Evaluation of Addition Rates of *p*-Chlorobenzenethiyl Radical to Vinyl Monomers by Means of Flash Photolysis

Osamu Ito and Minoru Matsuda*

Contribution from the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira-2, Sendai 980, Japan. Received July 13, 1978

Abstract: By flash photolysis of di(*p*-chlorobenzene) disulfide (RSSR) in cyclohexane at room temperature, the *p*-chlorobenzenethiyl radical (RS·) was generated. Enhancement of the decay rate of RS· was observed by the addition of vinyl monomer (CH$_2$=CHY) only when oxygen was added. This indicates that the reaction proceeds by a mechanism involving an equilibrium: RS· + CH$_2$=CHY (k_1) $\rightleftharpoons$ (k_{-1}) RSCH$_2$ĊHY (k_2, O$_2$) $\rightarrow$. Low reactivity of RS· toward oxygen was confirmed and high reactivity of oxygen toward the carbon-centered radical is well known. The radical species, RSCH$_2$ĊHY, was characterized by the flash photolysis of the degassed system containing both benzenethiol and 1,1-diphenylethylene. A transient band at 335 nm was attributed to PhSCH$_2$Ċ(Ph)$_2$. In the presence of oxygen, the decay rate of RS· increased linearly with increasing vinyl monomer concentration and was also affected by added oxygen concentration. Extrapolation to infinite oxygen concentration gives the absolute addition rate constant (k_1) and the ratio k_{-1}/k_2. The relative rate constants for various monomers calculated from our observed absolute rate constants agree with reported values obtained using the spin trapping method. A plot of log k_1 vs. log K ($K = k_1/k_{-1}$), in which k_{-1} was estimated by assuming $k_2 = 10^9$ M^{-1} s^{-1}, gives a linear relationship. The results suggest that increasing stability of RSCH$_2$ĊHY radical decreases the activation energy for the addition reaction.

A flash photolysis method with kinetic spectroscopy has been used to detect photochemically formed intermediates such as molecules in the triplet state, ion radicals, and free radicals. For the free-radical study, however, application of this method has been limited mainly to identification of free radicals responsible for the transient absorption band and determination of the recombination rate.[1,2] Recently, flash photolysis was applied to the determination of absolute rate constants for the addition reaction of the diarylcarbenes to vinyl monomers.[3] Enhanced decay resulting from addition of monomer has also been observed with the triplet anthracene and interpreted by formation of exciplexes.[4] A laser photolysis method has been applied to photoinduced ionic polymerization.[5] However, application of flash photolysis for the study of the addition reaction of free radical to vinyl monomers has not been reported.

In this paper we will report on the addition reaction of thiyl free radical to vinyl monomers by means of flash photolysis with kinetic absorption spectroscopy, whose reaction has already been pointed out to be reversible.[6] Addition of oxygen, however, could shift an equilibrium to the addition side. It may be interesting to compare our absolute rate constants with those obtained by other methods and to clarify the factors controlling the reactivity of the thiyl free radical toward vinyl monomer.

Results and Discussion

In general, a problem first encountered in the flash photolysis study is to identify the transient species responsible for the transient absorption band. In the case of *p*-chlorobenzenethiyl radical (RS·), however, the assignment was made without any ambiguity, since both disulfide and thiol gave the same absorption bands as shown in Figure 1. These spectra agree with the reported one.[7]

This radical decays with second-order kinetics in degassed solution as shown in the insert of Figure 1. This suggests that RS· decays exclusively with the recombination reaction. From the slope $2k_r/\epsilon$ (k_r is the rate constant for recombination and ϵ is the molar extinction coefficient) is given as $9.0 \pm 0.1 \times 10^5$ cm s^{-1}.

