Relative Reactivities in the Addition of Free Trichloromethyl Radicals to Substituted Styrenes. An Attempt to Separate Polar and Resonance Effects[1]

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Relative reactivities in dibenzoyl peroxide-catalyzed addition of bromotrichloromethane to nine nuclear-substituted styrenes have been investigated with unsubstituted styrene. The effect of *meta* substituents upon the relative rates was correlated with the simple Hammett equation using either σ or σ^+ constants. The relative rates of *para*-substituted styrenes, however, did not obey the simple Hammett relation, with the results best explained on the basis of polar ($\rho\sigma^+$) and resonance (E_D) terms. All *para* substituents examined increase the reactivity.

$$\log(k/k_H) = \rho\sigma^+ + E_D$$

The E_D term shows a striking correlation with log*Q* of the corresponding *para* styrene in Alfrey-Price's *Q-e* scheme of free-radical copolymerization. That the polar term originates in charge-transfer interactions between the olefin and the electrophilic trichloromethyl radical and can be expressed by $\rho\sigma^+$ is further supported by the evidence that charge-transfer energies of substituted styrenes showed good correlation with σ^+. Factors influencing the reactivity have been discussed.

There are few reactions of free-radical chemistry more extensively studied than addition to olefins, yet some of the basic problems of structure and reactivity remain unresolved. The substituent effects of styrenes, which should be studied as one of the most fundamental substrates, have not yet been investigated systematically in addition reactions except in copolymerization.[2]

Martin and Gleicher[3] have reported the addition of the trichloromethyl radical to substituted allylbenzenes, 3-butenylbenzenes and other 1-olefins where they observed linear correlations of the rate data by the Hammett-Taft equation.[4] More recently, Cadogan and Sadler[5] have reported the relative reactivities of addition of trichloromethyl and thiyl radicals to variously substituted olefins; in their report it was disclosed that the rate constant rations of substituted stilbenes and α-methylstyrenes toward these radicals obey the Hammett-Brown relation.[6]

$$\log(k/k_H) = \rho\sigma^+ \qquad (1)$$

However, only three substituents were chosen, *i.e.* methoxy, methyl and bromo, all at the *para* position, no *meta* or other appropriate substituent being included to check the possibility that enhanced delocalization of the odd electron in the free radical was increasing the reactivity. They noted at the same time, however, that the reactivity of 4-nitro-*trans*-stilbene was greater than that predicted from the proposed relation (eq. (1)).

Numerous studies[7] of hydrogen abstraction from substituted toluenes and other alkylbenzenes have demonstrated that the relative reactivities are generally correlated by the Hammett equation, and sometimes better by the Hammett-Brown equation. We have also reported recently examples in which the importance of polar effects was demonstrated.[8] As part of a program directed toward the relations of structure and reactivity in the homolytic process, we have investigated the relative reactivities of substituted styrenes toward the trichloromethyl radical derived from bromotrichloromethane. Our special interest was to separate the factors influencing the reactivity: both resonance and the polar effects should be operating in homolytic addition to conjugated olefins.

Results

Competitive Reactions. Addition of bromotrichloromethane to olefins by a free-radical mechanism has been well established.[3,5,9–11] Kharasch, Reinmuth, and Urry reported in their chassical study that styrene afforded the 1:1 adduct in 78% yield at 70°C using 2.3 wt% diacetyl peroxide as an initiator. Formation of a 1:1 adduct of styrene and bromotrichloromethane in photochemically induced reactions[12] and even in an uncatalyzed thermal reaction[13] have also been reported.

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[1] Presented in part at the 21st Annual Meeting of the Chemical Society of Japan, Suita, Osaka, Japan (April 1, 1968), Abstracts, III, p. 2060.

[2] a) C. Walling, E. R. Briggs, K. B. Wolfstein, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948), b) M. Imoto, M. Kinoshita, and M. Nishigaki, *Mackromol. Chem.*, **86**, 217 (1965), c) M. Imoto, M. Kinoshita, and M. Nishigaki, *ibid.*, **94**, 238 (1966).

[3] M. M. Martin and G. J. Gleicher, *J. Amer. Chem. Soc.*, **86**, 233, 238 ,242 (1964).

