Reactivity of Radical Cations. Effect of Radical Cation and Alkene Structure on the Absolute Rate Constants of Radical Cation Mediated Cycloaddition Reactions[1]

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Abstract: Absolute rate constants for the reactions of styrene, 4-methylstyrene, 4-methoxystyrene, and β-methyl-4-methoxystyrene radical cations with a series of alkenes, dienes, and enol ethers have been measured by laser flash photolysis. The measured rate constants correspond to either addition or electron transfer reactions, with the latter predominating when the oxidation potential of the alkene is lower than that of the styrene. The measured rate constants for the diene additions provide some of the first absolute kinetic data for the initial step in the synthetically-useful radical cation mediated Diels−Alder reaction. The addition reactions are sensitive to steric and electronic effects on both the radical cation and the alkene or diene. For example, the reactivity of the radical cations follows the general trend of 4-H > 4-CH_3 > 4-CH_3O > 4-CH_3O-β-CH_3. The effects of alkyl substitution on the relative reactivity of alkenes toward styrene radical cations may be summarized as 1,2-dialkyl < 2-alkyl < trialkyl ≤ 2,2-dialkyl < tetraalkyl. The addition of the 4-methoxystyrene radical cation to a series of ring-substituted styrenes gives a reasonable Hammett correlation with a ρ value of −5. Thus, the addition of radical cations to a variety of alkenes and dienes follows similar trends to those observed for the addition of other electrophiles, such as diarylcarbenium ions. The results are consistent with previous suggestions of a concerted pathway for radical cation mediated cycloaddition reactions, although direct spectroscopic evidence for the initial product radical cation is obtained only for the additions to substituted styrenes.

Introduction

The cycloaddition of neutral alkenes to alkene radical cations has recently been established as a useful method for the synthesis of cyclobutane derivatives and Diels−Alder products.[2−8] One of the main advantages of radical cation mediated cycloaddition reactions is the fact that they can be carried out under much milder reaction conditions (i.e., lower temperatures and shorter reaction times) than the analogous thermal [2 + 2] or [4 + 2] cycloadditions of neutral alkenes. In addition, the stereochemistry of the radical cation cycloaddition reactions can often be reliably predicted, and the reactions take place with stereospecificity that frequently rivals and sometimes surpasses that obtained in the corresponding cycloadditions of neutral alkenes.[5,6] Cycloadditions using radical cation chemistry are particularly useful in overcoming the limited success of Diels−Alder reactions involving neutral or electron-rich dienophiles. Radical cation mediated cyclobutanation and Diels−Alder reactions of anethole have also recently been used as the basis for intramolecular probe reactions to test for the intermediacy of radical cations in metalloporphyrin oxidations of alkenes and thermal cycloaddition reactions of tetracyanoethylene.[9−11]

Radical cation cycloaddition reactions involving electron-rich dienophiles are typically complete within minutes at low temperatures. Despite their obvious synthetic potential, little absolute kinetic data are currently available for these addition reactions. It is therefore difficult to predict the conditions required for efficient cycloaddition and to choose appropriate substrates that will lead to optimal cycloaddition yields. This is particularly problematic in cases where both dimerization and cross addition can occur. We recently reported that styrene radical cations can be conveniently generated and studied using nanosecond-laser flash photolysis.[12−15] We have used this method to measure second-order rate constants for the reaction of a series of substituted styrene radical cations with nucleophiles and with their parent styrenes in acetonitrile in reactions that are commonly termed radical cation dimerizations.[12,13] The

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rate constants in most cases were greater than 2×10^9 M^{-1} s^{-1}. The only exceptions were β-substituted styrenes, such as β,β-dimethylstyrene and β-methyl-4-methoxystyrene, for which rate constants for addition of the radical cations to the precursor styrenes were estimated at $<1 \times 10^8$ M^{-1} s^{-1}. The addition of a variety of styrene radical cations to their neutral precursors has also been studied using pulse radiolysis techniques.[16−19] Rate constants for radical cation mediated dimerizations of several other alkenes have been estimated by Stern−Volmer quenching and product studies[20−22] and by time-resolved methods.[23,24]

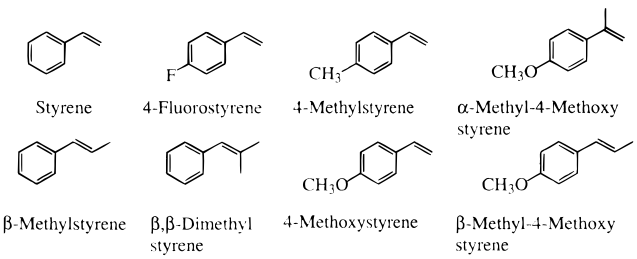
The data previously measured for the radical cation mediated dimerization of styrenes demonstrate the effects of structure on the rate constants for the initial cycloaddition. However, the fact that both the structure of the radical cation and the alkene were changed at the same time made it difficult to draw firm conclusions about the relative importance of steric and electronic effects on the individual partners. In the present work, we have studied the effects of independently varying the structure of both the radical cation and the alkene on the kinetics of cross addition reactions of substituted styrene radical cations with a range of alkenes. This allows for the determination of the influence of steric and electronic factors in both the alkene and radical cation and provides kinetic data that are essential for the design of synthetic strategies that utilize radical cation cycloaddition chemistry. A preliminary account of some of the data for two styrene radical cations with selected alkenes has been published.[25]

Experimental Section

Materials. α-Methyl-4-methoxystyrene was prepared according to a literature procedure.[26] All other styrenes and the alkenes used in the present work were commercially available. In each case, they were purified over silica or alumina prior to the laser photolysis experiments.

The laser flash photolysis apparatus has been previously described.[27] Either a Lumonics Nd:YAG (266 nm; ≤80 mJ/pulse; ~10 ns pulse width) or a Lumonics EX530 laser (308 nm; ≤40 mJ/pulse; ~8 ns pulse width) was used for sample excitation in these experiments. Samples were contained in 7×7 mm^2 quartz cells and when required were deaerated with nitrogen or oxygen for 15 min prior to laser irradiation. Absorption spectra were obtained using a flow system to ensure the presence of unphotolyzed precursor for each laser pulse. Static air-saturated samples were used in the quenching studies, with each sample being exposed to a maximum of two laser pulses. At least three observed rate constants for the decay of the styrene radical cations at each of five different concentrations of the alkene were measured. These observed rate constants were then plotted as a function of alkene concentration, and the second-order rate constants were determined by calculating the slopes of these plots.

Chart 1

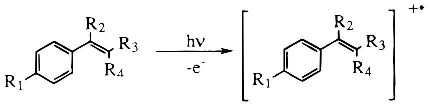


Electrochemical measurements were made using an EG&G Model 273A potentiostat. In each case, solutions containing 0.005 M purified samples of alkene or styrene in acetonitrile with 0.10 M tetrabutylammonium perchlorate were prepared. Half-wave oxidation potentials were obtained using a platinum electrode using scan rates of 200 mV/s. The reported half-wave potentials were measured relative to the oxidation potential of ferrocene and then converted to the SCE standard using a conversion factor of 0.441 V.

