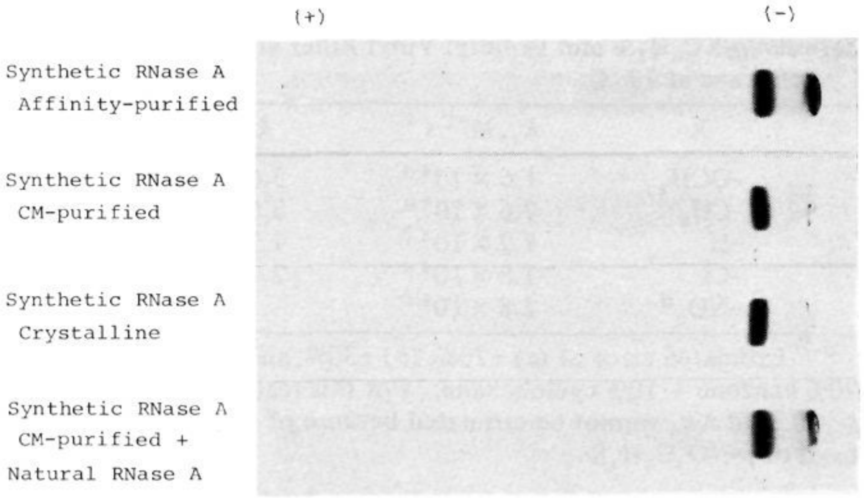

Figure 7. Disk isoelectrofocusing of synthetic RNase A on Ampholine, pH 3.5–10.0 (10 μg each).

A [Ampholine pH 3.5–10, at 200 V for 5 h, stained by Coomassie Brilliant Blue G-250 (Sigma)] (Figure 7); $[\alpha]^{20}{}_D$ −69.7° (*c* 0.2, in 0.1 M KCl) (lit.[11b] $[\alpha]^{20}{}_D$ −73.3° in 0.1 M KCl); UV $\epsilon_{max\ 277.5\ nm}$ 9734 in 0.1 M KCl (lit.[11b] 9800); Michaelis constant for yeast RNA, 1.21 mg/mL (lit.[23] 1.25 mg/mL). Amino acid ratios in 6 N HCl (48 h) hydrolyzate (numbers in parentheses are those of natural RNase A and numbers in brackets indicate the theory): Asp 14.94 (15.07) [15], Thr 9.79 (9.64) [10], Ser 13.80 (13.67) [15], Glu 12.53 (12.47) [12], Pro 4.27 (4.42) [4], Gly 3.38 (3.29) [3], Ala 11.96 (12.21) [12], Cys 3.82 (3.79) [4], Val 9.19 (8.92) [9], Met 4.20 (3.94) [4], Ile 2.28 (2.19) [3], Leu 2.00 (2.00) [2], Tyr 5.87 (5.94) [6], Phe 3.07 (3.11) [3], Lys 10.57 (10.44) [10], His 3.86 (3.66) [4], Arg 4.01 (4.11) [4], recovery of Leu 79% (77%).

Crystallization of the CM-Purified Product from Aqueous Ethanol. The CM-purified sample (3.4 mg) was dissolved in H_2O (50 μl). This solution was cooled to 5 °C and then 95% EtOH (60 μl) of the same temperature is added with gentle shaking until a very faint turbidity appeared. The solution was kept in a refrigerator for 3 months. During this period, a fine precipitate changed into a mass of small transparent, platelike crystals and then grew to multioriented polycrystals with rosettes (Figure 3a) or stalagmite shapes (Figure 3b). They were collected by centrifugation and washed with 95% EtOH; yield 1.92 mg. Activity against yeast RNA and 2′,3′-cyclic cytidine phosphate was 114% and 112% of natural RNase A, respectively. When measured at the protein concentration, 1.5 μg/ml, this crystalline sample exhibited the RNase A activity of 86.0 Kunitz U/mg.

