© 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 2474—2479 (1989) [Vol. 62, No. 8

ESR Studies on Chain Transfer Reactions: Rate Constants for the Reactions of Model Radicals of Polystyrene Growing Chain Ends with Tetrahalomethanes and Thiophenols

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(Received January 28, 1989)

The absolute rate constants for reactions of the model radicals of the growing chain ends of styrene and methacrylonitrile with tetrahalomethanes and thiophenols were determined by spin-trapping methods using ESR spectroscopy. The model radicals were produced by the photodecomposition of 1,1′-diphenylazoethane and 2,2′-azobisisobutyronitrile. In the case of the styrene model radical, the rate constants for the halogen abstraction reaction from CBr_4, $CBrCl_3$, and CCl_4 were 1.1×10^7, 2.0×10^6, and 1.1×10^5 $M^{-1}s^{-1}$, respectively, and increased with increasing electron affinity of tetrahalomethanes. The rate constants for the hydrogen abstraction reaction from thiophenols were of the order 10^6 $M^{-1}s^{-1}$, independent of the electron-donating and -accepting properties of the para substituents. In the case of the methacrylonitrile model radical, the rate constants for the halogen abstraction reaction from CBr_4 and $CBrCl_3$ were 1.1×10^5 and 4.5×10^3 $M^{-1}s^{-1}$, respectively. The rate constants for the hydrogen abstraction reaction from thiophenols with $-CH_3$, -H, and -Cl substituent in the para position were 4.5×10^4, 2.7×10^4, and 1.7×10^4 $M^{-1}s^{-1}$, respectively. The rate constants decreased with increasing the electron-withdrawing power of the substituent.

It has been well-known that tetrahalomethanes and thiol derivatives are strong chain-transfer reagents for the radical polymerization of styrene.[1,2] Although the chain-transfer constants (C_s) have been determined by the Mayo equation,[1] the values of C_s reported for strong chain-transfer reagents, such as CBr_4 and $CBrCl_3$, have varied over two orders of magnitude.[3–6] From a study of the dependence of C_s on the extent of polymerization, Thomson and Walter[6] pointed out the fact that this deviation is mainly due to the effect of a rapid removal of the transfer reagents on the degree of polymerization, since most of the strong transfer reagents are considered to be consumed at 0.5—0.7% conversion and the subsequent reaction probably similar to bulk polymerization. Since it is difficult to accurately estimate C_s for strong chain-transfer reagents by the Mayo equation, the value of C_s should be evaluated under the conditions where it is not influenced by the extent of polymerization.

Recently, we reported on a method for determining the absolute rate constants of model radicals of the propagating chain ends with tetrahalomethane using a spin-trapping ESR method.[12] In the present work, we applied this method to the halogen- and hydrogen-abstraction of the α-methylbenzyl radical ($CH_3\dot{C}HC_6H_5$), which is a model radical for the polystyrene end, from tetrahalomethanes and thiophenols.

The absolute rate constant, k_{trs}, provides more direct information concerning the mechanism of the chain-transfer reaction than C_s. An understanding of the mechanism of the chain-transfer reaction to strong transfer reagents possibly provides important information concerning the chemical properties of the propagating radical and the radical reaction control, such as the transformation of a radical reaction to an ionic reaction through the complex formation or electron transfer of the propagating radical to additives. In this paper, therefore, we determined the absolute rate constants for hydrogen abstraction of the 1-cyano-1-methylethyl radical (an electropositive radical) from thiophenols and reevaluated k_x for halogen-abstraction reactions of this radical from halomethanes. Additionally, these rate constants were compared with the corresponding ones of the α-methylbenzyl radical.

