Substituent Effect on the Rate Constants for the Reactions between Benzenethiyl Radicals and Stable Free Radicals Estimated by Flash Photolysis

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Abstract: Absolute rate constants for the reactions between para-substituted benzenethiyl radicals and stable free radicals such as di-*tert*-butyl nitroxide (DBNO·) and galvinoxyl (G·) were determined by means of xenon- and laser-flash photolysis. The rate constants were in the range of 3.3×10^8 to 1.6×10^9 M^{-1} s^{-1}. For both the stable free radicals, the rate constants were correlated with Hammett substituent constant σ^+ yielding positive ρ^+ values; $\rho^+(\text{DBNO}\cdot) = +0.75 \pm 0.02$ and $\rho^+(\text{G}\cdot) = +0.25 \pm 0.05$. The observed ρ^+ for G· most likely implies that the reactivities are determined mainly by the thermodynamic stabilities of the substituted benzenethiyl radicals. The ρ^+ for DBNO·, which is considerably larger than the ρ^+ for G·, may be explained by the contribution of the polar resonance structures to the transition state.

Rate constants for radical–radical reactions in solution have been measured by direct methods such as rotating sector, kinetic ESR, and kinetic absorption spectroscopy.[1] For the bimolecular self-reactions, flash photolysis with kinetic absorption spectroscopy can be applied only when molar extinction coefficients (ϵ) of the radicals are known. Since, in general, it is very difficult to estimate the exact values of ϵ of the free radicals, this method is applied to a few limited reactions.[1,2]

On the other hand, for the reaction between two different free radicals it may be expected that the rate constant can be measured by flash photolysis without use of ϵ when the following conditions are satisfied. One is the stable free radical and the other is the unstable radical produced by the flash photolysis. It is necessary that the absorption band of the unstable radical does not overlap with the absorption bands of the stable free radical. From these reasons, we selected the reactions between the para-substituted benzenethiyl radicals and di-*tert*-butyl nitroxide (DBNO·) or galvinoxyl (G·). In addition to the above reasons, these systems were selected since there is as yet little information about the sulfur-centered radicals. From the rate constants obtained in this study, we discussed whether the polar effect in the transition state is operating or not for these radical reactions.

Results and Discussion

The absorption spectra of para-substituted benzenethiyl radicals, except for the *p*-methoxy derivative, have been reported.[3-5] By the xenon-flash photolysis of *p*-methoxybenzenethiol, a transient absorption band appeared at 515 nm in cyclohexane, which is the same absorption band as that produced from the disulfide as shown in Figure 1. Thus, this absorption band was attributed to the *p*-methoxybenzenethiyl radical produced from the following reactions:

$$\text{RSH} \xrightarrow{h\nu} \text{RS}\cdot + \text{H}\cdot \tag{1}$$

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

where RS· refers to the thiyl radical.

This transient band disappeared with second-order kinetics as depicted in the insert in Figure 1. This indicates that the thiyl radical disappeared with the recombination predominantly (in reaction 3, k_r is the rate constant for the recombination reaction):

$$2\text{RS}\cdot \xrightarrow{k_r} \text{RSSR} \tag{3}$$

From the slope, $2k_r/\epsilon_{515\text{nm}} = 4.5 \times 10^5$ cm s^{-1} in cyclohexane was obtained. Since ϵ's of the para-substituted benzenethiyl radicals were not estimated by a conventional manner,[6] k_r could not be evaluated. However, we found the following fact: dependence of $2k_r/\epsilon_{\max}$ for *p*-chloro- and *p*-methylbenzenethiyl radicals on the reciprocal of solvent viscosity is higher than that for *p*-methoxybenzenethiyl radical, as shown in Figure 2. Assuming that there is no significant difference in their ϵ's at absorption maxima, the plots indicate that k_r's of the former two thiyl radicals are close to the diffusion-controlled rate constant and that k_r of the latter is considerably small.[7] The small k_r of *p*-methoxybenzenethiyl radical may be explained by the large repulsion between approaching sulfur atoms having relatively negative charge, which is caused by the strong electron-donating character of the methoxy group. In addition to this explanation, a slow recombination reaction may be realized when the thiyl radical is thermodynamically stable and the formed disulfide is unstable. In the case of the *p*-methoxy derivative, the above three effects may be cooperating.