By addition of oxygen, decay of RS· was promoted but only slightly and decay rate can be represented by:

$$-d[\text{RS·}]/dt = k_0[\text{O}_2][\text{RS·}] + 2k_r[\text{RS·}]^2 \qquad (1)$$

where k_0 is the rate constant for the reaction between RS· and O$_2$. To estimate the first- and second-order rate constants separately from a mixed-order decay curve, the following equation is applicable:[8]

$$-d \ln A_0/dt = k_I + 2(k_{II}/\epsilon l)A_0 \qquad (2)$$

where A_0 is the absorbance due to RS· at initial time, k_I and k_{II} are the first- and second-order rate constants, respectively, and l is the optical pass length. A plot of the left term vs. A_0 measured at various RS· concentrations gave a straight line, as shown in Figure 2a. The slope ($2k_{II}/\epsilon$) was found to be 9 × 10^5 cm s^{-1}, which is in agreement with the value obtained directly from Figure 1, and the intercept gives $k_I = 1.0 \times 10^3$ s^{-1}, including $k_0[\text{O}_2]$, where [O$_2$] is 11.5 mM in oxygen-saturated cyclohexane,[9] which is in excess compared with the RS· concentration, since [RS·] is estimated to be about 10^{-6} M by assuming diffusion-controlled recombination reaction. Thus, k_0 is found to be 8.7 × 10^4 M^{-1} s^{-1} with the experimental error of ±20%. An inherent error in this method may arise mainly from estimating the left term in eq 2, which is evaluated by the tangential line in the plot of ln A_t (A_t is the absorbance of RS· at time t) vs. t.

Computer simulation may afford another method to estimate k_I from a mixed-order decay curve. In general, A_t can be represented as follows:

$$1/A_t = (1/A_0' + 2k_{II}/\epsilon l k_I)e^{k_I t} - 2k_{II}/\epsilon l k_I \qquad (3)$$

In eq 3, $k_{II}/\epsilon l$ can be estimated from the experiment without substrates and A_0' is the absorbance at $t = 0$, which is estimated from extrapolating the second-order plot at the time when flash light intensity reaches maximum. Thus, k_I can be found easily. Although this method also contains an error due to ambiguity for setting of A_0', we obtained $k_0 = 9.0 \times 10^4$ M^{-1} s^{-1} with an error of ±20%, which is in agreement with the value given by the graphic method.

In the study of cooxidation of thiols with olefins, Oswald and his co-workers have presented a reaction mechanism in which even in the presence of oxygen the arylthiyl radicals react at first with olefins.[10] This suggests the low reactivity of the benzenethiyl radical to oxygen. On the other hand, it is shown by the pulse radiolysis study that alkanethiyl radicals react very rapidly with oxygen ($k_0 \approx 8 \times 10^9$ M^{-1} s^{-1} in water).[11] It may be impossible to deny the reversibility of the reaction between the benzenethiyl radical and oxygen, which will give a small rate constant in the flash photolysis. We could not recognize
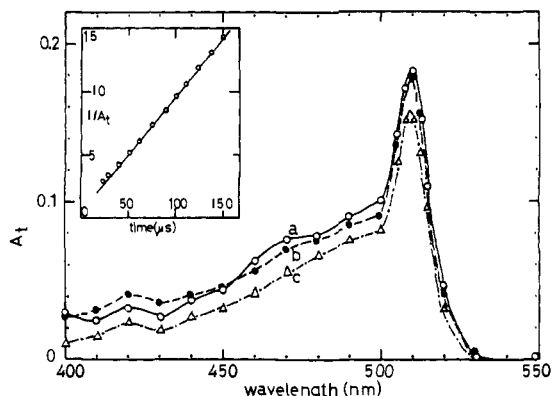
Figure 1. Transient absorption spectra due to p-chlorobenzenethiyl radical (RS·) in aerated cyclohexane: (a) flash photolysis of RSH (0.4 mM); (b) flash photolysis of RSSR (0.14 mM); (c) flash photolysis of RSSR in the presence of acrylonitrile (57 mM). A_t is the absorbance at 35 μs after triggering the flash lamp. Insert: Second-order plot of the decay curve at 510 nm in degassed solution.
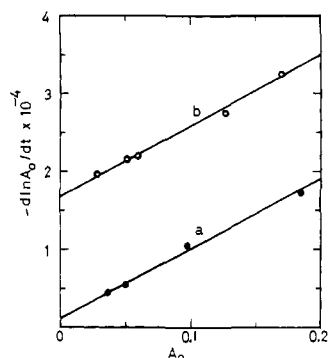

