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The Effect of Substituents in Radical Reactions: Reactivities of Substituted Cumenes to Attack by the Polystyryl Radical

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The polymerizations of styrene in a series of nuclear-substituted cumenes, using α, α'-azobisisobutyronitrile as an initiator, have been carried out at 60°C, and the chain transfer constants, C_s, for the substituted cumenes have been determined. It has been found that the C_s values for cumenes with electron-repelling groups are smaller than that for an unsubstituted cumene, while those for cumenes with electron-attracting groups are greater. The plot of $\log(k/k_0)$ against the corresponding Hammett's σ-constants failed to give a linear relationship. The modified Hammett's equation including the resonance effect for radical reactions, the equation which was proposed by the author and Azumi, *i. e.*,: $\log(k/k_0)=\rho\sigma+\gamma E_R$, could be adopted to the transfer with the usual precision, giving $\gamma=1$ and $\rho=0.7$. It is considered that the effects of substituents on the transfer reactivities of cumenes to the attack of the polystyryl radical depend on the contributions of polar and resonance factors.

In the radical polymerization of the vinyl monomer in the presence of a solvent, it is well known that the chain-transfer reaction of a growing polymer chain with the solvent occurs. A number of chain-transfer constants for various monomer-solvent systems have been measured and found to give useful information on the relation between structures and reactivities in chain transfers. However, in the study of the effects of meta- and para-substituents on the transfer reactivities of a series of nuclear-substituted compounds to any one vinyl polymer radical, we lack data covering wide enough ranges of substituents to discuss the Hammett relationship.

In the present experiments, in order to investigate the substituent effects on the chain-transfer reactivity, the polymerization of styrene in the presence of a cumene or a number of its meta- and para-substituted derivatives was carried out by using α, α'-azobisisobutyronitrile as an initiator at 60°C, and the transfer constants for styrene with a series of substituted cumenes were determined. Thus, the effects of substituents on the transfer reactivities of cumenes to attack by the polystyryl radical will be discussed on the basis of the Hammett relationship.

The series of nuclear-substituted cumenes used in the present study have the following substituents: *p*-OCH_3, *p*-*i*-C_3H_7, *p*-*t*-C_4H_9, *p*-Cl, *p*-Br, *p*-CN, *m*-OCH_3, *m*-Br and H.

Experimental

Materials. *p*-*t*-Butylcumene was prepared by the alkylation of purified cummene with *t*-butyl alcohol. Four hundred grams of cumene and *t*-butyl alcohol (3 : 1) were added to 700 m*l* of 92% sulfuric acid at −5−0°C.[1] After two hours the organic layer was separated and washed. Bp 125.5°C/44 mmHg, n_D^{20} 1.4918; lit.,[2] 1.4918.

p-Methoxycumene was prepared by treating 55 g of *p*-isopropylphenol, dissolved in 150 m*l* of a 1 : 1 water-ethanol mixture containing 25 g of potassium hydroxide, with 51 g of methyl sulfate. Thirty minutes after the drop-by-drop addition of the methyl sulfate, 200 m*l* of a 1 : 1 methanol-concentrated ammonium hydroxide solution was added to decompose any unreacted methyl sulfate. Bp 213°C, 103°C/20 mmHg, n_D^{20} 1.5032; lit.,[3] n_D^{20} 1.5033.

p-Diisopropylbenzene was synthesized from cumene. Propylene was added to a mixture of a cumene (300 g) and concentrated sulfuric acid (100 m*l*) at 0—5°C. Bp 121—121.5°C/56 mmHg, n_D^{20} 1.4898; lit.,[2] bp 121—121.5°C/56 mmHg, n_D^{20} 1.4898.

p-Chlorocumene was prepared by treating 120 m*l* of cumene with 110 m*l* of chlorobenzene in the presence of 20 g of anhydrous aluminum chloride for eight hours at 90°C. Bp 192—194°C, 72—73°C/11 mHg, n_D^{20} 1.5125; lit.,[4] 72—74°C/11 mmHg, n_D^{20} 1.5127.

p-Bromocumene was prepared by the bromination of cumene in the dark according to the procedure of Russell.[2] Bp 123.5°C/53 mmHg, n_D^{20} 1.5363; lit.,[2] bp 123.5°C/53 mmHg, n_D^{20} 1.5363.

p-Cyanocumene was prepared from *p*-cumic acid. *p*-Cumic acid was converted to the chloride by thionyl chloride, and the chloride was then converted to the methyl ester by treating it with methyl alcohol in the presence of pyridine. *p*-Cyanocumene was prepared by converting the acid chloride to the amide with ammonia. The amide was then dehydrated by thionyl

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1) H. Barbier, *Helv. Chem. Acta,* **19**, 1345 (1936).

