J. Am. Chem. Soc. 1982, 104, 1701-1703

Polar Effects in Addition Reactions of Benzenethiyl Radicals to Substituted Styrenes and α-Methylstyrenes Determined by Flash Photolysis[1]

Osamu Ito* and Minoru Matsuda

Contribution from the Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai, 980 Japan. *Received September 10, 1981*

Abstract: The absolute rate constants for the addition reactions of the benzenethiyl radical and its para-chloro derivative to para- and meta-substituted styrenes and α-methylstyrenes have been determined by the flash photolysis technique. The rate constants in the range of $\sim 10^7$–10^8 M^{-1} s^{-1} have been obtained. From the linear relationships in the Hammett plots vs. σ^+, the reaction constants (ρ^+) of $C_6H_5S\cdot$ toward substituted styrenes and α-methylstyrenes were estimated to be –0.26 and –0.30, respectively. The latter ρ^+ value is compatible with the value estimated from the relative reactivities (–0.38). The polar effects of p-$ClC_6H_4S\cdot$ toward styrenes ($\rho^+ = -0.56$) and α-methylstyrenes ($\rho^+ = -0.63$) are larger than those of $C_6H_5S\cdot$. The sign and magnitudes of these ρ^+ values are rationally interpreted in terms of the contribution of such polar resonance structure as $[XC_6H_4S^-, CH_2{=}C(R)C_6H_4Y^{+}\cdot]$ to the transition state.

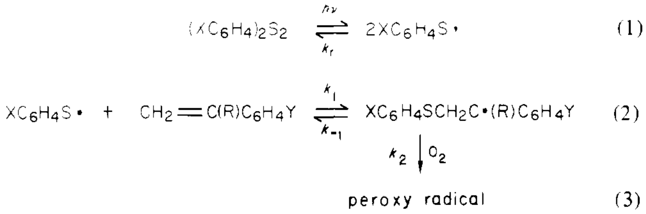
The polar effects in the addition reactions of free radicals to carbon–carbon double bonds have been studied by the application of Hammett-type linear free-energy treatments.[2-4] The sign and magnitudes of the Hammett reaction constants (ρ) reveal the polar nature of the transition state in the free-radical addition reactions. The interpretations, however, were made on the basis of the ρ values estimated from the relative reactivities by using a similar method. Thus, it is indispensable to compare those ρ values with the values estimated from the independent methods; Tanner et al. pointed out that the ρ value in hydrogen abstraction is changeable with the methods used for kinetic analysis of the relative reactivities.[5]

Church and Gleicher determined the relative reactivities of substituted α-methylstyrenes toward the benzenethiyl radical by assuming the irreversibility of the addition process.[6] We showed recently that it is possible to estimate the absolute rate constants of the reversible addition reaction of the benzenethiyl radicals to vinyl monomers by means of the flash photolysis technique.[7,8] Therefore, we will try to compare the absolute rate constants with the relative reactivities of the same reaction system. In order to confirm the results, substituted styrenes and the (p-chlorobenzene)thiyl radical have been examined. The sign and magnitudes of the Hammett reaction constants have been discussed.

Results and Discussion

Transient absorption bands were observed at 490 and 450 nm by the flash decomposition of diphenyl disulfide. They were attributed to the benzenethiyl radical, since similar transient absorption bands were produced from benzenethiol.[8,9] In a similar manner a transient band at 510 nm was attributed to p-$ClC_6H_4S\cdot$.[7,9] The transient absorption bands decayed with second-order kinetics in degassed solution, suggesting that the thiyl radicals decay with recombination. The slopes of the second-order plots yielded $2k_r/\epsilon$ where k_r refers to the rate constant of recombination and ϵ to molar extinction coefficient ($2k_r/\epsilon = 2.7 \times 10^6$ and 1.2×10^6 cm s^{-1} for $C_6H_5S\cdot$ and p-$ClC_6H_4S\cdot$, respectively). On the basis of the assumption that the recombination rates are the diffusion-controlling limit,[10] ϵ can be calculated to be 5.0×10^3 ($C_6H_5S\cdot$) and 1.1×10^4 M^{-1} cm^{-1} (p-$ClC_6H_4S\cdot$). Thus, the concentrations of the thiyl radicals produced by one flash exposure of the disulfides (5×10^{-4} M) were estimated to be ca. 10^{-6} M.[11,12]