Figure 2. Plot of $-d \ln A_0/dt$ vs. A_0 for the decay at 510 nm of RS· in the system (a) containing saturated oxygen and (b) containing acrylonitrile (38 mM) and oxygen (2.3 mM).
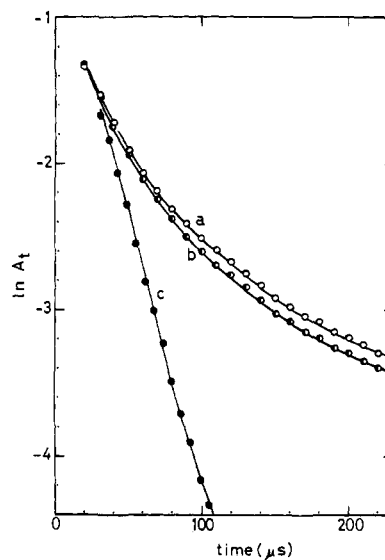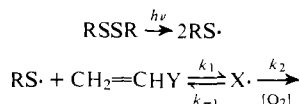

Figure 3. Plot of $\ln A_t$ at 510 nm of RS· vs. time: (a) decay in degassed cyclohexane in the absence of monomer; (b) decay in degassed solution in the presence of acrylonitrile (60 mM); and (c) decay in the oxygen-saturated solution in the presence of acrylonitrile (64 mM).
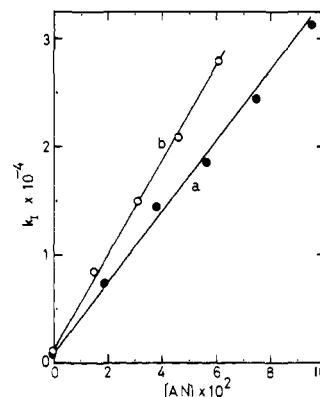

Figure 4. Plots of the first-order rate constants for the reaction of RS and acrylonitrile at various monomer concentrations: (a) in aerated solution and (b) in oxygen-saturated solution.

it, since the appropriate radical scavenger which is reactive only to RSO_2· cannot be identified. However, although the difference in reactivities between the alkanethiyl and benzenethiyl radicals to oxygen is significant (the ratio is about 10^5), it may be possible to attribute this mainly to the different reactivities of the two kinds of thiyl radicals.

In the absence of oxygen, the enhancement of the decay of RS· by the addition of monomer was very small, as shown in Figures 3a and 3b. On the other hand, enhanced decay was observed only when both monomer and oxygen were added (Figure 3c) and the first-order parts with respect to RS· (k_1 in eq 2 and 3) can be separated from the decay curves containing the first- and second-order decays by the methods mentioned above. A typical example for the graphic method is shown in Figure 2b. Thus, obtained k_1 values increase linearly with increasing monomer concentration, as shown in Figure 4. The slopes in Figure 4 increase with increasing concentrations of oxygen dissolved in the solution. These facts suggest a scheme for reaction including an equilibrium (Scheme I). The reversibility of the addition reaction of the thiyl radicals has been pointed out by many investigators using the product analysis method.[6] It is also clear that oxygen plays the role only of a scavenger of the intermediate radical (X·), which may be the carbon centered radical.[10] Thus, each slope in Figure 4 cannot be considered as a real addition rate constant.[12]

Scheme I

$$RSSR \xrightarrow{h\nu} 2RS\cdot$$

$$RS\cdot + CH_2{=}CHY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X\cdot \overset{k_2}{\underset{[O_2]}{\longrightarrow}}$$

Before further kinetic analysis, information about the properties of intermediate radical X· must be gathered. Since the shape of the transient absorption band due to RS· was not altered by the addition of monomer, as shown in Figure 1c, formation of a species such as charge-transfer complex I is not necessarily taken into consideration.

$$RS\cdot \longleftarrow \underset{CHY}{\overset{CH_2}{\|}}$$
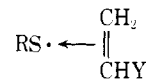
I

