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Reactivities of Radical Cations: Characterization of Styrene Radical Cations and Measurements of Their Reactivity toward Nucleophiles[1]

L. J. Johnston* and N. P. Schepp

Contribution from the Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada

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Abstract: A variety of substituted styrene radical cations (**2**) have been generated by 266- or 308-nm photoionization of the parent olefin in polar solvents or by electron-transfer quenching of triplet chloranil. The rate constant for decay of most of the radical cations is limited by a combination of nucleophilic addition of solvent and addition to the parent olefin. The latter rate constants are in the range of 10^9 M^{-1} s^{-1} for most of the radical cations without β-methyl substitutents. The reactivity of styrene radical cations toward nucleophiles such as alcohols, azide, and halides has also been examined. In acetonitrile or trifluoroethanol, azide, chloride, and bromide react with approximately diffusion-controlled rate constants ($\sim 10^{10}$ M^{-1} s^{-1}). However, the rate constants for addition of methanol and other alcohols are substantially slower and show the expected steric and electronic effects with variations in para-substituents, methyl substitution of the olefin, or modification of the alcohol structure. Transient absorption spectra demonstrate that the reaction with alcohols and halide ions involves addition to the β-position to generate the corresponding benzylic radical, in agreement with literature product studies for some of these systems. There is no evidence for competing electron transfer in cases where this would be exoergonic. Although the selectivity of anionic nucleophiles toward styrene radical cations is low in acetonitrile or water, most of these nucleophiles react much less rapidly in 4:1 aqueous acetonitrile. In some cases, decreases of 4 orders of magnitude are observed. The results agree well with data for nucleophilic addition to carbocations and are attributed to hydrogen-bonding of the nucleophile in the aqueous solvents.

Introduction

The wide-spread importance of photoinduced electron-transfer reactions in organic chemistry is well-recognized, and there have been extensive studies of the primary electron-transfer step.[2] As a result, the factors that determine the efficiency of electron-transfer reactions are now reasonably well-understood. In many cases it is possible to maximize reaction efficiencies by controlling the competition between the energy-wasting back electron transfer to regenerate ground-state reactants and either cage escape or incage reaction of the radical ions.[3] However, very little information is currently available on the dynamics of the radical ions produced by the initial electron transfer, despite the fact that their potential utility in synthetic strategies is now beginning to be exploited.[4] Radical cations are known to undergo a variety of reactions such as addition of nucleophiles, electron transfer, carbon–carbon bond cleavage, and deprotonation. Recent time-resolved studies have provided some absolute rate data for carbon–carbon and carbon–heteratom bond cleavage and deprotonation reactions of these species.[5,6] A few rate constants for additions of nucleophiles to radical cations have also been measured by either laser flash photolysis or electrochemical techniques.[7,8] However, the factors that control the competition between several possible reaction pathways are not well-understood at this time.

There have been several recent reports on the development and calibration of radical cation probes that can be used as radical cation clocks.[6,9] This approach has been widely used in free radical chemistry and involves the competition between an intramolecular reaction for which the rate is well-established and an intermolecular reaction.[10] Obviously, the successful development of similar radical cation clocks requires the calibration of a number of intermolecular and intramolecular reactions of radical cations.

We have undertaken a systematic study of the reactivity of a series of aryl olefin radical cations toward anionic, alcohol, and olefin nucleophiles using laser flash photolysis. Mechanistic and product studies have been carried out for electron-transfer reactions of a variety of aryl olefin radical cations.[11,12] These studies have demonstrated the importance of addition of nucleophiles such as solvent, of addition of the radical cation to the precursor olefin to give a dimer radical cation, and of deprotonation, isomerization, and electron-transfer reactions in deter-

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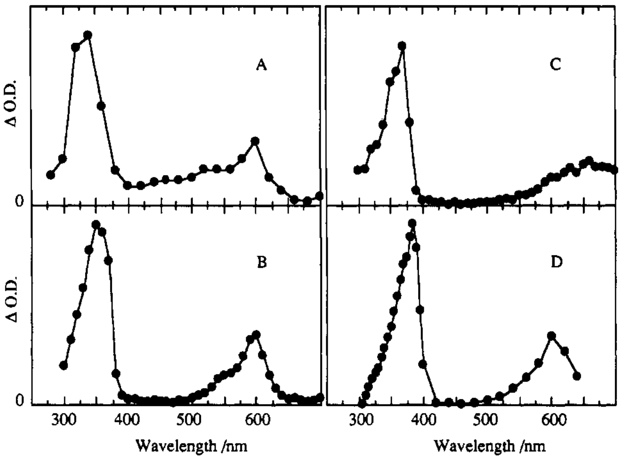
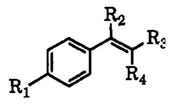


Figure 1. Absorption spectra of transients generated upon 266-nm irradiation of styrene (A) in TFE and 4-methoxystyrene (B), α-methyl-4-methoxystyrene (C), and β-methyl-4-methoxystyrene (D) in 4:1 water:acetonitrile.

mining the final product distributions. Our initial studies have focused on the reactivity of substituted styrene radical cations toward a variety of anionic nucleophiles and alcohols. These radical cations are readily generated for laser flash photolysis studies by using either photoionization or photosensitization techniques. Further, styrene provides a system in which it is straightforward to change substituents on either the aromatic ring or the double bond in order to assess the relative importance of steric and electronic effects in determining the reactivity of the radical cation.

Results

Characterization of Styrene Radical Cations. Excitation (266 nm) of aerated samples of the substituted styrenes **1a–g** in neat 2,2,2-trifluoroethanol (TFE) and **1h–j** in acetonitrile or 1:4 acetonitrile:water gave transients with two absorption bands, one in the UV at wavelengths ranging from 350 to 380 nm and the other in the visible near 600–680 nm. In each case, the two absorption bands decayed with the same first-order kinetics, indicating that both bands belong to one short-lived species. Representative transient absorption spectra are shown in Figure 1 for the transients produced by laser irradiation of styrene **1a** and the 4-methoxy-substituted styrenes **1h–j**; the absorption bands of the transients generated from all the substituted styrenes **1a–j** are summarized in Table I.

