Registry No. 1,5-Hexadiene, 592-42-7; 2-phenyl-1,5-hexadiene, 7399-52-2; 3-phenyl-1,5-hexadiene, 1076-66-0; 2,5-diphenyl-1,5-hexadiene, 7283-49-0; 2,5-dicyano-3-methyl-1,5-hexadiene, 63472-80-0; *threo*-3,4-dimethyl-1,5-hexadiene, 68701-55-3; *threo*-3,4-diphenyl-1,5-hexadiene, 80754-12-7; 2,4-diphenyl-1,5-hexadiene, 63779-63-5; allyl vinyl ether, 3917-15-5; allyl phenyl ether, 1746-13-0; allyl acetate, 591-87-7; 1,4-dimethylenecyclohexane, 4982-20-1; *cis*-1,2-dimethylcyclobutane, 16177-46-1; bicyclo[6.2.0]deca-2,6-diene, 77614-69-8; *cis*-1,2-divinylcyclopropane, 2984-58-9; 3,4-homotropilidene, 3725-20-0; bicyclo[6.1.0]nona-2,6-diene, 30767-77-2; semibullvalene, 6909-37-1; bullvalene, 1005-51-2.

Reactivities of Cycloalkenes toward Phenylthio Radicals

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The absolute rate constants for the addition reactions of the (*p*-chlorophenyl)thio radical toward cyclomonoalkenes, cycloalkadienes, and bicycloalkenes have been determined by the flash photolysis method by taking the reversibility of the addition process into consideration. The reactivities toward $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ are proportional to those toward the methyl radical. The rate constants (in $\text{M}^{-1}\ \text{s}^{-1}$) decrease in the order conjugated dienes (10^6–10^8) > bicycloalkenes (10^5–10^7) > cyclomonoalkenes (10^2–10^5). The reactivities are controlled by the resonance stabilization of the transition state, by the released strain energy, and by the polar nature of the transition state.

Introduction

The relative reactivities of cycloalkenes in free-radical addition reactions have been reported for the carbon-centered radicals,[1-3] the bromine atom,[4] and the thio radicals.[5-8] The reactivities, however, vary with the kinds of the attacking radicals. One of the origins of the difference in the reactivities is attributed to the reversibility of the addition step for radicals; in the case of the thio radicals reliable data have not been obtained since the reactivity ratios depend upon the concentrations of the chain-transfer reagents.[7] Therefore, a new kinetic approach that explicitly includes the reversibility of the addition step is required. We found that the flash photolysis method is useful to obtain the absolute rate constants for the reversible addition reactions of the phenylthio radicals with alkenes[9] and alkynes;[10] the difficulty of the reversibility can be overcome by addition of a selective radical trap that is not reactive to the thio radicals but reactive to the adduct carbon-centered radicals. In this study we have applied this method to cycloalkenes and examined the factors controlling the reactivities.

Results

The flash photolysis method of determining the rates of addition of the phenylthio radicals has been described in a previous paper;[9a] the procedure is briefly shown below.

Scheme I

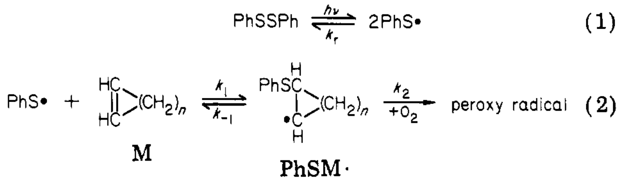

Table I. Addition Rate Constants (k_1) and Relative Equilibrium Constants (Kk_2) for Reactions of $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ toward Cyclomonoalkenes at 23 °C[a]

alkenes	k_1, $\text{M}^{-1}\ \text{s}^{-1}$	Kk_2, $\text{M}^{-2}\ \text{s}^{-1}$
cyclopentene[c]	4.2×10^4	2.7×10^6
cyclohexene[b]	3.3×10^3	2.0×10^5
cycloheptene[c]	1.1×10^5	8.2×10^6
cyclooctene[b]	2.5×10^3	1.9×10^5
cyclododecene[c]	8.2×10^2	8.3×10^4

[a] Each estimation error is ca. 10%. [b] In each alkene. [c] In cyclohexane.