To clarify the structure of X·, we attempted to detect X· in the system without oxygen. By flash photolysis of a degassed solution containing both benzenethiol and 1,1-diphenylethylene, a new transient band was observed at 335 nm (Figure 5). This band resembles that of diphenylmethyl radical reported by Porter and Windsor,[13] and both the intensity and decay curve of the 335-nm band were not affected by the addition of triplet quenchers such as perylene and ferrocene. Thus, this transient band can be attributed to the radical having a diphenylmethyl moiety, $PhSCH_2\dot{C}(Ph)_2$, which may be formed by anti-Markownikoff addition.[14,15] From this fact it may be supposed that RS· may form a radical of this type, $RSCH_2CHY$, even with other monomers.
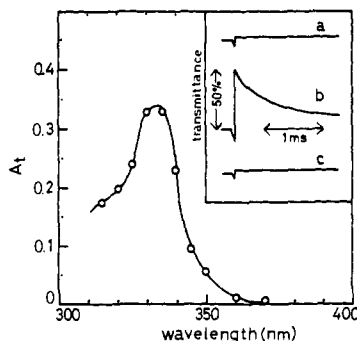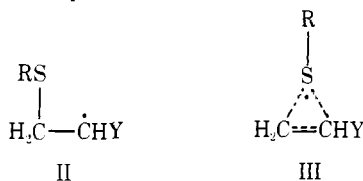
Figure 5. Transient absorption spectrum produced by the flash photolysis of the degassed cyclohexane solution containing benzenethiol (4.5 mM) and 1,1-diphenylethylene (3.1 mM). A_t is absorbance at 50 μs after triggering flash lamps. Insert: (a) decay curve at 335 nm of benzenethiol solution; (b) addition of 1,1-diphenylethylene to solution a; and (c) addition of oxygen to solution b.

Figure 6. Plot of k_{app} vs. $1/[O_2]$ (eq 6): (a) methyl methacrylate and (b) isobutyl vinyl ether.

Figure 7. First-order plots of p-chlorobenzenethiyl radical in cumene at 515 nm: (a) in mixed solvent (benzene and cyclohexane) having the same viscosity to cumene; (b) in aerated cumene; and (c) in oxygen-saturated cumene.

It is interesting to consider whether the interaction between the radical center on carbon of $RSCH_2\dot{C}HY$ and the sulfur atom exists or not. The observed absorption maximum at 335 nm coincides with that of diphenylmethyl radical within an experimental error of ± 2 nm. If the absorption band observed with the addition reaction is due to a structure involving symmetrically bridged radical III, a shift of the absorption maximum more than about 10 nm would be expected. Thus, it may be safely presumed that the structure of the radical rather resembles II, and even if there were interaction between the radical center on carbon and the sulfur atom, it may be less significant. The speculation agrees with the conclusion derived from the electron-spin resonance studies.[16,17]

RS
|
H_2C—$\dot{C}HY$

II

R
|
S
/`\
H_2C⋯$\dot{C}HY$

III

By addition of oxygen into the system, the carbon-centered radical, $RSCH_2\dot{C}HY$, disappeared as shown in the inserted oscilloscope trace (Figure 5c). This indicates that k_2 is so large that the carbon-centered radical decayed completely within flash duration, indicating $k_2[O_2] \gg 2 \times 10^5$ s^{-1}, where $[O_2]$ = 2 mM; it follows that $k_2 \gg 1 \times 10^8$ M^{-1} s^{-1}. This is a reasonable observation, since k_2 is known to be about 10^9 M^{-1}s^{-1} in the reaction of the carbon-centered radicals with oxygen.[18]

In Scheme I, the reaction between RS· and X· can be neglected experimentally, since the difference between Figure 3a and b was small. A slight increase in the decay of Figure 3b may be caused by this reaction, if each self-recombination reaction of RS· of X· was diffusion controlled. The decay of RS· can be written as:

$$-d[RS\cdot]/dt = 2k_r[RS\cdot]^2 + \{k_0[O_2] + k_1[M]\}[RS\cdot] - k_{-1}[X\cdot] \quad (4)$$

