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Enhancement of Chain Amplification in Photoreactions of *N*-Methoxypyridinium Salts with Alcohols[†]

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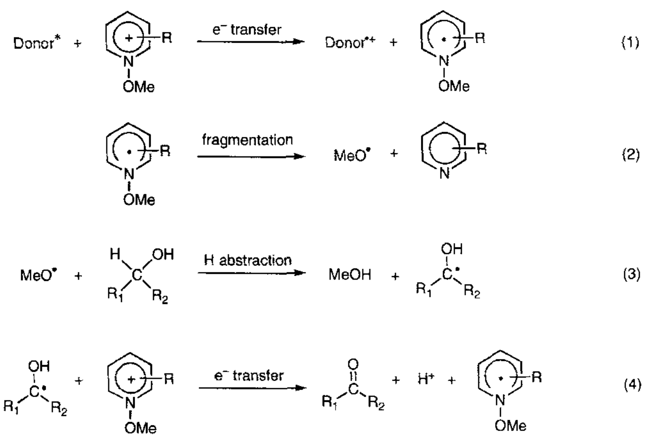
ABSTRACT

Recently we reported a chain-amplified photochemical reaction, initiated by electron transfer from an excited sensitizer to *N*-methoxypyridinium salts, which leads to N–O bond cleavage (26). Hydrogen atom abstraction by the methoxy radical from an alcohol yields an α-hydroxy radical, which reduces another *N*-methoxypyridinium molecule and propagates the chain. We now report that the chain amplification can be significantly enhanced in the presence of water. Detailed kinetic studies of the reaction of 4-cyano-*N*-methoxypyridinium salt (CMP) with benzhydrol (BH) showed that the rate constant for reduction of CMP by the diphenyl ketyl radical (1.1×10^6 M^{-1} s^{-1}) increases by more than an order of magnitude in the presence of water. This increase in the rate constant is the result of coupling of the electron transfer to a proton transfer from the ketyl radical to water, which decreases the endothermicity of the reaction. Unfortunately, this increase in the rate constant for one of the two propagation steps is accompanied by a larger increase in the rate constant(s) of the competing termination reaction(s) of the ketyl radical. The observed enhancement in chain amplification is the result of a significant increase in the ratio of propagation to termination rate constants of the reactions of the methoxy radical. The main chain-terminating reactions of the methoxy radical are deuterium abstraction from the solvent, CD_3CN, and reaction with the sensitizer, thioxanthone. The effect of increase in the ratios of the propagation rate constant of the methoxy radical (hydrogen abstraction from BH) to those of both termination reactions is larger than the unfavorable effect of water on the reactions of the ketyl radical. The increase in chain amplification depends on the concentration of the reactants; at 0.037 *M* of both reactants, the quantum yield increases form ~16 to ~45 in the presence of <1% water. The reaction of 4-phenyl-*N*-methoxypyridinium (PMP) with 4-methoxybenzyl alcohol does not proceed via chain amplification because of large endothermicity for electron transfer from the α-hydroxy radical to the pyridinium salt. However, chain amplification could be induced, simply by addition of water, where at ~10% water content, a quantum yield of ~5 was obtained. Water-induced, proton-coupled electron transfer increases the rate constant for reduction of PMP from a negligible level to becoming the dominant path.

INTRODUCTION

Quantum amplification in photoinduced reactions is limited to few concepts; most of them involve electron transfer reactions (1–25).‡ One of the challenges in these reactions is to minimize the ratio of chain termination to chain propagation reactions, which would enhance the quantum amplification. We reported recently on a chain reaction in which *N*-methoxypyridinium salt undergoes N–O bond cleavage upon one electron oxidation (26). In the presence of an alcohol, the cleaved methoxy radical abstracts a hydrogen atom at the α-position to generate a radical that can reduce another pyridinium molecule and propagates the chain, Scheme 1.



Scheme 1. Steps involved in photoinduced chain-amplified reaction between an *N*-methoxypyridinium salt and an alcohol.

