Laser flash photolysis studies of the reactivity of styrene radical cations

L. J. Johnston and N. P. Schepp

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

Abstract: Laser flash photolysis has been used to obtain kinetic and mechanistic
information for the reactions of substituted styrene radical cations with a variety of
anions, alcohols, nitrogen-centred nucleophiles and alkenes. The reactions studied
include nucleophilic addition to the β-position to give a substituted benzyl radical,
electron transfer to regenerate the starting styrene, deprotonation of the radical
cation for styrenes with a β-methyl group, and cycloaddition to give a cyclobutane
or Diels-Alder product. The importance of steric and electronic factors, solvent,
nucleophilicity, basicity and redox potentials in controlling the competition between
the different reaction pathways is discussed.

INTRODUCTION

There is currently considerable interest in the chemistry of radical ions (1-5). Much of this interest has
been prompted by the growing recognition of the importance of radical cations in synthetic strategies
and in biological systems. Olefin radical cations are of particular interest since they undergo a variety of
reactions such as addition of anionic and neutral nucleophiles, deprotonation, electron transfer and
[2 + 1] and [2 + 3] cycloaddition reactions (1-3, 5-8), and have been used recently in designing
intramolecular radical cation probes (9). Thus, they provide useful examples for studying the factors
that control the competition between various reaction pathways, with the ultimate aim of developing a
detailed understanding of radical cation reactivity that will allow one to predict and control the
chemistry of these important intermediates. Despite the fact that radical cations are key intermediates in
a wide range of electron transfer initiated chemistry, little information on the dynamics of these species
is currently available. We have recently initiated a study of the reactivity of olefin radical cations using
nanosecond and picosecond transient absorption techniques. Our initial studies are summarized herein
and have focused on the chemistry of styrene radical cations since they provide convenient substrates for
laser flash photolysis studies and have previously been the subject of a number of product and
mechanistic studies (7, 10-12).

GENERATION AND CHARACTERIZATION OF STYRENE RADICAL CATIONS

The radical cations of styrenes 1a–i can be readily generated by 266- or 308-nm laser irradiation of the
neutral olefin in polar solvents such as acetonitrile (ACN) or 2,2,2-trifluoroethanol (TFE) (13). The
photoionization has been shown to be biphotonic, presumably via the first excited singlet state of the
styrene. The radical cations (2a–i) have two characteristic absorption bands, one in the UV region
between 350-380 nm and a second visible band with λ_{max} between 585 and 670 nm, depending on the
substitution pattern. A representative spectrum for the 4-methylstyrene radical cation (2f) is shown in
Fig. 1. The assignment of the observed transient is supported by the formation of the same species in
matrices at low temperature (14) and by photosensitization using triplet chloranil as the acceptor.
Radical cations 2a–f have decay rate constants in the range of 10^5–10^7 s^{-1} in TFE and are too short-lived

for nanosecond experiments in ACN or aqueous ACN. By contrast, the methoxy-substituted radical cations 2g–i are substantially less reactive and decay with rate constants that are $\leq 4 \times 10^5$ s^{-1} in ACN or aqueous ACN. In most cases the lifetime of the radical cation is determined by nucleophilic trapping by solvent and/or reaction with the neutral styrene precursor and is the same in either nitrogen or oxygen-saturated solution. However, the β-methyl-4-methoxystyrene radical cation is sufficiently long-lived that its rate constant for reaction with oxygen can be estimated as 2.3×10^7 M^{-1}s^{-1} in ACN (13).

