Substituent Effects on the Free-radical Addition Reactions of Arylthiyl Radicals with Arylacetylenes

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Absolute rate constants for addition reactions of arylthiyl radicals ($YC_6H_4S^\bullet$) to arylacetylenes ($XC_6H_4C{\equiv}CH$) have been determined by a flash-photolysis method. The rate constants (in $dm^3\ mol^{-1}\ s^{-1}$) vary from 1.0×10^5 (X = *m*-NO_2 and Y = *p*-MeO) to 1.0×10^7 (X = *p*-MeO and Y = *p*-Br). For all arylthiyl radicals, a Hammett plot of the σ^+-constants for the X-substituents yields negative $\rho^+(Y)$ values. The $\rho^+(Y)$ values depend also on the Y-substituents on the arylthiyl radicals [$\rho^+(Y) = -0.22$ for Y = *p*-MeO and $\rho^+(Y) = -0.53$ for Y = *p*-Br]. These $\rho^+(Y)$ values are slightly smaller than the $\rho^+(Y)$ values reported for the corresponding arenesulphonyl radicals, reflecting the low electrophilicity of the arylthiyl radicals. On the other hand, for each arylacetylene a Hammett plot of the rate constants for $YC_6H_4S^\bullet$ *vs.* $\sigma^+(Y)$ yields positive $\rho^+(X)$ values which increase with the increasing electron density on the triple bond.

Since the importance of the polar effect in free-radical reactions was first revealed, the reactivity of free radicals with various substances has been extensively studied. In addition to the well known resonance stabilization of the attacking radicals and product radicals, the polar resonance contribution to the transition state has been taken into consideration.[1–4] The Hammett correlations which yield information about the polar effects have been systematically investigated for the addition reactions of arenesulphonyl radicals to substituted styrenes [5,6] and arylacetylenes.[7] Compared with the electrophilic sulphonyl radicals, less polar transition states are anticipated for the addition reactions of thiyl radicals. Although the addition reactions of thiyl radicals to alkenes supported a polar nature for the free-radical reaction,[8,9] systematic investigation has not been reported.

In this study, we determined the absolute rate constants for the addition reactions of several arylthiyl radicals to arylacetylenes taking the reversibility into consideration by using flash-photolysis techniques. It has been found that the absolute rate constants for the addition reactions of the arylthiyl radicals thus determined have an accuracy which permits an examination of substituent effects[10–13] and solvent effects.[14,15] By means of a determination of the absolute rates of the reactions between arylthiyl radicals and substituted arylacetylenes, we hoped to be able to give information about the reactivity and selectivity of these compounds.

Results and Discussion

The transient absorption bands which appear in the visible region (490–520 nm) from flash photolysis of diaryl disulphides were attributed to the corresponding arylthiyl radicals (Scheme 1).[16,17] An example is shown for *p*-$BrC_6H_4S^\bullet$ in the insert of Figure 1. It has recently been pointed out that the transient absorption bands attributed to adducts of $ArS^\bullet$ and ArSSAr appear in the u.v. region when the concentrations of ArSSAr are > *ca.* 10^{-4} mol dm^{-3}.[17] Since we used a dilute solution (<2 × 10^{-5} mol dm^{-3} of ArSSAr) and the positions of the absorption bands of $ArS^\bullet$ do not overlap with those of the adducts, the decay kinetics of $ArS^\bullet$ show no interference. The first-order decay plots are shown in Figure 1. The decay of the arylthiyl radical in the absence of arylacetylene [decay curve (*a*)] obeys second-order kinetics (1/absorbance *vs.* time), and so a recombination reaction to reform the disulphide is suggested. Even in the presence of oxygen, the decay rate was not affected, suggesting a low reactivity of $ArS^\bullet$ towards oxygen.[18,19] On addition of arylacetylene in a de-gassed solution of benzene the observed acceleration of the decay rate of $ArS^\bullet$ was not large, as already pointed out in our previous study;[20] this was attributed to the reversible addition process of the arylthiyl radical to acetylenes. Both the addition reaction rate ($k_1[ArS^\bullet][ArC{\equiv}CH]$) and its reverse rate ($k_{-1}[ArSCH{=}\dot{C}Ar]$) are faster than the recombina-

$$\tfrac{1}{2}\,ArSSAr \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} ArS^\bullet$$

Scheme 1.