When the stable free radical was added, decay of the transient absorption band of the thiyl radical was accelerated. In the case of xenon-flash photolysis, when the added stable free radical was in excess, the decay curve was deformed by the emission of the xenon-flash lamp. The pseudo-first-order rate constants less than 5×10^4 s^{-1} were measured accurately by our flash lamp. Low concentration of the stable free radical also may interfere with the analysis of pseudo-first-order kinetics because of mixing with second-order kinetics.

On the other hand, although the laser-flash photolysis method may afford first-order rate constants less than 10^7 s^{-1}, this method could yield the thiyl radical only from di(*p*-chlorobenzene) disulfide. The absorptions of the other disulfides at the wavelength of laser light (347.1 mm) are not strong enough for efficient S–S bond dissociation. Without any additives, the transient absorption band of the *p*-chlorobenzene thiyl radical produced by laser-flash photolysis decayed with second-order kinetics. By addition of a large excess of DBNO· (more than ca. ten times the initial concentration of the thiyl radical), the decay rate of the thiyl radical was promoted and decay kinetics approached first order as shown in Figure 3 and the insert. From the observed pseudo-first-order rate constant (k_1), the rate constant for the reaction between the thiyl radical and DBNO· (k_s in reaction 4) was estimated without any disturbance of the emission of flash light and of second-order kinetics. From $k_s = k_1/[\text{DBNO}\cdot]$, $k_s = 1.6 \times 10^9$ M^{-1} s^{-1} was obtained within an experimental error of ±20%.

$$\text{RS}\cdot + \text{Y}\cdot \xrightarrow{k_s} \text{RSY (Y}\cdot\text{: stable radical)} \tag{4}$$

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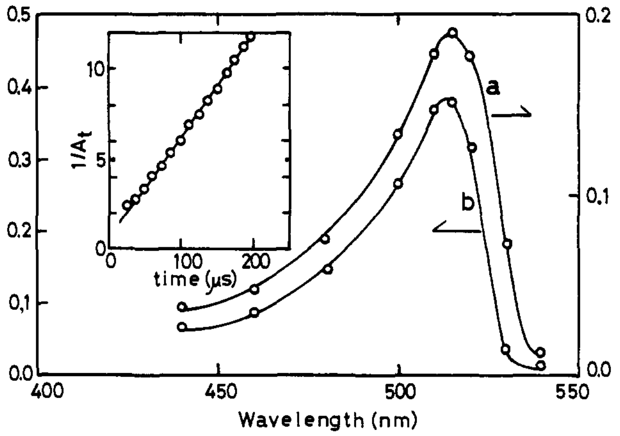


Figure 1. Transient absorption spectra observed immediately after xenon-flash photolysis: (a) *p*-methoxybenzenethiol (2.0 mM); (b) di(*p*-methoxybenzene) disulfide (0.13 mM) in cyclohexane. Insert: the second-order plot for the decay at 515 nm of the transient absorption band produced from the disulfide in a cylindrical optical cell (10 cm long).