2) G. A. Russel, *J. Am. Chem. Soc.,* **78**, 1047 (1956).

3) G. A. Russel and R. C. Williamson, Jr., *ibid.,* **86**, 2357 (1964).

4) T. Alfrey and J. G. Harrison, Jr., *ibid.,* **68**, 299 (1946).

chloride.5) Bp 110—110.5°C/24 mmHg, n_D^{20} 1.5285; lit.,2) bp 110—110.5°C/ 24 mmHg, n_D^{20} 1.5286.

m-Methoxycumene was synthesized from *m*-bromophenol. *m*-Bromophenol was converted to *m*-bromoanisole with dimethyl sulfate and sodium hydroxide.6,7) To a solution of the Grignard reagent derived from 93.5 g of *m*-bromoanisole there was added 182 g of freshly-distilled isopropyl sulfate at such a rate as to maintain gentle reflux for one hour. The mixture was then refluxed for thirty minutes, allowed to stand overnight, and hydrolyzed with iced dilute hydrochloric acid. The ether layer was separated, dried, and distilled. Bp 86—87°C/14 mmHg, lit.,8) bp 82—92°C/13—14 mmHg.

m-Bromocumene was prepared from 3-bromo-4-aminocumene in accordance with the procedure of Haworth and Barker9); that is, the 3-bromo-4-aminocumene was deaminated by diazotization and then treated with hypophosphorus acid. Bp 97—98°C/ 20 mmHg, lit.,9) bp 97—98°C/20 mmHg.

The cumene and styrene were commercial materials and were distilled before use.

Polymerization. Into a clean Pyrex tube there were pipetted 10 m*l* of a cumene solution of styrene and 1 m*l* of a benzene solution of α, α'-azobisisobutyronitrile (AIBN), the mixture was then diluted with benzene to a total volume of 15 m*l*. Each of the cumene derivatives was treated in the same way. The initial concentrations of AIBN and monomer in the contents were always kept constant: $[\text{AIBN}]=3.32\times10^{-3}$ mol/*l*. The contents of the tubes were frozen by dry ice in methanol and degassed in a vacuum line. The tubes were then sealed *in vacuo* and immersed in a water bath kept at 60°C±0.05°C. After polymerization to low conversions ($<10\%$), the polymer solution was stirred, drop by drop, into a large volume of methanol. After having been washed with methanol several times, the polymers were dried by being kept overnight *in vacuo* at 30°C. The rate of polymerization (R_p) was calculated from the weight of the dry polymer.

The Determination of the Degree of Polymerization. The intrinsic viscosities ($[\eta]$) of the polymer samples were determined by viscosity measurements of their dilute benzene solutions at 30°C, using Ostwald viscosimeters. The number-average degree of polymerization ($\overline{P}_n$) was calculated from the intrinsic viscosity, employing the following equation:10)

$$\log \overline{P}_n = 3.205 + 1.37 \log [\eta] \qquad (1)$$

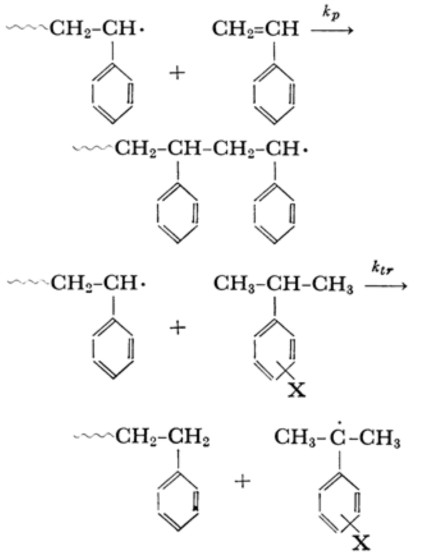
The chain-transfer constants (C_s) of substituted cumenes were determined by Mayo's equation:

$$\frac{1}{\overline{P}_n} = \text{const.} + C_s\frac{[\text{S}]}{[\text{M}]} \qquad (2)$$

where [S] and [M] are the initial concentrations of substituted cumenes and styrene respectively.

Results and Discussion

The reactions under consideration are:



(3)

(4)

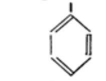
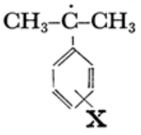
where  represents a growing polystyryl radical, which reacts with substituted cumenes to yield a dead polymer molecule and the  radical.

Figure 1 shows the relationship between the rate of polymerization of styrene in the presence of each substituted cumene and the concentration of each cumene.

