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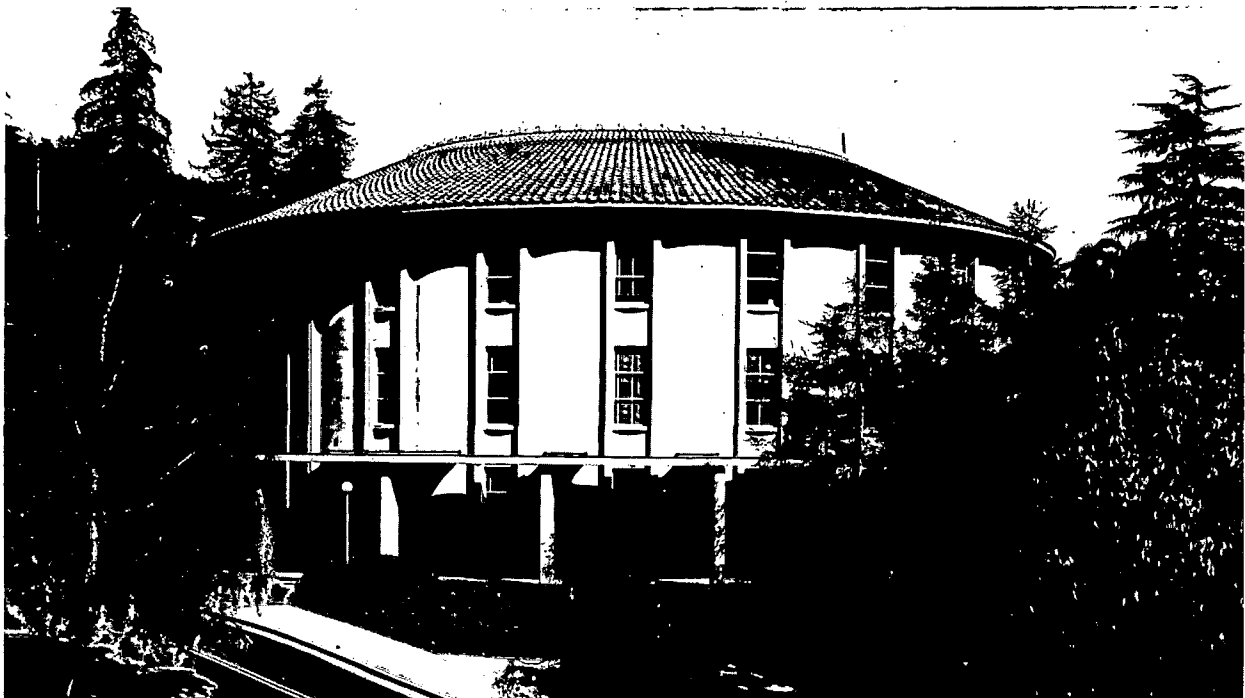## UNIVERSITY OF CALIFORNIA

CHEMICAL BIODYNAMICS DIVISION

POLYELECTROLYTES AS INTERFACES FOR RETARDING
BACK-REACTION IN PHOTOINDUCED ELECTRON TRANSFER

J.W. Otvos, T.E. Casti and M. Calvin

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DISCLAIMER

POLYELECTROLYTES AS INTERFACES FOR RETARDING
BACK-REACTION IN PHOTOINDUCED ELECTRON TRANSFER

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ABSTRACT

Flash photolysis experiments on the effect of the polyelectrolytes poly(styrene sulfonate) (PSS) and Poly(N,N-dimethyl-3,5-dimethylene piperidinium chloride) (PolyP) on the photoinduced electron transfer reaction between zinc(II) tetrakis(4-N-methylpyridinium)porphyin (ZnP) and propyl viologen sulfonate (PVS^o) show that PSS decreases both the forward and back- electron transfer reaction rates significantly, by a factor of ~ 50. The effect of PSS is due to hydrophobic envelopment of ZnP by the polyelectrolyte, hindering approach of reactants to it and thus reducing all bimolecular reaction rates between ZnP and species in solution. The cationic polyelectrolyte, PolyP, decreases the back-electron transfer rate by a factor of ~ 2 without affecting other bimolecular reaction rates. This effect is probably due to binding of the PVS^- to the polyelectrolyte, which then repels the oxidized porphyrin electrostatically.

I. INTRODUCTION

The electron transfer reaction between an excited photosensitizer molecule and an electron acceptor capable of hydrogen reduction is currently of interest as a means of solar energy conversion. (1,2) For efficient operation of a cyclic photochemical system (as shown in Figure 1) the exothermic back-reaction between oxidized sensitizer and reduced acceptor must be prevented. Several interfacial systems, e.g. SiO_2 colloids (3), micelles (4) and microemulsions (5) have been studied in an effort to reduce the back-reaction rate through electrostatic re-pulsion of oppositely charged photoproducts. Polyelectrolytes have also been shown to decrease the rate of reaction between oppositely charged species. (6) Extensive work in this area by Ise and co-workers (7) has shown that both electrostatic and hydrophobic (solvation) effects play major roles in the effects of polyelectrolytes on reaction rates.

