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Efficient Photoinduced Generation of Radical Cations in Solvents of Medium and Low Polarity

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The electron acceptors and donors most often used in organic photoinduced electron transfer (PET) reactions are neutral molecules, in which case the initially formed intermediates are radical anion/radical cation pairs.¹ Normally, efficient product formation is observed only when diffusive separation competes effectively with return electron transfer within the radical ion pairs.^{1,2} For this reason, PET reactions are usually performed in polar solvents such as acetonitrile, in which the Coulombic barrier to separation is greatly reduced compared to less polar solvents.³

The utility of PET reactions would be considerably extended if separated radical ions could be photochemically generated in nonpolar solvents. For example, it would permit a more direct comparison between PET chemistry and thermal electron transfer chemistry, which is usually performed in lower polarity solvents.⁴ More importantly, it is becoming increasingly clear that polar solvents may react rapidly with radical ions, whereas nonpolar solvents do not.^{2,5}

For these reasons we investigated the possible use of cationic acceptors⁶ as sensitizers in PET reactions in nonpolar solvents.

Table I. Quantum Yields for Formation of Separated Radical Cations in Various Solvents Using *N*-Methylacridinium (MA⁺) Hexafluorophosphate and 2,6,9,10-Tetracyanoanthracene (TCA) as Excited-State Electron Acceptors and the Relative Fluorescence Efficiencies of *N*-Methylacridinium Iodide and Hexafluorophosphate

solvent (ϵ) ^a	biphenyl (TCA) ^b	biphenyl (MA ⁺) ^b	($\Phi_{\text{I}}^{\text{f}}/\Phi_{\text{PF}_6}^{\text{f}}$) ^c
acetonitrile (35.9)	0.18	0.33 (0.33)	0.97
butyronitrile (24.3)	0.17	0.39	0.97
<i>o</i> -dichlorobenzene (9.93)	0.08	0.62	0.47
methylene chloride (8.93)	0.06	0.89 (0.88)	0.64
tetrahydrofuran (7.58)	0.02	0.43 (0.42)	0.23
fluorobenzene (5.42)	0.01	0.52	0.05
chloroform (4.81)	0.01	0.71 (0.75)	0.03
benzene (2.27)		0.34 ^d	

^aStatic dielectric constant at 25 °C. ^bThe ion yields were measured by using the transient absorption method described previously,⁷ except that stilbene, dimethylstilbene, dimethoxystilbene, and tritylamine were all used as monitors for the biphenyl radical cation, to correct for ion formation resulting from reactions of triplet MA⁺ and triplet TCA with the low oxidation potential monitors. The experimental details will be given elsewhere. The numbers in parentheses were measured by using photoacoustic calorimetry from $(1 - \phi_{\text{f}} - \alpha)E_{\text{hv}}/E_{\text{ip}}$, where E_{hv} is the photon energy, ϕ_{f} is the fluorescence quantum yield, and α is the fraction of photon energy released as heat in the photochemical reaction. The radical ion pair energies, $E_{\text{ip}} = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A})$,⁷ were calculated by using the redox potentials determined in acetonitrile and were corrected for triplet MA⁺ formation. The errors in the quantum yields are estimated to be ca. 15%. ^cRelative fluorescence efficiencies of *N*-methylacridinium iodide vs *N*-methylacridinium hexafluorophosphate. ^dThe benzene value was measured by using the more soluble *N*-decylacridinium hexafluorophosphate as the acceptor.

In this case, electron transfer to the excited state of the cationic acceptor from a neutral donor results in the formation of a neutral radical/radical cation pair in which there is no Coulombic barrier to separation. Therefore, the rate constants for separation of these pairs should be much less dependent on solvent polarity. In low-polarity solvents, these sensitizers are expected to benefit from an additional advantage. Because the return electron transfer reactions in the initial ion pairs are often in the Marcus "inverted" region,^{7,8} their rates can be decreased if the reaction reorganization energy can be decreased.⁹ Since most of the reorganization energy is associated with reorientation of the solvent, this can be achieved in less polar solvents.⁹ Described herein are experiments that confirm the utility of these sensitizers in nonpolar solvents.

The sensitizers used in this study were the salts of *N*-methylacridinium (MA⁺) and *N*-decylacridinium (DA⁺) hexafluorophosphate. The use of MA⁺ as an electron-transfer sensitizer

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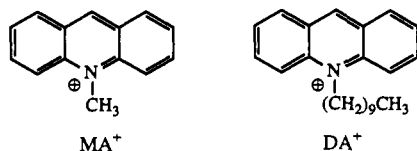
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and the properties of its excited state have been described previously.^{10,11} The transient absorption and photoacoustic techniques described earlier^{7,11} were used to measure the quantum yields for formation of separated radical ions produced upon quenching of the first excited singlet states of these sensitizers by biphenyl in a variety of solvents. Biphenyl was chosen as the electron donor since this compound is often used as a "cosensitizer" in electron-transfer reactions.^{2a,7,12}



Summarized in Table I are the quantum yields measured in solvents of varying polarity using MA⁺ as the sensitizer. Also included for comparison are the corresponding quantum yields for the neutral sensitizer 2,6,9,10-tetracyanoanthracene (TCA), which has a ground-state reduction potential, excited-state energy, and excited-state lifetime that are similar to those of MA⁺.¹¹ The yields of separated radical cations with MA⁺ as the sensitizer are higher than those with TCA in all of the solvents investigated. More importantly, the yields obtained by using MA⁺ are greater in solvents that are less polar than acetonitrile, reaching a value of ca. 0.9 in methylene chloride. Due to its limited solubility, MA⁺PF₆⁻ cannot be used in very nonpolar solvents. To overcome this problem, *N*-decylacridinium (DA⁺) hexafluorophosphate was synthesized.¹³ Remarkably, in benzene, quenching of the first excited singlet state of DA⁺ with biphenyl results in a quantum yield for biphenyl radical cation formation of 0.34.

