Nanosecond and Picosecond Dynamics of the Radical Cation Mediated Dimerization of 4-Methoxystyrene[1]

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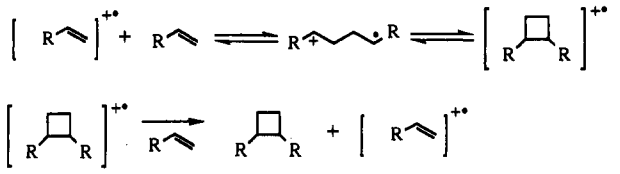
Abstract: The addition of the 4-methoxystyrene radical cation to neutral 4-methoxystyrene and the cleavage reactions of the 1,2-bis(4-methoxyphenyl)cyclobutane radical cation in acetonitrile have been studied by product analysis and by nanosecond and picosecond transient absorption spectroscopy. The main product upon radical cation mediated dimerization of 4-methoxystyrene using chloranil as the electron transfer sensitizer is a substituted dihydronaphthalene, 1,2-dihydro-7-methoxy-1-(4′-methoxyphenyl)naphthalene, at low concentrations of 4-methoxystyrene. At higher concentrations, the main product is 1,2-bis(4-methoxyphenyl)cyclobutane. Cleavage of the cyclobutane radical cation is found to give 4-methoxystyrene and the dihydronaphthalene in a 1:3 ratio. In the time-resolved experiments, the radical cations are generated from 4-methoxystyrene and 1,2-bis(4-methoxyphenyl)cyclobutane by 266-nm photoionization or by 355-nm photoinduced electron transfer using triplet chloranil as the sensitizer. A transient with an absorption maximum at 500 nm is observed as a short-lived intermediate in both the radical cation mediated 4-methoxystyrene dimerization and the cyclobutane radical cation cleavage experiments. Spectroscopic and kinetic considerations lead to the conclusion that this transient is a substituted hexatriene radical cation produced as an intermediate in the conversion of the 1,2-bis(4-methoxyphenyl)cyclobutane radical cation to the dihydronaphthalene. Observed rate constants for the decay of the 4-methoxystyrene radical cation measured at 4-methoxystyrene concentrations of 0.0001 to 0.015 M increase in a linear fashion with concentration, while at concentrations >0.2 M, the observed rate constant is found to be independent of concentration. Analysis of the kinetic data according to a rate law derived from a concerted [2 + 1] mechanism leads to the following rate constants: $k_1 = 1.4 \times 10^9$ M^{-1} s^{-1} for the addition reaction, $k_{-1} = 8 \times 10^7$ s^{-1} for the cycloreversion reaction, $k_2 = 2.5 \times 10^8$ s^{-1} for the rearrangement of the cyclobutane radical cation, and $k_3 = 1.5 \times 10^{10}$ M^{-1} s^{-1} for the reduction of the cyclobutane radical cation by neutral 4-methoxystyrene. Monitoring the kinetics of the reactions of the cyclobutane radical cation gives the same values for the rate constants k_2 and k_{-1}.

Introduction

Olefin radical cations undergo a variety of cycloaddition reactions, including dimerization and cross-additions leading to cyclobutanes and Diels Alder products.[2–6] These reactions are frequently much more facile than the analogous [2 + 2] or [2 + 4] cycloadditions of neutral olefins and often lead to different stereochemistry and regiochemistry. Radical cation mediated cycloaddition reactions are thus of considerable current mechanistic and synthetic interest,[4,7,8] and their use as radical cation clocks has been recently suggested.[9,10] The pioneering work by Ledwith on the triplet chloranil sensitized dimerization of *N*-vinylcarbazole led to the development of the mechanism outlined in Scheme 1 for this radical cation initiated chain process.[11] The key step is addition of the olefin radical cation to a neutral molecule to generate an acyclic 1,4-radical cation. This intermediate then cyclizes to a cyclobutane radical cation that is reduced by the neutral olefin and regenerates a second radical cation to carry on the chain (Scheme 1). This mechanism has been used to explain the radical cation mediated [2 + 2] dimerization of a variety of olefins, including aryl-substituted ethylenes, acetylenes, and vinyl ethers.[2,12,13] Later studies on the photochemical electron transfer sensitized cyclodimerizations established that the acyclic 1,4-radical cation could be trapped by nucleophiles and could also undergo 1,6-cyclization to give a substituted hexatriene radical cation that leads to dihydro- or tetrahydronaphthalene products.[14–16] More recently, Farid et al. suggested a further modification of the initial mechanism to explain their results on the dimerization of 1,1-diarylethylenes.[17] They invoked a competition between (1) diffusional separation of the initial geminate radical ion pair to give a free radical cation and (2) in-cage trapping of the monomer radical cation to give a dimer radical cation/radical anion pair. The free radical cation reacts with a neutral olefin to generate an acyclic dimer radical cation that undergoes predominantly 1,6-cyclization. In contrast,

Scheme 1



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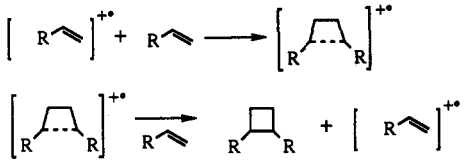
Scheme 2



the geminate radical cation/anion pair undergoes back electron transfer to generate a dimer biradical that cyclizes to cyclobutane.

Although the initial formation of an acyclic distonic radical cation explains much of the experimental data for radical cation-initiated olefin dimerizations, there is equally convincing stereochemical evidence from the work of Bauld[3] and Lewis[18] for a concerted (but non-synchronous) [2 + 1] cycloaddition to give a long-bond cyclobutane radical cation, Scheme 2. This intermediate is then reduced to the cyclobutane by neutral olefin or by sensitizer radical anion. The cyclobutane products retain the stereochemistry of the initial olefin double bond, a result that is not expected for an equilibrated acyclic 1,4-radical cation. It has also been pointed out that a 1,3-sigmatropic shift to give a hexatriene radical cation occurs for a number of cyclobutane radical cations and can thus explain the observation of 1,6-addition products *without* the intermediacy of an acyclic 1,4-radical cation.[3] The concerted cycloaddition mechanism shown in Scheme 2 is also supported by a variety of theoretical calculations on the ion–molecule reaction between ethene radical cation and ethene.[5,19–21] The most recent of these does not provide any evidence for a stable tetramethylene radical cation but does find that the addition of electron-donating substituents stabilizes long-bond cyclobutane radical cations to the extent that they become preferred over the more symmetric delocalized structures.[21]

The ring-cleavage reactions of the diarylcyclobutanes that are formed by radical cation mediated dimerization of styrenes also occur under photosensitized electron transfer conditions.[18,22,23] The results demonstrate that the rate of cleavage of the cyclobutane radical cation is strongly affected by the substituents as a result of changes in the relative charge densities on the cyclobutane ring and the aryl groups.

We have recently undertaken a systematic study of the reactivity of a variety of aryl olefin radical cations toward anionic, alcohol, amine, and olefin nucleophiles. Our initial work in this area indicated that substituted styrene radical cations react with their neutral olefin precursors with rate constants in the range of 10^9 M^{-1} s^{-1}.[24] We have now examined the radical cation mediated dimerization of 4-methoxystyrene and ring-cleavage reactions of its *trans*-cyclobutane dimer using a combination of product studies and nanosecond and picosecond transient absorption measurements. Our results are consistent with a mechanism in which addition of 4-methoxystyrene radical cation to neutral 4-methoxystyrene occurs in a concerted [2 + 1] manner to yield the same cyclobutane radical cation that is formed by oxidation of the neutral *trans*-cyclobutane. This radical cation then either cleaves to regenerate 4-methoxystyrene plus its radical cation or isomerizes to give a substituted hexatriene radical cation. In the presence of high concentrations of 4-methoxystyrene, reduction of the cyclobutane radical cation by the styrene competes with the other two reaction pathways. In addition, our results provide detailed insight into the dynamics of each step of the dimerization process, including rate constants for the addition of the radical cation to neutral 4-methoxystyrene and for the isomerization, cleavage, and reduction of the cyclobutane radical cation.