1a: X = H, R$_1$ = R$_2$ = R$_3$ = H
1b: X = H, R$_1$ = CH$_3$, R$_2$ = R$_3$ = H
1c: X = H, R$_1$ = H, R$_2$ = CH$_3$, R$_3$ = H
1d: X = H, R$_1$ = H, R$_2$ = CH$_3$, R$_3$ = CH$_3$
1e: X = F, R$_1$ = R$_2$ = R$_3$ = H
1f: X = CH$_3$, R$_1$ = R$_2$ = R$_3$ = H
1g: X = OCH$_3$, R$_1$ = R$_2$ = R$_3$ = H
1h: X = OCH$_3$, R$_1$ = H, R$_2$ = CH$_3$, R$_3$ = H
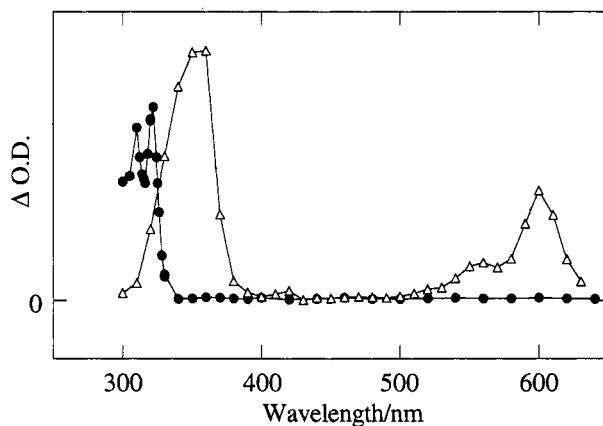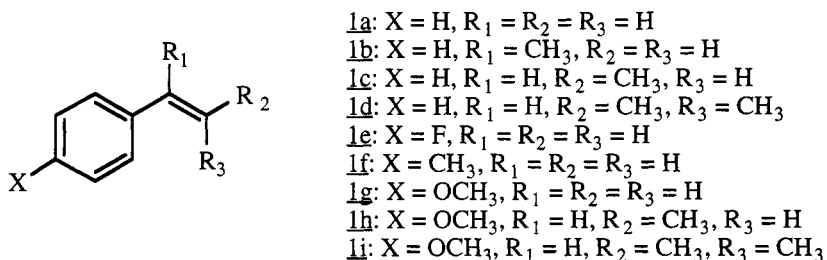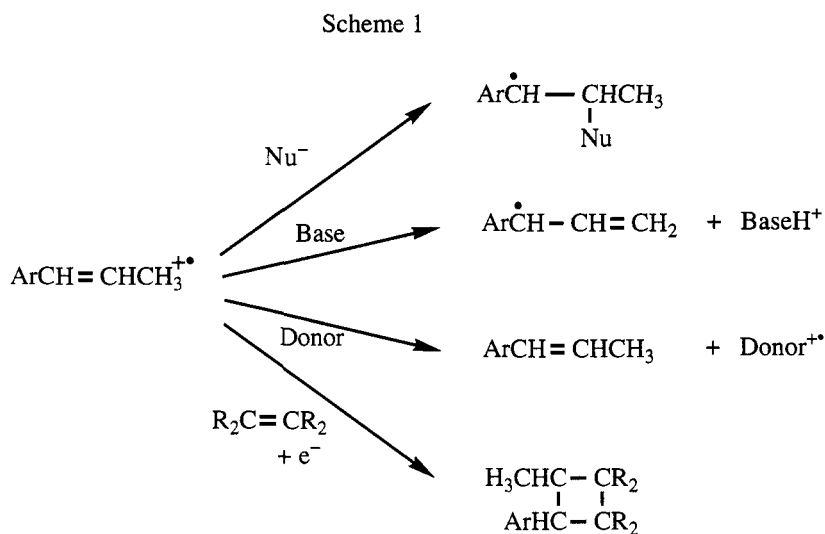1i: X = OCH$_3$, R$_1$ = H, R$_2$ = CH$_3$, R$_3$ = CH$_3$

Fig. 1. Transient absorption spectra in TFE of the 4-methylstyrene radical cation (△) generated by photoionization of 1f and the 2-methoxy-1-phenethyl radical (•) produced by addition of methanol to 2f.

Photoionization is a more suitable route than photosensitized electron transfer for the generation of styrene radical cations for kinetics studies since it permits the use of relatively low concentrations of the precursor and, thus, eliminates problems associated with addition of the radical cations to the neutral olefin. Furthermore, it is possible to measure transient spectra without the complications of signals due to sensitizer radical anions or to absorption of the ground state sensitizer at wavelengths ≤ 350 nm. For most of the time-resolved experiments discussed below direct photoionization was used to generate the radical cation of interest.

