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Kinetics for Reaction of ArS$^\bullet$ and PhSe$^\bullet$ with Methyl-Substituted Allenes in Solution

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The reactions of ArS$^\bullet$ and PhSe$^\bullet$ with methyl-substituted allenes have been studied by the flash photolysis method. Decay rates of ArS$^\bullet$ and PhSe$^\bullet$ increase with the concentration of the allenes without the carbon-radical scavengers such as oxygen which has low reactivity to ArS$^\bullet$ and PhSe$^\bullet$. From the decay rates, the rate constants of the addition reactions (k_1 in $M^{-1}\,s^{-1}$) were determined. For example, the k_1 value of PhS$^\bullet$ is 2.4×10^6 for $(CH_3)_2C{=}C{=}CH_2$, which is similar to that for $(CH_3)_2C{=}C{=}C(CH_3)_2$ ($k = 1.8 \times 10^6$). These findings seem to coincide with the reported regioselectivity that the central carbon of these allenes is attacked by ArS$^\bullet$. The reactivity of PhSe$^\bullet$ to allenes is higher than that of PhS$^\bullet$, whereas the opposite tendencies are observed for olefins and conjugated dienes. This indicates that the orbital size of the unpaired electron of the attacking radicals is an important factor in determining the reactivity of the allenes.

Introduction

Cumulated double bonds of allenes have specific reactivity to free radicals.[1-3] The regioselectivity of the free-radical addition to the π-bond of the allenes depends on the attacking free radicals. The carbon-centered radicals tend to attack the terminal carbon of the allenes, irrespective of the electrophilicity (or nucleophilicity) of the attacking radicals.[4-6] On the other hand, the bromine atom and stannyl radical attack to the central carbon of the allenes.[7-9] In the case of the thio radicals, although the regioselectivity depends on the substituents of the allenes and on the reaction conditions, the main route is the attack on the central carbon of the allenes.[10-14] It has been pointed out that the regioselectivity is closely related with the reversibility of the addition process.[7]

The kinetic approaches to the specific reactivity of the allenes to the free radicals also have been reported.[15,16] The conventional kinetic methods based on product analysis usually give the relative rate constants, from which it is difficult to compare the reactivities among the different attacking radicals. Furthermore, when the reaction proceeds reversibly, relative rate analysis is not easy. Therefore, it has been desired to obtain the absolute rate constants by a method which explicitly takes the reversibility into consideration.

In this study, the rate constants for the addition reactions of the arylthio radicals (ArS$^\bullet$) and phenylseleno radical (PhSe$^\bullet$) with the methyl-substituted allenes have been measured by the flash photolysis method, with the hope that it would reveal the details of the reaction process including the reversibility and irreversibility of the addition reactions.[17,18] Substituent effects on the side of ArS$^\bullet$ and allenes also disclose the electrophilicity and the steric effect. It would also be expected to clarify the size effect on the reactivity by changing the size of attacking radicals.

Experimental Section

Materials. Commercially available 3-methyl-1,2-butadiene, 2,4-dimethyl-2,3-hexadiene, 2,5-dimethyl-2,4-hexadiene, and 2-methyl-1-phenylpropene were purified by passing through an alumina column. The absence of reactive impurities such as 1,3-dienes in the allenes was checked by the lack of a UV-band in the wavelengths longer than 190 nm. Aryl disulfides and diphenyl diselenide were also commercially available, and were purified by recrystallization from alcohol. Solvents used were spectroscopic grade. The solution was degassed by vacuum pump. The oxygen-saturated solution was made by adding oxygen gas to the degassed solution.