Experimental

Materials. 1,1′-Diphenylazoethane was prepared according to the oxidation of the corresponding hydrazine derivatives. 2-(*t*-Butylthio)acrylonitrile was prepared by Viehe's method.[14] Thiophenols, commercially available, were purified by distillation or recrystallization. Azobisisobutyronitrile (AIBN) and tetrahalomethanes were purified as described previously.[12]

The ESR spectra were recorded on a Japan Electron Optics Laboratory Model JES-FE 1X ESR spectrometer under irradiation with a 500-W high-pressure mercury lamp (Ushio 500) at 80 °C. The temperature in the cavity of the ESR spectrometer was controlled with a variable temperature accessory (ES-VT-3A). The simulation for the overlap of two adducts was carried out using a JEOL ESR simulation program (0398) operating on a EC 6 computer.

A solution of an azocompound (2.0×10^{-2}—1.0×10^{-1} M; 1M=1 mol dm^{-3}), a trapping reagent (6.4×10^{-1}—6.4×10^{-3} M), and a transfer reagent (0.9—7.8×10^{-2}M) in toluene was put into a sample tube equipped with an ESR cell (spectrocil 3 mm) in the side arm, degassed by repeated melting and freezing under vacuum, and then sealed. The UV spectra were measured on a Hitachi 124 UV-visible spectrometer. Ionization potentials were measured by photoelectron spectroscopy with calibration by xenon as an internal standard (IP 12.130 eV).

An estimation of the kinetic parameter was carried out by a computer calculation using a nonlinear least-square method, whose program was Sals II written by Nakagawa et al. (Tokyo University).

Results

Addition Reaction of α-Methylbenzyl Radical to 2-(*t*-Butylthio)acrylonitrile. Figure 1 shows the ESR spectrum observed under irradiation of a mixture of 1,1′-diphenylazoethane and 2-(*t*-butylthio)acrylonitrile, a spin-trapping reagent (T). The ESR spectrum of a triplet of triplets of doublets with hyperfine splitting constants of 1.1, 0.28, and 0.08 mT, respectively, was reasonably assigned to the adduct of the model radical of the polystyrene propagating end to T.[12,14] The change in the ESR spectrum with the reaction time showed that the concentration of the adduct became stationary within several minutes after irradiation. The signal due to the α-methylbenzyl radicals (M·) could not be detected, indicating that the stationary concentration of M· was negligibly small, as compared with that of the adduct (MT·). Therefore, the bimolecular self-termination of M· was not taken into account in the kinetic treatment. Thus, the reactions are shown in Eqs. 1 to 4:

$$\text{M-N=N-M} \xrightarrow{I} \text{M}\cdot \qquad I\text{: Rate} \tag{1}$$

$$\text{M}\cdot + \text{T} \xrightarrow{k_1} \text{MT}\cdot \tag{2}$$

$$\text{MT}\cdot + \text{M}\cdot \xrightarrow{k_2} \text{product} \tag{3}$$

$$\text{MT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{product} \tag{4}$$

The assumption of the steady state for the concentrations of M· and MT· leads to

$$[\text{T}] = \frac{k_2}{k_2} \frac{[\text{MT}\cdot](1+k_3/I[\text{MT}\cdot]^2)}{(1-k_3/I[\text{MT}\cdot]^2)}. \tag{5}$$

The relation between the stationary concentration of MT· and T is shown in Fig 2. Ratios k_2/k_1 and k_3/I were determined from Eq. 5 by a computation using the data shown in Fig. 2: results are shown in Table 1, along with data for AIBN. The value of k_3/I for the reaction of 1,1′-diphenylazoethane is larger than that of AIBN. The difference is probably due to the difference in *I*.

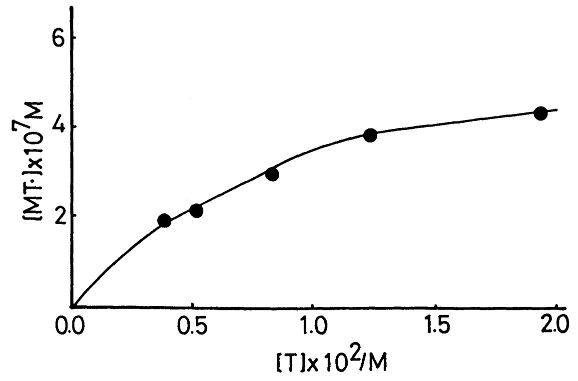


Fig. 2. Relation between MT· and T concentrations at 80 °C. [1,1′-diphenylazoethane]=5.0×10^{-2} M.