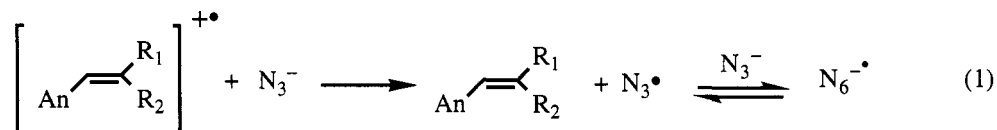## REACTIONS OF STYRENE RADICAL CATIONS

As noted above styrene radical cations undergo a variety of different reactions, and the products and mechanisms for some of these have been studied in detail. Examples of the nucleophilic addition, deprotonation, electron transfer and cycloaddition reactions that we have examined using laser flash photolysis are outlined in Scheme 1. The following sections discuss representative examples for each of these processes. The examples have been chosen to illustrate the importance of steric and electronic factors, solvent, redox potentials, nucleophilicity and basicity in controlling the competition between one

or more reaction pathways and in modulating the overall reactivity for a particular radical cation/substrate combination. It is also of interest to compare the results to similar data for carbocations, particularly in light of theoretical predictions that conclude that reaction of a radical cation with a nucleophile is formally forbidden, in contrast to the allowed addition of a nucleophile to a cation (15). This has led to the prediction that addition of a nucleophile to a radical cation should in general be slower than to a cation of similar electron affinity.

Scheme 1

$$\text{ArCH} = \text{CHCH}_3^{+\bullet}$$

Nu⁻ → ArĊH — CHCH₃ | Nu

Base → ArĊH – CH= CH₂ + BaseH⁺

Donor → ArCH= CHCH₃ + Donor⁺⁺

R₂C= CR₂ + e⁻ → H₃CHC– CR₂ | | ArHC– CR₂

Reaction of styrene radical cations with anions

Radical cations 2a–f react with anions such as azide, chloride and bromide with rate constants ($\sim 10^{10}$ $M^{-1}s^{-1}$) that approach the diffusion controlled limit in TFE and, thus, are not particularly sensitive to the structure of the radical cation (13). Transient spectra recorded after complete quenching of the radical cations by these nucleophiles in nitrogen-saturated solution provide evidence for the formation of the substituted benzyl radical formed by addition of the anion to the β-position of the radical cation. Reactions for methoxy-substituted radical cations 2g–i with azide, bromide and chloride in ACN also occur with diffusion-controlled rate constants (3-4×10^{10} $M^{-1}s^{-1}$). The transient spectra obtained in the presence of both chloride and bromide ions demonstrate that the substituted benzyl radical generated by nucleophilic addition to the β-position of the radical cation is formed in these reactions. By contrast, reaction of all three radical cations with azide in ACN occurs predominantly by electron transfer to generate azidyl radical and styrene. An electron transfer mechanism is clearly demonstrated by the observation of a transient assigned to $N_6^{-\bullet}$ produced by trapping of the azidyl radical by excess azide ion (eq 1, Fig. 2) (16). Completely different results are obtained upon reaction of the same three radical

$$\left[\begin{array}{c} \text{An} \diagdown = \diagup \begin{array}{c} R_1 \\ R_2 \end{array} \end{array} \right]^{+\bullet} + \ N_3^- \longrightarrow \ \text{An} \diagdown = \diagup \begin{array}{c} R_1 \\ R_2 \end{array} + \ N_3^\bullet \ \underset{}{\overset{N_3^-}{\rightleftharpoons}} \ N_6^{-\bullet} \qquad (1)$$

