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Charge-Density and Ring-Size Dependent Dimerization of 1-Arylcycloalkene Cation Radicals[#]

Masanobu Kojima,* Akito Ishida,† Yasunao Kuriyama,†† and Shigero Oishi††

Department of Bioscience and Biotechnology, Faculty of Agriculture, Shinshu University, Matsumoto, Nagano 390-8621

†The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047

††Department of Chemistry, School of Science, Kitasato University, Sagamihara, Kanagawa 228-8555

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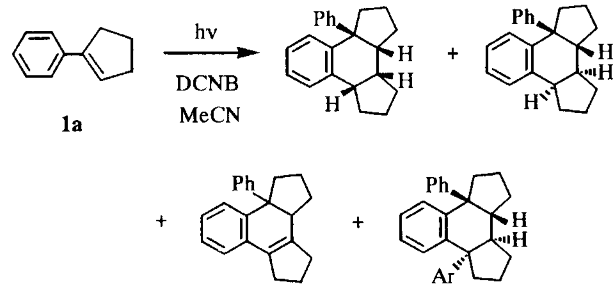
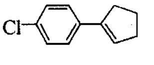
The γ-radiolysis of 1-arylcyclopentenes [Ar = Ph (**1a**); 4-ClC$_6$H$_4$ (**1b**); 4-MeC$_6$H$_4$ (**1c**); 4-MeOC$_6$H$_4$ (**1d**)] at 77 K initially gave transient absorption bands attributable to their monomer cation radicals ($\mathbf{1a}^{\bullet+}$—$\mathbf{1d}^{\bullet+}$), with $\lambda_{\max}$ around 400 and 650—730 nm. In the case of **1a**, **1b**, and **1c**, simultaneous formation of new absorption bands with $\lambda_{\max}$ around 480—500 nm, attributable to the dimer cation radicals, was clearly observed upon warming along with a decrease in the monomer cation radical absorption bands. Using 355-nm laser photolysis at room temperature and an *N*-methylquinolinium salt as an electron acceptor, the rate constants for the formation of the dimer cation radicals (k_{dimer}) and the reaction-rate constants for $\mathbf{1}^{\bullet+}$ with methanol (k_{MeOH}) were determined. The reactivities of $\mathbf{1}^{\bullet+}$ with **1** and with methanol are discussed on the basis of the results obtained by a semiempirical molecular orbital calculation using the PM3 method. The results indicate that the reactivities of $\mathbf{1}^{\bullet+}$ depend not on its structure but on the charge density of the ethylene bond. In addition, dimerization of the cycloalkene cation radicals with larger ring size than **1**, such as 1-phenylcyclohexene, 1-phenylcycloheptene, and 1-phenylcyclooctene cation radicals, was found to be remarkably dependent on the ring size.

As one of the most significant reactions for the aromatic alkene cation radicals, the photoinduced electron-transfer (PET) dimerization of arylalkenes like styrenes has been studied in detail.[1] Although the steric effect on dimerization using 1-arylcycloalkenes is potentially an especially interesting area of study, there had been no investigations concerning PET dimerization of these cycloalkenes, due to the complexity of the products. Recently, however, we reported that the irradiation of 1-phenylcyclopentene (**1a**) in the presence of 1,4-dicyanobenzene (DCNB) in MeCN gave the four kinds of [2+4] cyclodimers as the main products (Eq. 1), while under similar conditions 1-phenylcyclohexene (**2**) produced 2-phenylcyclohexane carbonitrile and the two kinds of 1 : 1 adducts between **2** and DCNB, without yielding any dimer products.[2] It was found in the above reactions that, firstly, the cation radicals of the alkenes ($\mathbf{1a}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$) were the initial intermediates, and secondly, by using a semiempirical molecular orbital calculation (the PM3 method), that the difference in their reactivities was due to their structures. The optimum structure of $\mathbf{1a}^{\bullet+}$ was calculated to be entirely planar, but that of $\mathbf{2}^{\bullet+}$ to be chairlike. In order to gain a deeper insight into the reactivities of 1-arylcycloalkene cation radicals, we investigated the formation of the dimer cation radicals of other 1-arylcyclopentenes [Ar = 4-ClC$_6$H$_4$ (**1b**); 4-MeC$_6$H$_4$ (**1c**); 4-MeOC$_6$H$_4$ (**1d**)], 1-phenylcycloheptene (**3**), and 1-phenylcyclooctene (**4**), and also determined the rate constants for $\mathbf{1a}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ with methanol, using γ-radiolysis and laser flash photolysis (Eq. 2). In conclusion, we suggest here that the reactivities of 1-arylcycloalkene cation radicals are controlled not only by their structures but also by the charge density of their ethylene bonds.

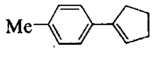


(Ar = 4-CNC$_6$H$_4$)

(1)



1b



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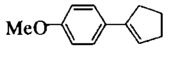
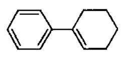


1d



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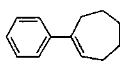

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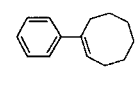


4

(2)

[#] Dedicated to the late Professor Setsuo Takamuku.

Experimental

γ-Radiolysis and Laser Flash Photolysis. γ-Radiolysis was carried out at 77 K, as reported previously.[2] At this low temperature, it seems likely that alkenes aggregate. Therefore, the formation of dimer cation radicals probably occurs readily upon warming the solution. Laser flash photolysis was carried out at room temperature using the third harmonic (355 nm, 7 ns of pulse width) of a Q-switched Nd : YAG laser (DCR-11, Spectra-Physics) for excitation. Probe lights were detected by a photomultiplier tube (R1477, Hamamatsu Photonics) and a photo-diode array with a microchannel plate (2 pixels/nm, 4 ns of gate; IRY-1024G/RB Princeton Instruments) for kinetic experiments and the measurement of the transient absorption spectra, respectively. Aerated sample solutions containing alkenes (4—100 mM; 1 M = 1 mol dm^{-3}), *N*-methylquinolinium hexafluorophosphate (NMQ : OD $\cong$ 0.5 at 355 nm), and toluene (1.0 M) in MeCN were used according to the literature.[3]

Molecular Orbital Calculation. Molecular orbital calculations were carried out using MOPAC 97 installed in CSC Chem3D Ver. 4.5. The geometry optimizations for cation radicals $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ were calculated using the PM3 method based on the structures of their neutral molecules optimized beforehand by the same method. An SCF convergence test was carried out on the total energy using the RHF/PM3 method. The convergence criterion was 1×10^{-6} and the RMS gradient was set at 0.04184 kJ Å^{-1} mol^{-1} as the terminal condition for the calculation. RHF/PM3 method calculations using optimized structures of **1** and $\mathbf{1}^{\bullet+}$ were also performed to give the charge and spin density, the dihedral angle between the aromatic and cyclopentene rings, the ionization potential, the heat of formation, and the bond length.

Irradiation of Cycloalkenes in the Presence of DCNB. Alkenes **1**—**4** (0.05—0.1 M, 3 ml) were irradiated with DCNB (0.05 M) under argon in MeCN using a 400-W high-pressure mercury lamp (Riko UVL-400HA) through a Pyrex filter for 15 h, except for **3** (60 h). The photoproducts were analyzed by a Shimadzu GC-14A gas chromatograph equipped with a flame-ionization detector and a 40-m capillary column (Chemicals Inspection & Testing Institutes G-450), and their molecular weights were determined by a Shimadzu GCMS-QP1000 gas-chromatograph mass spectrometer.