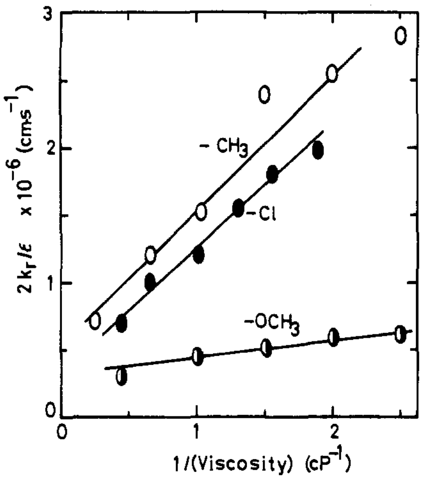


Figure 2. Dependence of the ratio of recombination rate constants (k_r) to ϵ's of p-$XC_6H_5S\cdot$ upon viscosities of solvents at 23 ± 1 °C. The second-order decay kinetics were analyzed at the absorption maxima: X = $-CH_3$, 505 nm; X = -Cl, 510 nm; X = $-OCH_3$, 515 nm. Solvents were liquid paraffin, cyclohexane, hexane, and their mixtures.

For the other derivatives, the rate constants must be evaluated from the xenon-flash photolysis. By addition of an appropriate amount of the stable free radical, the thiyl radical decayed with mixed-order kinetics containing first and second order. The former corresponds to reaction 4 and the latter to reaction 3. The rate of such decay may be expressed as

$$-d[RS\cdot]/dt = k_s[Y\cdot][RS\cdot] + 2k_r[RS\cdot]^2 \quad (5)$$

The mixed-order kinetics have been analyzed by the graphic method[8] and computer simulation.[9] Both of them need the initial concentration of the thiyl radical ($[RS\cdot]_0$) or initial absorbance (A_0), which contains uncertainty because of the emission of the flash lamp. Thus, we had to attempt to remove $[RS\cdot]_0$ or A_0 from the analysis.

Assuming that $[Y\cdot]$ in eq 5 is constant during the reaction and is equal to the feeded quantity ($[Y\cdot]_0$), eq 5 can be converted into eq 6 by integration:[9]

$$1/A_t = \{1/A_0 + 2k_r/(\epsilon l k_s[Y\cdot]_0)\}e^{k_s[Y\cdot]_0 t} - 2k_r/(\epsilon l k_s[Y\cdot]_0) \quad (6)$$

where $[RS\cdot]_t$ was substituted for absorbance A_t and l denotes the length of the optical cell. From differenciation of eq 6 by time at an appropriate absorbance A^*, eq 7 can be derived:

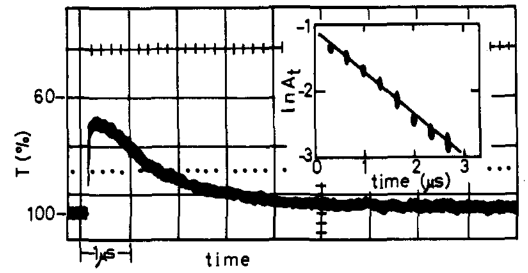


Figure 3. Decay curve of the transient absorption band at 510 nm produced by the laser-flash photolysis of di(*p*-chlorobenzene) disulfide in the presence of DBNO· (4.2×10^{-4} M) in cyclohexane. Insert: the first-order plot of the decay.

