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Chain Amplification in Photoreactions of *N*-Alkoxypyridinium Salts with Alcohols: Mechanism and Kinetics

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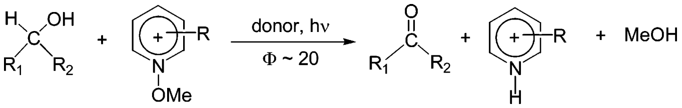

Photosensitized electron transfer from a variety of singlet- and triplet-excited donors to *N*-methoxypyridinium salts leads to N−O bond cleavage. Hydrogen atom abstraction by the resulting methoxy radical from an added alcohol generates an α-hydroxy radical that reduces another pyridinium molecule, thus leading to chain propagation. For example, thioxanthone-sensitized reactions of 4-cyano-*N*-methoxypyridinium, **P1**, with several aliphatic and benzyl alcohols gave quantum yields for products formation (an aldehyde or a ketone and protonated 4-cyanopyridinium) of ~15−20, at reactant concentrations of ~0.02−0.04 M. The reaction can also be sensitized with triplet benzopheone, which in this case acts as an electron donor. Energetic limitations on chain propagation are imposed by the relationship between the oxidation potential of the α-hydroxy radical and the reduction potential of the pyridinium salt. The chain reactions proceed despite ~0.25 eV endothermicity for the electron-transfer step. Chain reactions with the harder-to-reduce 4-phenyl-*N*-methoxypyridinium, however, are limited in scope because of increased endothermicity for electron transfer. The thioxanthone-sensitized reaction of **P1** with benzhydrol was studied in detail by a combination of steady state and transient kinetics. The bimolecular rate constants for the chain propagation reactions:hydrogen atom abstraction by the methoxy radical and electron transfer from the diphenylketyl radical to **P1** are ~6 × 10^6 and 1.1 × 10^6 M^{-1} s^{-1}, respectively. The kinetic data indicate that deuterium atom abstraction by the methoxy radical from the solvent, acetonitrile-d_3, is a dominant chain-terminating process. Because of a large deuterium isotope effect, ~7, the quantum amplification is strongly suppressed when the reaction is carried out in acetonitrile.

Introduction

Amplification of photochemical processes plays an important role in applications where high sensitivity is required. Generation of a species that can be used as a catalyst in a subsequent reaction is commonly used to amplify the effect of the primary photochemical reaction. Examples of these catalytic reactions are photogenerated acids, used in lithographic applications,[1] and photogenerated clusters of a few silver atoms, acting as a latent image in silver halide photography.[2] Chain propagation in photoinitiated radical or cationic polymerization is conceptually a different process, where the propagation simply increases the molecular weight of the forming polymer.[3]

Only few concepts of chain-amplified photoreactions are reported where one photon leads to the transformation of several reactant molecules to products. Well-known among these are the photoinduced electron-transfer reactions of electron donors, whose radical cations undergo valence isomerization or 2 + 2 cycloaddition/cycloreversion, where quantum yields of several tens can be achieved in polar solvents.[4] In these reactions, the chain is propagated via electron transfer from a reactant molecule to the radical cation of the product.

Whitten et al. reported an interesting chain-amplified, photoinduced electron-transfer reaction in which oxidative and reductive cleavage of *two* different pinacols produce a reducing and an oxidizing radical, respectively, capable of propagating the chain.[5]

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[1] (a) Tessier, T. G.; Frechet, J. M. J.; Willson, C. G.; Ito, H. *ACS Symposium Series*; American Chemical Society: Washington, DC, 1985; pp 266, 269. (b) Stewart, M. D.; Patterson, K.; Somervell, M. H.; Willson, C. G. *J. Phys. Org. Chem.* **2000**, *13*, 767.

[2] *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; MacMillan: New York, 1977.

[3] See, for example: Reiser, A. In *Photoreactive Polymers, The Science and Technology of Resists*; Wiley: New York, 1989; pp 102−177.

[4] (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Evans, T. R.; Wake, R. W.; Sifain, M. M. *Tetrahedron Lett.* **1973**, 701. (c) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

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A different kind of chain reaction, also involving two reactants, is that of onium salts. Upon one-electron reduction, eq 1, an onium salt ($Ar{-}X^+$) undergoes fragmentation to yield an aryl radical, eq 2, which in turn abstracts a hydrogen atom from an alcohol to give an α-hydroxy radical, eq 3. Chain propagation occurs via electron transfer from the α-hydroxy radical to another onium salt molecule, eq 4.

$$Ar{-}X^+ \xrightarrow{+\,e^-} Ar{-}X^\bullet \qquad (1)$$

$$Ar{-}X^\bullet \rightarrow Ar^\bullet + X \qquad (2)$$

$$Ar^\bullet + RCH_2OH \rightarrow Ar{-}H + R^\bullet CHOH \qquad (3)$$

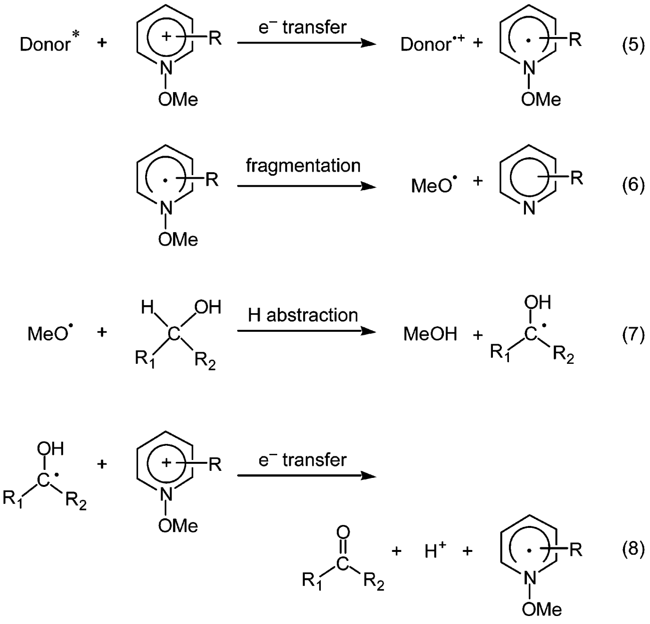
$$R^\bullet CHOH + Ar{-}X^+ \rightarrow RCHO + H^+ + Ar{-}X^\bullet \qquad (4)$$

This reaction sequence was first reported for diazonium salts[6] and was later extended to diaryl iodonium and to triaryl sulfonium salts.[7] In addition to alcohols such as methanol, ethers[8] (e.g., THF), triphenylphosphine,[9] formate,[10] and hypophosphite[11] were also found to undergo similar chain reactions with onium salts.

In a similar reaction, bromoacetate esters (in place of the onium salts) react with alcohols such as 2-propanol to yield the acetate ester, hydrogen bromide, and the oxidation product of the alcohol (acetone, in the case of 2-propanol). The chain is propagated through electron transfer from the hydroxy radical to a bromoacetate molecule, which fragments to a bromide ion and a radical that abstracts a hydrogen atom from the alcohol.[12]

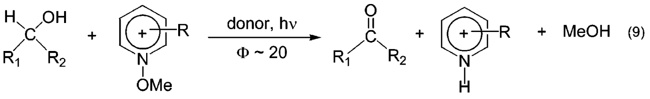
We now show that a chain-amplified reaction, analogous to that given by eqs 1−4, can be achieved in photoreactions of *N*-alkoxypyridinium salts, which have the advantage that their reduction potentials are readily modulated and that easy-to-reduce derivatives can still undergo fast fragmentation.[13−15] We also discuss several sensitization/initiation schemes in terms of the reaction energetics, as well as the limits of chain amplification based on a detailed kinetic studies to determine the controlling rate constants for propagation and termination reactions.

SCHEME 1



The reaction that we sought to investigate, Scheme 1, is based on one-electron reduction of *N*-methoxypyridinium salts, eq 5, which leads to N−O bond cleavage, eq 6. This fragmentation reaction yields a methoxy radical that abstracts an α hydrogen atom from an alcohol, eq 7, and if properly designed, the resulting α-hydroxy radical could transfer an electron to another molecule of *N*-methoxypyridinium salt, eq 8, and propagate the chain.

Thus, the net reaction would be dehydrogenation of the alcohol, with the two hydrogen atoms being formally inserted into the N−O bond of the methoxypyridinium salt to give protonated pyridinium and methanol, eq 9.