We report here our results on the effect of two polyelectrolytes, poly(styrene sulfonate) (PSS) and poly(N-N-dimethyl-3,5-dimethylene piperidinium chloride) (PolyP) on both the forward and back photoinduced electron transfer reactions between zinc-tetrakis(4-N-methylpyridinium)porphyrin and the neutral, zwitterionic electron acceptor, propyl viologen sulfonate (PVS^o). Continuous photolysis experiments using triethanolamine as a sacrificial electron donor demonstrate that addition of PSS increases the overall quantum yield of PVS^- formation by a factor of 2 relative to homogeneous solution, which is a much smaller effect than that observed when

colloidal silica particles with high surface charge density are added to the system. Flash photolysis experiments show that PSS addition decreases both the forward and back electron transfer rates, an effect that we ascribe to a hydrophobic envelopment of the positively charged porphyrin upon association with the anionic polyelectrolyte. In the case of the positively charged PolyP, no effect on the forward reaction is observed, while the back reaction is found to be decreased by a factor of about 2. This observation is consistent with a model in which the two reactants in solution do not interact with the polyelectrolyte because of charge considerations while one of the photoproducts, PVS⁻, does become associated with the oppositely charged PolyP. Thus the back reaction is reduced while the forward rate is unaffected.

II. MATERIALS AND METHODS

(1) MATERIALS

Zinc(II) tetrakis(4-N-methylpyridinium)porphyrin, perchlorate salt, (ZnP) was prepared by the method of Hambright and Fleischer. (8) Propyl viologen sulfonate (PVS⁰) was prepared by heating 1 g of 4,4'-dipyridine together with 3 g of 1,3-propane sultone in a sealed vial for 20 h at $120^{o}C$. The white product was precipitated three times from water by adding an excess of acetone. Elemental analysis and NMR were used to characterize the product. Poly(styrene sulfonate, sodium salt) (PSS), MW = 4000, was purchased from Polysciences, Inc. Poly-(N,N-dimethyl-3,5-dimethylene piperidinium chloride) (PolyP), MW = 10^{7} was purchased from Scientific Polymer Products, Inc. A suspension of colloidal silica particles, 40 Angstroms diameter, 24.5% w/v, NALCO

Chemical Co. #1115, was diluted to 0.2% w/v. Triethanolamine (TEOA) was purchased from Baker, Inc. Water was distilled and purified by a Millipore Milli-Q system before use.

(2) CONTINUOUS PHOTOLYSIS EXPERIMENTS

3 ml samples of ZnP (3.5×10^{-6} M), PVS^0 (2×10^{-3} M), TEOA (1×10^{-3} M) with and without PSS (3×10^{-4} eq/l) or colloidal SiO_2 (0.2%) were adjusted to pH 10.2, placed in airtight fluorimeter cells equipped with stopcocks and serum stoppers and deoxygenated by purging with pure argon. Simultaneous irradiation and spectrophotometric detection of photoproducts was accomplished through the use of a specially designed thermostated cell holder with provisions for magnetic stirring of the cell contents. Irradiation of the sample was by a 450 W xenon lamp directed through a fiber optics illumination system containing a 440 nm narrow bandpass interference filter. Photon flux was determined by Reinecke's salt actinometry (9) in conjunction with convolutive techniques described by Rougee, et al.(10)

(3) FLASH PHOTOLYSIS EXPERIMENTS

3 ml samples of ZnP (1×10^{-5} M), PVS^0 ($.25 - 1.0 \times 10^{-3}$ M) and PSS or PolyP ($0-1.25 \times 10^{-3}$ eq/l), pH 7, were deoxygenated as outlined in the previous section. Flash photolysis experiments were performed using 200 ns, 590 nm optical pulses from a Candela SLL-66A flashlamp-pumped dye laser. Transient absorbance changes at 480 and 600 nm were monitored by a single beam spectrometer consisting of a 75 W xenon lamp, narrow bandpass interference filters for wavelength selection, and a PIN-8-LC fast photodiode detector. The exciting and analyzing beams were in a crossed beam arrangement. Transient signals were recorded and