[4] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y. (1956), Chapter 13.

[5] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc., B*, **1966**, 1191.

[6] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[7] G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1963), and references cited therein.

[8] a) H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1968). b) H. Sakurai and K. Tokumaru, "Chemistry of Free Radicals," H. Sakurai and K. Tokumaru eds., Nankodo, Tokyo, 1967, Chapt. 17.

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[10] J. I. G. Cadogan and D. H. Hey, *Quart. Rev.* (London), **8**, 308 (1954).

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[12] M. S. Kharasch, E. Simon, and W. Nudenberg, *J. Org. Chem.*, **18**, 328 (1953).

[13] W. A. Skinner, E. Bishop, D. Tieszen, and J. D. Johnson, *ibid.*, **23**, 1710 (1958).

Kinetic investigations of the photochemical telomerization of styrene[14,15] also showed that at sufficiently low molar ratios of styrene to bromotrichloromethane, only a 1:1 adduct was formed. In our hands, the high yields of a 1:1 adduct from styrene are also confirmed under the conditions employed in competitive reactions. Therefore, any error originating in the possible comsumption of styrenes by polymerization can be ignored.

Cadogan and Sadler[5] published a very elaborate analysis to establish a valid competitive method of measuring the relattve reactivities of olefins toward thiyl and trichloromethyl radicals. We empolyed a procedure essentially the same as theirs[3,5] (see Experimental).

A reactant ratio of bromotrichloromethane: X:Y of 4:1:1 was empolyed generally in the competitive addition of the trichloromethyl radical derived from bromotrichloromethane to styrenes. Effects of variation of both the bromotrichloromethane ratios and the degree of conversion of the styrene into adduct were examined in some detail for *p*-chlorostyrene-styrene system, as shown in Table 1.

The reactivity of *p*-chlorostyrene relative to styrene was found to be fairly constant, regardless of experimental conditions. The value for k_{Cl}/k_H of 1.06±0.03 is consistent with the value 1.0, by Kharasch *et al.*[12]

TABLE 1. COMPETITIVE EXPERIMENT OF STYRENE (A) WITH *p*-CHLOROSTYRENE (B) TOWARD ADDITION OF BROMOTRICHLOROMETHANE

Run	A mmol	B mmol	$BrCCl_3$ mmol	Reaction time (hr)	k_B/k_A
1	2.503	2.501	5.01	3.0	1.03
2	2.503	2.501	10.02	3.0	1.04
3	2.503	2.501	20.05	3.0	1.02
4	10.05	10.17	40.38	2.0	1.09
5	10.07	10.25	40.68	2.0	1.09
6	10.07	10.25	40.68	3.0	1.10
7	10.05	10.17	40.38	3.0	1.10
8	10.07	10.25	40.68	4.0	1.06
9	10.07	10.25	40.68	5.0	1.06
10	5.079	5.006	20.58	3.0	1.02
11	5.177	5.079	20.21	3.0	1.03
12	5.091	5.129	20.23	3.0	1.04

TABLE 2. RELATIVE REACTIVITIES OF SUBSTITUTED STYRENES TOWARD TRICHLOROMETHYL RADICALS

Substituent	k/k_H[a]	
p-Methyl	1.74	±0.12
m-Methyl	1.08	±0.05
H	1.00	
m-Methoxy	1.05	±0.02
p-Chloro	1.06	±0.03
m-Chloro	0.767	±0.02
m-Trifluoromethyl	0.615	±0.00
p-Cyano	1.13	±0.04
m-Nitro	0.529	±0.02
p-Nitro	0.872	±0.07

a) Deviation listed for two to twelve runs.

