Captodative Effect on Rates of Addition Reactions of Arylthiyl Radicals to Disubstituted Olefins

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The rate constants for the addition reactions of the *para*-substituted phenylthiyl radicals ($ZC_6H_4\dot{S}$) to disubstituted olefins ($CH_2{=}CXY$) have been determined by the flash photolysis method. The substituents X and Y in the olefins were chosen in order to obtain kinetic evidence for a captodative effect on the free-radical addition reactions in which the captodative radicals ($PhSCH_2\dot{C}XY$) were formed. When X was an electron-withdrawing (captive) group such as CN, electron-donating (dative) substituents (Y) accelerated the reactions of the olefins with the arylthiyl radicals. The order of acceleration is as follows: $NR_2 > OR > Cl > OC({=}O)CH_3 > CH_3 > H$. This result was interpreted in terms of a lowering of the activation energy caused by captodative stabilization of the transition state. For substituted propenes [$CH_2{=}C(Y)CH_3$], the rate constants for addition increase with the electron-withdrawing power of the substituents Y. Localization energies for captodative-substituted olefins, from MO calculations, are well correlated with the kinetic data obtained in this study.

The captodative effect for radical stabilization which is caused by the combined interaction of electron-withdrawing (captive) and electron-donating (dative) substituents on the radical centre is of interest in free-radical chemistry.[1,2] This effect has been well established by theoretical considerations including MO calculations.[3-5] Experimentally, e.s.r. studies indicate that delocalization of the unpaired electron (spin) on the radical centre into the substituents is promoted by captodative substituents.[6] In spite of results from product analysis showing that captodative radicals mainly yield bis-adducts,[1,2] only a few kinetic studies of the captodative effect have been reported. Korth *et al.* reported that captodative-substituted methyl radicals dimerize with the rates close to the diffusion-controlled limit.[7,8]

Kinetic studies on reactions producing captodative radicals are further limited. In Gieses' preliminary observations cited in Viehe's review,[1] it is indicated that the relative rates for addition reactions of an alkyl radical to substituted acrylonitriles [$CH_2{=}C(Y)CN$] increase only when the substituents Y have electron-donating (dative) power with strong conjugation ability.

In this study, we measured the rate constants for free-radical addition reactions to captodative-disubstituted olefins. Arylthiyl radicals have been chosen as attacking radical, since the absolute rate constants could be easily determined by flash photolysis.[9-11] In order to distinguish the captodative effect from other factors controlling the radical reactivities such as the polar effect, the substituent effects of the attacking radicals for each olefin have also been examined.

Results and Discussion

Transient Absorption Bands of Arylthiyl Radicals.—The method for the determination of the rate constants for the addition reactions of the arylthiyl radicals to various olefins by flash photolysis has been described in our previous papers.[9,11] The arylthiyl radicals were produced by flash photolysis of the corresponding disulphides. Figure 1 shows the transient spectra produced by the photolysis of bis-*p*-chlorophenyl disulphide and its corresponding thiol; the transient absorption band at 515 nm is common to both radical sources, confirming the assignment to the *p*-chlorophenylthiyl radical.[9] The transient band at 325 nm was observed only for the disulphide, but not for the thiol. The transient absorption bands in the u.v. region produced from a concentrated solution of disulphide were examined by laser photolysis, modulation spectroscopy, and pulse radiolysis of disulphides;[12,13] it was revealed that the transient absorption bands in the region 320—375 nm are ascribable to the sulphuranyl radicals [$Ph\dot{S}(SPh)SPh$], which are radical adducts produced by addition of thiyl radicals to excess of disulphide. There is a possibility that the arylthiyl radicals observed were produced from sulphuranyl radicals because the rapid equilibrium $PhS^{\cdot} + PhSSPh \rightleftharpoons Ph\dot{S}(SPh)SPh$ is present.[12]

