Flash Photolysis Study of Solvent Effects in Addition Reactions of Thiyl Radicals to Styrene or α -Methylstyrene.¹ Interaction between p-Chlorobenzenethiyl Radical and Methylbenzenes

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The absorption spectra and the absolute rate constants of the addition reactions of the para-substituted benzenethiyl radicals to styrene and α -methylstyrene in cyclohexane and in π -electron-donor solvents such as benzene and mesitylene have been determined by flash photolysis. Broadenings of the absorption bands of the p-chlorobenzenethiyl radical observed in π -donor solvents were ascribed to the weak interaction between the radical center and π electrons of solvents; the addition rate constants to styrenes in mesitylene were smaller than those in cyclohexane (1:1.5). No appreciable solvent effect was observed both in the spectra and in the rates of the *p*-methylbenzenethiyl radical.

Introduction

An extensive study has revealed that solvents affect the reactivity and selectivity of free-radical reactions.² The solvent effects have mainly been interpreted in terms of solvent polarity³⁻⁵ or specific interactions such as electron donor-acceptor and hydrogen bonding.⁶⁻⁹ Direct evidence for the interaction between the iodine atom and π -donor solvents has been shown in the absorption spectra observed by flash photolysis.¹⁰ The π -donor solvent effects on the actual rates of free radical reactions, however, have not been reported. In this paper we will report our finding that the addition rates and the absorption bands of the benzenethiyl radical having an electron-withdrawing substituent vary with the π -donor solvents. Since the addition process of the thiyl radicals to vinyl monomers was reversible, oxygen was used as a selective radical trap (Scheme I).

Scheme I

$$\frac{1}{2}(p-XC_{6}H_{4})_{2}S_{2} \xrightarrow{h\nu}{k_{1}} p-XC_{6}H_{4}S \cdot$$

$$p-XC_{6}H_{4}S \cdot + CH_{2} = C(R)C_{6}H_{5} \xrightarrow{k_{1}}{k_{-1}}$$

$$p-XC_{6}H_{4}SCH_{2}\dot{C}(R)C_{6}H_{5} \xrightarrow{O_{2}}{k_{2}} \text{ peroxy radical}$$

Experimental Section

Disulfides, styrene, α -methylstyrene, and solvents were purified in the usual manner.¹¹ The flash photolysis apparatus was of standard design; the half-duration of the xenon flash lamps (Xenon Corp. N-851C) was ca. 10 μ s.

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The measurements were performed in a cylindrical cell (optical path = 10 cm) at 23 ± 1 °C. The oxygen concentration in the solvent was calculated from the Henry law after dissolving oxygen under an appropriate pressure into degassed solution.¹²

Results and Discussion

Solvent Effect on Absorption Band of $p-XC_6H_4S$. Figure 1 shows the transient absorption spectra observed by the flash decomposition of $(p-\text{ClC}_6\text{H}_4)_2\text{S}_2$ in various solvents. These absorption bands were ascribed to p- ClC_6H_4S since the same absorption band was observed by flash photolysis of p-ClC₆H₄SH in each solvent. The spectra were depicted with the absorbances immediately after flash (30 μ s) with the light between 310 and 400 nm, where the screening due to the absorptions of solvents is small. The quantum yields for the thiyl radical production in the solvents used in Figure 1 may be similar since the solvent viscosities are practically the same excepting benzene (0.65 cP): cyclohexane (0.98 cP), mesitylene (1.15 cP), and ethanol (1.08 cP).¹² Therefore, the spectra in Figure 1 can be qualitatively compared with each other. The sharp absorption band at 508 nm in cyclohexane was modified in benzene or in mesitylene; shifts in absorption peaks were not appreciable, but broadenings at the tails in the long-wavelength region were significant. These spectral changes in the aromatic solvents were more drastic than those in polar solvents such as ethanol. The broadening seems to increase with a decrease in the ionization potentials of the aromatic solvents. Spectral changes for the benzenethiyl radicals with electron-donating substituents such as the methyl group were small. Although a clear charge-transfer band was not found, these spectral changes shown in Figure 1 are probably attributable to the weak charge-transfer interaction between p-ClC₆H₄S· and π electrons of methylbenzenes.

The decay of p-ClC₆H₄S· obeyed second-order kinetics in cyclohexane and in mesitylene (insert of Figure 1), suggesting that the thiyl radicals decay with recombination (k_r) ; the hydrogen-abstraction ability of p-ClC₆H₄S· from the benzylic hydrogen atoms is very low.¹³⁻¹⁵ The slopes

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Figure 1. Transient absorption spectra produced by the flash photolysis of $(p-ClC_6H_4)_2S_2$ (4.4 × 10⁻⁴ M) in (a) cyclohexane, (b) benzene, (c) mesitylene, and (d) ethanol; spectra were depicted by the absorbance immediately after flash (30 μ s). Insert: second-order plots for decay of p-ClC₈H₄S· (O) in cyclohexane (at 515 nm) and (\bigcirc) in mesitylene (at 525 nm).