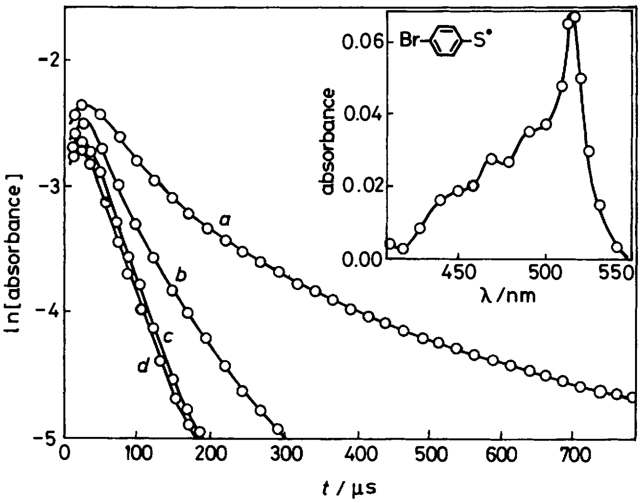


Figure 1. The plot of the first-order decay of *p*-$BrC_6H_4S^\bullet$ at 515 nm: (*a*) in cyclohexane without arylacetylene; (*b*), (*c*), and (*d*) with *p*-$MeOC_6H_4C{\equiv}CH$ (1.6 mol dm^{-3}) in degassed cyclohexane, in air-saturated solution, and in oxygen saturated solution, respectively. Insert: transient absorption spectrum after flash photolysis of (*p*-$BrC_6H_4)_2S_2$ (10^{-5} mol dm^{-3}).

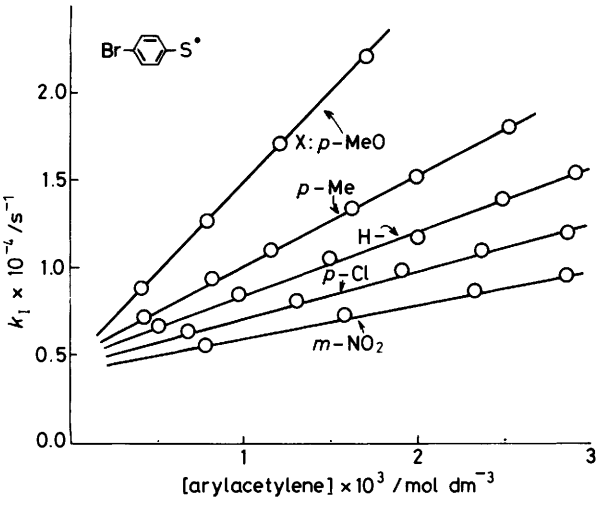


Figure 2. Pseudo-first order plots; slopes yield the second-order rate constants for the addition reactions of p-Br-$C_6H_4S^{\bullet}$ to $XC_6H_4C{\equiv}CH$. Intercept corresponds to the first-order component of the second-order recombination decay.

tion rate ($k_r[ArS^{\bullet}]^2$), which implies that the rate-determining step is the recombination reaction. These observations are shown in Scheme 2.

$$\tfrac{1}{2}\,\mathrm{ArSSAr} \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} \mathrm{ArS^{\bullet}} \underset{k_{-1}}{\overset{+[\mathrm{ArC{\equiv}CH}],\,k_1}{\rightleftharpoons}} \mathrm{ArSCH{=}\dot{C}Ar}$$

Scheme 2.

Since arylthiyl radicals with electron-withdrawing substituents interact with benzene,[15] we used cyclohexane as a non-interacting solvent in this study. In a de-gassed solution of cyclohexane containing an arylacetylene, the decay rate of ArS˙ increased [decay curve (*b*)] compared with the decay in de-gassed benzene, suggesting that the vinyl radical ($\mathrm{ArSCH{=}\dot{C}Ar}$) is quite reactive with cyclohexane (a hydrogen-atom abstraction reaction may occur). Since this phenomenon was not found for styrene, the reactivity of $\mathrm{ArSCH{=}\dot{C}HAr}$ is higher than that of $\mathrm{ArSCH_2\dot{C}HAr}$. This finding is shown in Scheme 3. On addition of molecular oxygen to this reaction system, the decay rates were further accelerated [decay curves (*c*) and (*d*)]. Since the arylthiyl radicals are unreactive towards oxygen, $\mathrm{ArSCH{=}\dot{C}Ar}$ was selectively scavenged by oxygen to yield the peroxyl radical (Scheme 4). Griesbaum *et al.* confirmed that the peroxyl radical changes into the monothiohemiacetal [ArSCH(OH)COAr].[21] The difference between decay curves (*b*) and (*c*) indicates that the reaction of $\mathrm{ArSCH{=}\dot{C}Ar}$ with oxygen is faster than that with cyclohexane. For de-gassed benzene solution up to 10^{-5} Torr,* the weak transient absorption bands appear in a longer-wavelength region than the absorption bands of ArS˙. These absorption bands are important only when arylacetylenes are used in high concentration. These transient absorption bands may be due to $\mathrm{ArSCH{=}\dot{C}Ar}$. In aerated solution, however, these bands disappear; thus, the decay kinetics of ArS˙ in aerated solution were not affected by these second transient species.