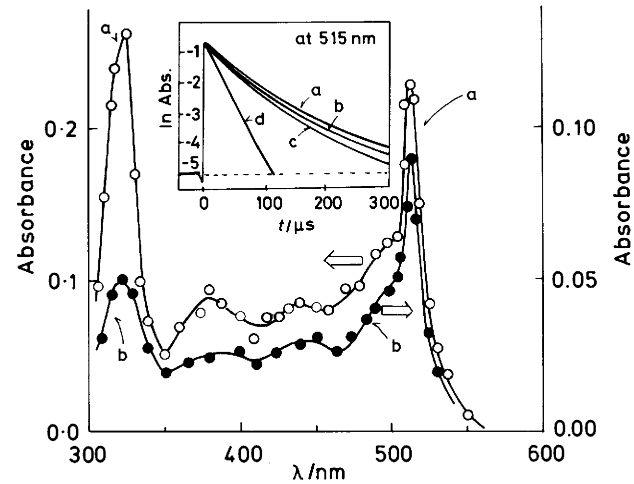
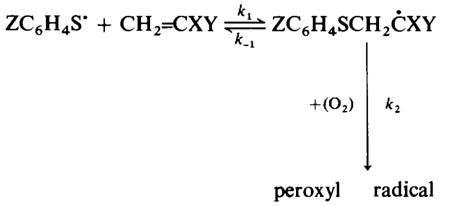


Figure 1. Transient absorption spectra observed by flash photodecomposition of a, $(p\text{-}ClC_6H_4S)_2$ (10^{-4} mol dm^{-3}) and b, $p\text{-}ClC_6H_4SH$ (10^{-3} mol dm^{-3}) in cyclohexane. Insert: First-order decay profiles of transient absorption band at 515 nm produced from disulphide: a, in cyclohexane without oxygen; b, in cyclohexane with oxygen; c, in hex-1-ene without oxygen; and d, in hex-1-ene with coexistence of oxygen

For other substituted phenylthiyl radicals, the transient absorption bands in the visible region (*ca.* 500 nm) are similarly attributed to the thiyl radicals. In this study, we followed the decay profiles of the 500 nm bands to determine the addition rate constants of the thiyl radicals. The coexistence of the sulphuranyl radicals which are inactive to olefins may not disturb the analysis of decay kinetics of the reactive thiyl radicals. Under our experimental conditions, the concentration of thiyl radical produced by one flash exposure is *ca.* 10^{-6} mol dm^{-3} and the concentration of olefin added in solution is 10^{-3}—10^{-1} mol dm^{-3}; thus, the concentrations of olefin is effectively constant during the reaction.

The decay rates of these transient absorption bands in the visible region were not changed substantially by the addition of molecular oxygen (decay curves **a** and **b** in the Insert in Figure 1), suggesting that the reactivity of the thiyl radicals to oxygen may be low.[14] As shown in the Insert in Figure 1 (decay curve d), the decay rates of the thiyl radicals were accelerated when both olefin (*i.e.*, hex-1-ene) and molecular oxygen were present. On the other hand, the decay rate of the transient species in the u.v. region was not accelerated by the coexistence of olefin and oxygen.

Determination of Rate Constants.—It is well established that the addition mode of arylthiyl radicals to olefins is, in general, reversible; if both the addition and the reverse reactions are fast enough, an equilibrium may be established within the time-scale of flash-exposure (10 μs). Indeed, the decay rate of the thiyl radical was only slightly affected by the addition of olefin to degassed solution (decay curve c in the Insert in Figure 1). Thus, it is necessary to add a selective radical scavenger which is solely reactive to the carbon-centred radicals, but not to arylthiyl radicals. Since oxygen is quite reactive to carbon-centred radicals but not to arylthiyl radicals, it is appropriate for this purpose. In the presence of both olefin and oxygen, the decay rates of the arylthiyl radicals were accelerated (decay curve d); the decay profiles changed from second-order to first-order kinetics. The slopes yield the first-order rate constants k_1 which linearly increase with the concentration of both olefin and oxygen.[9–11]



$$\begin{tikzcd} ZC_6H_4S^{\cdot} + CH_2{=}CXY \arrow[r, shift left, "k_1"] & ZC_6H_4SCH_2\dot{C}XY \arrow[l, shift left, "k_{-1}"] \arrow[d, "+(O_2)"', "k_2"] \\ & \text{peroxyl radical} \end{tikzcd}$$

Scheme.