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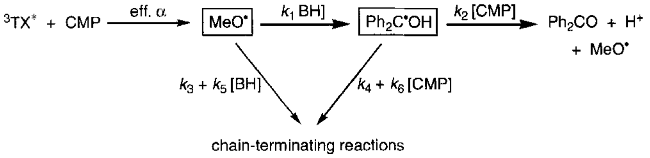
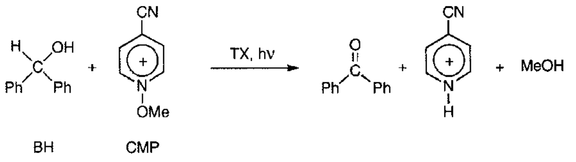
Abbreviations: CMP, 4-cyano-*N*-methoxypyridinium salt; BH, benzhydrol; PMP, 4-phenyl-*N*-methoxypyridinium; $Ph_2C^{\bullet}$–OH, diphenylketyl radical; TCB, 1,2,4,5-tetracyanobenzene; PCET, proton-coupled electron transfer; TX, thioxanthone; PMT, photomultiplier tube.

‡ The chain reaction of diazonium salts with hypophosphite (H_3PO_2) was the first to be reported (24).



Scheme 2. Reactions controlling chain propagation and chain termination in photoinduced reaction between 4-cyano-*N*-methoxypyridinium salt (CMP) and benzyl alcohol (BH). The reaction is initiated by photoexcitation of an electron donor with an efficiency α (equal to the intersystem crossing yield of the sensitizer, TX, 0.88). The two key intermediates are highlighted.

We also investigated the kinetics of the reaction of 4-cyano-*N*-methoxypyridinium (CMP) with benzhydrol (BH), $R_1 = R_2 = Ph$ in Scheme 1, induced by electron transfer from triplet excited thioxanthone (TX) in acetonitrile-d_3. The net reaction is given by



(5)

Eq. 5, where a quantum yield of 15–20 was obtained at reactants concentration of ~0.04 *M* (9).

The kinetic parameters were determined from steady state (changes in quantum yield as a function of concentration of both reactants) and from transient kinetics. The radical derived from the benzhydrol—diphenylketyl radical—is ideal for transient kinetic studies because of its well-characterized, strong absorption around 540 nm (27, 28). The data were analyzed in terms of the reactions shown in Scheme 2, in which the key intermediates are the methoxy radical and the diphenylketyl radical ($Ph_2C^•$–OH). The chain propagation reactions, k_1 and k_2, are in competition with chain terminating processes, (k_3, k_5) and (k_4, k_6), respectively, where k_5 and k_6 are side reactions with the reactants or impurities therein, and they play only a minor role.

According to Scheme 2, the dependence of the quantum yield for product formation (Φ_P) on the concentrations of the reactants is given by Eq. 6, which leads to Eq. 7.

$$\Phi_P = \alpha pq(1 + pq + p^2q^2 + p^3q^3 + \cdots\cdots) \qquad (6)$$

$$\Phi_P = \frac{\alpha}{\left(\frac{1}{p}\frac{1}{q} - 1\right)} \qquad (7)$$

$$\text{where} \quad \frac{1}{p} = \left(1 + \frac{k_5}{k_1}\right) + \left(\frac{k_3}{k_1}\right)\frac{1}{[BH]}$$

$$\text{and} \quad \frac{1}{q} = \left(1 + \frac{k_6}{k_2}\right) + \left(\frac{k_4}{k_2}\right)\frac{1}{[CMP]}$$

The following ratios of the termination to propagation rate constants were determined from fitting the data for the reaction with 6 m*M* thioxanthone in CD_3CN at various concentrations of CMP (Fig. 3), BH (Fig. 4) and both reactants (Fig. 5).

$$\left(\frac{k_5}{k_1} + \frac{k_6}{k_2}\right) = 9 \times 10^{-3} \quad \left(\frac{k_3}{k_1}\right) = 1.3 \times 10^{-3} \quad \left(\frac{k_4}{k_2}\right) = 2.1 \times 10^{-4}$$

The quantum amplification would increase, if these ratios can be further decreased. We here report an approach we took that led to higher quantum amplification because of decrease in termination to propagation ratio.

