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Onium Salt Effects on *p*-Terphenyl-Sensitized Photoreduction of Water to Hydrogen

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p-Terphenyl (TP) sensitizes photocatalytic reduction of water to H_2 under UV irradiation of homogeneous aqueous acetonitrile solution in the presence of triethylamine (TEA) as an electron donor and Ru^{3+} as a precursor of cocatalyst, Ru metal colloid. The addition of quaternary onium salts enhances the H_2 evolution, where the onium salts with longer alkyl groups become more effective. Dynamics studies of TP photosensitization reveal that the presence of the salts contributes to stabilization of the radical anion of TP ($TP^{\bullet -}$) formed through reductive quenching of the singlet state of TP ($^1TP^*$) and the triplet state of TP ($^3TP^*$) by TEA. The TP photosensitization accompanies competitive photo-Birch reduction via $TP^{-\cdot}$, but the presence of onium salts enhances the lifetime of $TP^{\bullet -}$ through the specific interaction, leading to the effective TP-photosensitized H_2 evolution.

Introduction

In our previous studies on photocatalysis or photosensitization of *p*-phenylene derivatives, we have focused our attention on photoinduced charge separation and electron-transfer reaction between electron donor and acceptor molecules in polar solvents.[1−4] Oligo(*p*-phenylene)s sensitize photoreduction of not only water molecule to H_2[1,2] but also CO_2 to CO and/or HCOOH[3] in the presence of triethylamine (TEA) as an electron donor under UV ($\lambda > 290$ nm) irradiation. Laser flash photolysis of *p*-terphenyl (TP) revealed that the radical anions from oligo(*p*-phenylene)s are the active intermediates for the photoreduction. The higher H_2 evolution in this system was observed in the presence of $RuCl_3$ with a short induction period. Therefore, we concluded that $RuCl_3$ should be reduced to colloidal Ru metal in situ by UV irradiation in the presence of oligo(*p*-phenylene)s and TEA, and the resulting Ru metal colloid worked as an electron mediator from the active intermediates of oligo(*p*-phenylene)s to water molecule.[2a] In those systems, however, a gradual decomposition of the sensitizer, which may be called photo-Birch reduction,[5] occurs competitively, resulting in inactivation of the photosensitization.

Salt effects on photoinduced electron-transfer reactions are often discussed and used to control or probe photochemical reactions.[6−10] Recently we reported the salt effect on photoinduced CO_2 fixation into benzophenone catalyzed by dispersed poly(*p*-phenylene) powder.[4] In these photoreaction systems, it is assumed that some soft cations of onium salts, such as tetraalkylammonium and tetraalkylphosphonium cations, may contribute to stabilization not only of the intermediary anionic species photoproduced from reacting substrates, but also of anionic species derived from the photocatalysts themselves. The stabilized anion species should have longer lifetimes and greater possibility of the following electron-transfer reactions or chemical reactions in the photocatalytic systems.

In this paper, we report significant onium salt effects on TP-photosensitized reduction of water to H_2, and reveal the role of the salts in the photoreaction system on the basis of dynamics studies of TP in the presence of the salts.

Experiments

Materials. *p*-Terphenyl (TP) which was obtained from nacalai tesque was purified by three time recrystallization from methanol. Extra-pure grade $RuCl_3 \cdot 1-3H_2O$ which was obtained from nacalai tesque was used without further purification. Triethylamine (TEA) was distilled in the presence of KOH, and acetonitrile (AN) was distilled in the presence of CaH_2 under a nitrogen atmosphere before use. Organic salts used in the photoreaction were obtained from the following source: Specially prepared grade tetraethylammonium bromide (TEAB) and tetra-*n*-butylammonium bromide (TBAB), and extra-pure grade tetra-*n*-octylammonium bromide (TOAB) were purchased from nacalai tesque. Tetra-*n*-butylammonium chloride (TBAC) was purchased from Tokyo Kasei.