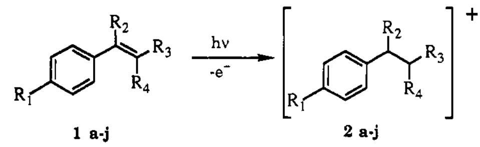


1a $R_1 = H; R_2 = H; R_3 = H; R_4 = H$
b $R_1 = H; R_2 = CH_3; R_3 = H; R_4 = H$
c $R_1 = H; R_2 = H; R_3 = CH_3; R_4 = H$
d $R_1 = H; R_2 = H; R_3 = CH_3; R_4 = CH_3$
e $R_1 = F; R_2 = H; R_3 = H; R_4 = H$
f $R_1 = CH_3; R_2 = H; R_3 = H; R_4 = H$
g $R_1 = CH_3; R_2 = CH_3; R_3 = H; R_4 = H$
h $R_1 = OCH_3; R_2 = H; R_3 = H; R_4 = H$
i $R_1 = OCH_3; R_2 = CH_3; R_3 = H; R_4 = H$
j $R_1 = OCH_3; R_2 = H; R_3 = CH_3; R_4 = H$

Table I. Absorption Maxima of Substituted Styrene Radical Cations **2a–j** Generated by 266-nm Laser Irradiation of the Corresponding Styrenes **1a–j** in TFE or 1:4 Acetonitrile:Water

radical cation	absorption maxima/nm	radical cation	absorption maxima/nm
2a	350, 600^a	**2f**	360, 600^a
2b	350, 650^a	**2g**	370, 670^a
2c	355, 370, 590^a	**2h**	350, 600^b
2d	380, 590^a	**2i**	370, 660^b
2e	350, 585^a	**2j**	380, 600^b

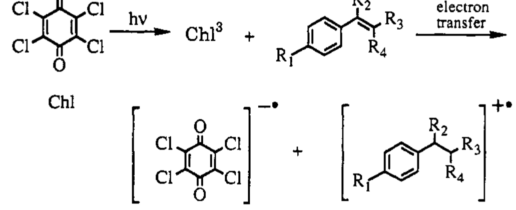
^{a} Measured in TFE. ^{b} Measured in 4:1 water:acetonitrile.



(1)

The transients are identified as the radical cations **2a–j**, eq 1, generated by photoionization of the corresponding styrenes **1a–j**. For radical cations **2a–c**, this identification is based on the close similarity between the spectra generated by photolysis of styrenes **1a–c** and the spectra of the same radical cations generated from the corresponding styrenes by pulse radiolysis in a glassy Freon matrix at 77 K[13] or by photoionization in a solid argon matrix at 20 K.[14] Similar comparisons are not available for the transients generated from styrenes **1d–j**. However, the spectra of these transients have absorption bands in regions similar to those for radical cations **2a–c**, and it is reasonable to conclude that the transient species produced by 266-nm laser irradiation of styrenes **1d–j** are the radical cations **2d–j**.

Experiments in which the styrene radical cations were generated by electron transfer from the styrene to triplet excited chloranil, eq 2, support these assignments. Selective excitation of chloranil with 355-nm laser light generates triplet chloranil ($\lambda_{max} = 530$ nm)[15] that is completely quenched by the addition of ca. 0.001 M 4-methoxystyrene. The resulting transient absorption spectrum consists of two visible bands, as shown in Figure 2. The band at ~450 nm is due to the chloranil radical anion[16] formed by electron transfer from the styrene to the triplet. The 600-nm band is due to the formation of the 4-methoxystyrene radical cation; this band is identical to that observed upon direct 266-nm irradiation of 4-methoxystyrene, thus confirming that the radical cation is formed by direct irradiation. In the triplet-sensitized experiment the styrene radical cation decays more rapidly than the chloranil radical anion (Figure 2). Under these conditions the radical cation decay is determined primarily by reaction with the parent olefin, as discussed in more detail in the following section, rather than by back electron transfer with the chloranil radical anion.



(2)

The yield of radical cation generated by direct 266-nm irradiation was measured as a function of laser dose to determine if the radical cations are produced in a one-photon or a multiphoton process. The results are presented in Figure 3. It is clear that there is a nonlinear dependence between the laser dose and the initial absorbance of the 4-methoxystyrene radical cation at both 360 and 600 nm immediately after the laser pulse, indicating that radical cation formation is not monophotonic.[17] When the radical cation absorption is plotted against the square of the laser dose

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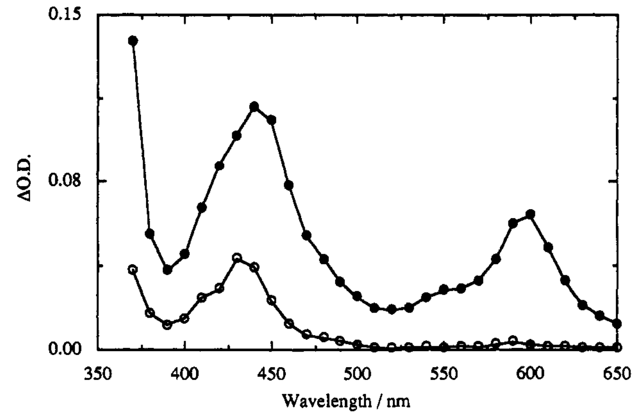


Figure 2. Transient absorption spectra generated upon 355-nm irradiation of chloranil (3×10^{-4} M) in acetonitrile with 0.001 M 4-methoxystyrene. Spectra were recorded immediately after the laser pulse (●) and 50 μs after the laser pulse (○).

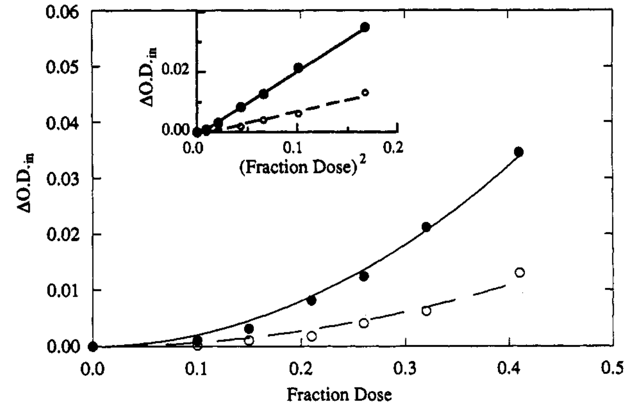
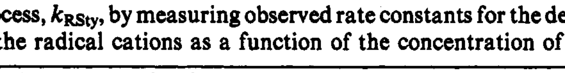


Figure 3. Magnitude of the initial absorption at 360 nm (●) and 600 nm (○) immediately after 266-nm laser irradiation of 4-methoxystyrene in 4:1 water:acetonitrile as a function of the laser dose. The inset shows the same data plotted against the square of the laser dose.