Results

Reaction of Substituted Styrene Radical Cations with Alkenes. We have previously shown that substituted styrene radical cations can be generated in acetonitrile or 2,2,2-trifluoroethanol (TFE) by direct 266- or 308-nm pulsed laser excitation of the corresponding neutral styrene or by photoinduced electron transfer using chloranil as the electron transfer sensitizer.[13] The chloranil-sensitized method in which the styrene radical cation is generated by electron transfer from the styrene to the triplet chloranil is useful because it often gives large yields of the radical cations of interest, and therefore allows their kinetic and spectral characteristics to be easily observed. However, in the present work in which we determine the rate constants for the quenching of styrene radical cations by aliphatic alkenes, high concentrations of alkenes were often required in order to observe significant quenching of the radical cations. Under these conditions, a significant fraction of the chloranil triplets are quenched by the alkene instead of the styrene, thus lowering the yields of the styrene radical cations and making their detection more difficult. For example, we measured observed rate constants for the decay of the chloranil triplet generated by 355-nm excitation of chloranil in acetonitrile as a function of concentration of three of the alkenes used in the present work. The triplet was indeed rapidly quenched with second-order rate constants ranging from 5×10^9 M^{-1} s^{-1} for quenching by 1-methylcyclohexene and ethyl propenyl ether to 1.8×10^9 M^{-1} s^{-1} for quenching by methylenecyclohexane. These rate constants are slightly less than the rate constant of ca. 1×10^{10} M^{-1} s^{-1} measured previously for electron transfer from triplet chloranil to substituted styrenes,[13] but are sufficiently large for the alkenes to be the dominant triplet quencher at high concentrations of the alkenes.

Due to the difficulties associated with the sensitized route for radical cation generation, we used exclusively the photoionization method[13] in which the substituted styrene radical cations were generated by direct 266- or 308-nm laser irradiation of the substituted styrenes shown in Chart 1, eq 1.



(1)

As described previously, the 4-methoxy substituted styrene radical cations are readily generated by photoionization of the neutral 4-methoxystyrene in acetonitrile, while the other styrene radical cations are generated in 2,2,2-trifluoroethanol (TFE).[13]

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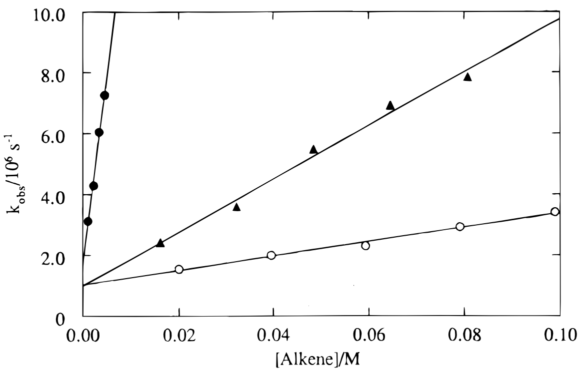


Figure 1. Relationship between the observed rate constants for the decay of the 4-methylstyrene radical cation and the concentration of ethyl vinyl ether (●), 1-hexene (△), and cyclohexene (○) in TFE.

The choice of solvents was determined by the reactivity of the radical cations such that the stabilized 4-methoxystyrene radical cations decay sufficiently slowly to be studied in acetonitrile, while the others are more reactive and must be studied in the non-nucleophilic solvent TFE. All the radical cations are easily characterized by an absorption maximum between 350 and 370 nm, and a second, slightly weaker absorption maximum that ranges from 600 to 650 nm.[13]

In the absence of added quenchers, the radical cations generally decay in a first-order manner either by reaction with solvent or by addition to the neutral precursor.[12,13,18] In the present work, observed rate constants for the first-order decay of the substituted styrene radical cations were measured as a function of the concentration of various alkenes. In most cases, the observed rate constants increased in a linear fashion with increasing alkene concentration according to eq 2.

$$k_{obs} = k_o' + k_{alk}[\text{alkene}] \qquad (2)$$

In this equation, k_{alk} is the second-order rate constant for the quenching of the styrene radical cation by the alkene, and k_o' is the sum of the rate constants for the reactions of the radical cation with solvent, k_o, and neutral precursor, k_{dim} ($k_o' = k_o + k_{dim}$[RSty]). To ensure that the observed rate constants measured in the present work were not influenced by changes in k_o', all quenching experiments were carried out by varying the concentration of the alkene but maintaining a constant concentration of the neutral precursor.

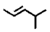
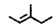
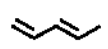
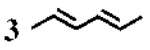
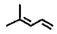
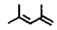
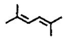
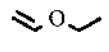
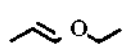
Quenching plots are shown in Figure 1 for the reaction of the 4-methylstyrene radical cation with cyclohexene, 1-hexene, and ethyl vinyl ether in TFE. In each case, a good linear relationship is observed, and linear least-squares analysis of the data gave second-order rate constants, k_{alk}, of 2.5×10^7, 8.3×10^7, and 1.3×10^9 $M^{-1}\ s^{-1}$ for quenching by cyclohexene, 1-hexene, and ethyl vinyl ether, respectively. Similar plots were obtained for the reaction of most of the styrene radical cations with cyclohexene and ethyl vinyl ether, and the second-order rate constants derived from these plots are summarized in Table 1. The radical cations of β,β-dimethystyrene, 4-methoxystyrene, and α-methyl-4-methoxystyrene were not quenched by cyclohexene even at concentrations as high as 1.0 M. Since the lifetimes of these radical cations are about 2 μs in the absence of any added quenchers, their reaction with cyclohexene takes place with rate constants $< 5 \times 10^5$ $M^{-1}\ s^{-1}$. The decay of the β-methyl-4-methoxystyrene radical cation was also unaffected by the addition of 1.0 M cyclohexene. In this case, the radical cation is slightly longer-lived with a lifetime of 10 μs, and we place an upper limit rate constant for quenching by cyclohexene at 1×10^5 $M^{-1}\ s^{-1}$.

Table 1. Second-Order Rate Constants for the Addition of Cyclohexene and Ethyl Vinyl Ether to Various Substituted Styrene Radical Cations

		$k_{alk}/M^{-1}\ s^{-1}$	
radical cation	$E_{1/2}^{ox\ a}$	cyclohexene (2.25 V)	ethyl vinyl ether (1.99 V)
styrene$^{\bullet+\ b}$	2.05	$(1.2 \pm 0.1) \times 10^9$	$(4.2 \pm 0.8) \times 10^9$
β-methylstyrene$^{\bullet+\ b}$	1.60	$(8.9 \pm 0.5) \times 10^6$	*d*
β,β-dimethylstyrene$^{\bullet+\ b}$	1.57	$<5 \times 10^5$	*d*
4-fluorostyrene$^{\bullet+\ b}$	*d*	$(3.5 \pm 0.2) \times 10^8$	$(3.9 \pm 0.4) \times 10^9$
4-methylstyrene$^{\bullet+\ b}$	1.87	$(2.5 \pm 0.2) \times 10^7$	$(1.3 \pm 0.2) \times 10^9$
4-methoxystyrene$^{\bullet+\ c}$	1.49	$<5 \times 10^5$	$(7.2 \pm 1.1) \times 10^7$
α-methyl-4-methoxystyrene$^{\bullet+\ c}$	*d*	$<5 \times 10^5$	$(8.2 \pm 0.7) \times 10^7$
β-methyl-4-methoxystyrene$^{\bullet+\ c}$	1.33	$<1 \times 10^5$	$(5.0 \pm 1.0) \times 10^5$

[a] Irreversible half-wave potentials in volts vs SCE in acetonitrile. [b] Rate constants measured in TFE. Errors are <±10%. [c] Rate constants measured in acetonitrile. [d] Not measured.