Photoreduction of H_2O to H_2. As reported in the previous paper,[2a] distilled TEA (0.5 mL), distilled water (0.5 mL) and AN solution (1 mL) of $RuCl_3$ (2 mM) and TP (2 mM) were placed in a Pyrex-glass tube (i.d. = 8 mm). After the mixture was purged with Ar, the tube was closed off with a gum stopper and then irradiated under stirring at $\lambda > 290$ nm using a 500 W high-pressure mercury-arc lamp. The salt effect was examined by introducing 80 mM of each salt in the photoreaction system.

Analysis. H_2 evolution was analyzed by GC using an activated carbon column (2 m × 3 mm) and a TCD detector on a Shimadzu Model GC-12A at 100 °C. Analysis of TP was carried out by GLC using an OV-1 column (25 m × 0.2 mm) and a FID detector on a Shimadzu Model GC-14A at 250 °C.

Laser Flash Photolysis. AN sample solutions for laser flash photolysis were prepared in a quartz cell and degassed by N_2 bubbling. Picosecond laser flash photolysis experiments were performed with the fourth harmonic laser pulses from a mode-

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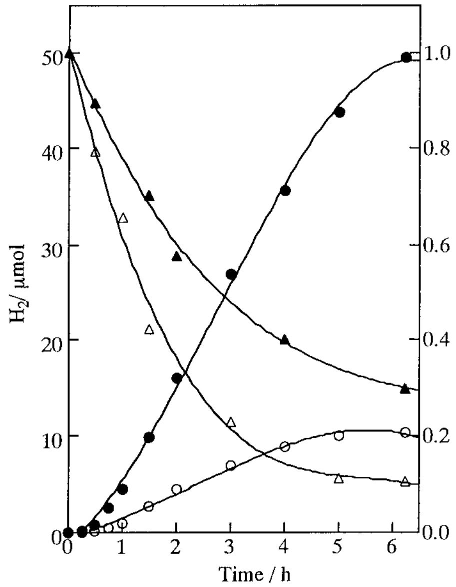

Figure 1. Time-conversion plots of H_2 formation (circle) and TP degradation (triangle) in the presence (closed) and absence (open) of TOAB.

locked Q-switched Continuum YG-501 DP Nd:YAG laser system ($\lambda = 266$ nm, output 1.2 mJ pulse^{-1}, pulse width < 18 ps). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D_2O/H_2O solution. The details of the experimental setup and its operation are described elsewhere.[11,12] Nanosecond laser flash photolysis experiments were performed with the fourth harmonic laser pulses from a Quanta-Ray CDR-1 Nd:YAG laser system ($\lambda = 266$ nm, output 10−50 mJ pulse^{-1}, pulse width 6 ns). A Xe lamp was used as a probe. A typical experiment consisted of 10 repetition shots per signal measurement. The average signal was processed with an LSI-11 microprocessor interfaced to a VAX computer. Details of the experimental setup are described elsewhere.[13] Each spectrum was an average of at least five individual scans. We estimated the errors as less than 10%.

Results

Salt Effects on TP-Photosensitized Water Reduction. We examined the photoreduction of water to hydrogen (H_2) sensitized by TP in the presence of TEA as an electron donor, $RuCl_3$ as a precursor of colloidal Ru metal working as an electron mediator, and in the presence and absence of some onium salts. Figure 1 shows time-conversion plots for the formation of H_2 and consumption of TP under UV irradiation ($\lambda > 290$ nm) in the presence and absence of TOAB. The presence of TOAB enhanced drastically the H_2 formation and suppressed the decomposition of TP. As a result, the turnover number for a 3-h photoreaction also increased from 4.5 in the absence of salt to 31 in the presence of the TOAB. Both systems have about 30 min of induction period, indicating that $RuCl_3$ was reduced to colloidal Ru metal before the photoreduction of water occurred.[2] The control experiment in the presence of colloidal Ru prepared by the method of Willner et al.[14] gave results similar to the irradiated system that included $RuCl_3$. After a longer irradiation period, the formation of H_2 leveled off because of the consumption of TP via photo-Birch reductions.[5]

The amounts of the evolved H_2 after a 3-h irradiation were plotted against concentrations of the added TOAB in Figure 2. The H_2 formation was increased by increase of TOAB up to 40 mM, and leveled off at higher concentration conditions.