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Evaluation of Addition Rates of Thiyl Radicals to Vinyl Monomers by Flash Photolysis. 3.[1] Polar Effect in Addition Reactions of Substituted Benzenethiyl Radicals

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Abstract: Rate constants for addition (k_1) of the para-substituted benzenethiyl radicals (p-$XC_6H_4S\cdot$) to vinyl monomers ($CH_2{=}CHY$) such as isobutyl vinyl ether and vinyl acetate (nonconjugated monomers) and acrylonitrile (conjugated one) have been determined by means of flash photolysis. The rate constants for the reverse reaction (k_{-1}) and the equilibrium constants ($K = k_1/k_{-1}$) have been estimated in the forms of k_{-1}/k_2 and Kk_2, respectively, where k_2 is the rate constant for the reaction between p-$XC_6H_4SCH_2C{\cdot}HY$ and oxygen; oxygen was used as a selective radical trap to the carbon-centered radicals. From the linear correlations obtained in the Hammett plots of log k_1, log (k_{-1}/k_2), and log Kk_2 vs. the substituent constants (σ^+), the reaction constants (ρ^+) were estimated for each vinyl monomer. The $\rho^+(Kk_2)$ values were invariant with a change in vinyl monomers ($\rho^+(Kk_2) = 1.37$). The $\rho^+(k_1)$ values increase with an increase in the electron densities of the double bonds in vinyl monomers. This suggests that a part of the polar effects in the reactivities is determined by the polar effect in the thermodynamic stabilities of the p-$XC_6H_4S\cdot$ and that another part of the polar effects is caused by the polar resonance structures in the transition state of which contribution varies with the electron-donating or -withdrawing ability of vinyl monomers.

Since Walling and Mayo applied the Hammett equation to radical addition reactions,[2] the polar effects in the free-radical reactions have been the subject of many studies.[3-5] The polar effects in various radical reactions have been rationalized in terms of the contributions of the polar resonance structures in the transition state. In the hydrogen abstraction, Zavitsas and Pinto have recently proposed an idea that the Hammett reaction constants (ρ or ρ^+) do not reflect the polar effects in the transition state but they reflect the exo- or endothermicity of the reactions.[6] Davis and Pryor[7] have presumed that both effects are effective, and Tanner and his co-workers[8] have pointed out that the discussion should be made on the basis of the accurate relative rate constants.

For the polar effects in the addition reactions, such arguments have not been made because of lack of thermodynamic data for both reactant radicals and product radicals. For reactions of the

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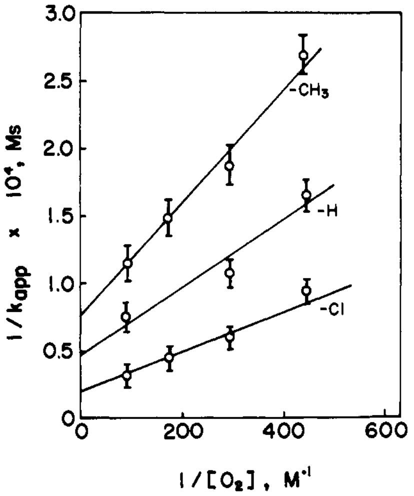

Figure 1. Plots of $1/k_{app}$ vs. $1/[O_2]$ (eq 5) for the reactions of $p\text{-}XC_6H_4S\cdot$ with vinyl acetate. $[O_2]$ = 1.4–12 mM and $[CH_2{=}CHY]$ = 200–1000 mM.

substituted polystyryl radicals towards substituted styrenes[2,5] and for the addition of thiyl radicals toward substituted α-methylstyrenes,[9–13] the sign and the magnitude of the ρ (or ρ^+) values were attributed to the contribution of the polar resonance structures in the transition state. In order to clarify the relative importance of the polar effect in the transition state and the exo- or endothermicity of the reactions, information about both kinetic and thermodynamic data may be necessary. In an earlier paper,[14] we reported that the absolute rate constants for the reversible addition reactions of the p-chlorobenzenethiyl radical ($p\text{-}ClC_6H_4S\cdot$) toward vinyl monomers ($CH_2{=}CHY$) and the relative equilibrium constants could be determined by the flash photolysis technique when oxygen was added in solution as a selective radical trap to the carbon-centered radicals ($p\text{-}ClC_6H_4SCH_2C\cdot HY$). It has also been clarified that the ρ^+ values for the reactivities of $p\text{-}XC_6H_4S\cdot$ toward methyl methacrylate and styrene are mainly determined by the polar effects in the thermodynamic stabilities of $p\text{-}XC_6H_4S\cdot$.[1]