Results

Production of [2 + 4] Cyclodimers through PET Reaction. As reported previously for **1a** (Eq. 1),[2] it was confirmed by means of a GCMS analysis of the products that similar irradiation of **1b**, **1c**, and **3** yielded their corresponding [2+4] cyclodimers through the PET reaction. For **1d**, in contrast, no cyclodimer was found in the reaction mixture, but the adducts of HCN and DCNB to **1d** were the major products detected, as in the case of **2** [*m*/*z* (rel intensity): M$^+$ = 201 (38%), 147 (100%), 121 (42%); M$^+$ = 275 (100%), 244 (M$^+$−OMe; 83%), 173 (M$^+$−*p*-CNC$_6$H$_4$; 30%)].[2] However, no reaction occurred for **4** under the conditions employed.

Transient Absorption Spectra of Monomer and Dimer Cation Radicals of 1-Arylcycloalkenes: γ-Radiolysis and Pulse Radiolysis. γ-Irradiated 1-chlorobutane (*n*-BuCl) solutions of **1a** (10 mM) at 77 K gave absorption bonds with $\lambda_{\max}$ around 400 and 670 nm, due to the presence of monomer cation radical $\mathbf{1a}^{\bullet+}$.[2] Upon warming the solution, a new transient absorption band with $\lambda_{\max}$ around 480 nm occurred with the decay of the initial absorption bands for $\mathbf{1a}^{\bullet+}$. Upon a pulse radiolysis of **1a** (10 and 50 mM) in *n*-BuCl under argon at room temperature, simultaneous formation of the 480-nm transient was observed along with decrease in the bands for $\mathbf{1a}^{\bullet+}$, thus resembling the spectra obtained by the γ-irradiation of **1a**.[2] The 480-nm band was attributed to the resulting dimer cation radicals, because an increase in the concentration of **1a** (10 to 50 mM) intensified the 480-nm band, and also because the cation radical generated by the γ-irradiation of the [2+4] dimer of **1a** gave a similar transient absorption band.[2]

Similar γ-irradiation at 77 K and pulse radiolysis at room temperature were performed for 1-phenylcycloalkenes (**3** and **4**) and other 1-arylcyclopentenes (**1b**—**1d**) with an electron-withdrawing or electron-donating group on their benzene rings. The absorption bands attributable to the monomer and dimer cation radicals of **3** and **4** were observed in a wavelength region similar to that of **1a**.[2] A red shift occurred only in the case of **1b**—**1d**, as shown in Figs. 1 and 2. It should be noted that the formation of the dimer cation radicals of **1b**—**1d** depended on the substituents introduced. In the case of **1b** with a chloro group on the benzene ring, the formation of the dimer cation radical was almost negligible in a 10 mM solution of **1b**, and a weak new band around 510 nm attributable to the dimer cation radical was observed at 100 mM, as can be seen in Fig. 1a. For **1c** with a methyl group on the benzene ring, the production of the dimer cation radical was clearly observed (Fig. 1b). However, compared with the case of **1a**, there was a slight suppression effect on the formation, and there were two absorption bands instead of just one: namely, the bands around 460 and 500 nm, which were attributed to the neutral dimer radical and dimer cation radical, respectively, as described later. For **1d** with a methoxy group on the benzene ring it is noteworthy that the absorption band around the 450—500-nm region, attributable to the dimer cation radical, was not observed when 50 and 100 mM solutions of **1d** were subjected to γ-radiolysis, as shown in Fig. 1c. However, as we show later in Fig. 3d, the absorption band attributable to the dimer cation radical for **1d** could be observed at around 475 nm. Interestingly, we observed a new transient band around 430 nm, which behaves like a dimer cation radical; however, this transient has not yet been identified, as will be discussed in the section "Transient Spectra Observed for $\mathbf{1d}^{\bullet+}$ ". These observations of dimer cation radicals on the γ-radiolysis of **1a**, **1b**, and **1c**, but not for **1d**, are consistent with the fact that the PET reaction for **1a**, **1b**, and **1c** in MeCN produced [2+4] cyclodimers, whereas **1d** did not.

On the other hand, as shown in Fig. 2a, 1-phenylcycloheptene cation radical ($\mathbf{3}^{\bullet+}$) generated by γ-irradiation, upon warming an *n*-BuCl solution, formed as in the case of **1a** and **1c** the new absorption band with $\lambda_{\max}$ around 480 nm, in this instance attributable to dimer cation radicals of **3**. In contrast, further expansion of the ring size caused a considerable suppression effect on the formation of the dimer cation radicals of **4** (Fig. 2b). These results agree with the fact that PET reaction of **3** in MeCN yielded [2+4] cyclodimers, whereas

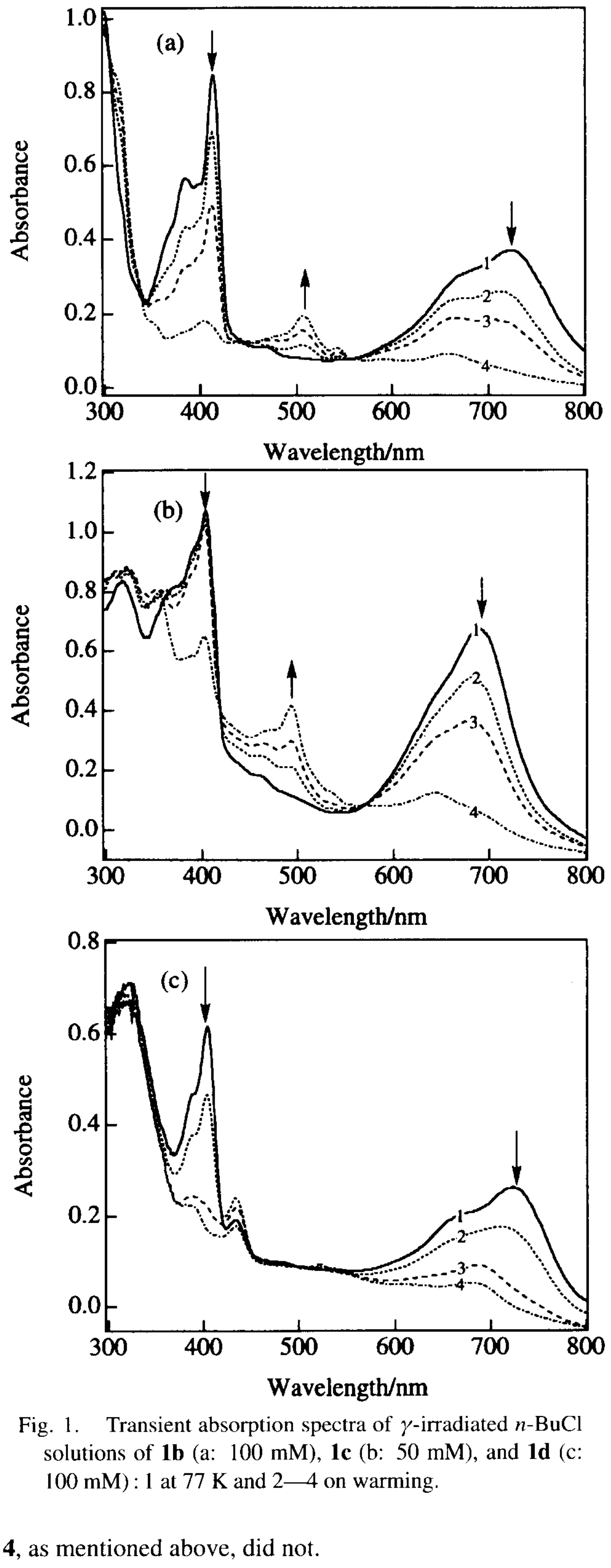


Fig. 1. Transient absorption spectra of γ-irradiated n-BuCl solutions of **1b** (a: 100 mM), **1c** (b: 50 mM), and **1d** (c: 100 mM) : 1 at 77 K and 2—4 on warming.