Table 1. Kinetic Data in Addition Reaction of Model Radicals to 2-(*t*-Butylthio)acrylonitrile[a,b]

	k_2/k_1	k_3/I
	10^{-4}	10^{10}M^{-2}
$(CH_3)_2\dot{C}CN$	0.10±0.014	39
$CH_3\dot{C}HC_6H_5$	0.54±0.21	58

a) 80 °C in toluene. [M-N=N-M]=5×10^{-2}M. b) Run number 3.

Halogen- and Hydrogen-Abstraction Reaction of the Model Radical from Tetrahalomethanes and Thiophenols. The intensity of the ESR spectra of the adducts (MT· and RT·) was much lower in the absence of UV light irradiation at 80 °C than that under UV irradiation. Accordingly, the adducts obtained thermally were neglected in the kinetic study under UV light irradiation. Figure 3 shows a typical example

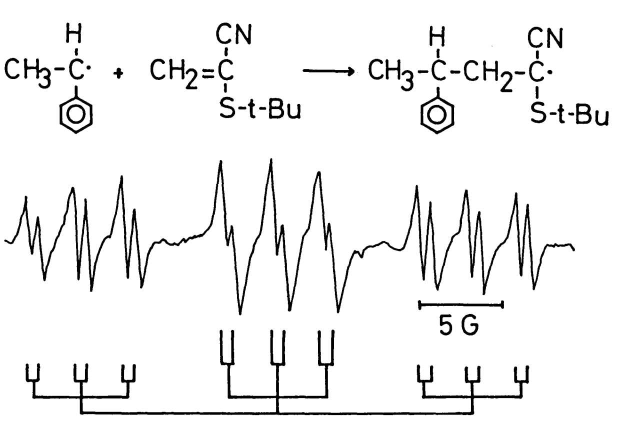


Fig. 1. ESR spectrum observed on irradiation of a mixture of 1,1′-diphenylazoethane and 2-(*t*-butylthio)acrylonitrile (T) in toluene at 80 °C. [1,1′-diphenylazoethane]=5×10^{-2} M and [T]=0.64 M.

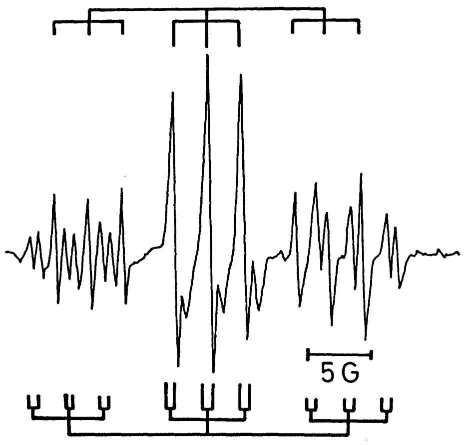


Fig. 3. ESR spectrum observed on the UV irradiation of a mixture of azo compound, thiophenol, and T in toluene at 80 °C. [1,1′-diphenylazoethane]=8.0×10^{-2} M, [thiophenol]=8.0×10^{-2} M, and [T]=0.32 M.