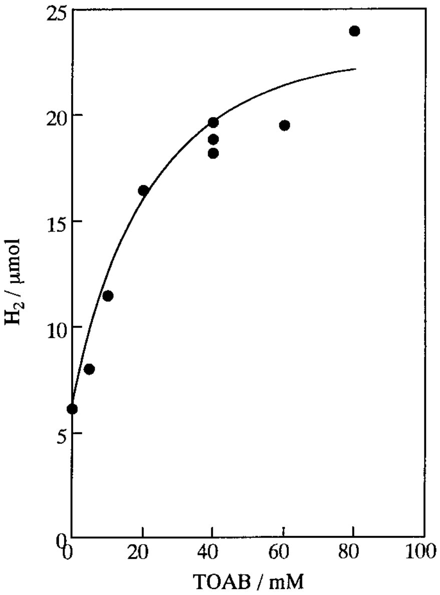

Figure 2. Additional effect of TOAB on the formation of H_2; the amount of H_2 after 3 h irradiation.

TABLE 1: Effect of Various Salts on TP-Sensitized Photoreduction of H_2O to H_2 in the Presence of $RuCl_3$ and TEA[a]

salt		H_2/μmol
none		6.5
$(C_2H_5)_4NCl$		12.0
$(n\text{-}C_3H_7)_4NCl$		16.8
$(n\text{-}C_4H_9)_4NCl$	(TBAC)	18.4
$(C_2H_5)_4NBr$	(TEAB)	11.9
$(n\text{-}C_3H_7)_4NBr$		13.0
$(n\text{-}C_4H_9)_4NBr$	(TBAB)	13.9
$(n\text{-}C_6H_{13})_4NBr$		18.8
$(n\text{-}C_8H_{17})_4NBr$	(TOAB)	24.0
$(n\text{-}C_4H_9)_4NI$		3.0
$(n\text{-}C_4H_9)_4NClO_4$		14.1
$(C_2H_5)_4PBr$		10.0
$(n\text{-}C_4H_9)_4PBr$		16.8

[a] Photoreaction conditions (TP 1 mM, $RuCl_3$ 1 mM, TEA 0.5 mL, H_2O 0.5 mL, and salt 80 mM in AN, total volume 2 mL, photoirradiation $\lambda > 290$ nm for 3 h).

Table 1 summarizes the effect of various onium salts on the photoformation of H_2. The presence of every onium salts except tetrabutylammonium iodide, which reduced the H_2 formation to half, led to an increase of the H_2 formation by two to three times when compared to the absence of any salts. The onium salts with longer alkyl chains were found more effective for the H_2 formation. The counteranion of the onium salt also affected the H_2 formation with an order of $Cl^- > ClO_4^- > Br^-$ ($>$ none $> I^-$).

Photoexcited States of TP. Figure 3 shows the transient absorption spectrum observed by the excitation with a picosecond laser pulse on a sample containing 0.1 mM of TP alone in AN. The transient absorption consists of a large peak at $\lambda = 550$ nm with a small peak at $\lambda = 450$ nm. The absorption at $\lambda = 550$ nm decayed much faster than that at $\lambda = 450$ nm, giving a decay rate $k_{obsd} = 6.5 \times 10^8$ s^{-1}. The absorption at 450 nm formed promptly after excitation and decayed slowly. The inset in Figure 3 shows the transient absorption spectrum observed by the excitation with a nanosecond laser pulse on the same sample. The absorption maximum at $\lambda = 450$ nm was observed, but that at $\lambda = 550$ nm was not detected in this time region. The decay of this absorption followed first-order kinetics and gave a decay rate $k_t = 2.4 \times 10^4$ s^{-1}. This absorption decreased