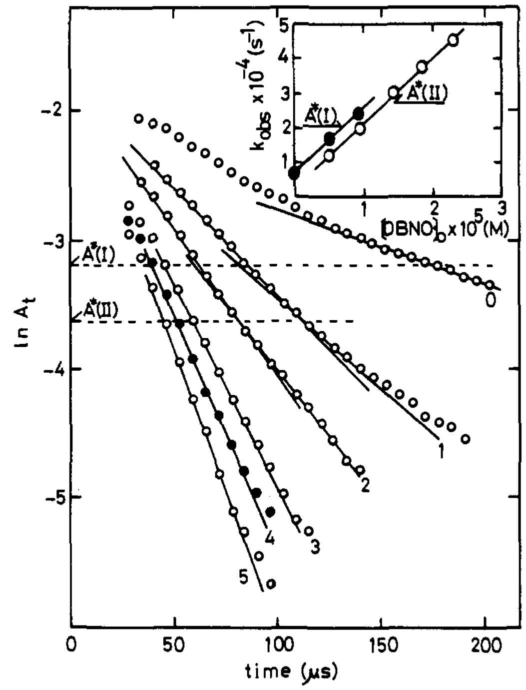


Figure 4. The first-order plots for the decay curves of the *p*-chlorobenzenethiyl radical at 510 nm in the presence of DBNO·. $[DBNO\cdot]_0$: 0, 0 M; 1, 4.6×10^{-6} M; 2, 9.3×10^{-6} M; 3, 1.4×10^{-5} M; 4, 1.9×10^{-5} M; 5, 2.3×10^{-5} M. Insert: plot of the left term of eq 7 vs. $[DBNO\cdot]_0$.

$$[d \ln A_t/dt]_{A^*} = -\{k_s[Y\cdot]_0 + (2k_r/\epsilon l)A^*\} \quad (7)$$

The left term is obtained from the tangential line at the appropriate absorbance in the first-order plot. The slope in the plot of these values against $[Y\cdot]_0$ yields k_s. An example is shown in Figure 4 for the reaction system of *p*-chlorobenzenethiyl radical and DBNO·, from which k_s can be estimated to be 1.6×10^9 M^{-1} s^{-1} within experimental error of ±20%. This value is in good agreement with the value obtained from the laser-flash photolysis. This suggests that this method also give considerably accurate rate constants.

In such a rapid reaction, assumption of $[Y\cdot]_t = [Y\cdot]_0$ must be examined; $[Y\cdot]_0$ should be in excess compared to $[RS\cdot]_0$. For this purpose, G· was more appropriate than DBNO· since the absorption peak at 428 nm of G· does not overlap with the absorption bands of the disulfides. At 428 nm a small change in [G·] can be measured by spectrophotometry using reported ϵ.[10] By flash photolysis of the system containing [G·] = 4.32×10^{-5} M and [di(*p*-chlorobenzene) disulfide]$_0$ = 4.13×10^{-4} M, the difference in [G·] between before-flash and after-dark reactions can be estimated to be 1.14×10^{-6} M.[11] In this system, since RS· decayed predominantly with first-order kinetices, $[G\cdot]_0 - [G\cdot]_{t=\infty}$ ($=\Delta[G\cdot]$) may be equal to $[RS\cdot]_0$. The observed value of 0.03 for $\Delta[G\cdot]/[G\cdot]_0$ may suggest that

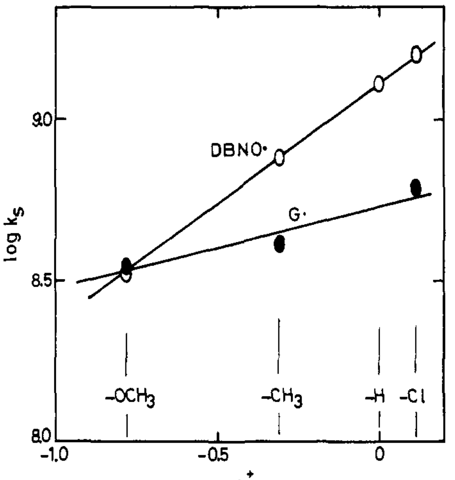


Figure 5. Plots of log k_s for the reactions between para-substituted benzenethiyl radicals and DBNO· or G· vs. Hammett substituent constants σ^+: (○) for DBNO·; (●) for G·.

$[G\cdot]_t$ is practically constant during the reactions.[12] In other systems, the initial concentrations of the thiyl radicals may be similar to the above system, and $[Y\cdot]_0$ ranging from 10^{-5} to 10^{-4} M may be sufficient for the assumption.