In this study we try to clarify whether the ρ^+ values for the reactivities vary with changing vinyl monomers. If the ρ^+ values for the reactivities vary with the stabilities of the product radicals ($p\text{-}XC_6H_4SCH_2C\cdot HY$), it might be presumed that the ρ^+ values are determined by the exo- or endothermicity in a manner similar to that proposed by Zavitsas and Pinto for hydrogen abstraction.[6] On the other hand, if the ρ^+ values vary with the electron-donating or -withdrawing ability of the substituents (Y) in $CH_2{=}CHY$, the changes in the ρ^+ values may be attributed to the polar resonance structures in the transition state. Acrylonitrile was chosen as a monomer having a conjugated and electron-poor double bond, and isobutyl vinyl ether and vinyl acetate as having nonconjugated ones.[15]

Results and Discussion

Determination of Rate Constants. It is established that xenon and laser flash photolysis techniques gave accurate rate constants for rapid free-radical and carbene reactions.[16–22] The thiyl radicals were produced by xenon flash photodecomposition of the corresponding disulfides. The transient absorption bands observed in the visible region were assigned to the thiyl radicals since the same transient bands were observed in flash photodecomposition of the corresponding thiols.[1,14,23,24] All thiyl radicals decayed with second-order kinetics in degassed cyclohexane. This suggests that the thiyl radicals decay via recombination which may occur at the diffusion-controlled limit since the slopes of the second-order plots, $2k_r/\epsilon$ (k_r refers to the rate constant for recombination and ϵ to the molar extinction coefficient), increased with a decrease in solvent viscosity. From the k_r value calculated from the Debye equation and the empirical factor,[25] the ϵ value was estimated; thus, the concentration of each thiyl radical immediately after a flash was calculated to be ca. 5×10^{-7} M.

The decay rates were only slightly affected by the addition of oxygen to solution. This indicates small rate constants for the reaction between the thiyl radicals and oxygen.[26] Even on addition

Table I. Rate Constants (k_1 and k_{-1}/k_2) for the Reactions between $p\text{-}XC_6H_4S$ and Isobutyl Vinyl Ether in Cyclohexane at 23 °C

X	k_1, $M^{-1}\ s^{-1}$	k_{-1}/k_2, M
$-OCH_3$	$1.6 \times 10^{4\ a}$	$3.6 \times 10^{-3\ b}$
$-CH_3$	$7.6 \times 10^{4\ a}$	$3.6 \times 10^{-3\ b}$
-H	$1.2 \times 10^{5\ b}$	$1.7 \times 10^{-3\ c}$
-Cl	$1.8 \times 10^{5\ a}$	$2.3 \times 10^{-3\ b}$
$-NO_2{}^d$	$2.8 \times 10^{6\ c}$	

[a–c] Estimated error of (*a*) ±20%, (*b*) ±30%, and (*c*) ±40%. [d] In 90% benzene + 10% cyclohexane. For this reaction system, k_{-1}/k_2 and Kk_2 cannot be estimated because of the weak transient band of $p\text{-}NO_2C_6H_4S\cdot$.

Table II. Rate Constants (k_1 and k_{-1}/k_2) for the Reaction between $p\text{-}XC_6H_4S\cdot$ and Vinyl Acetate in Cyclohexane at 23 °C

X	k_1, $M^{-1}\ s^{-1}$	k_{-1}/k_2, M
$-OCH_3{}^e$	$2.3 \times 10^{3\ a}$	
$-CH_3$	$1.3 \times 10^{4\ a}$	$5.2 \times 10^{-3\ b}$
-H	$1.7 \times 10^{4\ b}$	$3.9 \times 10^{-3\ c}$
-Cl	$4.6 \times 10^{4\ a}$	$6.3 \times 10^{-3\ b}$
$-NO_2{}^d$	$5.5 \times 10^{5\ c}$	

[a–d] See the footnotes for Table I. [e] For this reaction system, k_{-1}/k_2 and Kk_2 cannot be estimated because of small dependence of $1/k_{app}$ upon oxygen concentration.