In this study, the (*p*-chlorophenyl)thio radical was selected as a representative of the phenylthio radicals because the sharp transient absorption band yields precise data. The transient absorption band at 515 nm generated by the flash photodecomposition of bis(*p*-chlorophenyl) disulfide was ascribed to $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ since the same absorption band was observed by the flash photolysis of the corresponding thiol.[11] The initial concentration of the thio radical generated by one flash exposure is estimated to be ca. 10^{-6} M by assuming the diffusion-controlled rate constant for recombination of the thio radical.[9] Low reactivity of the phenylthio radical toward oxygen was confirmed since the decay rate of the phenylthio radical was not accelerated by the addition of oxygen into solution. The low hydrogen-abstraction ability of the phenylthio radical was also confirmed.[9a]

Figure 1 shows the first-order plots of the decay curves of $p\text{-ClC}_6\text{H}_4\text{S}\cdot$ in cyclohexane. Curve b is the plot in de-

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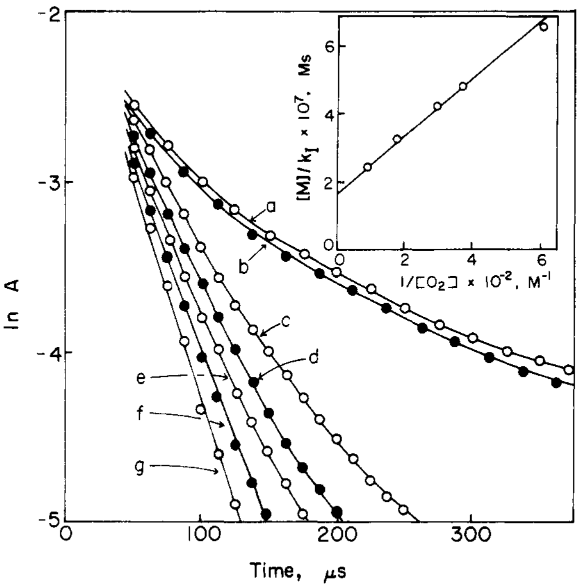

Figure 1. First order plots for decay of p-$ClC_6H_4S\cdot$ in the presence of bicyclo[2.2.1]-2-heptene and oxygen. [Olefin]: a, 0; b–g, 5.4 × 10^{-3} M. [O_2]: a and b, 0; c, 1.6 × 10^{-3}; d, 2.7 × 10^{-3}; e, 3.5 × 10^{-3}; f, 5.7 × 10^{-3}; g, 1.1 × 10^{-2} M. insert: plot of [olefin]/k_I vs. 1/[O_2].

gassed solution containing bicyclo[2.2.1]-2-heptene, which is similar to that without the alkene (curve a). By the addition of both alkene and oxygen, the decay rates are accelerated and decay kinetics approach first order (curves c–g); the slopes of the first-order plots (k_I) increase with the concentration of oxygen. These findings suggest that the addition step of the thio radical is reversible and that oxygen acts as a selective radical trap to the carbon-centered radical (Scheme I).[9] Here, p-$ClC_6H_4S\cdot$ is abbreviated as $PhS\cdot$. The decay of the thio radical can be written as in eq 3. By applying the steady-state approximation with

$$-d[PhS\cdot]/dt = 2k_r[PhS\cdot]^2 + k_1[M][PhS\cdot] - k_{-1}[PhSM\cdot] \qquad (3)$$

$$k_I = k_1[1 - k_{-1}/(k_{-1} + k_2[O_2])][M] \qquad (4)$$

$$[M]/k_I = 1/k_1 + k_{-1}/k_1k_2[O_2] \qquad (5)$$

respect to [$PhS\cdot$], the first-order rate constant (k_I) can be expressed as eq 4, whose reciprocal is eq 5.

Under our experimental conditions, the concentrations of oxygen (~10^{-4}–10^{-2} M) and cycloalkenes (~10^{-1}–10 M) are kept constant during the reaction with the thio radical, since the concentration of the thio radical generated by one flash exposure is very low (ca. 10^{-6} M). When the concentrations of oxygen and cycloalkenes are low, decay kinetics are mixed order, consisting of second order ($k_r[PhS\cdot]^2$) and first order ($k_I[PhS\cdot]$); the k_I values can be separated from the second-order term by a graphic method and/or computer simulation method by using the k_r/ϵ value estimated from the second-order plot in the absence of cycloalkenes.[12,13] The insert of Figure 1 shows the plot of eq 5; a linear line is obtained. From the intercept and slope, the reciprocals of the k_1 value and Kk_2 ($K = k_1/k_2$) value are estimated, respectively. In the same manner, the k_1 and Kk_2 values for other cycloalkenes are obtained. These values are summarized in Table I for cyclomonoalkenes, in Table II for cycloalkadienes, and in Table III for bicycloalkenes. For conjugated dienes, triene, and tetraene in Table II, the Kk_2 values can not be obtained since the dependences of the k_I values upon the concentration of oxygen were small; in these cases, k_I/[M] in oxygen-saturated solution can be made equal to the k_1 value.