Although usually exothermic, hydrogen atom abstractions by oxygen-centered radicals have rate constants only in the range of 10^5−10^7 M^{-1} s^{-1}, well below the diffusion-controlled limit.[16] These reactions, however, can be fast enough to become the dominant path for •OMe.

The reducing power of the α-hydroxy radical should be high enough for electron transfer to the pyridinium salt to proceed at a rate well above those of potentially competing processes. As shown below, this condition could be met, even if the electron transfer is an endothermic reaction.

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(5) Chen, L.; Lucia, L.; Whitten, D. G. *J. Am. Chem. Soc.* **1998**, *120*, 439.

(6) (a) DeTar, F. D.; Turetzky, M. N. *J. Am. Chem. Soc.* **1955**, *77*, 1745. (b) DeTar, F. D.; Kosuge, T. *J. Am. Chem. Soc.* **1958**, *80*, 6072. (c) Packer, J. E.; House, D. B.; Rasburn, E. J. *J. Chem. Soc. B* **1971**, 1574. (d) Packer, J. E.; Richardson, R. K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 751. (e) Smets, G.; Aerts, A.; Van Erum, J. *J. Polym.* **1980**, *12*, 539. (f) Kosynkin, D.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 4846. (g) Kosynkin, D.; Bockman, T. M.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2003.

(7) (a) Saeva, F. D. In *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1990; Vol. 156, p 59. (b) Knapczyk, J. M.; McEwen, W. E. *J. Org. Chem.* **1970**, *35*, 2539. (c) Ledwith, A. *Polymer* **1978**, *19*, 1217. (d) Ledwith, A. *Makromol. Chem. Suppl.* **1979**, *3*, 348. (e) Ledwith, A. *Pure Appl. Chem.* **1979**, *51*, 159. (f) Baumann, H.; Timpe, H.-J. *Z. Chem.* **1984**, *24*, 18. (g) Pappas, P. S.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77. (h) Crivello, J. V.; Jo, K. D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2143. (i) Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1994**, *59*, 1381.

(8) (a) Abdoul-Rasoul, A. M. F.; Ledwith, A.; Yagci, Y. *Polym. Bull.* **1978**, *1*, 1. (b) Abdoul-Rasoul, A. M. F.; Ledwith, A.; Yagci, Y. *Polymer* **1978**, *19*, 1219. (c) See also refs 7d, 7e, and 7f.

(9) Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1993**, *58*, 943.

(10) Packer, J. E.; Richardson, R. K.; Soole, P. J.; Webster, D. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1472.

(11) (a) The chain reaction of diazonium salts with hypophosphite (H_3PO_2) was the first to be reported.[10] (b) Kornblum, N.; Cooper, G. D.; Taylor, J. E. *J. Am. Chem. Soc.* **1950**, *72*, 3013.

(12) Fontana, F.; Kolt, R. J.; Huang, Y.; Wayner, D. D. M. *J. Org. Chem.* **1994**, *59*, 4671.

(13) Lee, K. Y.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1992**, *7*, 1011.

(14) (a) Lorance, E. D.; Kramer, W. H.; Gould, I. R. *J. Am. Chem. Soc.* **2004**, *126*, 14071. (b) Lorance, E. D.; Hendrickson, K.; Gould, I. R. *J. Org. Chem.* **2005**, *70*, 2014.

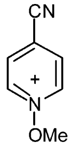
(15) Gould, I. R.; Shukla, D.; Giesen D.; Farid, S. *Helv. Chim. Acta* **2001**, *84*, 2796.

(16) (a) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520. (b) Scaiano, J. C. *J. Photochem.* **1973**, *2*, 81.

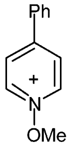
Results and Discussion

The reduction potential of the pyridinium salt sets the limits on the sensitizers and alcohols that can be used. In both cases the easier it is to reduce the pyridinium salt, i.e., the less negative its reduction potential, the broader the range of applicable sensitizers and alcohols. Reduction potentials of *N*-methoxypyridinium salts are not readily accessible through conventional electrochemical techniques because of the relatively fast reductive cleavage of these compounds.[14] However, on the basis of differences in absorption maxima between CT complexes of *N*-alkoxy- and *N*-alkyl-pyridinium salts, the *N*-alkoxy derivatives were estimated to have reduction potentials that are ~0.14 V less negative than those of the *N*-alkyl analogues.[13] Similar differences in reduction potentials between these sets of compounds are also supported by additional data.[15] Thus, the reduction potentials of *N*-alkoxy pyridiniums can be estimated from those of the corresponding *N*-alkyl analogues, many of which show reversible potentials by conventional cyclic voltametry.[13]

We compared reactions of two pyridinium salts, **P1** and **P2**, that have a large difference in reduction potentials: that of the 4-cyano derivative (**P1**) is estimated to be ca. −0.5 V vs SCE, and of the 4-phenyl analogue (**P2**) to be ca. −1.0 V vs SCE.[15]



P1



P2

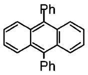
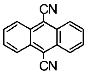
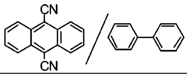
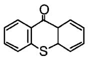
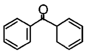
E^{red} (V vs SCE) ca – 0.5 ca – 1.0

Oxidation potentials of α-hydroxy radicals, which define the structure of the alcohols to be used, are also difficult to determine reliably because of sensitivity to hydrogen bonding and to medium basicity. For example, moderate to high concentrations of the parent alcohol could lower the oxidation potential owing to coupled electron/proton transfer.[17] The oxidation potential of the diphenyl ketyl radical, −0.25 V vs SCE, seems to be the most carefully established.[18] Interestingly, this α-hydroxy radical has the same oxidation potential as that of the corresponding methoxy radical. Because of the lack of potential complication from proton-coupled electron transfer in the case of the α-alkoxy radicals, their oxidation potentials could provide an estimate for the oxidation potentials of the corresponding α-hydroxy radicals.

1. Sensitization/Initiation. Based on the general derivation for energetic requirements for photoinduced electron transfer,[19] the driving force for electron transfer from an excited sensitizer to the methoxypyridinium salt depends on (a) the excitation energy of the sensitizing donor, $(E^{excit})_D$, (b) its oxidation potential, $(E^{ox})_D$, (c) the reduction potential of the pyridinium salt, $(E^{red})_A$, and (d) an energy increment Δ,[20] which varies from near zero in polar solvents, such as acetonitrile, to ca. 0.3 eV in nonpolar media. Thus, for the photoinduced electron transfer to be exothermic (i.e., for the energy stored in the excited state to exceed the energy stored in the electron-transfer products),[19] the relation shown in eq 10 has to be satisfied.

$$(E^{excit})_D > (E^{ox})_D - (E^{red})_A + \Delta \tag{10}$$

TABLE 1. Quantum Yields (Φ_P) and Chain Lengths of Photoreactions of Benzhydrol with 4-Cyano-*N*-methoxypyridinium (P1) at Equimolar Concentrations of 0.04 M, Initiated by Different Sensitizers in Acetonitrile

Entry	Sensitizer	Φ_P	Initiation Efficiency	Chain Amplification
1	 (DPA)	1.3	0.21	6
2	 (DCA)	1.3	0.054[a]	24
3		11	0.65	17
4	 (TX)	18	0.88	20
5	 (BP)	35	2.0[b]	18

[a] The measured quantum yield for formation of $DCA^{\bullet+}$ and pyridyl radical is 0.027. A second chain is initiated through oxidation of benzydrol by $DCA^{\bullet+}$. [b] Similar to the DCA reaction, two chains are generated from the reaction of $^3BP^*$, which is formed with a quantum yield of 1.

The excitation energy of the donor, $(E^{excit})_D$, could be that of the singlet or the triplet state, depending on which of these states react with the pyridinium compound. There are potential sources of inefficiencies in the initiation step. In the case of reactions via the singlet-excited state, energy-wasting return electron transfer can compete with the fragmentation of the *N*-methoxypyridyl radical, especially if the fragmentation of the pyridyl radical is not very fast. In the case of reactions via the triplet state, return electron transfer is spin forbidden and is unlikely to compete with the fragmentation. Inefficient intersystem crossing, however, will lower the initiation efficiency.

We first carried out experiments with benzhydrol because the α-hydroxy radical derived from this alcohol is a well-characterized intermediate with an absorption band at 540 nm that can be used to follow the reaction kinetics by flash photolysis.[21] In these experiments an equal concentration of benzhydrol and **P1** of ~0.04 M was used, and the conversion was kept under 20%. Irradiations using a number of sensitizers, Table 1, were carried out in CD_3CN, and the degree of conversion to products was determined by NMR. The three reaction products, benzophenone, protonated cyanopyridinium and metha-

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(17) Lilie, J.; Beck, G.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *75*, 458.