Experimental Section

Materials and General Techniques. GC analysis was carried out with a Hewlett-Packard 5890 gas chromatograph (cross-linked methylsilicone column), and GC-MS was performed using a Hewlett-Packard 5970 Series mass selective detector. Proton NMR spectra were recorded on a Bruker AM200 spectrometer. Continuous irradiation experiments were carried out using a Rayonet photoreactor equipped with either 300- or 350-nm lamps. The photoreactions were carried out in Pyrex cells. In some cases, the solutions were deaerated by bubbling with argon for 20 min. HPLC analysis of the products from chloranil sensitized irradiation of 1,2-bis(4-methoxyphenyl)cyclobutane was carried out using a Hewlett-Packard 1090 liquid chromatograph with a UV–vis diode-array detector (Hewlett-Packard ODS Hypersil 5-μm column). The solvent program for the HPLC experiments was 50:50 water–acetonitrile for 4 min followed by a 14-min gradient leading to a 25:75 water–acetonitrile mixture. Peak areas were calculated at 260, 280, or 330 nm.

Acetonitrile (HPLC Grade, Baker) was used without further purification. Chloranil was recrystallized from acetonitrile prior to use. 4-Methoxystyrene (Aldrich) was purified over silica. *cis*-1,2-Bis(4-methoxyphenyl)cyclobutane was prepared according to literature procedures[25] by irradiation (300 nm) of 4-methoxystyrene in argon-saturated acetonitrile for seven hours and purified over silica using benzene as the eluant. ^{1}H-NMR ($CDCl_3$) δ 6.16–6.40 (dd, 8H), 3.44 (m, 2H), 3.24 (s, 6H), 1.92 (m, 4H); GC/MS *m/e* (rel intensity) 240 (1), 134 ($M^+/2$, 100), 119 (14), 91 (12). *trans*-1,2-Bis(4-methoxyphenyl)cyclobutane was prepared[26] by irradiation (300 nm) of a solution of 1,4-dicyanobenzene and 4-methoxystyrene in argon-saturated acetonitrile for 24 h and purified by column chromatography. ^{1}H-NMR ($CDCl_3$) δ 6.34–6.72 (dd, 8H), 3.24 (s, 6H), 3.04 (m, 2H), 1.82 (m, 2H), 1.64 (m, 2H); GC/MS *m/e* (rel intensity) 240 (1), 134 ($M^+/2$, 100), 119 (14), 91 (13).

Dimerization of 4-Methoxystyrene. Irradiation (350 nm) of an aerated solution of chloranil (0.001 M) with low concentrations of 4-methoxystyrene (0.01 M) in acetonitrile for 1.5 h resulted in conversion of 4-methoxystyrene to two products present in a 23:1 ratio. The solvent was evaporated under reduced pressure and the major product isolated by column chromatography over silica using a 90:10 hexane–ethyl acetate mixture as the eluant. Analysis by GC/MS and ^{1}H-NMR was used to identify the product as 1,2-dihydro-7-methoxy-1-(4′-methoxyphenyl)-naphthalene. GC/MS, *m/e* (rel intensity) 266 (M^+, 100), 251 (21), 235 (25), 189 (10), 158 (17), 134 (11), 121 (56). ^{1}H-NMR ($CDCl_3$) δ 7.01–7.05 (d, 1H, J = 8.2 Hz), 6.82–7.15 (dd, 4H), 6.67–6.72 (dd, 1H, J = 8.2 Hz, J = 2.6 Hz), 6.40 (d, 1H, J = 2.3 Hz), 6.46–6.51 (d, 1H, J = 9.6 Hz), 5.82–5.91 (dt, 1H, J = 9.6 Hz, J = 4.2 Hz), 3.89 (s, 1H), 3.79 (s, 1H), 4.13 (t, 1H), 2.66 (m, 2H). The minor product was identified by GC/MS as the tetralin derivative, 1,2,3,4-tetrahydro-7-methoxy-1-(4′-methoxyphenyl)naphthalene. GC/MS, *m/e* (rel intensity) 268 (M^+, 57), 240 (13), 209 (15), 160 (100), 134 (14), 121 (11), 91 (8).

Irradiation carried out using concentrations of 4-methoxystyrene >0.05 M gave no dihydronaphthalene. Instead the major product was *trans*-1,2-bis(4-methoxyphenyl)cyclobutane as confirmed by GC/MS and ^{1}H-NMR analysis.

Cleavage of *trans*-1,2-Bis(4-methoxyphenyl)cyclobutane. Irradiation (350 nm) of chloranil (0.005 M) in the presence of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (0.01 M) in acetonitrile for 30 min led to the formation of 4-methoxystyrene and 1,2-dihydro-7-methoxy-1-(4′-methoxyphenyl)naphthalene. HPLC was used to determine quantitatively the relative yields of the two products instead of GC because *trans*-1,2-bis(4-methoxyphenyl)cyclobutane and the dihydronaphthalene have identical retention times on our GC OV1 column. At low conversion (13%) of the *trans* dimer, HPLC analysis showed that 12% of the consumed dimer is converted to 4-methoxystyrene while 34% is converted to the dihydronaphthalene. The remaining 54% of the product was unidentified and is likely due to polymerization.

Laser Photolysis. Nanosecond transient absorption spectra were obtained using a flow system in order to ensure the presence of unphotolyzed substrate for each laser pulse. Observed rate constants for the formation and decay of the radical cations were determined using static samples; in these experiments, each sample was exposed to one laser pulse. The samples in both the flow and static experiments were

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contained in 7 × 7 mm^2 quartz cells. Spectra and rate constants were measured in aerated solutions at room temperature (~20 °C). The laser system used has been described elsewhere.[27] A Nd:YAG laser (266 nm; 80 mJ/pulse; ~10 ns/pulse or 355 nm; 40 mJ/pulse; ~10 ns/pulse) or a Lumonics Model EX530 excimer laser (308 nm; ≤40 mJ/pulse; ~8 ns/pulse) was used as the laser excitation source.

