These salt effects arise because interactions between the anion and the cationic micelle make it more difficult for the hydroxide ion to attack the organic substrate which is incorporated into the micelle, and the stronger the interaction, *e.g.*, as with arenesulfonate ions, the greater the ability to exclude hydroxide ion.

The effect of the added salt upon the aggregation number of the cationic micelle also needs to be considered,[28] because some anions *e.g.*, Br^- and NO_3^-, increase the aggregation number of micelles of the cetylpyridinium ion, and others, *e.g.*, I^- and ClO_4^-, cause precipitation. An increase in the aggregation number should reduce the catalytic efficiency of the detergent, because of a reduction in the number of micelles, but our salt inhibitions were obtained at much lower concentrations of salt than that of 0.2 *m* used by Anacker and Ghose, suggesting that more than changes in micellar size and shape are involved in these salt effects.

The salt inhibition of the CTA-catalyzed hydrolysis of the dianions of 2,4- and 2,6-dinitrophenyl phosphate shows a similar dependence upon the charge density of the anions.[29]

Registry No.—2,4-Dinitrofluorobenzene, 70-34-8; hydroxide ion, 14280-30-9.

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Kinetics of Reactions of 4-Substituted 2-Nitrofluorobenzenes with Piperidine in Methanol[1]

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Received July 15, 1968

Rates of reaction of six 4-substituted 2-nitrofluorobenzenes with piperidine in methanol are determined, in part by conventional methods and in part by a stopped-flow technique. The reactions are first order in substrate and first order in piperidine; thus they are not base catalyzed. A satisfactory linear free-energy correlation of log k_A with σ^- exists, and ρ is +3.5. $\Delta S^\ddagger$ is substantially constant within this group of reactions.

The objectives of this research were twofold—to determine the effects of 4 substituents in 4-substituted 2-nitrofluorobenzenes on reactivity with piperidine in methanol and to ascertain whether reactions in this series are catalyzed by base.

A number of studies of substituent effects on aromatic nucleophilic substitution have been made in the last two decades. Many are summarized by Brieux, *et al.*,[4] and by Shein and Kozorez.[5] However, substituent effects have not previously been studied in the system of present interest.

Whether or not an aromatic substitution reaction involving an amine nucleophile is catalyzed by base is indicative of significant features of the energy profile of the reaction. In general, the absence of base catalysis (in hydroxylic solvents) indicates that the tetrahedral intermediate complex progresses to products faster than it reverts to reactants, while susceptibility to catalysis by base indicates the contrary.[6,7]

Reactions related to those studied in the present work differ in their susceptibility to catalysis by base. Those of piperidine with 2,4-dinitrochlorobenzene and 2,4-dinitroiodobenzene in aqueous dioxane are not catalyzed by base,[8] but the reactions of piperidine with 2,4-dinitrodiphenyl ether in aqueous dioxane[6] and with 2,4-dinitroanisole in aqueous dioxane[6b,9] or methanol[10] are accelerated by base. Reactions of 2,4-dinitrofluorobenzene with N-methylaniline in ethanol and aqueous dioxane are base catalyzed,[11] but those with *n*-butylamine and aniline are not.[12] The reaction of 2,4-dinitrofluorobenzene with piperidine in benzene solution is catalyzed by bases.[13,14] It was therefore of general interest as well as specific importance to our study of substituent effects to determine whether the present reactions are catalyzed by base.

The reactions studied are represented by eq 1. The 4-substituted 2-nitrophenylpiperidine products (II) are colored to the eye, having absorption maxima at *ca.* 375–440 mμ, and reaction rates are conveniently followed photometrically.

All rate determinations were performed with piperidine in large excess over the aryl fluoride substrate. Good pseudo-first-order kinetic plots were obtained in

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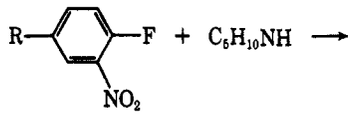

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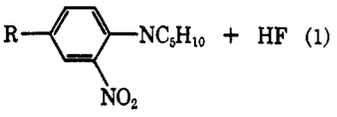

II

all cases. The pseudo-first-order rate coefficients (k_ψ) were divided by piperidine concentration to convert them into second-order coefficients, k_A. By having the amine in large excess, the complication of whether or not the hydrogen fluoride by-product combined with the piperidine to form a salt[15] was rendered inconsequential.