Table 2. Second-Order Rate Constants for the Quenching of Substituted Styrene Radical Cations by Various Alkenes in Acetonitrile or TFE

			$k_{alk}/M^{-1}s^{-1}$			
	Alkene	$E_{1/2}^{ox\ a}$	Styrene$^{+\bullet b}$ (2.05 V)	4-Methyl styrene$^{+\bullet b}$ (1.87)	4-Methoxy styrene$^{+\bullet c}$ (1.49 V)	β-Methyl-4-methoxy styrene$^{+\bullet c}$ (1.39 V)
1		2.85	$(1.9 \pm 0.3) \times 10^9$	$(8.3 \pm 0.9) \times 10^7$	$< 5 \times 10^5$	$< 1 \times 10^5$
2		2.62	$(3.6 \pm 0.6) \times 10^9$	$(3.1 \pm 0.4) \times 10^9$	$(2.4 \pm 0.4) \times 10^6$	$< 1 \times 10^5$
3		2.56 (2.6[d])	$(3.9 \pm 0.7) \times 10^9$	$(1.5 \pm 0.2) \times 10^9$	$(1.5 \pm 0.1) \times 10^6$	$< 1 \times 10^5$
4		2.32	$(1.2 \pm 0.2) \times 10^9$	$(9.5 \pm 2.2) \times 10^6$	$< 5 \times 10^5$	$< 1 \times 10^5$
5		2.25 (2.3[d])	$(1.2 \pm 0.1) \times 10^9$	$(2.5 \pm 0.3) \times 10^7$	$< 5 \times 10^5$	$< 1 \times 10^5$
6		2.08 (2.0[d])	$(4.0 \pm 0.6) \times 10^9$	$(3.0 \pm 0.3) \times 10^9$	$(1.4 \pm 0.3) \times 10^6$	$< 1 \times 10^5$
7		2.00 (1.9[d])	$(3.9 \pm 0.7) \times 10^9$	$(2.3 \pm 0.2) \times 10^9$	$(1.5 \pm 0.3) \times 10^6$	$< 1 \times 10^5$
8		1.98	$(6.4 \pm 1.4) \times 10^9$	$(2.6 \pm 0.2) \times 10^9$	$(7.2 \pm 1.4) \times 10^5$	$< 1 \times 10^5$
9		1.56 (1.6[d])	$(6.0 \pm 0.7) \times 10^9$	$(4.8 \pm 0.4) \times 10^9$	$(1.6 \pm 0.5) \times 10^7$	$< 1 \times 10^5$
10		2.18	$(5.8 \pm 0.7) \times 10^9$	$(4.8 \pm 0.2) \times 10^9$	$(3.5 \pm 0.4) \times 10^6$	$<1 \times 10^5$
11		2.03 (2.2[e])	$(4.9 \pm 0.6) \times 10^9$	$(5.4 \pm 0.5) \times 10^9$	2.5×10^6	$(1.9 \pm 0.2) \times 10^4$
12		1.96 (2.2[e])	$(5.9 \pm 0.6) \times 10^9$	$(4.2 \pm 0.2) \times 10^9$	$(2.8 \pm 0.5) \times 10^7$	$(7.4 \pm 1.8) \times 10^4$
13		1.82	$(5.9 \pm 0.5) \times 10^9$	$(4.2 \pm 0.4) \times 10^9$	$(2.6 \pm 0.2) \times 10^7$	$(5.9 \pm 1.2) \times 10^5$
14		1.82			$(7.0 \pm 1.1) \times 10^8$	$(5.6 \pm 0.9) \times 10^6$
15		1.83	$(5.2 \pm 0.5) \times 10^9$	$(4.0 \pm 0.2) \times 10^9$	$(2.7 \pm 0.2) \times 10^8$	$< 1 \times 10^5$
16		1.74	$(4.9 \pm 0.5) \times 10^9$	$(4.0 \pm 0.2) \times 10^9$	$(1.8 \pm 1.1) \times 10^9$	$(3.9 \pm 0.3) \times 10^6$
17		1.33 (1.2[e])	$(6.0 \pm 0.7) \times 10^9$	$(5.2 \pm 0.3) \times 10^9$	$(8.3 \pm 0.6) \times 10^9$	$(7.2 \pm 0.9) \times 10^9$
18		1.99	$(4.2 \pm 1.0) \times 10^9$	$(1.3 \pm 0.1) \times 10^9$	$(7.0 \pm 0.1) \times 10^7$	$(5.0 \pm 1.0) \times 10^5$
19		1.73	$(3.0 \pm 1.0) \times 10^9$	$(2.6 \pm 0.2) \times 10^9$	$(4.6 \pm 0.3) \times 10^8$	$(3.6 \pm 0.3) \times 10^6$
20		1.61	$(5.3 \pm 0.7) \times 10^9$	$(4.2 \pm 0.4) \times 10^9$	$(1.3 \pm 0.1) \times 10^9$	$(9.2 \pm 0.7) \times 10^6$

[a] Irreversible half-wave potentials in volts vs. SCE in acetonitrile. [b] Rate constants measured in TFE. Errors in the rate constants are <±20%. [c] Rate constants measured in acetonitrile. Errors in rate constants are <±10%. Some data have been published in ref 25. [d] Reference 28. [e] Reference 29.

Second-order rate constants for the reaction of the radical cations of styrene, 4-methylstyrene, 4-methoxystyrene, and β-methyl-4-methoxystyrene with a wide range of simple alkenes, dienes, and vinyl ethers were also measured. The radical cations of styrene and 4-methylstyrene were quenched upon the addition of all the alkenes with second-order rate constants summarized in Table 2. The rate constant for the decay of the 4-methoxystyrene radical cation increased in the presence of all alkenes except hexene, cyclohexene, and 4-methyl-2-pentene and the second-order rate constants are also included in Table 2. The radical cation of β-methyl-4-methoxystyrene was completely unreactive toward all of the simple alkenes up to 1.0 M

Table 3. Second-Order Rate Constants for the Addition of Substituted Styrenes to the 4-Methoxystyrene Radical Cation in Acetonitrile

styrene	$E_{1/2}^{\mathrm{ox}}$	k_{RSty}/M^{-1} s^{-1}
4-trifluoromethylstyrene	2.62	$(9.7 \pm 1.1) \times 10^6$
3-trifluoromethylstyrene		$<2 \times 10^5$
4-chlorostyrene	2.05	$<2 \times 10^6$
styrene	2.05	$(1.3 \pm 0.1) \times 10^7$
4-fluorostyrene		$(6.6 \pm 0.8) \times 10^6$
3-methylstyrene	1.95	$(3.2 \pm 0.2) \times 10^7$
4-methylstyrene	1.87	$(7.8 \pm 0.3) \times 10^7$
4-methoxystyrene	1.49	1.6×10^9 [a]
β-methylstyrene	1.60	$<2 \times 10^5$
β,β-dimethylstyrene	1.57	$<2 \times 10^5$
α-methylstyrene	1.85	$(1.2 \pm 0.2) \times 10^8$
α,β-dimethylstyrene	1.63	$(7.8 \pm 0.6) \times 10^7$

[a] Calculated number from ref 12.

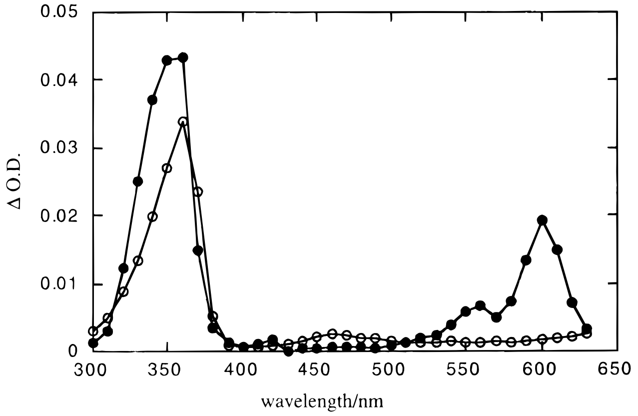


Figure 2. Absorption spectra obtained upon 308-nm laser irradiation of 4-methoxystyrene in acetonitrile with 0.001 M 2,5-dimethyl-2,4-hexadiene immediately (●) and 400 ns after the laser pulse (○).

concentrations, but reacted with several dienes and vinyl ethers with the rate constants shown in Table 2.

Oxidation potentials for the various styrenes and alkenes were measured by cyclic voltammetry. In all cases the oxidation was irreversible under our experimental conditions. The half-wave potentials obtained are reported in Tables 1, 2, and 3; in some cases literature data[28,29] for the same alkenes are provided for comparison.