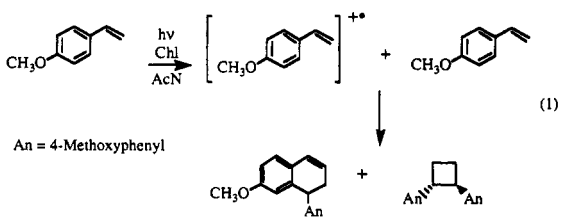
In the picosecond transient absorption experiments, a Continuum YG-601-C Nd:YAG laser giving pulses of 35-ps duration at 10 Hz is used to generate both the probe beam (1064 nm; 15 mJ/pulse) and the excitation beam (266 nm; 6 mJ/pulse). After exiting one port of the laser housing, the excitation beam is directed by a series of dichroic mirrors to a 7 × 7 mm^2 quartz sample cell through which is flowed a solution of the substrate of interest. The 1064-nm beam exits the laser housing through a second port and is sent via another series of dichroic mirrors to a retroflector mounted on the stage of a computer-controlled, precision rail table. The 1064-nm beam is then focused into a 25-cm-long tubular cell containing D_2O with 15% P_2O_5, causing the emission of 35-ps pulses of a broad continuum of light ranging from 400 to 800 nm. The white light continuum is focused onto a bifurcated quartz fiber optic cable (25 cm long) that carries one-half of the continuum light to the sample cell and the other half to a reference cell. The beams of light passing through the sample and reference cells are collected by lenses and focused separately onto two quartz fiber optic cables. These fiber optic cables carry the sample and reference data to a spectrograph which separates the white light continuum into its individual wavelengths and delivers the light to a Princeton Instruments dual diode array (DPDA-1024), with the sample cell data being recorded on one diode array and the reference cell data on the second. The data recorded on both diode arrays are sent to a Princeton Instruments ST-110 controller interfaced to a personal computer for analysis and storage. To obtain an absorption spectrum, the light transmitted through the reference cell, T_R, and through the sample cell, T_S, is recorded in an experiment in which the excitation beam is directed to the sample. A second experiment is then carried out in which the transmission through the reference, T_R', and sample, T_S', cells is recorded with the excitation beam blocked. The absorption spectrum is then calculated from these data using the following expression.

$$\Delta A = -\log(T_S T_R'/T_S' T_R)$$

Decay traces are obtained by measuring the absorption spectra of the sample at various times after the laser pulse and then plotting the absorption at a specific wavelength as a function of known delay times. The monitoring beam was delayed relative to the excitation beam by increasing or decreasing the path length of the 1064-nm light by changing the position of the reflector on the stage of the rail table.

Results

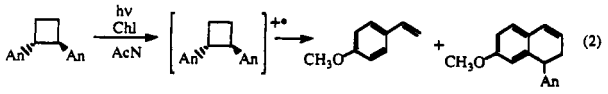
Product Studies. Products from the reactions of the 4-methoxystyrene radical cation were determined by generating the radical cation by photoinduced electron-transfer using chloranil as the electron-transfer sensitizer. Thus, 350-nm irradiation of chloranil in acetonitrile gives singlet chloranil that rapidly intersystem crosses within 30 ps[28] to give triplet chloranil that has been shown to readily oxidize 4-methoxystyrene to its radical cation.[24] The reactions of the 4-methoxystyrene radical cation generated in this way led to the formation of two major products. These products were identified by ^{1}H-NMR and GC/MS as the substituted dihydronaphthalene, 1,2-dihydro-7-methoxy-1(4′-methoxyphenyl)naphthalene and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane, eq 1.



The *trans* stereochemistry of the cyclobutane was established by comparison of the ^{1}H-NMR spectrum of the product isolated in the present work and the ^{1}H-NMR spectrum of the *trans* isomer in the literature, and also by determining that the ^{1}H-NMR and GC characteristics of the product are considerably different than those of an authentic sample of the *cis* isomer synthesized independently. The stereochemistry of the dihydronaphthalene with respect to the chiral center at the 4-position was not determined.

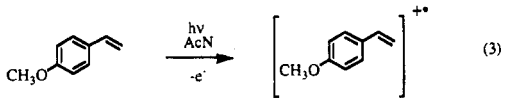
From experiments in which product yields were measured as a function of initial concentrations of 4-methoxystyrene ranging from 0.01 to 0.5 M, it was found that the product ratio was strongly dependent upon the initial concentration of 4-methoxystyrene. At low concentrations of 4-methoxystyrene (<0.02 M), only the substituted dihydronaphthalene was produced, while at higher concentrations, *trans*-cyclobutane formation was also observed. At 0.5 M 4-methoxystyrene, the cyclobutane was the exclusive product. Photoinduced electron-transfer dimerization of 4-methoxystyrene has been described previously[26,29-31] and in all cases the only dimerization product was the cyclobutane. Since these experiments were all carried out using >0.5 M 4-methoxystyrene, the absence of the dihydronaphthalene product is consistent with the present results.

We have also determined the products derived from the cyclobutane radical cation in acetonitrile. This radical cation was generated as described above by irradiation of chloranil in the presence of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane. Two products were formed and identified as 4-methoxystyrene and the same dihydronaphthalene produced in the dimerization reaction, eq 2.



HPLC analysis of the products from chloranil-sensitized irradiation showed that both 4-methoxystyrene and the substituted dihydronaphthalene were produced concomitantly with consumption of the substituted cyclobutane at low conversions, with the 4-methoxystyrene–dihydronaphthalene product ratio remaining unchanged at 1:3 from 2–10% conversion. Thus, both products are primary photoproducts generated from the reactions of the cyclobutane radical cation.

Nanosecond Laser Photolysis: Dimerization. As described previously,[24] 266- or 308-nm laser excitation of 4-methoxystyrene in acetonitrile results in biphotonic photoionization to give the 4-methoxystyrene radical cation, eq 3, with the absorption spectrum shown in Figure 1 (open circles).



The radical cation decays in a first-order manner with a rate constant that is largely determined by the initial concentration of 4-methoxystyrene. Observed rate constants for the decay of the radical cation were found to increase in a linear manner with increasing concentration of 4-methoxystyrene, Figure 2a, and these data lead to the rate constant for quenching of the 4-methoxystyrene radical cation by neutral 4-methoxystyrene, $k_q = 1.1 \times 10^9\ M^{-1}\ s^{-1}$.[24]

Because 4-methoxystyrene has a high extinction coefficient at the excitation wavelengths of 266 and 308 nm, the photoionization

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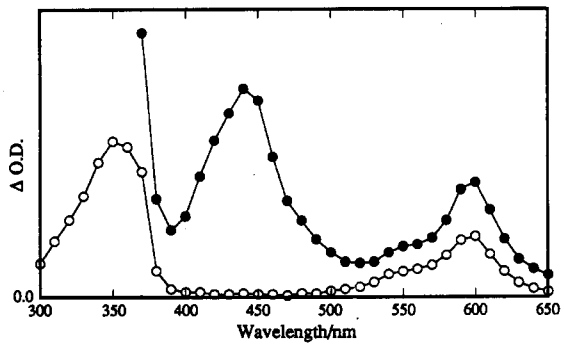
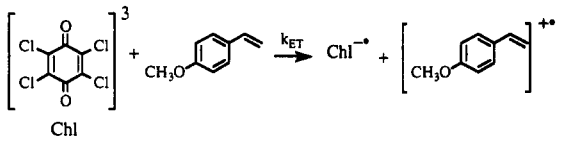


Figure 1. Transient absorption spectrum taken immediately after 266-nm laser irradiation of 4-methoxystyrene (0.0005 M) in acetonitrile (open circles). Absorption spectrum taken 1 μs after 355-nm irradiation of a solution of chloranil (0.003 M) and 4-methoxystyrene (0.001 M) in acetonitrile (filled circles).

method for the generation of the radical cation is limited to the use of relatively low concentrations (<0.0015 M) of 4-methoxystyrene. To study the decay of the 4-methoxystyrene radical cation at higher concentrations, the radical cation was produced by photoinduced electron-transfer from 4-methoxystyrene to triplet chloranil. High concentrations of the styrene can be used because chloranil can be selectively excited at 355 nm where 4-methoxystyrene has no significant absorption.