where [M] is added monomer concentration. The steady-state approximation with respect to X· can be applied for the following reasons: in the presence of oxygen, the dependence of [X·] on time seems to be negligibly small as shown in the inserted oscilloscope trace c in Figure 5 and [X·] is much smaller than in the absence of oxygen. The validity of the approximation is also supported from the fact that $k_2[O_2] \gg k_1[M]$, in which $k_2[O_2] \approx 2 \times 10^6$ s^{-1} in aerated solution from the literature[18] and $k_1[M] \ll 5 \times 10^4$ s^{-1} under our experimental conditions. The first-order part with respect to [RS·], abbre-
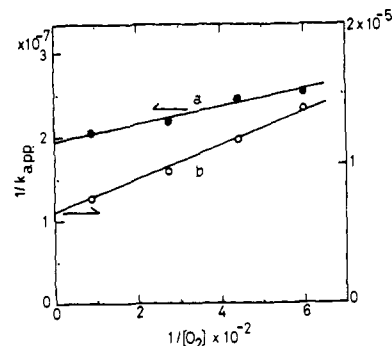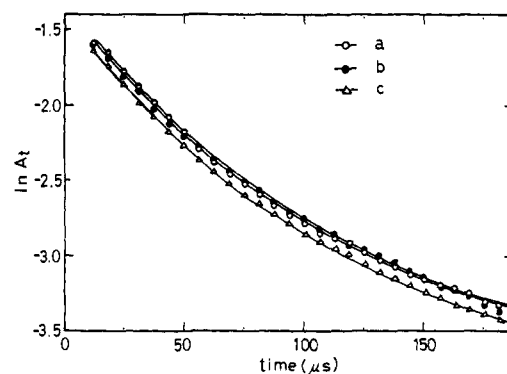
viated as k_1', is derived as eq 5:

$$k_1' = k_0[O_2] + k_1 \{1 - k_{-1}/(k_{-1} + k_2[O_2])\} [M] \quad (5)$$

Thus, it is now shown that the slopes in Figure 4 correspond to the second term in eq 5 and when this term is referred to k_{app}:

$$1/k_{app} = 1/k_1 + k_{-1}/k_1k_2[O_2] \quad (6)$$

Indeed, a plot of $1/k_{app}$ vs. $1/[O_2]$ gave a straight line as shown in Figure 6, which may also support the steady-state approximation. An actual k_1 is obtained from the intercept at $1/[O_2]$ = 0 and the ratio k_{-1}/k_1k_2 is obtained from the slope.[19] Assuming that all k_2's for carbon-centered radical formed from various monomers are 1×10^9 M^{-1}s^{-1},[18] k_{-1} can be estimated leading to the evaluation of equilibrium constant K (= k_1/k_{-1}). Estimated k_1 values are summarized in Table I, and k_{-1}/k_2 and K are in Table II.

In the case of the monomer containing hydrogen which is easily abstracted by the thiyl radical, it must be taken into consideration that k_1 contains not only the rate constant for addition but also for hydrogen abstraction. To estimate the hydrogen abstraction ability of RS·, cumene was chosen as hydrogen donor. The decay curve of RS· in cumene was very close to second order even in oxygen-containing solution and was similar to that in the mixed solution of cyclohexane and benzene, having the same viscosity as that of cumene as shown in Figure 7.[20] If the small difference in the plots of ln A_t vs. t is attributed to the abstraction reaction, the rate constant for the reaction with cumene is found to be less than 50 M^{-1}s^{-1}. The rate constant for the hydrogen abstraction of the alkanethiyl radical was reported to be about 10^6 M^{-1} s^{-1} at 70 °C by Pryor, Gojon, and Church.[21] Reactivity of the alkanethiyl radical is about 10^4 times larger than that of the p-

Table I. Rate Constants (k_1) for the Addition Reaction of p-Chlorobenzenethiyl Radical to Various Monomers

no.	monomer[a]	e	Q	k_1,[b] M^{-1} s^{-1}	rel k_1	[M],[d] mM
1	St	−0.8	1.0	5.1×10^7	1.0 (1.0)[c]	0.2–1.1
2	MMA	0.4	0.74	5.4×10^6	0.10 (0.083)[c]	2–10
3	MA	0.6	0.42	4.3×10^5	0.0078	20–110
4	MAN	0.81	1.12	2.3×10^6	0.045	3–12
5	AN	1.2	0.60	4.6×10^5	0.0090 (0.0064)[c]	15–100
6	IBVE	−1.77	0.023	1.8×10^5	0.0035	40–200
7	IPA	−0.5	0.045	3.5×10^4	0.0007	200–900
8	VAc	−0.22	0.026	4.6×10^4	0.0009 (0.000 36)[c]	200–1000

[a] St, styrene; MMA, methyl methacrylate; MA, methyl acrylate; MAN, methacrylonitrile; AN, acrylonitrile; IBVE, isobutyl vinyl ether; IPA, isopropenyl acetate; VAc, vinyl acetate. [b] Estimated errors are ±20%. [c] Relative values estimated by the spin trapping method.[23] [d] Monomer concentration range used in experiments and oxygen concentration was 1.4–12 mM.