(Figure 3, insert), a linear relationship is obtained. This leads to the conclusion that radical cation formation by photoionization of the styrene derivatives is a two-photon process.

Kinetics for the Decay of Styrene Radical Cations. All of the radical cations **2a–j** decayed in a first-order manner in aerated solvents. The observed rate constant for the decay of each radical cation was independent of oxygen concentration, except for the β-methyl-4-methoxystyrene radical cation **2j**. In this case the radical cation decayed with first-order kinetics in aerated acetonitrile but in a second-order manner in nitrogen-saturated solution, indicating that it does react with oxygen. Using the observed rate constant for decay of **2j** in aerated acetonitrile, $k = 4 \times 10^4\ s^{-1}$, and the known oxygen concentration for this solvent, we calculate a rate constant for oxygen quenching of $2.3 \times 10^7\ M^{-1}\ s^{-1}$. This agrees well with an earlier estimate based on product studies by Lewis and co-workers.[18]

Aryl olefin radical cations are well known to add to the precursor styrene to produce either cyclic or acyclic radical cation "dimers", eq 3.[11,18–20] We were able to determine rate constants for this



(3)

process, k_{RSty}, by measuring observed rate constants for the decay of the radical cations as a function of the concentration of the precursor styrene. As shown in Figure 4, the observed rate constants for decay of the 4-methoxystyrene radical cation increased in a linear manner with increasing styrene concentration according to eq 4. The slope of this plot leads to a second-order

$$k_{obs} = k_0 + k_{RSty}[RSty] \qquad (4)$$

rate constant for the addition reaction of $k_{RSty} = 1.0 \times 10^9\ M^{-1}\ s^{-1}$. Rate constants for addition of some of the other radical cations to their precursor styrenes were measured in the same way, and these are summarized in Table II.

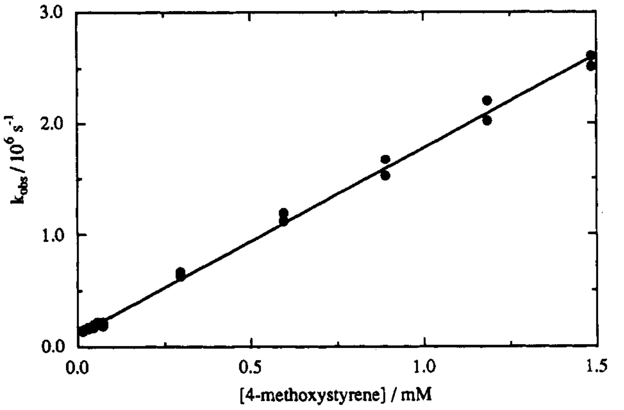


Figure 4. Relationship between the observed rate constant for the decay of the 4-methoxystyrene radical cation at 600 nm and the concentration of 4-methoxystyrene in 4:1 water:acetonitrile.

Table II. Rate Constants for the Reaction of Styrene Radical Cations **2a–j** with Solvent (k_0) and Precursor Styrene (k_{RSty}) in TFE, Acetonitrile (AcN), or 4:1 Water:Acetonitrile (H_2O/AcN)

radical cation	solvent	k_0/s^{-1}	$k_{RSty}/M^{-1}\ s^{-1}$
2a	TFE	2.5×10^7	
2b	TFE	1.2×10^7	
2c	TFE	$(2.2 \pm 0.1) \times 10^5$	$(1.4 \pm 0.1) \times 10^9$
2d	TFE	1.2×10^5	$<1 \times 10^8$
2e	TFE	6.0×10^6	
2f	TFE	$(3.4 \pm 0.3) \times 10^5$	$(2.9 \pm 0.2) \times 10^9$
2g	TFE	$(4.4 \pm 0.2) \times 10^5$	$(1.9 \pm 0.2) \times 10^9$
2h	H_2O/AcN	$(1.1 \pm 0.2) \times 10^5$	$(1.7 \pm 0.1) \times 10^9$
	AcN	$(1.3 \pm 0.3) \times 10^5$	$(1.1 \pm 0.1) \times 10^9$
2i	H_2O/AcN	$(4.0 \pm 0.2) \times 10^5$	$(2.1 \pm 0.1) \times 10^9$
	AcN	$(4.2 \pm 0.4) \times 10^5$	$(2.0 \pm 0.2) \times 10^9$
2j	AcN	4×10^4 [a]	$<1 \times 10^8$

[a] Observed rate constant for reaction with oxygen in aerated acetonitrile.

According to eq 4, the intercept, k_0, of the plot shown in Figure 4 represents the rate constant for decay of the radical cation in the absence of styrene precursor and can be used as a measure of the observed rate constant for reaction with solvent. The solvent rate constants for most of the substituted styrene radical cations were determined in this way and are summarized in Table II. The decay of the radical cations of styrene (**2a**), α-methylstyrene (**2b**), β,β-dimethylstyrene (**2d**), and 4-fluorostyrene (**2e**) did not depend on the concentration of the precursor styrenes up to ca. 0.001 M, an upper limit in our experiments due to the strong absorption of the precursor styrenes at the laser irradiation wavelength of 266 nm. The rate constants for reaction of these radical cations with solvent were therefore simply evaluated from the observed first-order decay. Presumably, the short-lived 4-fluorostyrene, α-methylstyrene, and styrene radical cations react with solvent too rapidly for addition of the styrene precursor to compete successfully, even though addition for these three radical cations may take place with rate constants greater than $10^9\ M^{-1}\ s^{-1}$. On the other hand, the fact that addition to the styrene precursor is not observed for the β,β-dimethylstyrene radical cation, which decays with a rate constant of $1.2 \times 10^5\ s^{-1}$ in

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Table III. Second-Order Rate Constants, k_{Nu}, for the Addition of Nucleophiles to Radical Cations **2a–j** (All rate constants are for reaction in TFE unless otherwise noted.)