The chloranil triplet (λ_{max} = 500 nm)[32] generated by 355-nm laser irradiation of chloranil in acetonitrile is quenched by 4-methoxystyrene with a second-order rate constant of $k_{ET} = 1.3 \times 10^{10}\ M^{-1}\ s^{-1}$. Triplet quenching is accompanied by the formation of the radical cation of 4-methoxystyrene with absorption at 600 nm and the chloranil radical ion at 450 nm,[33] Figure 1 (closed circles). These results indicate that triplet quenching involves electron transfer from 4-methoxystyrene to triplet chloranil to give the chloranil radical anion and the radical cation of the styrene, eq 4.



Observed rate constants for the decay of the 4-methoxystyrene radical cation generated by the chloranil sensitization method at low concentrations of 4-methoxystyrene (<0.002 M) parallel the rate constants determined using the photoionization method to generate the radical cation. However, at concentrations of 4-methoxystyrene greater than 0.01 M that are not accessible using the photoionization method, the observed rate constant levels off and reaches a maximum value of about $2.5 \times 10^7\ s^{-1}$ at concentrations >0.20 M, Figure 2b.

As expected from the rapid rate of electron transfer, triplet chloranil is completely quenched and the 4-methoxystyrene radical cation and the chloranil radical anion are produced within the 10-ns laser pulse at 0.01 M 4-methoxystyrene. The radical cation then decays by reaction with neutral 4-methoxystyrene with an observed rate constant of $8.3 \times 10^6\ s^{-1}$. Under these conditions, a transient with an absorption maximum at 500 nm is observed in addition to the chloranil radical anion at 450 nm and the 4-methoxystyrene radical cation at 600 nm, Figure 3. The transient is not produced within the laser pulse, but instead grows in with a rate constant identical to the rate constant for the decay of the radical cation, Figure 3 (inset). The 500-nm band is therefore due to a transient produced by reaction between the 4-methoxystyrene radical cation and neutral 4-methoxystyrene. The 500-nm species is quite reactive and decays in a first-order

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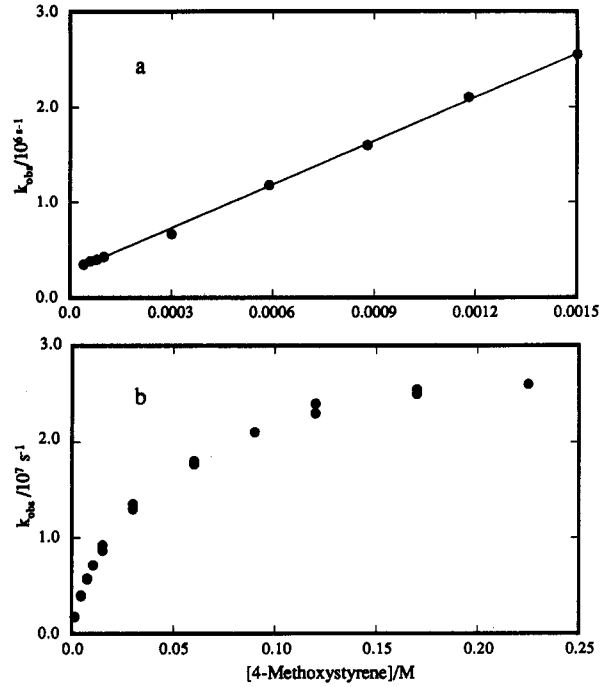


Figure 2. Relationship between the observed rate constant for the decay of the 4-methoxystyrene radical cation and (a) concentration of 4-methoxystyrene ranging from 0.00004 to 0.0015 M and (b) concentration of 4-methoxystyrene ranging from 0.002 to 0.23 M in acetonitrile.

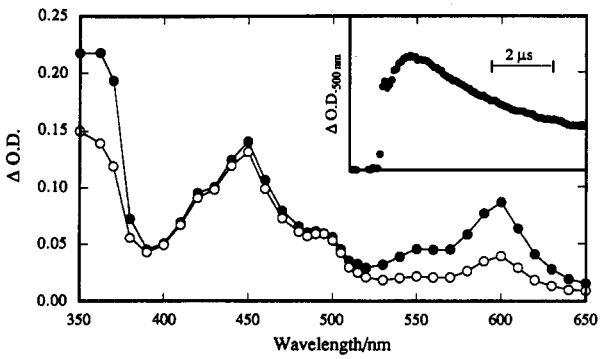


Figure 3. Transient absorption spectra after 355-nm laser irradiation of a solution of chloranil (0.003 M) and 4-methoxystyrene (0.01 M) in acetonitrile. Spectra were recorded immediately after the laser pulse (filled circles) and 100 ns after the laser pulse (open circles). The inset shows the growth and decay of the transient at 500 nm for the same sample.

manner with a rate constant of $k = 5 \times 10^6\ s^{-1}$. The decay remains constant in O_2- and N_2-saturated solution, indicating that the 500-nm transient is not reactive toward oxygen. It should be noted that the transient is not observed (Figure 1, closed circles) in the presence of low concentrations of 4-methoxystyrene because its decay would be faster than its formation by addition of the 4-methoxystyrene radical cation to neutral 4-methoxystyrene. In addition, the initial jump in absorption at 500 nm during the laser pulse and the residual absorption seen in the inset of Figure 3 are not due to the presence of the new transient but are instead due to the chloranil radical anion which has significant absorption in this region and decays quite slowly.

Nanosecond Laser Photolysis: Cyclobutane Ring-Cleavage. The kinetics and spectroscopy of the ring-cleavage reactions of the cyclobutane radical cation have been examined using both nanosecond and picosecond laser spectroscopy. The results from the nanosecond experiments show that the chloranil triplet generated by 355-nm laser excitation is rapidly quenched by the addition of the substituted cyclobutane with a second-order rate constant of $1.5 \times 10^{10}\ M^{-1}\ s^{-1}$ in acetonitrile. The triplet quenching

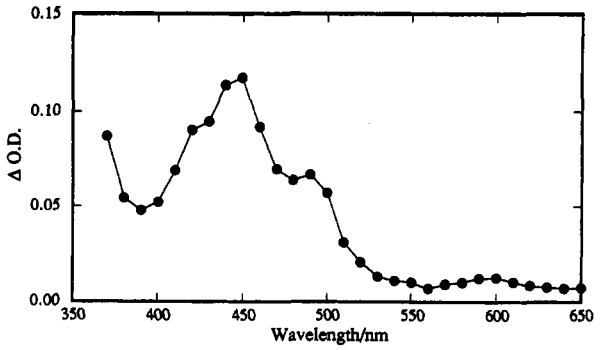
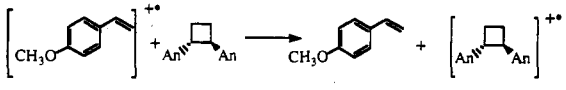


Figure 4. Transient absorption spectrum taken immediately after 355-nm laser photolysis of chloranil (0.003 M) and *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (0.01 M) in acetonitrile.

is accompanied by growth of the chloranil radical anion at 450 nm and by weak absorption at 600 nm due to the 4-methoxystyrene radical cation, Figure 4; the observed rate constant for the growth of the radical ions is the same as that for the triplet decay. An additional transient species is also observed with an absorption maximum at 500 nm, Figure 4, and a decay rate of 5×10^6 s^{-1} that are identical to those for the transient observed upon dimerization of the 4-methoxystyrene monomer radical cation described above. At cyclobutane concentrations of 0.01 M, the chloranil triplet is quenched and the 4-methoxystyrene radical cation and the 500-nm transient are formed within the duration of the 10-ns laser pulse. The prompt formation indicates that both the 4-methoxystyrene radical cation and the 500-nm transient are formed with rate constants $>10^8$ s^{-1}.