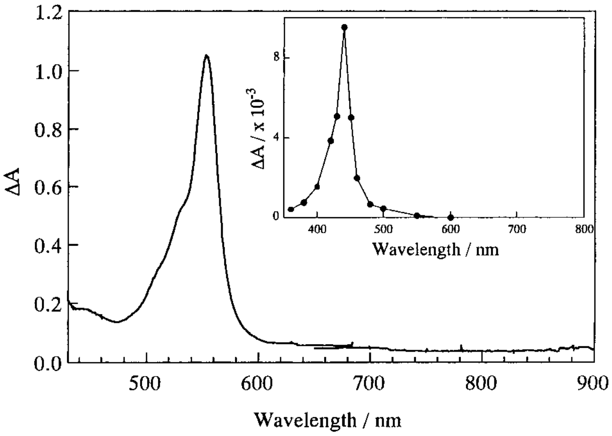

Figure 3. Transient absorption spectrum observed at 1 ns after excitation with a picosecond laser pulse on a sample containing 0.1 mM of TP alone in AN. Inset: transient absorption spectrum at 3.13 μs after excitation with a nanosecond laser pulse on the same sample.

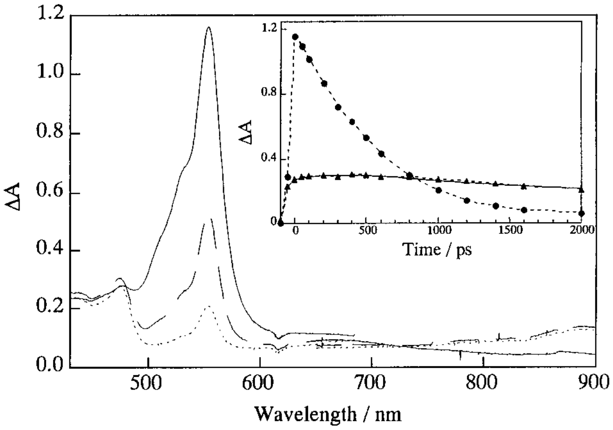

Figure 4. Transient absorption spectrum observed at 0 ps (solid), 500 ps (dash), and 1000 ps (dot) after excitation with a picosecond laser pulse on a sample containing 0.1 mM of TP and 0.1 M of TEA in AN. Inset: decay of transient absorption monitored at $\lambda = 470$ nm (triangle), 550 nm (circle) and those fitting curves.

by introduction of O_2 and a linear plots of the decay rate of this absorption versus concentration of O_2 gave a rate constant $k_{qO2} = 2.2 \times 10^9$ M^{-1} s^{-1}. This absorption spectrum was comparable with the transient absorption spectrum obtained in the electron pulse radiolysis of a toluene solution of TP in the presence of biphenyl (data not shown). On the basis of these facts, we assigned the transient absorption at $\lambda = 550$ nm to the excited singlet state of TP, ^{1}TP*, and the absorption at $\lambda = 450$ nm to the excited triplet state of TP, ^{3}TP*.

Reaction of the Excited State of TP with TEA. Figure 4 shows the transient absorption spectrum of TP (0.1 mM) in the presence of TEA (0.1 M) observed by the excitation with a picosecond laser pulse. The absorption of ^{1}TP* decreased and a new peak appeared at $\lambda = 470$ nm. The new peak at $\lambda = 470$ nm coincided with the reported spectrum of the TP radical anion, TP$^{\bullet-}$.[2a,3,15] The inset in Figure 4 shows the transient decay curves observed at $\lambda = 550$ and 470 nm, respectively. The transient absorbance monitored at $\lambda = 550$ nm followed first-order kinetics and gave a decay rate of 1.7×10^9 s^{-1}. We assumed that the transient absorption of ^{1}TP* and TP$^{\bullet-}$ must overlap at $\lambda = 470$ nm, and decay with the first-order rates for the decreasing of ^{1}TP* and the rising of TP$^{\bullet-}$. The calculated rate for rising of TP$^{\bullet-}$ was 2.0×10^9 s^{-1} and agreed with the decreasing rate in the transient absorption at $\lambda = 550$ nm. These results support that TP$^{\bullet-}$ should be formed through electron-transfer reaction from TEA to ^{1}TP* (reductive quenching of ^{1}TP* by TEA).

