

thermal parameters for the nonhydrogen atoms. Hydrogen positions were determined from the geometry of the molecule. All the hydrogen atoms were refined with one overall isotropic temperature factor (8.9 \AA^2). The final conventional R index was 0.061.

Photolysis of Oxaziridine 3. Nitrogen was bubbled through a cyclohexanic solution of oxaziridine **3** (100 mg/10 mL) for 30 min in order to remove all traces of air. The solution was then irradiated during 8 h in a Rayonet photochemical reactor, Model RPR 100, which was equipped with 16 RPR 2537-Å lamps.

The crude product (yellow oil) was purified by preparative TLC (Kieselgel 60 PF₂₅₄₊₃₆₆, 10% EtOH in CHCl₃). The yield of the pure lactam **4a** is ~80% from oxaziridine **3** (400 mg of starting substrate **3** yielded 311 mg of crystallized lactam **4a**): mp 90–95 °C; $[\alpha]^{20}_D -143^\circ$ (c 0.32, MeOH); $[\alpha]^{20}_{378} -153^\circ$ (c 0.32, MeOH); IR (CHCl₃) 1660 cm⁻¹ (C=O amide); ¹H NMR (CDCl₃) δ 0.85 (s, 9 H), 1.47 (d, 3 H, $J = 7.10$ Hz), 5.96 (q, 1 H, $J = 7.10$ Hz), 7.20 (m, 5 H, aromatics); mass spectrum is in accord with the structure.

X-ray Analysis of Lactam 4a. Single crystals grown from a chloroform-ethanol 90/10 solution of C₁₈H₂₇NO are monoclinic, space group $P2_1$ with $a = 10.767$ (8), $b = 6.584$ (3), and $c = 11.666$ (5) Å, $\beta = 100.41$ (5)°, $V = 813.4$ (8) Å³, $Z = 2$, $M_r = 273.40$, $\rho(\text{calcd}) = 1.12 \text{ Mg m}^{-3}$.

A total of 1321 reflections were collected, of which 1124 were considered as having been observed and were included in the refinement. All the experimental details that are not explicitly mentioned are the same as for oxaziridine **3**. For H atoms, B was 7.4 Å². The final conventional R index was 0.041.

Registry No. **1**, 98-53-3; (*S*)-**2**, 81583-85-9; **3**, 81583-86-0; **4a**, 81583-87-1; (–)-(*S*)- α -phenylethylamine, 2627-86-3.

Supplementary Material Available: Tables of the final thermal parameters and observed and calculated structure factors for oxaziridine **3** and lactam **4a** (12 pages). Ordering information is given on any current masthead page.

Determination of Addition Rates of Benzenethiyl Radicals to Alkynes by Flash Photolysis. Structures of Produced Vinyl-Type Radicals

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Abstract: The addition rate constants (k_1) of substituted benzenethiyl radicals to $\text{CH}\equiv\text{CR}$ ($R = \text{Ph}$, $n\text{-C}_3\text{H}_7$, and COOCH_3) have been determined by flash photolysis. The Hammett reaction constant (ρ^+) was estimated for each alkyne: $\rho^+(\text{CH}\equiv\text{CPh}) = +1.38$, $\rho^+(\text{CH}\equiv\text{CC}_3\text{H}_7) = +1.34$, and $\rho^+(\text{CH}\equiv\text{CCOOCH}_3) = +1.28$. A small ρ^+ value for $\text{CH}\equiv\text{CCOOCH}_3$ was attributed to a decrease in the polar effect in the transition state. Similar ρ^+ values were estimated for the corresponding alkenes. A small difference in the ρ^+ values suggests that the reactivities of the alkynes and alkenes toward a thiyl radical may be mainly determined by the thermodynamic stabilities of the produced radicals ($\text{PhSCH}=\dot{\text{C}}\text{R}$ and $\text{PhSCH}_2\dot{\text{C}}\text{HR}$). The rate constants (in $\text{M}^{-1} \text{ s}^{-1}$) for the benzenethiyl radical were as follows: $k_1(\text{CH}_2=\text{CHPh}) = 2.0 \times 10^7$, $k_1(\text{CH}\equiv\text{CPh}) = 7.9 \times 10^5$, $k_1(\text{CH}_2=\text{CHCOOCH}_3) = 2.7 \times 10^5$, $k_1(\text{CH}\equiv\text{CC}_3\text{H}_7) = 1.4 \times 10^6$, $k_1(\text{CH}_2=\text{CHC}_4\text{H}_9) = 1.0 \times 10^4$, and $k_1(\text{CH}\equiv\text{CCOOCH}_3) = 8.3 \times 10^3$. The unpaired electron of $\text{PhSCH}=\dot{\text{C}}\text{COOCH}_3$ may be localized, whereas the unpaired electron of $\text{PhSCH}_2\dot{\text{C}}\text{HCOOCH}_3$ is stabilized by the interaction with the ester group. The stability of $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ is intermediate between the linear π radical and the localized σ radical.