In the presence of 0.01 M *trans*-1,2-bis(4-methoxyphenyl)-cyclobutane, the 4-methoxystyrene radical cation decays with a rate constant of 6×10^6 s^{-1} that is significantly greater than the rate constant of 4×10^5 s^{-1} for its decay in neat acetonitrile.[24] This rapid decay indicates that the observed rate constant for the decay of the monomer radical cation depends on the concentration of the substituted cyclobutane. Thus, the observed rate constant for the decay of the 4-methoxystyrene radical cation increased linearly with the concentration of the substituted cyclobutane, with a second-order rate constant of 7×10^8 M^{-1} s^{-1}. Since the only products observed upon chloranil sensitized irradiation of the cyclobutane in acetonitrile are 4-methoxystyrene and the substituted dihydronaphthalene, quenching of the 4-methoxystyrene radical cation by the cyclobutane most likely occurs by electron transfer to give neutral 4-methoxystyrene and the cyclobutane radical cation, eq 5.



(5)

The spectrum in Figure 4 clearly shows that the absorption at 500 nm is significantly more intense than the absorption at 600 nm. After correction for the contribution from the chloranil radical anion, the 500-nm band is found to be 3 times more intense than the 600-nm band. However, different results were obtained upon generation of the cyclobutane radical cation by photoionization of 1,2-bis(4-methoxyphenyl)cyclobutane (0.0001 M) using 266-nm laser irradiation. In this case, the 4-methoxystyrene radical cation and the transient with absorption at 500 nm, Figure 5, were both produced within the duration of the 10-ns pulse. However, the intensity of the radical cation absorption at 600 nm is considerably greater than the absorption at 500 nm. Thus, while chloranil sensitized ring-cleavage gave a 600 nm–500 nm ratio of 1:3, photoionization resulted in a ratio of 3:1 of the two signals.

Picosecond Laser Photolysis: Cyclobutane Ring-Cleavage. Photoionization experiments similar to the nanosecond experiments described above were carried out using time-resolved picosecond absorption spectroscopy. Our results show that direct 35-ps 266-nm irradiation of the *trans* or *cis* isomer of the cyclobutane results in the formation of two transient species. One of these is readily identified as the 4-methoxystyrene monomer radical cation from its characteristic absorption at 600 nm, Figure 6. The time dependence for the growth of the 4-methoxystyrene radical cation, Figure 7a, clearly shows that the radical cation is formed within about 100 ps after the laser pulse.

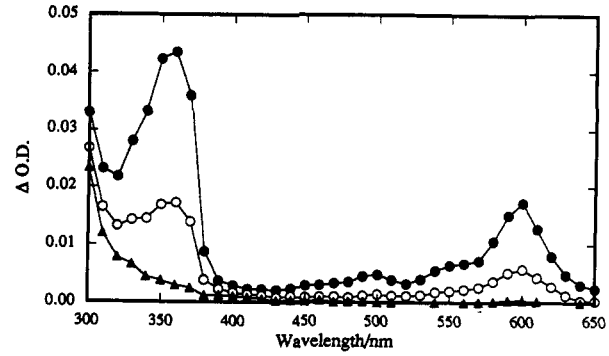


Figure 5. Transient absorption spectra after 266-nm irradiation of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (0.0005 M) in acetonitrile. Spectra were recorded immediately after the laser pulse (filled circles), 100 ns after the laser pulse (open circles), and 2 μs after the laser pulse (filled triangles).

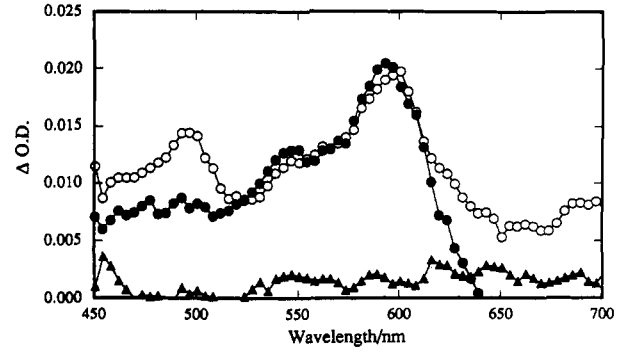


Figure 6. Transient absorption spectra after 266-nm picosecond irradiation of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (0.0005 M) in acetonitrile. Spectra were recorded at time intervals of 0 ps after the laser pulse (filled triangles), 250 ps after the laser pulse (filled circles), and 9 ps after the laser pulse (open circles).

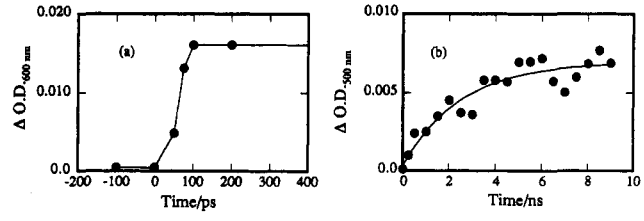


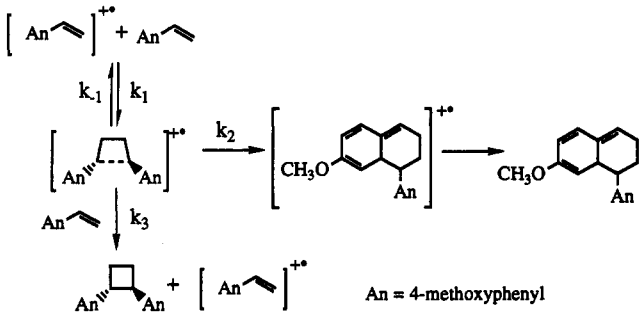
Figure 7. Time-dependent absorption changes upon 266-nm picosecond irradiation of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane (0.0005 M) in acetonitrile monitored at (a) 600 nm and (b) 500 nm.

The second transient produced upon direct 35-ps irradiation of the substituted cyclobutane is the 500-nm transient observed in the dimerization experiments, Figure 6. This species is not detected immediately after the laser pulse. Instead, its population grows to a maximum value at about 5 ns after the laser pulse, Figure 7b. The increase in absorption followed first-order kinetics well, with a rate constant of $k_{growth} = (4 \pm 1) \times 10^8$ s^{-1}.

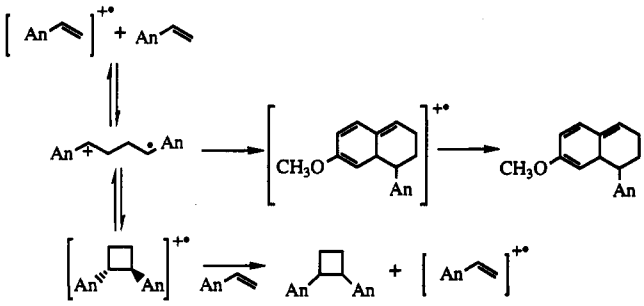
Discussion

The mechanism for the concerted cycloaddition of the 4-methoxystyrene radical cation to neutral 4-methoxystyrene proposed by Bauld[3] is shown in Scheme 3. The primary intermediate is

Scheme 3



Scheme 4



a long-bond cyclobutane radical cation that cleaves to regenerate the radical cation of 4-methoxystyrene and neutral 4-methoxystyrene, or rearranges via a 1,3-sigmatropic shift to the substituted hexatriene radical cation. Loss of a proton followed by electron transfer and loss of a second proton then gives the final observed product, the substituted dihydronaphthalene. The long-bond cyclobutane radical cation can also be reduced by electron transfer from neutral 4-methoxystyrene in a chain propagation step to give the neutral cyclobutane and the radical cation of 4-methoxystyrene. This mechanism differs from the step-wise process postulated by Ledwith in which the primary intermediate upon addition of the 4-methoxystyrene radical cation to neutral 4-methoxystyrene is the acyclic 1,4-radical cation, Scheme 4. In this case, dihydronaphthalene formation occurs by 1,6-cyclization of the acyclic radical cation, while cyclobutane formation takes place by 1,4-cyclization of the acyclic radical cation followed by electron transfer from 4-methoxystyrene.

