp[-(z_i e\psi/kT)] \tag{6}$$

where $n_i(R)$ is the concentration in mol/L of ion i at $r = R$, z_i is the signed valency of ion i, e is the electronic charge, ψ is the electrostatic potential, k is the Boltzmann constant, and T is the absolute temperature.

Measurement of the dipole moment of the BSV molecule was not found to be possible since it was too insoluble in nonpolar solvents. Thus, quantitative verification of the application of the Poisson–Boltzmann equation to describe the behavior of BSV in the polyelectrolyte field could not be carried out. However, the BSV molecule is found to follow the type of behavior predicted by the Poisson–Boltzmann equation as may be seen from the experimental results described in Figure 5. The figure gives a plot of the pseudo-first-order quenching rate constant, uncorrected for the concentration of BSV, as a function of the ratio of [BSV] to [PVS] at various coverages of the polyelectrolyte by doubly charged positive ions and at various concentrations of BSV. Note that the $Ru(bpy)_3^{2+}$ concentration was kept constant at 4 × 10^{-5} M and the required coverage of PVS by doubly positively charged ions was also kept constant, as the polyelectrolyte concentration was varied, by addition of the appropriate amount of inert Ba^{2+} ions. Note also that the range of coverage studied here is that in which all the doubly charged positive ions are condensed onto the polyelectrolyte, i.e., the range in which quenching reversal does not take place.

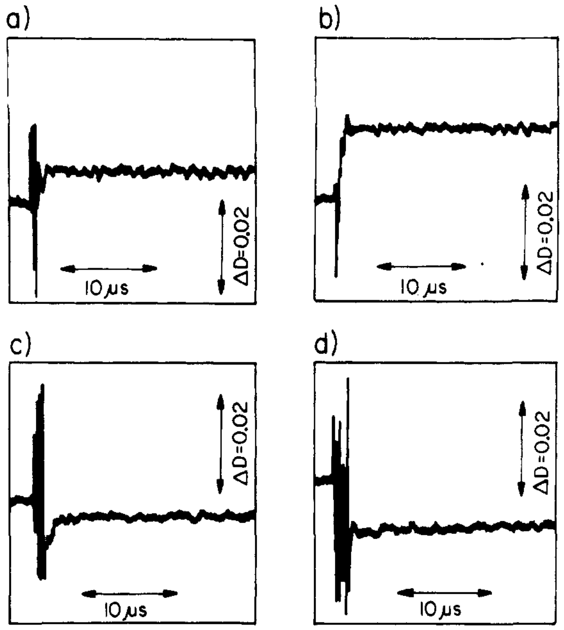


Figure 6. Transient absorption and bleaching signals obtained following laser flash photolysis of $Ru(bpy)_3^{2+}$–BSV solutions: (a) absorption signal at 590 nm in the absence of PVS and (b) in the presence of 8 × 10^{-3} M PVS; (c) bleaching signal at 450 nm in the absence of PVS and (d) in the presence of 8 × 10^{-3} M PVS.

As the coverage of the polyelectrolyte by doubly charged positive ions increases at constant BSV concentration, the accelerated quenching rate constant is seen to go down. This is because the electrostatic potential of the system, which is negative due to the negatively charged polyelectrolyte, is mainly determined by the degree of coverage or condensation of doubly positively charged ions on the polyelectrolyte and, as a result of applying eq 6 to the system, the acceleration factor is observed to decrease as the electrostatic potential becomes smaller due to higher coverages of the polyelectrolyte by doubly charged positive ions. However, the form of the distribution of BSV ions around the PVS polyion is given by the term $\exp[-(z_i e\psi/kT)]$ in eq 6 and does not depend on their average concentration in solution, n_{BSV}. This is observed to be so in Figure 5 since parallel lines are obtained at the same coverages of polyelectrolyte by doubly charged positive ions (i.e., at the same potential) but at different concentrations of BSV, thus confirming the applicability of the Poisson–Boltzmann equation to the distribution of the BSV zwitterions around the PVS polyion.

Such enhancement effects have not been observed in analogous photochemical systems using various zwitterionic viologen species as quenchers in the presence of micelles[16,17] or charged colloids,[14,25] and we assume that in these systems the quenchers possess little or no dipole.