Table III. Rate Constants (k_1 and k_{-1}/k_2) for the Reaction between $p\text{-}XC_6H_4S\cdot$ and Acrylonitrile in Cyclohexane at 23 °C

X	k_1, $M^{-1}\ s^{-1}$	k_{-1}/k_2, M
$-OCH_3$	$1.7 \times 10^{5\ a}$	$3.0 \times 10^{-3\ b}$
$-CH_3$	$4.3 \times 10^{5\ a}$	$9.4 \times 10^{-4\ b}$
-H	$4.6 \times 10^{5\ b}$	$5.9 \times 10^{-4\ c}$
-Cl	$5.0 \times 10^{5\ a}$	$3.3 \times 10^{-4\ b}$
$-NO_2{}^d$	$1.1 \times 10^{6\ c}$	

[a–d] See the footnotes for Table I.

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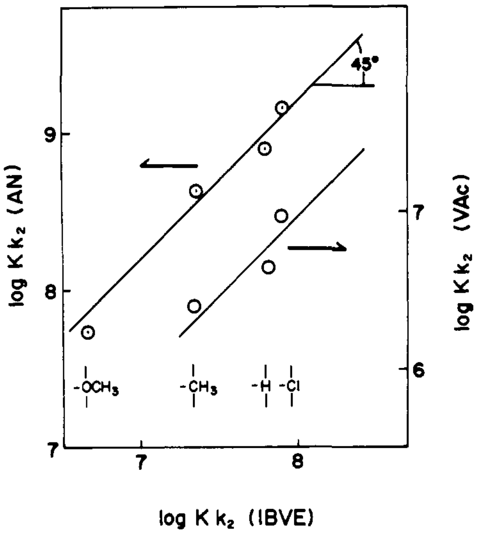

Figure 2. Correlations among log Kk_2 values obtained with three vinyl monomers; plots of log Kk_2 for acrylonitrile (AN) and log Kk_2 for vinyl acetate (VAc) vs. log Kk_2 for isobutyl vinyl ether (IBVE).

of vinyl monomers to degassed solutions, the decay rates were only slightly affected. On the addition of both vinyl monomers and oxygen, the decay rates of the thiyl radicals increased and the decay kinetics changed to first order. These findings suggest that the addition reactions of thiyl radicals to vinyl monomers occur reversibly and that oxygen reacts selectively with p-$XC_6H_4SCH_2C{\cdot}HY$,[27] which resulted in a shift of the equilibrium to the product as shown in Scheme I. Under the experimental conditions that both $[CH_2{=}CHY]$ and $[O_2]$ were in large excess compared with $[p\text{-}XC_6H_4S\cdot]$, decay kinetics of p-$XC_6H_4S\cdot$ obeyed a first-order relationship. The first-order rate constants (k_I) can be expressed according to eq 4 by applying the steady-state approximation with respect to $[p\text{-}XC_6H_4SCH_2C{\cdot}HY]$ in eq 3.[28] Then, a relation between the apparent second-order rate constants, k_{app} ($=k_I/[CH_2{=}CHY]$), and $[O_2]$ was derived as eq 5. Figure 1 shows the plots of $1/k_{app}$ vs. $1/[O_2]$ for the p-$XC_6H_4S\cdot$–vinyl acetate system as an example; the intercept and the slope yield $1/k_1$ and k_{-1}/k_1k_2, respectively. Similar plots were obtained for other reaction systems. The rate constants of the reverse reactions (k_{-1}) were estimated as a form of k_{-1}/k_2. These values are summarized in Table I for isobutyl vinyl ether, in Table II for vinyl acetate, and in Table III for acrylonitrile.[29] The equilibrium constants ($K = k_1/k_{-1}$) can be calculated as a form of Kk_2 from the k_1 and k_{-1}/k_2 values in the tables. Although the absolute rate constants for addition of the phenylthiyl radicals to vinyl monomers have not yet been reported, the relative values have been estimated by the spin trapping method;[30] the ratio of the reactivity of $C_6H_5S\cdot$ toward acrylonitrile to that toward vinyl acetate is 19, which is in good agreement with the ratio of the k_1 values, 27, determined in this study.[31]