Table II. Addition Rate Constants (k_1) for Reactions of p-$ClC_6H_4S\cdot$ toward Cycloalkadienes in Cyclohexane at 23 °C[a]

alkenes	k_1, M^{-1} s^{-1}
1,5-cyclooctadiene[b]	1.1 × 10^5
1,3-cyclohexadiene	2.4 × 10^8
1,3-cycloheptadiene	3.6 × 10^7
1,3-cyclooctadiene	2.1 × 10^6
cycloheptatriene	8.9 × 10^6
cyclooctatetraene	2.4 × 10^6

[a] Each estimation error is ca. 10%. [b] Kk_2 = 3.3 × 10^7 M^{-2} s^{-1}.

Table III. Addition Rate Constants (k_1) and Relative Equilibrium Constants (Kk_2) for Reactions of p-$ClC_6H_4S\cdot$ toward Bicycloalkenes in Cyclohexane at 23 °C[a]

alkenes	k_1, M^{-1} s^{-1}	Kk_2, M^{-2} s^{-1}
dicyclopentadiene	5.4 × 10^6	5.4 × 10^8
bicyclo[2.2.1]-2-heptene	6.1 × 10^6	1.2 × 10^9
bicyclo[2.2.1]hepta-2,5-diene	1.2 × 10^7	3.0 × 10^9

[a] Each estimation error is ca. 10%.

The relative reverse rate constants can be obtained in the form of k_{-1}/k_2 by dividing k_1 by Kk_2 in Tables I and III. Replacing the k_2 values by the reported one (10^8–10^9 M^{-1} s^{-1}),[14] we can estimate the k_{-1} values to be 10^5–10^8 s^{-1}. Such fast backward reactions are compatible with our observation that the equilibrium is established during the xenon flash duration of ca. 10 μs, as the similarity of decay curves a and b in Figure 1 suggests. In the same manner, the K values are estimated to be ~10^{-5}–30 M^{-1}; with a decrease in the K value, the addition reactions become more endothermic. In the case of conjugated dienes, independence of the k_I values upon [O_2] suggests that the second term in eq 5 is small ($1/k_1 > k_{-1}/k_1k_2$); i.e., k_{-1} is small. Thus, the reactions may be rather exothermic.

Discussion

Figure 2 shows the plot of log k_1 vs. the affinity of the methyl radical toward cycloalkenes as reported by Gresser, Rajbenbach, and Szwarc.[2] A fiarly good correlation is obtained except for cyclooctene. This linear relation shows the reliability of the k_1 values estimated in this study; our data is sensitive to the concentration of the reactive impuritys such as dienes in monoalkenes since in the flash photolysis method the consumption of small amounts of the phenylthio radical is observed, whereas the methyl affinities were estimated after the consumption of substrates in more than ca. 10%.[2]

In Figure 2, 1,3-cyclohexadiene is the most reactive; the rate constants for three conjugated dienes in Table II are comparable with that for indene (1.8 × 10^7 M^{-1} s^{-1}),[15] which is a cyclopentene with a conjugated phenyl ring. The reactivities of conjugated cycloalkadienes can be correlated with the absorption maxima of the dienes: 1,3-cyclohexadiene (256 nm), 1,3-cycloheptadiene (248 nm), and 1,3-cyclooctadiene (228 nm).[16] The reactivities increase

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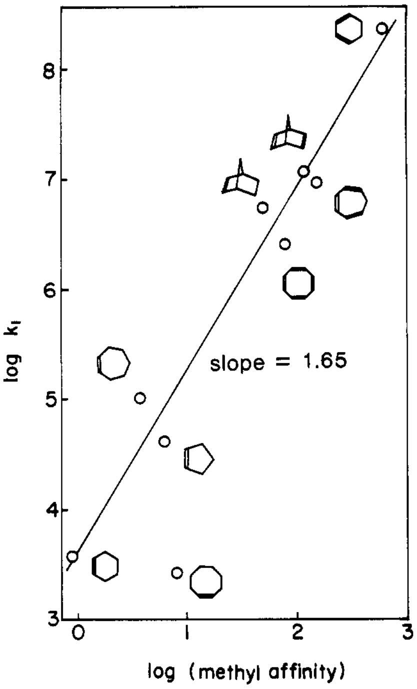

Figure 2. Plot of log k_1 vs. log (methyl affinity).

with the shift to longer wavelength, which may be proportional to the coplanarity of the two double bonds. Such coplanarity becomes more important in the resonance stabilization of the allyl-type adduct radical in the product (or in the transition state) than that in the reactant, which can be presumed from an interpretation of the bathochromic shift based on the coplanarity of the excited state of the diene (·C—C=C—C·).[16]

The reactivities of cycloheptatriene and cyclooctatetraene are compatible with those of the corresponding conjugated dienes, suggesting that the third double bond does not play any important role in the resonance stabilization of the adduct radical (or transition state) because of the nonplanarity of the triene and tetraene.