In Fig. 1, it may be seen that the rate of polymerization only slightly decreases linearly with

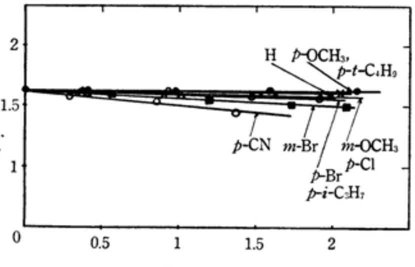


Fig. 1. Relationship between rates of polymerization (R_p) and the concentration of each cumene ([S]).

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5) S. M. McElvain and C. L. Stevens, *ibid.*, **69**, 2663 (1947).

6) F. Koelsch, *ibid.*, **61**, 969 (1939).

7) S. Nateson and S. P. Gottfried, *ibid.*, **61**, 1001 (1939).

8) H. Gilman, S. Avakian, R. A. Benkeser, H. S. Broadbent, R. M. Clark, G. Karmas, F. J. Marshall and S. M. Massie, *J. Org. Chem.*, **19**, 1064 (1954).

9) R. D. Haworth and R. L. Barker, *J. Chem. Soc.*, **1939**, 1302.

10) F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

an increase in the [S] value within the range of concentrations used. Thus, cumenes exhibited no appreciable retarding influences on the rate of polymerization of styrene.

The plots of the $1/\bar{P}_n$ values of the polymers against the ratio of the concentration of substituted cumenes to the styrene monomer are shown in Fig. 2; the chain-transfer constants were calculated from the slopes.

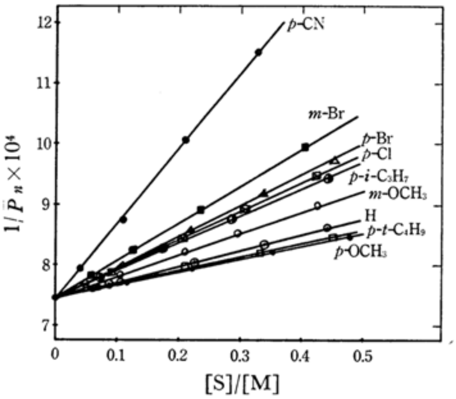

Fig. 2. Relationship between $1/\bar{P}_n$ and [cumene]/[styrene] for the polymerization of styrene initiated by AIBN in the presence of substituted cumenes at 60°C.

TABLE 1. CHAIN TRANSFER CONSTANTS OF SUBSTITUTED CUMENES ($C_s = k_{tr}/k_p$), 60°C

Substituent	$C_s \times 10^4$	Substituent	$C_s \times 10^4$
p-OCH_3	3.23	*p*-Br	7.57
p-*t*-C_4H_9	3.46	*p*-CN	18.6
p-*i*-C_3H_7	6.60	*m*-OCH_3	5.23
p-Cl	6.90	*m*-Br	8.29
H	3.88		

As is shown in Table 1, the values for the compounds with electron-repelling groups were generally smaller than that for the unsubstituted compound, while those for electron-attracting groups were greater. Thus, it may be considered that this order of values accords with the polar effect of substituents.

In order to examine this trend in more detail, we attempted to apply the Hammett equation:

$$\log (C_s/C_{s_0}) = \rho\sigma \qquad (5)$$

In Fig. 3, the logarithm of the ratios of the chain-transfer constants for substituted cumenes to that for an unsubstituted cumene is plotted against Hammett's σ values for the substituents in cumenes.

As is shown clearly in Fig. 3, the Hammett plots give not a straight line, but a concave one. Therefore, the effect of a substituent on the reactivity in the present reaction cannot be explained as only a polar effect.

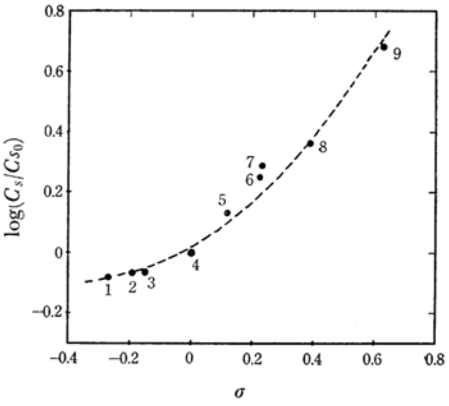

Fig. 3. Correlations between $\log(C_s/C_{s_0})$ and σ-constants for the attack of polystyryl radical upon substituted cumenes.

1 *p*-OCH_3
2 *p*-*t*-C_4H_9
3 *p*-*i*-C_3H_7
4 H
5 *m*-OCH_3
6 *p*-Cl
7 *p*-Br
8 *m*-Br
9 *p*-CN

Gregg and Mayo[11] demonstrated the importance of polar and resonance factors in evaluating the transfer reactivities of a number of organic compounds with a styrene monomer. These factors in chain-transfer reactions were also discussed in detail by Mayo and Walling.[12] Since, in the present reaction, it is not necessary to consider the steric effect of a substituent, the resonance effect may be regarded as being responsible for the deviation from the simple Hammett relation.