Both the concerted and step-wise mechanisms are compatible with the results from the dimerization product studies showing that the dihydronaphthalene is the only product at low concentrations of 4-methoxystyrene. The formation of the cyclobutane at higher concentrations of 4-methoxystyrene is also consistent with both mechanisms. In addition, reaction of the radical cation of *trans*-1,2-bis(4-methoxyphenyl)cyclobutane to give 4-methoxystyrene and the dihydronaphthalene agrees with both the concerted and step-wise mechanisms. Therefore, the results from the product studies alone are not sufficient to determine which of the two mechanisms applies to the radical cation mediated dimerization of 4-methoxystyrene and the ring-cleavage reactions of the corresponding cyclobutane. However, the kinetic and spectroscopic data for these two processes can be used to help distinguish between the concerted and stepwise mechanisms, as outlined below.

A 500-nm transient is observed in both the dimerization and ring-cleavage reactions and could in principle be assigned to one of three possible intermediates in Schemes 3 and 4: the acyclic 1,4-radical cation, the long-bond cyclobutane radical cation, or the hexatriene radical cation. Previous time-resolved studies of the radical cation mediated dimerization of styrene,[34,35] α-methylstyrene,[36] and 4-methoxystyrene[25] have all described the presence of similar transient species with absorption in the 450–500-nm region upon addition of the radical cation to the neutral precursor. In particular, Tojo et al.[25] showed that the decay of the 4-methoxystyrene radical cation generated by pulse radiolysis of 0.02 M 4-methoxystyrene in dichloromethane gave rise to an absorption band at 495 nm in a manner similar to that observed in the present work. The results in the previous studies were interpreted on the basis of the assumptions that the addition of the radical cation to the neutral styrene follows the step-wise mechanism, and that the absorption in the 450–500-nm range is due the presence of the acyclic 1,4-radical cation. If these assumptions are both valid, the radical cation mediated cleavage of the substituted cyclobutane should result in the rapid formation of the acyclic 1,4-radical cation at 500 nm. Subsequent decay of the 500-nm band should then be accompanied by a growth in the 600-nm region due to the formation of the 4-methoxystyrene radical cation. However, this is clearly not the case for the chloranil sensitized ring-cleavage experiments carried out in the present work since both the 500-nm transient and the radical cation absorption at 600 nm are formed promptly within the 10-ns laser pulse. Furthermore, the decay of the 500-nm band does not lead to the formation of the 4-methoxystyrene radical cation. Thus, these results lead to the conclusion that the assumption of a step-wise mechanism for the radical cation mediated dimerization of 4-methoxystyrene and the assignment of the 500-nm band to an acyclic 1,4-radical cation need to be reexamined.

Spectroscopic and kinetic considerations are also inconsistent with the assignment of the 500-nm transient to the acyclic 1,4-radical cation. If the radical cation exists in the open form, there should be little interaction between the cationic center and the radical center and its absorption spectrum should correspond to that of the isolated chromophores as has been observed for biradicals.[37] The acyclic 1,4-radical cation is therefore expected to have absorption maxima in the 300–340-nm region that correspond to the spectra of the 4-methoxyphenethyl cation, λ_{max} = 340 nm,[38] and 4-methoxybenzyl radical, λ_{max} = 310 nm,[39] and not at 500 nm. In addition, the minimum reactivity of the acyclic 1,4-radical cation should be a composite of the reactivity of the 4-methoxyphenethyl cation and the 4-methoxyphenethyl radical. However, the lifetime of about 200 ns measured in the present work for the 500-nm transient in acetonitrile is at least 10-fold longer than the lifetime of <20 ns for the 4-methoxyphenethyl cation in the same solvent.[38] In addition, since benzyl-like radicals are quenched by oxygen at diffusion-controlled rates, the insensitivity of the observed rate constant for the decay of the 500-nm transient to oxygen concentration also argues against the identification of this transient as the acyclic 1,4-radical cation.

Identification of the 500-nm band as the long-bond cyclobutane radical cation can be ruled out since its formation should also precede the formation of the 600-nm band upon cleavage of the cyclobutane radical cation. In addition, since reduction of the cyclobutane radical cation by 4-methoxystyrene leads to neutral cyclobutane formation, the observed rate constant for the decay of the cyclobutane radical cation should increase as the concentration of 4-methoxystyrene increases. However, our results show that the decay of the 500-nm transient is insensitive to 4-methoxystyrene concentration.

Thus, based on the spectroscopic and kinetic data, the 500-nm transient formed by addition of the radical cation to the neutral styrene and by reaction of the cyclobutane radical cation is unlikely

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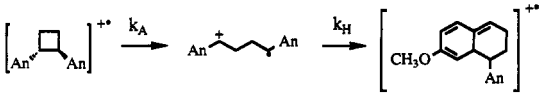
to be the acyclic 1,4-radical cation. We suggest that the 500-nm band is due to the substituted hexatriene radical cation produced by 1,3-sigmatropic rearrangement of the cyclobutane radical cation. This assignment is based on spectroscopic data for analogous hexatriene radical cations derived from *cis,cis,trans*-hexatriene[40] and methylenecyclohexadiene.[41] The matrix spectra for these hexatriene radical cations have absorption maxima in the visible near 430 nm. The absorption maximum of the transient observed in the present work is at a considerably longer wavelength, λ_{max} = 500 nm, but the additional methoxy and methyl groups in the hexatriene radical cation formed by rearrangement of the 1,2-bis(4-methoxyphenyl)cyclobutane radical cation would be expected to shift the absorption to higher wavelengths. It is also likely that the 450-nm transient observed in the radical cation mediated dimerization of styrene[34,35] is the corresponding hexatriene radical cation on the basis of the similarity between the absorption maximum at 450 nm and the absorption maximum of the methylcyclohexadiene radical cation at 430 nm, and from product studies which show that the naphthalene derivative is the major product.[42] Furthermore, it has been shown that the radical cation mediated dimerization of β-methyl-4-methoxystyrene and cleavage of the corresponding cyclobutane radical cation do not lead to the formation of naphthalene derivatives. The hexatriene radical cation is therefore not formed in the dimerization or cleavage reactions, and in this case, no absorption in the 450–550-nm range is observed in time-resolved studies.[25,43]

Stepwise or Concerted Mechanism. The results from the picosecond ring-cleavage experiments show that the hexatriene radical cation with absorption at 500 nm is produced with a rate constant of $(4 \pm 1) \times 10^8$ s^{-1} in acetonitrile. Thus, if the acyclic 1,4-radical cation is present as an intermediate along the pathway to the hexatriene radical cation as required by the stepwise mechanism, we can assume either that the cleavage of the cyclobutane radical cation to the acyclic 1,4-radical cation takes place with a rate constant of $k_A = 4 \times 10^8$ s^{-1} followed by cyclization to the hexatriene radical cation with a rate constant of $k_H \gg 4 \times 10^8$ s^{-1}, eq 6, or that cleavage to the acyclic 1,4-radical cation is fast, $k_A \gg 4 \times 10^8$ s^{-1}, followed by slower cyclization to the hexatriene radical with a rate constant of $k_H = 4 \times 10^8$ s^{-1}.