Scheme I



$$(XC_6H_4)_2S_2 \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2XC_6H_4S\cdot \quad (1)$$

$$XC_6H_4S\cdot + CH_2{=}C(R)C_6H_4Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XC_6H_4SCH_2C\cdot(R)C_6H_4Y \quad (2)$$

$$\downarrow k_2\ O_2$$

$$\text{peroxy radical} \quad (3)$$

The decay rates of the thiyl radicals were only slightly affected by the addition of oxygen to solution, suggesting the low reactivities of the benzenethiyl radicals toward molecular oxygen.[7] Figure 1 shows the effect of oxygen on the decay curves of $C_6H_5S\cdot$ in the presence of m-chlorostyrene. When oxygen was absent in solution, the decay rate was not accelerated by the addition of m-chlorostyrene to solution (Figures 1a and 1b). Only when both m-chlorostyrene and oxygen were present did the decay rate increase (Figures 1c and 1d) and decay kinetics approach first order (insert in Figure 1). This finding suggests that the addition reaction of $C_6H_5S\cdot$ toward m-chlorostyrene is reversible[13] and that oxygen acts as a selective radical trap for the carbon-centered radical ($C_6H_5SCH_2C\cdot HC_6H_4Cl$);[14] the high reactivity of the carbon-centered radicals toward oxygen has been reported.[15] Similar phenomena were observed for other reaction systems. The reactions were presumed as Scheme I.[16]

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(1) Evaluation of Addition Rates of Thiyl Radicals to Vinyl Monomers by Flash Photolysis. 5. For part 4 see: Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 568.

(2) Walling, C.; Briggs, E. R.; Wolfstirn, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.

(3) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Makromol. Chem.* **1966**, *94*, 238.

(4) Sakurai, H.; Hayashi, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945.

(5) Tanner, D. D.; Samal, P. W.; Ruo, T. C-S.; Henriquez, R. *J. Am. Chem. Soc.* **1979**, *101*, 1168.

(6) Church, D. F.; Gleicher, G. J. *J. Org. Chem.* **1975**, *40*, 536.

(7) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815.

(8) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732.

(9) Thyrion, F. C. *J. Phys. Chem.* **1973**, *77*, 1478.

(10) Nakamura, M.; Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1980**, *102*, 698.

(11) The diffusion rate constants calculated from the Debye equation are usually ca. $\sim$2–4 times larger than the values obtained experimentally;[12] thus the concentrations of the thiyl radicals estimated in this study may contain such an uncertainty.

(12) Ingold, K. U. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, p 37.

(13) Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1959**, *81*, 1144.

(14) The carbon-centered radicals can be represented as $XC_6H_4SCH_2C\cdot(R)C_6H_4Y$ since the addition reactions of the thiyl radicals to olefins are known as anti-Markownikoff. E.g.: Kellogg, R. M. In "Methods in Free Radical Chemistry", Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. III, p 2.

(15) Howard, J. A. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 1.

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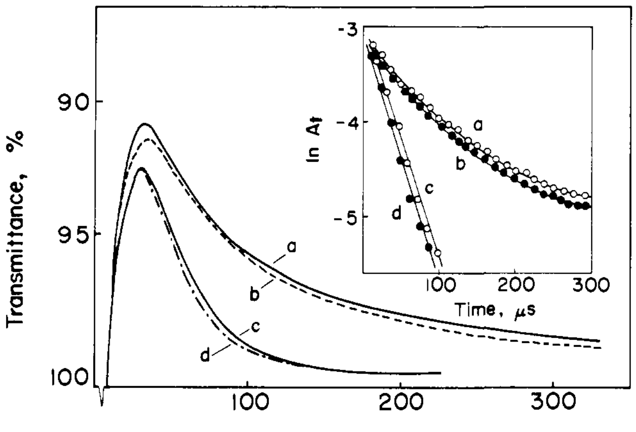