Apparatus. The flash photolysis apparatus was a standard design with two xenon flash lamps (Xenon Corp. N-810C; half duration of 8 μs and input energy of 100 J). The flash photolysis cell was made of Pyrex that was cylindrical with a diameter of 10 mm, and the optical path for monitor the transmission change was 100 mm. The photolysis light was selected between 310 and 400 nm by the band-path filters. All the measurements were performed at 23 ± 1 °C. The half-duration of 8 μs of the flash lamp allowed the measurement of the first-order rate constant ($k_{\text{first-order}}$) of less than ca. $10^5\ s^{-1}$. Thus, the concentrations of the substrates were controlled as $k_{\text{first-order}}$ did not to exceed ca. $10^5\ s^{-1}$.

Results and Discussion

The reversibility of the addition process of ArS$^\bullet$ to olefins has been revealed by the cis–trans isomerization reaction.[19]

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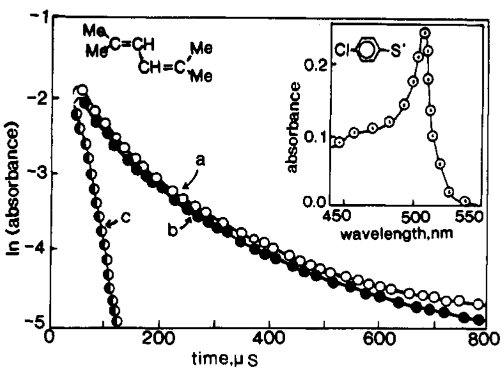
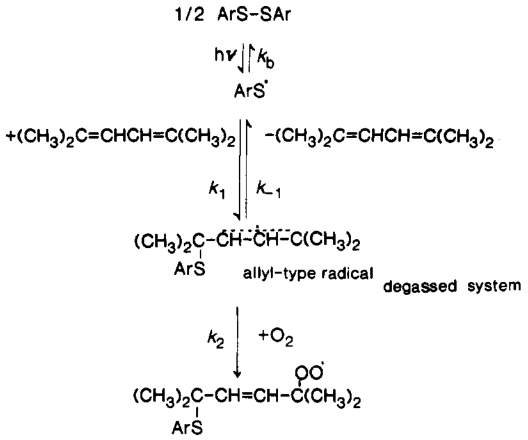


Figure 1. First-order plots for decay of p-$ClC_6H_4S^•$: (a) in cyclohexane, (b) with $(CH_3)_2C{=}CHCH{=}C(CH_3)_2$ (0.6 mM) in degassed solution, and (c) with $(CH_3)_2C{=}CHCH{=}C(CH_3)_2$ (0.6 mM) in aerated solution. Inset: transient absorption spectrum of p-$ClC_6H_4S^•$ observed immediately after the flash photolysis of $(p\text{-}ClC_6H_4S)_2$ in cyclohexane (0.05 mM).

By the flash photolysis method, the decay profiles of ArS• and PhSe• show the reversibility of the addition processes to olefins,[17,18] acetylenes,[20] and dienes.[21] An example is shown in Figure 1 for a 1,3-diene $[(CH_3)_2C{=}CHCH{=}C(CH_3)_2]$, which was selected to compare the rate constants with those of methyl-substituted allenes. The transient absorption band observed by the flash photolysis of $(p\text{-}ClC_6H_4S)_2$ has a sharp peak in the visible region (Figure 1 inset). This absorption band is attributed to p-$ClC_6H_4S^•$ because the same absorption band was observed from p-ClC_6H_4SH.[17,22] The absorption bands for other ArS• and PhSe• were also reported.[18,23,24] In the absence of the diene, ArS• decayed with recombination returning to the disulfide (curve **a**, Figure 1). The decay rate was not accelerated by the addition of O_2 to solution, indicating that the reactivity of ArS• to O_2 is very low.[17,25] When the solution was degassed, the decay of ArS• was not accelerated even by addition of the diene into solution (curve **b**, Figure 1). By adding O_2 to solution containing the diene, the decay of ArS• was accelerated (curve **c**, Figure 1). These findings suggest that ArS• is reproduced by the fast reverse C–S bond dissociation immediately after the addition reaction of ArS• to the diene forming the C–S bond.[17] When O_2 is added to solution, O_2 shifts the fast equilibrium to the product side by trapping selectivity the carbon-centered radical. These reactions for conjugated dienes are represented as shown in Scheme I.[21]