In 1960, assuming that the effect of structure on the activation free energies of radical reactions may be represented as the sum of the independent contributions of polar and resonance effects, as in ionic reactions, the present author and Azumi[13] proposed the following equation:

$$\log (k/k_0) = \rho\sigma + \gamma E_R \qquad (6)$$

TABLE 2. SEVERAL VALUES OF THE RESONANCE SUBSTITUENT CONSTANT, E_R

Substituent	E_R	Substituent	E_R
p-OCH_3	0.08	*p*-Br	0.12
p-*t*-C_4H_9	0.03	*p*-CN	0.52
p-*i*-C_3H_7	0.03	*m*-Br	0.12*
p-Cl	0.12	H	0.00

* Since there seems to be some doubt as to this numerical value, it is listed as a provisional value.

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[11] R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 3530 (1953).

[12] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

[13] T. Azumi and T. Yamamoto, *Reports of Himeji Institute of Technology*, **11**, 152 (1960); T. Yamamoto and T. Azumi, *ibid.*, **12**, 79 (1960); **13**, 77, 83 (1961).

where E_R is a resonance substituent constant, where γ is a reaction constant giving the degree of the resonance effect caused by the substituent, and where $\rho\sigma$ is a polar term indicated in the Hammett equation. For evaluating E_R, the addition reactions of both polystyryl[14] and polymethyl methacrylate radicals[15] to substituted styrenes[*1] were selected as standard reactions. Setting $\rho=0$ and $\gamma=1.0$ in Eq. (6) for these reactions, the E_R values for each substituents were calculated and averaged. In Table 2, the E_R values of the substituents used in the present reaction are listed.

Now, we attempted to apply Eq. (6) to this chain-transfer reaction. Equation 6 was put in the form of Eq. (7):

$$\log(C_s/C_{s_0}) - \gamma E_R = \rho\sigma \qquad (7)$$

In Fig. 4, setting $\gamma=1$ in Eq. (7), $\log(C_s/C_{s_0})-E_R$ is plotted against the Hammett σ value of each substituent.

As may be seen in this figure, there was here a better linear correlation than in Fig. 3. From the slope of the straight line, ρ is given as $+0.7$. It is thus demonstrated that the resonance effect of substituents on this chain transfer reactivity is important.

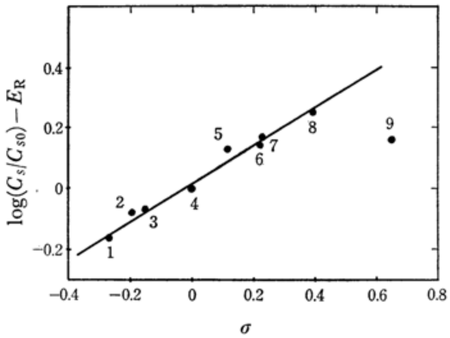

Fig. 4. Relationship between $\log(Cs/Cs_0)-E_R$ and the Hammett σ value.
1 p-OCH$_3$
2 p-t-C$_4$H$_9$
3 p-i-C$_3$H$_7$
4 H
5 m-OCH$_3$
6 p-Cl
7 p-Br
8 m-Br
9 p-CN

In Fig. 4 the plot of the p-cyano group deviates greatly form the line. Of course, the failure of Eq. (6) to apply to this group can not be concluded to result from a change in the reaction mechanism. The available value of E_R for the p-cyano group may be not so large as the numerical value shown in Table 2. The E_R value of the m-Br group in Table 2 could be used for the present purposes. However, it is doubtful whether this value can be used in the cases of other reactions. The present author intends hereafter to re-examine the desirable values of E_R for these substituents.

As has been mentioned above, the previously-calculated E_R values for some substituents are still under consideration. However, it is, in fact, undoubtedly true that Eq. (6) and its treatment of the resonance effect are better applied to the present reaction than the Hammett equation. Accordingly, the results clearly demonstrated that the effects of substituents on the transfer reactivities of cumenes to the attack of the polystyryl radical depend on the contributions of both polar and resonance factors.

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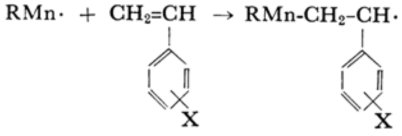
[14] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

[15] C. Walling, D. Seymour and K. B. Wolfstirn, *ibid.*, **70**, 1544 (1948).

[*1] These copolymerization reactions proceed as follows:



$$\text{RMn}\cdot + \text{CH}_2\text{=CH} \rightarrow \text{RMn-CH}_2\text{-CH}\cdot$$

where RMn· represents polystyryl and polymethyl methacrylate radicals.