chromatographed over silica gel (hexane/benzene: 80/20). The thiols were extracted with ethyl ether and dichloromethane with a Soxhlet extractor. The solvent was replaced by deuteriated chloroform, fumaronitrile (0.55 mg) added, and the sample was analyzed by ^{1}H NMR. The areas of peaks δ 2.85 (methine proton of one thiol isomer), 0.55 (methyl protons of both thiols), 0.32 (cyclopropyl protons of both thiols), and 6.15 (protons of fumaronitrile) were measured carefully. The ratio of the thiols were found to be 3:1, and the lower limit of quantum yield of formation of thiols was 0.03.

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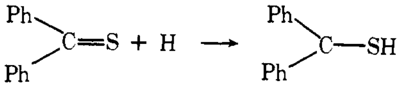

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Evaluation of Addition Rates of the Thiyl Radicals to Vinyl Monomers by Flash Photolysis. 2.[1] Substituent Effect on Addition of Substituted Benzenethiyl Radicals to Methyl Methacrylate or Styrene

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Abstract: Rate constants for the addition reactions (k_1) of the para-substituted benzenethiyl radicals to methyl methacrylate (MMA) or styrene (St) were determined by means of flash photolysis. Rate constants for reverse reaction (k_{-1}) and equilibrium constants ($K = k_1/k_{-1}$) were estimated as ratios of the rate constant for the reaction between the carbon centered radical and oxygen (k_2). Fairly good linear correlations were obtained for the Hammett plots of log k_1 vs. σ^+ for both monomers (ρ^+ ($k_{1,\mathrm{MMA}}$) = 1.05 ± 0.05 and ρ^+ ($k_{1,\mathrm{St}}$) = +1.37 ± 0.08). For MMA, log k_{-1}/k_2 and log Kk_2 also gave the linear correlations to σ^+ yielding ρ^+ ($k_{-1,\mathrm{MMA}}$) = −0.36 ± 0.05 and ρ^+ (K_{MMA}) = +1.35 ± 0.05. Decreasing order of log Kk_2 is closely related to increasing order of the thermodynamic stabilities of the thiyl radicals. For MMA which has an electron-poor double bond and St which has an electron-rich double bond, we attempted to assess the relative importance of stabilities of the radicals and of the possible contribution of polar structures to the transition state.

Substituent effect on addition reactions of the free radicals to vinyl monomers has been investigated by appling the Hammett equation correlations and the observed ρ values have been interpreted mainly in terms of the substituent effect on polar resonance structures in the transition state.[2,3] For the substituent effect on the hydrogen abstraction reactions by free

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radicals, the importance of the bond-dissociation energy has been pointed out by Zavitsas and Pinto.[4] Recently, Davis and Pryor have explained this effect on the basis of resonance stabilization in the transition state in addition to bond-dissociation energy.[5] For the radical addition reactions, it must be significant to assess the relative importance of product stabilities and of the possible contribution of polar structures to the transition state. However, it is well known to be difficult to obtain the experimental data to realize these two effects separately.

For the following reversible addition reaction of thiyl radicals

$$p\text{-XC}_6\text{H}_4\text{S}\cdot + \text{CH}_2{=}\text{CHY} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} p\text{-XC}_6\text{H}_4\text{SCH}_2\text{C}\cdot\text{HY} \xrightarrow[(\text{O}_2)]{k_2} \quad (1)$$

we reported in a preceding paper[1] that k_1, k_{-1}/k_2, and Kk_2 ($K = k_1/k_{-1}$) for systems with X = Cl and various Y were evaluated by the microsecond flash photolysis. In this paper, these rate parameters for the systems consisting of methyl methacrylate (MMA, as a vinyl monomer having electron-poor double bond) or styrene (St, as a monomer having electron-rich double bond) and a series of para-substituted benzenethiyl radicals are estimated to clarify the factors controlling the reactivity.