Scheme I

$$(p\text{-}XC_6H_4)_2S_2 \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2p\text{-}XC_6H_4S\cdot \qquad (1)$$

$$p\text{-}XC_6H_4S\cdot + CH_2{=}CHY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} p\text{-}XC_6H_4SCH_2C{\cdot}HY \xrightarrow[O_2]{k_2} \text{peroxy radical} \qquad (2)$$

$$-d[p\text{-}XC_6H_4S\cdot]/dt = 2k_r[p\text{-}XC_6H_4S\cdot]^2 + k_1[p\text{-}XC_6H_4S\cdot][CH_2{=}CHY] - k_{-1}[p\text{-}XC_6H_4SCH_2C{\cdot}HY] \qquad (3)$$

$$k_I/[CH_2{=}CHY] = k_1\{1 - k_{-1}/(k_{-1} + k_2[O_2])\} = k_{app} \qquad (4)$$

$$1/k_{app} = 1/k_1 + k_{-1}/(k_1k_2[O_2]) \qquad (5)$$

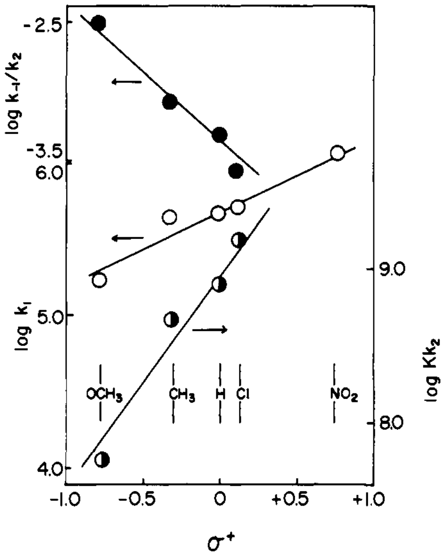

Figure 3. The Hammett plots of log k_1 (○), log (k_{-1}/k_2) (●), and log Kk_2 (◑) for acrylonitrile vs. σ^+.

Table IV. The Hammett Parameters for the Addition of the Para-Substituted Benzenethiyl Radicals to Isobutyl Vinyl Ether, Vinyl Acetate, and Acrylonitrile[a]

parameter	isobutyl vinyl ether	vinyl acetate	acrylonitrile
Q	0.023	0.026	0.60
e	−1.77	−0.22	1.2
$\rho^+(k_1)$	+1.43	+1.31	+0.46
$\rho^+(k_{-1}/k_2)$			−0.88
$\rho^+(Kk_2)$	+1.36	+1.38	+1.38
$\rho^+(k_1)/\rho^+(Kk_2)$	+1.05	+0.95	+0.33
$\rho^+(k_{-1}/k_2)/\rho^+(Kk_2)$			−0.64

[a] The values for methyl methacrylate and styrene have been reported in the preceding paper;[1] for methyl methacrylate (Q = 0.74 and e = 0.4), $\rho^+(k_1) = +1.05$, $\rho^+(k_{-1}/k_2) = -0.36$, $\rho^+(Kk_2) = +1.35$, $\rho^+(k_1)/\rho^+(Kk_2) = +0.78$, and $\rho^+(k_{-1}/k_2)/\rho^+(Kk_2) = -0.27$; for styrene ($Q$ = 1.0 and e = −0.8), $\rho^+(k_1) = +1.37$, $\rho^+(k_1)/\rho^+(Kk) = +1.00$. Each Hammett's parameter contains an estimated error of ca. 5%.