The absorption spectrum measured immediately after laser photolysis of 4-methylstyrene in the presence of 2,5-dimethyl-2,4-hexadiene in acetonitrile shows the presence of the 4-methylstyrene radical cation, Figure 2, with absorption maxima at 360 and 600 nm. The radical cation then decays by reaction with the diene to give a new transient species with a strong absorption maximum at 360 nm and a weaker band between 400 and 550 nm, Figure 2. The absorption spectrum of the new transient is identical to that of the radical cation of 2,5-dimethyl-2,4-hexadiene produced by γ-irradiation of the diene in a solid matrix,[30] or by photoinduced electron transfer from the diene-to-triplet chloranil in acetonitrile.[31] We therefore identify this transient as the radical cation of 2,5-dimethyl-2,4-hexadiene produced by electron transfer from the diene to the radical cation of the styrene. The same transient is also observed upon quenching of the styrene radical cation by the same diene in TFE and upon reaction of the 4-methoxystyrene[25] and β-methyl-4-methoxystyrene radical cations with the diene in AcN.

Alkene radical cations were not observed in the absorption spectra obtained after complete quenching of the styrene radical cation by the other alkenes used in the present work. The presence of transient species with weak absorptions at wavelengths below 340 nm that were quenched by the addition of oxygen was typically observed, but the absorption spectra in this region were not sufficiently diagnostic to identify the transient products.

Rate Constants for the Reaction of the 4-Methoxystyrene Radical Cation with Substituted Styrenes. As described in our previous work, the 4-methoxystyrene radical cation is rapidly quenched by 4-methoxystyrene in acetonitrile with a rate constant of 1.1×10^9 M^{-1} s^{-1}.[12,13] This radical cation can also be generated in the presence of the other substituted styrenes listed in Table 3 by selective photoionization of 4-methoxystyrene in acetonitrile with 308-nm laser light. Significant acceleration in the decay of the 4-methoxystyrene radical cation was observed upon the addition of sufficiently high concentrations of most of the substituted styrenes. Plots of the observed rate constant for the decay of the radical cation as a function of the concentration of the substituted styrene were linear. Second-order rate constants, k_{RSty}, for reaction of the styrenes with the 4-methoxystyrene radical cation were determined from the slopes of these plots and are summarized in Table 3.

The decay of the 4-methoxystyrene radical cation remained unchanged in the presence of 3-(trifluoromethyl)styrene, β-methylstyrene and β,β-dimethylstyrene at concentrations up to 0.5 M. This establishes an upper limit of $<2 \times 10^5$ M^{-1} s^{-1} for the rate constant for the reaction of the radical cation with these styrenes. The radical cation was also not quenched by 4-chlorostyrene. In this case, the relatively strong absorption of 4-chlorostyrene at the excitation wavelength of 308 nm limited its use to concentrations ≤ 0.05 M, resulting in a higher upper limit of 2×10^6 M^{-1} s^{-1} for the rate constant for reaction of 4-chlorostyrene with the radical cation of 4-methoxystyrene.

The absorption spectra measured immediately after 308 nm laser excitation of 4-methoxystyrene in nitrogen-saturated acetonitrile with high concentrations of styrene showed new absorption bands at 495 and 400 nm, Figure 3, in addition to the absorption bands of the 4-methoxystyrene radical cation at 360 and 600 nm. The transient at 400-nm was longer-lived than the 4-methoxystyrene radical cation, and the absorption spectrum of the solution after the radical cation had completely decayed shows more clearly the 400-nm band and also the presence of an additional weak absorption near 580 nm. The 400- and 580-nm bands decayed with identical rates and both were quenched in oxygen-saturated acetonitrile indicating that they belong to a single transient species. We identify this transient as the styrene radical anion on the basis of the similarity between the absorption spectrum that we obtain in acetonitrile and the spectrum of the same species generated in matrices.[30] This identification is also consistent with the observed oxygen quenching of the transients. The most likely mechanism for the formation of the radical anion is trapping of the electron produced by photoionization of 4-methoxystyrene. The 495-nm transient is more clearly observed in oxygen-saturated solution where the bands due to the radical anion are completely quenched, Figure 3b. The 495-nm transient was unaffected by the presence of oxygen and decayed with an observed rate constant of 5×10^6 s^{-1}.

Similar transients were observed in the absorption spectra obtained upon quenching the 4-methoxystyrene radical cation

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(28) Arnold, D. R.; Snow, M. S. *Can. J. Chem.* **1988**, *66*, 3012−3026.

(29) McManus, K. A.; Arnold, D. R. *Can. J. Chem.* **1994**, *72*, 2291−2304.

(30) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.

(31) Lew, C. S. Q.; Johnston, L. J. Unpublished results.

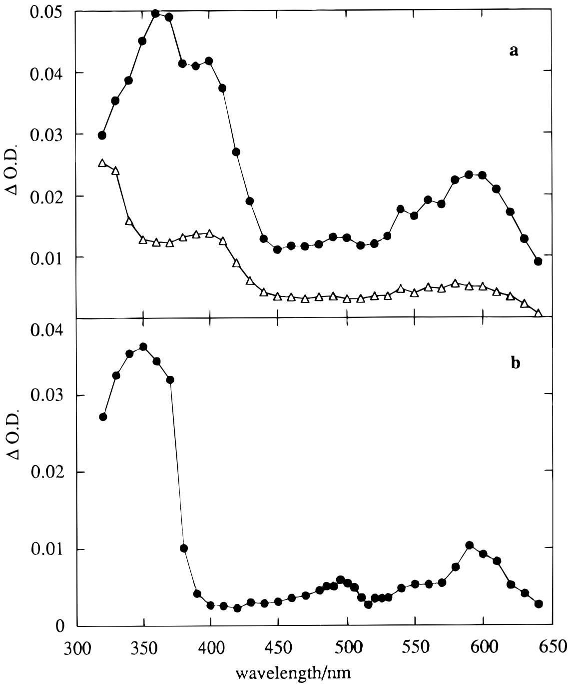
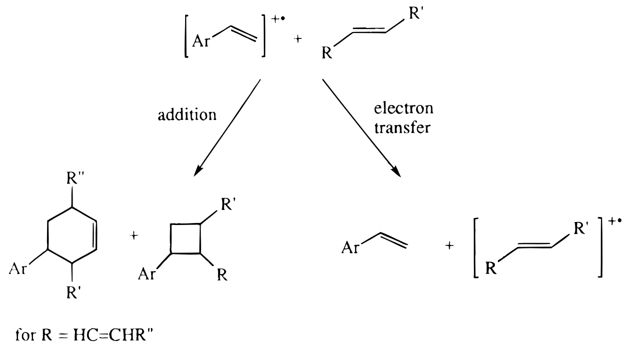


Figure 3. Absorption spectra obtained upon 308 nm laser irradiation of 4-methoxystyrene in nitrogen-saturated (a) and oxygen-saturated (b) acetonitrile with 0.5 M styrene immediately (●) and 1.1 μs after the laser pulse (△).

Scheme 1



with 4-methylstyrene. Absorption bands due to the 4-methylstyrene radical anion at 600 and 420 nm were quenched by oxygen and revealed an absorption at 495 nm that decayed with a rate constant of 5×10^6 s^{-1}. Similar results were also obtained upon complete quenching of the 4-methoxystyrene radical cation with 3-methylstyrene, α-methylstyrene, and α,β-dimethylstyrene.