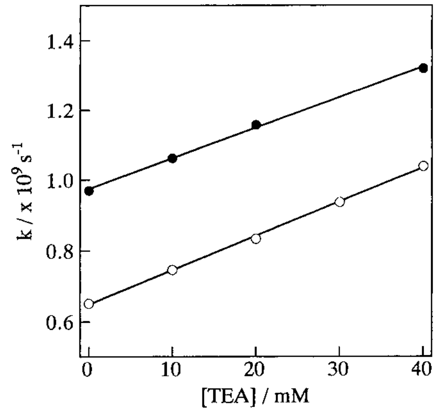

Figure 5. Kinetic behavior of the ^{1}TP* in the presence of TEA, as shown by a plot of the lifetime of ^{1}TP* versus TEA concentration in the absence (open) and presence (80 mM; closed) of TOAB.

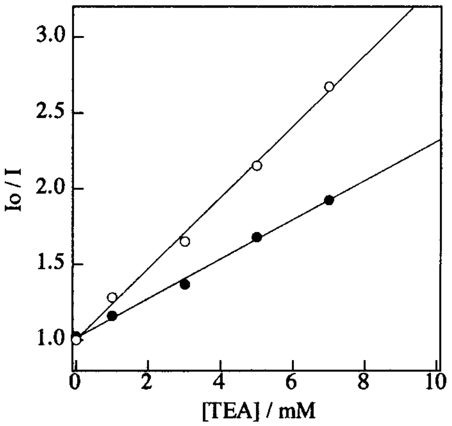

Figure 6. Stern−Volmer plots of the quenching of the emission of TP by TEA in the absence (open) and presence (80 mM; closed) of TOAB: least-squares fitting of the plots gave $K_{SV} = 23.5$ and 13.0 M^{-1}, respectively.

Figure 5 shows linear plots of the decay rate of the ^{1}TP* versus concentration of TEA in the absence and presence of TOAB, respectively. From the slope of the plots, the rate constants of quenching k_{qs} are calculated as 9.7×10^9 M^{-1} s^{-1} for the system without salt and 8.8×10^9 M^{-1} s^{-1} for the system with TOAB, respectively. These comparable rate constants are very close to the diffusion-controlled rate constant of ^{1}TP* in AN. We also found that the addition of TOAB (80 mM) reduced the natural lifetime of ^{1}TP* in AN from 1.5 to 1.0 ns, and decreased quantum yield of fluorescence from 0.90 to 0.50. Stern−Volmer plots of quenching of the emission of TP by TEA in the absence and presence of TOAB are shown in Figure 6. From the slope of the plots and the lifetime of ^{1}TP*, the rate constants of quenching k_{sv} are calculated as 1.5×10^{10} M^{-1} s^{-1} without TOAB and 1.3×10^{10} M^{-1} s^{-1} with TOAB, respectively. These values are quite comparable with those determined based on the dynamics of the transient absorption spectra (Figure 5). These results suggest that the addition of the onium salt, TOAB, enhances intersystem crossing of ^{1}TP* to ^{3}TP*,[16] but does not change the quenching rate of ^{1}TP* by TEA.