The rate constants for the reactions between the para-substituted benzenethiyl radicals and DBNO· or G· measured by xenon-flash photolysis are listed in Table I. The rate constant for the system of the benzenethiyl radical-G· could not be measured since the absorption bands of both species are superimposed on each other. The largest value (DBNO· for the *p*-chloro derivative) may be still slightly less than the calculated (or empirically estimated) diffusion-controlled rate constant in cyclohexane.[1,13] Our values for the thiyl radicals are larger than the reported values for the reactions between the unstable carbon-centered radicals and stable free radicals: k(polystyryl radical + DBNO·) = 1×10^7 M^{-1} s^{-1},[14] k(CH$_2$OH + triacetoneamine-*N*-oxyl) = 7.2×10^8 M^{-1} s^{-1},[15] and $k(CH_3\cdot + G\cdot) = 2 \times 10^7$ M^{-1} s^{-1}.[16]

As can be seen from Table I, it is apparent that electron-donating substituents tend to decrease the rate constants. These rate constants were correlated to Hammett substituent constants σ^+ as depicted in Figure 5.[17] The slopes yield ρ^+; $\rho^+(DBNO\cdot) = +0.75 \pm 0.02$ and $\rho^+(G\cdot) = +0.25 \pm 0.05$. In general, the polar effect observed in radical reactions such as hydrogen abstraction and addition to olefins has been explained by the contribution of the polar resonance structures to the transition state. If a similar effect is operating for the radical-radical reactions, polar resonance structures such as type I (RS$^+$, Y$^-$) and type II (RS$^-$, Y$^+$) can be written. In the case of type I, introduction of electron-donating substituents into the thiyl radicals may increase the contribution of the charge transfer from the thiyl radical to the stable free radical and may increase the rate constants; consequently, a negative ρ or ρ^+ may be realized. If there is interaction of type II in the transition state, a positive ρ or ρ^+ may be realized.

Table I. Rate Constants (k_s) for the Reactions between the Para-Substituted Benzenethiyl Radicals (*p*-XC$_6$H$_5$S·) and DBNO· or G· in Cyclohexane at 23 °C

X	k_s(DBNO·), M^{-1} s^{-1}	k_s(G·), M^{-1} s^{-1}
-Cl[a]	1.6×10^9	6.2×10^8
-H[b]	1.3×10^9	
-CH$_3$[a]	7.5×10^8	4.1×10^8
-OCH$_3$[a]	3.3×10^8	3.5×10^8

[a] Experimental error of ±20%. [b] Experimental error of ±30%.

Recently, it has been proposed that the thermodynamic stabilities of the radicals are playing an important role in the observed polar effect.[18] Mahoney and DaRooge reported that the stabilities of the substituted phenoxy radicals are controlling the reactivities of the hydrogen abstraction.[19] From their data the tendency that the electron-donating substituents stabilize the phenoxy radicals is clearly shown. Colle and Lewis have reported the activation energies for the hydrogen-abstraction reactions by the carbon-centered radical from the substituted benzenethiols.[20] From the observed activation energies, an increasing order of thermodynamic stabilities of substituted benzenethiyl radicals can be estimated as follows: *p*-Cl < H < *p*-OCH$_3$. From these results it may be suggested that the thermodynamic stabilities of the para-substituted benzyl-type radicals (*p*-XC$_6$H$_4$Z·) such as phenoxy and benzenethiyl radicals are also correlated with σ or σ^+. In the addition reaction of the thiyl radicals to vinyl monomers, we reported that para-substituted benzenethiyl radicals having electron-donating substituents are more stable than those having electron-withdrawing ones and that these stabilities are correlated to σ^+ yielding $\rho^+ = +1.35$.[21] In this case, even though there is no polar effect in the transition state, positive ρ^+ (reactivity) can be predicted by the linear free energy relationship as represented in eq 8 (Figures 6a, b):

$$\rho^+ \text{ (reactivity)} = \alpha\rho^+ \text{ (stability)} \quad (0 < \alpha < 1) \tag{8}$$

For the reaction between G· and RS·,[22] it can be presumed that the C-S bond is formed by attack of RS· on the aromatic