Discussion

Electron Transfer vs Addition. Two reactions that are likely to be responsible for the observed quenching of the substituted styrene radical cations by a variety of different alkenes are shown in Scheme 1. One is addition of the alkene to the styrene radical cation to give a radical cation that ultimately leads to an arylcyclobutane or Diels−Alder adduct, and the second is electron transfer from the alkene to the styrene radical cation to generate the neutral styrene and the radical cation of the alkene. It should, however, be noted that electron transfer may also lead to adduct formation, even if this is not the primary reaction. Since the main objectives of the present work were to provide kinetic data for the initial addition reaction and to establish the influence of styrene and alkene structure on this reaction, we must first identify which of the two reactions, electron transfer or addition, is responsible for the observed quenching. One means of differentiating between these two possibilities is to compare the experimental rate constants summarized in Table 2 to rate constants for electron transfer calculated using the Marcus equation[32] shown below,

$$\Delta G^{\ddagger} = \Delta G_o^{\ddagger}\left(1 + \frac{\Delta G_o'}{4\Delta G_o^{\ddagger}}\right)^2 \qquad (3)$$

where $\Delta G^{\ddagger}$ is the free energy of activation, $\Delta G_o^{\ddagger}$ is the intrinsic barrier, and $\Delta G_o'$ is the free energy of the electron transfer reaction calculated from the half-wave oxidation potentials of the alkenes and the styrenes, $\Delta G_o' = 23.01\,(E_{1/2}(\text{alkenes}) - E_{1/2}(\text{styrene}))$. The free energy of activation $\Delta G^{\ddagger}$ calculated using Marcus theory can be related to the observed rate constant for a bimolecular electron transfer in solution using eq 4.[33]

$$k_{\text{calc}} = \frac{k_d}{1 + \dfrac{k_d}{K_d Z}\exp\left[\dfrac{\Delta G_o^{\ddagger}}{RT}\left(1 + \dfrac{\Delta G_o'}{4\Delta G_o^{\ddagger}}\right)^2\right]} \qquad (4)$$

In this equation, k_d is the second-order rate constant for a diffusion-limited reaction, K_d is the ratio of the rate constants for the formation and diffusion apart of an encounter complex, and Z is the frequency factor.

A reasonable value for the parameter, $k_d/(K_dZ)$, can be calculated by assuming a rate constant for diffusion-controlled reactions in acetonitrile of $k_d = 1 \times 10^{10}$ M^{-1} s^{-1}, and using values of $K_d = 0.2$ M^{-1} and $Z = 5 \times 10^{11}$ s^{-1} that are typical for the reactions of a positively charged species with a neutral species in solution.[33] Although measured values of $\Delta G_o^{\ddagger}$ for electron transfer between alkenes and styrene radical cations are not available, values for bimolecular electron transfer reactions involving radical cations in solution are generally significantly greater than 3 kcal mol^{-1}.[33] Thus, upper limit rate constants for the electron transfer from the alkenes to the styrene radical cations can be calculated from eq 4 using $\Delta G_o^{\ddagger} = 3$ kcal mol^{-1} and $k_d/(K_dZ) = 0.1$ together with the values of $\Delta G_o'$ determined from the oxidation potentials of the alkenes and the styrenes.

Experimental rate constants for the quenching of the radical cations of styrene, 4-methylstyrene, 4-methoxystyrene and β-methyl-4-methoxystyrene with the alkenes shown in Table 2 are plotted as a function of $\Delta G_o'$ in Figure 4. Also included in these plots are curves calculated using eq 4 that represent upper limit rate constants for the electron-transfer reaction. These plots clearly indicate that when the electron-transfer reaction is endothermic ($\Delta G_o' > 0$) based on our measured oxidation potentials, the measured rate constants for the reaction of the styrene radical cations with the various alkenes are several orders of magnitude greater than the upper-limit rate constant calculated for an electron-transfer reaction.[34] Since the measured rate constants are much greater than those predicted by Marcus theory, we can rule out the possibility that the observed quenching is due to electron transfer, and conclude that the reaction between the substituted styrene radical cations and alkenes is addition when $\Delta G_o^{\ddagger} > 0$.

When the electron-transfer reaction is exothermic, $\Delta G_o' < 0$, reasonable agreement is observed between the measured rate constants and the calculated rate constants. This indicates that

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(32) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(33) Eberson, L. *Reactivity and Structure in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

(34) A range of values for the various parameters in eq 4 have been used to calculate the electron transfer rate constant, without improving the fit of the calculated and observed rate constants.

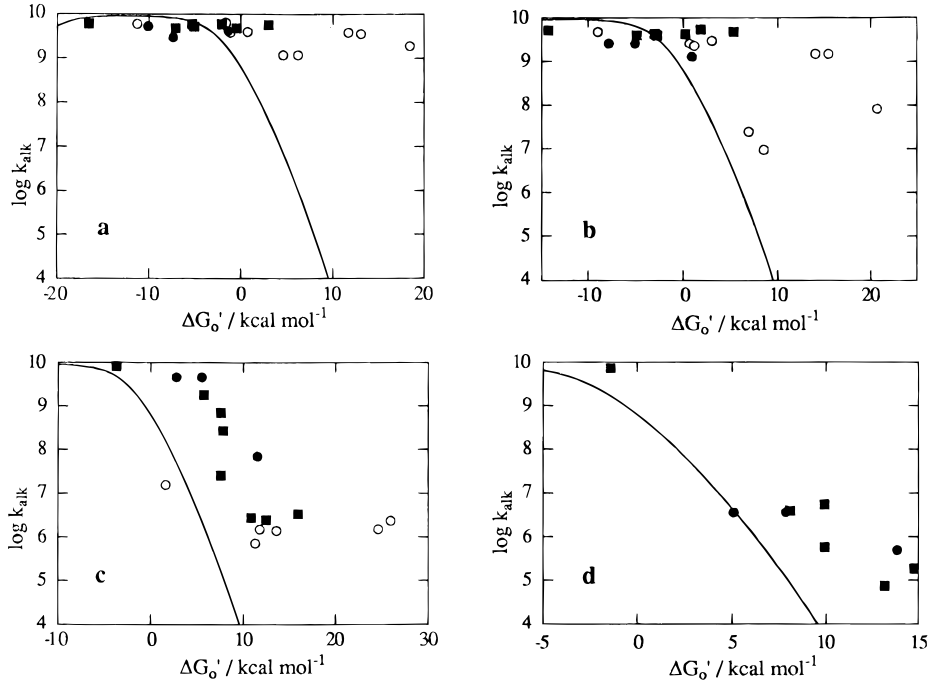

Figure 4. Relationship between second-order rate constants for the quenching of the radical cations of styrene (a) and 4-methylstyrene (b) in TFE and 4-methoxystyrene (c) and *β*-methyl-4-methoxystyrene (d) in acetonitrile by alkenes (○), dienes (■), and vinyl ethers (●) and the free energy for electron transfer. The curves were calculated using eq 4 and the parameters given in the text.

electron transfer from the alkene to the styrene radical cation is a feasible reaction. In fact, the observation that the radical cation of 2,5-dimethyl-2,4-hexadiene ($E_{1/2} = 1.33$ V) is produced upon quenching of each of the four styrene radical cations by neutral diene in either TFE or AcN provides direct evidence that electron transfer is an important process when the reaction is sufficiently exothermic. It is worth noting, however, that the close similarity between the measured and calculated rate constants for electron transfer in the region where $\Delta G_o' < 0$ does not rule out the possibility that some addition may take place. The fact that addition of the styrene and 4-methylstyrene radical cations to some alkenes occurs with rate constants that are close to the diffusion limit suggests that addition may be competitive with the thermodynamically allowed electron transfer in other cases as well.