4, as mentioned above, did not.

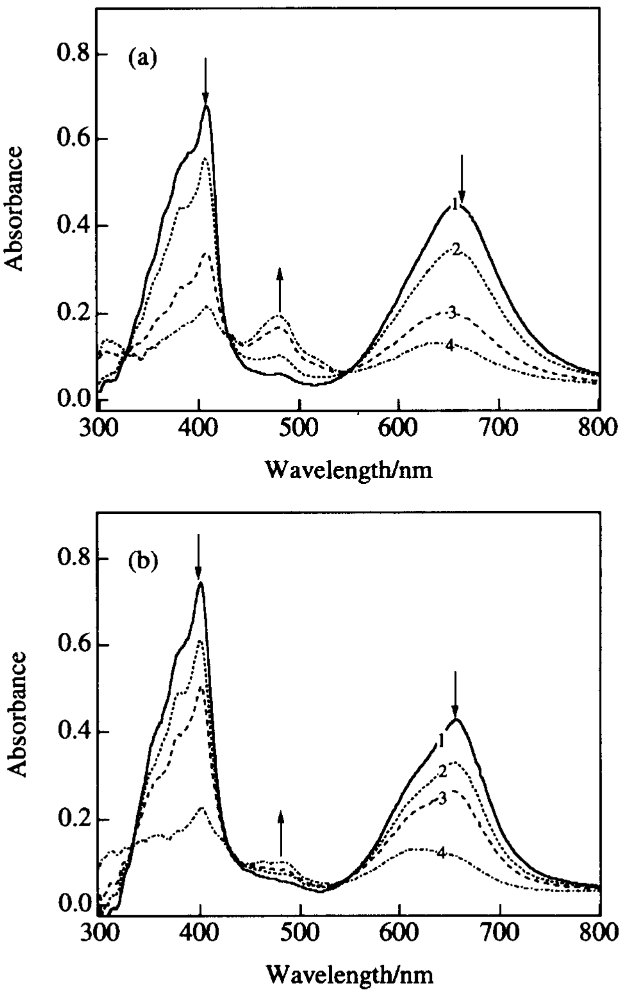


Fig. 2. Transient absorption spectra of γ-irradiated n-BuCl solutions of **3** (a: 10 mM) and **4** (b: 10 mM): 1 at 77 K and 2—4 on warming.

Laser Photolysis: a. Reaction of 1$^{\bullet+}$**—4**$^{\bullet+}$ **with Their Neutral Precursors.** The rate constants for the formation of the dimer cation radicals ($k_{\rm dimer}$) of **1**—**4** and the reaction rate constants ($k_{\rm alkene}$) for **1**$^{\bullet+}$—**4**$^{\bullet+}$ with their neutral precursors were determined by 355-nm (YAG) laser photolysis of **1**—**4** in aerated MeCN in the presence of NMQ as an electron acceptor and toluene as a co-sensitizer (Fig. 3),[3] and by using the following equation as reported for substituted styrene cation radicals:[4]

$$k_{\rm obsd} = k_0 + k_{\rm dimer}\ [\text{alkene}] \quad \text{or} \quad k'_{\rm obsd} = k'_0 + k_{\rm alkene}\ [\text{alkene}]. \qquad (3)$$

In this equation, $k_{\rm obsd}$ is the observed rate constant for the formation of the dimer cation radicals of **1**—**4** and $k'_{\rm obsd}$ is that for the decay of **1**$^{\bullet+}$—**4**$^{\bullet+}$; [alkene] is the initial concentration of **1**—**4**. For **1a** and **1c**, the observed rate constants increased in a linear manner on increase of the initial concentration, as shown in Fig. 4. The intercepts of the plot represent the rate constants (k_0 and k'_0) for the decay of **1**$^{\bullet+}$—**4**$^{\bullet+}$ in the absence of their neutral precursors. These values are taken as the observed rate constants for a reaction with an oxygen molecule (O_2) or superoxide anion radical ($O_2^{\bullet-}$) in MeCN. The measured rate constants ($k_{\rm dimer}$ and $k_{\rm alkene}$) are summarized in Table 1. Under the conditions described, **1a**$^{\bullet+}$ and **1c**$^{\bullet+}$ reacted with their neutral alkenes to give their dimer cation radicals at rate constants of $k_{\rm dimer} = (5.3 \pm 1.4)\times 10^8$ $M^{-1}\,s^{-1}$(monitored wavelength, 460 nm) and $(5.8 \pm 1.6)\times 10^8$ $M^{-1}\,s^{-1}$ (500 nm), respec-