Thiols and hydrogen bromide add to alkynes via a free-radical mechanism to yield substituted alkenes.^{1,2} The addition of radicals to a triple bond yields a vinylic radical; the stereoselectivity and reactivity are controlled by the structure of the vinylic radical. The relative reactivities of substituted alkynes and alkenes toward the methyl acrylate radical or the acrylonitrile radical estimated from the copolymer compositions by Doak³ were in agreement with those toward the methyl radical estimated by Gazith and Szwarc;⁴ styrene (3.5–4.5), phenylacetylene (1.0), 1-hexyne (0.05–0.06), and 1-hexene (0.02–0.07). Fairly high reactivity of phenylacetylene compared to 1-hexyne was attributed to higher resonance stabilization of the α -phenyl vinylic radical.^{3,4} This conclusion seems to be compatible with that from the ESR studies^{5,6} or some stereochemical studies,^{7–10} suggesting a linear

π radical for the α -phenyl vinylic radical. In this paper, however, we will report our finding that the absolute rate constants for the addition reactions of the benzenethiyl radicals to phenylacetylene estimated by flash photolysis are intermediate between styrene and 1-pentyne. We will discuss the relation between the rate constants and the structures of the vinylic radicals after examining the polar effects in the transition state of the addition reactions.

Results and Discussion

The para-substituted benzenethiyl radicals were produced by xenon flash decomposition of the corresponding disulfides; transient absorption bands at ca. 500 nm were ascribed to the thiyl radicals.^{11–13} They decayed with second-order kinetics, suggesting recombination (k_r) to produce the disulfides; from the slopes of the second-order plots ($2k_r/\epsilon$, where ϵ refers to the molar extinction coefficient of the thiyl radical), the concentrations of the thiyl radicals produced by one flash exposure were estimated to be $\sim 10^{-7}$ – 10^{-6} M on the basis of the assumption of the diffusion-

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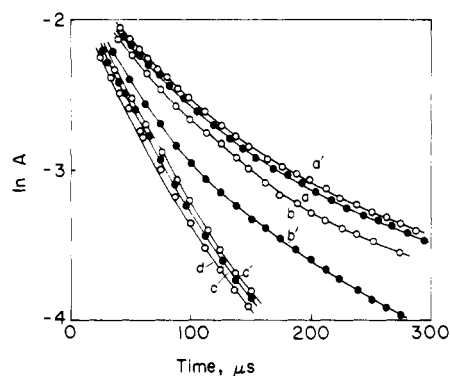


Figure 1. First-order plots for the decay curves of $p\text{-ClC}_6\text{H}_4\text{S}^\bullet$ (at 515 nm) in benzene (a–d) or in toluene (a'–c'); (a and a') in degassed solution, (b and b') in degassed solution with phenylacetylene (7.3×10^{-3} M), (c and c') addition of oxygen (1.0×10^{-3} M) to solution b or b', and (d) $[\text{O}_2] = 1.9 \times 10^{-3}$ M in solution b.

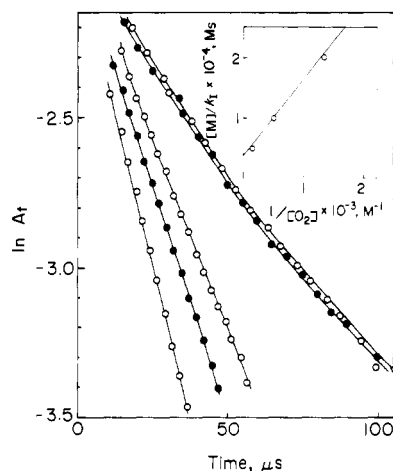
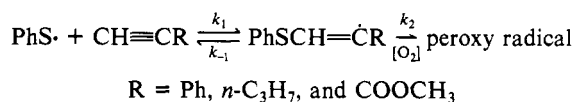


