Mechanism of Nonactivated Bimolecular Aromatic Nucleophilic Substitution. Reaction of *meta*- and *para*-Substituted Fluorobenzenes with Piperidine

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Summary An excellent linear correlation is obtained for second-order rate coefficients in the displacement of fluoride ion by piperidine in triethylene glycol from fluorobenzenes containing a wide variety of activating and nonactivating *meta*- and *para*-substituents.

THE bimolecular (intermediate complex) mechanism for aromatic nucleophilic substitution is well established for most activated (nitro-containing) aromatic compounds.[1] In contrast, however, little is known concerning the nature of the bimolecular mechanism for the nonactivated counterparts. We report the study of the effect of a wide variety of activating and nonactivating substituents on the rate of displacement of fluoride from *meta*- and *para*-substituted fluorobenzenes by piperidine in triethylene glycol at 194·5°. The Table summarizes the second-order rate coefficients.

An excellent linear correlation (log k_2 against σ^-) is obtained for second-order rate coefficients covering almost seven orders of magnitude in rate ($\rho = +4{\cdot}41$, $r = 0{\cdot}996$). This suggests that the same reaction mechanism is involved for all the substituted fluorobenzenes reported in this study.[2] Bunnett[3] and Suhr[4] have postulated that the reaction of *p*-nitrofluorobenzene (an activated substrate) with piperidine proceeds *via* a two-step mechanism in which the formation of the intermediate complex is rate-controlling. The observation that the *p*-nitro-substituent falls directly on the correlation line suggests that all of the other substituted fluorobenzenes proceed by the same two-step mechanism. Indeed, if there were any change in mechanism (as, for example, a concerted, one-step displacement)[5] or a change in rate-controlling step as one varied the activating power of the substituent on the ring, one would expect a nonlinear structure–reactivity correlation[2] instead of the linear correlation reported.

TABLE

X[a]	k(M^{-1} sec.$^{-1}$)
p-Me	$5{\cdot}56 \times 10^{-8}$
m-Me	$2{\cdot}21 \times 10^{-7}$
p-F	$1{\cdot}38 \times 10^{-7}$
H	$3{\cdot}14 \times 10^{-7}$
m-OH	$1{\cdot}18 \times 10^{-6}$
m-F	$7{\cdot}81 \times 10^{-6}$
m-CF_3	$1{\cdot}83 \times 10^{-5}$
m-NO_2	$2{\cdot}54 \times 10^{-4}$
p-NO_2	$1{\cdot}75 \times 10^{-1}$

[a] Detailed product analysis indicates the absence of benzyne intermediates.

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