In the Scheme, arylthiyl radicals add to olefins (CH_2=CXY) in an anti-Markownikoff fashion, which is well established in the literature.[15,16] The Scheme involving rapid equilibration and the selective radical scavenger (oxygen) was proposed by Gilbert *et al.* on the basis of e.s.r. experiments.[17] Plots of [CH_2=CXY]/k_l against 1/[O_2] give a straight line for each reaction system; from the intercept and slope, the values of $1/k_1$ and k_{-1}/k_1k_2 are obtained. For olefins which would be expected to produce resonance-stabilized carbon-centred radicals, the reverse rates are slow and the dependence of k_l[olefin] upon the concentration of O_2 is small. For such reaction systems, the k_1 values can be adequately approximated by the k_l/[olefin] values obtained in O_2-saturated solution.

$$[CH_2{=}CXY]/k_l = 1/k_1 + k_{-1}/k_1k_2[O_2] \quad (1)$$

Substituted Acrylonitriles.—The substituents on the olefins were selected in order to clarify the captodative effect; to make comparisons with Gieses' data cited in ref. 1, acrylonitrile derivatives (X = CN) with the dative substituents (Y) at the α-position were chosen. The addition rate constants (k_1) obtained for variations of substituents Y in the olefin and the substituent Z in the arylthiyl radical are summarized in Table 1 where the data for Y = H are cited from our previous study.[18] From the Alfrey–Price *Q–e* values for vinyl monomers, the CN substituent has large conjugation ability with strong electron-withdrawing (captive) power.[19] In order to clarify the effect of the second substituents (Y), it is necessary to select substituents exerting a weaker conjugation effect than CN, *i.e.*, non-conjugated substituents with *Q* values lower than 0.3, which is the higher limit for a non-conjugated monomer, were examined in this study. For the *e* values of Y, dative substituents with smaller (more negative) values than CN group are selected.

First, we examined the polar effect of the reaction systems on

Table 1. Addition rate constants ($10^{-4}k_1$/dm^3 mol^{-1} s^{-1} at 23 °C) and Hammett reaction constants [$\rho^+(k_1)$] of $ZC_6H_4S^{\cdot}$ to CH_2=C(CN)Y

	Z						
Y	OCH_3	CH_3	Bu^t	H	Cl	Br	$\rho^+(k_1)$
H[a]	4.6	29	30	43	43	48	0.5
CH_3	14	97	92	110	140	150	0.5
OC(=O)-CH_3	26	83	110	250	150	190	0.6
Cl	110	380	340	520	450	390	0.4
OC_2H_5	96	760	610	1 400	1 700	1 600	0.6
NR_2[b]		14 000	16 000	27 000	26 000	26 000	0.6

[a] Ref. 18. [b] NR_2 = Morpholino.