(6)

The second scenario in which $k_A \gg 4 \times 10^8$ s^{-1} can be ruled out because it implies that cleavage of the cyclobutane radical cation will be too fast for electron transfer to 4-methoxystyrene to compete successfully, and formation of the cyclobutane would not take place at 4-methoxystyrene concentrations of 0.05 M as observed in the present work. Thus, it appears that cleavage of the cyclobutane radical cation is the rate determining step in the formation of the hexatriene radical cation upon oxidation of the cyclobutane.

The above discussion leads to the conclusion that neither the product studies nor the time-resolved experiments require the formation of an acyclic 1,4-radical cation as an intermediate in the dimerization or cyclobutane ring-cleavage reactions. Furthermore, it is clear that the 500-nm transient, irrespective of its assignment to either the acyclic or hexatriene radical cations, cannot be the primary intermediate formed in either reaction.

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(43) Preliminary results from picosecond laser studies on the cleavage of the cyclobutane show no evidence for the presence of a transient in the 500-nm region at time scales as short as 50 ps. Johnston, L. J.; Schepp, N. P. Unpublished results.

On the basis of these conclusions, as well as detailed studies by Bauld[3] and Lewis[18] showing that some dimerization and ring-cleavage reactions occur by a concerted mechanism, we believe that the concerted mechanism with a long-bond cyclobutane radical cation as the primary intermediate provides a better model with which to explain our results. The kinetic analysis presented in the following section is derived on that basis and is independent of the assignment of the 500-nm transient.

Kinetic Analysis. According to the concerted mechanism shown in Scheme 3, the observed rate constant for the disappearance of the 4-methoxystyrene radical cation is given by the following rate law, eq 7,

$$k_{obs} = \frac{k_1 k_2 [\text{4-MeOSty}]}{k_{-1} + k_2 + k_3[\text{4-MeOSty}]} \tag{7}$$

derived by assuming the steady-state approximation with respect to the long-bond cyclobutane radical cation. In this equation, k_1 represents the rate constant for addition of the radical cation to the neutral styrene, k_{-1} is the rate constant for the cleavage of the cyclobutane radical cation to 4-methoxystyrene and its radical cation, and k_2 designates the rate constant for the rearrangement of the cyclobutane radical cation to a hexatriene radical cation. The parameter k_3 is the rate constant for the electron transfer from the long-bond cyclobutane radical cation to neutral 4-methoxystyrene. At low concentrations of 4-methoxystyrene where $k_{-1} + k_2 > k_3$[4-MeOSty], the rate law is simplified to that shown in eq 8.

$$k_{obs} = \frac{k_1 k_2 [\text{4-MeOSty}]}{k_{-1} + k_2} \tag{8}$$

This expression agrees well with the linear relationship between the observed rate constants for the decay of the 4-methoxystyrene radical cation and the 4-methoxystyrene concentration shown in Figure 2a.

The rate law shown in eq 7 is also consistent with the curvature shown in Figure 2b. At sufficiently high concentrations of 4-methoxystyrene, the observed rate constant will begin to level off and eventually become independent of the concentration when $k_{-1} + k_2 < k_3$[4-MeOSty], eq 9.

$$k_{obs} = \frac{k_1 k_2}{k_3} \tag{9}$$

Values for each of the rate constants in eq 7 can be obtained in the following way. According to eq 8, the slope of the linear plot in Figure 2a, $k_q = 1.1 \times 10^9$ M^{-1} s^{-1}, is made up of a combination of rate constants, slope = $k_1k_2/(k_{-1} + k_2)$. On the basis of the 3:1 ratio of the dihydronaphthalene and 4-methoxystyrene products obtained from the cyclobutane radical cation, we can estimate that $k_2/k_{-1} \approx 3$. Using this ratio together with the slope of the line in Figure 2a, we calculate a value for k_1 of 1.4×10^9 M^{-1} s^{-1}. The observed rate constant at high concentrations of 4-methoxystyrene where the decay of the 4-methoxystyrene radical cation is independent of 4-methoxystyrene concentration, $k_{obs} = 2.5 \times 10^7$ s^{-1}, is a combination of rate constants k_1, k_2, and k_3 as shown in eq 9. If the electron transfer from 4-methoxystyrene to the cyclobutane radical cation is sufficiently exothermic, the electron-transfer reaction will be diffusion controlled with a rate constant of $k_3 \approx 1.5 \times 10^{10}$ M^{-1} s^{-1}. This value and the rate constant $k_1 = 1.4 \times 10^9$ M^{-1} s^{-1} can be combined with the observed rate constant in the plateau region, $k_{obs} = 2.5 \times 10^7$ s^{-1}, to give a rate constant of $k_2 = 2.5 \times 10^8$ s^{-1} for the reaction of the long-bond cyclobutane radical cation to give the 500-nm transient that we assign to the hexatriene radical cation. Finally, on the basis of the rate ratio of $k_2/k_{-1} \approx 3$, a value of $k_{-1} = 8 \times 10^7$ s^{-1} can be calculated for the cleavage of

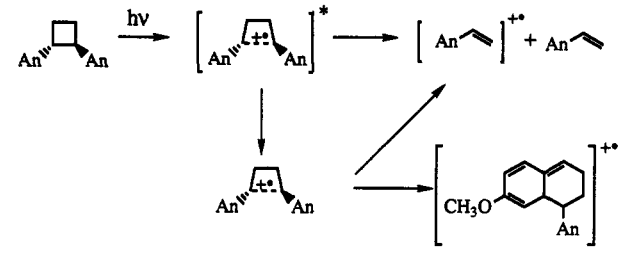
the cyclobutane radical cation to the 4-methoxystyrene radical cation and neutral 4-methoxystyrene.

Picosecond Photoionization: Cyclobutane Ring-Cleavage. As described above, the picosecond photoionization data show that the hexatriene radical cation at 500 nm grows in with a rate constant of $(4.0 \pm 1.0) \times 10^8$ s^{-1}. According to the mechanism in Scheme 3, this rate constant corresponds to the global rate constant for the decay of the cyclobutane radical cation, $k_{-1} + k_2$, and is identical within experimental error to the sum of $k_{-1} + k_2 = 3.3 \times 10^8$ s^{-1} calculated from the curvature shown in Figure 2b. The agreement between these two values verifies the assumption that the rate constant for the electron transfer from 4-methoxystyrene to the cyclobutane radical cation is diffusion controlled. In fact, by using the experimentally determined value of $(4.0 \pm 1.0) \times 10^8$ s^{-1} together with results from the product study showing that $k_2 \approx 3k_{-1}$, the rate constant k_2 can be calculated as $(3.0 \pm 0.8) \times 10^8$ s^{-1}. Substitution of this rate constant and the value of $k_1 = 1.4 \times 10^9$ M^{-1} s^{-1} determined earlier into eq 9 leads to an experimentally determined value of the rate constant for electron transfer from 4-methoxystyrene to the cyclobutane radical cation, $k_3 = (2.1 \pm 0.5) \times 10^{10}$ M^{-1} s^{-1}, that agrees well with the estimated value of 1.5×10^{10} M^{-1} s^{-1}.[44]