Reaction of the Triplet State of TP with TEA. We also observed quenching of ^{3}TP* by TEA using the excitation with a nanosecond laser pulse. The first-order curve fittings were performed on the observed transient absorption monitored at $\lambda = 440$ nm in the earlier time region ($t < 1$ μs). Linear plots of

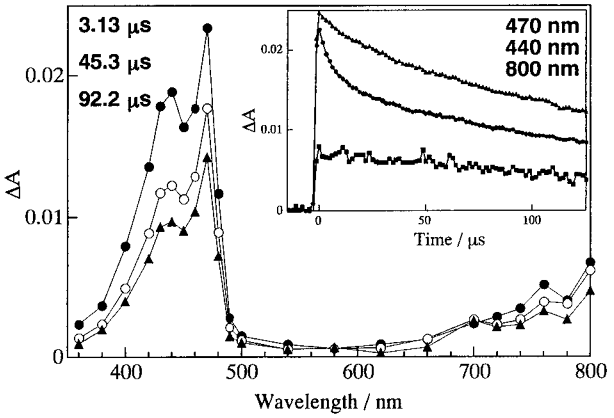

Figure 7. Transient absorption spectrum observed at 3.13 μs (closed circle), 45.3 μs (open circle), and 92.2 μs (closed triangle) after excitation with a nanosecond laser pulse on a sample containing 0.1 mM of TP and 0.1 M of TEA in AN. Inset: decay of the transient absorption monitored at λ = 440 nm (circle), 470 nm (triangle), and 800 nm (square).

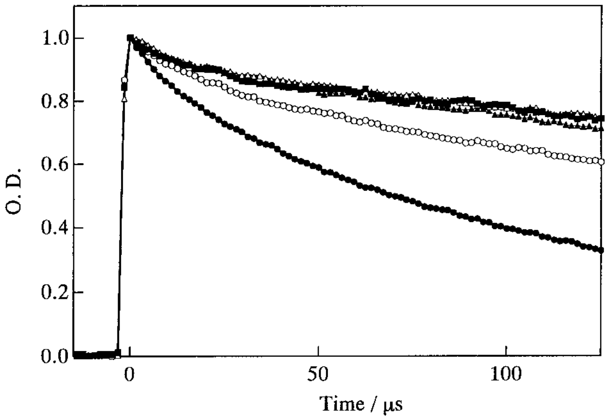

Figure 8. Decay of transient absorption monitored at λ = 470 nm in the presence of TOAB.; TOAB concentration is 0 mM (closed circle), 3.2 mM (open circle), 6.4 mM (closed triangle), 12.8 mM (open triangle), and 19.6 mM (closed square).

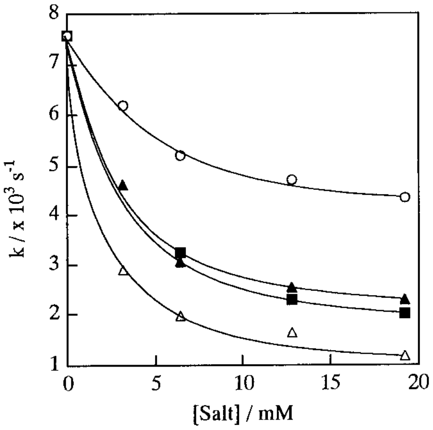

Figure 9. Kinetic behavior of the ^{1}TP* in the presence of TEA, as shown by a plot of the lifetime of TP$^{\bullet-}$ vs salt concentration. The salt added into the system is TEAB (open circle), TBAB (closed triangle), TOAB (open triangle), and TBAC (closed square).