MATERIALS AND METHODS

Materials. The pyridinium salts CMP and PMP were synthesized according to procedures in the literature (29). The crude salts were purified by repeated recrystallization from methanol. Thioxanthone (Aldrich, Milwaukee, WI) and benzhydrol (Aldrich) were commercially available and recrystallized (twice) from methanol before use. 4-Methoxybenzyl alcohol (Aldrich) was used as received. 1,2,4,5-Tetracyanobenzene (Aldrich) was recrystallized from chloroform before use.

Steady-state photolysis: reaction quantum yields measurements. The irradiations were carried out with an Oriel (Stratford, CT) medium-pressure Hg lamp. For 405 nm, a Corning 5–58 band-pass filter, a Corning 0–73 cut-off filter and a 405 nm interference filter were used. In a typical experiment, a 3 mL solution of an *N*-methoxypyridinium salt, an alcohol, specified amount of water and thioxanthone sensitizer in CD_3CN was placed in a 1 × 1 cm cell. Unless otherwise stated, the sensitizer concentration was 6 m*M*. The solution was purged with argon for ~2 min, and irradiated for 2–10 min to reach a conversion of ~10–20%. During photolysis, argon was continuously bubbled above the exposed area to purge and stir the solution. The percent conversion was determined from average ratios of integrated ^1H NMR signals of products and reactants. The difference in chemical shifts of the *N*-H-pyridinium signals from those of the starting *N*-methoxypyridinium salts (~0.2 ppm to lower fields) is sufficient to allow for accurate integration, for details see reference 26. Integration of signals from the three products: the *N*-H-pyridinium salt, oxidation product of the alcohol (benzophenone or 4-methoxybenzaldehyde) and methanol, clearly shows that they are formed in equal amounts. The reaction of phenanthrene quinone with *trans*-stilbene was used as chemical actinometer (26).

Laser flash photolysis. The samples in a 1 × 1 cm quartz cell were excited at right angle to the monitoring beam. The excitation source was a OPOTEK (Carlsbad, CA) frequency tripled Q-switched Nd:YAG laser system. The excitation pulses were attenuated, when necessary, using neutral density filters. A pulsed Oriel (Stratford, CT)150-W xenon lamp (Model 66007) was used as the monitoring beam. The analyzing beam was collected and focused on the entrance slit (2 nm) of a monochromator. A Hamamatsu R-446 photomultiplier tube (PMT) was attached to the exit slit of the monochromator. A computer-controlled Stanford Research Systems (Sunnyvale, CA) high-voltage power supply (Model PS310) was used with the PMT. The signals from the PMT were digitized using a Tektronix (Richardson, TX) TDS 620 oscilloscope and transferred to a PC via a National Instruments (Austin, TX) GPIB interface, for data storage and processing. A Quantum Composer (Bozeman, MT) pulse generator (Model 9318) provided TTL trigger pulses to control the timing for the laser, lamp and oscilloscope.

Kinetics of electron transfer from diphenyl ketyl radical to CMP. The diphenylketyl radical was generated by laser excitation (355 nm) of benzophenone (6 m*M*) in argon-purged acetonitrile in the presence of 0.05 *M* 1,2,4,5-tetracyanobenzene (TCB) and 0.05 *M* benzpinacol. Two transient species are generated in this experiment: $Ph_2C^•$–OH and $TCB^{•-}$, with absorption bands at 540 nm and at 465 nm, respectively (26). The effect of water on the bimolecular electron transfer rate constant from the diphenyl ketyl radical to CMP was determined from the change in decay rate constant of $Ph_2C^•$–OH at 540 nm (in the presence of 0.11 *M* CMP) as a function water concentration. Under these conditions, $TCB^{•-}$ was quenched very fast by CMP via an exothermic, probably diffusion controlled, electron transfer.