TABLE 3. CHARGE-TRANSFER ENERGIES AND IONIZATION POTENTIALS OF SUBSTITUTED STYRENES

Substituent	CT-Band (in CH_2Cl_2)		IP[b] eV
	mμ	eV[a]	
p-CH_3O	590 ± 5	2.10±0.02 (2.05)	7.9_9
p-CH_3	525 ± 3	2.36±0.02 (2.37)	8.2_5
m-CH_3O	520 ± 3	2.38±0.02	8.2_7
m-CH_3	485 ± 3	2.56±0.02	8.4_5
H	481 ± 3	2.58±0.02 (2.58)	8.4_7
p-Cl	481 ± 3	2.58±0.02 (2.57)	8.4_7
p-Br	481 ± 3	2.58±0.02	8.4_7
m-Cl	450 ± 5	2.75±0.03	8.6_4
m-CF_3	420 ± 3	2.95±0.02	8.8_4

a) Values in parenthesis were reported by M. Hatano, N. Tamura, and S. Kambara, *Kogyo Kagaku Zasshi*, **70**, 2012 (1967).

b) Calculated by Eq. (2).

In Table 2 are indicated the relative reactivities of nine nuclear-substituted styrenes toward the addition of the trichloromethyl radical.

Charge-transfer Spectra of Styrenes with Tetracyanoethylene. The charge-transfer spectra were taken in dichloromethane solution at an ambient temperature with tetracyanoethylene as an electron acceptor by the standard method.[16] The results are listed in Table 3. Ionization potentials (IP) were calculated from equation 2, and are also tabulated in the last column of the Table.

$$IP = (IP)_0 + (h\nu_{CT}) - (h\nu_{CT})_0 \qquad (2)$$

The charge-transfer energies are plotted against σ^+ parameters as shown in Fig. 1. A reasonably good (r=0.98)linear relationship was obtained omitting the point for *m*-methoxystyrene.

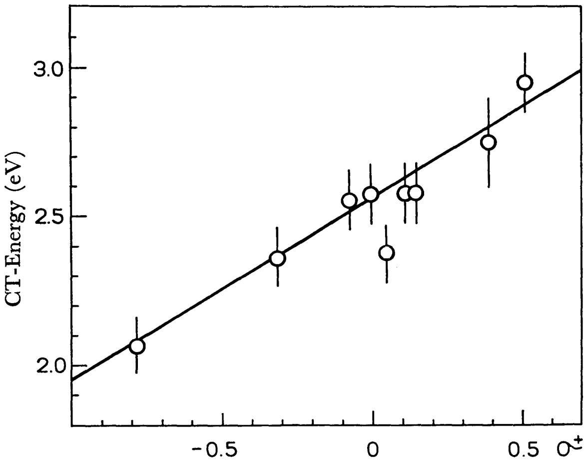

Fig. 1. Plots of charge-transfer energies of substituted styrenes-tetracyanoethylene complexes against σ^+ of the substituents.

Discussion

Figure 2 plots logarithm of the relative rates of additions against σ^+ constants. No very linear Ham-

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15) W. J. Kirkham and J. C. Robb, *ibid.*, **57**, 1757 (1961).

16) H. A. Benesi and T. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

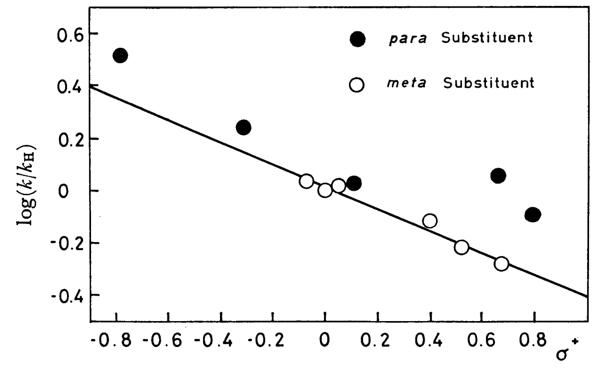

Fig. 2. Correlation of $\log(k/k_H)$ and σ^+ for addition of free trichloromethyl radicals to substituted styrenes in benzene at 80.0°.

mett correlation is found for the data as a whole, but clearly, the data for *meta*-substituted styrenes afford a nice linear relationship with σ or a somewhat better one with σ^+(*vide infra*).

$$\log(k_X/k_H) = -0.425\sigma + 0.019 \ (r = 0.9689) \tag{3}$$

$$\log(k_X/k_H) = -0.418\sigma^+ + 0.018 \ (r = 0.9847) \tag{4}$$

(r = correlation coefficient)