$$\tfrac{1}{2}\,\mathrm{ArSSAr} \overset{h\nu}{\rightleftharpoons} \mathrm{ArS^{\bullet}} \overset{+[\mathrm{ArC{\equiv}CH}],\,k_1}{\rightleftharpoons}$$
$$\mathrm{ArSCH{=}\dot{C}Ar} \xrightarrow{+[\mathrm{RH}]} \mathrm{ArSCH{=}CHAr}$$

Scheme 3.

$$\tfrac{1}{2}\,\mathrm{ArSSAr} \xrightarrow{h\nu} \mathrm{ArS^{\bullet}} \xrightarrow[k_1]{+[\mathrm{ArC{\equiv}CH}]}$$
$$\mathrm{ArSCH{=}\dot{C}Ar} \xrightarrow{+[\mathrm{O_2}]} \mathrm{ArSCH{=}C(O_2^{\bullet})Ar}$$

Scheme 4.

The first-order plots in an air-saturated solution [decay curve (*c*)] and in an oxygen saturated solution [decay curve (*d*)] are linear; since both slopes are similar, we adopted the slope of the first-order plot in air-saturated solution as the pseudo-first order rate constant (k_1). At low concentration of arylacetylene, the decay showed mixed-order kinetics consisting of first and second order; in such a case, k_1 was separated by the method described in the literature.[15,22]

Figure 2 shows the pseudo-first order plots (k_1 *vs.* [ArC≡CH]). The slopes yield the absolute rate constants for the addition reactions of the arylthiyl radicals to arylacetylenes. The addition-reaction rate constants for Scheme 5 are summarized in Table 1 for all the reactions shown below:

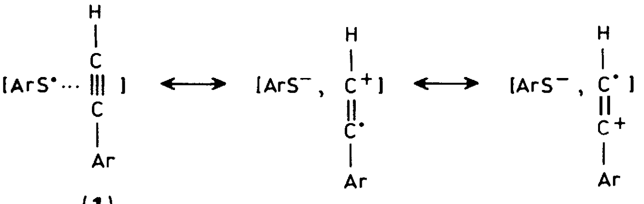
$$\mathrm{XC_6H_4C{\equiv}CH} + \mathrm{YC_6H_4S^{\bullet}} \xrightarrow{k_1} \mathrm{XC_6H_4\dot{C}{=}CHSC_6H_4Y}$$

X	Y
p-MeO	p-MeO
p-Me	p-Me
H	p-Bu^t
p-Cl	H
m-NO_2	p-Cl
	p-Br

Scheme 5.

The observed rate constants (in $dm^3\ mol^{-1}\ s^{-1}$) vary from 10^5 (m-$NO_2C_6H_4C{\equiv}CH$ and p-$MeOC_6H_4S^{\bullet}$) to 10^7 (p-$MeOC_6H_4C{\equiv}CH$ and p-$BrC_6H_4S^{\bullet}$). The rate constant for the reaction of PhS˙ with PhC≡CH (1.6×10^6) is smaller than that for PhS˙ with $PhCH{=}CH_2$ (2.7×10^7)[23] by a factor of *ca.* 1/20. From this large difference between addition-reaction rate constants, we assume that the orbital of the unpaired electron in $\mathrm{ArSCH{=}\dot{C}{-}Ar}$ is somewhat different from that in $\mathrm{ArSCH_2\dot{C}HAr}$.