The formation of the adduct carbon centered-radical under the condition observing decay curve **b** in Figure 1 is supported by the 1,4-addition product, when ArSH is present in degassed solution.[26] In the case of styrene, the transient absorption due to the benzyl-type radical was observed in the degassed solution, in which the decay of ArS• similar to decay curve **b** was observed.[17] For dienes, however, it was difficult to detect the transient absorption band of the allyl-type radical, which would be expected to appear in the short wavelength region (230–275 nm)[27,28] overlapping with other absorption bands. For various olefins, formations of the adduct carbon-radicals were confirmed by the spin-trapping EPR method.[29] Thus, it is certain that the addition of ArS• to the diene occurred even though the decay of ArS• was not accelerated in degassed solution.

Scheme I



Selective trapping of the carbon-centered radical with O_2 was also confirmed by the products including the C–O bond but not the S–O bond.[30] This is also supported with the reaction rate constants of O_2 with the carbon-centered radicals [$k_2 = (2\text{–}5) \times 10^9\ M^{-1}\ s^{-1}$][31] which are greater than that with ArS• by a factor of ca. 10^5.[17] Since this selective radical trapping method was first found in 1979 by Ito and Matsuda,[17] this method has been applied by other researchers to various reaction systems using the xenon-flash photolysis,[32] laser-flash photolysis,[33] and pulse radiolysis.[34]

The decay behavior of methyl-substituted allenes was quite different from that of the conjugated dienes. Figure 2 shows the decay of p-$ClC_6H_4S^•$ in cyclohexane for the reaction with $[(CH_3)_2C{=}C{=}C(CH_3)_2]$. By adding the allene, the decay of ArS• was accelerated even in degassed solution (curve **b**, Figure 2), suggesting that the reaction proceeds irreversibly. In the aerated solution, the decay of ArS• was further accelerated (curve **c**, Figure 2), indicating the irreversibility of the decay was not complete; O_2 further shifts the equilibrium to the peroxy radical side by trapping selectivity the incipient short-lived carbon-centered radicals. Reactions are shown in Scheme II with the assumption that ArS• attacks the central 2p-orbital of the methyl-substituted allenes, which was confirmed by product analyses.[14] Irreversibility (decay curve **b** in Figure 2) may occur by rearrangement of the

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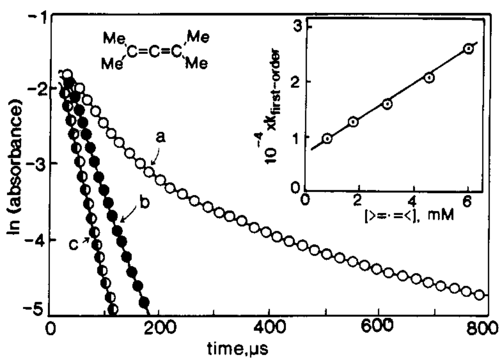
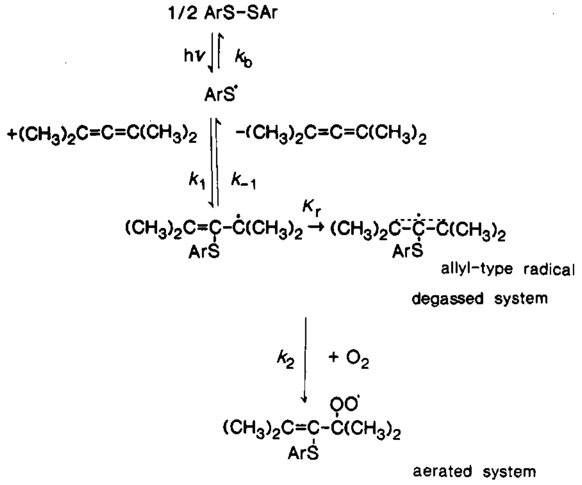


Figure 2. First-order plots for decay of $p\text{-ClC}_6\text{H}_4\text{S}^\bullet$: (a) in cyclohexane, (b) with $(\text{CH}_3)_2\text{C}{=}\text{C}{=}\text{C}(\text{CH}_3)_2$ (7.0 mM) in degassed solution, and (c) $(\text{CH}_3)_2\text{C}{=}\text{C}{=}\text{C}(\text{CH}_3)_2$ (7.0 mM) in aerated solution. Inset: pseudo-first-order plots in aerated solution.