(18) Lund, T.; Wayner, D. D. M.; Jonsson, M.; Larsen, A. G.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, *123*, 12590.

(19) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129.

(20) Arnold, B. R.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.

(21) (a) Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9. (b) Murov, S. L.; Carmichael, I.; Hug, G. L. In *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

nol, were formed, as expected, in similar amounts; see Experimental Section.

In Table 1, Φ_P is the measured product quantum yield of the reaction determined by NMR, initiation efficiency is the efficiency of the initial formation of the pyridyl radical from the reaction of **P1** with excited electron donors, and the chain amplification is obtained from the quantum yield divided by the initiation efficiency

Using 9,10-diphenylanthracene, DPA, as an electron-transfer sensitizer via the singlet excited state,[22] a product quantum yield of 1.3 was obtained, experiment. 1, Table 1. As shown by flash photolysis, the initiation efficiency of this reaction was only 0.21 (see Experimental Section for Quantum Yield for Initial Radical Formation). Thus, after correction for inefficient initiation, the chain length, in this case, is estimated to be ~6.

Although 9,10-dicyanoanthacene, DCA, is a widely used electron acceptor ($E^{\mathrm{excit}} = 2.97$ eV, $E^{\mathrm{red}} = -0.91$ V vs SCE),[23] its fluorescence is quenched by **P1** at a rate constant, 9×10^9 M^{-1} s^{-1}, approaching the diffusion-controlled limit. This suggests that, in this case, DCA is acting as an *electron* donor, and using it as a sensitizer for the benzhydrol/**P1** reaction, a quantum yield of 1.3 was obtained, experiment 2. After correcting for an initiation efficiency of 0.054,[24] a chain amplification of 24 is estimated.

In experiment 3, DCA was used in combination with biphenyl as a cosensitizer.[23] At high concentration of biphenyl, most of the singlet-excited DCA is intercepted by this electron donor, with only a small fraction of ^{1}DCA* being intercepted by **P1**. Under the reaction conditions, DCA$^{\bullet-}$ and biphenyl$^{\bullet+}$ are formed with a quantum yield of 0.65.[23] Thus, in this case the reducing agent is not an excited sensitizer, as in the previous two experiments, but it is a radical anion, DCA$^{\bullet-}$, an interaction that does not have a deactivation path. The measured quantum yield of this reaction was 11, which upon correction for the initiation efficiency of 0.65 yields a chain amplification of 17.

In experiment 4, a triplet sensitizer, thioxanthone (TX), was used to eliminate inefficiencies resulting from return electron transfer in the geminate pair, as encountered in experiments 1 and 2. Triplet TX is quenched by **P1** at a rate constant (8.8×10^9 M^{-1} s^{-1}) approaching the diffusion-controlled limit in acetonitrile. Shown in Figure 1 is the transient spectrum from this reaction, with an absorption maximum at 435 nm, similar to that reported for the thioxanthone radical cation, TX$^{\bullet+}$.[25] An additional, much stronger absorption band with ill-defined maximum at ca. 760 nm, which has not been reported before, is also observed. For evidence that both bands are due to the same species, see Experimental Section. A minor source of inefficiency, in this case, is the quantum yield of intersystem crossing, which is 0.88 for TX in acetonitrile.[26] Thus, the measured quantum yield of 18 would correspond to a chain length of 20.

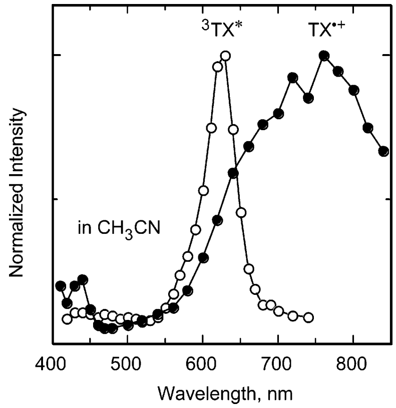

FIGURE 1. Absorption spectra of triplet thioxanthone (^{3}TX*) and of thioxanthone radical cation (TX$^{\bullet+}$), generated via electron transfer from ^{3}TX* to **P1**. ^{3}TX* and TX$^{\bullet+}$ spectra obtained 0.5 and 1 μs after laser pulse, respectively.

In experiment 5, our original intent was to initiate the benzhydrol/**P1** chain reaction through the well-known hydrogen-atom abstraction by triplet benzophenone, ^{3}BP*, from benzhydrol.[27] This reaction would yield two diphenyl ketyl radicals and, thus, an initiation efficiency of 2. Although the highest quantum yield was obtained using BP as a sensitizer, the actual mechanism, however, turned out to be a *double* electron-transfer reaction with initiation efficiency of 2.

Whereas the bimolecular rate constant for hydrogen abstraction from benzhydrol by ^{3}BP* is 5.1×10^6 M^{-1} s^{-1} (see Experimental Section), flash photolysis experiments showed that ^{3}BP* is quenched by **P1** at a rate constant of 1.7×10^8 M^{-1} s^{-1}, Figure 2.[28]

Thus, at equimolar concentrations of benzhydrol and **P1**, only 3% of ^{3}BP* molecules are intercepted by benzhydrol and 97% by **P1**. The latter process yields a species with a transient absorption at ~390 nm, Figure 3, which we assign to BP$^{\bullet+}$, a product of electron transfer from ^{3}BP* to **P1**.[29] Consistent with this assignment is its quenching by triphenylamine, TPA, at a rate constant that matches the concurrent formation of TPA$^{\bullet+}$; see

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(22) (a) DPA: $E_{\mathrm{excit}} \approx 3$ eV,[22b] $E^{\mathrm{ox}} = 1.22$ V vs SCE.[22c] (b) Berlman, I. B. In *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971. (c) Phelps, J.; Santhanam, K. V. S.; Bard, A. *J. Am. Chem. Soc.* **1967**, *89*, 1752.

(23) (a) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4291. (b) DCA fluorescence in CH$_3$CN is quenched by **P2** ($E^{\mathrm{red}} = -1.0$ V vs SCE) at a rate constant of $\sim 6 \times 10^9$ M^{-1} s^{-1}. Thus, the oxidation potential of DCA is estimated to be ≤ 1.9 V vs SCE.

(24) The measured quantum yield of free ions is 0.027. The radical cation of DCA can oxidize benzhydrol and initiate another chain; thus, the effective initiation efficiency is double the measured ion yield.

(25) (a) Fouassier, J. P.; Burr, D.; Crivello, J. V. *J. Photochem. Photobio., A* **1989**, *49*, 317. (b) Manivanan, F.; Fouassier, J. P.; Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1999.

(26) (a) Intersystem-crossing quantum yield for TX of 0.85 has been measured in benzene.[26b] In polar solvents, however, triplet quantum yields ranging from 0.66 to 1 have been reported.[26c] In view of the discrepancies in reported values, we measured Φ_{isc} for TX in acetonitrile and obtained a value of 0.88; see Experimental Section. (b) Amirzadeh, G.; Schnabel, W. *Makromol. Chem.* **1981**, *182*, 2821. (c) Allonas, X.; Ley, C.; Bibaut, C.; Jacques, P.; Fouassier, J. P. *Chem. Phys. Lett.* **2000**, *322*, 483 and references therein.

(27) Wagner, P. J. *Mol. Photochem.* **1981**, *1*, 71.

(28) Smets[6e] and Pappas[7h] have proposed that reactions of onium salts with alcohols were initiated by hydrogen atom abstraction by triplet ketones. In light of our kinetic data, however, initiation of these reactions through electron transfer from the triplet ketone to the onium salt should not be ruled out.

(29) (a) Similar electron transfer occurs in reaction of ^{3}BP* with methyl viologen leading to the formation of methyl viologen radical cation, suggesting formation of benzophenone radical cation.[29b] In our experiment absorption by BP$^{\bullet+}$ (~390 nm) could be detected because of the lack of contribution from other species in this spectral region. In the methyl viologen reaction, this region is masked by absorption by the reduced acceptor (viologen radical cation). (b) Das, P. K. *Tettrahedron Lett.* **1981**, *22*, 1307.