Quantum Yields and Back-Reactions of the System. The yields of products of the electron-transfer quenching reaction and their subsequent reactions were followed by using the technique of laser flash photolysis after excitation with light of wavelength 457 or 421 nm. The initial yields and subsequent disappearance of the photoinitiated redox products were monitored at the wavelength 450 nm, where the bleaching signal due principally to the depletion of $Ru(bpy)_3^{2+}$ could be observed, and at 590 nm, where the main absorbing species is expected to be the $BSV^{-\cdot}$ radical anion. Figure 6 shows examples of the initial traces obtained after laser excitation of the photochemical system in both the absence and presence of the polyelectrolyte, PVS. Figure 6, a and b, shows the initial absorption signal averaged over 64 laser pulses at the monitoring wavelength of 590 nm observed in solutions of $Ru(bpy)_3^{2+}$ and

TABLE I: Yields of Electron Transfer and Back-Reactions in the $Ru(bpy)_3^{2+}$–BSV System in the Absence of PVS[a]

						590 nm[d]			450 nm[d]	
$10^4 \times$ [BSV], M	pH[b]	[$NaClO_4$], mM	ϕ_{590}[c]	ϕ_{450}[c]	ϕ_{590}/ϕ_{450}	$10^3 \times \Delta D$[e]	$t_{1/2}^{1st}$,[f] ms	$t_{1/2}^{2nd}/t_{1/2}^{1st}$[g]	$t_{1/2}^{1st}$,[f] ms	$t_{1/2}^{2nd}/t_{1/2}^{1st}$[g]
1.5			0.19	0.14	1.4	4.4	0.12	1.5	0.26	1.7
3			0.16	0.10	1.6	6.2	0.14	1.6	0.22	1.8
3	2		0.16	0.13	1.3	6.8	0.14	1.3	0.29	1.8
3	4		0.13	0.12	1.1	5.4	0.13	1.2	0.24	2.0
3	10		0.12	0.07	1.8	5.2	0.13	1.2	0.22	1.2
3		1	0.17	0.09	1.9	7.7	0.20	1.8	0.21	1.4
3		3	0.17	0.09	1.9	8.5	0.17	1.8	0.24	1.4
3		10	0.14	0.10	1.4	7.3	0.21	1.6	0.25	1.4
3		30	0.18	0.12	1.5	8.0	0.20	1.6	0.22	1.6
3		100	0.15	0.09	1.7	8.4	0.20	1.3	0.27	1.3

[a] See Experimental Section for experimental conditions. [b] The pH was adjusted by using $HClO_4$ or NaOH. [c] ϕ_{590} and ϕ_{450} are the apparent limiting quantum yields extrapolated to infinite quenching, measured at 590 and 450 nm, respectively, assuming $Ru(bpy)_3^{3+}$ and $BSV^{-}\cdot$ are the sole products of electron transfer. They are derived from the absorption signal 5 μs after the pulse and calculated according to the extinction coefficients obtained from the absorption spectra of $Ru(bpy)_3^{2+}$, $Ru(bpy)_3^{3+}$, BSV, and $BSV^{-}\cdot$ at the appropriate wavelength. [d] Monitoring wavelengths. [e] Change in absorbance at 590 nm measured 5 μs after the laser pulse. [f] First half-lifetime for the decay of the absorption or bleaching signal following the laser pulse. [g] Ratio of the second to the first half-lifetimes for the decay of the absorption or bleaching signal.

TABLE II: Yields of Electron Transfer and Back-Reactions in the $Ru(bpy)_3^{2+}$–BSV System in the Presence of PVS[a]

						590 nm			450 nm	
$10^4 \times$ [BSV], M	$10^3 \times$ [PVS],[b] M	pH[a]	ϕ_{590}[c]	ϕ_{450}[c]	ϕ_{590}/ϕ_{450}	$10^3 \times \Delta D$[c]	$t_{1/2}^{1st}$,[c] ms	$t_{1/2}^{2nd}/t_{1/2}^{1st}$[c]	$t_{1/2}^{1st}$,[c] ms	$t_{1/2}^{2nd}/t_{1/2}^{1st}$[c]
1.5	8		0.15	0.12	1.2	10.8	0.69	1.2	0.45	1.5
3	8		0.15	0.08	1.9	14.8	0.80	1.2	0.52	1.2
3	8	2	0.13	0.09	1.4	12.8	0.41	1.1	0.41	1.2
3	8	4	0.15	0.08	1.9	15.3	1.06	1.5	0.39	1.5
3	8	10	0.15	0.10	1.5	13.8	0.86	1.4	0.58	1.2
3	20		0.17	0.09	1.8	14.3	0.86	1.5	0.59	1.2
3	4		0.14	0.06	2.3	14.9	0.94	1.1	0.53	1.0
3	2		0.12	0.06	2.0	15.2	0.88	1.2	0.56	1.2
3	0.8		0.08	0.03	2.4	12.2	0.69	1.1	0.52	1.1
3	0.2		0.03	≃0.003		4.6	0.47	1.4		
3[d]	8		0.12	0.09	1.3	12.4	0.40	1.1	0.52	1.1

[a] Experimental conditions as for Table I. [b] PVS concentration is given in terms of monomer units. [c] Symbols have same meanings as in Table I. [d] 1×10^{-2} M $NaClO_4$ was present in this solution.