cations with azide in TFE. In this case the transient spectra clearly indicate that nucleophilic addition to give a benzylic radical predominates, Fig. 2. This change in reaction mechanism is the result of an approximately 0.5 V increase in the oxidation peak potential of azide upon changing the solvent from ACN to TFE. The oxidation peak potentials for azide and the styrenes differ by ≤150 mV in TFE and addition is the major reaction, whereas electron transfer dominates in ACN where azide is ≥0.55 V easier to oxidize than any of the three styrenes. The oxidation potentials of styrenes 1a–1f are such that electron transfer is not expected to compete with addition, even in TFE.
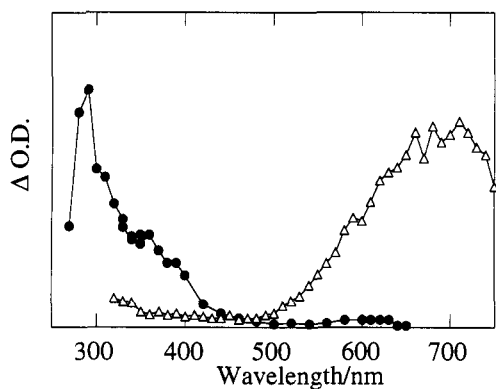
Fig. 2. Transient absorption spectra of $N_6^{-\bullet}$ ($\triangle$) and the substituted benzyl radical ($\bullet$) produced by reaction of azide with 2i in ACN and TFE, respectively.
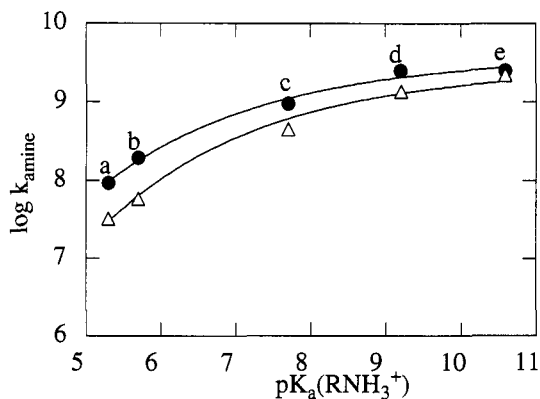
Fig. 3. Effect of amine ($X\text{-}CH_2NH_2$) basicity (pK_a) on the rate constant for reaction with 2g($\bullet$) and 2h($\triangle$): X = CN(a), CF_3(b), $CNCH_2$(c), CH_3OCH_2(d), $CH_3CH_2CH_2$(e).

Reaction of styrene radical cations with alcohols

The rate constants for reaction of styrene radical cations with alcohols are considerably slower than the diffusion controlled limit and occur exclusively by addition to give the substituted benzyl radicals, as illustrated in Fig.1 for methanol addition to 2f (13). Since the oxidation potentials of the alcohols are much higher than those of the alcohols, there is no possibility of competing electron transfer. Therefore, these substrates provide useful examples for examining the effects of changes in the steric and electronic properties of both the radical cation and the nucleophile. For example, the rate constants for methanol addition to 2a, 2f and 2g are 180, 5.9 and 0.03 x 10^6 $M^{-1}s^{-1}$, respectively, and demonstrate that methoxy-substitution decreases the reactivity by almost 4 orders of magnitude. The effects of alkyl-substitution of the double bond on the reaction with methanol have also been examined. In this case the measured rate constants of 180, 190, 9.7 and 0.2 x 10^6 $M^{-1}s^{-1}$ for 2a–d indicate that an α-methyl group has essentially no effect whereas one and two β-methyl groups lead to 20 and 1000-fold decreases in reactivity. Again, these results are consistent with the expected steric and electronic effects of β-methyl substituents.

Reaction of styrene radical cations with amines and pyridines

The reactions with nitrogen-centred nucleophiles such as pyridines and amines can in principle occur by one of three routes: electron transfer, nucleophilic addition or deprotonation. Representative data for reactions with amines and pyridines are listed in Table 1 for 2g and 2h. A combination of transient spectra, product studies and redox potentials can be used to establish which reactions are important for any particular substrate. Thus, the observation of amine radical cations upon reaction of both 2g and 2h with DABCO or aniline clearly demonstrates that electron transfer is the major reaction pathway, consistent with the fact that these amines are substantially easier to oxidize than either styrene. By contrast, reaction with primary amines occurs by nucleophilic addition which yields a transient in the 320 nm region that is assigned to the substituted benzyl radical. Comparison of the data for the tertiary and primary amines indicates that the electron transfer reactions with tertiary amines are relatively insensitive to the substituents on the double bond whereas the rate constants for nucleophilic addition decrease by approximately an order of magnitude when a β–H is replaced by a methyl group. In fact, this provides a useful means of distinguishing between electron transfer and addition reactions.