stored using a Nicolet digital oscilloscope interfaced with a VAX-11/780 digital computer for signal averaging and data manipulation.
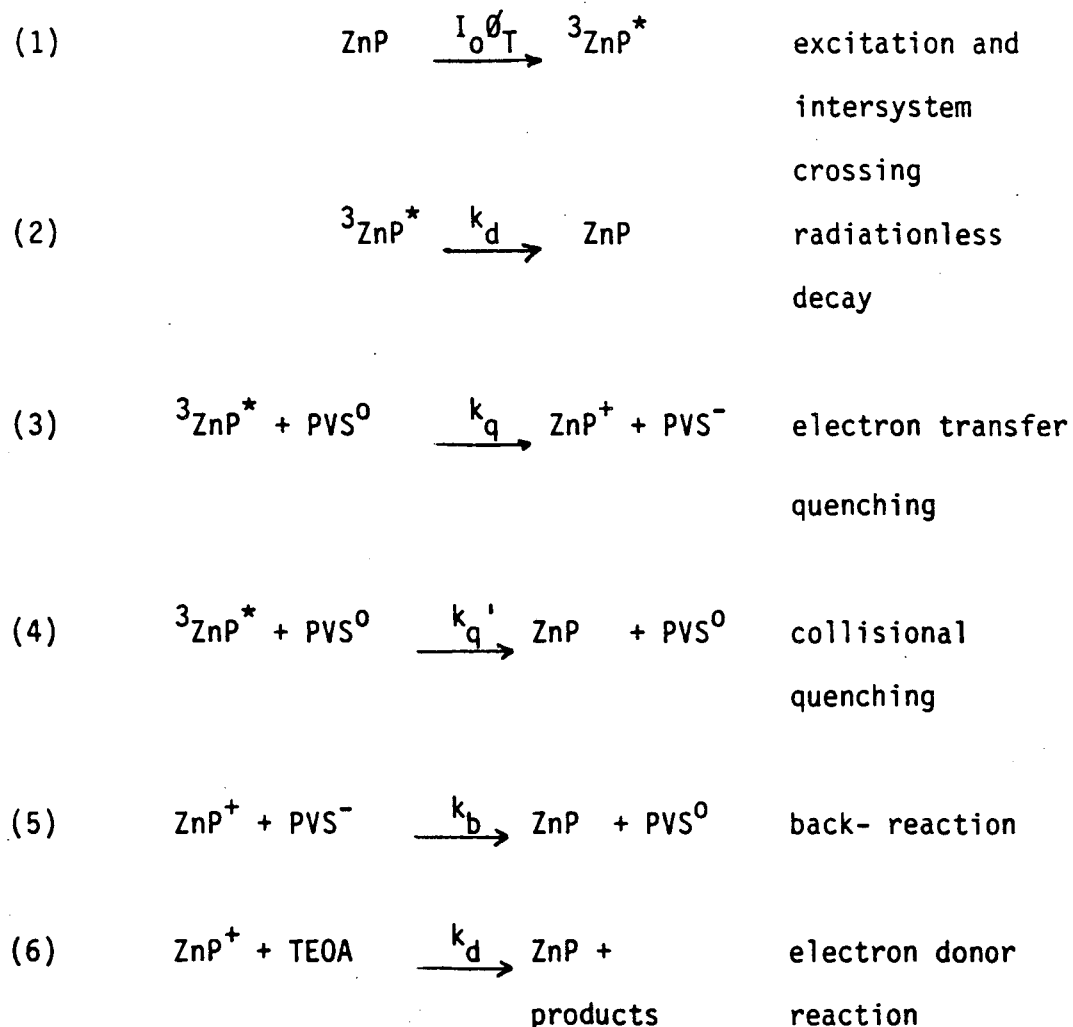
(4) FITTING OF FLASH PHOTOLYSIS DATA TO KINETIC MODEL

Fitting of transient absorbance data at 600 nm was performed as follows: There is a contribution to the absorbance at 600 nm from both $^3ZnP^*$ and PVS^-. To model the total absorbance change with time, the integrated form of equation 10 is converted to absorbance and added to equation 9, also converted to absorbance. Since there is no simple analytical solution for equation 10, numerical integration methods were used. $^3ZnP^*_o$ is determined by initial absorbance change measurements at 480 nm. k_d (300 s^{-1}) was determined by a separate measurement of the triplet lifetime in the absence of quencher. k_b is determined independently of k_q and k_q'; at times greater than $10/(k_q + k_q')[PVS^o]$ the exponential term in equation 10 becomes negligible and the second order constant, k_b, can be obtained from a plot of reciprocal absorbance change vs. time.

Because of the several distinct features in the experimental data, i.e., initial absorbance, height of maximum, time at the maximum, shape of the tail, etc., a good fit to the data lends credibility to the values of the parameters k_q and k_q'. Figures 2, 3 and 4 show typical experimental data and fits, which are are well within experimental noise.

III. <u>RESULTS AND DISCUSSION</u>

The kinetic scheme used to interpret both continuous irradiation and flash photolysis experimental data is shown below:

(1) $\quad ZnP \xrightarrow{I_0 \phi_T} {}^3ZnP^*$ excitation and intersystem crossing

(2) $\quad {}^3ZnP^* \xrightarrow{k_d} ZnP$ radiationless decay

(3) $\quad {}^3ZnP^* + PVS^0 \xrightarrow{k_q} ZnP^+ + PVS^-$ electron transfer quenching

(4) $\quad {}^3ZnP^* + PVS^0 \xrightarrow{k_q'} ZnP + PVS^0$ collisional quenching

(5) $\quad ZnP^+ + PVS^- \xrightarrow{k_b} ZnP + PVS^0$ back- reaction

(6) $\quad ZnP^+ + TEOA \xrightarrow{k_d} ZnP + products$ electron donor reaction

The actual chemistry of sacrificial electron donors in continuous photolysis systems is more complicated than is shown in equation 6 because the oxidized $TEOA^+$ has reducing properties and may react with PVS^0 to form another PVS^-, which means the overall quantum yield in this

system could have an upper limit of 2.0. (10) These reactions are not included here because our data do not relate to them in detail.

The results of continuous photolysis experiments at pH 10.2 are shown in Figure 5. The overall quantum yield of PVS⁻ formation increases by a factor of 2 upon the addition of the anionic polyelectrolyte PSS. While the increase is significant, it is not as dramatic as the effect observed when 40 A negatively charged colloidal SiO_2 particles are added to the same reaction mixture. The mechanism of quantum yield enhancement upon the addition of the silica particles is understood in terms of electrostatic binding of the positively charged porphyrin to the surface of the charged SiO_2 particle and repulsion of the negatively charged product, PVS⁻, from the vicinity of the particle-bound porphyrin.(3) This decreases the rate of reaction 5 and allows reaction 6 to drive the forward reaction effectively by regenerating ZnP.