Figure 3 shows the correlation between log k_1 and $\sigma^+(X)$ for reactions of different arylthiyl radicals with the same group of arylacetylenes. The negative Hammett reaction constants [$\rho^+(Y)$] indicate a polar transition state that may be represented by the resonance structures (**1**), (**2**), and (**3**).[1–4]



(**1**) (**2**) (**3**)

$$[\mathrm{ArS^{\bullet}}\cdots \mathrm{HC{\equiv}CAr}] \longleftrightarrow [\mathrm{ArS^-},\ \mathrm{H\overset{+}{C}{=}\dot{C}Ar}] \longleftrightarrow [\mathrm{ArS^-},\ \mathrm{H\dot{C}{=}\overset{+}{C}Ar}]$$

On introduction of electron-withdrawing substituents on the arylthiyl radicals, the $\rho^+(Y)$ constant increases (*vice versa* for electron-donating substituents). Since the Hammett relationships in Figure 3 were obtained from the absolute rate constants, we can deduce a reactivity–selectivity principle. With increasing reactivity of Y (p-Br > p-Cl > H > p-Bu^t > Me > p-MeO), the selectivities also increase. This clearly indicates that the reaction rates are determined by the contribution of the polar transition state rather than the reactivity–selectivity principle.

In Table 2, we summarize these $\rho^+(Y)$ values for the arylacetylenes, the values for substituted styrenes hitherto reported, and those for sulphonyl radicals. A comparison of the arylthiyl radicals with the arenesulphonyl radicals shows that

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* 1 Torr = 101 325/760 Pa.

Table 1. Rate constants for addition reactions of arylthiyl radicals ($YC_6H_4S^{\bullet}$) to arylacetylenes ($XC_6H_4C{\equiv}CH$) in cyclohexane at 23 °C.[a]

	$k_1 \times 10^{-5}/dm^3\ mol^{-1}\ s^{-1}$ of $YC_6H_4S^{\bullet}$					
$XC_6H_4C{\equiv}CH$	*p*-MeO	*p*-Me	*p*-Bu^t	H	*p*-Cl	*p*-Br
p-MeO	2.1	15	16	35	65	100
p-Me	1.5	7.5	9.0	22	38	54
H	1.3	5.4	6.8	16	26	38
p-Cl	1.2	5.0	6.5	12	20	28
m-NO_2	1.0	3.5	4.0	10	14	18

[a] The rate constants in benzene solution reported in the previous paper are about a half of the corresponding values in cyclohexane;[20] this phenomenon was ascribed to the solvent effect.[10]

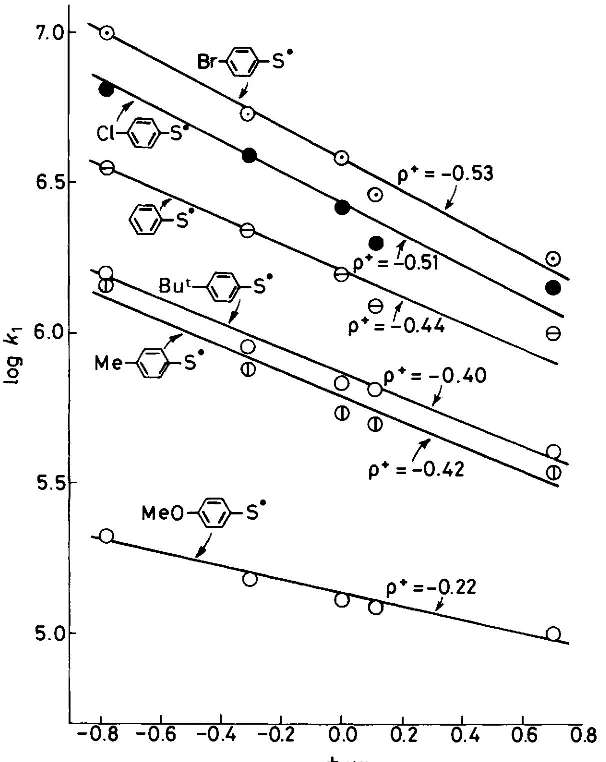

Figure 3. Hammett plots for the rate constants *vs.* σ^+ with variation of $XC_6H_4C{\equiv}CH$ for each $YC_6H_4S^{\bullet}$.

the $\rho^+(Y)$ values for arenesulphonyl radicals are slightly more negative than those of the corresponding arylthiyl radicals for both arylacetylenes and substituted styrenes. This indicates that the arenesulphonyl radicals are more electrophilic than the corresponding arylthiyl radicals. Since two oxygen atoms strongly withdraw the unpaired electron density on the sulphur atom, this tendency is reasonable; however, from the strong polarization of $S^+–O^-$, a greater electrophilicity for $ArSO_2^{\bullet}$ should be expected than those found in Table 2. It thus seems that the sulphur orbital in which the unpaired electron is involved is not strongly affected by the ionic polarization of $S^+–O^-$.