The reaction of 2g and 2h with primary amines of varying basicity but constant steric requirements has also been examined. As demonstrated in Fig. 3, the rate constants for nucleophilic addition increase with increasing basicity of the amine. The β-methyl-substituted radical cation is considerably more

TABLE 1. Rate constants for the reaction of 2g and 2h with selected amines and pyridines (Pyr) in ACN.

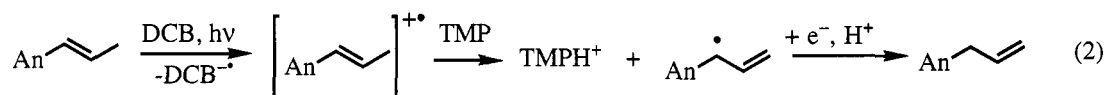| Amine or Pyridine	$k_q/10^9$ M^{-1} s^{-1}	
	2g	2h
aniline	13	12
DABCO	15	12
Et$_3$N	6.6	4.7
n-BuNH$_2$	2.5	2.2
t-BuNH$_2$	2.1	0.46
2,6-t-Bu$_2$Pyr	< 0.001	0.002
2,4,6-Me$_3$Pyr	0.039	0.003

TABLE 2. Rate constants for the reaction of radical cations 2a, 2f, 2g and 2h with selected alkenes in ACN or TFE.

Alkene	$k_q/10^9$ M^{-1} s^{-1}			
	2a[a]	2f[a]	2g[b]	2h[b]
1-hexene	1.9	0.083	<0.0005	<0.0001
4-methyl-2-pentene	1.2	0.0095	<0.0005	<0.0001
2-methyl-1-butene	3.9	1.5	0.0015	<0.0001
2-methyl-2-butene	4.0	3.0	0.0014	<0.0001
2,5-dimethyl-2,4-hexadiene	6.0	5.2	8.3	7.2
2-methyl-1,3-butadiene	4.9	5.4	0.003	0.0002
1,3-cyclohexadiene	--	--	0.70	0.0056
ethyl vinyl ether	4.2	1.3	0.07	0.0005

a- in TFE; *b*- in ACN

selective with rate constants that vary by a factor of ~65 over the pK$_a$ range in Fig. 3, as compared to a factor of 25 for the reactions of the unsubstituted analog. The plots are curved and reach a plateau at a rate constant of ~2.5 x 10^9 M^{-1}s^{-1}. Similar results have been observed in the addition of amines to diarylmethylcarbocations and 9-phenylanthracene radical cations (17, 18).

Reactions of 2g and 2h with hindered pyridines have also been examined (Table 1). For example di-*tert*-butylpyridine reacts with 2h with a rate constant of 2 x 10^6 M^{-1}s^{-1}, whereas its reaction with 2g is too slow to measure under our experimental conditions. The reaction with 2h must result in deprotonation to give the corresponding allylic radical since electron transfer to pyridines is endergonic by at least 0.7 V and since addition to 2h would be expected to be at least an order of magnitude slower for 2h than for 2g based on the effects of β-methyl substitution on nucleophilic addition of alcohols and amines. The reaction of 2h with 2,4,6-trimethylpyridine is also believed to be deprotonation. This is supported by preliminary product studies in which the tautomerized olefin is formed upon irradiation of a mixture of 1h, dicyanobenzene (DCB) and 2,4,6-trimethylpyridine (TMP) (eq 2).

$$An\diagdown\diagup \xrightarrow[-DCB^{-\bullet}]{DCB,\ h\nu} \left[An\diagdown\diagup\diagdown\right]^{+\bullet} \xrightarrow{TMP} TMPH^+ + An\diagdown\diagup^{\bullet} \xrightarrow{+\ e^-,\ H^+} An\diagdown\diagup \qquad (2)$$