Thermodynamic Stabilities of p-$XC_6H_4S\cdot$. For any vinyl monomer, the effects of the para substituents (X) in the reactivities toward oxygen and those in the thermodynamic stabilities of p-$XC_6H_4SCH_2C{\cdot}HY$ may be insignificant because of the intermediacy of one methylene group. Thus, the differences among the log Kk_2 values by changing the para substituents of the thiyl radicals are a relative measure of the thermodynamic stabilities of p-$XC_6H_4S\cdot$. This was supported by Figure 2 in which log Kk_2 for vinyl acetate or acrylonitrile was plotted against log Kk_2 for isobutyl vinyl ether; straight lines can be drawn so as to give a slope of unity.[32] The stabilities of p-$XC_6H_4S\cdot$ increase with a decrease in log Kk_2; $-OCH_3 > -CH_3 > -H > -Cl$. A similar tendency has been reported for the substituted benzenethiyl

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[27] The carbon-centered radicals may be expressed as p-$XC_6H_4SCH_2C{\cdot}HY$ since addition of the phenylthiyl radicals to olefins is known as anti-Markovnikov. E.g.; Kellogg, R. M. In "Methods in Free-Radical Chemistry", Huyser, E. S., Ed.; Marcel Dekker: New York, 1969; Vol. II, p 2.

[28] Under our experimental conditions written down in the caption of Figure 1, both $[CH_2{=}CHY]$ and $[O_2]$ are in large excess compared with $[p\text{-}XC_6H_4S\cdot]$; thus, both $[CH_2{=}CHY]$ and $[O_2]$ may be considered to be kept constant during the reaction.

[29] The values for p-$XC_6H_4S\cdot$–acrylonitrile in the previous paper[14] were slightly corrected.

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[31] Low ability of hydrogen abstraction of p-$XC_6H_4S\cdot$ was proven by flash photolysis;[14] this finding was supported by ESR studies.[30]

[32] A similar plot was obtained for the log Kk_2 values for methyl methacrylate reported in an earlier paper.[1]

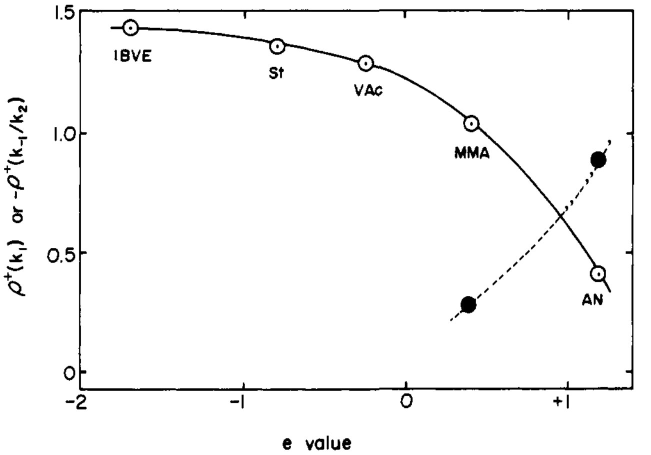

Figure 4. Plots of $\rho^+(k_1)$ (○) and $\rho^+(k_{-1}/k_2)$ (●) vs. the *e* values for vinyl monomers; abbreviations of vinyl monomers are cited in Figure 2. The ρ^+ values for styrene (St) and methyl methacrylate (MMA) are cited from the footnote of Table IV.

radicals[33] and phenoxy radicals.[34]

Hammett Correlations. Figure 3 shows the Hammett plots of the log k_1, log (k_{-1}/k_2), and log Kk_2 values for acrylonitrile vs. σ^+ as an example.[35] Similar Hammett plots were obtained for isobutyl vinyl ether and vinyl acetate. The slopes yielded the ρ^+ values as listed in Table IV, in which $\rho^+(k_1)$ refers to the slopes of the plots of the log k_1 values, $\rho^+(k_{-1}/k_2)$ to those of the log (k_{-1}/k_2) values, and $\rho^+(Kk_2)$ to those of the log Kk_2 values. For isobutyl vinyl ether and vinyl acetate, the log (k_{-1}/k_2) values did not depend on σ^+; $\rho^+(k_{-1}/k_2) \simeq 0$. In Table IV, the $\rho^+(Kk_2)$ values for three vinyl monomers are in good agreement with each other, and the $\rho^+(Kk_2)$ values are larger than the $\rho^+(k_1)$ and $\rho^+(k_{-1}/k_2)$ values. These observations suggest that a considerably large polar effect is present in the thermodynamic stabilities of p-$XC_6H_4S\cdot$ and that this polar effect plays an important role in determining the polar effects in the reactivities of p-$XC_6H_4S\cdot$. If there is no interaction between the reactants in the transition state, the signs and magnitudes of the ρ^+ values for the reactivities might be determined mainly by the linear free-energy relationship; the dependences of the $\rho^+(k_1)$ and $\rho^+(k_{-1}/k_2)$ values upon the $\rho^+(Kk_2)$ were referred to as α and $-\beta$, respectively ($0 < \alpha$, $\beta < 1$ and $\beta = 1 - \alpha$).[36] The fact that the observed $\rho^+(k_1)$ and $\rho^+(k_{-1}/k_2)$ values vary with vinyl monomers suggests that other effects also must be effective in determining the polar effect in the reactivities. Referring the deviation of the $\rho^+(k_1)$ value from α to γ, we can derive eq 6 and 7.