RESULTS AND DISCUSSION

In the above-mentioned reaction, Scheme 1, unimolecular fragmentation of the methoxypyridinium, upon one electron reduction, is a fast reaction (30–32) and is likely to occur with unit efficiency, especially when the electron transfer is from a triplet-excited donor, which precludes return electron transfer. The two key steps are the chain-propagating reactions: hydrogen atom abstraction by the methoxy radical from benzhydrol (BH), k_1; and electron transfer from the ketyl radical to the pyridinium salt (CMP), k_2.

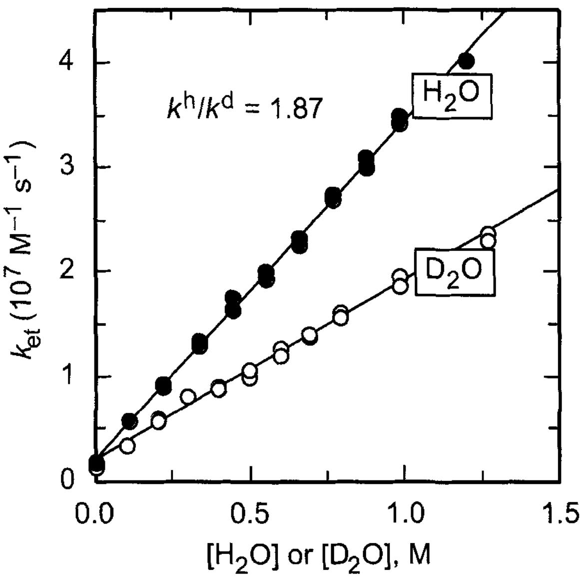
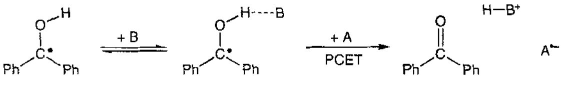


Figure 1. Plot of rate constant for electron transfer from diphenyl ketyl radical to 4-cyano-*N*-methoxypyridinium (CMP) in acetonitrile *vs* concentration of added H_2O or D_2O.

The oxidation potential of the ketyl radical is −0.25 V *vs* SCE (33), and the reduction potential of CMP is −0.5 V *vs* SCE (34). Thus, the electron transfer rate reaction (k_2) is endothermic by 0.25 eV, and as a result, proceeds in acetonitrile at a rate constant of 1.1×10^6 M^{-1} s^{-1}, ca 4 orders of magnitude lower than the diffusion controlled limit (26).

In another study, we have recently described a proton-coupled electron transfer (PCET) reaction in which the diphenyl ketyl radical, through hydrogen bonding to a pyridine base (B), can undergo very fast electron transfer to an electron acceptor (A), Eq. 8 (35). With 1,2,4,5-tetracyanobenze (TCB) as acceptor, direct electron transfer from the diphenyl ketyl radical is *endothermic* by 0.4 eV; with lutidine as a base, the overall reaction becomes *exothermic* by 0.4 eV, and the coupled proton/electron transfer takes place at a rate approaching the diffusion-controlled limit.



(8)

We tried a similar approach for the current chain reaction with CMP as acceptor, using water instead of a pyridine derivative as a potential base to lower the endothermicity of the electron transfer reaction. The rate constant for electron transfer from the diphenyl ketyl radical to CMP was determined by transient kinetics. In a laser flash photolysis experiment, the ketyl radical was generated, as described before, via energy transfer from triplet-excited benzophenone to TCB, followed by electron transfer from benzopinacol to ^{3}TCB* (35). The oxidized benzopinacol undergoes fast fragmentation to yield diphenyl ketyl radical, whose decay was monitored at 540 nm in the presence of 0.11 *M* CMP in acetonitrile as a function of added water. Figure 1 shows a steady increase in the rate constant for electron transfer from the diphenyl ketyl radical to CMP (k_{et} = k_{obs}/[CMP]) with increasing water concentration, where there is no detectable sign for leveling off up to a water concentration of 1.2 *M*. This lack of leveling off indicates a very small equilibrium constant (<<1 M^{-1}) for formation of the hydrogen-bonded complex. Note that the PCET reaction can occur only from the hydrogen-bonded complex in which the hydrogen on the diphenyl ketyl radical is involved, complex **1**. In this configuration, the hydrogen of the ketyl radical