Figure 2. First-order plots for the decay curves of $p\text{-}t\text{-C}_4\text{H}_9\text{C}_6\text{H}_4\text{S}^\bullet$ (at 505 nm) in benzene; (a) in degassed solution, (b) in degassed solution with methyl acrylate (1.4×10^{-1} M), (c) addition of oxygen (1.3×10^{-3} M) to solution b, (d) $[\text{O}_2] = 1.9 \times 10^{-3}$ M in solution b, and (e) $[\text{O}_2] = 1.0 \times 10^{-2}$ M in solution b. Insert: Plot of $[\text{CH}_2=\text{CHCOOCH}_3]/k_1$ vs. $1/[\text{O}_2]$.

controlled rate. Since second-order kinetics were also observed in aerated solutions ($[\text{O}_2] = 1.9 \times 10^{-3}$ M in benzene),¹⁴ the reactivities of the thiyl radicals toward molecular oxygen are low. Figure 1 shows the effects of the concentrations of oxygen and phenylacetylene on the first-order plots of decay of $p\text{-ClC}_6\text{H}_4\text{S}^\bullet$ in benzene or in toluene. On the addition of phenylacetylene to a degassed solution, decay of the thiyl radical was accelerated slightly (Figure 1a,b). The addition of oxygen to benzene solution containing phenylacetylene caused an acceleration in the decay rate, and decay kinetics approached first order (Figure 1c). This suggests the reversibility of the addition process in which oxygen acts as a selective trap to the carbon-centered radical (Scheme I).

Scheme I



Addition products of the benzenethiyl radicals to alkynes have been identified by Oswald et al.¹⁵ The decay rate of the thiyl radical in the presence of phenylacetylene in degassed toluene solution (Figure 1b') was accelerated compared to that in degassed

Table I. Addition Rate Constants (k_1), Reverse Rate Constants (k_{-1}/k_2), and Equilibrium Constants (Kk_2) for the Reactions of $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ toward Methyl Acrylate and k_1 Values for 1-Hexene in Benzene at $23 \pm 1^\circ\text{C}^a$

X	$\text{CH}_2=\text{CHCOOCH}_3$			$\text{CH}_2=\text{CHC}_4\text{H}_9$, $k_1, \text{M}^{-1} \text{s}^{-1}$
	$k_1, \text{M}^{-1} \text{s}^{-1}$	$k_{-1}/k_2, \text{M}$	$Kk_2, \text{M}^{-2} \text{s}^{-1}$	
Br	3.9×10^5	1.3×10^{-3}	3.1×10^8	1.2×10^4
Cl	4.9×10^5	3.2×10^{-3}	1.5×10^8	1.5×10^4
H	2.7×10^5	1.2×10^{-3}	3.8×10^8	1.0×10^4
CH_3	1.6×10^5	2.9×10^{-3}	5.6×10^7	4.2×10^3
$t\text{-C}_4\text{H}_9$	1.4×10^5	1.5×10^{-3}	9.3×10^7	3.5×10^3
CH_3O	3.1×10^4	7.5×10^{-3}	4.2×10^6	5.7×10^2

^a Estimation errors are ca. 10%.

Table II. Addition Rate Constants ($k_1, \text{M}^{-1} \text{s}^{-1}$) of $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ toward $\text{CH}=\text{CR}$ ($\text{R} = \text{Ph}, n\text{-C}_3\text{H}_7$, and COOCH_3) in Benzene at $23 \pm 1^\circ\text{C}^a$

X	$\text{CH}=\text{CPh}$	$\text{CH}=\text{CC}_3\text{H}_7$	$\text{CH}=\text{CCOOCH}_3$
Br	2.1×10^6	2.1×10^4	1.6×10^4
Cl	1.1×10^6	2.0×10^4	1.5×10^4
H	7.9×10^5	1.4×10^4	8.3×10^3
CH_3	3.7×10^5	5.3×10^3	3.4×10^3
$t\text{-C}_4\text{H}_9$	3.4×10^5	6.4×10^3	3.8×10^3
CH_3O	8.1×10^4	1.3×10^3	1.1×10^3

^a Estimation errors are ca. 10%.

benzene (Figure 1b). This suggests that the shift of the equilibrium to the product side was caused by the hydrogen abstraction of $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ from toluene.