Figure 1. Decay curves of the benzenethiyl radical produced by flash photodecomposition of diphenyl disulfide (5×10^{-4} M): (a) in degassed cyclohexane, (b) in the presence of *m*-chlorostyrene (8.1×10^{-4} M) in degassed solution; (c) in the presence of *m*-chlorostyrene and oxygen (9.5×10^{-4} M); and (d) in the presence of *m*-chlorostyrene and oxygen (1.2×10^{-2} M). Insert: First-order plots of the decay curves a–d.

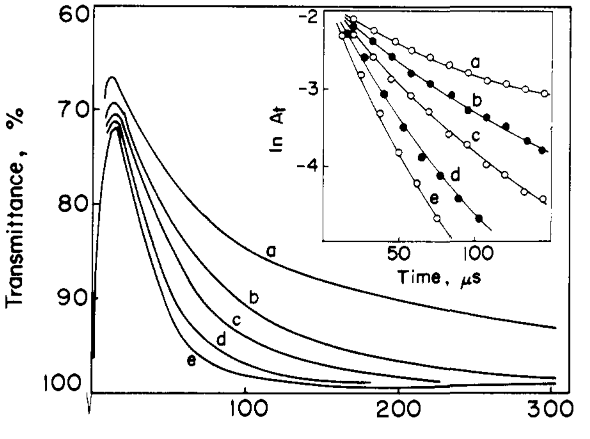

Figure 2. Decay curves of the (*p*-chlorobenzene)thiyl radical produced by flash decomposition of $(p\text{-}C_6H_4)_2S_2$ (5×10^{-4} M) in oxygen-saturated cyclohexane solution ($[O_2] = 1.2 \times 10^{-2}$ M). Concentration of *m*-methylstyrene; (a) 0, (b) 8×10^{-5}, (c) 1.7×10^{-4}, (d) 3.6×10^{-4}, and (e) 5.6×10^{-4} M. Insert: First-order plots of the decay curves a–d.

Since the decay rates of the thiyl radicals in the presence of styrenes were not practically influenced by the oxygen concentration more than ca. 10^{-3} M as shown in Figures 1c and 1d, the reverse process of the addition reaction does not contribute to decay kinetics in solutions containing such high oxygen concentration. This finding suggests that the addition reaction may be quite exothermic and that the decay rates in oxygen-saturated solution correspond to the forward reaction. The decay kinetics of the thiyl radicals can be expressed by

$$-d[XC_6H_4S\cdot]/dt = 2k_r[XC_6H_4S\cdot]^2 + k_I[CH_2{=}C(R)C_6H_4Y][XC_6H_4S\cdot] \quad (4)$$

Figure 2 shows the effect of the concentrations of *m*-methylstyrene on the decay rates of $p\text{-}ClC_6H_4S\cdot$ in oxygen-saturated solution. The first-order plots are shown in the insert of Figure 2; when the concentration of *m*-methylstyrene was high, the decay kinetics approached first order. Since [styrene] [(8.0×10^{-5})–(5.6×10^{-4} M)] and $[O_2]$ (1.2×10^{-2} M) were in large excess compared to $[XC_6H_4S\cdot]$ [($\sim 5 \times 10^{-7}$)–(1×10^{-6} M)] under our experimental conditions, the concentrations of styrene and oxygen were being kept constant during the reaction; thus the pseudo-first-order relationship would be anticipated. When [styrene] was small, decay kinetics was mixed order consisting of first order ($k_I[XC_6H_4S\cdot]$ where $k_I = k_I[CH_2{=}C(R)C_6H_4Y]$) and second order ($k_r[XC_6H_4S\cdot]^2$); the first-order part can be estimated by graphic methods[10,17] or a computer simulation method.[18] The first-order rate constants (k_I) thus estimated were plotted against the concentrations of substituted styrenes (Figure 3). The slopes yield the second-order rate constants (k_I) and these slopes vary with the substituents in styrene. They are summarized in Table I for substituted styrenes[19] and in Table II for substituted α-methylstyrenes. Since low hydrogen-abstraction ability of the phenylthiyl radicals has been proved by the ESR[20] and flash photolysis studies,[7] the rate constants in tables are solely attributed to the addition rate constants. The rate constants in the range of 10^7–10^8 M^{-1} s^{-1} in the tables suggest the exothermicity of the addition reactions. For each substituent in styrene and α-methylstyrene, the rate constant with $C_6H_5S\cdot$ is smaller than that with $p\text{-}ClC_6H_4S\cdot$; this can be interpreted both by the thermody-