Solvent effects

The reaction of 2g and 2h with a variety of nucleophiles has been measured in both ACN and aqueous ACN. The trends are illustrated in Fig. 4, as a plot of the log of the quenching rate constant for 2g vs. the nucleophilicity of the quencher. The data demonstrate that there is little selectivity for nucleophilic addition in ACN with all nucleophiles except NO$_3^-$ reacting at approximately diffusion controlled rates. Note that the two amines that react by electron transfer react with similar, although slightly slower, rate constants. In aqueous ACN the rate constants for some of the less nucleophilic quenchers are as much as four orders of magnitude slower than in ACN. Although there is a linear correlation between nucleophilicity and reactivity in aqueous ACN, azide is two orders of magnitude more reactive than expected. However, this is readily explainable by the change in mechanism from addition to electron transfer for this anion. The fact that Et$_3$N falls on the line may indicate that it reacts by addition in aqueous solvent in contrast to electron transfer in ACN. The large decreases in reactivity towards nucleophilic addition in aqueous ACN are attributed to hydrogen bonding between water and the nucleophile; similar effects have been observed for the reactions of diarylmethylcarbocations with amines and retinyl cations with
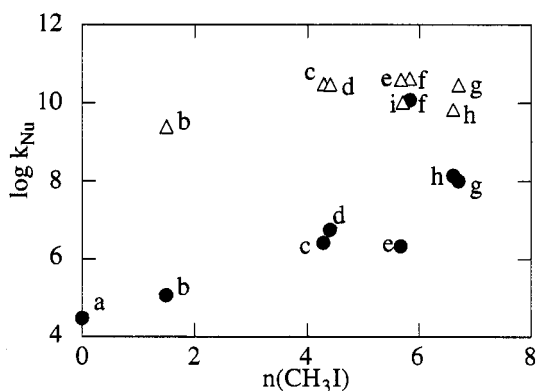
Fig. 4. Solvent effect on the rate constant for the reaction of $\underline{2g}$ with nucleophiles in ACN($\triangle$) and 30% aq. ACN($\bullet$): a-MeOH; b-NO_3^-; c-AcO^-; d-Cl^-; e-Br^-; f-N_3^-; g-CN^-; h-Et_3N; i-aniline.
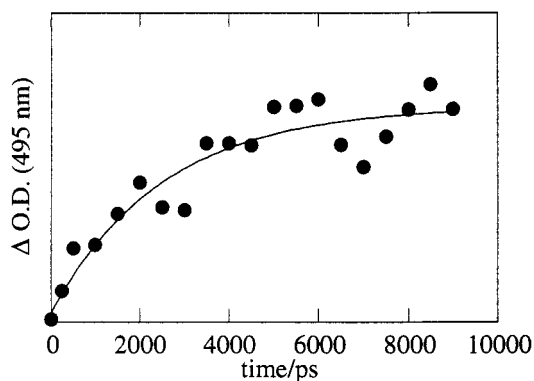
Fig. 5. Time-dependent growth at 495 nm upon 355-nm 35-picosecond irradiation of $trans$-1,2-bis(4-methoxyphenyl)cyclobutane in acetonitrile.

nucleophiles (17, 19). The observed solvent effects provide a useful method for modulating the reactivity of a particular radical cation/nucleophile combination and are expected to be of particular utility when nucleophilic addition competes with a reaction that is not greatly affected by solvent.