Scheme II



incipient carbon-centered radical to the coplanar allyl-type radical stabilized by the delocalization of the unpaired electron. Irreversiblity is evidence of the central attack as was shown in the addition reaction of bromine atom to the allenes.[7]

Similar decay phenomena were observed for the reactions of PhSe• with the allenes. The decay rates of ArS• (PhSe•) in O_2-saturated solution were similar to those in aerated cyclohexane solution ($[O_2] = 2.3$ mM)[35] for allenes and dienes, indicating that the reverse rate (k_{-1}) can be neglected in aerated solution ($k_{-1} \ll k_1 k_2[O_2]$).[17,20] The slope of the first-order plot for each decay of ArS• or PhSe• is the pseudo-first-order rate constant ($k_{\text{first-order}}$), which depends on the concentrations of substrates. An example of the plots is shown in the inset of Figure 2; the second-order rate constant for the forward addition process (k_1) was evaluated from the slope. The values of k_1 are summarized in Table I. Similarly, the values of k_1 were measured for $[\text{PhCH}{=}\text{C}(\text{CH}_3)_2]$ and $[\text{PhC}{\equiv}\text{C}(\text{CH}_3)]$ which were selected to examine the steric effect of the methyl group on the reactivity. For PhS•, the value of k_1 for dimethylallene is greater than the corresponding value of tetramethylallene by a factor of 1.3, which is in good agreement with the ratio from the relative rates (1.4) reported by Pasto et al.[14]

The rearrangement rate constant (k_r) from the localized incipient carbon-centered radical to the delocalized allyl-type radical (Scheme II) can be evaluated from $k_{\text{first-order}}$ in degassed solution, which is represented as eq 1 on assuming the steady-state concentration on the incipient radical $[>\text{C}{=}\text{C}(\text{SAr})\text{C}^\bullet<]$. In Figure 3, two examples of

$$1/k_{\text{first-order}} = (1 + k_{-1}/k_r)/k_1[\text{allenes}] \qquad (1)$$

the plots of eq 1 are shown for the reactions of $p\text{-ClC}_6\text{H}_4\text{S}^\bullet$ with two allenes. The values of k_{-1}/k_r were obtained as 0.10 and 0.16 for tetramethylallene and dimethylallene, respectively. The values of k_{-1} were already estimated to be ca. 10^6 s^{-1} for the reaction of $p\text{-ClC}_6\text{H}_4\text{S}^\bullet$ with nonconjugated olefins, which would be anticipated to have k_{-1} similar to the incipient radical from the allenes;[17] thus, the value of k_r was calculated to be ca. 10^7 s^{-1}. Small differences in the slopes in Figure 3 lead to a tendency that k_r(tetramethylallene) > k_r(dimethylallene), on assuming the same k_{-1} for both allenes. This order seems to reflect some steric effects on the rotation about the C–C of $>\text{C}{=}\text{C}(\text{SAr})\text{C}^\bullet<$.