of the ESR spectra observed upon irradiating a mixture of thiophenol, 1,1′-diphenylazoethane, and T. The spectrum (Fig. 3) showed an overlap of a triplet of triplets of doublets and a triplet of triplets, which were reasonably assigned to the adducts of the α-methylbenzyl radical and the sulfur-centered radical produced from thiophenol,[12,14] respectively. An overlap of two kinds of a triplet of triplets was observed in a mixture of thiophenol, AIBN, and T, which was assigned to the adducts of the 1-cyano-1-methylethyl radical and the sulfur-centered radical. Similar spectra were observed in mixtures of azo compounds, tetrahalomethane and T.[12] The hyperfine splitting constants of the adducts are shown in Table 2. The reactions are shown in the following schemes:

$$\text{M-N=N-M} \xrightarrow{I} \text{M}\cdot \tag{1}$$

$$\text{M}\cdot + \text{T} \xrightarrow{k_1} \text{MT}\cdot \tag{2}$$

$$\text{M}\cdot + \text{RX} \xrightarrow{k_x} \text{MX} + \text{R}\cdot \tag{6}$$

$$\text{R}\cdot + \text{T} \xrightarrow{k_{1x}} \text{RT}\cdot \tag{7}$$

$$\text{RT}\cdot + \text{RT}\cdot \xrightarrow{k_3} \text{RTTR} \tag{8}$$

$$\text{RT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{RTTM} \tag{9}$$

$$\text{MT}\cdot + \text{MT}\cdot \xrightarrow{k_3} \text{MTTM} \tag{10}$$

Since M· and R· were not observed in the ESR spectra, the self-coupling reactions of these radicals were not taken into account. The stationary state treatment on R·, RT·, and MT· yields

$$\frac{[\text{RT}\cdot]}{[\text{MT}\cdot]} = \frac{k_{1x}[\text{R}\cdot][\text{T}]}{k_1[\text{M}\cdot][\text{T}]} = \frac{k_x[\text{RX}]}{k_1[\text{T}]}. \tag{11}$$

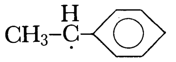
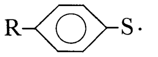
A typical example of a plot of [RT·]/[MT·] vs. the concentrations of transfer reagents is shown in Fig. 4. A linear relation was observed, the ratio, k_x/k_1, being calculated from the slope. Results are shown in Tables 3 and 4. Since the kinetic parameters obtained so far were k_x/k_1, k_2/k_1, and k_3/I, the absolute rate constants of each elementary process could not be directly estimated. If k_2 can be evaluated, k_1 could be estimated from k_2/k_1, and then k_x from k_x/k_1 using the obtained k_1. However, it is hard to directly measure the cross-coupling rate constant (k_2). If self-coupling reactions of M· and MT· are determined, the rate constants of a cross-coupling reaction can generally be estimated as the geometrical mean of the self coupling constants:

$$k_2 = (k_3 k_M)^{1/2}, \tag{12}$$

where k_M and k_3 are the rate constants for the self-coupling reactions of M· and MT·, respectively.

The k_M's for $CH_3\dot{C}HC_6H_5$ and $(CH_3)_2\dot{C}CN$ have already been reported to be 4.7×10^9 $M^{-1}\,s^{-1}$ [15] and 8×10^9 $M^{-1}\,s^{-1}$,[16] respectively. We determined k_3 to be $6.5\pm3\times10^8$ $M^{-1}\,s^{-1}$ as an average of data for 5 radicals estimated in a previous paper.[12] Accordingly, k_2's for these reactions were estimated from Eq. 12, being

Table 2. Hyperfine Splitting Constants for Adducts Obtained by Reaction of Carbon Radicals with 2-(*t*-Butylthio)acrylonitrile[a]

radical	a_H(mT)	a_{CN}(mT)	a_H(mT)
	11.0	2.8	0.8
$(CH_3)_2\dot{C}$-CN	8.8	2.8	—
·CBr_3	7.7	2.6	—
·CCl_3	8.0	2.6	—
	9.6	2.6	—

a) 80 °C in toluene.