Quantitative yields of the expected products (II) were indicated by the photometric data except in one case. 4-Trifluoromethyl-2-nitrofluorobenzene (I, R = CF_3) gave "infinity" absorbances only about 90% of those expected for complete reaction. A complication of competing methoxydefluorination, stemming from the reaction $C_5H_{10}NH + CH_3OH \rightleftarrows C_5H_{10}NH_2^+ + CH_3O^-$, was suspected,[16] but addition of piperidine hydrochloride had little effect on the "infinity" absorbance. It is probable that our sample of I, R = CF_3, was contaminated with an unreactive impurity. We have treated the data on that assumption. If the assumption is unjustified, the error is only about 10%.

In Table I, the rate coefficients determined for five substrates are presented. These were all determined by conventional techniques which are described in the Experimental Section.

TABLE I

REACTIONS OF 4-SUBSTITUTED 2-NITROFLUOROBENZENES WITH PIPERIDINE IN METHANOL

4 substituent	Temp, °C	$[C_5H_{10}NH]$, M	10^3k_ψ, sec^{-1}	10^4k_A, l. mol^{-1} sec^{-1}
H	25.0	0.098	1.34 ± 0.01[a]	1.37
		0.102	1.23	1.21
		0.201	2.48	1.23
		0.304	3.98	1.31
		0.401	5.17	1.29
		0.502	6.74	1.34
	45.0	0.098	5.36 ± 0.04[b]	5.49
	46.6	0.102	5.38	5.27
		0.303	18.14	5.99
Br	24.7	0.0393	6.08 ± 0.06[a]	15.4
	46.0	0.0393	25.0[c]	63.6
CF_3[d]	0.0	0.0394	41.9 ± 1.2[b]	106
		0.3094[e]	45.2[c]	115
	20.0	0.0393	168	427
		0.0393[e]	172	438
CH_3CO	0.0	0.0198	87.5[c]	442
	10.1	0.0198	178 ± 5[f]	898
	20.0	0.0198	326 ± 2[a]	1640
CH_3SO_2	0.0	0.0393	671 ± 11[b]	1710
	10.2	0.0393	1260 ± 20	3200
	19.8	0.0393	2070 ± 100	5260

[a] Average of two runs. [b] Average of three runs. [c] Two identical runs gave identical results. [d] The presence of about 10% unreactive impurity is suspected; see text. [e] Piperidine hydrochloride, 0.0197 M, also present. [f] Average of four runs.

In Table II, most of the data obtained for the reaction of 2,4-dinitrofluorobenzene with piperidine are listed. These were obtained by direct observation of the increase in absorbance of the reacting solution, and all measurements at piperidine concentrations over 0.01 M were made in a Durrum–Gibson stopped-flow spectrophotometric kinetics apparatus.

TABLE II

REACTION OF 2,4-DINITROFLUOROBENZENE[a] WITH PIPERIDINE IN METHANOL

$[C_5H_{10}NH]$, M	10^3k_ψ, sec^{-1} 15.0°	25.0°	40.0°	k_A, l. mol^{-1} sec^{-1} 15.0°	25.0°	40.0°
0.00131	3.65	6.40	11.4	2.79	4.92	8.70
0.00328	10.7	17.6	30.6	3.26	5.43	9.35
0.00656	23.6	33.6		3.54	5.59	
0.0180	64.8[b]	110	205	4.05[b]	6.50	11.3
0.0205	90.4	132	235	4.47	6.46	11.3
0.0470	182	264	474	4.49	6.43	11.6
0.0820	377	565	1030	4.60	6.89	12.5
0.205	948	1450	2480	4.62	7.10	12.3
0.410	2170	2990	5400	5.29	7.26	13.0

[a] $[(O_2N)_2C_6H_3F]_0$, *ca.* 5×10^{-5} M. [b] $[C_5H_{10}NH]$, 0.0160 M.

Extrapolation of the data in Table II (at 0.205 M piperidine) gives a k_A of 2.38 l. mol^{-1} sec^{-1} at 0.0°. This is about 60% higher than reported by Bunnett, Garbisch, and Pruitt.[16] The earlier determinations involved taking aliquots from the reaction solutions by pipet, a technique only marginally applicable to such a fast reaction.