As seen in Figure 2, bicycloalkenes are also more reactive than monocycloalkenes. Such high reactivities can be attributed to the released strain energies by the addition of the attacking radical, which is measured by the heat of hydrogenation of one double bond (ΔH); the strain energies of bicycloalkenes ($-\Delta H = \sim 35$ kcal mol^{-1}) are greater than those of monocycloalkenes ($-\Delta H = \sim 25$ kcal mol^{-1}).[17] The log Kk_2 values can be thought of as a measure of the exothermicity of the addition reactions on the basis of the assumption that the k_2 value is constant with the change of alkenes. Figure 3 shows the plots of log k_1 vs. log Kk_2; a fairly good linear correlation is found. In the case of the cycloalkenes shown in Figure 3, the log Kk_2 values may increase with the released strain energy. The reactivity of bicyclo[2.2.1]hepta-2,5-diene is about twice that of the corresponding monoene; this finding suggests that the stabilization of the adduct radical on account of a homoallyl-type resonance is not important. Although the reactivity of 1,5-cyclooctadiene is 44 times higher than that of cyclooctene, the greater strain energy of the diene than that of the monoene (ca. 7 kcal mol^{-1}), which is estimated from the heats of hydrogenation, may be sufficient to explain the difference in the reactivities; the interannular interaction as would be expected for 1,5-cyclooctadiene is not evident.

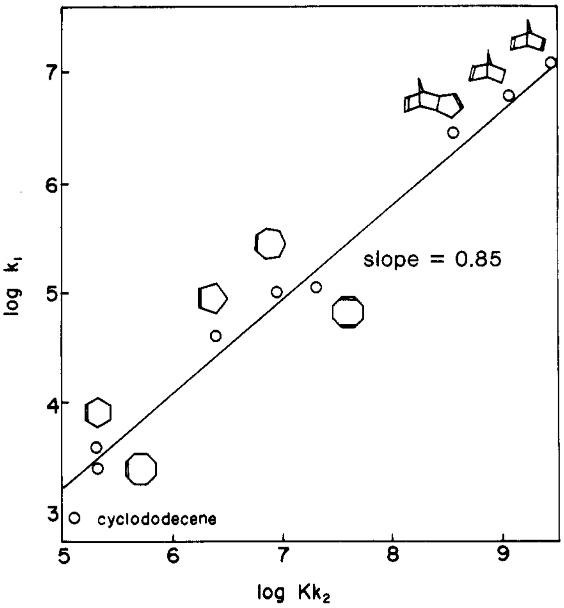

Figure 3. Plot of log k_1 vs. log Kk_2.

Since the thio radicals are highly electrophilic, the transition state may be stabilized with alkenes having low ionization potentials by the participation of the polar resonance structures such as [PhS$^-$,alkene$^{+\cdot}$].[1,9] In Figure 2, the most reactive 1,3-cyclohexadiene has a low ionization potential (8.2 eV), bicycloalkenes have modest ionization potentials (ca. 8.5 eV), and less reactive cyclomonoalkenes have high ionization potentials (ca. 9.0 eV).[18] The effect of the polar transition state on the rates is concealed in the linear relation of Figure 3, because the ionization potentials vary with the same order of the exothermicity of the reaction such as the released strain energy or the resonance stabilization of the adduct radical. On the other hand, the methyl radical is not electrophilic; thus, such a polar effect is not superimposed upon the exothermicity. The higher selectivity of the thio radical than the methyl radical, which is measured from the slope of Figure 2 (1.65), is attributed to the difference in the polar nature of the transition state. Such a difference in the selectivity cannot be attributed to the Hammond postulate in this case,[19] since the absolute rate constants for addition of the methyl radical toward alkenes are reported to be ca. 10^3–10^4 M^{-1} s^{-1}, which are similar to those of the thio radical.[20]

In Figure 2, a disagreement was found for cyclooctene; although the origin of such difference could not be pointed out, the ratio of the k_1 values of cyclooctene to cyclohexene is in good agreement with that estimated from product analysis at low temperature by Gale.[3]

Experimental Section

Commercially available cycloalkenes were distilled in a usual manner after the photoillumination of diphenyl disulfide in the presence of benzenethiol and oxygen to eliminate substances reactive toward the phenylthio radical. Presence of conjugated dienes in monoalkenes was checked by their characteristic absorption bands at ca. 240 nm. Bis(*p*-chlorophenyl) disulfide was purified by recrystallization. Cyclohexane used as solvent was of spectrophotometric grade.