Figure 2. Effects of oxygen on the decay curves of p-CIC₆H₄S- in mesitylene at 525 nm: (a) in degassed solution, (b) in degassed solution containing α -methylstyrene (2.3 × 10⁻⁴ M), (c) in air-saturated solution $([O_2] = 2 \times 10^{-3} \text{ M})$ containing α -methylstyrene (2.3 $\times 10^{-4} \text{ M})$, and (d) in O₂-saturated solution ($[O_2] = 10^{-2}$ M) containing α -methylstyrene $(2.3 \times 10^{-4} \text{ M})$. Insert: first-order plots for the decay curves.

yield $2k_r/\epsilon$, where ϵ refers to the molar extinction coefficient of the thiyl radical; although similar $2k_r/\epsilon$ values in both solvents were estimated at the wavelength where the initial absorbance was the same, precise k_r values could not be compared with each other because of a lack of data for the ϵ values and the quantum yields. Since the $2k_r/\epsilon$ values depend upon the solvent viscosity, k_r may be the diffusion-controlled limit.¹⁶ From the Debye equation for the diffusion-controlled rate, the k_r value can be calculated to be 7×10^9 M⁻¹ s⁻¹ when the solvent viscosity is 1.0 cP;¹⁴ the ϵ and the initial concentration of the thiyl radical were estimated to be ca. 10⁴ M⁻¹ cm⁻¹ and ca. 10⁻⁶ M, respectively.17

Solvent Effect on Addition Rates. The low reactivity of the benzenethiyl radicals toward molecular oxygen was confirmed by the finding that the decay rate of the thiyl radical was only slightly affected by the addition of oxygen



Figure 3. Effects of the concentration of α -methylstyrene on the decay curves of *p*-CIC₆H₄S in O₂-saturated mesitylene at 525 nm; [α -methylstyrene]: (a) 0, (b) 7.7 × 10⁻⁵, (c) 1.5 × 10⁻⁴, (d) 2.3 × 10⁻⁴, and (e) 3.0×10^{-4} M. Insert: first-order plots for the decay curves.

TABLE I: Addition Rate Constants (k_1) of p-ClC₆H₄S. and p-CH₃C₆H₄S toward Styrene and α -Methylstyrene in Various Solutions at 23 °C^a

solvent	$10^{-7}k_1, M^{-1} s^{-1}$		
	p-ClC ₆ H ₄ S·		<i>p</i> -CH ₃ C ₆ - H.S./
	styrene	α-methyl- styrene	α-methyl- styrene
cyclohexane	5.2	14	1.6
etnanoi benzene mesitylene	$\frac{5.0}{4.3}$	$14 \\ 12 \\ 8.5$	$\begin{array}{c} 1.5\\ 1.4 \end{array}$

^{*a*} Estimation error of $\pm 10\%$.

to solution. Figure 2 shows that the acceleration of the decay curve of p-ClC₆H₄S· in the presence of α -methylstyrene was observed only when oxygen coexists in solution. These findings suggest the reversibility of the addition process where oxygen acts as a selective radical trap for the carbon-centered radical, since the high reactivity of the carbon-centered radicals toward oxygen has been reported (Scheme I).^{18,19} The fact that the equilibrium was established during the flash duration (ca. 10 μ s) suggests that the k_{-1} value may be greater than 10^5 s^{-1} ; on the basis of the assumption of $k_2 = 10^9 \text{ M}^{-1} \text{ s}^{-1}$, oxygen concentrations of more than ca. 10⁻⁴ M may be necessary to scavenge all of the carbon-centered radicals. Figure 2, c and d, shows that the decay rate of the thiyl radical in the presence of α -methylstyrene was not influenced by oxygen concentrations of more than 2×10^{-3} M; thus, the decay rates in the oxygen-saturated solution (ca. 10⁻² M) correspond solely to the forward reaction. Decay kinetics of the thivl radicals can be expressed by eq 1.

$$d[p-XC_{6}H_{4}S\cdot]/dt = 2k_{r}[p-XC_{6}H_{4}S\cdot]^{2} + k_{1}[CH_{2}=C(R)C_{6}H_{5}][p-XC_{6}H_{4}S\cdot]$$
(1)

Figure 3 shows the effect of the concentrations of α methylstyrene on the decay rates of p-ClC₆H₄S· in oxygen-saturated solution. The first-order plots are shown in the insert of Figure 3; decay kinetics approached first order with an increase in the concentration of α -methyl-

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⁽¹⁷⁾ The k, values calculated from the Debye equation are usually \sim 2–4 times larger than the values determined experimentally; ¹⁴ thus the ϵ values and concentrations of the thiyl radicals estimated in this method may contain such an uncertainity.