BSV in the absence and in the presence of PVS, respectively. The addition of PVS is found to enhance considerably the absorption signal and this is attributed to the more efficient quenching of the excited state of $Ru(bpy)_3^{2+}$ by BSV in the presence of PVS. The corresponding bleaching signals of the absorption of $Ru(bpy)_3^{2+}$ at 450 nm with and without PVS in solution may be seen in Figures 6, d and c, respectively. It should be noted that the bleaching signals at 450 nm are somewhat smaller than the corresponding absorption signals at 590 nm.

The regeneration of the initial reactants from the photoproduced electron-transfer products, as monitored at the two analytical wavelengths 450 and 590 nm, may be seen in Figure 7. The decay of the absorption and bleaching signals in the absence of PVS are shown in Figures 7, a and c, respectively, whereas the slower decay of these signals on addition of 8×10^{-3} M PVS to solution may be observed in parts b and d of Figure 7. It should also be noted that the absorption signals at both wavelengths decayed back to their original value observed before laser irradiation. Indeed, on steady-state illumination for several hours, from a 60-W tungsten lamp, of solutions of $Ru(bpy)_3^{2+}$ and BSV both with and without PVS present, no overall change in the optical absorption spectrum of the solutions was observed, indicating that the original ground-state reactants are regenerated in this photochemical system.

Solutions of $Ru(bpy)_3^{2+}$ and BSV at various conditions of pH, ionic strength, and concentration of polyelectrolyte were laser irradiated and the results obtained in the absence and in the presence of PVS, after averaging the absorption signals following irradiation of 64 laser pulses, are summarized in Tables I and II, respectively. Certain features of the photochemical system may be described on considering the experimental results.

It is immediately clear that the products of photoinitiated electron transfer are not simply $Ru(bpy)_3^{3+}$ and $BSV^{-}\cdot$ and that their subsequent reactions cannot be solely explained by a single back-reaction of the type given by eq 7. The apparent quantum yield of photoinduced electron transfer assuming such a mechanism

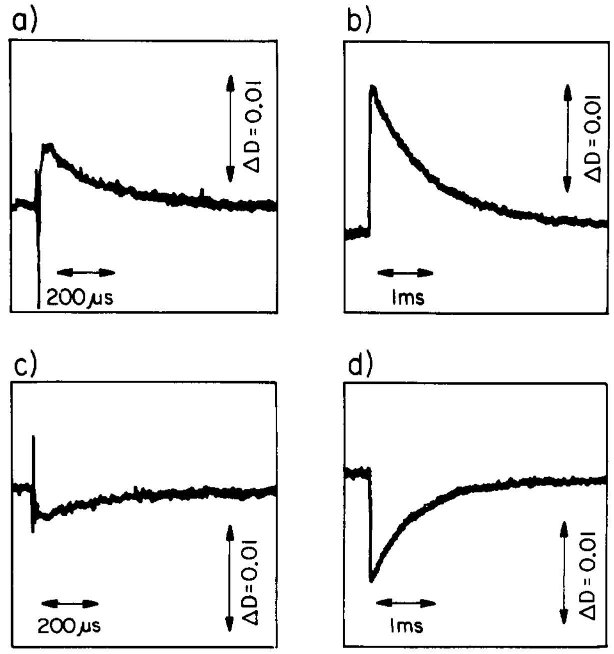


Figure 7. Decays of the absorption and bleaching signals following laser irradiation of solutions of $Ru(bpy)_3^{2+}$ and BSV: (a) decay of transient absorption signal at 590 nm in the absence of PVS and (b) in the presence of 8×10^{-3} M PVS; (c) decay of transient bleaching signal at 450 nm in the absence of PVS and (d) in the presence of 8×10^{-3} M PVS.

$$\mathrm{Ru(bpy)_3^{3+} + BSV^{-\cdot} \rightarrow Ru(bpy)_3^{2+} + BSV} \qquad (7)$$

as calculated from the absorbance change at 590 nm is about 1.6 times the value calculated from the change in absorption of the solution at 450 nm as compared to the theoretical value of 1. This is true under almost all the conditions used and this ratio is virtually unaffected by the addition of 8×10^{-3} M PVS to the solution. The overall absorption change is greater when PVS is present in solution, as may be observed by comparing Figure 6, a and c to Figure 6, b and d. This is because of the increase in the efficiency of quenching of $\mathrm{Ru(bpy)_3^{2+*}}$ by BSV in the presence of PVS.