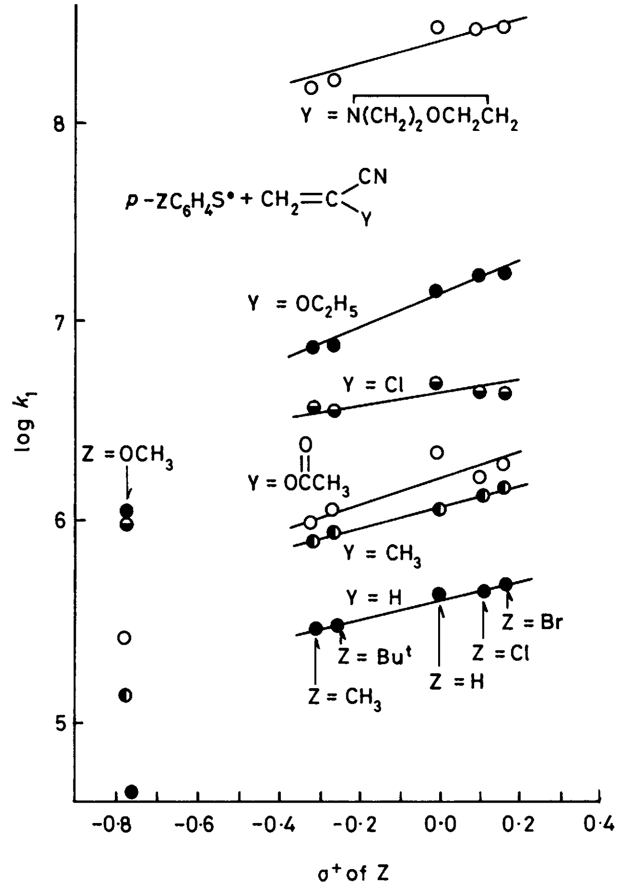


Figure 2. Hammett plot of rate constants of acrylonitrile derivatives *versus* σ^+ of substituent Z in arylthiyl radicals; lines are drawn excluding Z = OCH_3

Table 2. Rate parameters of propene derivatives (X = CH_3); $10^{-4}k_1$/dm^3 mol^{-1} s^{-1} and $10^{-6}Kk_2$/dm^3 mol^{-1} s^{-1}

		Z						
Y		OCH_3	CH_3	Bu^t	H	Cl	Br	ρ^+
C_3H_7	k_1	0.14	1.4	1.7	2.1	15	15	2.0
	Kk_2	0.34	1.4	1.5	6.2	18	17	1.8
$OC(=O)CH_3$	k_1	0.045	0.28	0.31	0.78	0.93	1.3	1.6
OCH_3	k_1	0.56	2.4	3.7	5.8	12	14	1.5
CO_2CH_3[a]	k_1	46	270		320	540		1.1

[a] Ref. 23.

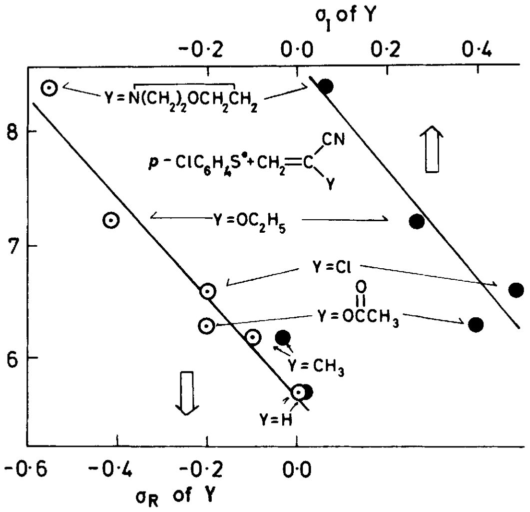


Figure 3. Plot of rate constants for reaction of acrylonitriles with p-$ClC_6H_4S^{\bullet}$ *versus* Taft constants (σ_R and σ_I) of substituents Y in $CH_2{=}C(Y)CN$

k_1 values. For each olefin in Table 1, the k_1 values decrease with the electron-donating power of Z in the arylthiyl radicals, but the size of the decrease is small except for Z = OCH_3. Hammett plots for the rate constants (k_1) *versus* σ^+ are shown in Figure 2; the slopes yield the reaction constant $\rho^+(k_1)$ values. The $\rho^+(k_1)$ values are summarized in Table 1; these values were calculated by excluding the data for OCH_3 because of their large deviation. Positive $\rho^+(k_1)$ values are obtained but they are not large compared with those for vinyl monomers having electron-donating substituents such as styrene [$\rho^+(k_1)$ 1.8][18] and vinyl sulphide [$\rho^+(k_1)$ *ca.* 2].[11] For the substituted acrylonitriles, the changes are small. Indeed, for each olefin, any inversion of the rate constants was not found with a change of the substituents Z (Figure 2). Thus, we can compare the reactivities of olefins with changing substituents Y for each thiyl radical.