Reactions of styrene radical cations with alkenes

Reactions of radical cations $\underline{2a}$–$\underline{2h}$ with a number of substituted alkenes have also been examined, and a few representative second-order rate constants are summarized in Table 2. Cycloaddition and electron transfer are expected to be the two major reactions leading to the quenching of the styrene radical cations by alkenes, and evidence from transient absorption and redox potentials can be used to establish which of these dominates. For example, reaction of the styrene radical cations with 2,5-dimethyl-2,4-hexadiene in ACN or TFE occurs by electron transfer, as indicated by the formation of the diene radical cation. Furthermore, the rate constants for the reaction between the styrene radical cations and 2,5-dimethyl-2,4-hexadiene are all $\geq 5 \times 10^9$ M^{-1} s^{-1} (Table 2) and are insensitive to the structure of the radical cation as noted previously for the electron-transfer reactions with anionic nucleophiles and amines. On the other hand, rate constants for the reactions of the same radical cations with other alkenes are strongly influenced by the nature of the radical cation. Thus, $\underline{2h}$ is one to two orders of magnitude less reactive toward simple alkenes such as 2-methyl-1-butene and dienes such as 1,3-cyclohexadiene than $\underline{2g}$ due to the presence of the β-methyl group in $\underline{2h}$. In addition, the rate constants for addition of simple alkenes such as 1-hexene or 4-methyl-2-pentene decrease by at least three orders of magnitude upon going from the unsubstituted parent styrene radical cation $\underline{2a}$ to the methoxy-substituted derivative $\underline{2g}$. These steric and electronic effects are similar to those observed for the nucleophilic addition of methanol to the same radical cations, and are therefore consistent with the rate determining step involving bond formation between the radical cation and the alkene.

The structure of the alkene also has a dramatic effect on the rate constants. For example, 1,1-dialkyl substituted alkenes such as 2-methyl-1-butene are significantly more reactive than 1-hexene, presumably due to the fact that the electron-donating methyl group increases the alkene nucleophilicity. On the other hand, the 1,2-dialkyl alkene, 4-methyl-2-pentene, is less reactive than 1,1-dialkyl alkenes and 1-hexene, suggesting that the rate accelerating influence of the second methyl group is offset by an unfavorable steric interaction. Similarly, 1,1,2-trialkyl substituted derivatives such as 2-methyl-2-butene have about the same reactivity as the 1,1-dialkyl substituted alkenes such as 2-methyl-1-butene. Substitution of the double bond with other electron-donating groups such as methoxy or alkenyl also has a dramatic rate accelerating effect, with ethyl propenyl ether and 2-methyl-1,3-butadiene reacting considerably more rapidly than 1-hexene. All of these effects are in qualitative agreement with,

although of lesser magnitude than, the trends for addition of carbocations to alkenes (20). The mechanism for radical cation mediated cycloaddition reactions of alkenes has been the subject of a number of mechanistic studies and theoretical calculations (2). There is now considerable evidence in favor of a concerted [2 + 1] mechanism to give a cyclobutane radical cation as opposed to a stepwise addition to give an acyclic 1,4-radical cation. Transient experiments have so far failed to yield any direct evidence for either of these intermediates in the addition of styrene radical cations to alkyl-substituted alkenes. However, they have been used to provide detailed mechanistic and kinetic information for the radical cation mediated dimerization of styrenes, as outlined in the following section.

Radical-Mediated Dimerization

A common reaction of styrene radical cations is addition to their neutral precursor to give dimeric products such as substituted 1,2-diarylcyclobutanes and dihydronaphthalenes. Rate constants for the reaction of styrene radical cations with their neutral precursors in ACN or TFE have been measured and are in the range of 1 - 3 x 10^9 M^{-1} s^{-1} for radical cations such as 2c, 2e, 2f and 2g. The presence of β-methyl groups in the radical cations of 2d and 2h significantly reduces the rate constants for addition to values that are too slow to measure under our experimental conditions (13).