Results and Discussion

The transient absorption bands generated by flash photolysis of di-para-substituted diphenyl disulfides appeared at 450 nm for -H, 505 nm for $-\text{CH}_3$, and 510 nm for -Cl in cyclohexane. Each of them was attributed to the corresponding thiyl radical.[6,7] For *p*-methoxybenzenethiyl radical, whose absorption band was not reported, the transient band at 515 nm in cyclohexane was attributed to this radical since the same absorption bands were observed in the photolyses of both the disulfide and the thiol.[8]

In the case of di-*p*-nitrobenzene disulfide, the transient absorption bands appeared at ca. 520 nm and ca. 450 nm in benzene solution containing 10% cyclohexane (benzene was used to raise the solubility of the disulfide). Since both bands are observed even in aerated nonpolar solvents, ion radicals are evidently not involved. No transient absorption band was observed in the visible region in the flash photolysis of *p*-nitrobenzenethiol or di-*p*-nitrobenzene sulfide. However, the addition rate constants to vinyl monomers, which were obtained from the decay curves of the transient bands produced from the disulfide, agree fairly well with the extrapolated values from the Hammett plots for the rate constants of other para-substituted benzenethiyl radicals (see Figures 2 and 3). Thus, the transient bands generated from the disulfide may be attributed to its thiyl radical.[9] Even if these bands should be attributable to other species, similar slopes in the plots of linear free-energy relationship can be drawn irrespective of the data of the nitrobenzenethiyl radical.

The thiyl radicals decay with second-order kinetics in degassed solutions. The decay rates were little affected by the addition of oxygen into the solution, indicating small rate constants for the reaction between oxygen and the thiyl radicals. The decay rates of the thiyl radicals were promoted only slightly by the addition of vinyl monomer in degassed solution, and the decay kinetics were still showing the second-order behavior. Only when both vinyl monomer and oxygen were present was the decay rate of the thiyl radical accelerated significantly, and the decay curve approached first-order kinetics. These facts suggest that thiyl radicals react with vinyl monomers reversibly and that oxygen reacts rapidly with the carbon-centered radicals, $p\text{-XC}_6\text{H}_4\text{SCH}_2\text{C}\cdot\text{HY}$, as shown in eq 1. Thus, the decay of the thiyl radical can be expressed as follows (k_r denotes the recombination rate constant of the thiyl radical).

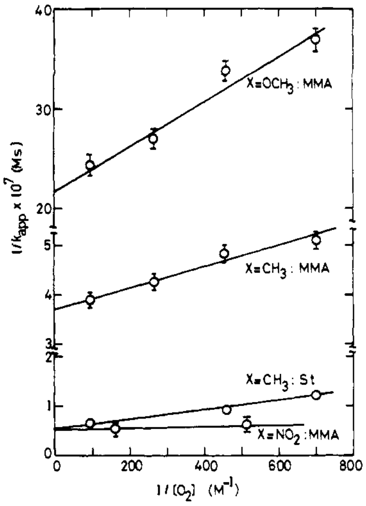

Figure 1. Plots of $1/k_{\text{app}}$ vs. $1/[\text{O}_2]$ (eq 4) for the reactions of para-substituted benzenethiyl radicals ($p\text{-XC}_6\text{H}_4\text{S}\cdot$) with MMA or St.

$$-\text{d}[\text{RS}\cdot]/\text{d}t = 2k_r[\text{RS}\cdot]^2 + k_1[\text{CH}_2{=}\text{CHY}][\text{RS}\cdot] - k_{-1}[\text{RSCH}_2\text{C}\cdot\text{HY}] \quad (2)$$

In eq 2, the reaction of the thiyl radical (RS·) and oxygen has been eliminated because of its small contribution.[1] By applying the steady-state approximation with respect to $[\text{RSCH}_2\text{C}\cdot\text{HY}]$ in reaction 1, eq 2 can be converted into eq 3:

$$k_\text{I} = k_1\{1 - k_{-1}/(k_{-1} + k_2[\text{O}_2])\}[\text{CH}_2{=}\text{CHY}] \quad (3)$$

where k_I is the first-order rate constant with respect to the thiyl radical which can be easily estimated from mixed-order decay kinetics by the methods described in the literature.[1,10,11] The slope (k_{app}) in the plot of k_I vs. $[\text{CH}_2{=}\text{CHY}]$ at constant oxygen gives eq 4:

$$1/k_{\text{app}} = 1/k_1 + (k_{-1}/k_1k_2)[\text{O}_2] \quad (4)$$

Fairly good straight lines were obtained in the plot of $1/k_{\text{app}}$ vs. $1/[\text{O}_2]$ for each substituted benzenethiyl radical, as shown in Figure 1 for some examples. The intercept and slope of the plots yield $1/k_1$ and k_{-1}/k_1k_2, respectively.