By changing the substituent X in $p\text{-XC}_6\text{H}_4\text{S}^\bullet$, we can examine the polar nature of the transition state of the addition reaction to the methyl-substituted allenes, 1,3-dienes, and olefins. Figure 4 shows the Hammett plots of the values of k_1 for $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ against the Brown–Okamoto σ^+-constants,[36] in which good linear relations are obtained. For the plots against other substituent constants such as σ_p and $\sigma^\bullet$, a good linear relationship was not obtained, indicating that the reactivity of the sulfur atom in $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ was influenced by both inductive and resonance factors of X.[37,38]

In Figure 4, positive slopes that are denoted as ρ^+ are obtained. In Table II, observed ρ^+ values for $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ are summarized with the values of k_1 for PhS• and PhSe•. The reliability of the ρ^+ value evaluated by this flash photolysis method was confirmed for arylacetylenes by the product analysis method.[37] For olefins, it is quite difficult to examine the substituent effects with changing the attacking radicals by the relative rate measurements.[38,39] The reversibility of the addition process further makes the estimation of the relative rates complex.[40]

The observed ρ^+ values seem quite large compared with those of other free-radical reactions. In the case of $p\text{-XC}_6\text{H}_4\text{S}^\bullet$, it has already been revealed that the thermodynamic stabilities of $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ are greatly varied by X,[41] which affects the activation energy in terms of the linear free-energy relationship (Evans–Polanyi relationship).[42] Thus, only a part of each observed ρ^+ value is attributed to the polar nature of the transition state.[43] The positive sign in the polar contribution implies the charge-transfer interaction from the C=C (or C≡C) to the radical center of ArS• in the transition state,[41,43] indicating the electrophilicity of ArS•. Similarity of the slopes in Figure 4 suggests that the polar natures of the transition state are similar except for that of phenylacetylene. This indicates that the addition reactivities are

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Table I. Rate Constants for Addition Reaction of ArS$^{\bullet}$ and PhSe$^{\bullet}$ to Methyl-Substituted Allenes, Diene, and Styrene in Cyclohexane at 23 ± 1 °C[a]

	$10^{-5} \times k_1$, M^{-1} s^{-1}						
	p-XC$_6$H$_4$S$^{\bullet}$						
X =	Br	Cl	H	t-Bu	Me	MeO	PhSe$^{\bullet}$
$(CH_3)_2C{=}C{=}CH_2$	68	46	24	6.8	9.0	1.6	31
$(CH_3)_2C{=}C{=}C(CH_3)_2$	51	33	18	5.8	4.8	1.1	32
$(CH_3)_2C{=}CH{-}CH{=}C(CH_3)_2$	560	500	240	80	93	13	0.46
$PhCH{=}C(CH_3)_2$	0.86	0.71	0.48	0.17	0.15		<0.02

[a] The concentrations of substrates were varied in the range of 0.1–1000 mM. For the largest k_1, 0.1–1 mM. For the smallest k_1, 100–1000 mM. Each k_1 contains an error of ±5%.

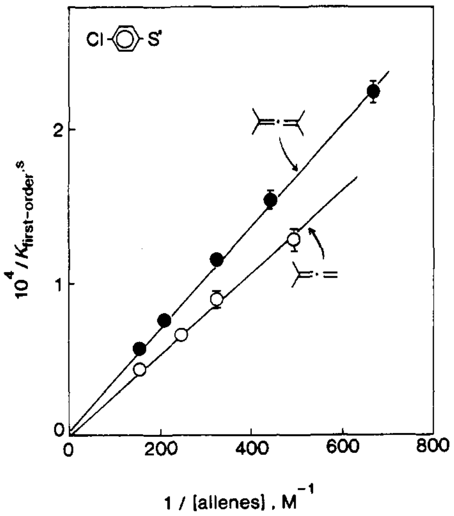

Figure 3. Plots of eq 1 for reaction systems of p-ClC$_6$H$_4$S$^{\bullet}$ and allenes in degassed solution.

determined mainly by the resonance ability of the transition state and by the steric factors for allenes, dienes, and styrenes.