The rate of the decay of the absorption and bleaching signals at the two monitoring wavelengths, 590 and 450 nm, follows neither true first-order nor true second-order kinetics. This may be concluded from inspection of the ratio of the second half-lifetime of the decay to the first half-lifetime which should be equal to 1 for a first-order reaction and to 2 for a second-order reaction. In the absence of PVS this ratio is equal to about 1.5 whereas in the presence of PVS in solution in decreases to approximately 1.2. Any difference in the overall order of the decay of the absorption signal at the two monitoring wavelengths cannot be resolved under our experimental conditions. However, when PVS is absent from the reaction solution, the first half-lifetime for the decay of the absorption signal is usually found to be somewhat lower at 590 nm than at 450 nm, indicating the observation of an initially slightly faster process at 590 nm than at 450 nm. The reverse effect is observed in solutions containing PVS where the initial rate of decay of the absorption signal is a little faster at 450 nm than at 590 nm.

It is also clear from comparison of the results listed in the two tables that inhibition of the process of regeneration of the ground-state reactants is achieved on addition of PVS. For example, the first half-lifetime for regeneration of the ground-state species averaged over both the monitoring wavelengths is about 3.5 times longer in the presence of 8×10^{-3} M PVS than in the absence of PVS.

Furthermore, increasing the ionic strength of solutions of $\mathrm{Ru(bpy)_3^{2+}}$ and BSV in the absence of PVS by the addition of from 1 to 100 mM $\mathrm{NaClO_4}$ causes virtually no change either in the size of the absorption signals or in their rates of decay as may be seen from the results given in Table I.

Several reasons for the apparently anomalous results obtained were ruled out on carrying out further experiments. Electronic or optical artifacts were found not to be present since the same results were obtained on changing the detection system or the excitation wavelength. The possibility of a biphotonic effect[29,47] causing a change in the ratio of $\mathrm{BSV^{-\cdot}}$ to $\mathrm{Ru(bpy)_3^{3+}}$ produced is unimportant on account of the pulse radiolysis results obtained in this work. In any case the laser intensity was usually sufficiently small such that biphotonic effects were negligible. The formation of an intermediate compound by protonation or deprotonation of one of the electron-transfer products and the possibility of small traces of oxygen catalyzing a slow back-reaction due to its rapid reaction with the viologen radical anion[48-50] were also ruled out. This was because there is no effect on the results on varying the pH of the solution in the range 2–10 or on using a vacuum deaeration technique to remove the final traces of oxygen from solution.

The possibility that the electron-transfer products may react with one of the original components in solution or with impurities in the system was also considered. However, $\mathrm{BSV^{-\cdot}}$ is known from the pulse radiolytic experiments to be stable in the presence of $\mathrm{Ru(bpy)_3^{2+}}$ and the possibility that $\mathrm{Ru(bpy)_3^{3+}}$ can oxidize one of the components in the system was checked by adding a solution of $\mathrm{Ru(bpy)_3^{3+}}$ to BSV and PVS solutions. No production of $\mathrm{Ru(bpy)_3^{2+}}$ in these solutions greater than that in a control solution of water at the same pH was observed on addition of $\mathrm{Ru(bpy)_3^{3+}}$, indicating that such oxidation reactions do not take place. The likelihood of impurities being involved is very small since both the original components of the photochemical system were recrystallized several times from water and gave good microanalysis results while the concentration of impurities present would have to be quite large in order to cause the discrepancies observed.