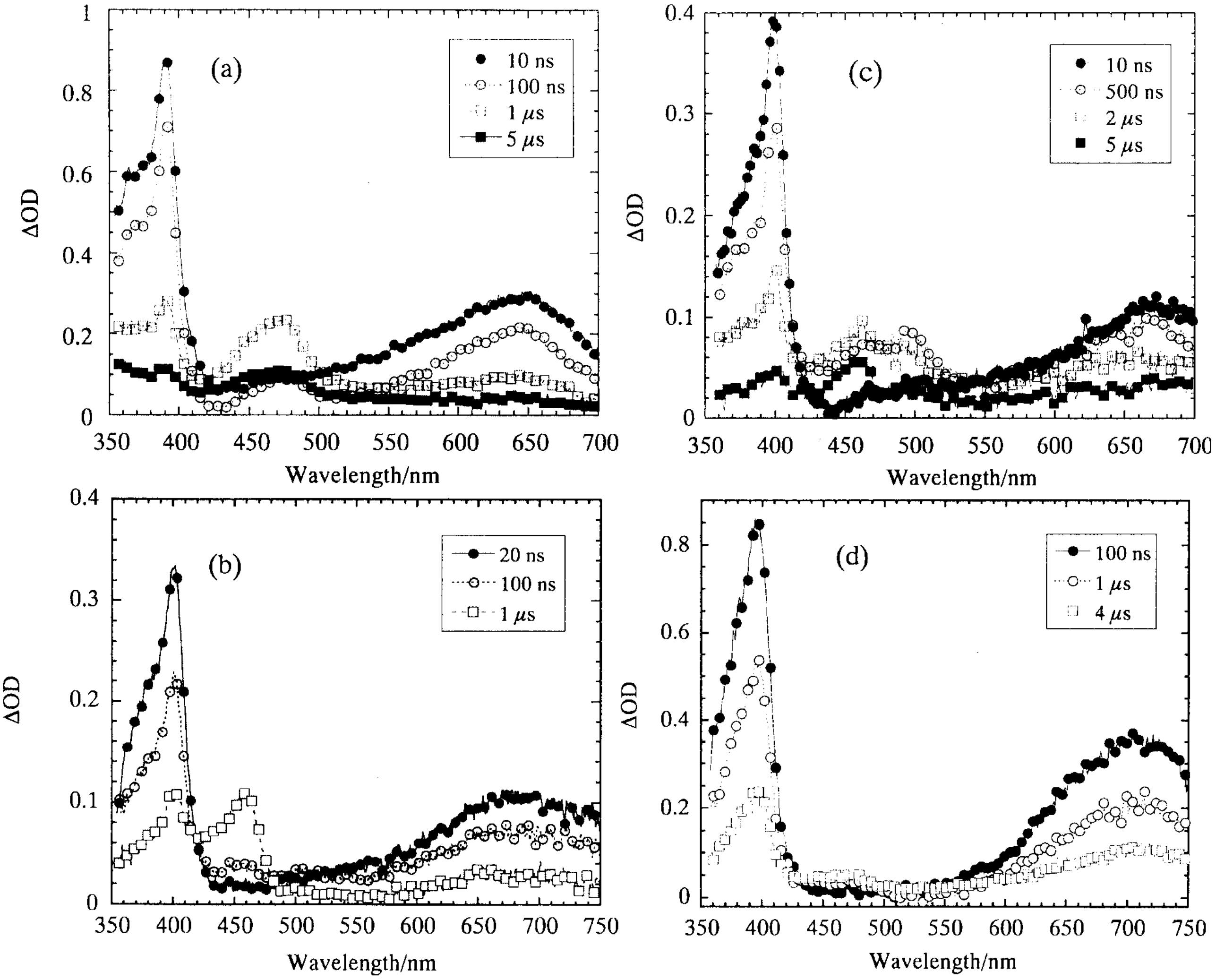


Fig. 3. Transient absorption spectra of **1a** (a: 4 mM), **1b** (b: 50 mM), **1c** (c: 15 mM), and **1d** (d: 50 mM) obtained by 355-nm laser flash photolysis using NMQ/toluene co-sensitization in aerated MeCN.

Table 1. Second-Order Rate Constants for 1-Arylcycloalkene Cation Radicals with MeOH (k_{MeOH})[a] and Their Neutral Alkenes (k_{dimer} and k_{alkene})[b] in MeCN

Alkene	$k_{\mathrm{MeOH}}/\mathrm{M^{-1}\,s^{-1}}$	$k_{\mathrm{dimer}}/\mathrm{M^{-1}\,s^{-1}}$		$k_{\mathrm{alkene}}/\mathrm{M^{-1}\,s^{-1}}$	
1a	$(6.8 \pm 0.4)\times 10^7$	$(5.3 \pm 1.4)\times 10^8$	(460 nm)[c]	$(2.9 \pm 0.4)\times 10^8$	(650 nm)[c]
1b	$(6.7 \pm 0.7)\times 10^7$	—[d]		—[d]	
1c	$(1.1 \pm 0.09)\times 10^7$	$(6.1 \pm 0.6)\times 10^7$	(460 nm)[c]	$(2.0 \pm 0.7)\times 10^8$	(660 nm)[c]
		$(5.8 \pm 1.6)\times 10^8$	(500 nm)[c]		
1d	$(6.7 \pm 1.6)\times 10^4$	—[d]		—[d]	
2	$(2.9 \pm 0.1)\times 10^7$	—[d]		—[d]	
3	$(5.4 \pm 0.4)\times 10^7$	—[d]		—[d]	
4	$(3.6 \pm 0.2)\times 10^7$	—[d]		—[d]	

a) Rate constants were determined in MeCN by 355-nm (YAG) laser photolysis of the alkenes (ca. 0.01 M) in the presence of NMQ (OD ≅ 0.5 at 355 nm) as an electron accepting sensitizer and toluene (1.0 M) as a co-sensitizer under similar conditions according to Ref. 3: [MeOH] ≅ 0.05—0.6 M except for **1d** (0.5—5 M). b) [**1a**—**1d**] ≅ 0.004—0.04 M; [**2**—**4**] ≅ 0.01—0.1 M. c) Wavelength monitored. d) Not determined (< $10^5\ \mathrm{M^{-1}\,s^{-1}}$).

tively. These rate constants are in relatively close agreement with $k_{\mathrm{alkene}} = (2.9 \pm 0.4)\times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ (650 nm) for **1a** and $(2.0 \pm 0.7)\times 10^8\ \mathrm{M^{-1}\,s^{-1}}$ (660 nm) for **1c**, respectively, although an overlap in absorption between the monomer and dimer cation radicals seems to occur around 600—800 nm, which makes it difficult to determine k_{alkene} accurately. As in the case of the transient absorption spectra obtained by γ-radiolysis of **1c**, another absorption band around 460 nm was also observed in laser photolysis. As shown in Table 1, k_{dimer} for **1c** at 460 and 500 nm is significantly different:

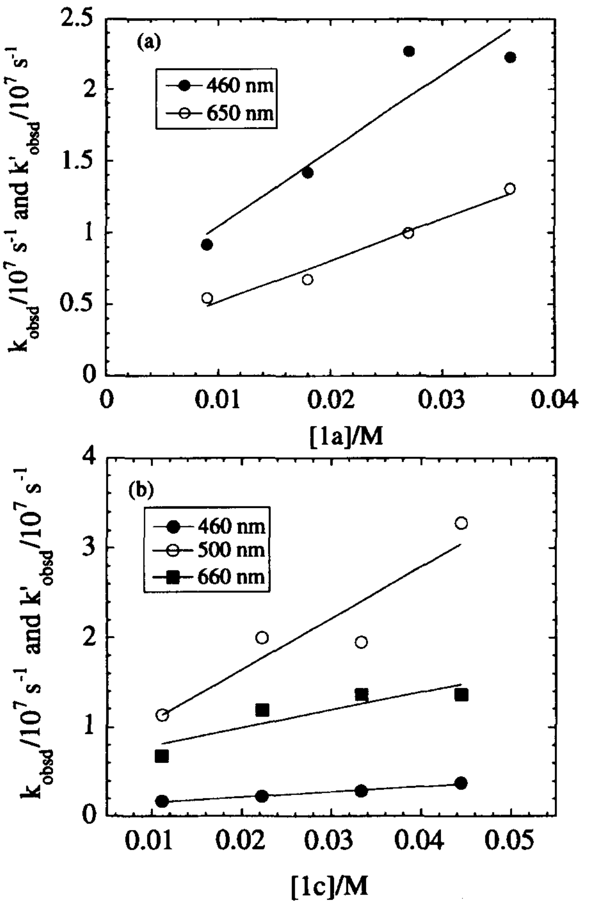


Fig. 4. Linear plots of observed rate constants (k_{obsd}) for the formation of dimer cation radicals of **1** and that (k'_{obsd}) for the decay of $\mathbf{1}^{\bullet+}$ vs. initial concentration of **1**: (a) **1a** and (b) **1c**.