For usual olefins, 1,3-dienes, and acetylenes, it would be anticipated that the rate constants are decreased by the methyl groups at the terminal carbon because they hinder the approach of the attacking radical to olefinic double bond and acetylenic triple bond. In Table II, it is shown that the steric effect of two β-methyl groups is quite large for styrene; the decrease in k_1 is $^1/_{500}$ (PhS$^{\bullet}$) to $^1/_{1100}$ (PhSe$^{\bullet}$). By the methyl substitutions at the terminal carbons of the 1,3-butadiene, the value of k_1 was decreased by a factor of $^1/_{3.7}$ (PhS$^{\bullet}$) to $^1/_{50}$ (PhSe$^{\bullet}$). For phenylacetylene,[20] the reaction rate was decreased by the methyl group by a factor of ca. 3 (PhS$^{\bullet}$). It seems reasonable that the steric effect of large attacking radical (PhSe$^{\bullet}$) is greater than that of small radical (PhS$^{\bullet}$) for these conjugated dienes, olefins, and acetylenes.

In the case of the allenes, however, the steric effect by replacing the four terminal hydrogen atoms with the methyl groups is quite small compared with the allene with two hydrogen atoms [$^1/_{1.3}$ (PhS$^{\bullet}$) to $^1/_{1.0}$ (PhSe$^{\bullet}$)]. This is strong support for the attack of ArS$^{\bullet}$ and PhSe$^{\bullet}$ on the central carbon of the allenes.

For 1,3-diene, styrene, and phenylacetylene, PhSe$^{\bullet}$ is less reactive than PhS$^{\bullet}$ by factors of $^1/_{11}$ to $^1/_{39}$, even when their terminal carbon is unsubstituted. This order might be attributed to the difference in the electronic factors between PhSe$^{\bullet}$ and PhS$^{\bullet}$. Such lower reactivity of PhSe$^{\bullet}$ to these substrates is ascribed to the higher thermodynamic stability of PhSe$^{\bullet}$ than that of PhS$^{\bullet}$ as pointed out in the previous paper.[18] On the other hand, in the case of the allenes, the reactivities of PhSe$^{\bullet}$ are slightly higher than those of PhS$^{\bullet}$ by factors of 1.3–1.8. Although this factor seems to be small, the increment in the reactivities of PhSe$^{\bullet}$ from $CH_2{=}C(CH_3)C(CH_3){=}CH_2$ to the allenes is 50–70 times larger than that of PhS$^{\bullet}$. On the basis of unsubstituted styrene and phenylacetylene the increments are 14–20. From these findings, one can deduce a tendency that the reactivity to the allenes increases with the size of the attacking radicals, which is completely opposite to the tendency of olefins, 1,3-dienes, and acetylenes. It is noteworthy that this effect is quite specific to the allenes.

As for the reaction mechanism for the allenes, two routes can be presumed as shown in Figure 5. The potential energy curves for two reaction routes are schematically shown in Figure 6 comparing with nonconjugated olefin and 1,3-diene without methyl groups at the terminal carbons. In Figure 6, the reaction with 1,3-diene is represented as slightly endothermic in order to emphasize the reversibility of the reaction, although an exoergic reaction was presumed from the bond-dissociation energies and the resonance stabilization energies.[13] In the reactant, the potential energy of allene is shown to be similar to that of nonconjugated olefin rather than 1,3-diene because λ_{max} of the allenes is shorter than that of 1,3-dienes (Table II).[44]

In route **a** in Figure 5, the attacking radical approaches one of the central 2p-orbitals (**1**) producing the incipient carbon radical **2**, in which the 2p-orbital of the unpaired electron is perpendicular with the remaining C=C. The delocalization of the unpaired electron is prevented as in a nonconjugated olefin. In this route, which is denoted as single orbital interaction in Figure 5, the value of k_1 would be anticipated to be similar to that of the nonconjugated olefins such as 1-hexene [$k_1 = 1.0 \times 10^4$ M^{-1} s^{-1} (PhS$^{\bullet}$)],[20] because the activation energy for the reaction with allene might be similar to that for nonconjugated olefin as shown in Figure 6, route **a**. Then, the rotation about C$^{\bullet}$–C in the incipient radical may occur giving the stable delocalized allyl-type radical **3**. The characteristic of the route **a** and its potential energy is that the transition state is reactant-like. By this potential energy curve for route **a**, however, the observed higher reactivities of the methyl-substituted allenes than nonconjugated olefin could not be explained.