radical cation	k_{Nu}—$M^{-1}\ s^{-1}$			
	N_3^-	Br^-	Cl^-	MeOH
2a	$(1.4 \pm 0.1) \times 10^{10}$	$(1.1 \pm 0.1) \times 10^{10}$	$(9.4 \pm 0.4) \times 10^{9}$	$(1.8 \pm 0.1) \times 10^{8}$
2b	$(1.2 \pm 0.1) \times 10^{10}$	$(1.0 \pm 0.1) \times 10^{10}$	$(9.5 \pm 0.4) \times 10^{9}$	$(1.9 \pm 0.1) \times 10^{8}$
2c	$(1.1 \pm 0.1) \times 10^{10}$	$(1.0 \pm 0.1) \times 10^{10}$	$(6.0 \pm 0.4) \times 10^{9}$	$(9.7 \pm 1.1) \times 10^{6}$
2d	$(7.9 \pm 1.2) \times 10^{9}$		$(8.0 \pm 0.5) \times 10^{7}$	$(2.0 \pm 0.4) \times 10^{5}$
2e	$(1.3 \pm 0.3) \times 10^{10}$	$(1.0 \pm 0.1) \times 10^{10}$	$(9.8 \pm 0.8) \times 10^{9}$	$(5.1 \pm 0.1) \times 10^{7}$
2f	$(1.0 \pm 0.1) \times 10^{10}$	$(1.3 \pm 0.1) \times 10^{10}$	$(8.9 \pm 0.4) \times 10^{9}$	$(5.9 \pm 0.8) \times 10^{6}$
2g	$(1.1 \pm 0.2) \times 10^{10}$	$(8.2 \pm 1.2) \times 10^{9}$		$(5.6 \pm 0.8) \times 10^{6}$
2h	$(1.2 \pm 0.1) \times 10^{10}$ [a]	$(2.2 \pm 0.1) \times 10^{6}$ [a]	$(6.4 \pm 0.4) \times 10^{6}$ [a]	$(3.0 \pm 0.5) \times 10^{4}$ [a]
	$(4.2 \pm 0.5) \times 10^{10}$ [b]	$(4.0 \pm 0.5) \times 10^{10}$ [b]	$(3.0 \pm 0.2) \times 10^{10}$ [b]	
2i	$(8.0 \pm 0.5) \times 10^{9}$ [a]			
	$(4.0 \pm 0.2) \times 10^{10}$ [b]	$(3.2 \pm 0.2) \times 10^{10}$ [b]		
2j	$(9.7 \pm 0.4) \times 10^{9}$ [a]			
	$(2.9 \pm 0.2) \times 10^{10}$ [b]	$(3.0 \pm 0.3) \times 10^{10}$ [b]		

[a] In 4:1 water:acetonitrile. [b] In neat acetonitrile.

Table IV. Second-Order Rate Constants, k_{ROH}, for the Reaction of β-Methylstyrene (**2c**) and 4-Methylstyrene (**2f**) Radical Cations with Methanol, Ethanol, 2-Propanol, and *tert*-butyl Alcohol in TFE

radical cation	$k_{ROH}/M^{-1}\ s^{-1}$			
	MeOH	EtOH	2-PrOH	*t*BuOH
2c	$(1.1 \pm 0.2) \times 10^{7}$	$(4.3 \pm 0.1) \times 10^{6}$	$(2.1 \pm 0.3) \times 10^{6}$	$(1.0 \pm 0.1) \times 10^{6}$
2f	$(5.9 \pm 0.8) \times 10^{6}$	$(3.6 \pm 0.3) \times 10^{6}$	$(3.0 \pm 0.1) \times 10^{6}$	$(1.8 \pm 0.1) \times 10^{6}$

aerated TFE, indicates that addition to the styrene precursor takes place with a rate constant considerably less than $1 \times 10^8\ M^{-1}\ s^{-1}$. The rate constant for the decay of the β-methyl-4-methoxystyrene radical cation was also independent of the precursor olefin concentration up to 0.001 M, again indicating that the rate constant for addition is less than $1 \times 10^8\ M^{-1}\ s^{-1}$. This result is in agreement with an estimate of the rate constant for dimerization of ca. $2 \times 10^6\ M^{-1}\ s^{-1}$ for β-methyl-4-methoxystyrene radical cation.[18]

The data in Table II show that the observed rate constants for the three 4-methoxy-substituted styrene radical cations (**2h–j**) were measured in acetonitrile or 4:1 water:acetonitrile, while the others were measured in TFE. TFE is not a suitable solvent in which to generate the 4-methoxystyrene and α-methyl-4-methoxystyrene radical cations because photoprotonation to give the corresponding 4-methoxyphenethyl cations[21,22] dominates over photoionization. It should be noted that some carbocation formation may also occur in aqueous acetonitrile; however, in this solvent, the 4-methoxyphenethyl cations would decay too rapidly to be observed with nanosecond flash photolysis equipment.[22]

The phenethyl cations that may be formed upon 266-nm irradiation of styrenes **1a–f** are too reactive to be observed in TFE,[22] and the radical cations are the only detectable transients. In aqueous acetonitrile or neat acetonitrile, no transients were detected by nanosecond flash photolysis of styrenes **1a–f**, suggesting that in these solvents, the radical cations **2a–f** are too short-lived to be observed. This was confirmed by picosecond transient absorption experiments in which we were able to generate the 4-methylstyrene radical cation in aqueous acetonitrile. The 3.4-ns lifetime measured in this solvent is considerably shorter than is accessible by nanosecond flash photolysis.

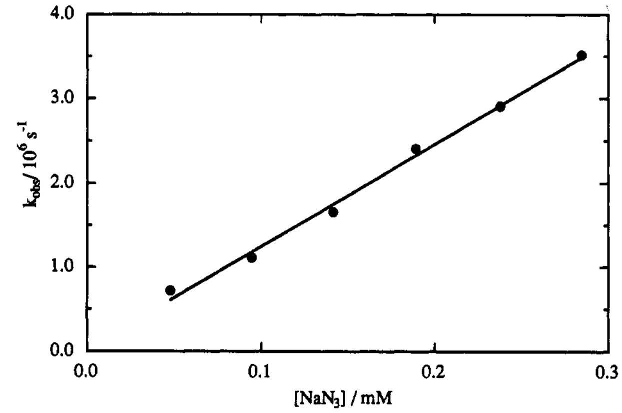

Figure 5. Relationship between the observed rate constant for the decay of the 4-methoxystyrene radical cation at 600 nm and sodium azide concentration in 4:1 water:acetonitrile.