$(6.1 \pm 0.6) \times 10^7$ and $(5.8 \pm 1.6) \times 10^8$ M^{-1} s^{-1}, respectively. Therefore, it is likely that the 460-nm transient is a different species from the 500-nm transient attributed to the dimer cation radical of **1c**.

In the case of **1b** and **1d**, the formation of dimer cation radicals was considerably suppressed compared to **1a** and **1c**, as can be seen from Fig. 3; accordingly, a higher concentration (50 mM) was used for the alkenes. For **1d**, in particular, a higher laser power was needed to observe the absorption band attributable to the dimer cation radical. Quenching of the monomer cation radicals by the alkenes did not occur in a concentration of between 10—40 mM. This is probably because k_{dimer} and k_{alkene} for **1b** are too slow to determine under the conditions employed ($< 10^5$ M^{-1} s^{-1}), while it is likely that the formation of the dimer cation radical of **1d** is a negligible process because no dimer product was obtained, as described above. Although we have no evidence for the reversible addition of the 1-arylcycloalkene cation radicals to their neutral precursors, this might be responsible for some of the apparent lack of reactivity of **1b** and **1d**. As in the case of **1b**, k_{dimer} and k_{alkene} for **3** and **4** were not determined because the reaction processes are probably too slow ($< 10^5$ M^{-1} s^{-1}).

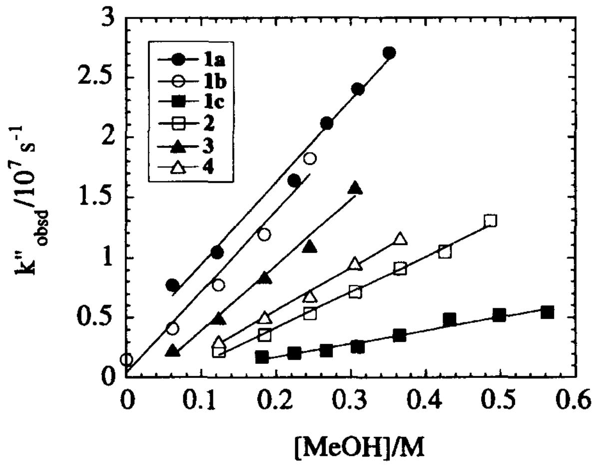


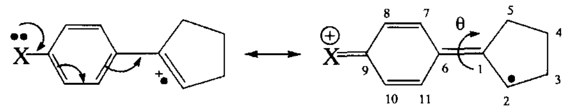
Fig. 5. Linear plots of the observed rate constants (k''_{obsd}) for the decay of $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ vs. initial concentration of MeOH.

b. Reaction of $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ with MeOH. The reaction rate constants (k_{MeOH}) for $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ with MeOH were determined using Eq. 4. The observed rate constants (k''_{obsd}) for the decay of $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ were obtained by the 355-nm laser photolysis of **1** in aerated MeCN using NMQ/toluene cosensitization. The decay rate constants, k''_{obsd}, were found to increase in a linear fashion upon increase in the initial concentration of MeOH ([MeOH]) according to Eq. 4, as shown in Fig. 5, where the intercepts of the plot represent the rate constants (k''_0) for the decay of $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ in the absence of MeOH. These values are taken as the observed rate constant for a reaction with the neutral precursors, O_2, and $O_2^{\bullet-}$. The quenching plots shown in Fig. 5 cover a limited range in relation to the rate constants, because in a low concentration of MeOH the plots did not become linear, most likely due to the competing reactions of the cation radicals with the neutral precursors, O_2, and $O_2^{\bullet-}$. The rate constants for $\mathbf{1}^{\bullet+}$—$\mathbf{4}^{\bullet+}$ with these species are presumably greater than those with MeOH, and thus in a low concentration of MeOH k''_0 would be still greater than or compatible with k_{MeOH} [MeOH]; for example, the reaction rate constants for 1,1-diarylethene cation radicals with $O_2 \cong 3$—9×10^8 M^{-1} s^{-1}.[5] As shown in Table 1, k_{MeOH} for $\mathbf{1}^{\bullet+}$ decreases in the following order: $\mathbf{1a}^{\bullet+}$ $[(6.8 \pm 0.4) \times 10^7$ M^{-1} $s^{-1}] \cong \mathbf{1b}^{\bullet+}$ $[(6.7 \pm 0.7) \times 10^7$ M^{-1} $s^{-1}] > \mathbf{1c}^{\bullet+}$ $[(1.1 \pm 0.09) \times 10^7$ M^{-1} $s^{-1}] \gg \mathbf{1d}^{\bullet+}$ $[(6.7 \pm 1.6) \times 10^4$ $M^{-1} s^{-1}]$. Furthermore, it was found that k_{MeOH} depended on the ring size of 1-phenylcycloalkenes: $\mathbf{1a}^{\bullet+}$ $[(6.8 \pm 0.4) \times 10^7$ M^{-1} $s^{-1}] > \mathbf{3}^{\bullet+}$ $[(5.4 \pm 0.4) \times 10^7$ M^{-1} $s^{-1}] > \mathbf{4}^{\bullet+}$ $[(3.6 \pm 0.2) \times 10^7$ M^{-1} $s^{-1}] > \mathbf{2}^{\bullet+}$ $[(2.9 \pm 0.1) \times 10^7$ M^{-1} $s^{-1}]$.