Figure 2 shows the first-order plots for the reaction between the thiyl radical and alkenes such as methyl acrylate; the decay curve in the presence of methyl acrylate in degassed solution (Figure 2b) seems to be exactly the same as that without methyl acrylate (Figure 2a). In Figure 2c–e, a clear dependence of the decay rates upon the oxygen concentration was seen. Since the concentration of the thiyl radicals produced by one flash exposure was very low ($\sim 10^{-7}$ – 10^{-6} M), both the concentrations of alkenes or alkynes ($\sim 10^{-4}$ – 10^{-1} M) and oxygen ($\sim 10^{-4}$ – 10^{-2} M) were kept constant during the reaction. The first-order rate constant (k_1), which can be estimated from the slope of the first-order plot, can be expressed in eq 1 and 2 on the basis of the steady-state assumption (M refers to alkenes or alkynes).¹² When the con-

$$k_1 = k_1\{1 - k_{-1}/(k_{-1} + k_2[\text{O}_2])\}[M] \quad (1)$$

$$[M]/k_1 = 1/k_1 + k_{-1}/k_1k_2[\text{O}_2] \quad (2)$$

centrations of O_2 and M were low, the decay kinetics was mixed order, consisting of second order ($k_1[\text{PhS}^\bullet]^2$) and first order ($k_1[\text{PhS}^\bullet]$). In this case, the k_1 value could be estimated from graphic^{12,16} or computer simulation methods.^{13,17} The plot of $[\text{CH}_2=\text{CHCOOCH}_3]/k_1$ vs. $1/[\text{O}_2]$ yielded a straight line (insert in Figure 2); the k_1 value was estimated from the intercept, and the reverse rate constant (k_{-1}) and the equilibrium constant ($K = k_1/k_{-1}$) were estimated from the slope in the forms of k_{-1}/k_2 and Kk_2 . These values obtained for methyl acrylate are summarized in Table I. Since the dependencies of $[\text{O}_2]$ upon the decay curves for 1-hexene were small, the k_1 values were estimated from the $k_1/[M]$ values in aerated solution; in eq 2 the first term may be larger than the second term. The k_1 and k_{-1}/k_2 values for styrene have been reported in our previous paper.¹⁸

Dependencies of $[\text{O}_2]$ upon the decay curves of the thiyl radicals in the presence of phenylacetylene were small (Figure 1c,d). This behavior is attributable to the high reactivity of $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ toward oxygen since a large k_2 value makes the second term in eq 2 small compared to the first term. Therefore, the $k_1/[\text{CH}=\text{CPh}]$ value in aerated solution (Figure 3) was ascribed to

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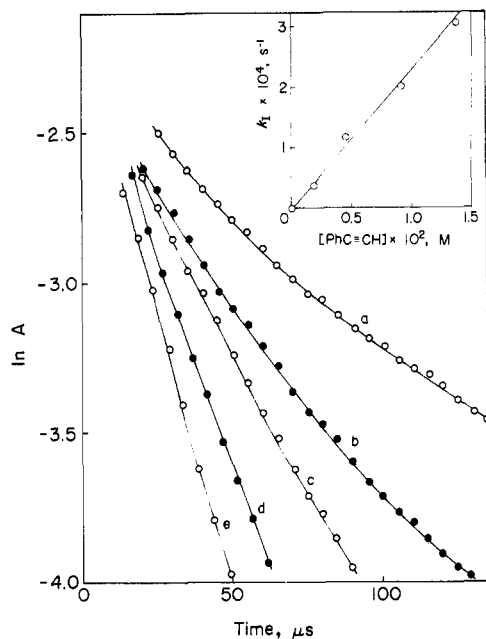


Figure 3. First-order plots for decay of $p\text{-BrC}_6\text{H}_4\text{S}^\bullet$ at 515 nm in aerated benzene ($[\text{O}_2] = 1.9 \times 10^{-3} \text{ M}$); $[\text{CH}\equiv\text{CPh}]$: (a) 0, (b) $1.8 \times 10^{-3} \text{ M}$, (c) $4.6 \times 10^{-3} \text{ M}$, (d) $9.1 \times 10^{-3} \text{ M}$, and (e) $1.4 \times 10^{-2} \text{ M}$. Insert: pseudo-first-order plot.

the k_1 value. These k_1 values are summarized in Table II, in which the k_1 values for $\text{CH}\equiv\text{CC}_3\text{H}_7$ and $\text{CH}\equiv\text{CCOOCH}_3$ estimated in a similar manner are also shown.