The effect of PSS on the individual reactions in the kinetic scheme was further studied by flash photolysis experiments in which no sacrificial electron donor was present. In these experiments the only reaction possible for the primary oxidized and reduced photoproducts is back- reaction with each other, i.e. reaction 5. Also, because of the short duration of the laser pulse (200 ns) compared to the time scale of the experiment (>300 μs), step 1 need not be included in the kinetic treatment.

Flash photolysis experiments were performed by monitoring changes in absorbance at both 600 and 480 nm to follow PVS⁻ and $^3ZnP^*$ concentrations, respectively. Relevant extinction coefficients are given in Table 1. Note that the excited triplet extinction coefficient is decreased when PSS is added. This is due to a shift in the maximum of

the triplet-triplet absorption of the porphyrin upon complexation with the polyelectrolyte. The ground state absorption spectrum of the porphyrin also changes upon addition of PSS. No change in the triplet-triplet absorption spectrum is observed upon addition of PolyP, however, presumably because the positively charged porphyrin does not complex with the positively charged polyelectrolyte.

TABLE 1

EXTINCTION COEFFICIENTS USED IN KINETIC ANALYSIS[+]

$$E$$

$$M^{-1}cm^{-1}$$

SPECIES	480 nm	600 nm
ZnP	2530	5000
ZnP/PSS	2290	4400
^{3}ZnP*	63300 (12)	8000
^{3}ZnP*/PSS	52500	6600
PVS$^-$		12800 (3)
ZnP$^+$		5000 (13)

[+] Determined by flash photolysis experiments based on extinction coefficients from ref. 11 except where otherwise noted.

Changes in absorbance at 600 nm after the laser pulse are due both to the decay of the excited triplet porphyrin and the buildup and decay

of PVS^-. The differential equations describing these two processes based on the proposed model are:

(7) $d[PVS^-]/dt = k_q[PVS^0][^3ZnP^*] - k_b[PVS^-][ZnP^+]$

(8) $d[^3ZnP^*]/dt = (-k_d - (k_q + k_q'))[PVS^0][^3ZnP^*]$

Equation 8 can be integrated to give

(9) $[^3ZnP^*] = [^3ZnP^*]_0 \exp(-k_d - (k_q + k_q')[PVS^0])t$

Combining equations 7 and 9, and noting that in experiments without sacrificial electron donor present $[ZnP^+] = [PVS^-]$ gives

(10) $d[PVS^-]/dt = [^3ZnP^*]_0 \exp(-k_d - (k_q + k_q')[PVS^0])t - k_b[PVS^-]^2$

Table 2 lists the values for k_q, k_q' and k_b determined by the methods outlined in the Materials and Methods section for systems containing no polyelectrolyte, PSS and PolyP. In the case of the homogeneous system, experiments were performed with different initial $^3ZnP^*$ concentrations (altered by changing the laser power) between 2.1×10^{-6} and 3.9×10^{-6} M and with PVS^0 concentrations ranging between .0025 and .001 M. Calculated values of k_q and k_b were insensitive to these changes, as the model requires. k_q', however, steadily decreases with increasing $[PVS^0]$. This does not seem to be caused by decreasing activity of PVS^0 with increasing concentration, as k_q does not vary with $[PVS^0]$. The problem may be that collecting all bimolecular processes

TABLE 2

CALCULATED RATE CONSTANTS FOR PROPOSED KINETIC SCHEME[+]

$[^3ZnP^*]_0$ M	$[PVS^0]$ M	$k_q' \times 10^{-7}$ $M^{-1}s^{-1}$	$k_q \times 10^{-7}$ $M^{-1}s^{-1}$	$k_b \times 10^{-7}$ $M^{-1}s^{-1}$
a) With no polyelectrolyte				
2.14	.00025	6.0 (0.2)	6.5 (0.1)	650 (30)
2.38	.00025	5.7	6.5	660
3.45	.00025	5.8	6.5	670
3.70	.00025	5.8	6.5	670
3.78	.00025	5.8	6.5	670
2.06	.0005	4.0	6.5	690
3.78	.0005	4.0	6.5	710
2.55	.001	1.5	6.5	700
b) With PSS, 0.001 eq/l				
3.98	.001	0.04 (.002)	0.065 (.002)	16 (2)
c) With PolyP, 0.00125 eq/l				
3.45	.001	1.4 (0.2)	6.5 (0.2)	390 (30)

+ All rate constants were determined by fitting transient
absorbance data at 600 nm by the procedures outlined in the
Materials and Methods section using the extinction coefficients
in Table 1. Absolute errors are in parenthesis following the
determined rate constants.

that deactivate $^3ZnP^*$ without electron transfer into one constant, k_q', may be too much of a simplification.