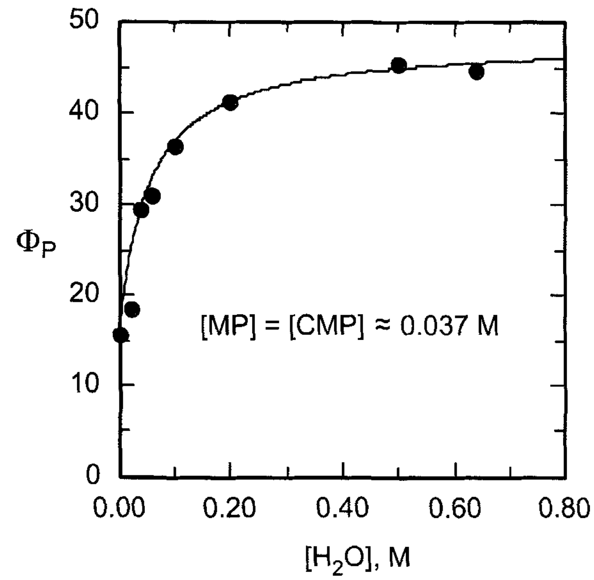
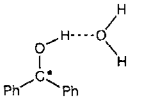


Figure 2. Plot of quantum yield for product formation (Φ_P) *vs* concentration of added water.



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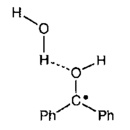

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can be transferred as a proton to the bonded water molecule in the PCET step. This is not the case, however, for the hydrogen-bonded complex **2**, because in this complex, the hydrogen of the ketyl radical is not bonded to a water molecule, and therefore, cannot undergo a *coupled* proton/electron transfer.

A lower slope by a factor of 1.87 for the dependence of the rate constant was obtained when H_2O was replaced by D_2O. The decrease in slope reflects a deuterium isotope effect on the electron transfer rate constant, consistent with a PCET reaction (35).

The water-induced effect of PCET on the electron transfer rate constant is substantial. At 0.5 *M* water, the rate constant increases by a factor of ~15, and at 1 *M*, by a factor of ~30. In principle, however, an increase in rate constant for chain propagation may not necessarily lead to an increase in chain amplification. The latter is achieved only if the *ratio* of competing propagation to termination rate constants increases.

We first investigated the effect of water on the quantum yield and the extent of change as a function of water concentration. As shown in Figure 2, keeping the concentrations of CMP and BH constant (average ~0.037 *M*), the quantum yield for product formation, Φ_P, increases with increasing water concentration, from ~16 in the absence of water, and levels off, starting at ~0.5 *M*, to a quantum yield of ~45.

To determine the individual contributions from the two branching propagation/termination reactions to the quantum yield in the presence of water, we carried out different experiments at

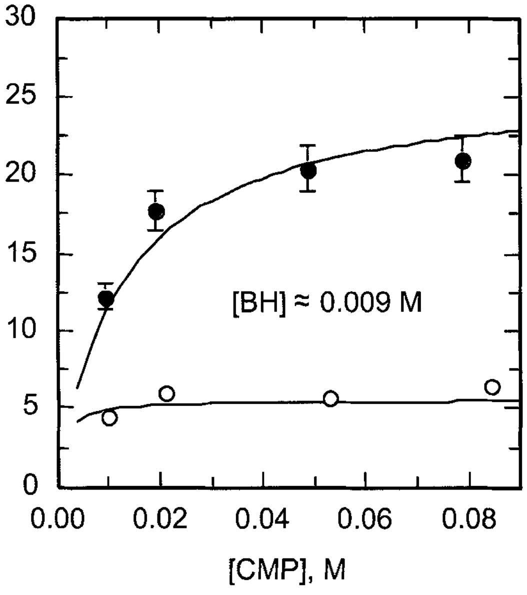


Figure 3. Quantum yield for product formation (Φ_P) *vs.* concentration of 4-cyano-*N*-methoxypyridinium (CMP), at constant concentration of benzhydrol (BH) in acetonitrile (open circles) and in the presence of 0.5 *M* water (closed circles). The curves are the calculated quantum yields according to Eq. 7 and the parameters given in the text.