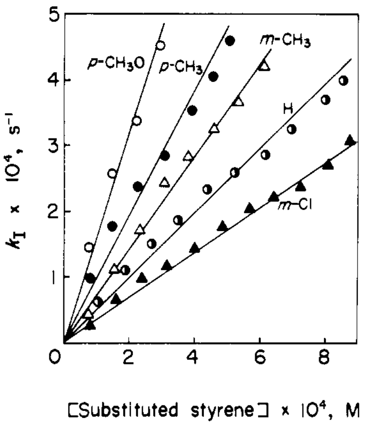

Figure 3. Pseudo-first-order plots for the decay of the (*p*-chlorobenzene)thiyl radical by the addition of substituted styrenes in oxygen-saturated cyclohexane.

Table I. The Rate Constants (k_1) for the Addition Reactions of the Benzenethiyl and (*p*-Chlorobenzene)thiyl Radicals to Para- and Meta-Substituted Styrenes in Cyclohexane at 23 °C[a]

	k_1, M^{-1} s^{-1}	
$YC_6H_4CH{=}CH_2$	$C_6H_5S\cdot$	$p\text{-}ClC_6H_4S\cdot$
m-Cl	2.3×10^7	3.4×10^7
p-Cl	2.6×10^7	3.9×10^7
p-Br	2.9×10^7	4.6×10^7
H	2.7×10^7	5.2×10^7
m-CH_3	2.9×10^7	7.3×10^7
p-CH_3	3.4×10^7	8.0×10^7
p-CH_3O	5.4×10^7	1.5×10^8

[a] Each value contains the estimation error of ca. 10%.

Table II. The Rate Constants (k_1) for the Addition Reactions of the Benzenethiyl and (*p*-Chlorobenzene)thiyl Radicals toward Para- and Meta-Substituted α-Methylstyrenes in Cyclohexane at 23 °C[a]

	k_1, M^{-1} s^{-1}	
$YC_6H_4C(CH_3){=}CH$	$C_6H_5S\cdot$	$p\text{-}ClC_6H_4S\cdot$
m-Cl	5.5×10^7	7.5×10^7
p-Cl	6.5×10^7	1.1×10^8
H	7.1×10^7	1.4×10^8
p-CH_3	8.6×10^7	2.4×10^8

[a] Estimation error is ca. 10%.

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(16) Subsequent reactions of reaction 3 have been studied and the addition products containing oxygen atoms have been isolated. E.g.: Oswald, A. A.; Gresbaum, K.; Hudson, B. E. *J. Org. Chem.* **1963**, *28*, 2361.

(17) Zwicker, E. F.; Grossweiner, L. I. *J. Phys. Chem.* **1963**, *67*, 549.

(18) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

(19) The value for $C_6H_5S\cdot$–styrene in the previous paper[8] has been slightly corrected.

(20) Sato, T.; Abe, M.; Otsu. T. *Makromol. Chem.* **1979**, *180*, 1165.