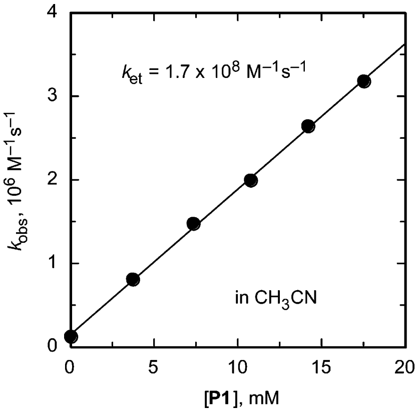


FIGURE 2. Observed decay rate constant of benzophenone triplet (^{3}BP*) as a function of added pyridinium salt **P1**.

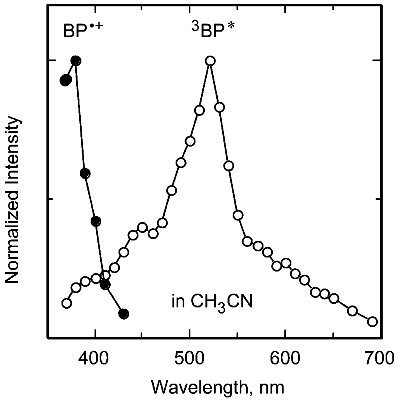


FIGURE 3. Absorption spectra of benzophenone triplet (^{3}BP*) and of benzophenone radical cation (BP$^{•+}$), generated via electron transfer from ^{3}BP* to **P1**. ^{3}BP* and BP$^{•+}$ spectra obtained 1.5 and 2 μs after laser pulse, respectively.

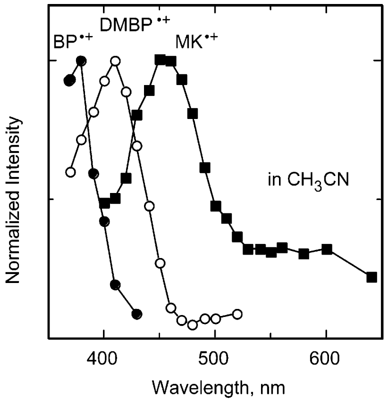
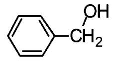
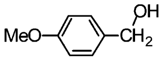
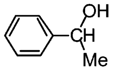
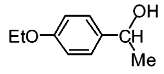


FIGURE 4. Absorption spectra of the radical cations of benzophenone (BP$^{•+}$), 4,4′-dimethoxybenzophenone (DMPB$^{•+}$), and Michlers ketone (MK$^{•+}$). BP$^{•+}$, DMPB$^{•+}$, and MK$^{•+}$ spectra obtained 1.2, 1.5, and 2 μs after laser pulse, respectively.

TABLE 2. Quantum Yields[a] of Photoreactions of Benzyl Alcohols with *N*-Methoxypyridinium Salts P1 and P2 at Equimolar Concentrations of 0.02 M, Initiated with Thioxanthone (TX) in CD$_3$CN

Benzyl Alcohol	**P1**	**P2**
	10	1
	16	1
	20	1
	20	5 (8)[b]

[a] Error margin ≈ 10%. [b] The value in parentheses is the quantum yield measured at 0.04 M concentration of both reactants.

Supporting Information. For comparison with spectra of radical cations of other well-characterized benzophenone derivatives, see Figure 4. We believe this is the first identification of benzophenone radical cation by transient absorption.

The fact that electron transfer from ^{3}BP* to **P1** occurs with a rate constant that is ca. 1/100th of the diffusion-controlled limit indicates that this reaction is isoenergetic within 0.1 eV. Given that BP triplet energy is 3.0 eV and the reduction potential of **P1** is ca −0.5 V, the oxidation potential of BP is likely to be ~2.5 ± 0.1 V vs SCE.[30] Because of such high oxidation potential, the BP radical cation should be a powerful enough oxidant to oxidize benzhydrol. This was confirmed in a flash photolysis experiment where a rate constant for interception of BP$^{•+}$ by benzhydrol of $\sim 1 \times 10^9$ M^{-1} s^{-1} was measured. One-electron oxidation of benzhydrol will yield a radical cation, which upon deprotonation will yield a ketyl radical, and this in turn will reduce **P1** and start another chain. Therefore, the initiation efficiency is most likely ~2, and thus the chain length is ~18.

At a concentration of benzhydrol and **P1** of ~0.04 M, the chain amplification in experiments 2−5 seem to fall within a narrow range of 17−24, regardless of the sensitizer/initiator system. In the case of experiment 1, the amplification is considerably less, which is probably due to higher rates for termination reactions.

2. Scope and Limitations. To explore the scope of this chain process, we also investigated reactions with other alcohols and the effect of substituents on the chain propagation. An electron-donating substituent, such as an alkoxy group, on the phenyl ring of a benzyl alcohol lowers the oxidation potential of the corresponding α-hydroxy radical because of the increased stabilization of the resulting cation.[31] An α-methyl substituent also increases the reducing power of the radical because, in general, tertiary radicals have lower (more negative) oxidation potentials than the corresponding secondary radicals.[32] An α-methyl substituent, and to a lesser degree a 4-alkoxy group, will also lower the bond dissociation

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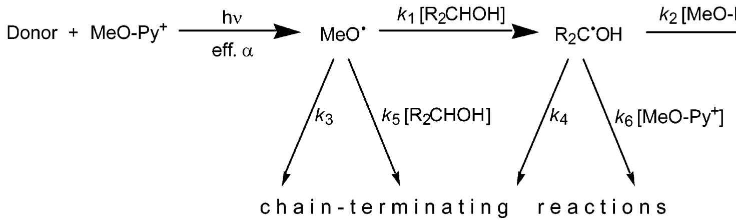
(30) (a) Independent experiments led, through bracketing, to a similar conclusion. The fluorescence of 2,6,9,10-tetracyanoanthracene (E^{excit} = 2.87 eV, E^{red} = −0.44 V vs SCE)[23] is not quenched by BP, i.e., E^{ox}_{BP} > 2.43 V. In addition, BP triplet (E_T = 3.00 eV)[21b] is quenched by 4-cyano-*N*-methylpyridinium (E^{red} = −0.64 V, reversible)[15] at a rate constant of 1.7×10^7 M^{-1} s^{-1}, corresponding to endothermicity of ≤0.17 eV, i.e., $E^{ox}_{BP} \leq$ 2.53 V, hence our estimate of ~2.5 V. A literature value of 2.33 V is reported for the oxidation potential of BP.[30b] (b) Raumer, M. v.; Suppan, P.; Jacques, P. *J. Photochem. Photobiol., A* **1997**, *105*, 21.

(31) Workentin, M. S.; Wayner, D. D. M. *Res. Chem. Intermed.* **1993**, *19*, 777.

(32) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

SCHEME 2. Chain Propagation (k_1 and k_2) and Chain Termination (k_3–k_6) Steps in the Oxidation of Alcohols by *N*-Methoxypyridinium Salts, Initiated by Photoexcitation of an Electron Donor with an Efficiency α



energy of the α-C−H bond of the benzyl alcohol.[33] Thus, the energetics of the two propagation steps in our scheme, the hydrogen atom abstraction from the alcohol by the methoxy radical and the electron transfer from the radical to the methoxypyridinium salt, will be more favored by these substitution patterns.

The oxidation potential of α-methoxybenzyl radical (−0.33 V vs SCE)[31] is slightly more negative than that of the diphenylketyl radical (−0.25 V vs SCE) which is the chain-propagating species in the first set of experiments, Table 1. If α-hydroxybenzyl radical has a similar oxidation potential as that of the α-methoxybenzyl radical, see above, then the chain reaction between benzyl alcohol and **P1** should be feasible. Indeed, with thioxanthone as a sensitizer, a quantum yield of 10 was obtained at 0.02 M concentrations of both benzyl alcohol and **P1**, Table 2. Further increase in the quantum yield up to 20 was observed in reactions with benzyl alcohol derivatives that produce radicals with more reducing power, Table 2.

With benzyl alcohol, the 4-alkoxy- or the α-methyl analogues, no chain amplification was observed with the phenylpyridinium salt **P2**, which is harder to reduce than **P1** by ~0.5 V. This indicates that electron transfer from the α-hydroxy radicals derived from these alcohols to **P2** is too endothermic to proceed at a rate that competes with the termination reactions. Chain propagation with **P2** was observed only in the reaction with the most reducing radical derived from this set of compounds, 4-alkoxy-α-methylbenzyl alcohol. Thus, with proper substitution of the alcohol, chain amplification can be achieved, even with a pyridinium salt that has a reduction potential of ca −1 V vs SCE.