0.5 *M* water as a function of the concentration of the two reactants. Shown in Figs. 3 and 4 is the dependence of the quantum yield on the concentration of CMP, keeping that of BH constant and vice versa. The reaction was also investigated at varying concentration of *both* reactants, keeping [CMP] = [BH] (Fig. 5).

From these three experiments, conclusions can be drawn about the ratios of the different termination to propagation reactions. This was achieved by a global fitting of the data in Figs. 3–5 according to Eq. 7. Of the four ratios of termination to propagation rate constants, the fitting is insensitive to the individual values of (k_5/k_1) and (k_6/k_2), but their sum is ~0.002, much smaller than the value of 0.009 observed in the absence of water.

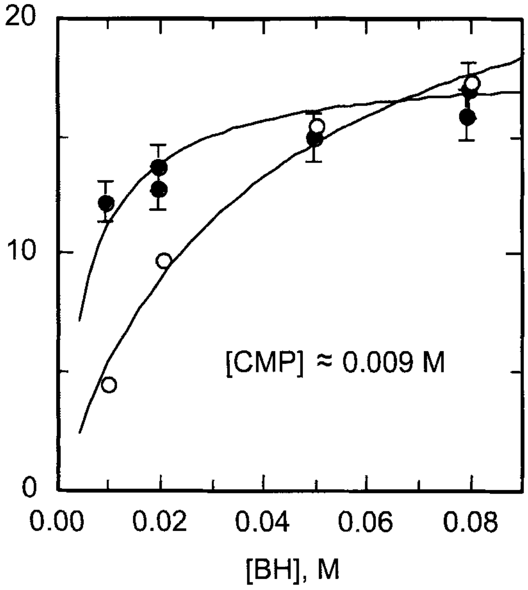


Figure 4. Quantum yield for product formation (Φ_P) *vs* concentration of benzhydrol (BH), at constant concentration of 4-cyano-*N*-methoxypyridinium (CMP) in acetonitrile (open circles) and in the presence of 0.5 *M* water (closed circles). The curves are the calculated quantum yields according to Eq. 7 and the parameters given in the text.

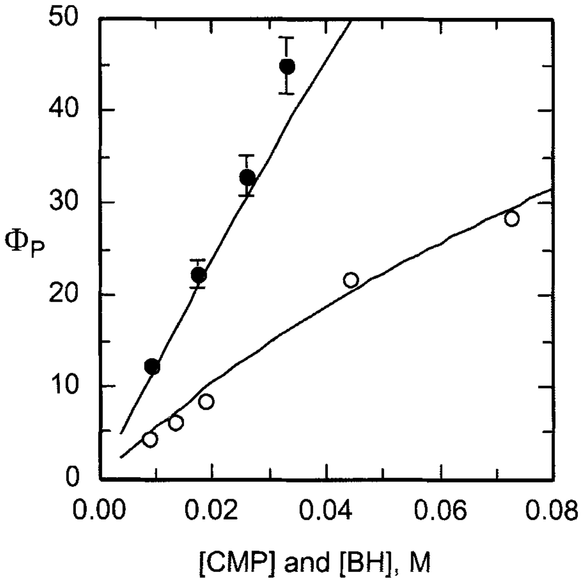


Figure 5. Quantum yield for product formation (Φ_P) *vs* concentration of 4-cyano-*N*-methoxypyridinium (CMP) and of benzhydrol (BH), keeping [CMP] = [BH], in acetonitrile (open circles) and in the presence of 0.5 *M* water (closed circles). The curves are the calculated quantum yields according to Eq. 7 and the parameters given in the text.

Surprisingly, the termination to propagation ratio (k_4/k_2) *increased* in the presence of 0.5 *M* water from 0.00021 to 0.00041, despite the ~15-fold increase in the electron transfer rate constant, k_2. This indicates that the rate constant(s) of the termination reaction(s), k_4, increased by a factor of almost 30 in the presence of water. In the absence of water, the chain termination process, k_4, could be attributed to reaction with trace amounts of residual oxygen and to dimerization. It seems that an additional path for reaction of the diphenyl ketyl radical is introduced in the aqueous acetonitrile medium. Further work is needed to determine the nature of this additional chain-terminating process.