$$k''_{obsd} = k''_0 + k_{MeOH}\ [\mathrm{MeOH}]. \qquad (4)$$

Discussion

Factors Controlling the Reactivities of $\mathbf{1}^{\bullet+}$ with 1 and MeOH. The results of the MO calculation for **1** and $\mathbf{1}^{\bullet+}$ using the PM3 method provided satisfactory explanations for the reactivities of $\mathbf{1}^{\bullet+}$ with **1** and MeOH: for example, the optimized structure, heat of formation ($\Delta_f H$, kJ mol^{-1}), charge and spin density, and bond length, as can be seen in Table 2. The geometries of **1** optimized by the PM3 method indicate that in all cases of neutral cyclopentenes **1**, there are two energy minimums at around 0° and 33° of the dihedral angle (θ) between the aromatic ring and the cyclopentene ring. The difference in the energy is less than 0.84 kJ mol^{-1}; therefore, it is likely that the cyclopentenes exist in both conformers. On the other hand, the optimum geometries of the cation radicals **1**$^{\bullet+}$ are calculated to be entirely planar, regardless of the substituents on the benzene rings. This result shows that the introduction of electron-withdrawing and electron-donating groups, such as Cl, Me, and MeO, into the para-position on the benzene ring of **1a** causes no change in the optimum geometries in either **1a**—**1d** or **1a**$^{\bullet+}$—**1d**$^{\bullet+}$. Therefore, the remarkable difference in the reactivities of **1a**$^{\bullet+}$—**1d**$^{\bullet+}$, particularly with MeOH, must be caused by an electronic effect of the substituents on the resonance, as shown in Eq. 5. This conclusion is supported by the following calculation results. First of all, the entirely planar structures of **1a**$^{\bullet+}$—**1d**$^{\bullet+}$ have the most significant effect on the resonance. Secondly, the difference in the heat of formation ($\Delta\Delta_fH$, kJ mol^{-1}) between **1** and **1**$^{\bullet+}$ for **1c** and **1d** is smaller than that for **1a** and **1b**; namely, **1c**$^{\bullet+}$ and **1d**$^{\bullet+}$ are more stable than **1a**$^{\bullet+}$ and **1b**$^{\bullet+}$. Thirdly, the bond length between C1 and C6 of **1a**$^{\bullet+}$—**1d**$^{\bullet+}$ (1.41 Å) is shorter by 0.05 Å than that of **1a**—**1d**. Accordingly, it is likely that the reactivities of **1**$^{\bullet+}$ with **1** and MeOH are controlled by the charge and/or spin density of the C2 carbon of **1**$^{\bullet+}$,[6] due to the resonance effect of the substituents. We draw this conclusion because precedent studies suggest that the addition of **1** and MeOH to **1**$^{\bullet+}$ occurs on the C2 carbon of **1**$^{\bullet+}$, and finally produces head-to-head [2+2] and/or [2+4] cyclodimers[7—13] and anti-Markovnikov adducts.[14—18] The increase in the electron deficiency and spin density on the C2 carbon probably accelerates the reactivity of the cation radical with neutral alkenes and nucleophiles. The result of the calculation for charge density on the C2 carbon of **1**$^{\bullet+}$ (**1a**$^{\bullet+}$ > **1c**$^{\bullet+}$ > **1b**$^{\bullet+}$ > **1d**$^{\bullet+}$) is consistent with the fact that the k_{dimer} and k_{alkene} observed for **1a** and **1c** are considerably larger than those for **1b** and **1d**. The difference in the charge density of the C2 carbons between **1** and **1**$^{\bullet+}$ (ΔCD) is also in relatively close agreement with the k_{dimer} and k_{alkene} observed. In fact, **1a** and **1c** with a relatively large value for ΔCD (0.252 and 0.247, respectively) have rate constants greater than **1b** and **1d** (0.231 and 0.238, respectively). Furthermore, the change in the spin density of the C2 carbon of **1**$^{\bullet+}$ due to the substituents (**1a**$^{\bullet+}$ > **1c**$^{\bullet+}$ > **1d**$^{\bullet+}$ > **1b**$^{\bullet+}$) also suggests that **1a**$^{\bullet+}$ and **1c**$^{\bullet+}$ are more reactive on the formation of the dimer cation radicals than **1b**$^{\bullet+}$ and **1d**$^{\bullet+}$.



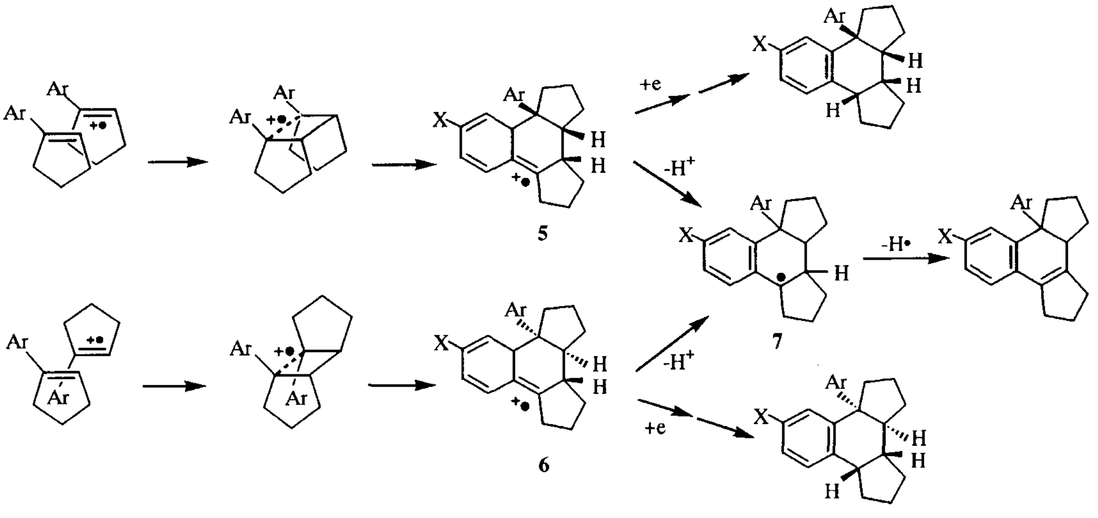
(5)

460-nm Transient Observed for 1c$^{\bullet+}$. It is interesting that for **1b** and **1c** the appearance of another new transient was observed at around 460 nm (Figs. 3b and 3c), which is likely to be another kind of dimer species. The rate constant for production was determined to be $(6.1 \pm 0.6) \times 10^7$ M^{-1} s^{-1} for **1c**, but not for **1b**. The PET reaction of **1c** in the presence of DCNB in MeCN was found by a GCMS analysis of the reaction mixture to yield the three kinds of [2+4] cyclodimers (M$^+$ = 316 and 314) and two isomeric adducts of HCN to **1c** (M$^+$ = 185), similar to the case of **1a**. It seems probable that the 500-nm transient indicates the presence of tetralin-type dimer cation radicals **5** and **6**, as shown in Scheme 1, because k_{dimer} and k_{alkene} for **1c** are almost the same as for **1a**.[2] On the other hand, the 460-nm transient might be the neutral radical dimer **7** generated by deprotonation from **5** and **6**. The grounds for this hypothesis are as follows. It has been reported that the initial electron-transfer process resulting from laser photolysis using NMQ/toluene co-sensitization gives the reduced NMQ, *N*-methylquinolyl radical (NMQ·), and toluene cation radical. NMQ· reacts with O_2 at a rate constant close to the diffusion-controlled limit, probably due to electron transfer, to form $O_2^{\bullet-}$.[3] The toluene cation radical is reduced by neutral **1c** to generate **1c**$^{\bullet+}$, which reacts with another **1c** to form **5** and **6**. Deprotonation from **5** and **6** may accelerate in the presence of $O_2^{\bullet-}$ as a proton acceptor to give neutral dimer radical **7**. This seems to be a dialkyl substituted benzyl radical. Most benzylic radicals have a modest absorption band at around the 320-nm wavelength region, but negligible absorption beyond 400 nm. Therefore, we should consider the possibility that **7** might π-interact with another aromatic ring. Although we made further attempts to identify the 460-nm transient by means of the quenching experiments using O_2 and MeOH, we only observed a decrease in the intensity of the optical density (ΔOD) for both the 460 and 500-nm bands and no

Table 2. Results of MO Calculation for **1** and **1**$^{\bullet+}$ Using the RHF/PM3 Method

1	IP$^{a)}$	$\Delta_fH^{b)}$		$\Delta\Delta_fH^{c)}$	$\theta^{\circ\ d)}$		Charge density$^{e)}$			Spin density$^{g)}$	
		1	**1**$^{\bullet+}$		**1**	**1**$^{\bullet+}$	C1: **1**/**1**$^{\bullet+}$	C2: **1**/**1**$^{\bullet+}$	ΔCD$^{f)}$	C1	C2
1a	8.90	112.0	915.0	803.0	33.5	0.0	−0.091/−0.026	−0.143/0.109	0.252	0.150	0.296
1b	8.86	83.4	884.2	800.8	33.2	0.0	−0.096/−0.090	−0.138/0.093	0.231	0.101	0.218
1c	8.76	72.8	863.2	790.4	32.9	0.0	−0.088/−0.053	−0.146/0.101	0.247	0.126	0.271
1d	8.50	−47.2	724.1	771.3	32.4$^{h)}$	0.0	−0.080/−0.079	−0.156/0.082	0.238	0.097	0.245

a) Ionization potential (eV) of **1**. b) Heat of formation (kJ mol^{-1}). c) $\Delta\Delta_fH$ (kJ mol^{-1}) = $\Delta_fH(\mathbf{1}^{\bullet+}) - \Delta_fH(\mathbf{1})$. d) Dihedral angle of C11–C6–C1–C2 (See Eq. 5). e) Charge density of C1 and C2 carbons of **1** and **1**$^{\bullet+}$. f) Difference in the charge density of a C2 carbon between **1** and **1**$^{\bullet+}$. g) Spin density of C1 and C2 carbons of **1**$^{\bullet+}$. h) There is another energy minimum ($\Delta_fH = -47.2$ kJ mol^{-1}) at $\theta = 0°$.