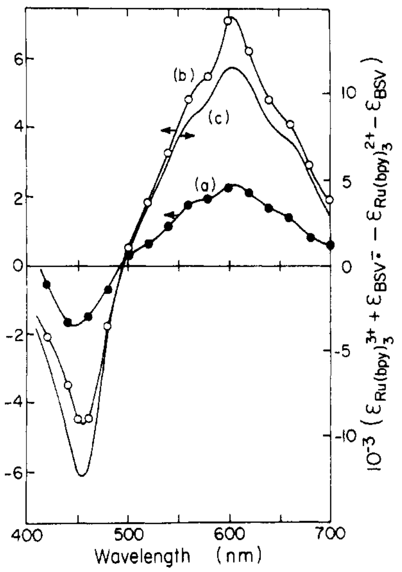


Figure 8. Transient absorption spectra obtained approximately 5 μs after laser irradiation of solutions of $\mathrm{Ru(bpy)_3^{2+}}$ and BSV (a) in the absence of PVS and (b) in the presence of 8×10^{-3} M PVS. Wavelength of excitation = 457 nm except for the wavelength range 440–480 nm when excitation wavelength = 421 nm. Number of photons deposited per unit volume per laser pulse = 8×10^{-5} photons/cm^3. (c) Transient absorption spectrum expected if $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{BSV^{-\cdot}}$ are the sole products of photoinduced electron transfer. The theoretical difference spectrum is calculated from the difference between the extinction coefficients of $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{BSV^{-\cdot}}$, and those of $\mathrm{Ru(bpy)_3^{2+}}$ and BSV.

The complex results that are observed for the yields of products of electron transfer and for their subsequent reactions do however clearly seem to indicate either the formation of more than one set of products and/or the subsequent occurrence of more than one reaction. We conclude that the major products formed are $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{BSV^{-\cdot}}$. This is supported by the fact that the transient difference spectra obtained 5 μs after laser excitation of solutions of $\mathrm{Ru(bpy)_3^{2+}}$ and BSV in both the absence and presence of PVS are of a form similar to that expected from the absorbances of $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{BSV^{-\cdot}}$ as may be seen in Figure 8. Additional evidence for such a supposition comes from the inhibition of the decay of the transient signals which is observed to occur on addition of PVS. Such retardation would be expected to occur for reaction 7 on addition of the negative polyelectrolyte. Furthermore, the addition of 0.01 M triethanolamine at pH 10 to the reaction solution both with and without PVS present, which leads to the overall removal of $\mathrm{Ru(bpy)_3^{3+}}$,[51] yields a transient absorption spectrum similar to that expected from $\mathrm{BSV^{-\cdot}}$ while in air-saturated reaction solutions, in which $\mathrm{BSV^{-\cdot}}$ is very rapidly oxidized to BSV,[48-50] the transient different spectra produced both in the absence and in the presence of PVS are of the same form as that expected if $\mathrm{Ru(bpy)_3^{3+}}$ is produced.

However, the deviations which are observed both in the transient absorption spectra obtained and in the kinetics and wavelength dependence of the rates of decay of the absorption signals suggest that presence of additional species formed in solution after quenching takes place. It is not clear what the nature of the additional species is but we suggest that possibly a complex between $\mathrm{Ru(bpy)_3^{3+}}$ and $\mathrm{BSV^{-\cdot}}$ may be formed. Complexes of a

---

(47) C. D. Jonah, M. S. Matheson, and D. Meisel, *J. Am. Chem. Soc.*, **100**, 1449 (1978).

(48) J. A. Farrington, M. Ebert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, **314**, 372 (1973).

(49) L. K. Patterson, R. D. Small, and J. C. Scaiano, *Radiat. Res.*, **72**, 218 (1977).

(50) F. Rauwel and D. Thevenot, *J. Electroanal. Chem.*, **75**, 579 (1977).

(51) K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, **61**, 2720 (1978).

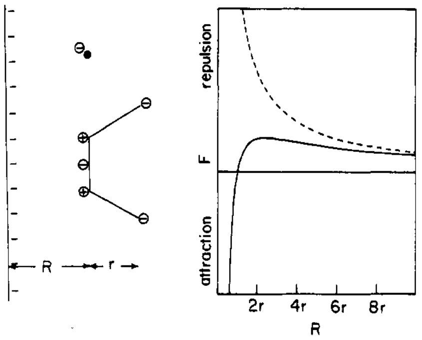


Figure 9. Simplified representation of the variation of Coulombic forces exerted by poly(vinyl sulfate) on the $BSV^{-}\cdot$ radical anion (—) and on an anion bearing a single negative charge (---) with perpendicular distance from the polyanion.

similar nature have been reported[52-55] and evidence for weak association of $Ru(bpy)_3{}^{2+*}$ with viologen analogues to BSV has also been found.[36,56,57] The difference in the apparent quantum yields at the monitoring wavelengths may then be accounted for by the additional absorption of the complex at these wavelengths and the order and wavelength dependence of the decays of the absorption signals may be explained by a complex reaction mechanism in which the complex itself also decays back to the ground-state reactants.

