

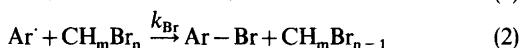
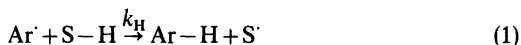
Short Communications

Selectivities of 4-Substituted Phenyl Radicals in Hydrogen, Deuterium and Bromine Atom Abstraction Reactions in Acetonitrile

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We recently observed that relative rate constant ratios (k_H/k_{Br}) in reactions (1) and (2) were greater when Ar \cdot was 4-nitrophenyl than when the aryl



radical was α -naphthyl reacting with the solvent, DMF, or with bromomethanes.¹ We found this somewhat surprising since the more electrophilic radical would be expected to preferentially attack the electron-rich halogen atoms. The comparison is not very meaningful since the structures of Ar \cdot differed considerably. We have now carried out competitive kinetic experiments on the atom abstraction reactions of a series of 4-substituted aryl radicals which resulted in clearly evident trends in the electrophilic–nucleophilic character of the radicals.

Results of reactions carried out in CH₃CN or CD₃CN are summarized in Table 1. The radicals reacting in (1) where S–H is the solvent were generated by the electron transfer reduction of the appropriate 4-substituted phenyldiazonium fluoroborate with iodide ion. The relative rate constants for reaction (1) compared to reaction (2) where CH₃Br_n was dibromomethane were obtained by GLC analysis of the resulting reaction mixtures as described earlier.¹ The data indicate that k_H/k_D decreases as the aryl radical becomes less electrophilic. On the other hand, k_H/k_{Br} increases in the opposite sense, i.e. as the radical becomes more nucleophilic. The latter trend is even more

evident in the k_D/k_{Br} ratios. The data were correlated using the Hammett relationship (3)² where c has no

$$\log(k_X/k_H) = \rho\sigma_p + c \quad (3)$$

significance. In all cases, the correlation coefficient was greater than 0.99.

The most interesting feature of the data is that D–CD₂CN is much more prone to attack by the more nucleophilic radical, 4-methoxyphenyl than by electrophilic 4-nitrophenyl. The relative rate constant for the two reactions is equal to 6.7, as evident from the last column of Table 1. The corresponding relative rate constant for the reactions of the radicals with H–CH₂CN is of the order of 2.5 (next to last column of Table 1). These relative reactivities then result in the deuterium kinetic isotope effect being very dependent upon the electrophilicity–nucleophilicity of the aryl radical.

Table 1. Deuterium kinetic isotope effects and selectivities in atom transfer reactions of 4-substituted phenyl radicals.^a

Radical	k_H/k_D	$10^2 k_H/k_{Br}$	$10^2 k_D/k_{Br}$
4-Nitrophenyl	9.53	3.54	0.371
4-Chlorophenyl	5.50	6.35	1.16
4-Methoxyphenyl	3.53	8.70	2.47

^aThe radicals were generated by the reaction of equimolar amounts of the appropriate diazonium fluoroborate with Bu₄NI in solvent at 20 °C. The analysis procedure has been described.¹

Table 2. Hammett equation correlations of the relative rate constants for atom abstraction reactions of 4-substituted phenyl radicals.^a

Rate constant ratio	ρ^b	r^c
k_H/k_{Br}	–0.373	0.990
k_H/k_D	+0.411	0.999
k_D/k_{Br}	–0.786	0.996

^aData from Table 1. ^bThe slope of the Hammett correlation using ρ_p from Ref. 2. ^cThe correlation coefficient from b .

The overall conclusion from the data in Tables 1 and 2 is that the more electrophilic the aryl radical is, the more favorable abstraction of Br from CH_2Br_2 is relative to abstraction of either H or D from acetonitrile. Nucleophilic radicals have a more pronounced tendency to abstract deuterium from acetonitrile than do electrophilic radicals.

The electrophilic–nucleophilic character of free radicals has been discussed in a number of instances.^{3–5} However, we are not aware of any data on the reactions of 4-substituted phenyl radicals which so clearly show the effect of substituents on the relative nucleophilicity as that reported here. A number of Hammett correlations of the rates of halogen atom abstraction has been carried out.⁶ However, these have involved substituent changes in the halogen compound^{7–10} rather than in the radicals.

1. Tilset, M. and Parker, V. D. *Acta Chem. Scand. B* 36 (1982). *In press*.
2. Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*, Cambridge Univ. Press, London 1979, Chapter 3.
3. Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London 1976, pp. 182–185.
4. Nonhebel, D. C., Tedder, J. M. and Walton, J. C. *Radicals*, Cambridge Univ. Press, London 1979, pp. 131–133.
5. Huyser, E. S. *Free Radical Chain Reactions*, Wiley-Interscience, New York 1970, p. 77.
6. Danen, W. C. In Huyser, E. S., Ed., *Methods in Free Radical Chemistry*, Dekker, New York 1974, Vol. 5, Chapter 1.
7. Danen, W. C. and Winter, R. L. *J. Am. Chem. Soc.* 93 (1971) 716.
8. Danen, W. C. and Saunders, D. G. *J. Am. Chem. Soc.* 91 (1969) 5924.
9. Gardner, I. J. and Noyes, R. M. *J. Am. Chem. Soc.* 83 (1961) 2409.
10. Kuivila, H. G. and Walsh, E. J. *J. Am. Chem. Soc.* 88 (1966) 571.

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