From these values, k_1, k_{-1}/k_2, and Kk_2, where K is equilibrium constant ($K = k_1/k_{-1}$), were calculated as listed in Table I (MMA) and Table II (St), in which the values for the *p*-chlorobenzenethiyl radical are quoted from our preceding report.[1] Values of k_{-1}/k_2 for the three systems of MMA-*p*-nitrobenzenethiyl radical, St-*p*-chloro-, and St-*p*-nitrobenzenethiyl radicals could not be estimated since the dependence of each k_{app} on concentration of oxygen for these systems was small. The k_1 values for *p*-nitrobenzenethiyl radical include rather large experimental errors because of weak transient absorptions. The k_1 ratio of MMA to St obtained for the benzenethiyl radical, $k_{1,\text{H,MMA}}/k_{1,\text{H,St}} = 0.16$, is in agreement with the ratio of the reported relative values estimated by the spin trapping method (0.083)[12] within experimental error.

When Y is fixed the effect of X on the reaction of oxygen with the radical center of $p\text{-XC}_6\text{H}_4\text{SCH}_2\text{C}\cdot\text{HY}$ may be insignificant, since its effect is decreased by the intermediacy of one methylene group; k_2 may be taken as constant for each vinyl monomer. For the rate constants for the reactions between oxygen and the carbon centered radicals, the values of $10^8 \sim 10^9$ M^{-1} s^{-1} have been reported.[13,14] By assuming an appropriate k_2 value, k_{-1} and K values can be calculated from the values in Tables I and II.

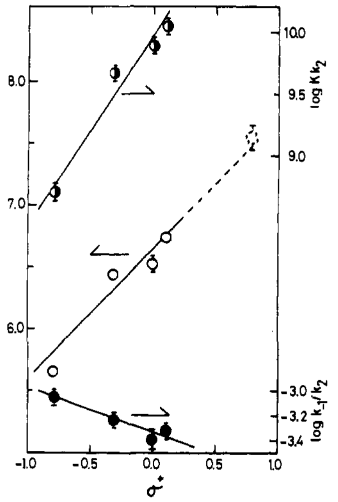

Figure 2. Hammett equation plots of log k_1 (○), log k_{-1}/k_2 (●), and log Kk_2 (◐) for MMA vs. σ^+.

Table I. Estimated k_1, k_{-1}/k_2, and Kk_2 for MMA in Cyclohexane at 23 °C

X	k_1, $M^{-1}\ s^{-1}$	k_{-1}/k_2, M	Kk_2, $M^{-2}\ s^{-1}$
$-OCH_3$	4.6×10^5 [a]	9.1×10^{-4} [c]	5.0×10^8 [c]
$-CH_3$	2.7×10^6 [a]	5.8×10^{-4} [c]	4.7×10^9 [c]
$-H$	3.2×10^6 [b]	4.1×10^{-4} [d]	7.8×10^9 [d]
$-Cl$	5.4×10^6 [a]	4.9×10^{-4} [c]	1.1×10^{10} [c]
$-NO_2$ [e]	1.8×10^7 [c]		

[a] Estimated error of ±20%; [b] ±30%; [c] ±40%; and [d] ±60%. [e] In 90% benzene + 10% cyclohexane.

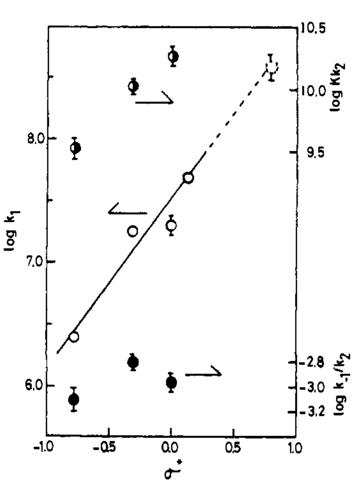

Figure 3. Hammett equation plots of log k_1 (○), log k_{-1}/k_2 (●), and log Kk_2 (◐) for St vs. σ^+.