The radical-cation mediated dimerization of 4-methoxystyrene in ACN was investigated in detail using both product studies and laser flash photolysis (21). A single product, dihydronaphthalene 3, is formed in product studies using low concentrations of 4-methoxystyrene, while at higher concentrations the *trans*-bis(4-methoxyphenyl)cyclobutane, 4, is the major product. Radical-cation mediated cycloreversion of the cyclobutane gives the formal cycloreversion product, 4-methoxystyrene, as well as the same dihydronaphthalene observed in the dimerization reaction. Transient experiments show that the rate constant for decay of the 4-methoxystyrene radical cation increases linearly with concentration for low concentrations of 4-methoxystyrene, while at higher concentrations, the observed rate constant is independent of 4-methoxystyrene concentration. These results are consistent with the concerted cycloaddition postulated by Bauld (2) and supported by results from Lewis (7) for the radical cation mediated dimerization of mono-aryl ethylene radical cations, Scheme 2.
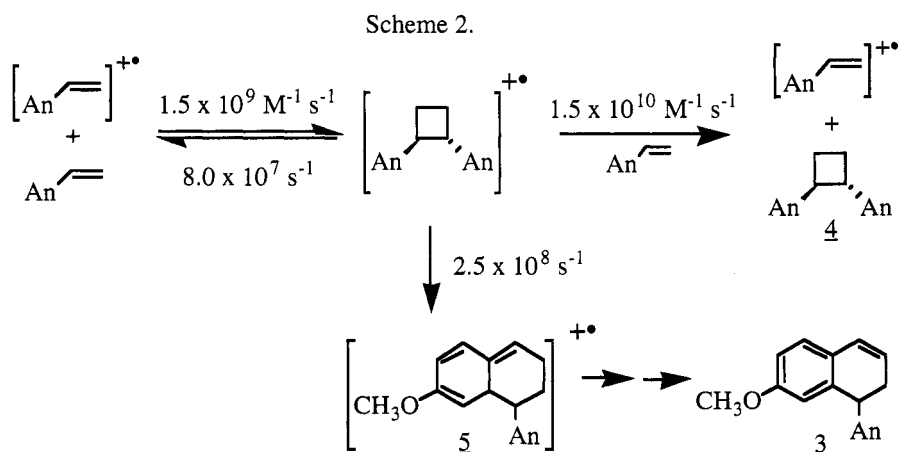
Scheme 2.

Kinetic analysis of the data for the dimerization of the 4-methoxystyrene radical cation as a function of 4-methoxystyrene concentration led to rate constants for each step of the mechanism shown in Scheme 2. The kinetic data indicate that the actual cycloaddition step is very rapid, taking place with a second-order rate constant of 1.5 x 10^9 M^{-1}s^{-1}. In addition, the key intermediate in this reaction sequence, the cyclobutane radical cation, has a lifetime of only 3 ns in ACN. This lifetime is determined by a competition between cycloreversion to give neutral 4-methoxystyrene and its radical cation, and rearrangement to the hexatriene radical cation 5 that is the precursor to the dihydronaphthalene product, 3. We were able to confirm the results from the nanosecond experiments by carrying out picosecond

laser flash photolysis experiments in which the hexatriene radical cation $\underline{5}$ with an absorption maximum at 495 nm was observed to grow in with a rate constant of 3 x 10^8 s^{-1} (Fig. 5). This rate constant corresponds to a 3-ns lifetime for the cyclobutane radical cation, in excellent agreement with the value determined from the nanosecond experiments.

SUMMARY

The reactions of styrene radical cations with anionic, alcohol and amine nucleophiles occur by either nucleophilic addition to the β-position to give a substituted benzyl radical or by electron transfer. Addition is observed for alcohols, primary amines and most anions, while electron transfer is the dominant pathway for tertiary amines. Azide can react by either electron transfer or addition depending on the solvent. Both electron transfer and addition are also observed in the reaction of styrene radical cations with olefins and dienes. The combined results suggest that addition will only compete effectively with electron transfer in cases where the oxidation potential of the styrene is 0.1-0.2 V lower than that of the quencher, and demonstrate the importance of redox potentials and solvent in controlling the overall chemistry. Both nucleophilic addition and cycloaddition to alkenes are subject to the same steric and electronic effects that are observed in carbocation chemistry. Moreover, the measured rate constants indicate that nucleophilic additions to radical cations are just as rapid as those to related carbocations. The results on the dimerization of 4-methoxystyrene provide the first detailed kinetic analysis for all of the intermediates involved in a concerted [2 + 1] cycloaddition reaction. Further the kinetic data summarized herein lays a firm foundation for the use of radical cation chemistry in synthetic strategies and in the development of radical ion probes.

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