The sensitivity of electron-density to substituent is not very different between the double bond and the triple bond, although only a few $\rho^+(Y)$ values have been reported for reactions between $ArS^{\bullet}$ and styrenes. These results are compatible with the fact that the effect of substituent on the ^{13}C chemical shifts of arylacetylenes—which reflects the charge density of the carbon in the triple bond—is similar to that on substituted styrenes.[24,25]

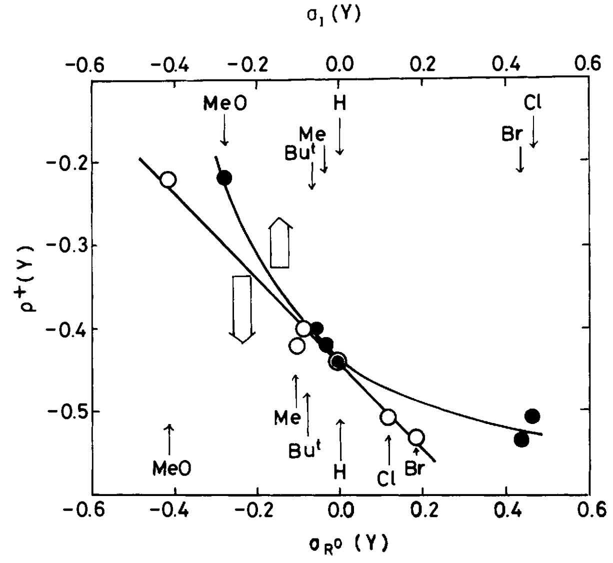

Figure 4. Correlation of ρ^+ obtained with variation of $XC_6H_4C{\equiv}CH$ for each $YC_6H_4S^{\bullet}$ [denoted as $\rho^+(Y)$] *vs.* the Taft substituent constants.

Figure 4 shows a plot of the $\rho^+(Y)$ values obtained from Figure 3 *vs.* the Taft substituents σ_I and $\sigma_{R°}$, in order to determine which is more effective, the resonance or the inductive effect. The linear relationship for $\sigma_{R°}$ is better than for σ_I. This may show that, even in the polar reaction transition state, resonance stabilization of the unpaired electron (or of the partially negative charge) on the arylthiyl radicals plays an important role.

Figure 5 shows the Hammett plots of log k_1 against $\sigma^+(Y)$ for $YC_6H_4S^{\bullet}$ for reactions with each arylacetylene. It is unusual that linear correlations are also found for Hammett plots with the same σ^+ constants used in Figure 3. With Hammett plots for $\sigma(Y)$, straight lines can be drawn from Y = *p*-Br to Y = *p*-Me, but points for Y = *p*-MeO deviate downward for all arylacetylenes. This suggests that a large interaction between the methoxy oxygen lone pair and sulphur unpaired electron stabilizes *p*-$MeOC_6H_4S^{\bullet}$.[26] Since the σ^+ constants can compensate for this interaction, we used the Hammett plots for $\sigma^+(Y)$ as shown in Figure 5.

The slopes in Figure 5 are positive for all arylacetylenes examined in this study. The $\rho^+(X)$ values are summarized in Table 3 together with the ^{13}C chemical shift for the β-carbon.[24] With electron-donating substituents on the arylacetylene, the $\rho^+(X)$ values increase; *vice versa* for electron-withdrawing substituents. These $\rho^+(X)$ values correspond to the sensitivity of the arylacetylene triple bond to the attacking electrophilic radicals. Since these sensitivities were determined by changing the attacking radicals, they may reflect the intrinsic electron densities (or polarizability) of the triple bonds of the arylacetylenes (*cf.* the e-values of the Alfrey–Price *Q*–e scheme and the β values of the Bamford–Jenkins α–β parameter for vinyl monomers).[27,28] In the case of the arylacetylenes, these dual parameters have not been reported, since reliable co-polymerization data were not obtained. Thus the $\rho^+(X)$ values obtained in this study become important. The relationship between these $\rho^+(X)$ values and the electron density of the triple bond, (which increases with decreasing ^{13}C chemical shift at $\delta_{C\beta}$) is seen in Figure 6.

Table 2. The $\rho^+(Y)$ values for addition reactions of the sulphur-centred radicals $[YC_6H_4S(O)_n^{\bullet}]$ obtained by changing the substituents X on arylacetylenes ($XC_6H_4C≡CH$) and substituted styrenes ($XC_6H_4CH=CH_2$).