$$\rho^+(k_1)/\rho^+(Kk_2) = \alpha + \gamma \quad (6)$$

$$\rho^+(k_{-1}/k_2)/\rho^+(Kk_2) = -(\beta - \gamma) \quad (7)$$

In the case of acrylonitrile, a relation $\rho^+(k_1)/\rho^+(Kk_2) - \rho^+(k_{-1}/k_2)/\rho^+(Kk_2) \simeq 1$ was confirmed from Table IV; this shows the reliability of the ρ^+ values observed in this study.

In Figure 4, the $\rho^+(k_1)$ and $\rho^+(k_{-1}/k_2)$ values were plotted against the *e* values of vinyl monomers which are one of the measures of the electron-donating or -withdrawing ability.[15,37] This suggests that the γ value is a measure of the contribution of the polar resonance structure to the transition state. When the polar resonance structure such as $[(p\text{-}XC_6H_4S)^-, (CH_2{=}CHY)^{+}\cdot]$ contributes to the transition state, γ has a positive value; the oppositely charged polar resonance structure changes the sign of γ to a negative value. We assume that the α value is equal to +0.75 from Semenov's empirical estimation for endothermic radical reactions;[38] all the reaction systems in this study may be endothermic since K values less than unity can be estimated from Kk_2 values by assuming k_2 = ca. 1×10^9 M^{-1} s^{-1}.[39] Therefore, for the reaction systems having $\rho^+(k_1)/\rho^+(Kk_2)$ larger than +0.75, the difference, $\rho^+(k_1)/\rho^+(Kk_2) - 0.75$, can be ascribed to γ; isobutyl vinyl ether, vinyl acetate, and styrene belong to this group. On the other hand, in the reaction system of acrylonitrile having $\rho^+(k_1)/\rho^+(Kk_2)$ smaller than +0.75, the oppositely charged polar resonance structure may contribute to the transition state. This suggests that an unpaired electron on the sulfur atom in p-$XC_6H_4S\cdot$ may be mobile in the transition state.

On the other hand, if the ρ^+ values in the reactivities vary with the exo- or endothermicity of the reactions as was proposed by Zavitsas and Pinto[6] and Hammond,[40] the ρ^+ values must be determined by the change in the stabilities of p-$XC_6H_4SCH_2C\cdot HY$ with changing Y; the stabilities of p-$XC_6H_4SCH_2C\cdot HY$ due to the delocalization of an unpaired electron may be determined by the *Q* values of the vinyl monomers.[15,37] However, the $\rho^+(k_1)$ values listed in Table IV do not show any correlation to the *Q* values.

In conclusion, the polar effect in the reactivities of p-$XC_6H_4S\cdot$ toward vinyl monomers has two origins; one part is governed by the polar effect in the thermodynamic stabilities of p-$XC_6H_4S\cdot$ and another part, which varies with the electron-donating or -withdrawing ability of vinyl monomers, is caused by the polar resonance structures in the transition state.

Experimental Section

Disulfides were purified by recrystallizing the commercial reagents. Vinyl monomers were distilled under a reduced pressure before use. Oxygen concentration in the cyclohexane solutions was controlled by the partial pressure of oxygen and calculated from Henry's law.[41] Xenon flash photolysis apparatus was of standard design; half-duration of xenon flash lamps (Xenon Corp. N851C) and flash energy was ca. 10 μs and ca. 100 J, respectively.

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