The ρ-values were calculated by the method of least squares, the negative ρ-value being consistent with the view that the trichloromethyl radical is of an electrophilic nature. In *meta*-substituted styrenes, the odd electron of the 1-phenyl-3,3,3-trichloropropyl radicals is conjugated not with the substituent but only with the π-electrons of the benzene ring. Thus further resonance stabilization of the resulting radicals due to the presence of the *meta*-substituent does not occur, and it is quite natural that the second-order substituent effect, seen in the relative rates, is polar for the *meta* series

The ρ-value obtained here is considerably lower than that of ionic reactions such as hydration of styrenes ($\rho = -3.42$ with σ^+ including *para* substituents).[17] This fact indicates that the polar effect in the addition of the trichloromethyl radicals is much smaller than in ionic reactions, although the polar effect is the crucial factor in determining the relative rates in *meta* styrenes.

The rate constant ratios of *para*-substituted styrenes, however, do not obey the Hammett relation. These data deviate considerably upward from the line of *meta* series. All *para* substituents examined increase the reactivity.

We have tried to get the relative rate for *p*-methoxystyrene, but the tendency of this monomer toward spontaneous polymerization was too high to obtain a reliable value. However, there is a close resemblance in the relative reactivity sequences of styrenes, α-methylstyrenes and *trans*-stilbene toward the trichloromethyl radical. Thus, the increase in reactivity toward the trichloromethyl radical due to the interaction of a given substituent group in the *para* position, as shown in Table 4, is the same within the limits of experimental error for these.[5] Therefore we may assume the relative rate for *p*-methoxystyrene to be around 3. 3.

Table 4. Relative reactivities toward trichloromethyl radicals in olefins

X	$X\text{-}C_6H_4\text{-}CH{=}CH_2$[a]	$X\text{-}C_6H_4\text{-}CH{=}CH\text{-}C_6H_4\text{-}X$[b] (*trans*)	$X\text{-}C_6H_4\text{-}CMe{=}CH_2$[b]
4-MeO	——	3.4	3.2
4-Me	1.74	1.7	1.7
4-H	1.0	1.0	1.0
4-Br	——		0.7

a) Present study
b) Cadogan and Sadler[5]

It is an unlikely assumption that these *para*-substituent effects are due entirely to the stabilization of the somewhat electron-deficient free-radical in the transition state by an inductive effect, since the reactivities of substrates containing a deactivating substituent group such as *p*-nitro- and *p*-cyanostyrene are far greater than those predicted on the basis of this polar effect alone. Therefore, the high observed relative rates for *para*-substituted styrenes are certainly due, at least in part, to the extra delocalization of the odd electron in the radicals.

Investigations of homolytic arylation by Simamura and co-workers[18] have shown that the influence of a substituent may be divided into resonance and inductive effects. Since in substitution at the *meta*-position of the substituted benzenes the conjugation of the odd electron dose not extend into the substituent group, as for *meta*-styrenes, the partial rate factors for arylations at the *meta* position are correlated only with the polar term; thus the Hammett relation holds. On the other hand, partial rate factors for *para* substitution are expressed by

$$\log(k_p/k) = \rho\sigma_p + \tau_p \tag{5}$$

where τ_p is a term for additional stabilization due to the conjgaution of the substituent group correlated with the difference of the extra resonance energy. That τ_p is a constant dependent only on the nature of the substituent group in the substrate is also demonstrated.

If it is assumed that the free-energy changes for the *para*-substituted styrense in free-radical addition can be also divided into polar and delocalization terms, with the former expressed by ρσ or ρσ+, the relative rates may be formulated as

$$\log(k_p/k_H) = \rho\sigma_p(\text{or } \rho\sigma_p^+) + E_D \tag{6}$$

where E_D is a term for additional stabilization due to extra delocailzation by the *para* substituent group.

Combining this equation with eqs. 3 and 4, numerical values of E_D are calculated with σ and σ^+ -parameters, respectively. The results are listed in Table 5.

Meanwhile, Alfrey and Price[19] proposed an empirical formula that expresses the monomer reactivity ratios, r, in free-radical copolymerization in terms of Q and e. Table 5 contains also log Q for the respective styrenes. There is a striking resemblance between the

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[17] W. M. Schubert, B. Lamm, and J. R. Reefe, *ibid.*, **86**, 4727 (1964).