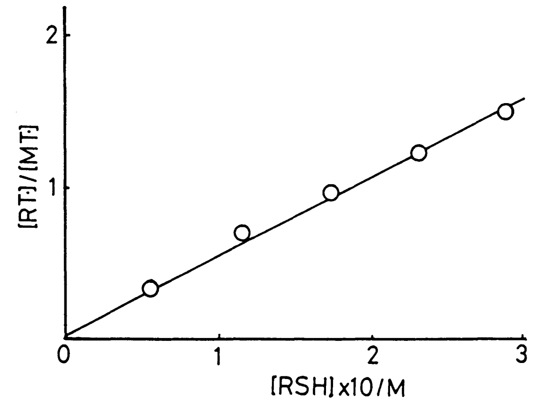


Fig. 4. Plot of [RT·]/[MT·] vs. [RSH] in the stationary concentration of RT· and MT·. [1,1′-diphenylazoethane]=5.0×10^{-2} M and T=0.32 M.

Table 3. Relative Rate Constants for Radicals $CH_3\dot{C}R_1R_2$ in Halogen Abstraction[a,b]

R_1	R_2	k_x/k_1		
		CBr_4	$CBrCl_3$	CCl_4
$-CH_3$	-CN	5.0±0.4	0.20±0.019	—
-H	-Ph	37 ±0.15	6.6 ±0.64	0.38±0.029

a) 80 °C in toluene, [M-N=N-M]=5×10^{-2} M. b) Run number 3.

Table 4. Relative Rate Constants for Radicals $CH_3\dot{C}R_1R_2$ in Hydrogen Abstraction from Thiophenol ($HS-C_6H_4-Z(p)$)[a,b]

R_1	R_2	k_x/k_1		
	Z=	-Cl	-H	$-CH_3$
$-CH_3$	-CN	0.76±0.020	1.2±0.14	2.1±0.12
-H	-Ph	23 ±1.5	25 ±1.1	23 ±1.5

a) 80 °C in toluene, [M-N=N-M]=5×10^{-2} M. b) Run number 3.

Table 5. Rate Constants for Halogen Abstraction of $CH_3\dot{C}R_1R_2$ from Tetrahalomethanes[a)]

R_1	R_2	k_x / $10^5M^{-1}s^{-1}$		
		CBr_4	$CBrCl_3$	CCl_4
$-CH_3$	$-CN$	2.1	0.084	—
-H	-Ph	110	20	1.1

a) 80 °C in toluene.

Table 6. Rate Constants for Hydrogen Abstraction of $CH_3\dot{C}R_1R_2$ from Thiophenols ($HS\text{-}C_6H_4\text{-}Z(p)$))[a)]

R_1	R_2	k_x / $10^7M^{-1}s^{-1}$		
	Z=	-Cl	-H	$-CH_3$
$-CH_3$	$-CN$	3.1×10^{-2}	5.0×10^{-2}	8.8×10^{-2}
-H	-Ph	0.68	0.74	0.68

a) 80 °C in toluene.

Table 7. Ionization Potential of Thiophenols (eV)

-Cl	-H	$-CH_3$
8.54	8.44	8.26

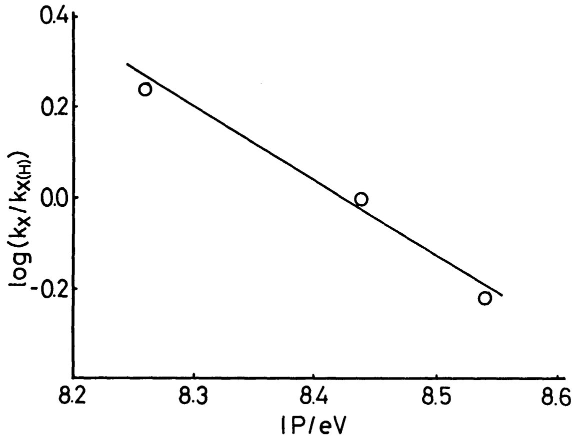


Fig. 5. Relation between rate constants and ionization potentials of thiophenols in the hydrogen abstraction reactions of $(CH_3)_2\dot{C}CN$ from the S-H bonds.