A further point needs to be discussed concerning the yields of the products of eq 5 and their subsequent back-reactions. The addition of polyelectrolyte is found not to have any effect on the apparent quantum yield of photoinduced-electron-transfer products, whereas their subsequent back-reactions are retarded on addition of PVS. In most electron-transfer systems a quantum yield of separated oppositely charged redox products greater than zero is indicative of a rate of geminate back-recombination less than diffusion controlled.[7,8] In such systems the addition of an appropriate polyelectrolyte would therefore be expected to lead to both an increase in the yield of separated electron-transfer products and an inhibition of the rate of their back-reaction following diffusion of one of the products into the bulk of solution. This lack of effect of addition of PVS to the system on the yield of $Ru(bpy)_3{}^{3+}$ and $BSV^{-}\cdot$ may be understood by reference to Figure 9, in which the electrostatic forces exerted by the negative polyelectrolyte on the $BSV^{-}\cdot$ radical anion are considered as a function of the distance of $BSV^{-}\cdot$ away from the polyanion.

The electrostatic force, F, exerted on an ion carrying a charge, ze, by an infinitely long cylindrical polyelectrolyte of linear charge density, σ, is given by the equation

$$F = z\sigma e / 2\pi\epsilon_0\epsilon R \tag{8}$$

where ϵ_0 is the permittivity of a vacuum, ϵ is the dielectric constant of the medium, and R is the perpendicular distance of the ion from the polyelectrolyte. The force of repulsion exerted on the $BSV^{-}\cdot$ radical anion by the negative polyelectrolyte, PVS, is then given by eq 9 on consideration of the dispersal of charge over the BSV

$$\begin{aligned} F &= \frac{\sigma e}{2\pi\epsilon_0\epsilon}\left(\frac{1}{R} - \frac{2}{R} + \frac{2}{R+r}\right) \\ &= \frac{\sigma e}{2\pi\epsilon_0\epsilon}\left(\frac{2}{R+r} - \frac{1}{R}\right) \end{aligned} \tag{9}$$

radical anion. In this case R is the distance between the polyelectrolyte and the charges on the $BSV^{-}\cdot$ radical anion closest to the polyelectrolyte, and r is the distance between the positive charges on the nitrogen atoms of the bipyridine grouping and the negative charges of the sulfonate groups in the ion, on an axis perpendicular to the polyelectrolyte.

On plotting this force as a function of R we obtain the graph given by the solid line in Figure 9. This is compared to the plot given by the broken line which represents the variation with distance away from the polyelectrolyte of the force of repulsion on a point negative electronic charge exerted by the same PVS polyion. The plot for the $BSV^{-}\cdot$ radical anion shows that, when it is in very close proximity to the polyelectrolyte, attraction of the overall negative species occurs since the highly attractive forces acting on the two positive charges in the radical anion species are considerably larger than the total repulsive force acting on the three negative charges in the radical anion, two of which are certainly significantly more distant from the polyelectrolyte molecule than the positive charges. The electrostatic force exerted on $BSV^{-}\cdot$ by the PVS polyanion becomes a repulsive force as the $BSV^{-}\cdot$ species is more distant from the polyelectrolyte since the repulsive force acting on the three negative charges will then clearly exceed the attractive force acting on the two positive charges of $BSV^{-}\cdot$. The retarding electrostatic force is at a maximum when $R \simeq 2.4r$. No account is taken of the electrostatic forces acting on the $BSV^{-}\cdot$ radical anion by the $Ru(bpy)_3{}^{3+}$ ion although this will not change the qualitative nature of the situation described.

When the bipyridine backbone of the $BSV^{-}\cdot$ radical anion lies at a distance of approximately r away from the PVS polyelectrolyte, i.e., when $R \simeq r$, then no electrostatic force is exerted upon $BSV^{-}\cdot$. This is approximately in the vicinity in which the forward electron-transfer reaction is assumed to take place and hence no large driving force for enhanced charge separation is expected on addition of PVS, leading to no dramatic change in the net quantum yield of electron-transfer products. However, when the bipyridine backbone of $BSV^{-}\cdot$ is at a distance greater than about r away from the polyion, it experiences a repulsive force which produces a small retarding potential energy barrier for the $BSV^{-}\cdot$ species to overcome when it diffuses from the bulk of solution to react back with the $Ru(bpy)_3{}^{3+}$ species, lying in the PVS field. Thus, the rate of back-electron-transfer is observed to be reduced.