With changing olefins (Table 1), the rate constant for each thiyl radical increases for the following order of substituents Y: $NR_2 > OC_2H_5 > Cl > OC(=O)CH_3 > CH_3 > H$. This order is in good agreement with the general tendency for the increase in the electron-donating power of the substituents Y.[20] For p-$CH_3OC_6H_4S^{\bullet}$, a similar tendency was observed. Thus, we confirm that captodative-substituted olefins are reactive toward arylthiyl radicals.

In general, the activation energy of the transition state is affected by a polar contribution and resonance stabilization. The positive $\rho^+(k_1)$ implies that charge transfer may occur from the olefinic double bond to the attacking radical centre. Resonance stabilization of the transition state may be caused mainly by delocalization of the unpaired electron produced in the olefin. The polar effect is invariant with the change of the substituents Y for each thiyl radical for the reaction systems in Table 1, since the Hammett reaction constants [$\rho^+(k_1)$] are essentially constant. Thus, it can be concluded that the activation energy of the transition state is mainly affected by resonance stabilization. Our kinetic data obtained in this study indicate that transition states which are similar to the product-side (the carbon-centred radicals $PhSCH_2\dot{C}XY$) are stabilized by the captodative effect.

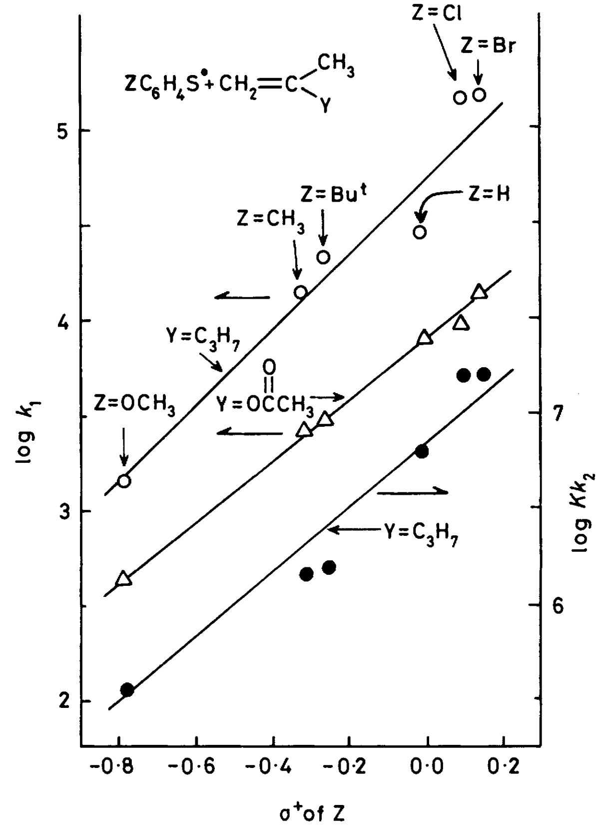


Figure 4. Hammett plot of addition rate constants and relative equilibrium constants *versus* σ^+(Z) for propenes

In order to investigate in more detail the factors controlling the acceleration of the rate constants for captodative-substituted olefins, plots of the rate constants for changing substituent Y against various substituent parameters such as the Alfrey–Price *e* value,[19] Hammett σ,[21] and Taft σ_R and σ_I were tried.[22] In Figure 3, plots of k_1 values (Z = Cl) against Taft σ_R and σ_I are shown; for σ_R a fairly good linear relationship can be seen. For plots against σ_I, k_1 values for heteroatom-substituted olefins seem to be correlated well, although some deviations are seen for H and CH_3. For σ_m, there is a similar tendency to σ_I.