In addition to the experiments summarized in Table II, a series of ten determinations of the rate of reaction of 2,4-dinitrofluorobenzene with piperidine at 40.0° was made with piperidine hydrochloride present in a constant concentration of 8.87×10^{-4} M and piperidine present in variable concentration between the extremes of 1.75×10^{-3} and 0.157 M. The resulting k_A values varied randomly with piperidine concentration between 12.0 and 12.9 l. mol^{-1} sec^{-1}; the mean value was 12.5 l. mol^{-1} sec^{-1} which is in agreement with the k_A values in Table II at higher piperidine concentrations. This series of runs provides not the least suggestion of catalysis by the base piperidine.

In Table III, our rate data at 25° are summarized, and the activation parameters calculated by means of standard expressions[17] are tabulated.

TABLE III

RATES, ENTHALPIES, AND ENTROPIES OF ACTIVATION[a]

4 substituent	k_A at 25.0°, l. mol^{-1} sec^{-1}	k_A, relative	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}
H	1.29×10^{-4}	1.00	12.5	−34
Br	1.57×10^{-3}	12.2	12.0	−31
CF_3	5.86×10^{-2}	455	10.4	−29
CH_3CO	2.22×10^{-1}	1720	9.9	−28
CH_3SO_2	6.93×10^{-1}	5370	8.6	−30
NO_2	6.46[b]	50100	6.3[c]	−33[c]

[a] Based on data in Tables I and II, with extrapolation to 25° as necessary. [b] At $[C_5H_{10}NH]$ 0.0205 M. [c] Average of values derived from the last five lines of data in Table II.

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Discussion

Absence of Base Catalysis.—Concerning the *o*-fluoronitrobenzene data in Table I for 25.0°, the determinations at 0.098 *M* piperidine were made in one laboratory and all the rest in another. The latter suggest a modest increase in the second-order rate coefficient (k_A) as piperidine concentration increases from 0.1 to 0.5 *M*. For 2,4-dinitrofluorobenzene, the k_A values in Table II span a wider range of piperidine concentrations (on a logarithmic scale) than do the *o*-fluoronitrobenzene values in Table I, and they show a somewhat greater increase with increase in piperidine concentration.

Part of the small variations observed can be attributed to the basic dissociation of piperidine in methanol, for which K_b has been reported to be 7.3×10^{-6}.[18] Using this value, one calculates that about 8% of the piperidine was ionized to piperidinium methoxide at the lowest piperidine concentration in Table II, but less than 1% at piperidine concentrations of 0.07 *M* or greater. Basic dissociation decreases the concentration of piperidine available to react with the aryl fluoride, and therefore depresses the measured rate coefficient. However, on the basis of these calculations this factor can only account for a small part of the trend among the k_A values in Table II, and its effect on the *o*-fluoronitrobenzene data in Table I is negligible.

A further consideration is that reactions at the lowest three piperidine concentrations in Table II were too slow for convenient study in the stopped-flow apparatus, but rather fast for study by more conventional techniques. Moreover, there was some possibility of interference by atmospheric carbon dioxide at such low concentrations of a strongly basic reagent. For these reasons, we have somewhat less confidence in those k_A values than in those at higher piperidine concentrations. The trend among the k_A values at the highest six piperidine concentrations in Table II is less accentuated.

On the other hand, as described above a series of runs with constant piperidine hydrochloride concentration and variable piperidine concentration (between 0.0018 and 0.157 *M*) showed only random variation in k_A. Thus some of our data indicate a mild increase in rate with increase in piperidine concentration while other data indicate no increase at all. Certainly there is no suggestion of the strong acceleration which is characteristic of reactions which are truly catalyzed by base. These reactions thus are not base catalyzed. Mild accelerations of uncertain character have been observed in certain other reactions of amines with activated aryl halides.[12,19]

Substituent Effects on Rate.—When linear free-energy correlations were attempted between log k_A from Table III and σ values of the original Hammett type,[20] or with the "normal" mean σ of van Bekkum, Verkade, and Wepster,[21] or the special σ of the latter authors for anilinium ion dissociation (their reaction 26a), rather unsatisfactory plots were obtained. On the other hand, the plot of log k_A *vs.* Jaffé's σ^- (originally designated σ^*) values[20,22,23] was agreeable; it is presented as Figure 1. The slope of the line drawn is +3.52. This ρ is similar in magnitude to ρ observed for many other aromatic nucleophilic substitutions in nitro-activated aryl halides.[5]