**Table II.** Observed k_{-1}/k_2 and Estimated k_{-1} and K ($=k_1/k_{-1}$)

no.	monomer	k_{-1}/k_2,[a] M^{-1}	k_{-1},[b] s^{-1}	K,[b] M^{-1}
1	St	$<1 \times 10^{-4}$ [c]	$<1 \times 10^5$	>500
2	MMA	4.9×10^{-4}	4.9×10^5	11
3	MA	1.3×10^{-3}	1.3×10^6	0.34
4	MAN	3.0×10^{-4}	3.0×10^5	7.5
5	AN	1.0×10^{-5}	1.0×10^6	0.45
6	IBVE	2.3×10^{-3}	2.3×10^6	0.08
7	IPA	4.0×10^{-3}	4.0×10^6	0.009
8	VAc	6.3×10^{-3}	6.3×10^6	0.008

[a] Each value contains an estimated error of ±20%. [b] k_{-1} and K values are calculated by assuming $k_2 = 1 \times 10^9$ M^{-1} s^{-1}. [c] Dependence on oxygen concentration was very small in the range of [O_2] = 1.4–12 mM.

Figure 8. Correlation between log k_1 or log k_{-1} and log K. Monomers 1–8 refer to Table I.

Figure 9. Correlations between log k_1 and e values of monomers. Monomers 1–8 refer to Table I.

chlorobenzenethiyl radical. A similar fact is found in rate constants for both thiyl radicals to oxygen. Pryor et al. have determined the rate constant of hydrogen abstraction by comparison with that for the reaction between the alkanethiyl radical and trialkyl phosphite. The latter rate constant was reported to be 2.5×10^8 M^{-1} s^{-1} at 80 °C by Walling and Pearson.[22] In our flash photolysis experiment, the rate constant for the reaction between the p-chlorobenzenethiyl radical and trimethyl phosphite was estimated to be about 2×10^3 M^{-1} s^{-1} at 23 °C. The ratio between the alkanethiyl and arylthiyl radicals is again as large as about 10^5. It may not be unreasonable that these differences should be attributed to rather low reactivity of the arylthiyl radical regarding the hydrogen abstraction and addition to oxygen or to trialkyl phosphite.

In the case of *tert*-butoxyl radical, it is reported that the hydrogen donor ability of the methyl group located at the α position of the vinyl monomers is similar to that of benzylic hydrogen in cumene.[23] Assuming that it also holds for the thiyl radicals, the rate constant for hydrogen abstraction from monomers is not included in k_1 values estimated by this study, since the decay curves of RS· were not affected by the addition of cumene (Figure 7). Even for the nonconjugated monomers, whose k_1 values are smaller, contamination by hydrogen abstraction may be neglected, because the hydrogen which is easily abstracted is not included in these monomers.

In Table I, ratios among addition rate constants for p-chlorobenzenethiyl radical to vinyl monomers are compared with the relative values for the benzenethiyl radical estimated by the spin trapping method.[23] The latter method gives slightly smaller relative values than the corresponding value obtained by our flash photolysis method. Taking into account the difference of the thiyl radicals and the experimental errors included in both methods, it may be considered that the agreement is fairly good. Using the rotating sector method, Sivertz reported the absolute addition rate constants of the n-butylthiyl radical to be 8×10^8 M^{-1} s^{-1} for styrene and 7×10^6 M^{-1} s^{-1} for 1-pentene.[24,25] Although the value for styrene by the rotating sector method is one order larger than our value, the
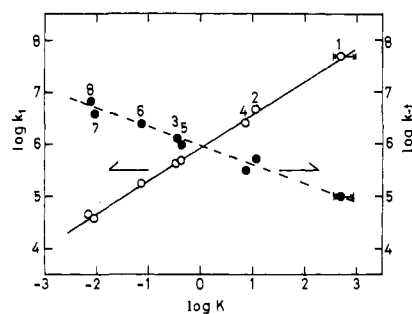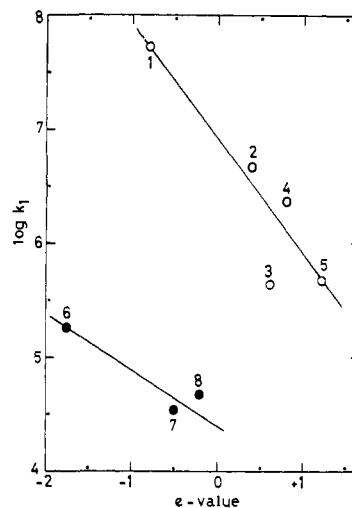
difference may again be attributed mainly to the difference between the reactivities of alkanethiyl and arylthiyl radicals. The value for 1-pentene is 10^2–10^3 larger than our value for nonconjugated monomer. This may also be attributed to the different reactivity of the two thiyl radicals for nonconjugated monomers. The difference of the reactivities between alkanethiyl and arylthiyl radicals to vinyl monomers is smaller than those of reactivities to hydrogen donor, oxygen, and trialkyl phosphate.