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The flash experiments were made at room temperature controlled at 23 ± 1 °C. The flash apparatus was of standard design;[21] half-duration and flash energy of the xenon flash lamp (Xenon Corp. N-851C) were ca. 10 μs and 150 J, respectively. A flash light in the range of 350–400 nm was selected by the use of appropriate light filters to prevent the excitation of alkenes. Kinetic observations of the thio radical were made with a continuous monitor light source and photomultiplier detector. The oxygen concentrations of solutions were calculated from Henry's law by dissolving oxygen under partial pressure after degassing the solution.[22]

Registry No. p-ClC$_6$H$_4$S, 31053-91-5; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclododecene, 1501-82-2; 1,5-cyclooctadiene, 111-78-4; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9; dicyclopentadiene, 77-73-6; bicyclo[2.2.1]-2-heptene, 498-66-8; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; methyl, 2229-07-4; bis(p-chlorophenyl) disulfide, 1142-19-4.

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Surface Photochemistry: Decomposition of Azobis(isobutyronitrile) on Dry Silica Gel[1]

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The generation of cyanopropyl radical pairs by the photolysis of azobis(isobutyronitrile) (AIBN) adsorbed on dry silica gel–benzene slurries has been investigated. The results require revision of an earlier observation that restrictions on the rotational motion of cyanopropyl radicals at a silica gel–benzene interface prevented the formation of the unsymmetrical coupling product dimethyl-N-(2-cyano-2-propyl)ketenimine. Both tetramethylsuccinodinitrile and the ketenimine were formed on the silica gel surface, even when dry, although the latter was partially hydrolyzed to the corresponding amide. Measurements of geminate recombination of radicals produced by direct photolysis of mixtures of deuterated and nondeuterated AIBN indicated that some radicals could escape, by translational motion, from their original geminate partners. The amount of translational motion was increased for the same cyanopropyl radical pair generated by triplet-sensitized AIBN decomposition. This latter observation supports the view that the triplet-sensitized decomposition of AIBN occurs *directly* from an excited state rather than by isomerization to a thermally labile cis isomer.

The behavior of both singlet and triplet spin-correlated radical pairs has been extensively investigated in solution.[2] It has been found that a geminate radical pair generated within a solvent cage has a number of pathways available to it: (1) it may react to form products either by recombination or disproportionation, or may recombined to regenerate starting material, (2) it may be transformed into a new radical pair, or (3) it may undergo diffusional separation to form free radicals. The first process can occur only with singlet radical pairs, whereas the latter two are independent of the radical pair multiplicity. Since intersystem crossing must precede geminate reaction of a triplet radical pair, processes 2 and 3 compete more effectively with process 1 from triplet than from singlet pairs. The amounts of geminate recombination may be varied by changing either the rate of intersystem crossing of the radical pair or the rate of its diffusional separation. The latter may be achieved by, for example, altering the viscosity of the medium. Changes in the relative importance of the above processes (1–3) are to be expected when the radical pair is generated in an environment where its motion is restricted, as, for example, in the crystalline state,[3] in a micelle,[4] or on a solid surface.[5,6] Variations in the amount of geminate radical pair reaction can provide a useful measure of such effects.

The behavior of adsorbed radical pairs and, in particular, the possibilities for their rotational and translational movement of inorganic surfaces such as silica gel, alumina, and porous Vycor have not been widely studied.[7] Similarly, there have been few studies of the photochemistry and mobility of adsorbed organic molecules, although the nature of the surface and the adsorbate–surface binding interaction have been extensively examined.

In the case of silica gel there are two types of surface functional groups: the siloxane and the silanol, as well as physisorbed water molecules.[13] It is generally accepted that for equilibrated surfaces there are ~5 silanols/nm^2, but there has been no general consensus concerning the relative contributions from isolated, vicinal and geminal silanols.[14] The adsorption of organic molecules on silica is believed to occur through London dispersion forces, electrostatic interactions, and hydrogen bonding. The

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