5.5×10^9 M^{-1} s^{-1} and 4.2×10^9 M^{-1} s^{-1} for $CH_3\dot{C}HC_6H_5$ and $(CH_3)_2\dot{C}CN$, respectively. Then, the k_l's were estimated from k_l/k_2 and the k_x's from k_x/k_l (Table 5). It can be seen that the k_x's for reactions between $CH_3\dot{C}HC_6H_5$ and tetrahalomethanes decreased in the order $CBr_4>CBrCl_3>CCl_4$: k_x of $CH_3\dot{C}HC_6H_5$ with CBr_4 was 6 and 10^2 times as large as those with $CBrCl_3$ and CCl_4, respectively. A similar trend in k_x for the halogen-abstraction reaction of $(CH_3)_2\dot{C}CN$ from tetrahalomethanes was observed (Table 5). The k_x's for the reaction of $CH_3\dot{C}HC_6H_5$ with CBr_4 and $CBrCl_3$ were about 50 and 200 times as large as those of $(CH_3)_2\dot{C}CN$ with the corresponding tetrahalomethanes, respectively.

In the case of thiophenols, k_x's of $CH_3\dot{C}HC_6H_5$ were in order of 10^7, being independent of the nature of para substituents (Table 6), while k_x's of $(CH_3)_2\dot{C}CN$ were in the order of 10^5 and decreased with electron-accepting substituents. The value of $\ln k_x$ for $(CH_3)_2\dot{C}CN$ was linearly correlated with the ionization potential of thiophenols (Fig. 5).

Discussion

To our knowledge, the absolute rate constants for the halogen-abstraction reaction of carbon radicals from tetrahalomethanes have been reported for only a few radicals, such as the methyl, *t*-butyl,[17)] and phenyl radicals.[18,19)] Therefore, we could not check the reliability of our data by comparison with other data. The k_x's for the halogen-abstraction reaction of the phenyl radical from CBr_4 and CCl_4 have been reported to be 5×10^9 [19)] and 5.8×10^6 M^{-1} s^{-1},[18)] respectively, two orders of magnitude larger than the corresponding k_x of $CH_3\dot{C}HC_6H_5$, (Table 5). This difference can reasonably be explained by the lower reactivity of $CH_3\text{-}\dot{C}HC_6H_5$ due to resonance stabilization than that of the phenyl radical. The k_x's for the halogen abstraction reactions of $CH_3\cdot$, $(CH_3)_3C\cdot$, and $(CH_3)_2\text{-}\dot{C}OCH_2CH_3$ from CCl_4 have been reported to be 3.35×10^2 (80 °C),[7)] 4.9×10^4 (30 °C),[17)] and 1.0×10^8 M^{-1} s^{-1},[20)] respectively. The k_x of $CH_3\dot{C}HC_6H_5$ from CCl_4 is larger than that of $\cdot CH_3$, and less than that of $(CH_3)_2\dot{C}OCH_2CH_3$. The k_x of $CH_3\dot{C}HC_6H_5$ at 80 °C is twice as large as that for $(CH_3)_3\dot{C}$ at 30 °C. When the k_x of the latter radical at 80 °C is calculated on the assumption that its activation energy is 13.8 kJ mol^{-1},[17)] it is estimated to be 1.06×10^5 M^{-1} s^{-1}, being of the same order as the k_x for the former. The k_x for the halogen abstraction reaction of carbon radicals has been found to be of the following order:

$$(CH_3)_2\dot{C}OCH_2CH_3>\dot{C}(CH_3)_3=CH_3\dot{C}HC_6H_5>\dot{C}H_3.$$

This order seems to be correlated with the electron-donating property of the α-substituents. These results show that our method for the determination of the rate constant of the halogen-abstraction reaction leads to reasonable rate constants. However, when the k_x's of $(CH_3)\dot{C}HC_6H_5$ were compared with the corresponding k_{trs}'s which were calculated from k_p and C_s's for the radical polymerization of styrene, a remarkable difference between k_x and k_{trs} was found (Table 5).