Despite the above-mentioned unfavorable course of reactions of the diphenyl ketyl radical, the presence of water causes a dramatic *decrease* in the ratio of termination to propagation reactions of the methoxy radical, (k_3/k_1), from 0.0013 to 0.00028. This led to the observed increase in quantum amplification. Note that the main limiting factor affecting the chain length *in the absence of water* is the competition between k_3 with k_1. As we showed earlier, k_3 represents the cumulative effect of two reactions of the methoxy radical: abstraction of a deuterium atom from the solvent, CD_3CN, k^{d}_{solv} and reaction with the sensitizer, thioxanthone (TX), k_{TX}. Thus, the ratio (k_3/k_1) can be represented as a sum of two components Eq. 9.

$$\frac{k_3}{k_1} = \frac{k^{d}_{solv}[CD_3CN]}{k_1} + \frac{k_{TX}}{k_1}[TX] \qquad (9)$$

We investigated the effect of TX concentration on the quantum yield to quantify the role these two components play (Fig. 6). In the presence of water, the quantum yield is clearly much less dependent on [TX]. Best fit of the data in Fig. 6 was obtained using the values given in Table 1; the corresponding ratios from the reaction in absence of water are also listed for comparison.

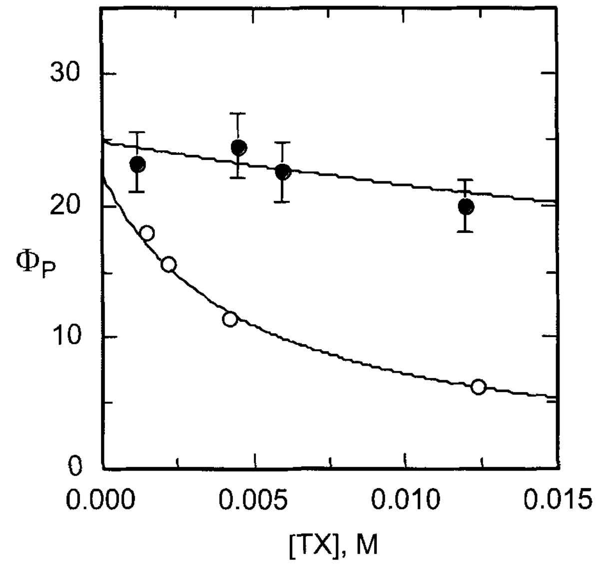


Figure 6. Quantum yield for product formation (Φ_P) *vs* concentration of the sensitizer, thioxanthone (TX). The average concentration (from before and after irradiation) of 4-cyano-*N*-methoxypyridinium (CMP) and of benzhydrol (BH) is 0.019 *M*, in acetonitrile (open circles) and in the presence of 0.5 *M* water (closed circles). The curves are the calculated quantum yields according to Eq. 7 and the parameters given in the text.

Although both ratios of termination-to-propagation rate constants are lower in the presence of water, that due to reaction with the sensitizer decreased much more than that with the solvent. For example, at the sensitizer concentration of 0.006 *M* used in these experiments, contributions to chain termination due to reactions of the methoxy radical in the absence of water are 73% interception by the sensitizer and 27% by the solvent, CD_3CN. The corresponding contributions in the presence of 0.5 *M* water are 21% and 79%, respectively.

Consistent with deuterium abstraction from the solvent by $MeO^{\bullet}$ as a chain-terminating reaction, we had previously observed significant decrease in the quantum yield when the reaction was carried out in CH_3CN. From that study in the absence of water, a deuterium isotope effect of ~7.7 was determined (26). In the presence of 0.5 *M* water, at average concentrations of both reactants of 0.019 *M* and with 0.006 *M* thioxanthone, the quantum yield for product formation drops from ~23 in CD_3CN to ~7.5 in CH_3CN. From the ratios of termination to propagation reactions listed above and the parameters given in Table 1, a very similar deuterium isotope effect of 7.6 can be calculated by substituting in Eq. 7 (36, 37).§ The similarity between the deuterium isotope effect for reactions in the presence and absence of water provides additional support for the validity of the kinetic analysis and for the conclusions about the different roles in which water affects the chain reaction between CMP and BH.