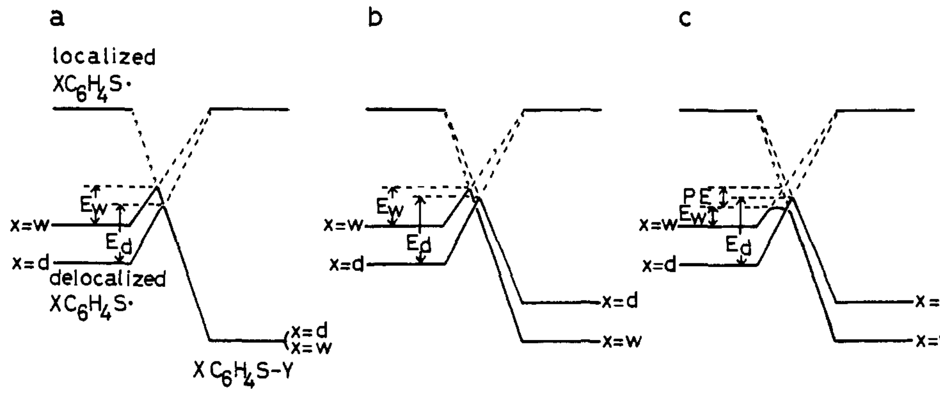
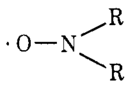


Figure 6. Schematic representations of the potential energies for the reactions between the radicals. Case (a): potential energies at the products are not changed by the para substituents in the benzenethiyl moieties, and the polar effect is nonexistent in the transition state. Case (b): potential energies at the products are changed by para substituents in the benzenethiyl moieties without a polar effect in the transition state. Case (c): a polar effect exists in the transition state in addition to case (b). **w** and **d** refer to the electron-withdrawing and electron-donating substituents, respectively. E_w and E_d are respective activation energies, and PE is the stabilization energy caused by a polar effect in the transition state.

ring of G· in a similar manner to attack of the carbon-centered radical.[10] For this case, the potential energy of the product may be practically constant because the strength of the C-S bond can be considered to be invariant irrespective of the kind of para substituents in the benzenethiyl moiety. For the radical reactions, α values in eq 8 were estimated empirically by Semenov; $\alpha \approx 0.25$ for exothermic radical reactions and $\alpha \approx 0.75$ for endothermic radical reactions.[23] Since it is presumed that the radical-radical reactions producing molecules are exothermic, α for the reaction systems of the thiyl radicals-stable radicals may be ca. 0.25. Assuming that ρ^+ (stability) for the substituted benzenethiyl radicals is 1.35,[21] ρ^+ (reactivity)/ρ^+ (stability) can be calculated to be ca. 0.20 for the reaction system of thiyl radical-G·. This value may be nearly equal to α. Thus, it is suggested that the reactivities of the systems of the thiyl radicals-G· are mainly controlled by the stabilities of the thiyl radicals.

If RS· reacts with the oxygen atom in G·, the strength of the S-O bond may be sensitive to X in p-XC_6H_4SG because of repulsion between lone-pair electrons on S and O atoms. The potential energy diagrams must be written so as to represent that the products are destabilized by the electron-donating substituents (Figure 6b). Taking into consideration the instability effect in the products, we can predict that the value of ρ^+ is slightly larger than that of case (a); from the geometric consideration the calculated ρ^+ for case (b) is only ca. 10% larger than that of case (a), even though the energy difference in the products was set equal to that in the reactants. Thus, the observed ρ^+(G·) may suggest that the reactivities are determined mainly by the energy differences between the reactants and products; reactivities can be explained without the interaction in the transition state.