Reaction of Styrene Radical Cations with Nucleophiles. Rate constants for the decay of the radical cations increased significantly upon the addition of a variety of anionic nucleophiles, such as azide, bromide, and chloride, and nucleophilic alcohols. Observed rate constants for the decay of the radical cations (k_{obs}) were found to increase in a linear fashion with increasing nucleophile concentration according to eq 5.

$$k_{obs} = k_0 + k_{Nu}[Nu] \qquad (5)$$

A typical plot is shown in Figure 5 for the quenching of the 4-methylstyrene radical cation with azide ion in TFE. The slope of this plot gives the second-order rate constant, $k_{Az} = 1.0 \times 10^{10}\ M^{-1}\ s^{-1}$. Second-order rate constants for the reaction of all the styrene radical cations with a variety of nucleophiles were determined in the same way and are summarized in Table III. Rate constants for quenching of the β-methylstyrene and 4-methylstyrene radical cations with a series of alcohols and for reaction of 4-methoxystyrene and β-methyl-4-methoxystyrene radical cations with a larger series of anionic nucleophiles and methanol are shown in Tables IV and V, respectively.

Complete quenching with methanol of the β-methylstyrene, 4-methylstyrene, and styrene radical cations in nitrogen-saturated TFE leads to transient species with absorption bands near 305–310 and 315–320 nm, Figures 6A–C, open circles. These species are readily identified as the 2-methoxy-1-arylethyl radicals **3** formed by addition of methanol to the β-position of the radical cations, eq 6, by comparison with the absorption and kinetic characteristics of similar benzyl and phenethyl radicals.[23] For example, the 2-hydroxy-1-phenylethyl radical produced by pulse

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Table V. Second-Order Rate Constants, k_{Nu}, for the Reaction of 4-Methoxystyrene (**2h**) and β-Methyl-4-methoxystyrene (**2j**) Radical Cations with Various Nucleophiles in 4:1 Water:Acetonitrile (H_2O/AcN) or Neat Acetonitrile (AcN)

	k_{Nu}/M^{-1} s^{-1}			
	2h		**2j**	
nucleophile	H_2O/AcN	AcN	H_2O/AcN	AcN
N_3^-	$(1.2 \pm 0.1) \times 10^{10}$	$(4.2 \pm 0.5) \times 10^{10}$	$(9.7 \pm 0.4) \times 10^{9}$	$(2.9 \pm 0.2) \times 10^{10}$
CN^-	$(1.0 \pm 0.1) \times 10^{8}$	$(2.9 \pm 0.1) \times 10^{10}$	$(1.9 \pm 0.1) \times 10^{7}$	$(1.4 \pm 0.1) \times 10^{10}$
HO^-	$(5.3 \pm 0.2) \times 10^{7}$	$(2.3 \pm 0.1) \times 10^{10}$	$(1.2 \pm 0.1) \times 10^{7}$	$(2.0 \pm 0.3) \times 10^{10}$
Cl^-	$(6.4 \pm 0.4) \times 10^{6}$	$(3.0 \pm 0.2) \times 10^{10}$	*a*	$(3.2 \pm 0.2) \times 10^{10}$
$CH_3CO_2^-$	$(2.6 \pm 0.4) \times 10^{6}$	$(4.0 \pm 0.6) \times 10^{10}$	$(7.2 \pm 0.1) \times 10^{5}$	$(1.5 \pm 0.1) \times 10^{10}$
Br^-	$(2.2 \pm 0.1) \times 10^{6}$	$(4.0 \pm 0.5) \times 10^{10}$	*a*	$(3.0 \pm 0.3) \times 10^{10}$
$CF_3CO_2^-$	$(1.6 \pm 0.1) \times 10^{6}$	*b*	$(3.5 \pm 0.4) \times 10^{5}$	*b*
MeOH	$(3.0 \pm 0.5) \times 10^{4}$	*b*	*a*	*b*
NO_3^-	*a*	$(2.4 \pm 0.2) \times 10^{9}$	*a*	$(2.2 \pm 0.2) \times 10^{9}$

[a] No rate acceleration was observed for up to 1.0 M nucleophile. [b] Not measured.

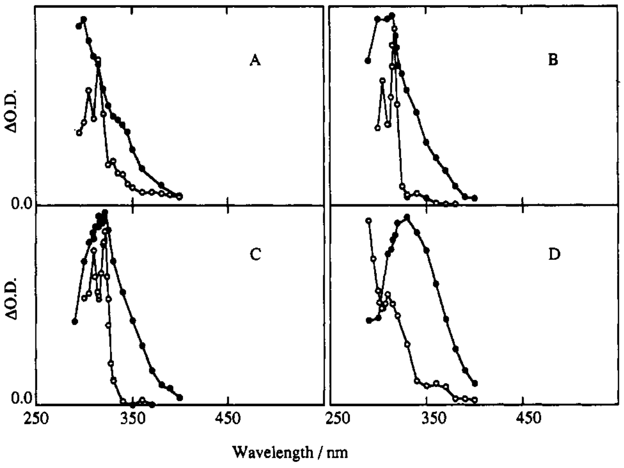
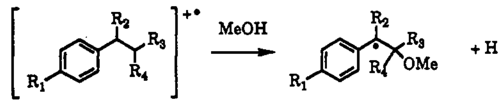


Figure 6. Absorption spectra of the radicals produced by addition of methanol (○) and bromide ion (●) to: (A) styrene radical cation in nitrogen-saturated TFE; (B) β-methylstyrene radical cation in nitrogen-saturated TFE; (C) 4-methylstyrene radical cation in nitrogen-saturated TFE, and (D) 4-methoxystyrene radical cation in nitrogen-saturated acetonitrile.



(6)

2 3

radiolysis of styrene in aqueous solution has absorption maxima at 305 and 315 nm[24] similar to those observed for the transient produced by reaction of methanol with the styrene radical cation. This identification is also supported by observations that the transients decay in a second-order manner and are quenched by the addition of oxygen, kinetic behavior that is typical of carbon-centered radicals. The much broader absorption band of the transient produced by addition of methanol to the 4-methoxystyrene radical cation (Figure 6D, open circles) is consistent with the effect of 4-methoxy groups on the spectra of benzyl radicals.[25] Spectra consistent with β-substituted phenethyl radicals were also observed upon reaction of various styrene radical cations with chloride ion in acetonitrile and TFE and azide ion in TFE.