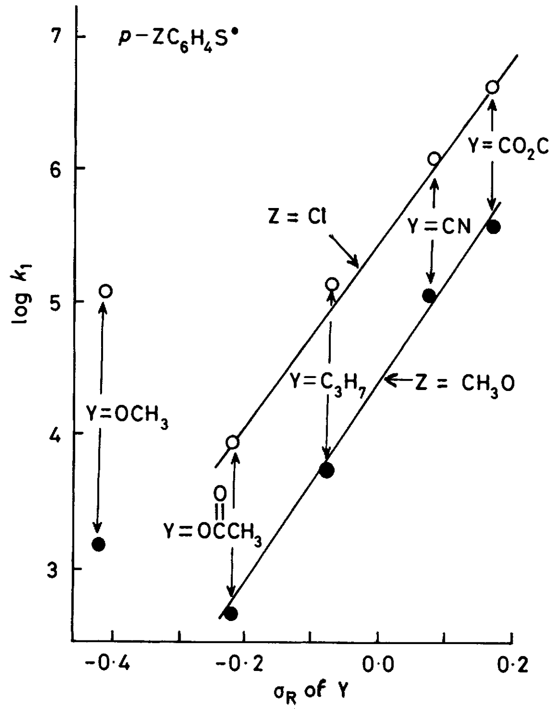


Figure 5. Plot of rate constants for reactions of propenes with p-ClC$_6$H$_4$S$^•$ and p-CH$_3$OC$_6$H$_4$S$^•$ *versus* Taft σ_R of substituents Y in CH$_2$=C(Y)CH$_3$

For the e value, a negative correlation is seen except for the chloro derivative. From Figure 3, it can be presumed that captodative stabilization mainly originates from both resonance and inductive effects. If the deviations of H and CH$_3$ from the straight line with σ_I are meaningful, the resonance contribution may be larger than the inductive contribution.

Substituted Propenes.—For an electron-donating substituted vinyl monomer, electron-withdrawing substituents such as CN, CO$_2$CH$_3$, and OC(=O)CH$_3$ may be expected to accelerate the addition rates. In this study, methyl was selected as the electron-donating substituent, although it is weak and is similar to the non-conjugated substituent in vinyl monomers. The observed rate constants are summarized in Table 2 where the data for Y = CO$_2$CH$_3$ are cited from our previous study.[23] In Table 2, the relative equilibrium constants ($K = k_1/k_{-1}$) obtained from the slope of the plot of equation (1) are added. In the Hammett plot for σ^+, fairly good linear lines are obtained as shown in Figure 4. A large positive ρ^+ value was obtained not only for the reactivities but also for the equilibrium constants. A part of the ρ^+ value of the reactivity results for the linear free-energy relationship [$\rho^+(k_1)$ = constant × $\rho^+(Kk_2)$]; the remaining part is attributed to the polar transition state in the addition reaction.[17,24] Since the former contribution does not vary with the nature of the olefin, the change of observed $\rho^+(k_1)$ values can be attributed to the change in contribution of the polar transition state. Positive $\rho^+(k_1)$ values for propenes are larger than those for acrylonitriles, which indicates that the amount of charge transfer from the propenyl double bond to the sulphur radical centre (ZC$_6$H$_4$S$^•$ —← >C=C<) in the transition state is greater than for the acrylonitriles.

In Figure 5, the rate constants for p-ClC$_6$H$_4$S$^•$ and p-CH$_3$OC$_6$H$_4$S$^•$ are plotted against the Taft σ_R parameter. An opposite tendency to substituted acrylonitriles (Figure 3) is found. This tendency is invariant with the substituents in the arylthiyl radicals. An upward deviation of the methoxy derivative from each line was observed; this indicates that for the weak CH$_3$ substituent, the relatively strong perturbation of a second substituent such as methoxy affects the reactivity and overcomes the captodative effect.