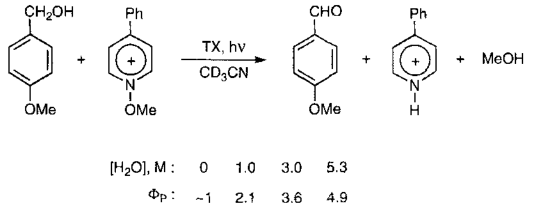
A similar increase in chain amplification in the presence of water was observed in reaction of CMP with 4-methoxybenzyl alcohol. In this case, the quantum yield at ~0.04 *M* concentration of both reactants and 6 m*M* TX in CD_3CN increases from 16 in the absence of water to 27 at 1 *M* water concentration. Although the kinetics of the reaction with the methoxybenzyl alcohol has not been fully investigated, it is likely to be analogous to that of the reaction with BH. Discussed below, however, is another reaction in which water plays a different role.

Table 1. Ratios of termination-to-propagation rate constants of methoxy radical with CD_3CN and sensitizer, TX, in the presence and absence of water.

Solvent	$k^{d}_{solv}[CD_3CN]/k_t$	k_{TX}/k_t
CD_3CN + 0.5 M H_2O	0.00022	0.01
CD_3CN	0.00036	0.16

As mentioned above, the driving force for the electron transfer reaction, Eq. 4, is a function of the oxidation potential of the α-hyrdroxy radical and the reduction potential of the pyridinium salt. As the endothermicity for electron transfer increases, a point will be reached that the reaction will become too slow to compete with other processes, and no chain amplification will be observed. This was the case of reactions of several alcohols with 4-phenyl-*N*-methoxypyridinium (PMP), which is harder to reduce than CMP by 0.5 V.

As mentioned above, the rate constant for the moderately (~0.25 eV) endothermic electron transfer form diphenyl ketyl radical to CMP increases by more than an order of magnitude in the presence of water. This increase in rate constant is because of a coupled electron/proton transfer, which leads to lower-energy products, and thus, to decreased reaction endothermicity. It was of interest to find out whether the reactions of PMP with 4-methoxybenzyl alcohol, which does *not* proceed via a chain process, could be altered in the presence of water. A PCET could increase the rate constant for reduction of the pyridinium salt by the α-hydroxy radical to an extent that would allow chain amplification. Indeed, the quantum yield for product formation steadily increases with increasing water content (Eq. 10). In this case, the



(10)

lack of a chain reaction in the absence of water is definitely due to the large endothermicity for electron transfer, and it is remarkable that a water-induced PCET can change the course of the reaction to such an extent that at ~10% (v/v) water, a five-fold increase in quantum yield is achieved.

CONCLUSIONS

Chain amplification in photoinduced electron transfer reactions of *N*-methoxypyridinium salts with alcohols can be enhanced in the presence of water by two different mechanisms. In the reaction of CMP with BH, a factor of ~3 enhancement in quantum yield could be achieved in the presence of 0.5 *M* water. Detailed kinetic studies showed that an increase in the *ratio* of propagation to termination

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§ Reported deuterium isotope effects for hydrogen atom abstraction by *tert*-butoxy radical from different substrates vary over a wide range (36), up to ~6 for the reaction with toluene (36, 37), which is several orders of magnitude faster than that with acetonitrile.

rate constants of the methoxy radical, but not in that of the α-hydroxy radical, causes this enhancement in chain amplification. The reaction of PMP with 4-methoxybenzyl alcohol does not proceed via a chain process because of a large endothermicity for electron transfer from the α-hydroxy radical to the pryidinium salt. At ~10% water content, however, the quantum yield increases from ~1 to 5, because the negligible, conventional electron transfer is now replaced by a PCET, and becomes a dominant path (>80%) for reactions of the α-hydroxy radical.

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