	$\rho^+(Y)$ of $YC_6H_4SO_n^{\bullet}$						
	p-MeO	*p*-Me	*p*-Bu^t	H	*p*-Cl	*p*-Br	*m*-NO$_2$
n = 0; [ArS$^{\bullet}$]							
ArC≡CH	−0.22	−0.42	−0.40	−0.44	−0.51	−0.53	
ArCH=CH$_2$[a]				−0.26	−0.56		
n = 2; [ArSO$_2^{\bullet}$]							
ArC≡CH[b]	−0.53	−0.66		−0.58	−0.64		−0.93
ArCH=CH$_2$[c]	−0.35	−0.50			−0.75		−0.88

[a] Ref. 23. [b] Ref. 7. [c] Refs. 5 and 6.

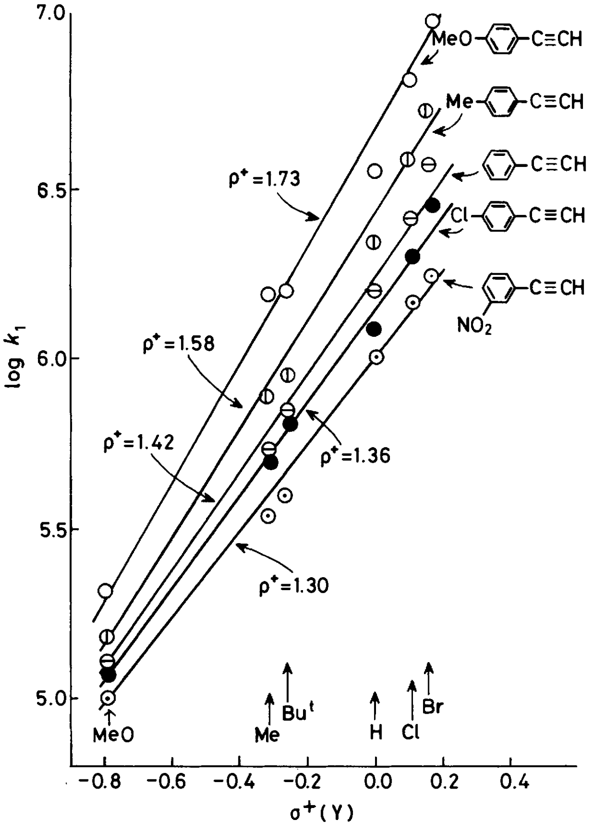

Figure 5. Hammett plot of the reaction rate constants with variation in the substituents $YC_6H_4S^{\bullet}$ for each $XC_6H_4C≡CH$.

Table 3. $\rho^+(X)$ and ^{13}C chemical shift ($\delta_{C\beta}$) values for the arylacetylenes.

$XC_6H_4C≡CH$	$\rho^+(X)$	$\delta_{C\beta}$[a]/p.p.m.
p-MeO	1.73	75.67
p-Me	1.58	76.36
H	1.42	77.06
p-Cl	1.36	78.03
m-NO$_2$	1.30	

[a] Ref. 24.

Experimental

Arylacetylenes were prepared by the methods described in the previous paper.[7] Diaryl disulphides were prepared from the appropriate thiol by the action of iodine. Cyclohexane used as a solvent was of spectroscopic grade.

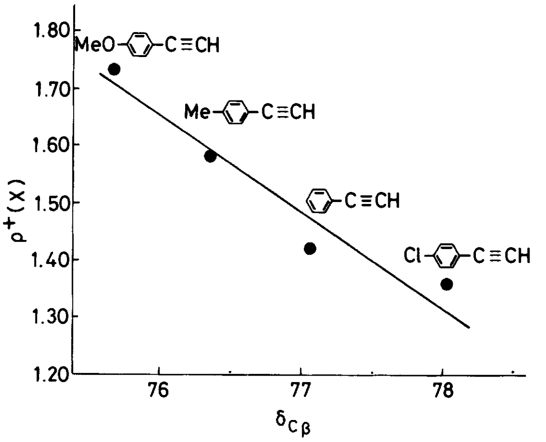

Figure 6. Correlation of $\rho^+(X)$ *vs.* ^{13}C chemical shift at the β-carbon of $XC_6H_4C≡CH$.

Flash-photolysis experiments were performed at 23 °C using an apparatus of standard design; the input energy into xenon flash lamps was *ca.* 65 J and the half-duration of the flash lamps (Xenon Co. N-815C) was *ca.* 8 μs. Diaryl disulphides were flash-photolysed in a cylindrical quartz cell with light of wavelength 330–420 nm, selected by light filters. In this wavelength region, the absorption of the arylacetylenes was negligible.

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