TABLE 2: Comparison of the Rate Constant, and a Quantum Yield of Fluorescence of ^{1}TP* in the Absence and Presence of TOAB[a]

	without TOAB	with TOAB
$k_s/10^8$ s^{-1}[b]	6.5	9.7
$k_f/10^8$ s^{-1}[c]	5.8	4.9
$k_i/10^8$ s^{-1}[d]	0.6	4.9
Φ_s[e]	0.90	0.50
$k_{qs}/10^9$ M^{-1} s^{-1}[f]	9.7	8.8
$k_{SV}/10^9$ M^{-1} s^{-1}[g]	1.5 × 10	1.3 × 10

[a] The system consists of TP (0.1 mM) and TOAB (80 mM) in AN. [b] A natural decay rate of ^{1}TP*. [c] A fluorescence rate of ^{1}TP*. [d] A intersystem crossing rate of ^{1}TP*. [e] A quantum yield of fluorescence. [f] A quenching rate constant from a plot of a decay rate of ^{1}TP*. [g] A quenching rate constant from a plot of TP emission.

the decay rate of the ^{3}TP* versus concentration of TEA gave a second-order rate constant $k_{qt} = 2.3 \times 10^6$ M^{-1} s^{-1}. This result suggests that ^{3}TP* may also contribute to the formation of TP$^{\bullet-}$ through electron-transfer reaction from TEA. However, the rise of transient absorption of TP$^{\bullet-}$ with the decrease of the transient absorption of ^{3}TP* could not be detected because the absorbance was so weak and overlapped with very intense absorption from ^{1}TP*, hence the salt effect on the quenching of ^{3}TP* by TEA was not clearly confirmed.

Salt Effect on TP$^{\bullet-}$ Decay. Figure 7 shows the transient absorption spectra observed by the excitation with a nanosecond laser pulse on a sample containing 0.1 mM of TP and 0.1 M of TEA in AN. The absorption spectrum at 92.2 μs after excitation is identical with the reported absorption spectrum of TP$^{\bullet-}$ (Figure 4).[2a,3,15] The decay of TP$^{\bullet-}$ monitored at λ = 800 nm followed single-exponential decay and gave a rate constant of 7.6×10^3 s^{-1} in the present system (Figure 7, insert). The decay at λ = 440 and 470 nm consisted of two components, which must be due to the mixture of the fast decay of ^{3}TP* and the slow one of TP$^{\bullet-}$.

The lifetime of TP$^{\bullet-}$ was increased by the addition of salts, while the shape of absorption spectrum is not affected by the addition of any salts. Figure 8 shows the transient decay monitored at λ = 470 nm in the presence of different amounts of TOAB. The slower component of the decay attributed to TP$^{\bullet-}$ was slowed with increase of TOAB concentration, and leveled off in higher concentration conditions. Figure 9 shows the relationship between concentration of various salts such as TEAB, TBAB, TOAB, and TEAC and the decay rate constants of TP$^{\bullet-}$. When the salt with longer alkyl chain was used, the decay was slowed more effectively. The lifetime of TP$^{\bullet-}$ in the presence of TBAC is comparable with that of TBAB, implying that the stabilization of TP$^{\bullet-}$ is mainly due to an electrostatic interaction between TP$^{\bullet-}$ and tetrabutylammonium cation.

Discussion

Effect of Onium Salts on Excited States of TP. In our previous paper concerning photoreduction of water in the TP/TEA/RuCl$_3$/THF system,[2a] we discussed the photosensitization based only on the singlet excited state of TP, because the fluorescence quantum yield of TP is unity in THF. In the system of AN, the fluorescence quantum yield of TP was found to be 0.90 and the presence of the onium salts led to the decrease of the quantum yield of the fluorescence.