Log K is a measure of the stability of the radical $RSCH_2\dot{C}HY$ and log k_1 or log k_{-1} may be proportional to the corresponding activation energy. Plots of log k_1 or log k_{-1} vs. log K each gave fairly good linear relationships with the opposite slope, as shown in Figure 8. This indicates that an increase in the stability of the radical $RSCH_2\dot{C}HY$ causes a decrease in the activation energy of the forward reaction and an increase in k_1. On the other hand, the increase in the activation energy in the reverse reaction, that is, a decrease in k_{-1}

is caused by the increase in stability of $RSCH_2CHY$. Furthermore, these linear relationships suggest that an interaction between the radical and monomer in the transition state giving stabilization due to charge-transfer interaction seems to be insignificant, coinciding with our preceding discussion concerning the structure of the intermediate radical. These results are a good example of qualitative verification for Evans and Polanyi's law.[26] According to Bagdasariyan's considerations, the decrease in the activation energy is caused by the increase in the conjugation of the $RSCH_2\dot{C}HY$ by the substituent Y.[27] As shown in Tables I and II, the difference in k_1 values between the conjugated and nonconjugated monomer having the same e value is quite significant (its ratio is about 10^3), and a similar difference is also seen in the equilibrium constants. Thus, it is shown that as a factor governing the stability of $RSCH_2\dot{C}HY$, the resonance factor of the corresponding monomer may be important.

As proposed by Alfrey and Price, the addition rate is controlled not only by the resonance effect but also by a polar effect.[28] A plot of log k_1 of various monomers vs. their e values is shown in Figure 9. The conjugated and nonconjugated monomers are correlated on the two distinguishable straight lines. This shows that the rate constants are determined not only by a resonance factor but also by a polar factor. As is expected from Figure 8, similar relationships are seen in the plot of log K vs. e values. Thus, the stability of $RSCH_2\dot{C}HY$ is also affected by both effects. Negative slopes in Figure 9 indicate the electrophilic character of the *p*-chlorobenzenethiyl radical, which is in agreement with the other thiyl radicals such as alkanethiyl,[6,29] benzenethiyl,[30] and benzoylthiyl radicals.[23]

Conclusions

Absolute rate constants for the addition of *p*-chlorobenzenethiyl radical to various vinyl monomers were determined by means of the flash photolysis method. Equilibrium constants of the reversible addition reaction were also estimated. By comparison of both values, it is confirmed that the addition rate is mainly governed by the stability of the formed radical $RSCH_2\dot{C}HY$. An increase in stability is reflected by the increase in rate and is affected by both resonance and polar effects.

Experimental Section

p-Chlorobenzenethiol and disulfide were purified by recrystallization. Benzenethiol and all vinyl monomers used were purified by distillation under reduced pressure. Ferrocene and perylene, which were used as triplet quenchers, were purified by recrystallization and sublimation. Cyclohexane and hexane used as solvent were spectrophotometric grade.

The flash photolysis apparatus was standard design as described elsewhere.[15] The xenon flash lamp reaches to peak at 10 μs after triggering and decays with a half-life of 9 μs, which permitted the observation of an apparent first-order rate constant less than about 5×10^4 s^{-1}. To avoid the excitation of monomers, flash light of 310–400 nm was exposed to the solution in a cylindrical cell (diameter of 8 mm and length of 100 mm) using band-path and cut-off filters.

Degassed solutions were made by degassing up to 10^{-5} Torr. The solutions containing a definite amount of oxygen were made by the absorption of oxygen and the concentration was calculated by Henry's law. All experiments were performed at room temperature controlled at 23 ± 1 °C.

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