The constants in Table 2 show that addition of PSS to the system causes approximately a 60-fold decrease in both k_q and k_b. This is not in agreement with the electrostatic model of polyelectrolyte influence on intermolecular reactions, which in this case would predict no effect on k_q, a reaction between a neutral and a cationic species, and an inhibitory effect on k_b, a reaction between oppositely charged species. Studies of the role of solvation in polyelectrolyte "catalysis" have shown that the solvating properties of the polyelectrolyte can contribute significantly to the effect of the polymer in solution, and that these hydrophobic effects may even predominate over electrostatic effects. (13,14)

In a study of the effect of PSS on the fluorescence lifetime of a cationic probe molecule, Turro and Okubo found the probe to be strongly associated with the polyelectrolyte molecule in an environment whose apparent microviscosity is ca. 150 cP. (15) This effect is analogous to envelopment of ZnP by the PSS macroion upon binding and decreases the rate of all bimolecular reactions because of hindrance to the approach of reactants in solution to bound ZnP molecules. Such hydrophobic effects appear to dominate with the polyelectrolyte PSS. Sassoon and Rabani have studied the effect of poly(vinyl sulfate), a nonhydrophobic polyelectrolyte, on the forward and back reaction between $Ru(bpy)_3^{2+}$ and the zwitterionic electron acceptor, dibenzyl sulfonate viologen (BSV^0), a system similar to the one that we have studied. (16) Addition of poly(vinyl sulfate) increased k_q by a factor of 40 and decreased k_b by 10-fold. These results are interpreted in terms of coulombic attraction

of $Ru(bpy)_3^{2+}$ and BSVo through electrostatic and dipolar forces, respectively, and coulombic repulsion of BSV⁻ from the polyelectrolyte. Clearly, charge considerations determine the effect of the polyelectrolyte in this case, unlike in the experiments performed using PSS.

Also shown in Table 2 are the calculated rate constants for k_q and k_b in the presence of PolyP, a cationic polyelectrolyte. In this case, electrostatic considerations predict that addition of the poly-electrolyte should have no effect on k_q and a retarding effect on k_b, as the cationic macroion should only interact with PVS⁻. This is indeed what is observed, i.e., k_q is not changed significantly, while k_b is decreased by a factor of 2 relative to its value in the homogeneous solution.

The effect of PSS on k_b is much greater than that of PolyP. The overall quantum yield of PVS⁻ in a continuously irradiated system, however, depends on the ratio of k_q to k_b. Since PSS affects k_q and k_b about equally, no overall improvement in quantum yield is predicted. Our continuous photolysis experiments using PSS showed an improvement in overall quantum yield of 2, which must be due to the influence of PSS on some other reaction, possibly involving the sacrificial electron donor, TEOA.

IV. CONCLUSIONS

Flash photolysis experiments to study the effect of PSS on the forward and back electron transfer reactions between ZnP and PVS⁰ show that both k_q and k_b are drastically decreased by PSS addition. It

appears that hydrophobic interactions of ZnP with PSS result in envelopment of the porphyrin by the polyelectrolyte, hindering approach of reactants to ZnP and decreasing all bimolecular reaction rates involving PSS- bound ZnP. The polyelectrolyte has little effect on the ratio k_q/k_b, which determines the quantum yield in continuous photolysis experiments. The increased quantum yield that we observed is probably due to the effect of the polyelectrolyte on reactions involving the sacrificial electron donor.

Flash photolysis experiments have also shown that PolyP does decrease k_b by a factor of 2 without significantly decreasing k_q. The effect of PolyP is probably by association of PVS⁻ to the cationic polyelectrolyte. This association would shield the PVS⁻ electrostatically from the approach of oxidized porphyrin molecules. It would also reduce k_b by slowing down the diffusion of PVS⁻ in solution.

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FIGURE CAPTIONS
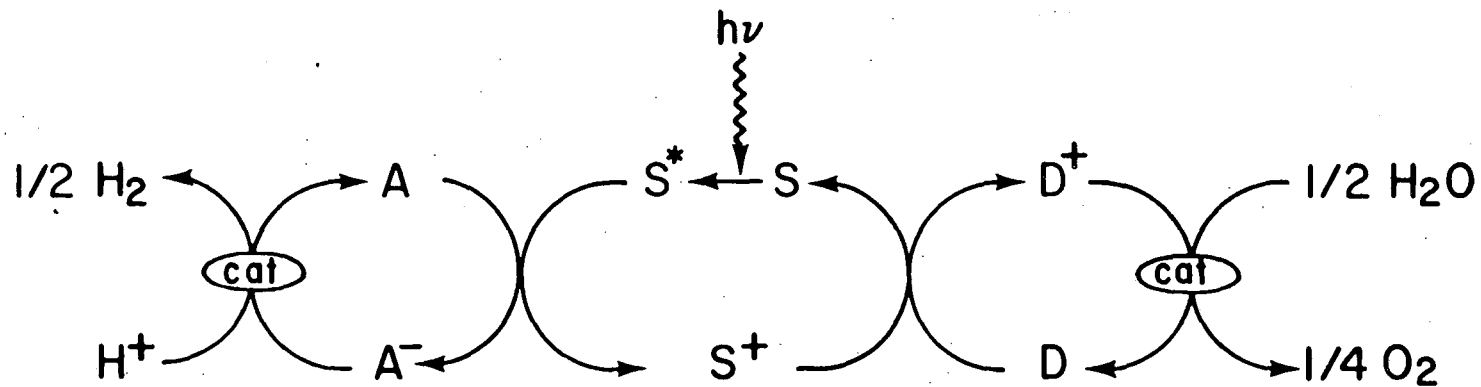
Figure 1   Cyclic photochemical scheme for decomposition of water

