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BROMINE ABSTRACTION BY ARYL RADICALS FROM SUBSTITUTED BENZYL BROMIDES

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The relative reactivities of substituted benzyl bromides toward bromine abstraction by substituted phenyl radicals were determined at 60°C. The nature and the extent of polar and conjugative effects were found to depend on the substituents on the radicals.

Among abstractions of univalent atoms by radicals, hydrogen abstraction has been extensively studied in view of the structure-reactivity relationship, but halogen abstractions have received attention for only these several years.1) Systematic researches showed the positive ρ value for iodine abstraction by the phenyl radical, and the polar effect oversides the effect of differences in the bond dissociation energy, particularly in abstraction from aryl iodides.1) We wish to communicate the facts which seem to indicate that the rate-controlling factors in bromine abstractions by substituted phenyl radicals from the benzylic bromides vary with the nature of the aryl radicals.

The measures of the reactivities of substituted benzyl bromides toward aryl radicals were determined by carrying out competitive reactions of the radicals derived from thermal decomposition (at 60°C) of arylazotriphenylmethanes between carbon tetrachloride and the benzyl bromides.

$$\mathrm{Ar}\cdot \quad + \quad \mathrm{CCl_4} \xrightarrow{k_{Cl}} \mathrm{ArCl} \quad + \quad \mathrm{CCl_3}\cdot$$

$$\mathrm{Ar}\cdot \quad + \quad \mathrm{XC_6H_4CH_2Br} \xrightarrow{k_{Br}} \mathrm{ArBr} \quad + \quad \mathrm{XC_6H_4CH_2}\cdot$$

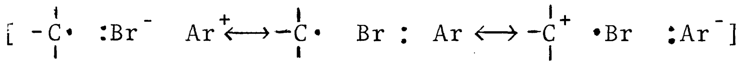
Relative rate constants k_{Br}/k_{Cl} were calculated from the yields of the aryl bromides and chlorides. Variations of initial concentrations of the radical generators and relative concentrations of the substrates did not affect seriously the observed rate constants. Relative rate constants obtained are listed in Table 1, and their Hammett plots are shown in Fig. 1, 2, and 3. Each value represents the average of several independent runs.

Although the selectivities of the bromine abstractions are generally low, some interesting tendencies can be found from the results. Fig. 1 shows that relative reactivities of m-substituted benzyl bromides toward phenyl radical hold Hammett's relation, indicating slightly nucleo-seeking selectivity ($\rho = +0.13$, $r = 0.99$) of the abstraction by the phenyl radical, and that p-substituted benzyl bromides are always more reactive than expected from the above Hammett line, irrespectively of the polar natures of the substituents. This tendencies imply that the conjugative effects of the p-substituents are operative, as had been observed in homolytic aromatic substitutions[2] and free radical additions to substituted styrenes,[3] although the activating effect of p-methyl group appears anormally large.

As can be seen in Fig. 2, the abstraction by p-chlorophenyl radical shows similar tendencies, but the nucleo-seeking selectivity is even slighter ($\rho = +0.05$, $r = 0.87$), and the activation by the conjugative effects of the p-substituents are also smaller than in the reaction of the phenyl radical.

Interestingly, furthermore, the activating effects of the p-substituents, especially of the p-nitro group, could not be observed in the abstraction by the p-nitrophenyl radical. Instead, as shown in Fig. 3, the relative reactivities of all benzylic bromides tolerably correlate with σ^+ ($\rho^+ = -0.19$, $r = 0.87$) or with σ ($\rho = -0.22$, $r = 0.77$), indicating the electron-seeking feature of the abstraction.