[18] R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

[19] T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).

Table 5. Extra-delocalization terms for addition of trichloromethyl radicals to *para*-substituted styrenes

X	E_D with σ	E_D with σ^+	log Q[a]
MeO[b]	0.40_4	0.19_2	0.13
Me	0.16_8	0.11_0	0.04
Cl	0.12_3	0.07_1	0.01
CN	0.33_4	0.32_9	0.27
NO_2	0.27_2	0.27_1	0.21

a) Taken from L. J. Young, *J. Polym. Sci.*, **54**, 411 (1961).
b) Estimated values.

values of log Q and E_D calculated with σ^+.

$$\log Q_p = 1.022E_{D(\sigma^+)} - 0.067 \quad (r = 0.9995) \tag{7}$$

The correlation of log Q with the value of E_D calculated with σ is less satisfactory (r=0.7090).

Therefore, if we assume that the E_D term in eq. 6 can be given by log Q log(k_m/k_H) of *meta* styrenes and log(k_p/k_H) −log Q of *para* derivatives should express the free-energy change of the reaction corrected for extra-resonance effect of the substituents. As shown in Fig. 3, these are plotted against σ^+ to give a nicely linear relation even with the hypothetical value of *p*-methoxystyrene.

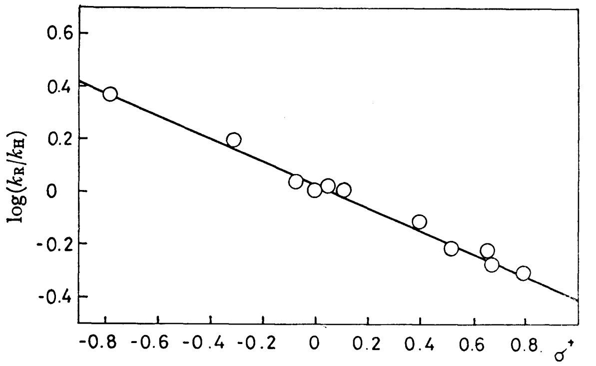

Fig. 3. Correlation of log(k_R/k_H) and σ^+ for addition of free trichloromethyl radicals to substituted styrenes in benzene at 80.0°. Reduced rates, k_R, are defined as k_m for *meta*-substituted styrenes, whereas k_p/Q for *para* series.

These findings now raise the question of why the polar term is given by $\rho\sigma^+$ instead of $\rho\sigma$ and/or why the resonance term should be log Q.

In the case of free-radical addition to olefins there is good indication that in the absence of any specific polar effects the rate of addition and the orientation are governed primarily by the localization energy of the substrate.[20] However, when an electrophilic radical such as the trichloromethyl radical is approaching to an olefinic double bond, the electrostatic interaction leads to a lowering of the potential energy of the system, and this should be an origin of the polar effect in addition reaction. It is not clear that electrophilic radicals can form a π-complex with olefin, but such interaction must originate in the charge-transfer interaction between the free radical and olefin. Therefore, the more developed the charge-transfer interaction at the transition state, the more the lowering of the potential energy of the system, and the relative extent of such a lowering effect of the free energy may be evaluated by ionization potential difference of olefins.

We have measured the charge-transfer frequencies of substituted styrene-tetracyanoethylene complex, and as seen in Fig. 1, there is a good correlation between the charge-transfer energy or ionization potential and σ^+ substituent constants. This correlation implies that the substituent effect in the charge-transfer interaction, *viz.*, the polar effect of the addition reaction, is governed by the $\rho\sigma^+$ relation.

It is established that in hydrogen abstraction reaction at non-benzylic position rates are correlated with σ, and that rates of abstraction of benyzlic and phenolic hydrogen by electron-seeking radicals follow generally the $\rho\sigma^+$ relation.[21] It should be emphasized that the latter $\rho\sigma^+$ relation is concerned with the polar effect of the substituent in stabilization of the benzylic carbonium ions and not with the extra stabilization of the benzylic radicals due to the delocalization of unpaired electron by the substituent. For addition reaction, the $\rho\sigma^+$ relation should be also recognized as a result of the charge-transfer interaction responsible for the polar effect.