The formation of the 4-methoxystyrene radical cation within 100 ps after direct 266-nm irradiation of the cyclobutane suggests that the cyclobutane radical cation produced by photoionization decays with a rate constant $>1 \times 10^{10}$ s^{-1}. This rate constant is considerably greater than that determined above and is incompatible with the mechanism shown in Scheme 3 because electron-transfer from 4-methoxystyrene to the cyclobutane radical cation would not compete with cleavage of the cyclobutane radical cation occurring with a rate constant $>10^{10}$ s^{-1}. We considered a mechanism in which the cyclobutane radical cation is formed in a quasi-concerted process, but breaks down in $<10^{-10}$ s to give the 4-methoxystyrene radical cation and the acyclic 1,4-radical cation. The acyclic 1,4-radical cation then undergoes a 1,6-cyclization to give the dihydronaphthalene, or at sufficiently high concentrations of neutral 4-methoxystyrene is reduced by electron transfer from the 4-methoxystyrene to give the 1,4-butanediyl biradical that closes to the cyclobutane and to regenerate the 4-methoxystyrene radical cation. However, since the reduction potentials of the radical center and the cation center of the acyclic 1,4-radical cation should be similar to those of the 4-methoxybenzyl radical[45] and the 4-methoxybenzyl cation,[45] respectively, the electron-transfer between 4-methoxystyrene and the acyclic 1,4-radical cation will be endothermic by at least 25 kcal.[46] The rate constant for electron-transfer would therefore be much slower than the diffusion controlled rate constant of 1.5×10^{10} M^{-1} s^{-1} and the curvature in the plot shown in Figure 2b would not be observed.

The rapid formation of the 4-methoxystyrene radical cation upon direct picosecond irradiation of the cyclobutane therefore indicates that photoionization provides an additional mechanism for the rapid cleavage of the cyclobutane radical cation. This suggestion is reinforced by the increased yield of the 4-methoxystyrene radical cation relative to the hexatriene radical cation at 500 nm in the photoionization experiment as compared to the chloranil sensitized irradiation. We considered the possibility that the dimer undergoes direct photochemical cleavage to give 4-methoxystyrene which is then photoionized. Since the photoionization of 4-methoxystyrene has been shown to be biphotonic, the overall process would require three photons and is, thus, unlikely even if the direct photochemical cleavage is rapid (i.e. <35 ps). A more likely explanation for the enhanced yield is that direct 266-nm excitation of the cyclobutane leads to an electronically or vibrationally excited cyclobutane radical cation that breaks apart to give the 4-methoxystyrene radical cation in competition with deactivation to give the ground state cyclobutane radical cation, Scheme 5. Cleavage of photochemically excited cyclobutane radical cations has been observed for the parent cyclobutane radical cation which is stable in a low-temperature matrix but undergoes unimolecular rearrangement reactions upon irradiation.[47,48]

Scheme 5



Cyclobutane Radical Cation Cleavage. The results in the present work provide a clear picture of the dynamics of the dimerization and ring-cleavage reactions and lead to the conclusion that the reactions of the cyclobutane radical cation are the prime factor in determining the course of the dimerization reaction. This species could not be observed directly by nanosecond laser photolysis because of its short 3-ns lifetime. The failure to detect the intermediate by picosecond spectroscopy suggests that the radical cation has absorption below 400 nm in a region that is not accessible with our picosecond spectrometer.

The 3-ns lifetime of the cyclobutane radical cation is considerably greater than the <1-ns lifetime estimated for the 1,2-diphenylcyclobutane radical cation generated by addition of styrene radical cation to styrene.[23] The increased lifetime of the 4-methoxy-substituted cyclobutane radical cation can be attributed to stabilization of the positive charge by the electron-donating 4-methoxy groups. On the other hand, the 3-ns lifetime is considerably less than the lifetime of 100 ns[18,23] estimated for the radical cation of 1,2-bis(4-methoxyphenyl)-3,4-dimethylcyclobutane produced by addition of anethole radical cation to anethole. Some of this difference is due to the reluctance of the anethole cyclobutane radical cation to undergo a sigmatropic shift; in this case, only cleavage to starting material or reduction by electron-transfer from anethole occurs.[18] Thus, the 100-ns lifetime of the radical cation represents a rate constant for cycloreversion of 1×10^7 s^{-1} which is about 8-fold slower than the cycloreversion of the 4-methoxystyrene cyclobutane radical cation determined in the present work, $k_r = 8 \times 10^7$ s^{-1}.

Rate constants for the cleavage of the radical cations of substituted 2,3-bis(4-methoxyphenyl)butanes, which are acyclic analogs of the 1,2-bis(4-methoxyphenyl)cyclobutane radical

(44) The rate constants 2.1×10^{10} M^{-1} s^{-1} for the reduction of the cyclobutane radical cation by 4-methoxystyrene and 7×10^8 M^{-1} s^{-1} for the reduction of the 4-methoxystyrene radical cation by neutral cyclobutane lead to $\Delta E° = 90$ mV for the two redox couples. Verification of this difference from electrochemical measurements is difficult because oxidation of 4-methoxystyrene is irreversible, and oxidation of the cyclobutane is not a simple one-electron oxidation. However, $\Delta E° = 90$ mV is consistent with the small $\Delta E° = 10$ mV determined from peak potential measurements for the irreversible oxidation of the analogous *trans*-anethole and its cyclobutane dimer system in acetonitrile.[18]

(45) Sim, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1990**, *112*, 6635–6638.

(46) Based on oxidation potentials of 1.4 and 0.26 eV for 4-methoxystyrene and 4-methoxyphenethyl radical, respectively, and a reduction potential of −1.81 for 4-methoxyphenethyl cation.[45]

(47) Toriyama, K.; Nunome, K.; Iwasaki, M.; Shida, T.; Ushida, K. *Chem. Phys. Lett.* **1985**, *122*, 118–123.

(48) Further support for an alternative mechanism being responsible for rapid cleavage of the cyclobutane dimer comes from the observations that the 2,3-dimethyl-1,2-bis(4-methoxyphenyl)cyclobutane radical cation has a lifetime of ca. 100 ns in acetonitrile,[18,23] while 266-nm picosecond irradiation of the same cyclobutane in acetonitrile leads to the complete formation of the anethole radical cation within 100 ps. Johnston, L. J.; Schepp, N. P. Unpublished results.

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cation discussed in the present work, have recently been measured.[49,50] The data show that acyclic analogues cleave rapidly with rate constants of 6×10^8 s^{-1} for 2,3-bis(4-methoxyphenyl)-2,3-dimethylbutane radical cation[50] and $<5 \times 10^7$ s^{-1} for the cleavage of 2,3-bis(4-methoxyphenyl)butane radical cation[49] that are similar to the rate constant of 8×10^7 s^{-1} measured in the present work for the cleavage of the 1,2-bis(4-methoxyphenyl)-cyclobutane radical cation.

Conclusions

Our results are consistent with a mechanism in which the 4-methoxystyrene radical cation adds in a concerted manner to neutral 4-methoxystyrene to give a cyclobutane radical cation with a rate constant of 1.4×10^9 M^{-1} s^{-1}. This radical cation undergoes a 1,3-sigmatropic shift with a rate constant of 2.5×10^8 s^{-1} to give a substituted hexatriene radical cation with absorption at 500 nm. The cyclobutane radical cation also cleaves to regenerate 4-methoxystyrene and its radical cation with a rate constant of ca. 8×10^7 s^{-1}. When the cyclobutane radical cation is generated in the presence of high concentrations of 4-methoxystyrene, an additional reaction pathway becomes available involving electron transfer to give the neutral cyclobutane product and the 4-methoxystyrene radical cation, indicating that cyclobutane formation is a chain process.

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