Figure 2   Calculated vs. experimental transient absorbance change at 600 nm. $(ZnP) = 1.0 \times 10^{-5}$ M; $(^{3}ZnP^{*})_{0} = 2.6 \times 10^{-6}$ M; $(PVS^{0}) = .001$ M

Figure 3   Calculated vs. experimental transient absorbance change at 600 nm. $(ZnP) = 1.0 \times 10^{-5}$ M; $(^{3}ZnP^{*})_{0} = 4.0 \times 10^{-6}$ M; $(PVS^{0}) = .001$ M; $(PSS) = 1.0 \times 10^{-3}$ eq/l

Figure 4   Calculated vs. experimental transient absorbance change at 600 nm. $(ZnP) = 1.0 \times 10^{-5}$ M; $(^{3}ZnP^{*})_{0} = 3.5 \times 10^{-6}$ M; $(PVS^{0}) = .001$ M; $(PolyP) = 1.25 \times 10^{-3}$ eq/l

Figure 5 PVS^{-} formation as a function of light absorbed under continuous illumination conditions; $(ZnTMPyP^{4+}) = 3.5 \times 10^{-6}$ M, $(PVS^{0}) = 2 \times 10^{-3}$ M, $(TEOA) = 1 \times 10^{-3}$ M. All experiments performed at pH 10.2.