To explain such high reactivity of the allenes, the transition state for the reaction with allene should be rather similar to the delocalized allyl-type radical. Thus, the transition state may be a bent structure with partially delocalization as shown in **2′** of route **b** in Figure 5. For the formation of **2′**, it is presumed that the orbital of unpaired electron of the attacking radical interacts in the same time with two perpendicular 2p-orbitals at the central carbon of the allene as shown in **1′** in Figure 5 (dual-orbital

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Table II. Methyl Substitution Effect of Allenes, Conjugated Dienes, Olefins, and Acetylenes on Addition Reaction Rate Constants for PhS$^\bullet$ and PhSe$^\bullet$

	$10^5 \times k_1$, $M^{-1}\,s^{-1}$				
	PhS$^\bullet$ (ρ^+)	PhSe$^\bullet$	(PhS$^\bullet$)/(PhSe$^\bullet$)	IE^a (eV)	$\lambda_{max}{}^b$ (nm)
$(CH_3)_2C{=}C{=}CH_2$	24 (1.79)	31	0.77	8.95	<190
$(CH_3)_2C{=}C{=}C(CH_3)_2$	18 (1.83)	32	0.56	8.47	<190
k_1 (>=$\cdot$=)/k_1(>=$\cdot$=<)	1.3	1.0			
$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	900 (1.71)^c	23	39	8.79	226
$(CH_3)_2C{=}CHCH{=}C(CH_3)_2$	240 (1.80)	0.46	500	8.39	244
k_1(=-=)/k_1(>=-=<)	3.7	50			
$PhCH{=}CH_2$	270 (1.70)^d	22^e	12	8.47	
$PhCH{=}C(CH_3)_2$	0.48 (1.73)	<0.02	>24		
k_1 (Ph=)/k_1 (Ph=<)	560	>1100			
$PhC{\equiv}CH$	7.9 (1.38)^f	0.75^e	11	8.81	
$PhC{\equiv}CCH_3$	2.0				
k_1 (Ph≡)/k_1 (Ph≡Me)	3.2				

[a] Ionization energy from ref 45–47. [b] Reference 44. [c] Reference 21. [d] Reference 37. [e] Reference 18. [f] Reference 20.

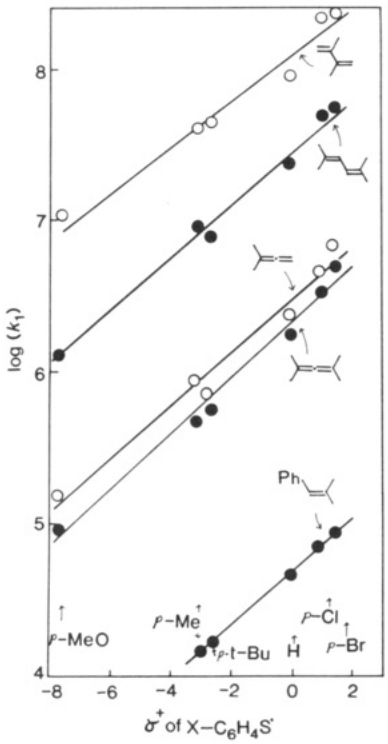

Figure 4. Hammett plots of log k_1 vs Brown–Okamoto σ^+ (X)-constants of p-XC$_6$HS$^\bullet$; values of k_1 for $CH_2{=}C(CH_3)$-$C(CH_3){=}CH_2$ are cited from ref 21.