For the reaction between DBNO· and RS·, if the S-O bond is formed,[22,24] the potential energy diagram is represented by case (b). The calculated ratio of ρ^+(case b)/ρ^+(case a) is not large enough to explain the fact that the observed ρ^+(DBNO·) was three times larger than ρ^+(G·) as described above. Thus, to explain the observed ρ^+(DBNO·), it may be reasonable to introduce the idea that there is a contribution of polar resonance structures to the transition state (Figure 6c). It is well known that the electron distribution of DBNO· is represented by the two resonance structures **1** and **2**.[25] When the thiyl radical having an electron-withdrawing substituent approaches **2**, electron transfer from DBNO· to the thiyl radical may easily occur. Thus, the rate is increased by an electron-withdrawing substituent; consequently ρ^+ may increase.



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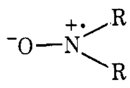

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If RS· attacks the nitrogen atom in DBNO· having a relatively positive charge, a negative ρ (or ρ^+) may be predicted. From the observed positive ρ^+(DBNO·) this possibility can be eliminated.

Conclusions

The rates of the reactions between para-substituted benzenethiyl radicals and stable free radicals such as DBNO· and G· were determined. The reactivities of the thiyl radicals are slightly higher than those reported for the unstable carbon-centered radicals. From the Hammett-equation correlations, the observed ρ^+ for G· (=+0.25) may suggest that the reactivities for G· are controlled mainly by the stabilities of the thiyl radicals. For DBNO·, the large positive ρ^+ (=+0.75) may suggest that the reactivities are controlled not only by the stabilities of the thiyl radicals but also by the participation of polar resonance structures in the transition state.

Experimental Section

p-Methoxybenzenethiol and its disulfide were prepared by the method described in the literature.[26] Other disulfides were purified by recrystallizing the commercial reagents. Di-*tert*-butyl nitroxide was prepared by the method described in the literature.[27] Galvinoxyl was commercial grade and its concentration was determined with spectrophotometry using the reported ϵ.[10] The xenon- and laser-flash photolysis apparatus was of standard design.[28] The half-duration of the xenon-flash lamp was ca. 10 μs, which permitted the observation of first-order rate constants less than $5 \times 10^4\ s^{-1}$. For the laser-flash experiment the second-harmonic light (347.1 nm) of the ruby laser was used as the excitation flash. The irradiation vessel was a cylindrical quartz cell (10 cm long and 1 cm diameter). Experiments were performed at room temperature (controlled at 23 ± 1 °C).

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(6) In ref 12 we attempted to estimate ϵ of the thiyl radical qualitatively.
(7) Assuming the diffusion-controlled reaction for p-chloro- and p-methylbenzenethiyl radicals, rate constants can be calculated from the Debye equation, $8RT/3000\eta$ (η = solvent viscosity).[1] From the calculated rate constants and observed k_r/ϵ, it is possible to evaluate each ϵ for both the radicals. In Figure 2, however, extrapolated lines to $1/\eta \rightarrow 0$ do not pass through the origin. This means that each ϵ obtained by this method depended upon the solvent viscosity, though, in general, ϵ does not. Thus, we could not adopt this method for the estimation of ϵ.
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(11) This was calculated on the assumption that the absorption bands due to the reaction products (RSG) do not overlap with the 428-nm band of G·.
(12) Assuming that A_0 (initial absorbance) is the extrapolated value to the time at which the intensity of the flash light reaches a maximum, $\epsilon_{510nm}(p\text{-}ClC_6H_5S\cdot)$ can be estimated to be 8000–9000 $M^{-1}\ cm^{-1}$ using the equation $\Delta[G\cdot] = [RS\cdot]_0\ (\equiv A_0)$. We found another method to calculate ϵ. Assuming that RS· formed by a flash exposure of RSH gives RSSR predominantly, $[RS\cdot]_0$ can be set equal to $[RSSR]/2$. Thus, $\epsilon_{510nm}(p\text{-}ClC_6H_4S\cdot)$ can be calculated to be 5000–6000 $M^{-1}\ cm^{-1}$. Although agreement between both values is fairly good, these values are 20–30 times larger than the reported value.[4] Sometimes these discrepancies among ϵ values for free radicals are found in the literature and these suggest that ϵ should not be used without due consideration.
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