      (A)   No polyelectrolyte added

      (B)   With 3.5×10^{-5} M polystyrene sulfonate, MW = 4000
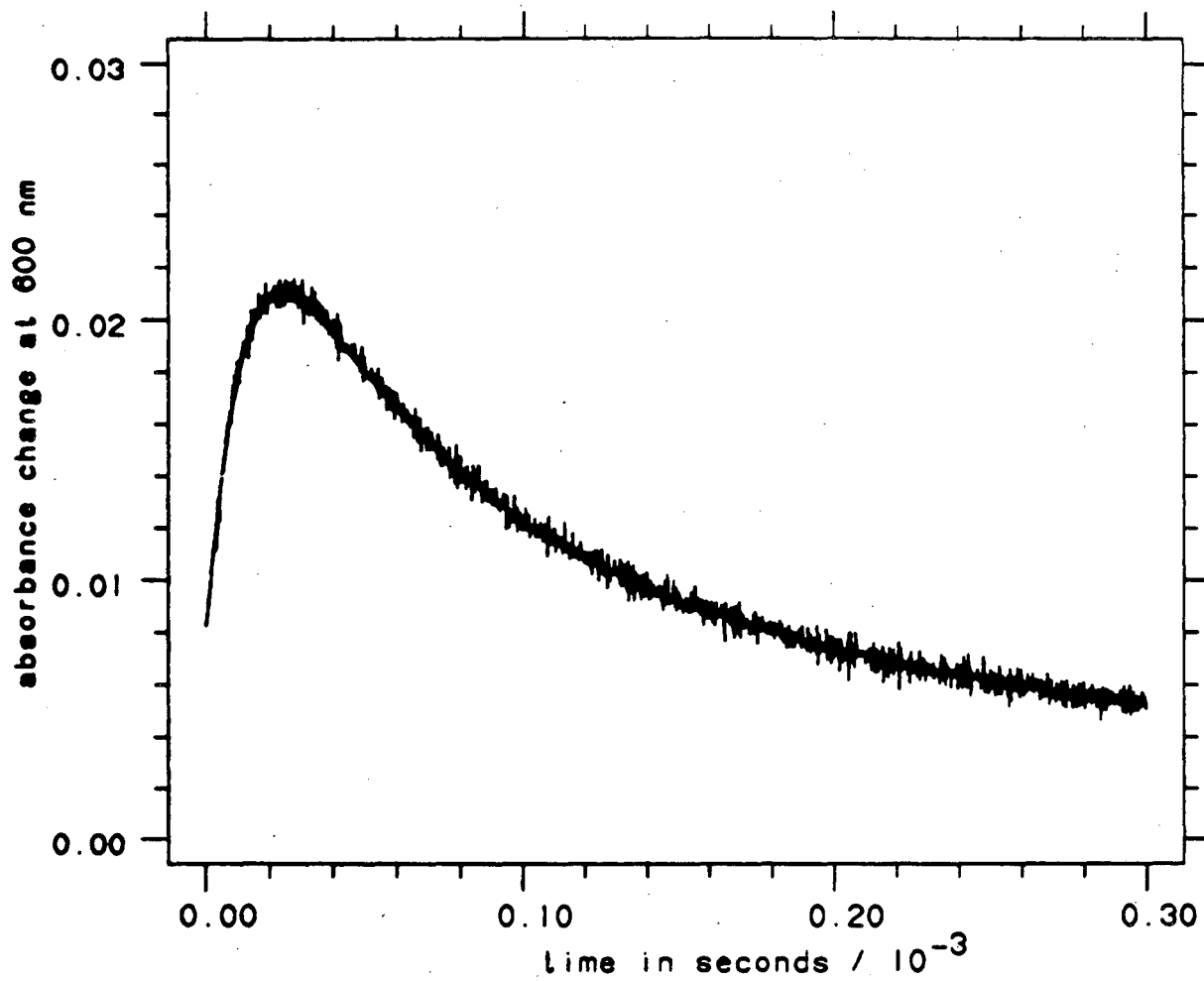
      (C)   With 0.1% W SiO_{2} colloid (NALCO 1115)
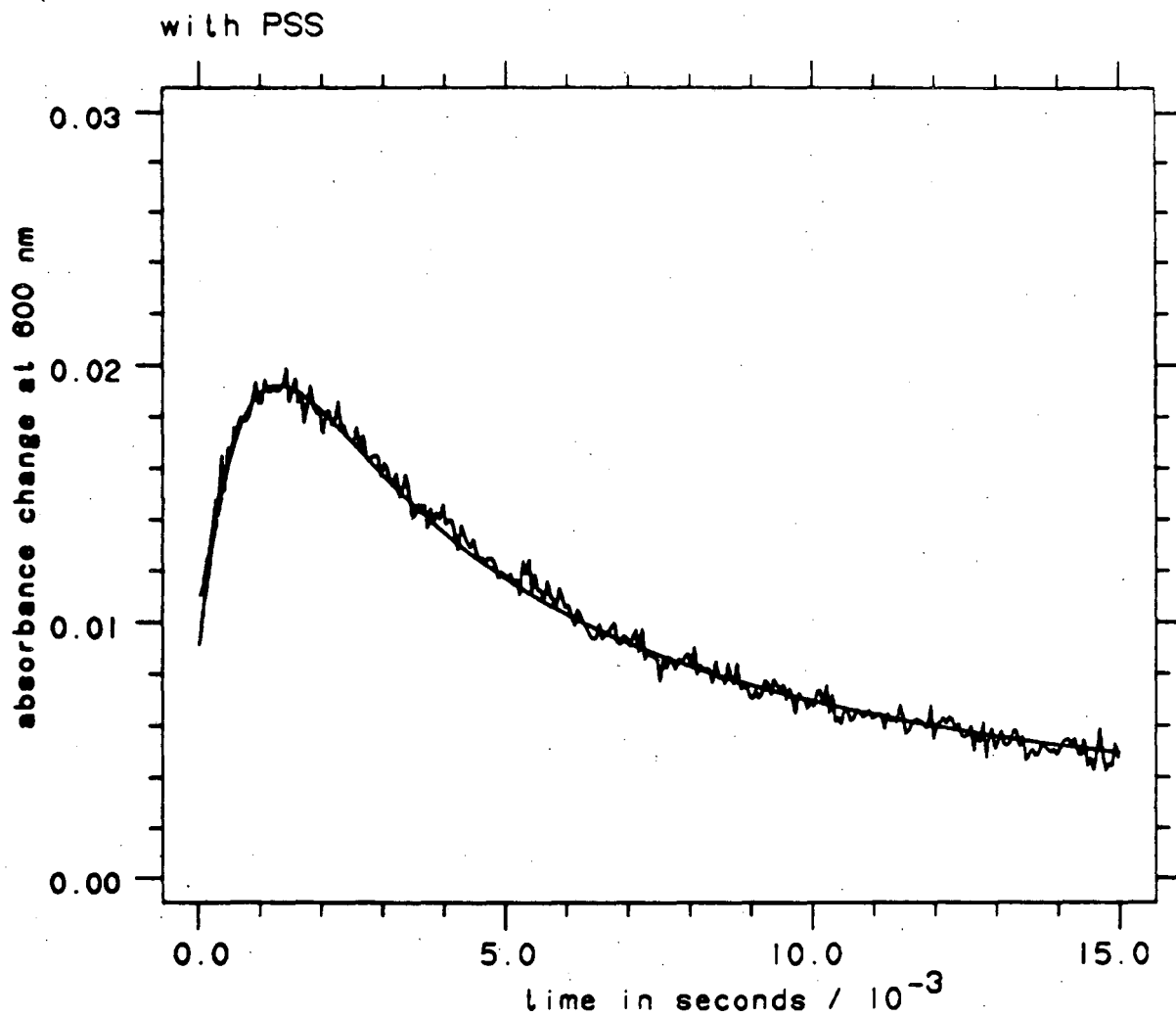
Cyclic Photochemical Scheme for
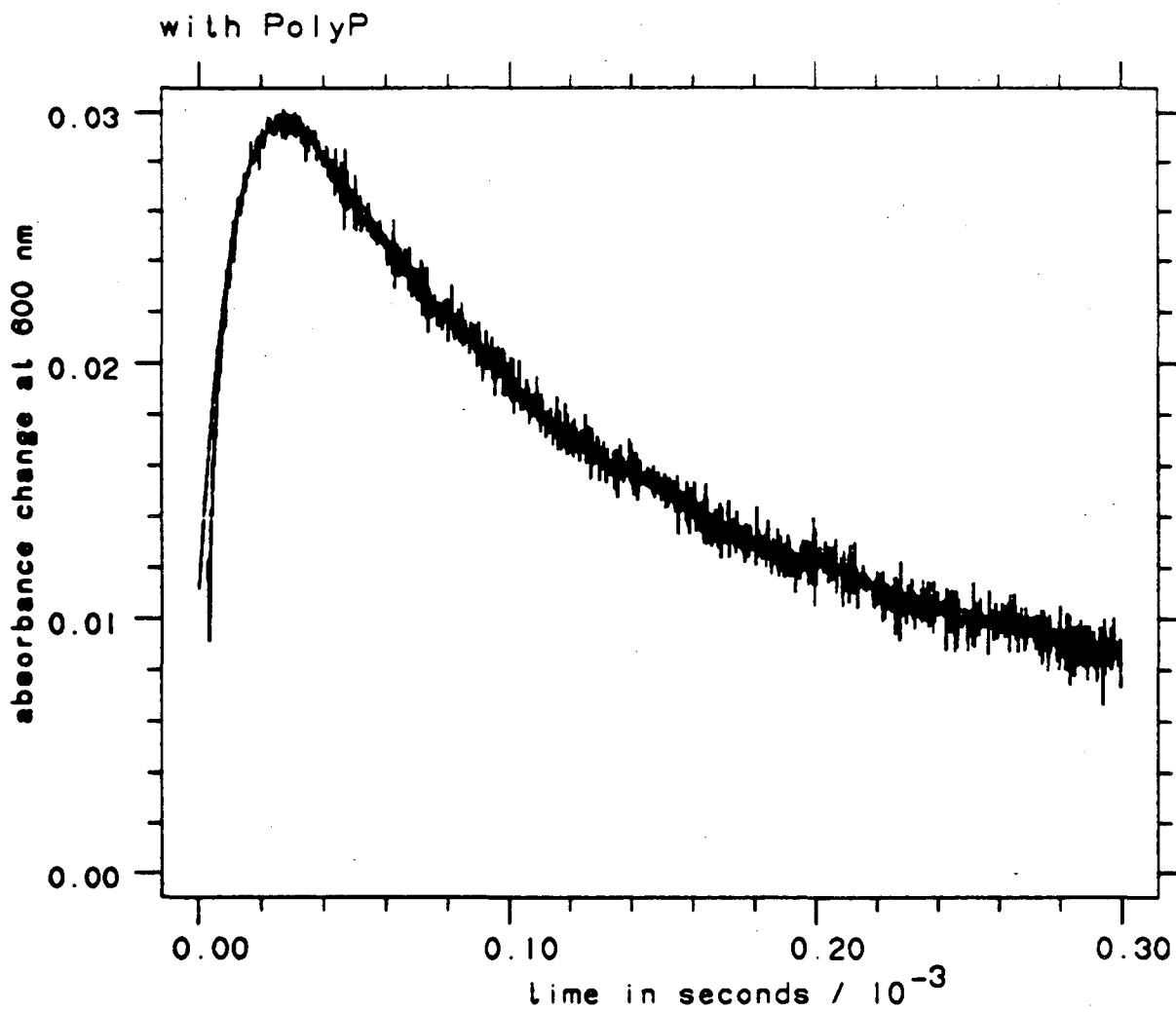Decomposition of Water