The formation of diene radical cations via electron transfer quenching of styrene radical cations by diene was observed only for 2,5-dimethyl-2,4-hexadiene (**17**). This is somewhat surprising since electron transfer is expected to compete favorably with addition for reactions of both styrene and 4-methylstyrene with dienes such as **13**−**16** and since the radical cations of these dienes have been generated either in matrices or in solution and have similar absorption properties to **17**$^{\bullet+}$.[30,31] However, recent laser flash photolysis results for 2,4-hexadiene (**13**) and 2,4-dimethyl-2,4-pentadiene (**16**) demonstrate that these radical cations are relatively short-lived in AcN and decay by addition to their neutral precursors at the concentrations of diene required to quench the styrene radical cations.[31]

The above discussion leads to the conclusion that the measured rate constants for reaction between the styrene radical cations and alkenes are those for addition when the oxidation potential of the alkene is greater than that of the styrene. For the styrene radical cation reaction with alkenes **1**−**6** and diene **10** occurs by addition, whereas electron transfer contributes or predominates for the other quenchers used. Similarly the 4-methylstyrene radical cation reacts with alkenes **1**−**8** and dienes **10**−**12** by addition. The lower oxidation potential for both 4-methoxystyrene and *β*-methyl-4-methoxystyrene makes the calculated rate constant for electron transfer too slow to account for our measured rate constants for all the alkenes used, except for diene **17** and enol ether **19**. These conclusions are also supported by the fact that both [2 + 1] and [4 + 1] cycloadducts are formed by the reaction of various styrene radical cations with a variety of alkenes under hole transfer catalysis conditions.[5,35−37]

Effect of Styrene Radical Cation Structure on Rate Constant for Addition. The data in Table 1 show the effect of the structure of the styrene radical cations on the rate constants for addition of cyclohexene and ethyl vinyl ether. Except where noted, electron transfer from the alkene to the styrene radical cations is significantly endothermic, and the rate constants are those for addition not electron transfer. The rate constants for the reaction with cyclohexene are strongly influenced by two factors, namely the electron-donating ability of the aromatic substituent and the presence or absence of methyl groups in the *β*-position of the styrene. The influence of the phenyl substituent is clearly illustrated by comparing the rate constants for the reaction of the parent styrene radical cation with cyclohexene to those for the 4-fluoro-, 4-methyl, and 4-methoxystyrene radical cations. The styrene radical cation is quenched by cyclohexene with a rate constant of 1.2×10^9 M^{-1} s^{-1} which is about 3-fold greater than the rate constant for quenching of the 4-fluorostyrene radical cation, and 50 times greater than the rate constant for quenching of the 4-methylstyrene radical cation by the same alkene. The 4-methoxystyrene radical cation is so unreactive toward cyclohexene that no measurable increase in the rate constant for its decay is observed up to 0.5 M cyclohexene. Thus, the reactivity of the substituted radical cations decreases as the electron-donating ability of the 4-substituent increases, such that the reactivity order is 4-MeO < 4- Me < 4-F < 4-H. The rate constants for the reaction of the same radical cations with ethyl vinyl ether approach the diffusion-controlled limit for all but the 4-methoxy-substituted

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(35) Bauld, N. L.; Bellville, D. J.; Pabon, R.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378−2382.

(36) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158−5159.

(37) Reynolds, D. W.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6189−6194.

radical cation. Although these reactions are less selective than those with cyclohexene, the same reactivity order is observed.

The β-methyl effect is established from the observations that the β-methylstyrene radical cation is more than two orders of magnitude less reactive toward cyclohexene than the styrene radical cation and that the addition of a second β-methyl group in β,β-dimethylstyrene renders the decay of the radical cation completely insensitive to the presence of cyclohexene up to 1.0 M. Furthermore, a large 140-fold decrease in the rate constant for the reaction with ethyl vinyl ether is observed upon adding a methyl group to the β-position of the 4-methoxystyrene radical cation.

The rate constant for the reaction of the α-methyl-4-methoxystyrene radical cation with ethyl vinyl ether is almost identical to that for the reaction of 4-methoxystyrene radical cation. Thus, while a single methyl group in the β-position has a strong influence on the kinetics of the addition reaction, the presence of a methyl group in the α-position has no effect. This is similar to our earlier results which showed that the rate constants for the reactions of the same radical cations with nucleophiles are insensitive to the presence of methyl groups at the α-position, but decrease significantly upon the addition of a β-methyl group.[13]

Additional information concerning the effect of the structure of the styrene radical cation on the rate constants for the addition of a wider range of alkenes can be obtained from Table 2. The second-order rate constants for quenching of the radical cation by alkenes **1**−**6** decrease in the order styrene > 4-methylstyrene > 4-methoxystyrene > β-methyl-4-methoxystyrene. The difference between the rate constants for quenching of the styrene and the 4-methylstyrene radical cations by alkenes **2** and **3** is small since the rate constants approach the diffusion-controlled limit in TFE. On the other hand, the reactivity of the styrene radical cation toward hexene, cyclohexene, and 4-methyl-2-pentene is significantly greater than that of the 4-methylstyrene radical cation. The data in Table 2 also show that the 4-methoxystyrene radical cation is considerably less reactive toward dienes **10**−**20** than the 4-methylstyrene radical cation, but more reactive than the β-methyl-4-methoxystyrene radical cation. Thus, the decreased reactivity of the radical cation toward carbon nucleophiles upon addition of either a β-methyl group or an electron-donating group at the 4-position of the phenyl ring is a general trend followed by each alkene examined in the present work.

Effect of Alkene Structure on Rate Constant for Addition. Examining the data in each column in Table 2 highlights the effect of the alkene structure on the rate constants for the addition of alkenes to the radical cations of styrene, 4-methylstyrene, 4-methoxystyrene, and β-methyl-4-methoxystyrene. The data in the first column show that the parent styrene radical cation is essentially nonselective in its reactions with the entire group of alkenes, with rate constants varying from 1.2×10^9 M^{-1} s^{-1} for cyclohexene to 5.9×10^9 M^{-1} s^{-1} for 2,3-dimethyl-1,4-pentadiene. Rate constants for reactions with alkenes **1**−**6** vary by only a factor of 2, indicating that there is little effect of alkene structure on the second-order rate constant for addition. The low selectivity of the styrene radical cation is similar to previous results on the addition of nucleophiles to styrene radical cations[13] and reflects the high reactivity of the radical cation due to the absence of electron-donating groups. Thus, the styrene radical cation reacts sufficiently rapidly that its rate constant for addition to alkenes is unaffected by either the nucleophilicity of the alkene or steric factors.

The radical cation of 4-methylstyrene is considerably more selective in its addition to alkenes **1**−**6** than the styrene radical cation, with rate constants ranging from 9.5×10^6 M^{-1} s^{-1} for reaction with 4-methyl-2-pentene (**4**) to almost 3.1×10^9 M^{-1} s^{-1} for reaction with methylenecyclohexane (**2**). These results indicate that terminal 2,2-dialkyl-substituted alkenes such as **2** and **3** are considerably more reactive than terminal alkenes such as **1**, and suggest that the number of alkyl substituents on the carbon−carbon double bond has an important influence on the reactivity of the alkene toward the radical cation. On the other hand, trialkyl-substituted alkenes such as **6**−**8** are no more reactive than terminal dialkyl-substituted alkenes **2** and **3**, and nonterminal 1,2-dialkyl substituted alkenes such as **4** and **5** are significantly less reactive than the dialkyl-substituted terminal alkenes **2** and **3**, and slightly less reactive than 1-hexene. Thus, not only the number of alkyl substituents but also their position on the carbon−carbon double bond are important factors in determining the reactivity of the alkenes toward the radical cations.

The effects of alkene structure on the rate constants for addition reactions of the 4-methoxystyrene radical cation show similar trends to those observed for the reactions of the 4-methylstyrene radical cation. The least reactive alkenes were 1-hexene (**1**), cyclohexene (**5**), and 4-methyl-2-pentene (**4**), all of which have rate constants of $<5 \times 10^5$ M^{-1} s^{-1}. In addition, the 4-methoxystyrene radical cation was effectively quenched by the dialkyl-substituted terminal alkenes **2** and **3** with rate constants slightly greater than those for quenching by the trialkyl substituted alkenes **6**−**8**.