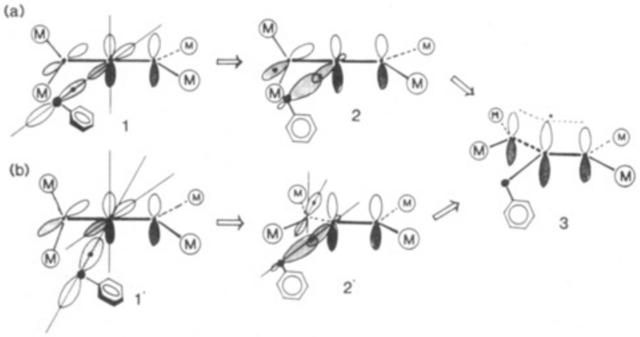

Figure 5. Schematic representation of radical addition reaction process of PhS$^\bullet$ (PhSe$^\bullet$) with $(CH_3)_2C{=}C{=}C(CH_3)_2$. Route **a**: **1**, single orbital interaction, **2**, incipient radical with perpendicular structure; and **3**, allyl-type radical with coplanar structure. Route **b**: **1′**, dual-orbital interaction; and **2′**, allyl-type radical with bent structure.

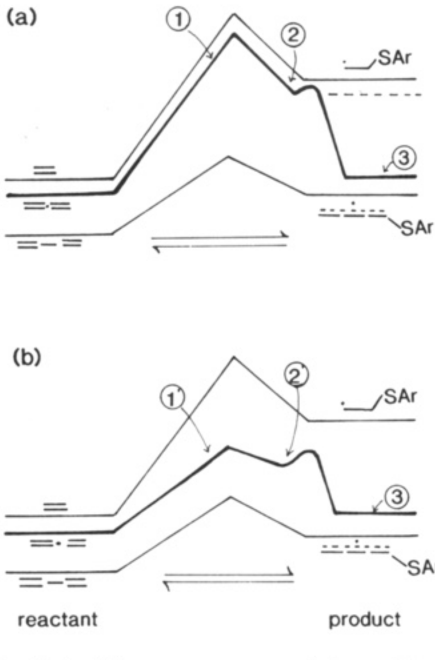

Figure 6. Potential energy curves of free-radical addition reactions to different double bonds such as nonconjugated olefin, allene, and conjugated diene. **a** and **b** correspond to reaction routes **a** and **b** in Figure 5, respectively.

interaction). This interaction may delocalize the unpaired electron into the whole p-orbitals of the allene molecule resulting in the decrease of the activation energy (Figure 6, route **b**). In the case of PhSe$^\bullet$, the reactivity to the allenes is slightly higher than that of 1,3-dienes. To explain such high reactivity of allenes to PhSe$^\bullet$, it needs to increase in the overlap integral between the orbital of the attacking radical center with the central two 2p-orbitals of allene.

The regioselectivity of the radical addition reaction to allenes has, so far, been interpreted mainly in terms of the reversibility of the reaction.[7,12] To $(CH_3)_2C{=}C{=}C(CH_3)_2$, the addition product of ArS$^\bullet$ shows exclusively the central attack;[14] the irreversibility of the central attack was confirmed in this flash photolysis study especially by the decay curve **b** of ArS$^\bullet$ in Figure 2. In the case of $(CH_3)_2C{=}C{=}CH_2$, although the reversible terminal addition is possible prior to the irreversible central attack, no clear evidence for the terminal attack is obtained by the product analysis[14] and by the decay kinetics of ArS$^\bullet$ (PhSe$^\bullet$) in this flash photolysis study.

In general, the radical reactivity is determined by energy levels between SOMO of the attacking radical and HOMO of the double bond and by the overlap integral between them. No correlation was found between the observed k_1 values and the ionization energies of substrates in Table II.[45–47] On the other hand, it is clearly shown that the orbital size of unpaired electron of the attacking radical infuences strongly the rates of addition reactions to the 2p-orbitals of the central carbon of allene. The central attack was also observed for the other attacking radicals having large orbital such as bromine atom (4p-orbital)[8] and stannyl radical (5p-orbital).[1,9] Thus, the orbital size of the unpaired electron of the attacking radicals is an important factor for determining both the reaction rates and the regioselectivity.

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