The "Q and e" treatment must be regarded as empirical, but there is a good deal of evidence showing a satisfactory correlation of the localization energy with log Q of various types of vinyl monomers.[22] It is still a matter of question whether the E_D term observed in the present study can be equated to log Q. We might propose a new set of parameters equated directly to E_D. However, considering our basis for representing the polar effect as $\rho\sigma^+$, and the fact that the calculated E_D values based on the $\rho\sigma^+$ relation resemble nicely log Q, relative rates of addition of the trichloromethyl radical to substituted styrenes are best expressed by the following equation.

$$\log(k/k_H) = \rho\sigma^+ + \log Q_p \tag{8}$$

Experimental

Materials. Bromotrichloromethane was of reagent grade purchased from Aldrich Chemical Co. and was used after distillation through a 35-cm column packed with glass helicoils. Styrene and *m*-nitrostyrene were commercial samples. *p*-Methoxy- and *m*-methoxystyrenes were prepared by decarboxylation of the corresponding cinnamic acids. *p*-Methyl-, *m*-methyl-, *p*-chloro, *m*-chloro-, *p*-bromo-, *p*-cyano-, and *m*-trifluoromethylstyrenes were obtained by dehydration of the corresponding secondary alcohols. *p*-Nitrostyrene was prepared by dehydrobromination of 2-(4′-nitrophenyl)ethyl bromide with triethanolamine. All samples were stored in a freezer and distilled under reduced pressure immediately before use. All physical constants and glpc analyses confirmed the purity of the materials used.

Procedure for Kinetic Runs. Samples of substituted

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20) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Symposium, 1958, Butterworth Scientific Publications, London, (1959), p. 291.

21) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **35**, 993 (1970).

22) a) G. S. Levinson, *J. Polym. Sci.*, **60**, 43 (1962), b) T. Fueno, T. Tsuruta, and J. Furukawa, *Nippon Kagaku Zasshi*, **78**, 1075 (1957).

styrene (X), styrene (Y, standard olefin), and an internal standard were accurately weighed into a flask, to which 5 m*l* of bromotrichloromethane and 10 m*l* of benzene containing dibenzoyl peroxide were added. A reactant ratio of bromotrichloromethane/styrene/substituted styrene/internal standard/dibenzoyl peroxide of 4:1:1:0.75:0.012 was employed. The reaction mixture was then placed in a glass tube and degassed by repeated freezing and melting in a vacuum. The tube was then sealed in a vacuum and immersed in a constant-temperature bath kept at 80° for 0.5—1 hr. The extent of total olefin consumption varied from 30—60%. The mixtures were analyzed by glpc on a column packed with polyethylene glycol 20 M or Apiezon L using helium as a carrier gas. In each run, the amount of chloroform was negligibly small, and hardly detectable, indicative of the absence of hydrogen abstraction by the trichloromethyl radical as a side reaction.

A survey of the literature and arguments above indicated that side reactions other than addition could be ignored and that the rate determining step should be the addition of the trichloromethyl radical to the olefins. The relative rates were thus followed by the disappearance of the styrenes. The ratio of rate constants for disappearance of the two styrenes was calculated from the usual expression

$$(k_X/k_Y) = \log([X_0])/[X_f])/\log([Y_0]/[Y_f]) \tag{6}$$

where $[X_0]$ and $[X_f]$ were the initial and final concentrations of styrene $X\text{-}C_6H_4CH{=}CH_2(X)$, respectively, and $[Y_0]$ and $[Y_f]$ have a similar significance for $Y\text{-}C_6H_4CH{=}CH_2(Y)$.

Charge-transfer Spectra. Charge-transfer spectra were run on a Shimadzu Model SV-50A automatic recording spectrophotometer using 10 mm quartz cell. Dichloromethane was used as the solvent throughout the experiment, concentrations of tetracyanoethylene and styrenes being kept at 10^{-4}—10^{-3} and 10^{-2}—10^{-1} mol/*l*, respectively. The solutions were made up and mixed immediately before measurements. These solutions decolorize fairly rapidly, but were stable enough to record the charge-transfer maxima two or three times.

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