For assessment of the contribution of the polar effect in the transition state of the reaction to the reactivity, the $\log k_1$ values are plotted vs. the Hammett constants of the para substituents of the benzenethiyl radicals. The linear correlations are observed in the plots vs. σ^+ (Figure 4); the Hammett reaction constants (ρ^+) for the alkynes and alkenes were estimated in the range of +1.20–1.51. A line was obtained in the plots of $\log Kk_2$ for methyl acrylate vs. σ^+ ($\rho^+(Kk_2) = \text{ca.} +1.40$). The variation of $\log Kk_2$ with the change of X in $p\text{-XC}_6\text{H}_4\text{S}^\bullet$ for each monomer may be thought of as a relative measure of the thermodynamic stabilities of $p\text{-XC}_6\text{H}_4\text{S}^\bullet$, since both the k_2 value and the thermodynamic stability of $p\text{-XC}_6\text{H}_4\text{SCH}_2\text{CHR}$ are independent of the substituent X. If the proportional constant (α) in the linear free-energy relationship ($\rho^+(\text{reactivity}) = \alpha\rho^+(\text{stability})$) was chosen to be +0.75, as reported by Semenov for the endothermic reactions,¹⁹ it is suggested that a large part of the $\rho^+(\text{reactivity})$ value is governed by the polar effect in the stabilities of the reactant thiyl radicals. Thus, the remaining small part of the ρ^+ values for the reactivities may be attributed to the contribution of the polar resonance structures in the transition state such as $[p\text{-XC}_6\text{H}_4\text{S}^\bullet, \text{CH}_2=\text{CHR}^+]$ and $[p\text{-XC}_6\text{H}_4\text{S}^\bullet, \text{CH}\equiv\text{CR}^+]$. Smaller $\rho^+(k_1)$ values for $\text{CH}\equiv\text{CCOOCH}_3$ and $\text{CH}_2=\text{CHCOOCH}_3$ than those for other alkynes and alkenes may be interpreted by a decrease in the latter contribution with the electron-withdrawing ester group.²⁰ Since the intersection of the lines in the Hammett plots was not seen except in the plots for $\text{CH}_2=\text{CHC}_4\text{H}_9$ and $\text{CH}\equiv\text{CCOOCH}_3$, the reactivities of the alkynes and alkenes toward a thiyl radical were mainly determined by the stabilities of the radicals produced such as $\text{PhSCH}=\text{CR}$ and PhSCH_2CHR .

The reactivity ratio of $k_1(1\text{-hexene})/k_1(\text{phenylacetylene})$ toward $\text{C}_6\text{H}_5\text{S}^\bullet$ was estimated to be 0.018, which is in good agreement with that toward the acrylonitrile radical (0.02) estimated by Doak.³ The ratio of $k_1(\text{styrene})/k_1(\text{phenylacetylene})$ toward $\text{C}_6\text{H}_5\text{S}^\bullet$ was 25, which is greater than the reported values (3.5–4.5),^{3,4} a part of this difference may be attributable to the properties of the attacking radicals and part to estimation errors.

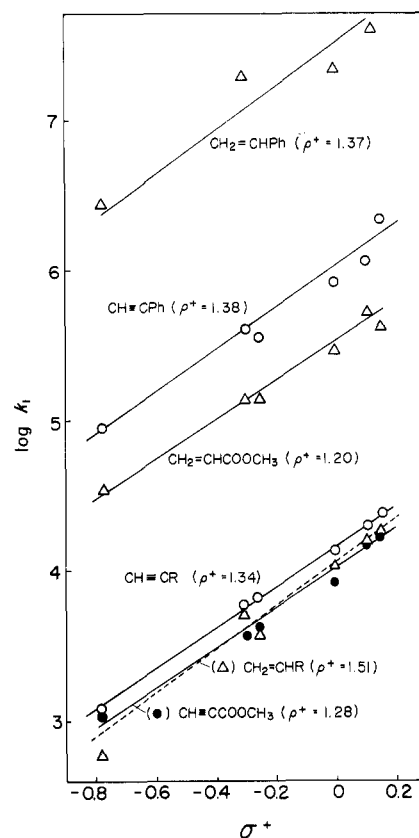


Figure 4. Hammett plots of $\log k_1$ vs. σ^+ ; the data for styrene were cited from ref 18.