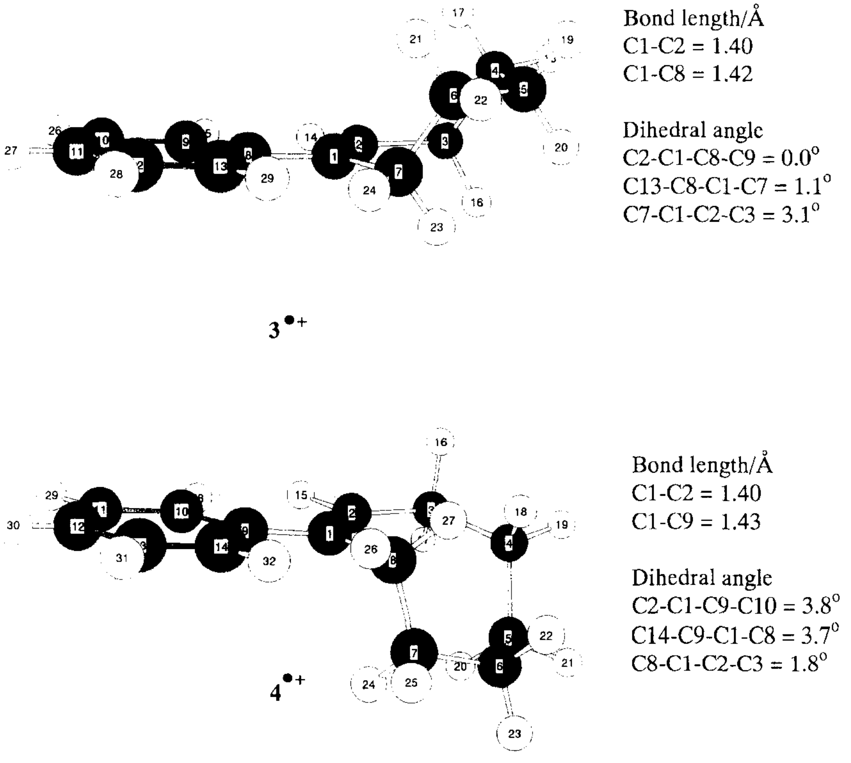
Ar = Ph, 4-ClC$_6$H$_4$, and 4-MeC$_6$H$_4$; X = H, Cl, and Me.

Scheme 1.

significant spectra change. Accordingly, it was tentatively attributed at this stage to **7**.

Transient Spectra Observed for 1d$^{•+}$. When the NMQ/toluene co-sensitized laser photolysis of a solution containing ca. 50 mM **1d** in MeCN was performed (Fig. 3d), the 430-nm transient band, observed by γ-radiolysis of **1d** in *n*-BuCl (Fig. 1c), did not appear. Instead, an extremely weak new absorption band around 475 nm, probably attributable to the dimer cation radical of **1d**, appeared at 1 µs after the laser pulse. However, no dimer product was yielded upon the irradiation of **1d** with DCNB in MeCN; therefore, it is thought that the formation of the dimer cation radical is a relatively minor process. On the basis of these results, the 430-nm transient might be some radical species generated by the reaction between **1d$^{•+}$** and nucleophiles produced under the conditions, for example Cl$^-$.

Ring-Size Dependent Dimerization of 1-Phenylcycloalkene Cation Radicals. The optimum structures for **3**$^{•+}$ and **4**$^{•+}$ were also calculated using the PM3 method, as for **1a**$^{•+}$ and **2**$^{•+}$.[2] As shown in Fig. 6, their optimized geometries have a partially planar structure consisting of the C7–C1–C2–C3 (dihedral angle $\theta = 3.1°$) carbons for **3**$^{•+}$,



Bond length/Å
C1-C2 = 1.40
C1-C8 = 1.42

Dihedral angle
C2-C1-C8-C9 = 0.0°
C13-C8-C1-C7 = 1.1°
C7-C1-C2-C3 = 3.1°

Bond length/Å
C1-C2 = 1.40
C1-C9 = 1.43

Dihedral angle
C2-C1-C9-C10 = 3.8°
C14-C9-C1-C8 = 3.7°
C8-C1-C2-C3 = 1.8°

Fig. 6. Optimized structures of monomer cation radicals of **3** and **4** obtained by a semiempirical molecular orbital calculation with the PM3 method.

whereas the dihedral angle for the C8–C1–C2–C3 carbons for **4**$^{\bullet+}$ was calculated to be 1.8°. In addition, the dihedral angles of C2–C1–C8–C9 and C13–C8–C1–C7 for **3**$^{\bullet+}$ were calculated to be 0.0° and 1.1°, respectively, while those of C2–C1–C9–C10 and C14–C9–C1–C8 for **4**$^{\bullet+}$ were calculated to be 3.8° and 3.7°. These data suggest that **3**$^{\bullet+}$ should have a more planar structure than **4**$^{\bullet+}$. As we reported previously,[2] the optimum structure of **1a**$^{\bullet+}$ was calculated to be entirely planar, but that of **2**$^{\bullet+}$ chairlike. Moreover, as can be seen from Fig. 2, the build-up of the absorption band attributable to the dimer cation radicals for **3** and **4** was more suppressed compared to that for **1a**. Therefore, we concluded that the formation of 1-phenylcycloalkene dimer cation radicals depends on the planarity of the monomer cation radicals.

Ring-Size Dependent Reactivities of 1-Phenylcycloalkene Cation Radicals with MeOH. As shown in Table 1, there were significant differences in the reactivity among **1a**$^{\bullet+}$ and **2**$^{\bullet+}$—**4**$^{\bullet+}$ with MeOH. It has been found that the addition of MeOH to **1a**, **2**, and **3** through the PET reaction gives *cis*- and *trans*-isomers of anti-Markovnikov adducts.[15,18] Using a semiempirical molecular orbital calculation (PM3), we have found that the *cis*/*trans* ratio depends on the structures and stabilities of the free-radical and anion intermediates generated in the reaction.[18] It is notable that the anti-Markovnikov addition of MeOH to **1a**$^{\bullet+}$ and **3**$^{\bullet+}$ yields the *cis*- and *trans*-isomers at a ratio of approximately 50 : 50 in MeCN, but for **2**$^{\bullet+}$ the isomers are produced at *cis*/*trans* = approximately 80 : 20 in the same solvent. These results indicate that **3**$^{\bullet+}$ has a reactivity with MeOH similar to that of **1a**$^{\bullet+}$. As mentioned above, **3**$^{\bullet+}$ probably has a higher degree of planarity than **4**$^{\bullet+}$. Therefore, we conclude that, as in the dimerization reaction, the difference in k_{MeOH} for 1-phenylcycloalkene cation radicals is also due to the planar structures.