Table II. Estimated k_1, k_{-1}/k_2, and Kk_2 for St in Cyclohexane at 23 °C

X	k_1, $M^{-1}\ s^{-1}$	k_{-1}/k_2, M	Kk_2, $M^{-2}\ s^{-1}$
$-OCH_3$	2.6×10^6 [a]	7.7×10^{-4} [d]	3.4×10^9 [d]
$-CH_3$	1.8×10^7 [a]	1.6×10^{-3} [c]	1.1×10^{10} [c]
$-H$	2.0×10^7 [b]	1.1×10^{-3} [d]	1.9×10^{10} [d]
$-Cl$	5.1×10^7 [d]		
$-NO_2$ [e]	4.0×10^8 [d]		

[a] Estimated error of ±20%; [b] ±30%; [c] ±40%; and [d] ±60%. [e] In 90% benzene + 10% cyclohexane.

Table III. Parameters of Linear Free-Energy Relationships obtained from Reversible Addition Reactions of the Para-Substituted Benzenethiyl Radicals to Vinyl Monomers in Cyclohexane

parameter	MMA[a]	St[b]
$\rho^+(k_1)$	+1.05	+1.37
$\rho^+(k_{-1})$	−0.36	
$\rho^+(K)$	+1.35	
$\rho^+(k_1)/\rho^+(K) = S(k_1)$[c]	+0.78	+1.00[d]
$\rho^+(k_{-1})/\rho^+(K) = S(k_{-1})$[c]	−0.27	

[a] Estimated error of ±0.05 and [b] ±0.08. [c] $S(k_1) - S(k_{-1}) \fallingdotseq 1$. [d] $\rho^+(k_{1,St})/\rho^+(K_{MMA})$.

We attempted to plot the values in Tables I and II as a function of Brown–Okamoto's Hammett σ^+ constants as depicted in Figure 2 for MMA and Figure 3 for St.[15] In Hammett plot with σ, the values for the p-methoxybenzenethiyl radical deviate significantly from linearity. In reactions concerned with thiyl radicals, a V-shaped Hammett correlation was suggested in a few papers,[16,17] and this has been explained by the reason that the rate of radical reactions are controlled not only by polar term but also by resonance term.[2,3,5] Contrary to this, in our figures the straight lines are much more appropriate than V-shaped curve as can be seen from Figures 2 and 3. In the reactions of stable free radicals with para-substituted benzenethiyl radicals, linear correlations were also obtained in the Hammett plot with σ^+.[8] The slopes yield ρ^+'s which are listed in Table III. For St, $\rho^+(k_{-1})$ and $\rho^+(K)$ were not obtained from only three plotted points.

Logarithm of Kk_2 is proportional to the difference in the thermodynamic stabilities between reactant and product. For one vinyl monomer, the stability of $p\text{-}XC_6H_4SCH_2C{\cdot}HY$ with changing para substituent may depend on the strength of the σ-bond between sulfide sulfur and methylene carbon ($-S-CH_2-$), which may depend mainly on the repulsion energy between the lone pair electrons on S and carbon atom of methylene group. Since this repulsion energy may be small, the stability of the radical may not be influenced largely by X. This leads to an important conclusion. When Y is fixed, the differences among log Kk_2 by changing the para substituent of the benzenethiyl radicals are a relative measure of the thermodynamic stabilities of the thiyl radicals. The smaller the log Kk_2 the more stable the thiyl radical is, which depends on the magnitude of the electron-donating power of X; $\rho^+(K) = +1.35$ for MMA.

The same tendency has been reported for the reversible hydrogen abstraction by the substituted phenoxy radicals by Mahoney and DaRooge;[18] from their data, ρ^+ for equilibrium constants can be estimated to be ca. 3.4, which may indicate that the thermodynamic stabilities of the phenoxy radicals are increased by the electron-donating substituents. Our $\rho^+(K)$ for the para-substituted benzenethiyl radicals obtained with MMA is less than a half of $\rho^+(K)$ for the phenoxy radicals. Recently, Colle and Lewis have reported the activation energies for the hydrogen abstraction reactions by the carbon-centered radical from substituted thiophenols.[19] It may be expected that the activation energies are inversely proportional to the thermodynamic stabilities of the benzenethiyl radicals formed from hydrogen abstraction; the order of the stabilities is p-Cl < H < p-OCH_3, which agrees with our results.