Figure No. 1

without polyelectrolyte

XBL 848-3453

Figure No. 2
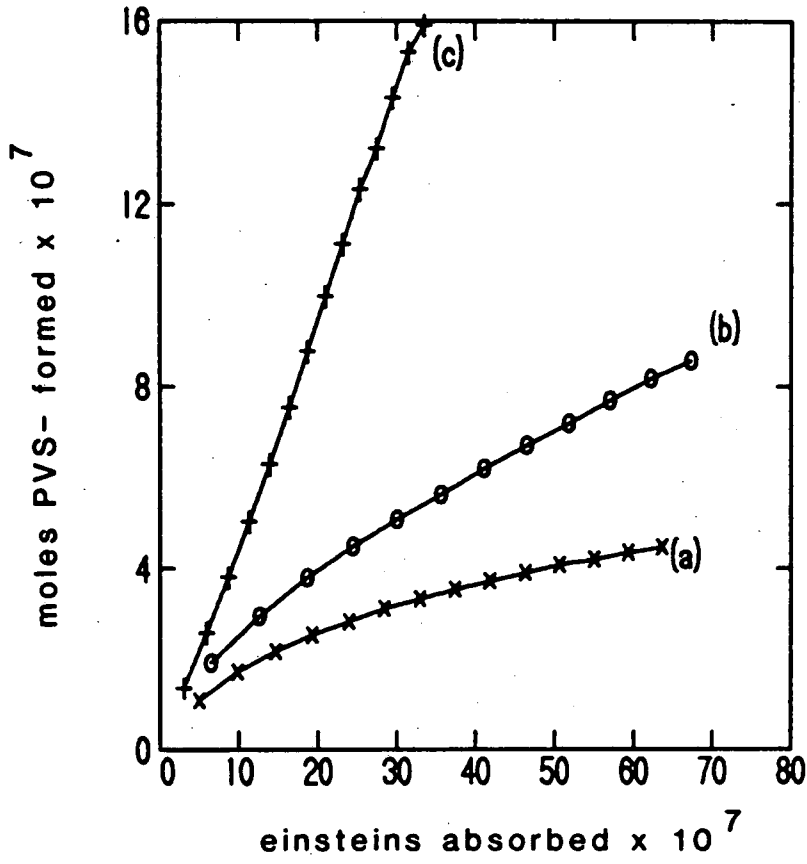
Figure No. 3

XBL 848-3452

with PolyP

Figure No. 4

XBL 848-3451

PVS- radical formation as a function of photons absorbed

XBL 838-11110

Figure No. 5