The increased yields of separated radical cations obtained by using MA⁺ and DA⁺ clearly demonstrate that separation within the initially formed radical/radical cation pairs can indeed compete more effectively with return electron transfer in solvents with polarities lower than that of acetonitrile. Preliminary investigations of the ion yields for two other donors, fluorene and 4,4'-dimethylbiphenyl, in the solvents mentioned in Table I, also indicate that the ion yields decrease with decreasing donor oxidation potential (i.e., in the order biphenyl > fluorene > 4,4'-dimethylbiphenyl), as observed previously for reactions in the inverted region.⁷

Interestingly, the data in Table I reveal that as the solvent polarity becomes very low, the radical cation yields for MA⁺ decrease, in spite of the prediction that return electron transfer should be slowest in these solvents. In the less polar solvents, however, the effects of ion pairing might have to be taken into account. The extent of ion pairing was investigated by comparing the fluorescence efficiencies of MA⁺I⁻ and MA⁺PF₆⁻. In the less polar solvents, the fluorescence of the iodide salt is considerably lower than that of the hexafluorophosphate salt (Table I), which can be attributed to quenching of the excited state of the acridinium cation by iodide when these species are paired.¹⁴ This ion pairing may play a role in decreasing the radical cation quantum yields with decreasing solvent polarity. For example,

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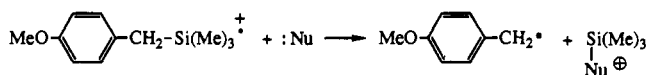
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(13) Prepared by alkylation of acridine with *n*-decyl iodide in refluxing acetonitrile followed by treatment of the resulting *N*-decylacridinium iodide with silver hexafluorophosphate in methanol.

(14) All experiments were performed with <10⁻⁵ M salt; therefore, intermolecular quenching should not be important. The quenching mechanism was not investigated but presumably involves interion electron transfer or heavy atom induced intersystem crossing.^{10a}

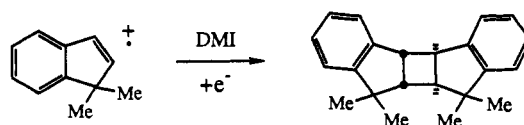
separation of the acridine radical/radical cation pair might require "transfer" of the anion from the sensitizer to the radical cation in the less polar solvents. This transfer step may be a relatively slow process and thus allow return electron transfer to compete with the separation process and thus lower the yield of separated radical ions. In addition, intersystem crossing leading to triplet MA⁺ could also compete with separation of the geminate pair to further decrease the yield of free-radical ions. Preliminary experiments suggest that such intersystem crossing does indeed occur, especially in the low-polarity solvents. A quantitative analysis of these three competing reactions will be reported elsewhere.

The utility of the acridinium ions as sensitizers in time-resolved experiments was next explored. In previous experiments, the radical cation of (*p*-methoxybenzyl)trimethylsilane was generated by pulsed laser photolysis in acetonitrile and was observed to decay by a first-order process.^{5a} On the basis of several lines of evidence, this decay was attributed to a nucleophilic cleavage of the benzylic C-Si bond by acetonitrile. With MA⁺ as the sensitizer, this radical cation can also be generated in high yield in methylene chloride in a pulsed laser experiment. In this solvent, the radical cation



is observed to be much longer lived and decays mainly by second-order recombination with the acridine radical, MA[•]. Upon addition of a sufficient concentration of a nucleophile, the decay becomes pseudo first order, and the second-order rate constants for reaction of several nucleophiles could be obtained in the usual manner.^{5c} The second-order rate constant for reaction of the radical cation with acetonitrile in methylene chloride (5.5 × 10⁵ M⁻¹ s⁻¹) is similar to that estimated in neat acetonitrile (1.2 × 10⁵ M⁻¹ s⁻¹).^{5c} This correspondence of rate constants lends further support to the previously proposed nucleophilic cleavage mechanism.^{5a}

In order to investigate the use of MA⁺ as a sensitizer in steady-state product formation experiments, the MA⁺-sensitized dimerization of 1,1-dimethylindene (DMI) was investigated. Previous studies have shown that, in acetonitrile, the radical cation of DMI gives a head-to-head dimer via a radical cation chain mechanism.^{2a,6b} This same dimer can also be prepared in good yield (80%) in methylene chloride by irradiation of MA⁺ (10⁻² M) and DMI (0.1 M).¹⁵



In summary, the combined experiments described above clearly illustrate the advantages of using *N*-alkylacridinium salts as photosensitizers for producing radical cations in low-polarity solvents. Our results suggest that these sensitizers should dramatically increase the scope and utility of photoinduced electron transfer reactions in general. It seems likely that this methodology could be similarly applied to the photogeneration of radical anions in low-dielectric solvents by the use of anionic excited-state sensitizers.

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Registry No. MA⁺PF₆⁻, 85191-66-8; DA⁺PF₆⁻, 132832-87-2; DMI, 18636-55-0; DMI^{•+}, 91549-06-3; Ph₂, 92-52-4; *p*-MeOC₆H₄CH₂TMS^{•+}, 123621-33-0; H₃CCN, 75-05-8.

(15) Yield measured at 40% conversion of DMI. Dimerization via the triplet state of DMI was ruled out by the observation that the addition of 1.0 M tetrachloroethylene, which adds to the triplet state of DMI,^{6b} did not affect the dimerization.