To date, in many addition reactions of the free radicals (R·) to vinyl monomers (M), the magnitude and sign of ρ have been explained mainly by the polar effect on the transition state (R^+, $M^-\cdot$ or R^-, $M^+\cdot$).[2,3] However, our observation that log Kk_2 can be correlated to σ^+ may suggest that the thermodynamic stabilities of the para-substituted benzenethiyl radicals play an important role in determining the reactivities for reaction 1. Degree of dependence of the reactivities for forward and backward reactions on the stabilities of the thiyl radicals can be expressed by the ratios of $\rho^+(k_1)/\rho^+(K) = S(k_1)$ and $\rho^+(k_{-1})/\rho^+(K) = S(k_{-1})$, respectively; these values are listed in Table III.

When polar effect on the transition state is not taken into consideration, the Evans–Polanyi's relationship can be applied to the forward and backward reactions, and the following equations can be derived:

$$\Delta(\log k_1) = -\alpha\Delta(\log K) \text{ or } \rho^+(k_1) = -\alpha\rho^+(K) \quad (5)$$

$$\Delta(\log k_{-1}) = \beta\Delta(\log K) \text{ or } \rho^+(k_{-1}) = \beta\rho^+(K) \quad (6)$$

where $0 < \alpha,\beta < 1$ and $\alpha = 1 - \beta$. In Table III, a relation of $S(k_1) - S(k_{-1}) \fallingdotseq 1$, which may show reliability of the data, is satisfied for MMA.

The value of α was estimated by Semenov empirically; for exothermic reactions $\alpha = 0.25$ and for endothermic reactions $\alpha = 0.75$.[20] Assuming that the addition reactions (k_1) for MMA were endothermic, the observed $S(k_1) = 0.78$ can be set equal to α (= 0.75); consequently, $S(k_{-1}) = 0.27$ is equal to β (= 0.25). This means that the reactivities are controlled by the stabilities of the thiyl radicals in reactants. This may be supported by the electrophilic character of the thiyl radicals;[21] the case that polar effect in transition state is insignificant should be rather expected for the vinyl monomer having the electron-poor double bond (positive e value). MMA ($e = +0.4$) may correspond to this case.

As can be seen from Table III, the $S(k_1)$ value for St is larger than that for MMA.[22] In Figure 3, plots of $\log k_{-1}/k_2$ seem to afford $\rho^+(k_{-1,\mathrm{St}}) \fallingdotseq 0$; $S(k_{-1}) \fallingdotseq 0$. One of possible explanations is that this difference could be attributed to the different positions of the transition state; α changes to ca. 1 from ca. 0.75. However, this may not be accepted since rate constants for St do not differ significantly from those for MMA. It is more likely that $S(k_1) \fallingdotseq 1$ (and $S(k_{-1}) \fallingdotseq 0$) may suggest some interactions in the transition state. For St having an electron-rich double bond ($e = -0.8$), polar resonance interaction of the type of $[(p\text{-XC}_6\text{H}_4\text{S})^-, (\text{CH}_2{=}\text{CHY})^{+\cdot}]$ can be expected when X is electron withdrawing; consequently, $S(k_1)$ may increase and $S(k_{-1})$ may decrease. If a smaller value rather than 0.75 was attributable to α, even for MMA there may exist the same kind of interaction in the transition state and this effect for St may increase, or vice versa.

Conclusions

For the reactions between para-substituted benzenethiyl radicals and vinyl monomers such as MMA and St, the rate constants for forward and backward reactions were determined. The logarithm of the equilibrium constant is a measure of the thermodynamic stability of the thiyl radical; stability increases in the order: $\text{-Cl} < \text{-H} < \text{-CH}_3 < \text{-OCH}_3$. For an electron-poor monomer (MMA) and electron-rich monomer (St), we attempted to assess the relative importance of stabilities of the radicals and of the possible contribution of polar structures to the transition state.

Experimental Section

Disulfides excepting the p-methoxy derivative were purified by recrystallizing the commercial reagents. Di(p-methoxybenzene) disulfide,[23] di(p-nitrobenzene) sulfide,[24] and p-nitrobenzenethiol[25] were prepared by the method described in literatures. MMA and St were distilled under reduced pressure before use. Cyclohexane and benzene used as solvents were spectrophotometric grade. Concentration of oxygen was calculated by Henry's law by using the data cited in the text.[26] All experiments were performed at the room temperature controlled at 23 ± 1 °C. Flash photolysis apparatus was standard design as described elsewhere.[1] The apparent first-order rate constants less than $5 \times 10^4\ \mathrm{s}^{-1}$ can be estimated.

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