On the basis of our data, we discuss the relation between the reactivities and the structures of the adduct radicals. The stabilities of the carbon-centered radicals formed from the alkenes are well established. An unpaired electron is in the 2p orbital of the sp^2 -hybridized carbon, and the stabilities increase with the Q values of the monomers as follows:²¹ $\text{PhSCH}_2\text{CHC}_4\text{H}_9 < \text{PhSCH}_2\text{CHCOOCH}_3 < \text{PhSCH}_2\text{CHPh}$. The order of the k_1 values of the alkenes toward each thiyl radical is in agreement with the above order. A number of studies indicate that the vinylic radicals substituted by the alkyl group such as $\text{PhSCH}=\text{CC}_3\text{H}_7$ are the σ radicals where an unpaired electron is located in sp^2 orbital.²² A similarity of the reactivity of 1-pentyne toward each thiyl radical to the corresponding one for 1-hexene suggests that the stability of an unpaired electron in the localized sp^2 orbital is similar to that in the localized p orbital. The slightly higher reactivity of 1-pentyne than 1-hexene may be ascribed to the larger frequency factor of the cylindrical symmetry of a triple bond.⁴

The k_1 value for $\text{CH}\equiv\text{CCOOCH}_3$ toward $\text{C}_6\text{H}_5\text{S}^\bullet$ is similar to that for 1-pentyne, whereas the k_1 value for $\text{CH}_2=\text{CHCOOCH}_3$ is greater than that for 1-hexene by a factor of ca. 30. This shows that an unpaired electron of $\text{PhSCH}_2\text{CHCOOCH}_3$ is stabilized by the interaction with the ester group, whereas the electron of $\text{PhSCH}=\text{CCOOCH}_3$ is not stabilized. If $\text{PhSCH}=\text{CCOOCH}_3$ is ascribed to the linear π radical, as suggested from the ESR studies and the MO calculations,^{6,23} the large reactivity ratio ($k_1(\text{CH}_2=\text{CHCOOCH}_3)/k_1(\text{CH}\equiv\text{CCOOCH}_3) = \text{ca.} 30$) must be attributed to the faint difference between the p orbital on the sp^2 -hybridized carbon and that on the sp -hybridized carbon. From our data for the reactivities, there is a possibility that $\text{PhSCH}=\text{CCOOCH}_3$ is the localized σ radical.^{24,25}

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The k_1 value for phenylacetylene toward each thiyl radical is smaller than the corresponding value for styrene by a factor of ca. 25, whereas it is larger than that for 1-pentyne by a factor of ca. 70. If $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ is the linear π radical,^{5,6,22} the reactivity ratio of phenylacetylene to styrene must be attributed to the different conjugation properties of the π radicals, which involve the sp - and sp^2 -hybridized carbons, respectively. However, the spin densities of the phenyl ring of the α -styryl radical calculated on the assumption of the linear π radical were practically the same as those of the benzyl radical;^{23,26} thus, such difference in the conjugation properties between both π radicals is not so large. The high reactivity of $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ toward oxygen or hydrogen donors, as deduced from Figure 1, was not observed in the case of styrene or methyl acrylate (Figure 2); this seems to correspond to an increase in the s character of the half-filled orbital of $\text{PhSCH}=\dot{\text{C}}\text{Ph}$. If $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ is the σ radical, we must consider the stabilization of an unpaired electron in the sp^2 orbital by the interaction with the adjacent phenyl ring through space²⁷ or through σ bonds; however, there may be a doubt whether such interaction is strong enough to explain the high reactivity of phenylacetylene compared to 1-pentyne (ca. 70 times). From our

data for the reactivities, another possible explanation, that the actual α -styryl-type radical has an intermediate character between the localized σ radical and the linear π radical, was suggested.

In summary, we have estimated the absolute rate constants for the addition reactions of $p\text{-XC}_6\text{H}_4\text{S}\cdot$ to $\text{CH}\equiv\text{CR}$ and $\text{CH}_2=\text{CHR}$ ($\text{R} = \text{Ph}$, alkyl, and COOCH_3) by flash photolysis. From the Hammett plots, it was suggested that the reactivities are mainly determined by the stabilities of the adduct radicals. An unpaired electron of $\text{PhSCH}_2\text{CHCOOCH}_3$ is stabilized with the interaction with the ester group, whereas $\text{PhSCH}=\dot{\text{C}}\text{COOCH}_3$ may be a localized σ radical. $\text{PhSCH}=\dot{\text{C}}\text{Ph}$ may have an intermediate character between the σ radical and the π radical.