So in the case of zwitterionic dipolar quenchers such as BSV, the addition of a negative polyelectrolyte may cause an inhibition of the back-electron-transfer reaction between the charge-separated photoelectron-transfer products without affecting their net yield of formation via the process of charge separation as is indeed observed in this investigation.

Addition of Oxygen to the Photochemical System. BSV may be used as a shuttle or relay species in the photochemical system described above, on addition of an electron-acceptor species which may be rapidly reduced by $BSV^{-}\cdot$. For example, under our experimental conditions, addition of O_2, while it quenches some of the $Ru(bpy)_3{}^{2+*}$, also removes all the $BSV^{-}\cdot$ via reaction 10

$$BSV^{-}\cdot + O_2 \rightarrow BSV + O_2^{-} \tag{10}$$

producing O_2^{-}.[48,49] Any complex formed probably also disappears very rapidly while the oxidized product, $Ru(bpy)_3{}^{3+}$, may remain until it reacts back with O_2^{-} via reaction 11.

$$Ru(bpy)_3{}^{3+} + O_2^{-} \rightarrow Ru(bpy)_3{}^{2+} + O_2 \tag{11}$$

The decay of the bleaching signal at 450 nm obtained after laser irradiation of air-saturated solutions of $Ru(bpy)_3{}^{2+}$ and BSV, which represents the re-formation of $Ru(bpy)_3{}^{2+}$ via reaction 11, could be followed and the effect of adding PVS to these solutions was studied. The rate constant for reaction 11 in homogeneous aqueous solution was measured to be 3.5×10^{10} M^{-1} s^{-1}, which in the presence of 8×10^{-3} M PVS decreased to a value of 8.3×10^{8} M^{-1} s^{-1}, indicating a factor of inhibition of about 40 due to the addition of the anionic polyelectrolyte. This represents a considerably larger degree of retardation of the back-reaction than obtained for the back-electron-transfer reaction between $Ru(bpy)_3{}^{3+}$ and $BSV^{-}\cdot$ and is probably due to the greater potential energy barrier to be overcome for the diffusion of the O_2^{-} species

---

(52) J. W. Verhoeven, A.-M. A. Verhoeven-Schoff, A. Masson, and R. Schwyzer, *Helv. Chim. Acta*, **57**, 2503 (1974).

(53) A. T. Poulos, C. K. Kelley, and R. Simone, *J. Phys. Chem.*, **85**, 823 (1981).

(54) (a) A. Deronzier and F. Esposito, *Nouv. J. Chim.*, **7**, 15 (1983); (b) A. Deronzier, *J. Chem. Soc., Chem. Commun.*, 329 (1982).

(55) (a) J. C. Curtis, B. P. Sullivan, and T. J. Meyer, *Inorg. Chem.*, **19**, 3833 (1980); (b) B. P. Sullivan, W. J. Dressick, and T. J. Meyer, *J. Phys. Chem.*, **86**, 1473 (1982).

(56) M. A. J. Rodgers and J. C. Becker, *J. Phys. Chem.*, **84**, 2762 (1980).

(57) K. Kalyanasundaram and M. Neumann-Spallart, *Chem. Phys. Lett.*, **88**, 7 (1982).

from the bulk of solution to the polyelectrolyte as compared to that for the BSV$^{-\cdot}$ species, as explained schematically in Figure 9. It should be noted that the degree of inhibition of reaction 11 on addition of PVS is of the same order of magnitude as that found for several other chemical reactions between oppositively charged species in polyelectrolyte systems.[1,3]

Acknowledgment. We are indebted to Mr. G. Dolan and Mr. Y. Ogdan for technical assistance and to Profs. Y. Klein and I. Shahak for helpful discussions concerning the synthesis of BSV. This research was supported by the Israel National Research Council, The Balfour Foundation, and The Schrieber Hebrew University Center for Hydrogen.

Chlorine-35 Nuclear Magnetic Resonance Study of Aqueous Sodium Perchlorate Association†

Allan G. Miller,‡

Rockwell Hanford Operations, Richland, Washington 99352

James A. Franz,

Battelle Pacific Northwest Laboratories, Richland, Washington 99352

and John W. Macklin*

Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195
(Received: April 10, 1984)

Variation of the ^{35}Cl nuclear magnetic resonance chemical shift and quadrupolar relaxation rate in aqueous NaClO$_4$ and NaClO$_4$–NaOH mixtures with changing concentration and temperature is explained based on contact ion pairing and hydrogen bonding of ClO$_4^-$ with water. Arrhenius activation energies for ^{35}Cl quadrupolar relaxation range from −2 to −9 kcal/mol. The variation of this activation energy as a function of concentration is analogous to the concentration-dependent changes in chemical shift.