The addition of bromide ion to the same radical cations is expected to give the β-bromo radicals **4**, eq 7. A transient species that is quenched by oxygen and decays with second-order kinetics typical for radicals is produced upon reaction of the radical cations with bromide, but the absorption bands for these species are considerably broadened and shifted relative to the corresponding 2-methoxy-1-arylethyl radicals, Figure 6 (filled circles). The absorption shift is particularly significant for the 1-(4-methoxyphenyl)ethyl radical, which shifts from 310 to 335 nm upon replacing the 2-methoxy group with a bromo group. To confirm our assignments of the transients, we generated the same β-bromo radicals by photohomolysis of substituted 1,2-dibromo-1-phenylethane derivatives **5**, eq 8. As shown in Figure 7A, the β-bromo radical (filled circles) produced by laser photolysis of 1,2-dibromo-1-(4-methylphenyl)ethane in nitrogen-saturated acetonitrile has

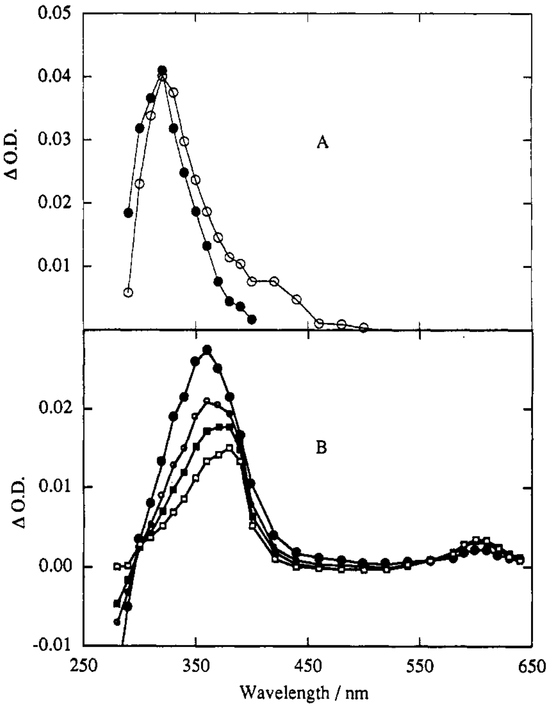
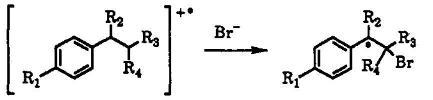
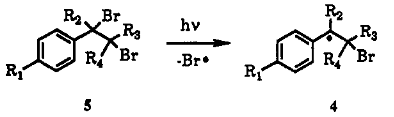


Figure 7. (A) Absorption spectra of 2-bromo-1-(4-methylphenyl)-1-ethyl radical produced by 266-nm laser irradiation of 1,2-dibromo-1-(4-methylphenyl)ethane (●) and by quenching of the 4-methylstyrene radical cation with bromide (○) in nitrogen-saturated acetonitrile. (B) Time-dependent absorption changes produced upon 266-nm irradiation of 1,2-dibromo-1-(4-methoxyphenyl)propane in nitrogen-saturated acetonitrile. Spectra were recorded 500 ns (●), 1.6 μs (○), 3.2 μs (■), and 6 μs (□) after the laser pulse.



(7)

2 4



(8)

5 4

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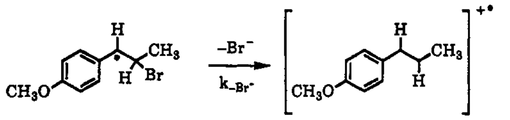
the same absorption spectrum as the product from the addition of bromide ion to the β-position of radical cation **2f** (open circles). Reasonably good agreement was also observed between the spectra obtained by photolysis of 1,2-dibromo-1-phenylethane and 1,2-dibromo-1-(4-methoxyphenyl)ethane and the radicals produced by quenching of the corresponding radical cations by bromide ion.

Photolysis of 1-(4-methoxyphenyl)-1,2-dibromopropane in nitrogen-saturated acetonitrile also gave a β-bromo radical (Figure 7B) with an absorption spectrum very similar to that produced by addition of bromide to the radical cation of β-methyl-4-methoxystyrene. As the β-bromo radical decays, it gives rise to the formation of a new transient that had not been observed from the three other β-bromo radicals. This species is identified from its absorption spectrum, Figure 7B, open squares, as the β-methyl-4-methoxystyrene radical cation generated by elimination of bromide ion from the β-bromo radical, eq 9. The radical cation is not observed in oxygen-saturated acetonitrile, indicating that only in the absence of oxygen is the formation of the radical cation sufficiently rapid to be competitive with other decay processes of the radical.

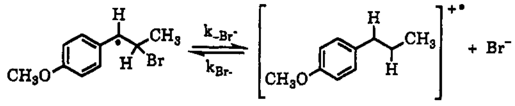


(9)

The formation of the radical cation was a first-order process that took place with a rate constant of $5.8 \times 10^5\ \text{s}^{-1}$. Assuming that loss of bromide is the only decay mode for the radical, this rate constant is equal to $k_{-\text{Br}^-}$. Using the relation shown in eq 10,

$$K_{\text{dis}} = \frac{k_{-\text{Br}^-}}{k_{\text{Br}^-}} \qquad (10)$$

the value of k_{Br^-} can be combined with the measured rate constant for the addition of bromide ion to the radical cation, $k_{\text{Br}^-} = 2.9 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$, to give the experimentally measured dissociation constant, $K_{\text{dis}} = 2 \times 10^{-4}$ M, for the equilibrium shown in eq 11.



(11)

Discussion

Styrene radical cations (**2a–j**) are readily generated by photoionization of the parent olefin in polar solvents such as acetonitrile or TFE. Dose dependence plots indicate that ejection of an electron is a biphotonic process, presumably via the first excited singlet state. Absorption of a second photon by the triplet state is unlikely with the 10-ns laser pulse used in our experiments, given that most singlet styrenes have lifetimes (2–14 ns)[26] that are comparable to the laser pulse width. Further, the production of the 4-methylstyrene radical cation using a picosecond laser pulse cannot possibly involve the intermediacy of triplet styrene. Although styrene radical cations can also be readily generated by electron-transfer quenching of a sensitizer such as triplet chloranil, photoionization is the method of choice for these particular experiments since it allows the use of relatively low concentrations of the precursor olefin and eliminates complications associated with addition of the radical cation to the precursor.