Experimental Section

Commercially available phenylacetylene, 1-pentyne, methyl propiolate, 1-hexene, and methyl acrylate were distilled under reduced pressure before use. Diphenyl disulfides were purified by recrystallization from ethanol. Solvents were of spectrophotometric grade. The oxygen concentration in solution was controlled by dissolving oxygen under an appropriate pressure after degassing up to 10^{-5} torr; the oxygen concentration was calculated from Henry's law by using the reported oxygen concentration in aerated benzene (1.9×10^{-3} M).¹⁴ The flash photolysis experiments were made at room temperature controlled at $23 \pm 1^\circ\text{C}$. A xenon flash photolysis apparatus of standard design was used; the flash energy was ca. 100 J, and the half-duration of the xenon flash lamps was ca. 10 μs .

Registry No. $p\text{-BrC}_6\text{H}_4\text{S}\cdot$, 31053-90-4; $p\text{-ClC}_6\text{H}_4\text{S}\cdot$, 31053-91-5; $\text{C}_6\text{H}_5\text{S}\cdot$, 4985-62-0; $p\text{-CH}_3\text{C}_6\text{H}_4\text{S}\cdot$, 31053-92-6; $p\text{-(t-C}_4\text{H}_9\text{)C}_6\text{H}_4\text{S}\cdot$, 81372-23-8; $p\text{-CH}_3\text{OC}_6\text{H}_4\text{S}\cdot$, 31053-93-7; $\text{CH}_2=\text{CHCOOCH}_3$, 96-33-3; $\text{CH}_2=\text{CHC}_4\text{H}_9$, 592-41-6; $\text{CH}\equiv\text{CPh}$, 536-74-3; $\text{CH}\equiv\text{CC}_3\text{H}_7$, 627-19-0; $\text{CH}\equiv\text{CCOOCH}_3$, 922-67-8.

(25) There is a possibility that the prediction of the σ and π radicals from the MO energies is reversed by the methods used for the MO calculations: Kasai, P. H.; Clark, P. A.; Whipple, E. B. *J. Am. Chem. Soc.* **1970**, *92*, 2640.

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(27) Intramolecular charge-transfer interaction between the electron-deficient σ orbital and the electron-rich phenyl ring can be considered as a through-space interaction. In the case of $\text{PhSCH}=\dot{\text{C}}\text{COOCH}_3$, such interaction cannot be expected since both the carbonyl double bond and the σ orbital are electron deficient.

Determination of the Orientation of Aromatic Molecules Adsorbed on Platinum Electrodes.^{1,2} The Effect of Solute Concentration

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Abstract: Accurate measurements of the amounts of aromatic molecules adsorbed on smooth polycrystalline platinum electrodes in aqueous solutions are reported as a function of concentration. The measurements were made by electrochemical methods using thin-layer cells. A plot of adsorbed amount against concentration shows that most of the subject compounds display multiple plateaus separated by abrupt transitions to higher densities at higher concentrations. Comparison of plateau values with model calculations, based upon covalent and van der Waals radii tabulated by Pauling, reveals that a series of definite orientations are adopted as the adsorbate concentration is increased; each individual orientation was stable over an appreciable range of concentration. Twenty-six compounds, representing a variety of structures and chemical properties, were studied: simple diphenols; alkyldiphenols; polyhydroxybenzenes; halogenated diphenols; N heteroaromatics; diphenols having surface-active side chains; polycyclic phenols and quinones; and hydroquinone mercaptans.

The orientation of aromatic molecules adsorbed from solution on smooth polycrystalline platinum electrodes has been studied as a function of adsorbate molecular structure and supporting electrolyte.^{1,2} At low concentrations (≤ 0.1 mM), in the absence of competing surfactants, aromatic molecules generally adopt a flat orientation on the Pt surface. Deviations from this orientation occur for heteroaromatics and when electronegative or surface-

active functional groups are present on the aromatic ring.¹ Also, when a layer of molecules adsorbed in the flat orientation was exposed to a solution of a surface-active anion, iodide, reorientation to an edgewise orientation occurred for most of the compounds.² The present article describes the concentration dependence of the orientations of 26 aromatic compounds adsorbed on platinum.

Measurement of Adsorbed Aromatics

An accurate method, based upon thin-layer electrochemistry, for measurement of the amount of aromatic compound adsorbed on Pt has been described.¹ Only details unique to the present study

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