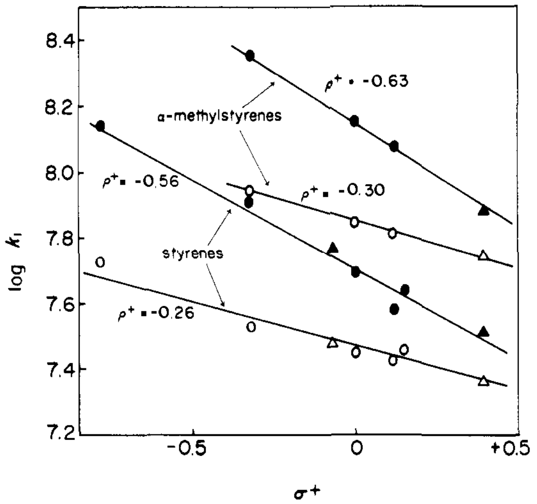

Figure 4. The Hammett plots for the addition rate constants (k_1) vs. σ^+. (○) and (△) refer to the reactions of $C_6H_5S\cdot$ with para- and meta-substituted styrenes, respectively; (●) and (▲) refer to the reactions of p-$ClC_6H_4S\cdot$. The ρ^+ values contain the estimation errors of ca. 5%.

Scheme II

Addition

$$RS\cdot + X \underset{k_{-X}}{\overset{k_X}{\rightleftharpoons}} RSX\cdot$$

$$RS\cdot + Y \underset{k_{-Y}}{\overset{k_Y}{\rightleftharpoons}} RSY\cdot$$

Displacement

$$RSX\cdot + RSH \xrightarrow{k_{XH}} RSXH + RS\cdot$$

$$RSY\cdot + RSH \xrightarrow{k_{YH}} RSYH + RS\cdot$$

namic stabilities of the thiyl radicals and by the contribution of the polar resonance structures to the transition state.[8] For each thiyl radical, the k_1 value of α-methylstyrene is larger than that of styrene by a factor of ca. 2; this also can be ascribed to greater contribution of the polar transition state and the exothermicity of the reaction, which can be deduced from a more negative e value ($e = -1{,}27$ for α-methylstyrene and $e = -0.8$ for styrene)[21] and from the more stable product radical (the 1-phenylethyl radical is more stable than the benzyl radical).

Figure 4 shows the Hammett plots of the k_1 values vs. σ^+; fairly good linear correlations were obtained.[22] The slopes yield the reaction constants (ρ^+) as shown in Figure 4. The ρ^+ value for $C_6H_5S\cdot$ toward substituted α-methylstyrenes had been estimated from the relative reactivities by Church and Gleicher[6] on the basis of the assumption that the addition process is irreversible. The reversibility of the addition reaction, however, was confirmed from our experiment (Figure 1); thus the reaction systems used by Church and Gleicher should be revised as Scheme II, where X and Y refer to substituted α-methylstyrenes. In the case of the reversible addition reactions, the reactivity ratios cannot be determined by measuring the consumption of X and Y (or the formation of RSXH and RSYH), but the rate constants such as k_{-X}, k_{-Y}, k_{XH}, and k_{YH} are necessary as Cadogan and Sadler have pointed out.[23] Otherwise, when $k_{XH}[RSH] \gg k_{-X}$ and $k_{YH}[RSH] \gg k_{-Y}$, the procedure for the estimation of the reactivity ratio agrees with that from the method adopted by Church and Gleicher. The result that their ρ^+ value (−0.38) is compatible with our value (−0.30) may suggest that these conditions are satisfied.[24-26]

All ρ^+ values estimated in this study are negative; this suggests the contribution of the polar resonance structures such as $[XC_6H_4S^-, CH_2{=}C(R)C_6H_4Y^{+}\cdot]$ to the transition state. The results that the magnitudes of the ρ^+ values of p-$ClC_6H_4S\cdot$ ($\rho^+ = -0.56$ for styrenes and $\rho^+ = -0.63$ for α-methylstyrenes) are greater than those of $C_6H_5S\cdot$ ($\rho^+ = -0.26$ for styrenes and $\rho^+ = -0.30$ for α-methylstyrenes) indicate that the electron-withdrawing substituent in the benzenethiyl radical increases the contribution of the above resonance structure. Since the ρ^+ values of α-methylstyrenes were not accurately obtained from only four derivatives, we could not decide if the differences from those of styrenes are significant or not.