⁽¹⁸⁾ Since the addition reactions of the thiyl radicals to vinyl monomers are known as anti-Markovnikov, the carbon-centered radicals can be represented as p-XC₆H₄SCH₂C(R)C₆H₅. (19) Howard, J. A. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New

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Figure 4. Pseudo-first-order plots for the addition reaction of p-ClC₆H₄S• to α -methylstyrene or styrene in O₂-saturated solutions: (a) α -methylstyrene in cyclohexane, (b) α -methylstyrene in mesitylene, (c) styrene in cyclohexane, and (d) styrene in mesitylene.

styrene. The pseudo-first-order relationship would be anticipated since the concentration of vinyl monomers was being kept constant during the reaction under our experimental conditions; [α -methylstyrene] or [styrene] (0.4 $\times 10^{-4} - 4.5 \times 10^{-4}$ M) was higher than [p-XC₆H₄S·] (ca. 10^{-6} M). When the concentration of vinyl monomers was small, decay kinetics was mixed order consisting of second order ($k_r[p$ -XC₆H₄S·]²) and first order ($k_I[p$ -XC₆H₄S·] where $k_I = k_1[CH_2=C(R)C_6H_5]$); the k_I values for such cases can be estimated by graphic methods^{13,16} or a computer simulation method.²⁰ The $k_{\rm I}$ values thus estimated were plotted against the concentrations of α -methylstyrene or styrene (Figure 4). The slopes yield the second-order addition rate constants (k_1) which vary with the solvents. They are summarized in Table I. Although the difference of the k_1 values of p-ClC₆H₄S· in benzene from those in cyclohexane was small, the difference observed in mesitylene was significantly larger than the estimation errors of $\pm 10\%$ which were derived from the several manipulations needed to extract the k_1 values from the experimental flash data. The effect of polar solvent or hydrogen-bonding solvent such as ethanol on the k_1 value is quite small. No appreciable change was observed for the k_1 values of the $p-CH_3C_6H_4S-\alpha$ -methylstyrene system (Table I). Since these findings for the k_1 values correspond to the spectral changes, the weak interaction of p-ClC₆H₄S with π -donor solvents may cause a decrease in the rate constants; π donor solvents may stabilize the reactant by surrounding p-ClC₆H₄S· and may desolvate when the thivl radical approaches the double bond of vinyl monomers.

The k_1 value of p-ClC₆H₄S· toward α -methylstyrene is larger than that toward styrene in each solvent; this can be ascribed to a greater contribution of the polar transition state such as [p-XC₆H₄S⁻, CH₂=C(R)C₆H₅⁺·] and to the exothermicity of the reaction, which can be deduced from the *e* value and from the stability of the product radical, respectively.^{11,21} The larger k_1 value of p-ClC₆H₄S· toward α -methylstyrene than that of p-CH₃C₆H₄S· in each solvent can be interpreted both by the thermodynamic stability of the thiyl radials and by the polar transition state.¹¹

Rate Constant for Scavenging e_{ac} in N₂O-Saturated Solutions¹

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The rate constant for reaction of hydrated electrons with N_2O in aqueous solutions has been determined to be $(9.1 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from pulse radiolysis observations on the growth and the decay of the absorption of e_{aq}^{-} . Improvements in instrumental response have allowed observations to be carried out directly on solutions saturated with N_2O at atmospheric pressure where the reaction period is only 2.9 ns. An approach to numerical simulation of the observed time dependence is described which allows one to take into account in detail the track processes which occur on this time scale as well as the pulse profile and instrumental characteristics. Critical comparisons of the observed growth and decay with the results of these simulations establish well-defined limits for the reaction period. By using the simulated responses to provide reference information we show that it is possible to use the integrated absorbance to evaluate the reaction period with an accuracy of a few percent. The approaches used here allow rate information to be obtained for reaction periods as low as ~0.3 ns even though the pulse duration and recording response periods are 1 order of magnitude greater.

Nitrous oxide is used in many radiation chemical studies of aqueous systems to convert e_{aq}^- into hydroxyl radicals

$$\mathbf{e}_{aq}^{-} + \mathbf{N}_2 \mathbf{O} + \mathbf{H}_2 \mathbf{O} \xrightarrow{\kappa_1} \mathbf{N}_2 + \mathbf{O} \mathbf{H}^- + \mathbf{O} \mathbf{H}$$
(1)

in order to produce a system that is predominantly oxidizing and to simplify the processes that must be considered in the ensuing chemistry. Because of the importance of this electron scavenger, it is desirable to have an accurate rate constant available for reaction 1 so that one can take its contribution into account quantitatively, particularly in studies involving solutes which react competitively with e_{aq} . Gordon et al. reported a value of $(8.7 \pm 0.6) \times$

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