NOTES

Effects of Substituents of the Chain-transfer Reactivities of Nuclear-substituted Acetophenones toward the Polymethyl Methacrylate Radical

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(Received March 27, 1968)

In previous papers,[1-5] the effects of substituents on the reactivities of substituted cumenes toward polymer radicals have been reported. The observed reactivities were not correlated with the ordinary Hammett equation, but they showed a good correlation with the Hammett equation[6] modified to include the resonance term:

$$\log (k/k_0) = \rho\sigma + \gamma E_R \qquad (1)$$

where $\rho\sigma$ is the polar term and γE_R is the resonance term. The ρ and γ show the degree of polar and resonance contributions of the substituents to the reactivities respectively.

This paper will describe the substituent effects on the chain-transfer reactivities of nuclear-substituted acetophenones toward the polymethyl methacrylate (PMMA) radical. Since the acetophenone has a carbonyl group between the benzene ring and the reacting methyl group, the nuclear-substituent effects on the reactivities of its derivatives toward a radical may be different from those observed in the abstraction of a benzylic hydrogen, as has been reported in previous papers.[1-5]

Experimental

A series of nuclear-substituted acetophenones (see Table 1), but not acetophenone itself, were synthesized. By using the method described in a previous paper,[1] the polymerizations of the methyl methacrylate in each acetophenone derivative were carried out at 60°C in the presence of 2,2′-azobisisobutyronitrile (3.32×10^{-3} mol/l) as an initiator. The polymerizations were performed below 5% conversion.

The number-average degree of the polymerization ($\overline{P}_n$) of the polymers was calculated from their intrinsic viscosities, $[\eta]$, determined in benzene, according to the following equation[7]:

$$\log \overline{P}_n = 3.420 + 1.13 \log [\eta]$$

The chain-transfer constants (C) of acetophenones were determined by means of Mayo plots[8] between $1/\overline{P}_n$ and the concentrations of the acetophenones.

Results and Discussion

The C values obtained are listed in Table 1, in which the E_R and σ values are the resonance[6] and the Hammett substituent constants[9], respectively.

As may be seen in Table 1, all of the C values for the substituted acetophenones were larger than that (C_0) for the unsubstituted compound. Figure 1 shows the plots using the ordinary Hammett equation and using Eq. (1).

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TABLE 1. CHAIN-TRANSFER CONSTANTS (C) OF NUCLEAR SUBSTITUTED ACETOPHENONES IN THE POLYMERIZATION OF METHYL METHACRYLATE AT 60°C

Substituent	σ	E_R	$C\times10^4$
p-CH_3O	−0.268	0.11	1.16
p-t-C_4H_9	−0.197	0.03	0.64
H	0.000	0.00	0.57
p-Cl	0.227	0.10	0.90
p-Br	0.232	0.12	1.15
m-Cl	0.373	0.08	0.83
p-CH_3CO	0.502	0.24	2.86 (1.43)*
p-CN	0.660	0.24	2.18

* This value indicates the value per CH_3CO group.

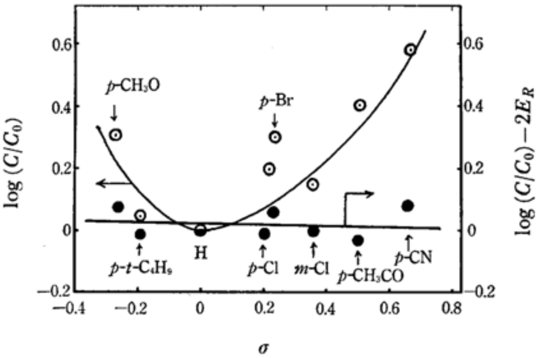

Fig. 1. Application of the Hammett equation and Eq. (1).

As is shown in Fig. 1, the ordinary Hammett plots for this reaction series failed to give a linear relationship. However, when the γ value in Eq. (1) was assumed to be 2.0, the plots with Eq. (1) gave linear relationship. From the slope of this line, the ρ value was obtained as nearly zero.

TABLE 2. APPLICATION OF EQ. (1) TO THE CHAIN-TRANSFER REACTIONS TOWARD THE PMMA RADICAL AT 60°C

Substrate	ρ	γ	Lit.
Cumenes	0.03	0.9	4)
Toluenes	0.01	0.6	10)
Dibenzoyl disulfides	0.07	0.75	11)
Diphenyl disulfides	0.01	0.75	12)
Phenylacetylenes	0.0	1.7	13)
Acetophenones	−0.01	2.0	This work

Table 2 summarizes the reaction constants obtatined from the application of Eq. (1) to the chain-transfer reactions of various substrates toward the PMMA radical.

As can be seen from Table 2, the ρ values in these reactions are very small or are negligible in comparison with the γ values. This finding strongly demonstrates that the polar substitutent effect on the chain-transfer reactivities of these substrates toward the PMMA radical is rather small. On the other hand, the γ value in the present reaction series is much larger than those in the other reaction series. Therefore, it may be considered that the effects of substituents in the acetophenones on the chain-transfer reactivities toward the PMMA radical depend on the contributions of their resonance factors.

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