Difference in the Reactivities between 1-Arylcycloalkene and Styrene Cation Radicals. Although there have been few studies concerning the formation of the dimer cation radicals of **1**—**4**, similar reactions in styrenes [**8**: ArCH=CH$_2$; Ar = Ph (**8a**), 4-ClC$_6$H$_4$ (**8b**), 4-MeC$_6$H$_4$ (**8c**), 4-MeOC$_6$H$_4$ (**8d**), etc.] have been more thoroughly investigated by pulse radiolysis,[19—22] γ-radiolysis,[19,20,22] and laser flash photolysis.[20,21,23] The reaction-rate constants for styrene monomer cation radicals (**8**$^{\bullet+}$) with their neutral precursors in MeCN or 2,2,2-trifluoroethanol have been measured using laser flash photolysis to be in the range of $< 10^8$ to $(2.9 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, and those with MeOH to be in the range of $(1.9 \pm 0.1) \times 10^8$ to $(3.0 \pm 0.5) \times 10^4$ M^{-1} s^{-1}.[23b] Compared to the findings presented here for **1**$^{\bullet+}$ with MeOH, the reaction rate constant for **8a**$^{\bullet+}$ is estimated to be approximately three-times greater than that for **1a**$^{\bullet+}$, and that for **8d**$^{\bullet+}$ approximately two-times slower than that for **1d**$^{\bullet+}$. However, the reactivities of **1a**$^{\bullet+}$ and **1d**$^{\bullet+}$ are expected to be more analogous to those of 1-phenylpropene (**8e**) and 1-(4-methoxyphenyl)propene (**8f**) cation radicals (**8e**$^{\bullet+}$ and **8f**$^{\bullet+}$, respectively) than to those of **8a**$^{\bullet+}$ and **8d**$^{\bullet+}$. The reaction rate constants for **8e**$^{\bullet+}$ with **8e** and with MeOH have been measured to be $(1.4 \pm 0.1) \times 10^9$ and $(1.1 \pm 0.1) \times 10^7$ M^{-1} s^{-1}, respectively.[23b] On the other hand, that for **8f**$^{\bullet+}$ with **8f** has been found to be 2×10^6 M^{-1} s^{-1}, although that for **8f**$^{\bullet+}$ with MeOH has not yet been determined.[11] Therefore, there is no doubt, as in the case of **1**$^{\bullet+}$, that the introduction of a methyl group on the β-position and a methoxy group on the *para*-position of styrene cation radicals causes decrease in the reactivity, probably due to steric and electronic effects.

Conclusion

By means of γ-radiolysis and laser photolysis, a lack of reactivity on the formation of dimer cation radical was observed for **1b** and **1d**, but not for **1a** and **1c**; in addition, a remarkable decrease in the reactivity of **1d**$^{\bullet+}$ with MeOH was found. On the basis of a semiempirical molecular orbital calculation, it was found that the introduction of Cl, Me, and MeO groups into the para-position on the benzene ring of **1a** caused a significant change in the charge and spin density of the C2 carbon of **1a**$^{\bullet+}$—**1d**$^{\bullet+}$, but no significant change in the structure. 1-Phenylcycloalkenes with a ring size larger than **1a**, except for **3**, caused suppression of the formation of their dimer cation radicals due to the steric effect. These results suggest that the dimerization of alkene cation radicals is controlled by both steric and electronic effects.

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References

1 a) F. D. Lewis, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part C, pp. 1—69. b) K. Mizuno and Y. Otsuji, "Topics in Current Chemistry," ed by J. Mattay, Springer-Verlag, Berlin (1994), Vol. 169, pp. 301—346.

2 M. Kojima, A. Kakehi, A. Ishida, and S. Takamuku, *J. Am. Chem. Soc.*, **118**, 2612 (1996).

3 K. P. Dockery, J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, and W. P. Todd, *J. Am. Chem. Soc.*, **119**, 1876 (1997).

4 a) L. J. Johnston and N. P. Schepp, *J. Am. Chem. Soc.*, **115**, 6564 (1993). b) N. P. Schepp and L. J. Johnston, *J. Am. Chem. Soc.*, **118**, 2872 (1996).

5 M. Kojima, A. Ishida, and S. Takamuku, *Bull. Chem. Soc. Jpn.*, **71**, 2211 (1998).

6 D. R. Arnold, X. Du, and J. Chen, *Can. J. Chem.*, **73**, 307 (1995).

7 A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972).

8 a) M. Yamamoto, T. Asanuma, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 53. b) T. Asanuma, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, **1975**, 608.

9 N. L. Bauld and R. Pabon, *J. Am. Chem. Soc.*, **105**, 633 (1983).

10 a) S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **108**, 7356 (1986). b) S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, **105**, 1386 (1983).

11 F. D. Lewis and M. Kojima, *J. Am. Chem. Soc.*, **110**, 8664

(1988).

12 a) N. L. Bauld, *Adv. Electron Transfer Chem.*, **2**, 1 (1992). b) N. L. Bauld, *Tetrahedron*, **45**, 5307 (1989).

13 M. Kojima, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **62**, 3863 (1989).

14 R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973).

15 Y. Shigemitsu and D. R. Arnold, *J. Chem. Soc., Chem. Commun.*, **1975**, 407.

16 A. J. Maroulis and D. R. Arnold, *Synthesis*, **1979**, 819.

17 K. Mizuno, I. Nakanishi, N. Ichinose, and Y. Otsuji, *Chem. Lett.*, **1989**, 1095.

18 a) M. Kojima, A. Ishida, S. Takamuku, Y. Wada, and S. Yanagida, *Chem. Lett.*, **1994**, 1897. b) M. Kojima, A. Ishida, Y. Kuriyama, Y. Wada, and H. Takeya, *Bull. Chem. Soc. Jpn.*, **72**, 1049 (1999).

19 a) S. Egusa, Y. Tabata, A. Kira, and M. Imamura, *J. Polym. Sci.*, **16**, 729 (1978). b) S. Egusa, S. Arai, A. Kira, M. Imamura, and Y. Tabata, *Radiat. Phys. Chem.*, **9**, 419 (1977).

20 M. Irie, H. Masuhara, K. Hayashi, and N. Mataga, *J. Phys. Chem.*, **78**, 341 (1974).

21 O. Brede, F. David, and S. Steenken, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 23.

22 a) S. Tojo, S. Toki, and S. Takamuku, *Radiat. Phys. Chem.*, **40**, 95 (1992). b) S. Tojo, S. Toki, and S. Takamuku, *J. Org. Chem.*, **56**, 6240 (1991).

23 a) L. J. Johnston and N. P. Schepp, *Pure Appl. Chem.*, **67**, 71 (1995). b) N. P. Schepp and L. J. Johnston, *J. Am. Chem. Soc.*, **116**, 6895 (1994).