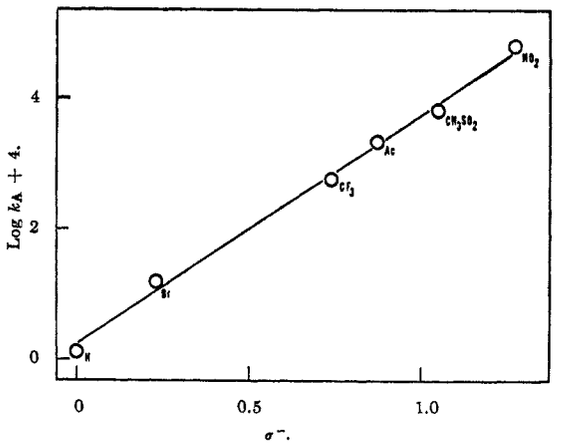

Figure 1.—Hammett plot of log k_A *vs.* σ^-. The slope of the line drawn, ρ, is +3.52. Data are from Table III.

Activation Parameters.—The $\Delta S^\ddagger$ values in Table III are nearly equal to those for reactions of piperidine with several 1-substituted 2,4-dinitrobenzenes in methanol solution.[16] The differences between the $\Delta S^\ddagger$ in Table III are not much greater than the probable experimental error, and they show no consistent trend. Differences in rate are governed mainly by differences in the enthalpy of activation.

Experimental Section

4-Substituted 2-Nitrofluorobenzenes (I).—*o*-Fluoronitrobenzene,[24] bp 78–79° (8 mm), further purified by preparative glpc, 4-fluoro-3-nitroacetophenone,[25] mp 49–50°, and 4-fluoro-3-nitrobenzotrifluoride,[24] bp 148–149° (150 mm) (this boiling point is from the final distillation of a series through good columns at various pressures), were made by standard methods.

4-Fluoro-3-nitrophenyl methyl sulfone was made by heating 4-chloro-3-nitrophenyl methyl sulfone[26] (25.1 g) with anhydrous potassium fluoride (12.4 g) at reflux in dimethylformamide (40 ml) for 3.5 hr with vigorous stirring;[24] the product (3 g, 13%) had mp 156–157° (lit.[27] mp 156°).

4-Bromo-2-nitrofluorobenzene.—Efforts to obtain this compound by the Sandmeyer method of van Hove[28] or from 2,5-dibromonitrobenzene by the methods of Finger and Kruse[24] were fruitless. The compound was obtained in 54% yield by bromination of *o*-fluoronitrobenzene after Derbyshire and Waters.[29] A mixture of 28.2 g of *o*-fluoronitrobenzene, 34 g of silver sulfate, 20 ml of water, and 180 ml of concentrated sulfuric acid was stirred until solution was complete (about 1 hr), 10.4 ml of bromine was added dropwise, and stirring was continued another 17 hr with occasional gentle heating by means of a steam bath. The product, isolated by standard procedures, had bp 89–90° (4 mm), fp 18.3–18.5° (lit.[28] fp 19°).

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4-Iodo-2-nitrofluorobenzene.—Attempted preparation by the diazonium method of van Hove[28] or by iodination of *o*-fluoronitrobenzene[30] at room temperature was unsuccessful. However, the latter reaction at *ca.* 100° produced the desired compound, mp 34.5–35° (lit.[28] mp 35.5°). The procedure was otherwise much as described above.

4-Fluoro-3-nitro-N,N-dimethylaniline was obtained in 27% yield by nitration of *p*-fluoro-N,N-dimethylaniline[31] by nitric acid in concentrated sulfuric acid at *ca.* −5°. The product was obtained as brilliant orange crystals, mp 46°, by crystallization from petroleum ether (bp 60–90°).

Anal. Calcd. for $C_8H_9FN_2O_2$: C, 52.17; H, 4.92. Found:[32] C, 51.99; H, 5.03.

N-(4-Substituted 2-nitrophenyl)piperidines (II).—*o*-Nitrophenylpiperidine,[33] mp 80–81°, 3-nitro-4-piperidinoacetophenone,[34] mp 92–93°, and 4-bromo-2-nitrophenylpiperidine were made by standard methods. The bromo derivative was obtained in two modifications, the one of mp 45–45.5° previously reported,[35] the other of mp 61–62°. The former was converted into the latter by crystallization from petroleum ether (bp 30–60°) with introduction of a seed crystal.