The decay of some of the styrene radical cations is controlled by a competition between nucleophilic addition of solvent and addition to the precursor styrene. The reaction with either water or alcohol as solvent is presumed to occur via addition to the β-position to give a benzylic radical, as discussed in more detail below for methanol and various anionic nucleophiles. In the case of acetonitrile, addition to solvent can give a nitrilium ion that will react with water to give an acetamide product, as observed for diarylmethyl carbocations.[27] In several cases (styrene, 4-fluorostyrene, and α-methylstyrene), the rate constants for solvent addition are sufficiently fast that reaction with the precursor olefin cannot compete under our experimental conditions and it is, therefore, not possible to measure the rate of addition of the radical cation to the styrene. For the other radical cations the addition rate constants are in the range of $10^9\ \text{M}^{-1}\ \text{s}^{-1}$, except for β,β-dimethylstyrene and β-methyl-4-methoxystyrene, for which we were only able to estimate an upper limit of $<1 \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$. These results are consistent with the fact that electron-transfer dimerization is known to result in addition to the β-position to give cyclobutane dimers for a variety of styrenes.[18–20,28] A rate constant of $\sim 2 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$ has been estimated from steady-state product studies for β-methyl-4-methoxystyrene.[18] The rate constants in Table II are also substantially faster than those for electron-transfer dimerization of stilbene ($2 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$), as expected on the basis of steric effects.[29]

It is not straightforward to draw conclusions from the data on the rates of addition of the radical cations to the parent styrenes since in all cases both the radical cation and the olefin are changing at the same time. The relative steric and electronic effects in these reactions could obviously be better established by studying the addition of a particular radical cation to a series of olefins. These experiments, as well as a more detailed study of the intermediates involved in the styrene radical cation/olefin additions, will be reported separately.[30]

Rate constants for addition of several anionic nucleophiles (azide, chloride, bromide) and alcohols have been measured for a variety of substituted styrene radical cations and are summarized in Tables III and IV. The rates of azide addition are all close to the diffusion-controlled limit and show little selectivity, with the possible exception of the β,β-dimethyl derivative **2b**, which has a slightly slower rate constant ($7.9 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$). Similarly, the rate constants for addition of bromide or chloride ions in either acetonitrile or TFE are all $(1.0 \pm 0.2) \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$, except for reaction of β-methylstyrene and β,β-dimethylstyrene radical cations with chloride (6×10^9 and $8 \times 10^7\ \text{M}^{-1}\ \text{s}^{-1}$, respectively).

The effects of changing the substituents on both the aromatic ring and the olefin are more clearly illustrated by the rate constants for addition of methanol since these are all substantially slower than the diffusion-controlled limit. For example, the rate constants for methanol addition decrease in the order $\text{H} > \text{F} > \text{CH}_3 > \text{OCH}_3$ for para substituents with the parent styrene radical cation being almost 4 orders of magnitude more reactive than the 4-methoxy-substituted analogue (Table III). Marked changes in reactivity are also observed upon methyl substitution of the olefin. Although an α-methyl group has essentially no effect on the rate constant for reaction with methanol, substitution of one or two methyls at the β-position leads to 19- and 900-fold decreases in reactivity, respectively. Estimates of 9.6×10^6 and $1.6 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$ for the rate constants for addition of methanol to 1,1-dimethylindene and 1,1-diphenylethylene radical cations are available from earlier steady-state photolysis experiments.[31,32] The rate constant for dimethylindene is in excellent agreement with our measured rate constant of $9.7 \times 10^6\ \text{M}^{-1}\ \text{s}^{-1}$ for addition of methanol to β-methylstyrene radical cation.

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The above results on the variation of radical cation reactivity as a function of the substitution pattern of the olefin are consistent with addition of methanol to the β-position of the olefin to give a stable benzylic radical as the product. This is also in agreement with results of product studies for nucleophile addition in these and related systems.[11,12,31–35] Transient absorption spectra measured in the presence of sufficient methanol to quench >95% of the radical cations further confirmed the production of substituted benzyl radicals as the products in the methanol additions. Spectra for selected examples are shown in Figure 6. In each case the spectrum shows one or two sharp maxima in the 305–320-nm region, as expected for a benzyl radical.[23] The transients are also quenched by oxygen, again as expected for a free radical intermediate. Benzylic radical intermediates are also observed when the styrene radical cations are quenched with chloride ion.

Transient absorption spectra measured after quenching of the styrene radical cations with bromide ion also indicated the formation of a long-lived, oxygen quenchable intermediate absorbing in the 300–350-nm region (Figure 6). However, in this case the spectra are considerably broader than those typically observed for benzylic radicals. Initially we considered the possibility that the observed transient was $Br_2^{\bullet-}$ formed via initial electron transfer to give styrene plus a bromine atom that was then scavenged by excess bromide ion in solution.[36] Note that such an electron transfer is exergonic for some of the radical cations. However, this possibility can be eliminated on the basis of the fact that different spectra are obtained when the various radical cations are quenched by bromide. We were able to confirm that the transients produced in these reactions were the substituted β-bromobenzyl radicals by generating the same intermediates by photohomolysis of substituted 1,2-dibromo-1-phenylethanes. This demonstrated that the β-bromo-substituted radicals are indeed the products of bromide addition to the radical cations and that these radicals have substantially broader spectra than the β-methoxy or β-chloro analogs.

The β-bromo radical generated by photohomolysis of 1,2-dibromo-1-(4-methoxyphenyl)propane decays at least partly to give the β-methyl-4-methoxystyrene radical cation which is readily identifiable by its characteristic absorptions at 360 and 600 nm. A combination of the rate constant for bromide addition to the radical cation and the rate constant for growth of the radical cation from the β-bromo radical allows us to estimate an equilibrium constant of 2×10^{-4} M for reaction 11. There is some literature precedence for reversible addition of bromide ion to radical cations.[8,37] For example, bromide ion has been suggested to add reversibly to dioxole radical cations, although in this case the loss of bromide ion from the radical is estimated to be much more rapid ($\geq 10^9$ s^{-1}).[8] It is also possible that the apparent loss of bromide ion from the β-bromo radical to give the radical cation actually occurs in a two-step reaction: loss of bromine atom to generate β-methyl-4-methoxystyrene, followed by electron transfer to give radical cation and bromide ion. Such a mechanism may be feasible based on the known oxidation potentials of ~1.40 V (vs SCE) for both β-methyl-4-methoxystyrene and bromide ion in acetonitrile[38] and the known propensity of β-bromo radicals to lose bromine atom.[39]