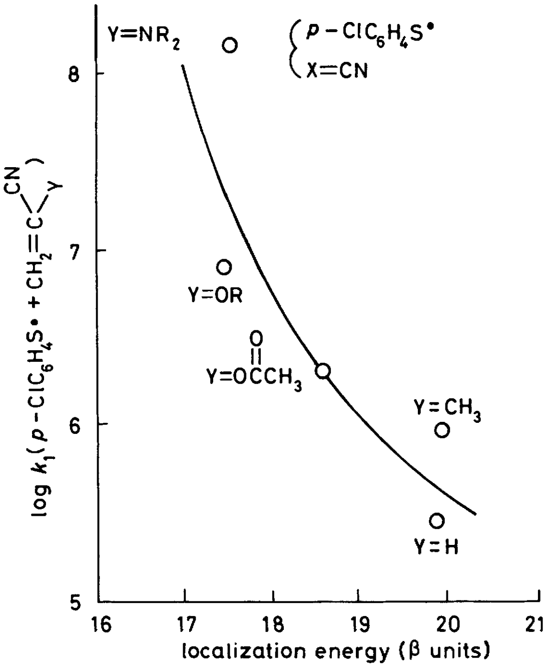


Figure 6. Correlation between observed rate constants (k_1 for substituted acrylonitriles) and calculated localization energies for CH$_2$=CXY (X = F) with varying Y

Although the rate constants for substituents Y such as CO$_2$CH$_3$ and CN fit well on the lines in Figure 5 along the captodative effect, the increase in the rate constants does not solely originate from the captodative effect. It is reasonable to draw a comparison with methyl-substituted acrylate, acrylonitrile, and acetate with the corresponding vinyl monomers without a methyl group at the α-position; the ratios of the rate constants are 11, 5, and 1, respectively.[8,17,22] This increasing order in the ratio is in good agreement with the captodative effect.

Correlation with Localization Energy.—In order to consider the origin of the lowering of the activation energies in the free-radical addition reactions to captodative-substituted olefins, it is useful to perform MO calculations. As a model of substituted acrylonitriles, we take olefins with a strong electronegative substituent without conjugation ability as the first substituent and various electron-donating substituents at the α-position as the second one, since the inductive effect is underestimated in MO calculations compared with the conjugation effect when both effects are involved in one substituent such as C≡N. In the simple Hückel MO method, we chose the parameters of the coulomb and resonance integrals for F as a strong electron-withdrawing substituent, since it has a similar σ_I value to C≡N.[25,26] Among the quantities obtained from MO calculations, it is well known that the localization energy (destabilization energy between the carbon-centred radical (PhSCH$_2\dot{C}$Y) and olefin (CH$_2$=CXY)] is correlated with the reactivities for radical addition. In Figure 6, the rate constants evaluated in this study for substituted acrylonitriles are plotted against the localization energies calculated by using the reported parameters of the substituents.[25,26] We can find a smooth tendency for the rate constants to increase with a decrease in the localization energy; this implies that the stabilization of the adduct radical is increased by the captodative substituents. This causes lowering of the activation energies which result in the acceleration of the rate of radical addition.

Experimental

Disubstituted olefins except for α-ethoxy- and α-morpholino-acrylonitrile were commercially available; they were distilled under reduced pressure at least twice before use. Ethoxy-[27] and morpholino-acrylonitrile[28] were prepared by methods described in the literature. The former was distilled and the latter recrystallized twice before use. Disulphides were prepared from the corresponding thiols. Thiol used to observe the transient species (Figure 1) was freshly prepared or distilled to prevent contamination by disulphides which may be produced by photolysis or air oxidation during storage. The solvent used for the flash experiments is cyclohexane of spectroscopic grade.

The flash photolysis apparatus was of standard design with two xenon flash lamps of 10 μs half-duration (*ca.* 100 J).[29] Rate measurements were performed at 23 °C. For standard experimental conditions, disulphides of *ca.* 10^{-4} mol dm^{-3} were flash-photodecomposed with light of 330—400 nm which was selected so as not to excite olefins in solution.

The concentration of molecular oxygen in cyclohexane was controlled by introducing oxygen into the solution after degassing. The oxygen concentration was calculated from Henry's law using the Ostwald coefficient in the literature.[30]

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