It is noteworthy that, in addition to the usual products, the reactions of the 4-alkoxybenzyl alcohols with **P1** also lead to the formation of the corresponding dibenzyl ethers. These benzyl alcohols are readily transformed to the ethers in a fast (dark) acid-catalyzed reaction at room temperature. This unintended reaction demonstrates the potential for "double amplification": a chain reaction leading to the formation of a reagent that can be used to catalyze another reaction. No ether formation was observed in the reactions with **P2**, presumably because protonated 4-phenylpyridinium is a weaker acid than protonated 4-cyanopyridinium.

To further explore the scope of these chain-amplified reactions, we investigated the photoreaction of 2-propanol with **P1**, sensitized with benzophenone, and obtained (at a 0.025 M concentration for both reactants) a quantum yield of 18 for products formation: acetone, protonated 4-cyanopyridinium, and methanol. Similarly, 2,4-pentanediol and **P1**, both at 0.04 M concentration, sensitized with BP, yielded 4-hydroxy-2-pentanone with a quantum yield of 15, which upon extended exposure underwent further oxidation to acetylacetone.

3. Kinetics and Chain Termination Processes. Having addressed the scope of the chain reactions of *N*-alkoxypyridinium salts and different initiation schemes, we now consider the kinetics of propagation and termination reactions, which are the parameters that control the chain length, Scheme 2.

Chain termination can result from side reactions of the intermediates (the methoxy radical and the α-hydroxy radical), k_3 and k_4, respectively. Other chain termination processes could be side reactions of these intermediates with the reactants or with impurities in the reactants, k_5 and k_6. Chain terminations resulting from reactions with the reactants, or with impurities therein, are kinetically equivalent. In the latter case, k_5 and k_6 would correspond simply to the rate constants times the molar fraction of the impurities. The effect of k_3 and k_4 on the quantum yield should decrease with increasing concentrations of the reactants, whereas that of k_5 and k_6 should not be a function of the concentrations of the reactants.

The quantum yield for product formation, Φ_P, the conversion of methoxypyridinium to the protonated pyridinium with the concomitant dehydrogenation of R_2CHOH (a primary or a secondary alcohol) to R_2CO (an aldehyde or a ketone), according to Scheme 2, is given by eq 11, which yields eq 12.

$$\Phi_P = \alpha pq\ (1 + p^2q^2 + p^3q^3 + \ldots) \tag{11}$$

$$\frac{\alpha}{\Phi_P} = \frac{1}{pq} - 1 \tag{12}$$

where

$$p = \frac{k_1[R_2CHOH]}{(k_1 + k_5)[R_2CHOH] + k_3}$$

and

$$q = \frac{k_2[\text{MeO-Py}^+]}{(k_2 + k_6)[\text{MeO-Py}^+] + k_4}$$

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[33] Shukla, D.; Young, R. H.; Farid, S. *J. Phy. Chem. A* **2004**, *108*, 10386.

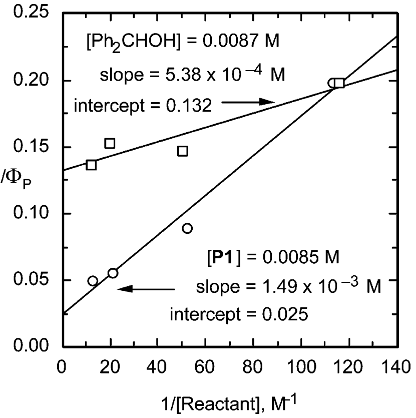


FIGURE 5. Plot of α/Φ_P at [TX] = 6 mM, where α is the initiation efficiency of the reaction (equal to the intersystem crossing yield of the sensitizer, TX, 0.88) and Φ_P is the quantum yield for product formation, vs the reciprocal of the concentration of the reactants: (□) the concentration of the pyridinium salt, **P1**, was varied, keeping the concentration of benzhydrol constant; (○) the concentration of benzhydrol was varied keeping the concentration of **P1** constant. The lines are least-squares fits for the data points.

Equation 12 leads to the following very good approximation, eq 13, by eliminating terms with negligible contributions:

$$\frac{\alpha}{\Phi_P} \approx \left(\frac{k_5}{k_1} + \frac{k_6}{k_2}\right) + \left(\frac{k_3}{k_1}\right)\frac{1}{[\mathrm{R_2CHOH}]} + \left(\frac{k_4}{k_2}\right)\frac{1}{[\text{MeO-Py}^+]} + \left(\frac{k_3}{k_1}\frac{k_4}{k_2}\right)\frac{1}{[\mathrm{R_2CHOH}]}\frac{1}{[\text{MeO-Py}^+]} \tag{13}$$

The kinetics of thioxanthone (TX)-sensitized reactions of the pyridinium salt **P1** with benzhydrol (i.e., R = Ph) were evaluated in terms of this model. The data indicated that, within the concentration range we used (<0.1 M), the magnitude of the last term in eq 13 is negligible compared to the other terms. The contribution of this quadratic term to the total value is no more than 2%, well within experimental error. Equation 13, therefore, can be further simplified to eq 14:

$$\frac{\alpha}{\Phi_P} \approx \left(\frac{k_5}{k_1} + \frac{k_6}{k_2}\right) + \left(\frac{k_3}{k_1}\right)\frac{1}{[\mathrm{R_2CHOH}]} + \left(\frac{k_4}{k_2}\right)\frac{1}{[\text{MeO-Py}^+]} \tag{14}$$

The three parameters of eq 14 given in parentheses can be determined by varying [R_2CHOH] while keeping [MeO-Py^+] constant and vice versa, Figure 5, as well as by varying an equimolar concentration of *both* reactants, Figure 6.

As shown in Figure 5, the quantum yield is much less dependent on the concentration of the pyridinium salt, **P1**, than it is on the concentration of the reacting alcohol, benzhydrol. According to eq 14, estimates for the fixed parameters can be obtained from the slopes and intercepts of the linear plots. More accurate values for these parameters were obtained, however, from a global analysis of the combined data from the three experiments.

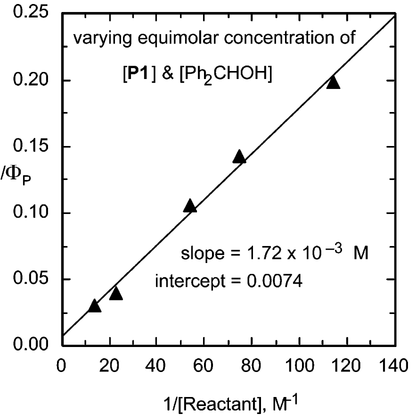


FIGURE 6. Plot of α/Φ_P at [TX] = 6 mM, where α is the initiation efficiency of the reaction (equal to the intersystem crossing yield of the sensitizer, TX, 0.88) and Φ_P is the quantum yield for product formation, vs the reciprocal of equimolar concentration of *both* reactants, the pyridinium salt **P1** and benzhydrol.

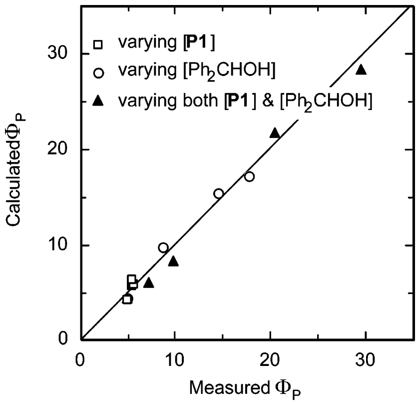


FIGURE 7. Plot of calculated vs measured quantum yield for product formation according to eq 14, using the parameters given in text.

The best correlation between measured and calculated quantum yields, Figure 7, was obtained using the following values:

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

These parameters represent ratios of rate constants of chain-termination reactions to those of chain propagation. Thus, the smaller these parameters become, the higher the chain amplification. It is useful to identify the sources of these chain-termination processes.