Introduction

Chemical shifts and relaxation times from ^{35}Cl nuclear magnetic resonance (NMR) measurements afford a means of studying environmental changes around perchlorate ions in solution. The results are used in a relative and qualitative manner since an explicit theoretical description of perchlorate ^{35}Cl relaxation is not available. Reimarsson et al.[1] have pointed out that the relationships describing relaxation rates of atoms and ions with noble-gas electronic structure developed by Hertz[2–4] may be inappropriate for the tetrahedral perchlorate ion since they do not account for distortions from tetrahedral symmetry or for the fact that the tetrahedral symmetry of perchlorate allows a field gradient of first order to be induced by an external field. Moreover, the Sternheimer antishielding factor is required for the Hertz computations and no estimate of its value for perchlorate ion exists.

Berman and Stengle[5] report studies of ^{35}ClO$_4^-$ relaxation rates in a number of solvents. While large line width variations attributable to contact ion pairing were observed with varying concentration of NaClO$_4$ in some polar organic solvents, such changes could not be measured for aqueous solutions since they were small and within the limits of magnet inhomogeneity. These authors point out that for simple systems quadrupolar relaxation is only affected by polarizing ions at close distances, so that solvent-separated ion pairs yield line broadening that is negligible when compared with the effect of ions in contact. Consequently, they conclude that only solvent-separated sodium perchlorate ion pairs exist in aqueous solution. Reimarsson and Lindman measured relaxation times for a number of aqueous M(ClO$_4$)$_n$ solutions.[6] Divalent and trivalent cations gave large increases in relaxation rates with increasing concentration, but the change for sodium was very small. The effect of NaClO$_4$ concentration up to 5 *m* on the ^{35}Cl chemical shifts was found by Blaser et al.[7] to be small and linear. The general application of NMR to studies of ^{35}ClO$_4^-$ in solution has been reviewed by Forsen and Lindman.[8,9]

The chemical shift and relaxation rate of the ^{23}Na resonance have been measured for various concentrations of aqueous sodium perchlorate and sodium hydroxide by Templeman and Van Geet.[10] Both parameters vary linearly with increasing mole fraction of the salt up to saturation. These changes are interpreted in terms of short-lived contact ion pairs with a formation constant close to 1.

We have carried out a careful investigation of Raman spectra of sodium perchlorate solutions[11] that indicates contact ion pairing in aqueous solution. In order to develop independent experimental support for the interpretation of these vibrational spectroscopic results, ^{35}Cl NMR measurements were taken on the same two series of NaClO$_4$–H$_2$O and NaClO$_4$–NaOH–H$_2$O solutions. In this paper we describe the corresponding ^{35}Cl NMR chemical shifts and relaxation rates that were measured to complement the Raman information.

[†] Presented in parts to: the 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979; the 37th Northwest Meeting of the American Chemical Society, Eugene, OR, June 1982.

[‡] Current address: U.S. Testing Co., 2800 George Washington Way, Richland, WA 99352.

(1) Reimarsson, P.; Wennerstrom, H.; Engstrom, S.; Lindman, B. *J. Phys. Chem.* **1977**, *81*, 789.

(2) Hertz, H. G. *Ber. Bunsenges, Phys. Chem.* **1973**, *77*, 531.

(3) Hertz, H. G.; Holz, M.; Klute, R.; Stalidis, G.; Versmold, H. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 24.

(4) Hertz, H. G. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 688.

(5) Berman, H. A.; Stengle, T. R. *J. Phys. Chem.* **1975**, *79*, 1001.

(6) Reimarrsson, P.; Lindman, B. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 449.

(7) Blaser, J.; Lutz, O.; Steinkilberg, W. *Z. Naturforsch., A* **1972**, *27A*, 72.

(8) Forsen, S.; Lindman, B. In "Basic Principles and Progress in NMR"; Diehl, P., Gluck, E., Kosfeld, R., Eds.; Springer-Verlag: West Berlin, 1976; Vol. 12.

(9) Lindman, B.; Forsen, S. In "NMR and the Periodic Table;" Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1979.

(10) Templemna, G. L.; Van Geet, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 5578.

(11) Miller, A. G.; Macklin, J. W. *J. Phys. Chem.*, following paper in this issue.

0022-3654/85/2089-1190$01.50/0 © 1985 American Chemical Society