As summarized in Table 2, the natural decay rate, k_s, of ^{1}TP* in AN was determined to be 6.5 and 9.7×10^8 s^{-1} (Figure 5) for the absence and presence of TOAB (80 mM, maximum), respectively. The quantum yield of fluorescence was 0.90 and 0.50 in the absence and presence of TOAB (80 mM), respectively. When ^{1}TP* decay is assumed only by fluorescence and intersystem crossing (no thermal relaxation), the fluorescence rate, k_f, and the intersystem crossing rate, k_i, are calculated as 5.8 and 0.6×10^8 s^{-1} for the system of the absence of salt, and 4.9 and 4.9×10^8 s^{-1} for the system of the presence of TOAB, respectively. In case of the photoreaction using 1.8 M of TEA, the quenching rate of $^1TP^*$ with TEA can be calculated on the basis of either $k_{qs} \times$ [TEA] or $k_{sv} \times$ [TEA]. The calculations of the quenching rate in the presence of TOAB give the values more than 1.1×10^{10} s^{-1}, that is much faster than the intersystem crossing rate, k_i. It is now clear that the quenching of $^1TP^*$ with TEA is much more operative than the intersystem crossing to $^3TP^*$. In addition, since the concentration of the salt is less than 80 mM and k_i should be less than the estimated value because of contribution of thermal relaxation of $^1TP^*$, the contribution of $^3TP^*$ for the formation of $TP^{\bullet -}$ must be less than 5% in the present system.

Ion−Ion Interaction. The presence of onium salts may stabilize $TP^{\bullet -}$ due to an electrostatic interaction between the soft anion, $TP^{\bullet -}$, and soft onium cation, which will be explained on the basis of the hard−soft acid−base (HASB) principle.[17] According to the HASB principle, the softer anion interacts with softer cation rather than harder one, and vice versa. The softness of the onium cation is increased by alkyl chain length because of delocalization of positive charge on alkyl chains. The softer onium cations with longer chains stabilize $TP^{\bullet -}$ more effectively through the more specific interaction. The pronounced salt effect can be observed especially for the steady-state photoreaction at high concentration of the onium salt. The onium salts with the long alkyl groups may form some aggregates such as micels or reversed micels in the photoreaction medium, since the medium consists of water, AN, and TEA. TP molecules may locate in the vicinity of larger numbers of the onium cations and their aggregates, and the photoformed $TP^{\bullet -}$ may be readily stabilized through the favorable electrostatic interaction.[18−23] In addition, $^1TP^*$ is reductively quenched by TEA to produce the radical anion $TP^{\bullet -}$ and $TEA^{\bullet +}$ radical. $TEA^{\bullet +}$ readily undergoes deprotonation to give *N*,*N*-diethylamino-1-ethyl radical ($Et_2NC^{\bullet}HCH_3$), which is promptly oxidized to $Et_2NC^{+}HCH_3$. These facts suggest that the back electron transfer hardly occur in the present system. Thus, the stabilization of $TP^{\bullet -}$ suppresses the degradation of TP and improves H_2 evolution in the photoreduction.

The salt effects also suggest that not only the cation of salts but also the counteranion should affect the TP photosensitization. The presence of onium salts decreased the lifetime of $^1TP^*$ and the quantum yield of fluorescence. The intersystem crossing to $^3TP^*$ must be enhanced probably due to the external heavy atom effects of the counter halogen anions.[16] However, the contribution of $^3TP^*$ to the $TP^{\bullet -}$ formation is very small in the present system, as discussed in the former section. It is interesting to note that onium chlorides showed the best efficiency for the H_2 evolution. Chloride anion must be harder than $TP^{\bullet -}$, so it might tend to interact favorably with much harder cations such as protonated TEA and diethylamine, or other intermediates produced by oxidation of TEA rather than the softer tetraalkylammonium cation.

Conclusions

The presence of the soft onium salts such as tetraalkylammonium and phosphonium chlorides enhanced the TP-photosensitized reduction of water to H_2 in the presence of TEA as a sacrificial electron donor and Ru colloids as an electron mediator. Picosecond laser dynamic studies of TP photosensitization revealed that $TP^{\bullet -}$ is formed mainly from reductive quenching of $^1TP^*$ by TEA. The presence of the soft onium cations with long alkyl groups enhances the stabilization of $TP^{\bullet -}$ through electrostatic soft−soft interaction. The intimate soft−soft interaction and the stabilization may contribute to suppression of the degradation of TP which proceeds through protonation of $TP^{\bullet -}$ as the photo-Birch reduction, leading to the enhanced H_2 formation in the photoreduction.

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