A. Reactions of the Methoxy Radical (MeO•). Hydrogen atom abstraction from benzhydrol by the methoxy radical, k_1, Scheme 2, is one of the two key steps in the chain reaction under investigation. Determined from an independent experiment (see Experimental Section), k_1 is ~6 × 10^6 M^{-1} s^{-1}. This rate constant is similar to the value of 6.7 × 10^6 M^{-1} s^{-1}, which is reported for hydrogen atom abstraction by *tert*-butoxyl radical from benzhydrol in benzene.[16]

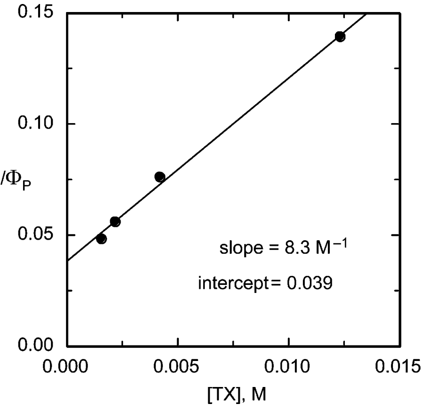


FIGURE 8. Plot of α/Φ_P, where α is the initiation efficiency of the reaction (= $(\Phi_{isc})_{TX}$) and Φp is the quantum yield of product formation for reaction of **P1** with benzhydrol vs the concentration of the sensitizer, thioxanthone (TX). Both **P1** and benzhydrol were at an average concentration (before and after irradiation) of 0.019 M.

In addition to potential reactions of MeO$^{\bullet}$ with impurities in the reactants, Figure 5 clearly shows that termination reactions involving this radical compete with the propagation step. These are collectively expressed in terms of a pseudo first-order rate constant, k_3. A likely source for chain termination is deuterium abstraction from the solvent, CD_3CN, by the methoxy radical to form methanol and $^{\bullet}CD_2CN$, which is a nonreducing radical. This hypothesis is supported by the data given below, which also indicates that there is an additional chain termination from the reaction of MeO$^{\bullet}$ with the sensitizer, thioxanthone (TX). Thus, k_3 represents the sum of two pseudo first-order processes, eqs 15−17:

$$\mathrm{MeO}^{\bullet} + \mathrm{CD_3CN} \xrightarrow{k^{\mathrm{d}}_{\mathrm{solv}}} \mathrm{MeOD} + {}^{\bullet}\mathrm{CD_2CN} \qquad (15)$$

$$\mathrm{MeO}^{\bullet} + \xrightarrow{k_{\mathrm{sens}}} \text{addition product} \qquad (16)$$

$$k_3 = k^{\mathrm{d}}_{\mathrm{solv}}[\mathrm{CD_3CN}] + k_{\mathrm{sens}}[\mathrm{TX}] \qquad (17)$$

We found that the quantum yield for product formation decreases with the increasing concentration of TX. A plot of $\alpha/\Phi P$ vs [TX] at an average, equimolar concentration of the reactants of 0.019 M, showed as expected, a linear dependence with an intercept of 0.039 and a slope of 8.3 M^{-1}, Figure 8. It is unlikely that this decrease in quantum yield is due to interception of $R_2C^{\bullet}OH$ by TX, which would yield benzophenone and TX-H$^{\bullet}$, because the latter radical would also be effective in propagating the chain by reducing **P1** with no net change in the outcome. The dependence of the quantum yield on [TX] is more likely due to the reaction of MeO$^{\bullet}$ with TX and is given by eq 18, which is derived from eqs 14 and 17:

$$\frac{\alpha}{\Phi_P} \approx \left\{\left(\frac{k_5}{k_1} + \frac{k_6}{k_2}\right) + \left(\frac{k_4}{k_2}\right)\frac{1}{[\mathrm{MeO\text{-}Py^+}]} + \left(\frac{k^{\mathrm{d}}_{\mathrm{solv}}[\mathrm{CD_3CN}]}{k_1\,[\mathrm{R_2CHOH}]}\right)\right\} + \frac{k_{\mathrm{sens}}}{k_1\,[\mathrm{R_2CHOH}]}[\mathrm{TX}] \qquad (18)$$

According to eq 18, the slope of the linear plot of Figure 8 corresponds to $k_{sens}/k_1[Ph_2CHOH]$. From the measured slope (8.3 M^{-1}), the above-mentioned value of k_1 (6×10^6 M^{-1} s^{-1}) and the concentration [Ph_2CHOH] used in this experiment (0.019 M), the rate constant for the reaction of MeO$^{\bullet}$ with thioxanthone, k_{sens} (eq 16), is calculated to be 9.5×10^5 M^{-1} s^{-1}.

The intercept of Figure 8, which is 0.039, corresponds to

$$\left\{\left(\frac{k_5}{k_1} + \frac{k_6}{k_2}\right) + \left(\frac{k_4}{k_2}\right)\frac{1}{[\mathrm{MeO\text{-}Py^+}]} + \left(\frac{k^{\mathrm{d}}_{\mathrm{solv}}[\mathrm{CD_3CN}]}{k_1\,[\mathrm{R_2CHOH}]}\right)\right\}$$

From this intercept, the rate constant of the chain-terminating reaction of the methoxy radical with deuterioacetonitrile, $k^{\mathrm{d}}_{\mathrm{solv}}$, can be determined. The sum of the first two terms of the intercept is available from the data mentioned above, (0.009) + (0.00021)/0.019 = 0.02, and from this, the third term is obtained, 0.039−0.02 = 0.019. From the values of k_1 (6×10^6 M^{-1} s^{-1}) and the benzhydrol concentration (0.019 M), the pseudo first-order rate constant for the reaction of MeO$^{\bullet}$ with CD_3CN, $k^{\mathrm{d}}_{\mathrm{solv}}$ [CD_3CN], is 2.2×10^3 s^{-1}. Neat CD_3CN is 19.2 M; thus, $k^{\mathrm{d}}_{\mathrm{solv}}$ (eq 15) is estimated to be 1.1×10^2 M^{-1} s^{-1}.

In accordance with the conclusion that some of the chain termination is due to abstraction of a deuterium atom from the solvent by the methoxy radical, a significant drop in quantum yield was observed when the reaction was carried out in CH_3CN instead of CD_3CN. As determined from the data in Figure 4, at an average equimolar concentration of benzhydrol and **P1** of 0.019 M, and at a TX concentration of 0.0023 M, the quantum yield for product formation (Φ_P) in CD_3CN is 15.1. Under the same conditions, the corresponding quantum yield in CH_3CN is only 4.7. Three of the four terms on the right-hand side of eq 10 are the same in both experiments, and their magnitudes are known from the data given above. For the reaction in CD_3CN, the third term

$$\left(\frac{k^{\mathrm{d}}_{\mathrm{solv}}[\mathrm{CD_3CN}]}{k_1[\mathrm{R_2CHOH}]}\right)$$

as mentioned above, equals 0.019. Similarly the corresponding term for the reaction in CH_3CN

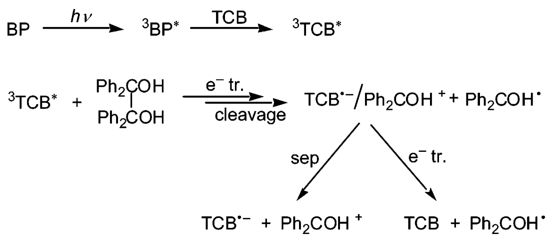
$$\left(\frac{k^{\mathrm{h}}_{\mathrm{solv}}[\mathrm{CH_3CN}]}{k_1[\mathrm{R_2CHOH}]}\right)$$

is calculated to be 0.147. This corresponds to a significant deuterium isotope effect ($k^{\mathrm{h}}_{\mathrm{solv}}/k^{\mathrm{d}}_{\mathrm{solv}}$) of 7.7 and a bimolecular rate constant for hydrogen abstraction by MeO$^{\bullet}$ from CH_3CN, $k^{\mathrm{h}}_{\mathrm{solv}}$ (eq 19) of 8.5×10^2 M^{-1} s^{-1}. Reported deuterium isotope effect for hydrogen atom abstraction by *tert*-butoxy radical from different substrates vary over a wide range,[34a] up to ~6 for the reaction with toluene,[34] which is several orders of magnitude faster than that with acetonitrile.

$$\mathrm{MeO}^{\bullet} + \mathrm{CH_3CN} \xrightarrow{k^{\mathrm{h}}_{\mathrm{solv}}} \mathrm{MeOH} + {}^{\bullet}\mathrm{CH_2CN} \qquad (19)$$

B. Reactions of the α-Hydroxy Radical ($Ph_2C^{\bullet}$-OH). The second chain-propagating reaction is

SCHEME 3



the electron transfer from the ketyl radical, $Ph_2C^{\bullet}$-OH, to the pyridinium salt (**P1**), k_2, Scheme 2. In general, whenever electron-transfer reactions are exothermic by ~0.2 eV or more, they proceed at the diffusion-controlled limit. The reduction potential of **P1** is ca. −0.5 V vs SCE,[15] see above, and the oxidation potential of the ketyl radical, $Ph_2C^{\bullet}$-OH, is −0.25 V vs SCE.[18] Thus, electron transfer from $Ph_2C^{\bullet}$-OH to **P1** is estimated to be *endothermic* by ~0.25 eV.