In addition to the reactions of methanol and azide, chloride, and bromide ions with styrene radical cations, we have also measured rate constants for addition of a series of nucleophiles to several of the radical cations. The data shown in Table IV for reaction of methanol, ethanol, 2-propanol, and *tert*-butyl alcohol with β-methylstyrene and 4-methylstyrene radical cations in TFE show the expected trend of decreasing reactivity with decreasing nucleophilicity and increasing steric bulk of the alcohol. The reactivity trends are identical to those observed for nucleophilic addition of alcohols to diphenylmethyl, cyclohexadienyl and vinyl cations.[40–42]

Data for addition of a series of nucleophiles to 4-methoxystyrene and β-methyl-4-methoxystyrene radical cations in both acetonitrile and 4:1 water/acetonitrile are listed in Table V. For both of these radical cations the reactions with nucleophiles in acetonitrile are nonselective with only the nitrite ion reacting at significantly less than 10^{10} M^{-1} s^{-1}. In contrast, the rate constants for addition of the same series of nucleophiles in aqueous acetonitrile vary by over 5 orders of magnitude. Similar solvent effects have been observed recently for addition of anionic[43,44] and amine[45] nucleophiles to di- or triarylmethyl cations and for nucleophilic additions to pentenyl cations.[46] The marked decreases in rate constant for a given nucleophile as the water content of the solvent is increased are attributed to hydrogen-bonding between water and the nucleophile. A detailed study of the reaction between amines and di- and triarylmethyl cations in a range of water/acetonitrile mixtures has led to the conclusion that the hydrated amine is unreactive and equilibrium desolvation to form the unhydrated amine precedes reaction with the cation.[45] It is clear from our data that styrene radical cations follow trends similar to those observed for cations in terms of the selectivity of their reactions with nucleophiles and the effects of hydrogen-bonding solvents on reactivity/selectivity patterns.

Our kinetic data lead to the conclusion that the reactions of styrene radical cations with nucleophiles follow the same trends that have been observed for nucleophilic additions to carbocations. This is illustrated by our results on the effects of (1) steric and electronic factors, (2) nucleophilicity of the nucleophile, and (3) solvent effects on the reactivity of the radical cations. Further, the rate constants are similar in magnitude to those observed for related arylmethyl, diarylmethyl, and vinyl cations. The unpaired electron in radical cations does not appear to have much effect on the reactivity of these species toward nucleophiles. These results are of particular interest with regard to the recent theoretical predictions of Shaik and Pross.[47] They have used the curve crossing model to assess the reactivity of cations and radical cations toward nucleophiles and have concluded that the reaction between a radical cation and a nucleophile is formally forbidden, in contrast to the allowed addition of a nucleophile to a cation. This leads to the prediction that addition of a nucleophile to a radical cation will, in general, be slower than to a cation of similar electron affinity. Our results certainly show that reactivity/selectivity patterns for styrene radical cations are very similar to those for related cations. However, any direct comparison of rate constants for particular radical cation/cation pairs leads to a problem in terms of selecting model species that are sufficiently similar that a direct comparison is valid. For example, although it is tempting to compare the styrene radical cation results to those for phenethyl cations, it is not clear that this approach is

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justified, given the fact that nucleophilic addition occurs at different positions in the two cases.

The combination of kinetic and transient absorption data for reaction of styrene radical cations with anionic and alcohol nucleophiles indicates that reaction occurs via nucleophilic addition to the β-position. For none of the radical cation/nucleophile/solvent combinations for which we have measured transient absorption spectra do we find any evidence for competing electron-transfer reactions. However, it should be noted that an initial electron transfer followed by rapid addition of the products would be feasible on energetic grounds for some nucleophile/radical cation combinations. Similarly, there is no evidence for competing deprotonation of the radical cation for the β-methyl styrene derivatives, although this reaction is well-documented for related aryl olefin radical cations in the presence of sterically hindered pyridine bases.[48] The rate constants for reactions with nucleophiles approach the diffusion-controlled limit in solvents such as acetonitrile and TFE. However, changing the solvent composition provides a straightforward means of varying the reactivity of a particular nucleophile/radical cation combination by several orders of magnitude. A detailed knowledge of the kinetics for a variety of other intra- and intermolecular radical cation reactions will obviously be of primary importance in controlling the chemistry of these important reactive intermediates.

Experimental Section

Materials and General Techniques. Styrene, α-methylstyrene, β-methylstyrene, β,β-dimethylstyrene, 4-methylstyrene, 4-fluorostyrene, 4-methoxystyrene, and β-methyl-4-methoxystyrene were commercially available (Aldrich) and were purified by column chromatography (Silica) before use. α-Methyl-4-methylstyrene and α-methyl-4-methoxystyrene were prepared according to a literature procedure.[49] 1,2-Dibromophenylethane, 1,2-dibromo-(4-methylphenyl)ethane, 1,2-dibromo-(4-methoxyphenyl)ethane, and 1,2-dibromo-(4-methoxyphenyl)propane were prepared by addition of bromine to the corresponding substituted styrene.[50–52] Chloranil was recrystallized before use. The anionic nucleophiles used for the quenching studies were either the sodium (aqueous solutions) or tetrabutylammonium (TFE or acetonitrile) salts. The tetrabutylammonium salts were purified by recrystallization before use. All other quenchers and solvents were commercially available and were used as received.

Laser Flash Photolysis Experiments. A Nd^{3+}:YAG laser (266 nm, 80 mJ/pulse, ~10 ns/pulse or 355 nm, 40 mJ/pulse, ~10 ns/pulse) or a Lumonics EX-530 excimer laser (XeCl, 308 nm, ≤45 mJ/pulse, ~8 ns/pulse) was used as laser excitation source. The rest of the laser system used has been described elsewhere.[53] A flow system was used to obtain transient absorption spectra in order to ensure the presence of unphotolyzed substrate for each laser pulse. Static samples were used to obtain observed rate constants for the decay of the radical cations in the presence of quenchers; in these experiments, each sample was exposed to one laser pulse. All quenching rate constants were measured at room temperature (~20 °C). Samples were contained in 7 × 7 mm^2 quartz cells. Most experiments were carried out using aerated samples. For the picosecond experiments, a Continuum YG-601-C Nd:YAG laser was used to generate both the pump (266 nm, mJ/pulse) and probe beams (1064 nm, 15 mJ/pulse, H_2O/D_2O for continuum generation), and a Princeton Instruments dual diode array (DPDA-1024) with a ST-110 controller was used as the detection system.

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