These results suggest the transition state of the bromine abstraction by aryl radical from benzylic bromide being expressed by the following resonance formula;



$$[\ -\overset{|}{\underset{|}{C}}\cdot\ \ :Br^-\ \ Ar^+ \longleftrightarrow -\overset{|}{\underset{|}{C}}\cdot\ \ Br:\ Ar \longleftrightarrow -\overset{|}{\underset{|}{C}}{}^+\ \ \cdot Br\ \ :Ar^-\ ]$$

and the relative importance of contribution of each canonical structure and the extent of breaking of the starting C–Br bond may depend on the nature of the attacking radical. The fact that no correlation with σ^- was observed even in the nucleo-seeking abstraction by the phenyl radical suggests unimportance of contribution of any structure bearing negative charge on the benzylic carbon. This could be understandable in the case of abstraction by the aryl radical from the benzylic substrate, considering the difference in s-character of carbon atoms of the reaction sites between the attacking radicals and the benzylic substrates.

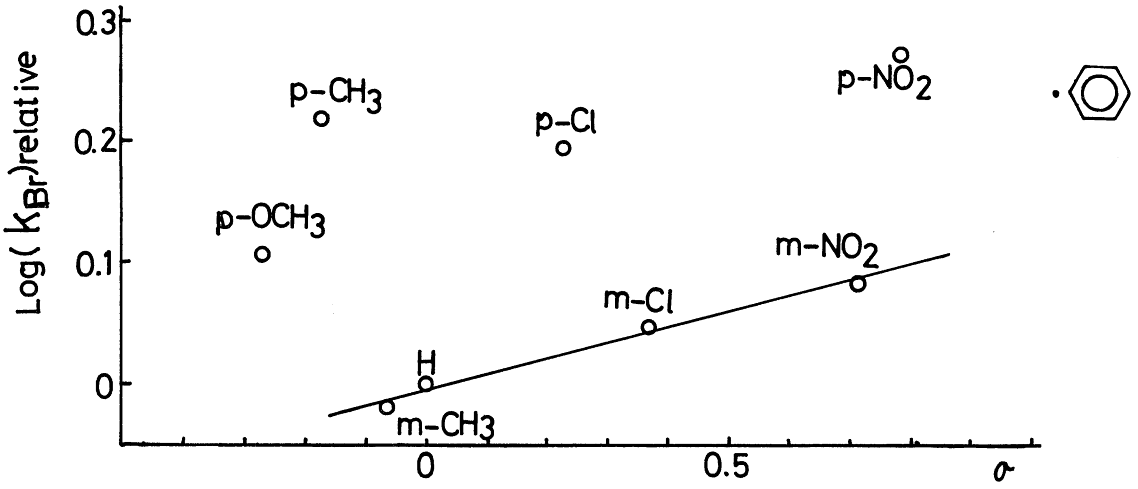


Fig. 1. Hammett Plot for Bromine Abstraction by Phenyl Radical

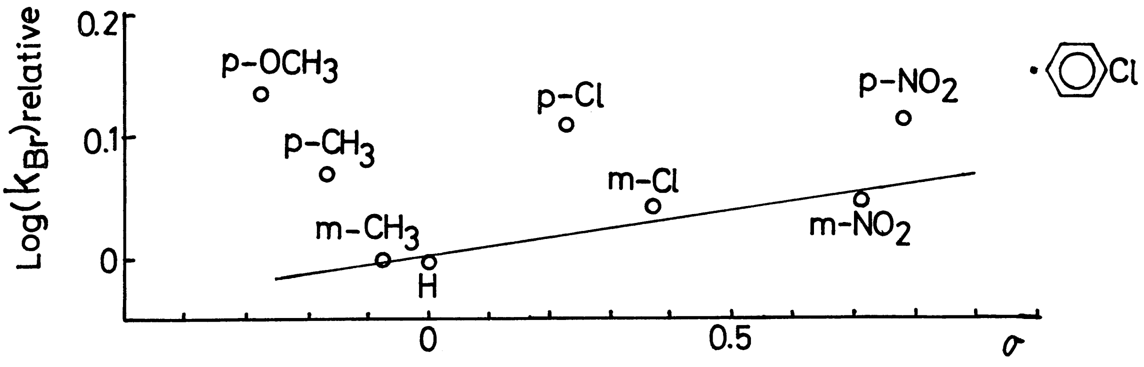


Fig. 2. Hammett Plot for Bromine Abstraction by p-Chlorophenyl Radical

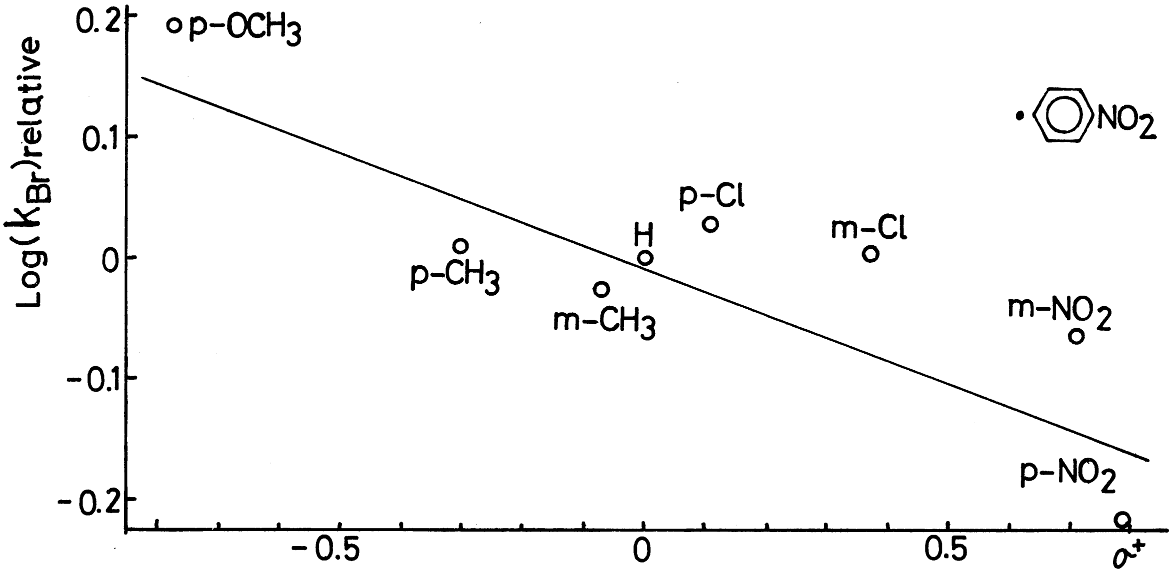


Fig. 3. Hammett-Brown Plot for Bromine Abstraction by p-Nitrophenyl Radical

Table 1. Rates of Bromine Abstraction from Benzyl Bromides Relative to Chlorine Abstraction from Carbon Tetrachloride at 60°

$XC_6H_4CH_2Br$ X =	$C_6H_5\cdot$ k_{Br}/k_{Cl}	$p\text{-}ClC_6H_4\cdot$ k_{Br}/k_{Cl}	$p\text{-}O_2NC_6H_4\cdot$ k_{Br}/k_{Cl}
$p\text{-}CH_3$	6.17 ± 0.45	9.56 ± 0.92	26.5 ± 0.9
$m\text{-}CH_3$	3.54 ± 0.10	8.14 ± 0.30	24.3 ± 0.3
$p\text{-}CH_3O$	4.78 ± 0.32	11.1 ± 0.4	40.2 ± 2.0
H	3.71 ± 0.25	8.13 ± 0.50	25.9 ± 1.8
m-Cl	4.17 ± 0.16	8.98 ± 0.31	26.1 ± 0.7
p-Cl	5.79 ± 0.25	10.5 ± 0.2	27.5 ± 0.5
$m\text{-}NO_2$	4.50 ± 0.30	8.82 ± 0.74	22.4 ± 0.9
$p\text{-}NO_2$	6.97 ± 0.50	10.7 ± 1.0	15.7 ± 0.7

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