Based on the reaction scheme used in this work, the rate constant k_2 is not readily determined by transient kinetics because chain propagation will continue to reform the ketyl radical during the course of the reaction. We were able, however, to determine k_2 by using another approach to generate the ketyl radical *in the absence* of benzhydrol. On the basis of a reaction scheme that we reported recently, triplet benzophenone ($^3BP^*$) transfers energy to 1,2,4,5-tetracyanobenzene (TCB), which in an electron-transfer reaction (e$^-$ tr.) with benzopinacol, followed by fragmentation of the pinacol radical cation yields the ketyl radical, Scheme 3.[35]

A plot of the ketyl radical decay rate vs the concentration of added **P1**, Figure 9, gives a slope corresponding to k_2 of 1.1×10^6 M^{-1} s^{-1}. This rate constant is ca. 4 orders of magnitude lower than the diffusion-controlled limit, not unreasonable for an electron-transfer reaction estimated to be endothermic by 0.25 eV. From the abovementioned ratio of k_4/k_2 of 2.1×10^{-4} M, the competing, pseudo first-order rate constant, k_4, is estimated to be 2.3×10^2 s^{-1}. This chain-terminating process might represent a sum of more than one reaction. A possible reaction could be that of $Ph_2C^{\bullet}$-OH with residual oxygen in the argon-purged solutions used in these experiments. Quenching of the ketyl radical by oxygen is likely to be diffusion controlled (~10^{10} M^{-1} s^{-1}), and thus, an oxygen concentration in the range of ~10^{-8} M could account for such chain-terminating process. It is also possible that dimerization (radical/radical coupling) could contribute to chain termination via the ketyl radical.

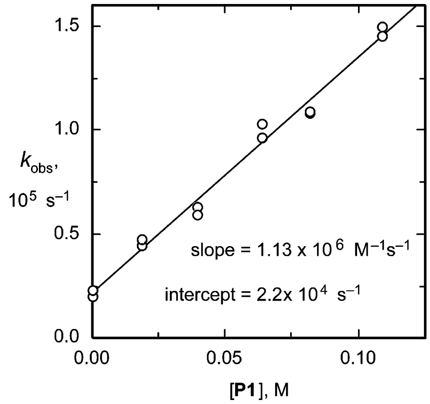
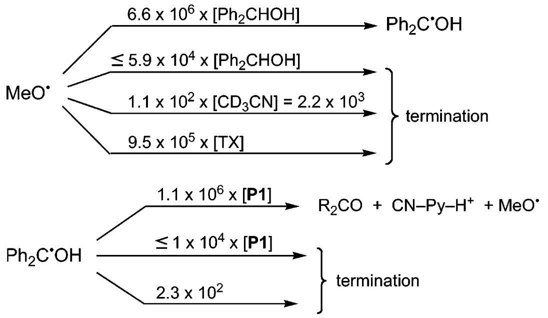


FIGURE 9. Observed rate constant for decay of the ketyl radical (generated according to Scheme 3, monitored at 540 nm) vs concentration of added pyridinium salt, **P1**, in acetonitrile. The slope corresponds to the bimolecular rate constant for electron transfer from the ketyl radical to **P1**.

SCHEME 4



Summary

Photosensitized electron-transfer reactions of *N*-methoxypyridinium salts with alcohols of diverse structures proceed via a chain process. Chain lengths of ~10−20 can be achieved, even at modest reactant concentrations of 0.02−0.04 M, and despite endothermicity of the critical electron-transfer step from the intermediate α-hydroxy radical to the pyridinium salt. The reactions can be initiated by a number of singlet or triplet sensitizers, with varying degrees of initiation efficiencies that can be as high as 2.

Summarized in Scheme 4 are rate constants for the propagation and termination steps in the thioxanthone-sensitized reaction of the methoxypyridinium salt, **P1**, with benzhydrol determined from a combination of steady-state and transient kinetics.

The data reveal the different sources that affect the propagation efficiency and clearly indicate that chain-terminating reactions of the methoxy radical play a more important role in limiting the extent of chain amplification than those of the ketyl radical. To illustrate this point, the measured quantum yield at 0.04 M concentration of both benzhydrol and **P1** in CD_3CN is ~19. If the chain-terminating reactions of the methoxy radical (with the solvent and the sensitizer) were eliminated, the quantum yield would increase to ~62. However, if the chain-terminating reactions of the ketyl radical (probably with residual oxygen and dimerization) were eliminated, the quantum yield would be only ~21. Because of a large deuterium isotope effect for hydrogen-atom abstraction by the methoxy radical from acetonitrile, the quantum yields in CD_3CN are substantially higher than those in CH_3CN.

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[34] (a) Manchester, J. I.; Dinnocenzo, J. P.; Higgins, L.-A.; Jones, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 5069. (b) Kim, S. S.; Kim, S. Y.; Ryou, S. S.; Lee, C. S.; Yoo, K. H. *J. Org. Chem.* **1993**, *58*, 192.

[35] In a less polar solvent (1,2-dichloroethane), the geminate pair $TCB^{\bullet-}/Ph_2COH^+$, Scheme 3, leads exclusively, via electron transfer, to TCB and $Ph_2COH^{\bullet}$. In acetonitrile, however, out-of-cage separation competes with the electron transfer. From the relative intensities of $Ph_2COH^{\bullet}$ and $TCB^{\bullet-}$ (see Supporting Information) and their extinction coefficients 3,800 and 15,900 M^{-1} cm^{-1}, respectively,[33] the partitioning between separation and electron transfer is estimated to be 30:70.

Experimental Section

Materials. The pyridinium salts **P1** and **P2** were synthesized according to literature procedure.[13] The crude salts were recrystallized from methanol. The sensitizers and alcohols were commercially available. 4-Ethoxy-1-phenylethyl alcohol was prepared by reduction of 4-ethoxyacetophenone with sodium borohydride in ethanol.[36] The products were identified by comparison with known authentic samples.

Steady-State Photolysis: Reaction Quantum Yields Measurements. The irradiations were carried out with a PEK 125-W super-high-pressure Hg lamp. For 365 nm, a combination of a Kodak Wratten ultraviolet filter, no. 18A, a Corning 0-52 cutoff filter, and a 365 nm interference filter were used. For 405 nm, a Corning 5-58 band-pass filter, a Corning 0-73 cutoff filter, and a 405 nm interference filter were used.

In a typical experiment, a 3-mL solution of an *N*-methoxypyridinium salt, an alcohol, and a sensitizer in CD_3CN was placed in a 1 × 1 cm cell. The sensitizer concentration was 6 mM, unless otherwise stated. The solution was purged with argon for ~10 min and irradiated for 2−10 min to reach a conversion of ~8−18%. 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 ^{1}H NMR signals of products and reactants. For example, before photolysis the ^{1}H NMR spectrum of an equimolar solution of **P1** and benzhydrol, with catalytic amount of thioxanthone, TX, in acetonitrile-d_3 shows characteristic signals due to P1 (δ 9.17 (m, 2H), 8.47 (m, 2H), 4.47 (s, 3H)) and to benzhydrol (δ 7.45−7.20 (m, 10H), 5.81 (d, 1H), 3.90 (d, 1H)). After irradiation at 405 nm the ^{1}H NMR spectrum of the photolyzate clearly showed appearance of new diagnostic signals due to formation of *N*-H-4-cyanopyridinium (δ 8.92 (m, 2H) and 8.33 (m, 2H)), benzophenone (δ 7.83−7.50 (m, 10H)) and CH_3OH (δ 3.30). The identity of these products was established by comparison with ^{1}H NMR spectra of authentic samples. Integration of *N*-H-4-cyanopyridinium, benzophenone, and methanol signals relative to P1 signals clearly shows that the three products, as required by the stoichiometery of the reaction, are formed in equal amounts. Additional details of the NMR data are given in Supporting Information.

The photon flux was determined by using the photocycloaddition reaction of phenanthrenequinone to *trans*-stilbene in benzene as an actinometer.[37] The light intensity was 7 to 9 × 10^{-8} Einstein min^{-1}. The quantum yield for product formation was determined from the percent conversion and the light intensity, corrected for incomplete absorption by the sensitizer.