In conclusion, the Hammett reaction constant (ρ^+) for substituted α-methylstyrenes toward $C_6H_5S\cdot$ estimated from the absolute rate constants by means of flash photolysis was compatible with the reported one estimated from the relative reactivities. The signs and magnitudes of the ρ^+ values for the reaction systems of substituted styrenes (or α-methylstyrenes)–$C_6H_5S\cdot$ (or p-$ClC_6H_4S\cdot$) were rationally interpreted in terms of the contribution of the polar resonance structures such as $[XC_6H_4S^-, CH_2{=}C(R)C_6H_4Y^{+}\cdot]$ to the transition state.

Experimental Section

Commercially available substituted styrenes were distilled under reduced pressure before use. Substituted α-methylstyrenes were prepared and purified by the methods in the literature.[6,27] The oxygen-saturated cyclohexane solutions were made by the replacement of air dissolved in solution by oxygen after degassing. The concentration of oxygen was calculated by the Henry law.[28] The flash photolysis experiments were made at room temperature controlled at 23 ± 1 °C. A xenon-flash photolysis apparatus of standard design was used; the flash energy was ca. 100 J and the half-duration of xenon-flash lamps was ca. 10 μs.

Acknowledgment. We are grateful to Dr. M. Hirooka of Sumitomo Chemical Co. Ltd. for his kind donation of p-methyl-α-methylstyrene.

Registry No. $C_6H_5S\cdot$, 4985-62-0; p-$ClC_6H_4S\cdot$, 31053-91-5; m-$ClC_6H_4CH{=}CH_2$, 2039-85-2; p-$ClC_6H_4CH{=}CH_2$, 1073-67-2; p-$BrC_6H_4CH{=}CH_2$, 2039-82-9; $PhCH{=}CH_2$, 100-42-5; m-$CH_3C_6H_4CH{=}CH_2$, 100-80-1; p-$CH_3C_6H_4CH{=}CH_2$, 622-97-9; p-$CH_3OC_6H_4CH{=}CH_2$, 637-69-4.

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(21) Brandrup, J.; Imergut, E. H. "Polymer Handbook", Wiley: New York, 1974; p II-387.

(22) In the Hammett plots vs. σ for the para substituents in styrene, curves having upward curvature were obtained; this suggests the presence of the resonance effect.[3,4]

(23) Cadogan, J. I. G.; Sadler, I. H. *J. Chem. Soc. B* **1966**, 1191.

(24) When the addition reactions are not quite exothermic, the k_{-1} (k_{-X} or k_{-Y}) values have been estimated to be $\sim 10^5$–10^6 s^{-1} from the oxygen effects on the decay rates of the thiyl radicals.[7,8] The k_{-1} values of α-methylstyrenes may be smaller about one order because of an increase in exothermicity. In Church and Gleicher's experiment the concentration of RSH in Scheme II is ca. 1 M; thus only when k_{XH}, $k_{YH} \gg 10^4$–10^5 M^{-1} s^{-1} is their procedure valid.

(25) Both the sign and magnitudes of the ρ^+ values for the addition reactions of the substituted benzenethiyl radicals to α-methylstyrene estimated from the relative reactivities by Geers, Gleicher, and Church[26] differ from those obtained by the flash photolysis technique. The reason will be discussed in a subsequent paper.

(26) Geers, B. N.; Gleicher, G. J.; Church, D. F. *Tetrahedron*, **1980**, *36*, 997.

(27) We did not measure the rate constants for p-methoxy-α-methylstyrene, since the boiling point reported in the literature differs greatly.

(28) Murov, S. I. "Handbook of Photochemistry"; Mercel Dekker: New York, 1973; p 89.