Trends reflecting the nucleophilicity of the hydrocarbon alkenes **1**−**8** as a function of methyl substitution can be summarized as follows. Both the number of alkyl groups attached to the carbon−carbon double bond and their position influence the rate constants for the cycloaddition reaction. Thus, 1,2-dialkyl-substituted alkenes are less reactive than 1-hexene and than 2,2-dialkyl-substituted alkenes such as methylenecyclohexane and 2-methyl-1-butene. Trialkyl-substituted alkenes are slightly less reactive than the 2,2-dialkyl alkenes. Finally, the tetrasubstituted alkene, 2,3-dimethyl-2-butene, is the most reactive alkene of those studied in the present work. This leads to the following trend for the relative reactivity of the alkenes toward the styrene radical cations: 1,2-dialkyl < 2-alkyl < trialkyl ≤ 2,2-dialkyl < tetraalkyl.

The reactions of the styrene and 4-methylstyrene radical cations with dienes **10**−**17** take place with diffusion-controlled rate constants of ca. 5×10^9 M^{-1} s^{-1} and occur predominately by electron transfer rather than addition. However, electron transfer from dienes **10**−**16** to the radical cations of 4-methoxystyrene and β-methyl-4-methoxystyrene is endothermic by ≥250 mV, and the reactions are all expected to be addition. The only exception is diene **17** which has a sufficiently low oxidation potential to undergo electron transfer with all four radical cations. The data show that the rate constants for the addition of dienes to the 4-methoxy-substituted styrene radical cations are considerably greater than those for addition of simple alkenes. For example, 4-methoxystyrene radical cation adds to the terminal diene **11** about one order of magnitude more rapidly than to the terminal alkene **2**, and the β-methyl-4-methoxystyrene radical cation is quenched by diene **11**, but is completely insensitive to alkene **2**. Similarly, dienes **13** and **14** quench both 4-methoxy substituted radical cations with rate constants that are at least an order of magnitude greater than the rate constants for quenching by the corresponding alkenes **4** and **5.**

The rate constants for the addition of vinyl ethers **18**−**20** to the 4-methoxy substituted styrene radical cations are also significantly greater than the rate constants for addition of the

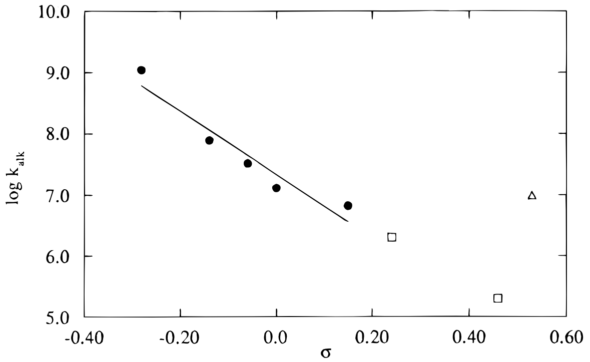


Figure 5. Relationship between the second order rate constants for the quenching of 4-methoxystyrene radical cation with phenyl substituted styrenes in acetonitrile. The line was calculated using the data points represented by (●). The points for 4-chlorostyrene and 3-(trifluoromethyl)styrene are upper limits and are represented by (□). The point for 4-(trifluoromethyl)styrene is represented by (△).

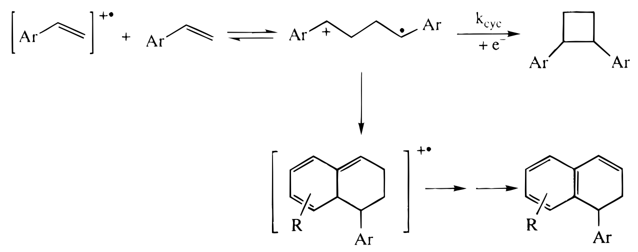
corresponding alkenes and dienes. Therefore, the nucleophilicity of the substituted alkenes toward the styrene radical cations follows the order alkyl < alkene < alkoxy.

Quenching of 4-Methoxystyrene Radical Cation by Substituted Styrenes. The rate constants for the reaction of the 4-methoxystyrene radical cation with substituted neutral styrenes show clearly that electronic effects are important in determining the reactivity of the olefin. Thus, the rate constant for the addition of the electron-rich 4-methoxystyrene to the radical cation of 4-methoxystyrene is almost 3 orders of magnitude greater than the rate constant for styrene addition, and at least 4 orders of magnitude greater than that for the addition of 4-chlorostyrene. The effect of phenyl substituent on the rate constant for addition is shown more clearly in the plot of the rate constants for the addition of the phenyl-substituted styrenes to 4-methoxystyrene radical cation versus Hammett σ parameters, Figure 5. This plot is reasonably linear ($\langle r \rangle = 0.96$), with a large negative slope of $\rho = -5$ which demonstrates that the rate constant for addition decreases considerably as a function of decreasing electron-donating ability. The rate constant for addition of the 4-CF_3 derivative falls considerably above the line determined from the other five data points, indicating that the reaction of the radical cation with this styrene is considerably faster than expected. The reason for this anomalous behavior is not understood at the present time, but may indicate a change in mechanism for this particular styrene.

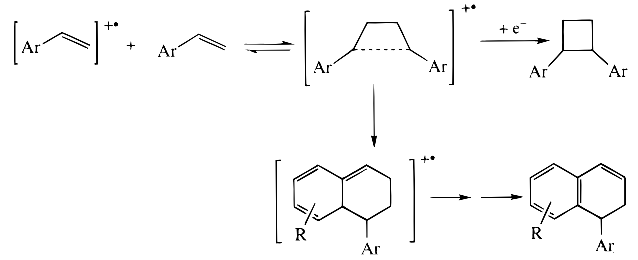
While an electron-donating phenyl substituent such as 4-methyl accelerates the addition reaction, the presence of a methyl group at the β-position clearly has the opposite result. This is exemplified by the observations that β-methylstyrene and β,β-dimethylstyrene quench the radical cation of 4-methoxystyrene with rate constants at least 1000-fold smaller than that measured for styrene itself. On the other hand, the presence of a methyl group at the α-position causes a significant acceleration in the rate constant, with α-methylstyrene adding to the 4-methoxystyrene radical cation with a rate constant that is 10-fold larger than the addition of the parent styrene to the same radical cation. These results are consistent with the trend established for the reaction of the styrene radical cations with alkenes in that a disubstituted terminal alkene such as α-methylstyrene is more reactive than both the parent styrene and the trisubstituted α,β-dimethylstyrene.

Mechanism for Addition. The addition of a radical cation to an alkene can in principle occur via either a stepwise or concerted pathway. The initial work on the radical cation initiated dimerization of *N*-vinylcarbazole was proposed to occur via stepwise addition to generate a 1,4-butanediyl radical cation as the key intermediate (Scheme 2).[38] The formation of dihydronaphthalene products in some arylalkene cyclodimerizations was also taken as evidence for the intermediacy of a 1,4-acyclic radical cation that could either cyclize to give a cyclobutane product (directly or via initial reduction to a biradical) or rearrange.[21,39,40] However, there is now considerable evidence from both product studies and theoretical work that argues in favor of a concerted but nonsynchronous cycloaddition to give a long-bond cyclobutane as the primary intermediate (Scheme 3).[6,41] For example, the stereospecificity of the cyclobutane products observed in the dimerization of *cis*- and *trans*-anethole is inconsistent with the formation of a freely-rotating 1,4-acyclic radical cation as an intermediate.[22,42] Our recent detailed study of the dimerization of 4-methoxystyrene is also consistent with formation of a cyclobutane radical cation as the key intermediate.[12] In this case the cyclobutane radical cation can ring open to give neutral 4-methoxystyrene and its radical cation, undergo reduction to generate cyclobutane, or rearrange to give a substituted hexatriene radical cation that ultimately gives dihydronaphthalene products (Scheme 3). The experimental results do not require the presence of an acyclic radical cation, although transients assigned to this intermediate have been reported in other studies.[16,18,19]

Scheme 2



Scheme 3



The addition of an alkene radical cation to a diene can give mixtures of cyclobutane and Diels−Alder products, although the latter usually predominate for dienes with at least modest s-cis conformer populations.[6] The formation of the two possible products raises the possibility that the Diels−Alder adduct arises either by secondary chemistry of the cyclobutane or via an initial cyclobutane radical cation rather than via direct cycloaddition. It has been clearly demonstrated that the cyclobutanation and Diels−Alder cycloadditions are independent reaction paths in some systems.[6] However, there are also examples where Diels−Alder adducts arise via rearrangement of initial divinyl cyclobutane products.[6] Despite a large amount of mechanistic and theoretical work, it is clear that neither the concerted nor the stepwise mechanism can satisfactorily explain all the available data. Furthermore, both the solvent and the method

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for generating the radical cation (photosensitization versus hole transfer catalysis with arylaminium salts) will play a role in determining the overall mechanism. For example, the solvent may change the relative energies of the acyclic and cyclobutane radical cations and the sensitizer frequently plays a role in determining the fate of the initial adduct radical cation.