Laser Flash Photolysis. The samples in a 1 cm × 1 cm quartz cell were excited at a right angle to the monitoring beam. The excitation source was a Q-switched Nd:YAG laser system. The laser can be tuned between 330 and 500 nm (pulses of 5 ns, 0.5−0.8 mJ) using the output of the 266 nm pumped OPO. The excitation pulses were attenuated, when necessary, using neutral density filters. A pulsed Oriel 150-W xenon lamp was used as the monitoring beam. The analyzing beam was collected and focused on the entrance slit (2 nm) of a monochromator. A photomultiplier tube (PMT) was attached to the exit slit of the monochromator. A computer-controlled high-voltage power supply was used with the PMT. The signals from the PMT were digitized using an oscilloscope and transferred to a PC. A pulse generator provided TTL trigger pulses to control the timing for the laser, lamp, and oscilloscope.

Triplet Thioxanthone (TX) as Electron Donor. Pulsed laser excitation of TX at 400 nm in an argon-purged acetonitrile solution led to the formation of a transient species with λ_{max} at 630 nm (Figure 1) and $\tau \approx 4$ μs. Based on the rapid quenching by oxygen and similarity to the previously reported spectrum,[38] the transient species was assigned to triplet thioxanthone (^{3}TX*). The decay of ^{3}TX* at 630 nm was enhanced in the presence of **P1** and from the slope of a linear plot of the observed decay rate constant (k_{obs} vs [**P1**]), a quenching rate constant of 8.8×10^9 M^{-1} s^{-1} was obtained.

At [**P1**] = 0.05 M, the ^{3}TX* spectrum was completely quenched and a new species with a weak transient absorption band, λ_{max} of 435 nm, and a much stronger, broad long-wavelength absorption with a $\lambda_{max} \approx 760$ nm was formed (Figure 1). Identical decay kinetics for *both* bands showed that they belong to a single species. Based on its rapid quenching by electron donors, the transient was assigned to the thioxanthone radical cation ($TX^{\bullet+}$). In the presence of 1,4-dimethoxybenzene (DMB) (10^{-3} M; $E^{ox} = 1.30$ V vs SCE), the decay at 435 and 780 nm occurred with the same rate constant (9.7 ± 0.2×10^9 M^{-1} s^{-1}) as the growth of DMB radical cation at 470 nm.[39]

Triplet Benzophenone (BP) as Electron Donor. Laser excitation of benzophenone (BP) at 360 nm in argon-purged acetonitrile led to the formation of triplet benzophenone (^{3}BP*) with characteristic absorption[33,40] having λ_{max} at 525 nm and τ of ~9 μs. ^{3}BP* was quenched by **P1**, and from a plot of the observed decay rate constant, k_{obs}, vs [**P1**], a second-order quenching rate constant of 1.7×10^8 M^{-1} s^{-1} was obtained (Figure 2).

Quenching of ^{3}BP* by **P1** (ca. 0.04 M) was accompanied by the formation of a weakly absorbing transient at 390 nm, $\tau \approx$ 10 μs, assigned to $BP^{\bullet+}$ on the basis of fast quenching by triphenylamine (TPA). The decay of $BP^{\bullet+}$ at 440 nm in the presence of added TPA and the concomitant rise of TPA radical cation ($TPA^{\bullet+}$) at 680 nm occurred at the same rate; see Supporting Information. The absorbance of $BP^{\bullet+}$ at 440 nm although low is enough to allow for measurement of its decay. It was necessary to monitor decay at 440 nm since triphenylamine radical cation has strong absorption below 400 nm. In a similar experiment, **P2** (0.05 M) failed to quench ^{3}BP*.

The triplet state of 4,4′-dimethoxybenzophenone was quenched by **P1** with a rate constant of 8.2×10^9 M^{-1} s^{-1}, and Michlers ketone triplet was quenched by **P1** and by **P2** with a rate constant of 1.6×10^{10} and of 1.2×10^{10} M^{-1} s^{-1}, respectively. The spectra of the resulting radical cations are shown in Figure 4.

Hydrogen Abstraction by Triplet Benzophenone (^{3}BP*). The decay of ^{3}BP* ($\lambda_{max} = 530$ nm) was measured in acetonitrile at different concentrations of benzhydrol (λ_{excit} = 360 nm). The reaction was monitored at 610 nm to avoid absorption by the reaction product, diphenylketyl radical. A rate constant of 5.1×10^6 M^{-1} s^{-1} was obtained, which is slightly lower than that reported in benzene, 8.9×10^6 M^{-1} s^{-1}.[27]

Quantum Yield for Initial Radical Formation. The efficiency of the initial formation of the pyridyl radical from the reaction of **P1** with excited electron donors was measured using the reaction of ^{1}DCA* with durene (0.05 M) in aerated acetonitrile as actinometer.[23] In each case, 4,4′-dimethoxystilbene (DMS) was used as a monitor (5×10^{-4} M) to intercept the primary radical cation. The concentration of the monitor was increased up to 3.2×10^{-3} M when DCA was used as sensitizer in order to ensure complete interception of $DCA^{\bullet+}$. The quantum yield of the free radical ions from the actinometer is 0.239.[23] Solutions having matched optical densities at the excitation wavelength were irradiated at 400 nm and monitored at 525 nm, where only $DMS^{\bullet+}$ absorbs, with $DCA^{\bullet-}$ being quenched by molecular oxygen present in the aerated solution. The quantum yields for the formation of the donor

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radical cation (and thus for that of the pyridyl radical) were 0.21 for DPA and 0.027 for DCA.

Triplet Yield of Thioxanthone (TX). The quantum yield for intersystem crossing of TX in acetonitrile was measured using, as an actinometer, the energy transfer from triplet benzophenone ($E_T = 69.1$ kcal/mol)[21b] to 1-cyanonaphthalene ($E_T = 57.4$ kcal/mol).[21b] The intersystem-crossing quantum yield for BP in acetonitrile was taken to be 1.0.[21b] Acetonitrile solutions of BP and TX were matched for optical density (0.67) at the excitation wavelength, 363 nm, and an equal amount of 1-cyanonaphthalene (3.4×10^{-3} M) was added to each sample. The solutions were thoroughly purged with argon and the formation of triplet 1-cyanonaphthalene was monitored at 430 nm. An intersystem crossing quantum yield, Φ_{isc}, of 0.88 ± 0.04 was obtained for TX in acetonitrile.

Kinetics of Hydrogen Abstraction from Benzhydrol by MeO$^•$. The methoxy radical was generated by laser excitation (355 nm) of *N*-methoxyphenanthridinium hexaflurophosphate in argon-purged acetonitrile. Cleavage of the N−O bond yields a methoxy radical and phenanthridine radical cation. 1,2-Dimethoxybenzene (0.01 M) was added to intercept the radical cation and remove its absorption between 500 and 700 nm. The rate of hydrogen atom abstraction was determined from the growth of the diphenylketyl radical at 530 nm in the presence of varying concentrations of benzhydrol. A plot of the observed growth rate at 530 nm, k_{obs}, vs [benzhydrol] was linear, and from the slope, a rate constant for hydrogen atom abstraction of 5.8×10^6 M^{-1} s^{-1} was obtained.

Kinetics of Electron Transfer from Diphenylketyl Radical by P1. The ketyl radical was generated in the absence of benzhydrol, as outlined in Scheme 3. Laser excitation (355 nm) of benzophenone (6 mM) in argon-purged acetonitrile in the presence of 1,2,4,5-tetracyanobenzene (TCB), 0.05 M, and benzpinacol, 0.05 M, gave two transient species: TCB$^{•-}$ and $Ph_2C^•$-OH with absorption bands at 465 nm and at 540 nm, respectively. The decay of the ketyl radical was monitored as a function of added **P1**. The slope of a plot of the observed decay rate constant vs [**P1**], Figure 9, corresponds to the bimolecular electron-transfer rate constant from $Ph_2C^•$-OH to **P1** (1.13×10^6 M^{-1} s^{-1}). TCB$^{•-}$ was completely quenched at the lowest concentration of **P1** (0.02 M) because of a much faster (probably diffusion controlled), exothermic electron transfer from TCB$^{•-}$ to **P1**.

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Supporting Information Available: NMR data of the pyridinium salts, figures for the decay of BP$^{•+}$ and TX$^{•+}$ with the concurrent growth of the radical cation of added donors, and spectra of the $Ph_2COH^•$ and TCB$^{•-}$, generated according to Scheme 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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