The determination of C_s has usually been carried out using the Mayo equation:[21)]

$$1/P_n = 1/P_{n0} + C_s[S]/[M], \tag{13}$$

where P_n and P_{n0} are the number degree of polymerization of the polymer produced in the presence and absence of transfer reagents[S], respectively; [S]/[M] is the molar ratio of the transfer reagent to the monomer. Thomas et al.[6] pointed out the fact that C_s in a CBr_4–styrene system was dependent on the extent of polymerization: C_s was 420 in the extent of polymerization to 0.5%, and 2.1 when the reaction was performed to 5% conversion. In addition, an accurate determination of the number average degree of polymerization is necessary for an accurate determination of C_s. Since a significant loss of low-molecular-weight polymer obtained in the low extent of polymerization leads to an overestimation of P_n, the C_s obtained by the Mayo equation seems to be smaller than the true value.

When thiophenols were used as chain-transfer reagents, the k_x's for the hydrogen-abstraction reactions of the styrene model radical from thiophenols was of the 10^6 order of magnitude, being consistent regarding the order of magnitude with the rate constant for the hydrogen abstraction of benzyl radical from thiophenol at 80 °C, which was estimated from the rate constant at 25 °C and the activation energy.[22,23] In addition, our results show that the k_x's is one order smaller than its halogen abstraction rate constant from CBr_4.[24] Since the C_s's of thiophenol derivatives have been reported to be one or two orders smaller than that of CBr_4[24] in the radical polymerization of styrene, the k_x for the hydrogen abstraction of α-methylbenzyl radical from thiophenol seems to be reasonable. To our knowledge, only a few absolute rate constants for the hydrogen abstraction of carbon radicals from thiophenol have been reported: The k_x's of the hydrogen-abstraction of phenyl, butyl, octyl, isopropyl, and t-butyl radicals from thiophenol are 1.9×10^9,[18] 1.36×10^8,[23] 9.2×10^7,[23] 1.05×10^8,[23] and $8.0\times10^7=1.47\times10^8$ [23] $M^{-1}s^{-1}$, respectively. These values are one or two orders of magnitude larger than the k_x of $CH_3\dot{C}HC_6H_5$. This styrene model radical is considered to be less reactive than phenyl radical and alkyl radicals, since the former radical is more stabilized through a delocalization of unpaired electron than the latter radicals. Accordingly, the difference in the rate constants between the model radicals and the others can be reasonably explained on the basis of the stabilization of the radical.

The k_x of $(CH_3)_2\dot{C}CN$ with thiophenols were an order of magnitude of 10^2 smaller than that of $CH_3\dot{C}HC_6H_5$, being dependent on the nature of the substituent binding to the benzene ring of thiophenol: the larger the electron-donating property of the substituent, the larger the k_x. The values of $\ln k_x$ were linearly correlated with the ionization potential of thiophenols. This result suggests the possibility that the hydrogen abstraction of $(CH_3)_2\dot{C}CN$ from thiophenol takes place through electron transfer or the charge-transfer complex of the radical. The k_x for the halogen abstraction of the styrene model radical from thiophenols might be too large for the substituent effect to be observed.

In conclusion, the rate constants for the halogen-abstraction reaction of the model radicals from tetrahalomethanes decreased in the order

$$CBr_4 > CBrCl_3 > CCl_4.$$

The rate constants (k_x) obtained by this method were larger than the corresponding chain-transfer rate constants (k_{trs}) calculated from the largest C_s and propagation rate constants of styrene (k_p).[12] This difference between k_x and k_{trs} can possibly be ascribed to an underestimation of C_s due to the removal of a fraction of a lower molecular weight polymer in the determination of the C_s values. In benzenethiols, the hydrogen-abstraction rate constants of the styrene model radical were an order of magnitude of 10^7, being independent of the substituents which were introduced in the para-positions of the aromatic ring; however, the rate constants of the methacrylonitrile model radical were an order of magnitude of 10^4, and decreased with increasing the electron-accepting power of the substituent.

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