The kinetic data obtained in the present study clearly demonstrate the effects of varying the structure of both the arylalkene radical cation and the alkene or diene on the rate constants for the initial step in the radical cation mediated cycloaddition reaction. However, the transient spectra measured after complete reaction of the styrene radical cations with simple alkyl- or alkoxy-substituted alkenes or dienes provide no evidence for either of the possible product radical cations. This could be taken as evidence for a concerted pathway, since in at least some cases the distonic radical cation generated by addition of a substituted styrene would be expected to have a reasonable chromophore in the UV−visible region, whereas considerably weaker absorptions might be expected for a cyclobutane radical cation. However, in the absence of detailed product studies for any particular reactant combination, it would certainly be premature to interpret our laser flash photolysis results in terms of either mechanistic scenario.

The addition of the 4-methoxystyrene radical cation to various substituted styrenes yields transient products that are similar to the 495-nm transient observed in the radical cation-mediated dimerization of 4-methoxystyrene. By analogy with the earlier work, it is likely that the observed transients are also the hexatriene radical cations. In the present case we do not observe curvature in the plots of observed rate constant for decay of the 4-methoxystyrene radical cation as a function of added styrene concentration. In our earlier work this curvature was a result of the reduction of the cyclobutane radical cation by excess styrene. This may be less important in the present examples because either the relative oxidation potentials of the cyclobutane and the styrene or changes in the lifetime of the cyclobutane radical cation make this process energetically unfavorable.

Comparison with Additions of Other Electrophilic Species. Absolute kinetic data for the addition of diarylcarbenium ions to a wide range of alkenes, dienes, and enol ethers have been measured by Mayr and co-workers during the last decade.[43,44] The trends observed in the present work show some similarity to those observed for the carbenium ion additions. As an example, Figure 6 shows a plot of the log of the rate constant for the addition of 4-methyl- and 4-methoxystyrene radical cations to selected alkenes versus the log of the rate constant for addition of the bis(4-chlorophenyl)methyl cation to the same substrates.[45] This particular cation was selected since the rate constants have been measured at room temperature in acetonitrile using laser flash photolysis techniques and cover a similar kinetic range to the data for the 4-methoxystyrene radical cation. The plot demonstrates that there is a reasonable correlation between the data for this radical cation and the carbenium ion data for a range of terminal and substituted alkenes. The rate constants for the 4-methylstyrene radical cation are all in excess of 10^9 M^{-1} s^{-1}, and thus show little selectivity.

The addition to substituted styrenes may also be compared with similar data for carbenium ions. For example, the rate constants for addition of the bis(4-methylphenyl)methyl cation with a series of ring-substituted styrenes give ρ and $\rho+$ values of −5.2 and −5.0, respectively.[43] These results have been interpreted in terms of a high positive charge density on the α-carbon of the styrene in the transition state. The ρ value measured in the present work for the addition of the 4-methoxystyrene radical cation is comparable to those observed for carbenium ion additions. The latter reactions have been suggested to proceed via a partially bridged transition state.[43] Therefore, addition of a radical cation to an alkene via a concerted but nonsynchronous mechanism to give a cyclic radical cation might be expected to show similarities to carbenium ion additions.

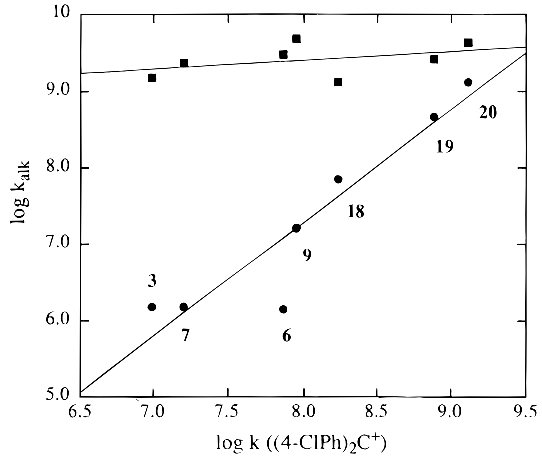

Figure 6. Plot of the log of the observed rate constant for addition of the 4-methyl- (■) and 4-methoxystyrene (●) radical cations to substituted alkenes and dienes vs the log of the rate constant for addition of the bis(4-chlorophenyl)methyl cation to the same substrates.

The rate constants for addition of the 4-methylstyrene and 4-methoxystyrene radical cations do not correlate particularly well with the ionization potential of the alkene or diene, even if only terminal alkenes or dienes are used to minimize steric effects. A similar lack of correlation with ionization potential has been observed for additions of carbenium ions and in fact has been used to argue against a rate-determining electron-transfer step.[43] By contrast, the addition of carbenium ions to enol ethers does correlate with ionization potential as does the addition of electrophilic radicals such as azidyl and perfluoroalkyl to substituted alkenes.[46,47] The addition of azidyl and perfluoro-*n*-octyl radicals to substituted styrenes can also be correlated with Hammett constants with ρ values of −1.5 and −0.53, respectively, that illustrate the electrophilic nature of the additions.

Conclusions

Rate constants for the reaction of four styrene radical cations with a series of alkenes, dienes, and enol ethers have been measured by laser flash photolysis and have been shown to correspond to either addition or electron-transfer reactions. The results demonstrate that electron transfer to generate an alkene or diene radical cation is a competitive, if not the predominant, process when the oxidation potential of the alkene is lower than that of the styrene. The absolute kinetic data obtained for the addition reactions provide the first detailed results on steric and electronic effects on the initial step in radical cation mediated cycloaddition reactions. The observed trends in reactivity are similar to those observed for the addition of diarylcarbenium ions to alkenes and dienes. Although the transient experiments

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do not provide any spectroscopic evidence for the initial product radical cation formed in the cycloaddition reactions of simple alkyl- or alkoxy-substituted alkenes, our results are consistent with previous suggestions of a concerted pathway to give a cyclobutane radical cation.

The synthetic utility of radical cation-mediated chemistry, and in particular cyclobutanation and Diels−Alder reactions, has been demonstrated.[2−8] However, it is clear that the rational design of synthetic strategies based on this chemistry requires detailed kinetic and mechanistic information for all the potential reaction pathways of the various intermediates. For example, cyclodimerization of an arylalkene radical cation will frequently compete with cross-addition to give, for example, a Diels−Alder product. Knowledge of the rate constants for the two competing processes allows the appropriate choice of concentrations and conditions to maximize the yield of the desired product. Of course, this is only one step in the reaction sequence and both the rate constant for generation of the initial radical cation and the possibility of partitioning of the initial radical cation adduct between cycloadduct formation and other reactions such as rearrangement and addition of nucleophiles must also be considered. The kinetic and mechanistic data provided herein for styrene radical cation additions to alkenes and dienes and that previously published for cyclodimerizations of the same radical cations[12,13] provide the basis for the exploitation of radical cation chemistry by the synthetic chemist.

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