Anal. Calcd for $C_{11}H_{13}BrN_2O_2$: C, 46.33; H, 4.60. Found:[32] C, 46.23; H, 4.71.

The following are new compounds, made by condensing the relevant 4-substituted 2-nitrochlorobenzenes with piperidine: **N-(4-trifluoromethyl-2-nitrophenyl)piperidine,** mp 54.5–55.2° (from aqueous ethanol) (*Anal.* Calcd for $C_{12}H_{13}F_3N_2O_2$: C, 52.55; H, 4.78. Found:[32] C, 52.53; H, 4.97); **N-(4-methylsulfonyl-2-nitrophenyl)piperidine,** mp 124–125.5° (from carbon tetrachloride) (*Anal.* Calcd for $C_{12}H_{16}N_2O_4S$: C, 50.69; H, 5.67. Found:[32] C, 50.47; H, 5.68); and **N-(4-iodo-2-nitrophenyl)piperidine,** mp 41–42° (from ethanol) (*Anal.* Calcd for $C_{11}H_{13}IN_2O_2$: C, 39.76; H, 3.91. Found:[32] C, 39.64; H, 3.90).

Kinetic Measurements.—For the most part, reactions were followed by photometric measurements at *ca.* 420 mμ on acid-quenched aliquots, according to a technique previously described.[16] The runs with *o*-fluoronitrobenzene at 46.6 and at 25.0° (except at 0.098 *M* piperidine), and the runs with 2,4-dinitrofluorobenzene at piperidine concentrations less than 0.01 *M* were followed by photometric measurements on the reaction solutions. The runs with 2,4-dinitrofluorobenzene at piperidine concentrations greater than 0.01 *M* were performed in a Durrum–Gibson stopped-flow spectrophotometric kinetics apparatus, the essential features of which are due to Gibson,[36] with observation at 375 mμ.

Registry No.—Piperidine, 110-89-4; methanol, 67-56-1; I (R = H), 1493-27-2; I (R = Br), 364-73-8; I (R = CF_3), 367-86-2; I (R = CH_3CO), 400-93-1; I (R = CH_3SO_2), 453-72-5; I (R = NO_2), 70-34-8; 4-fluoro-3-nitro-N,N-dimethylaniline, 18542-98-8; II (R = Br), 5465-66-7; II (R = CF_3), 1692-79-1; II (R = CH_3SO_2), 18543-01-6; II (R = I), 18543-02-7.

Acknowledgments.—Nearly all the preparative work described herein was done by Messrs. Ray M. Conner, James M. Jung, and Stanley M. Williamson. Some of the kinetic determinations with *o*-fluoronitrobenzene were performed by Mrs. Carol King. We are grateful for this assistance.

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Phosphinic Acids and Derivatives. III. The Mass Spectra of Diarylphosphinates[1]

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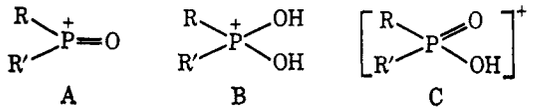
Received September 9, 1968

Rather than simply fragmenting as do dialkylphosphinates, diarylphosphinates cyclize to give biphenyl-2,2′-phosphorus ions, especially the biphenylphosphinylium ion, as intense peaks in their mass spectra. The fragmentation of benzophenone-2,2′-phosphinic acid does not proceed through the same pathway. This phosphorus heterocycle and diphenylmethane-2,2′-phosphinic acid apparently tend to form phosphorus heteroaromatic ions. The spectra of phenyl-*o*-tolylphosphinic acid and di-*o*-tolylphosphinic acid show that the cyclic fragmentation in these cases also involves formation of biphenylphosphorus ions rather than an alternative pathway previously found in *o*-tolyl sulfones.

We recently reported the mass spectra of some dialkylphosphinic acids and their alkyl esters.[1b,3] The most important fragments are phosphacylium ions (A), protonated phosphinate ions (B), and phosphinate ions (C).[4] We predicted that ions of type A would probably be a general phenomenon in the mass spectra



of organophosphorus compounds. Accordingly it was of some interest to examine the mass spectra of diarylphosphinic acids and esters which were available as a result of other studies carried out in this laboratory.[5] We have also included other arylphosphorus compounds which aid in the assignment of fragmentation pathways.[6]

(1) Supported in part by grants from the National Science Foundation. (a) Part I: P. Haake and G. H. Hurst, *J. Amer. Chem. Soc.*, **88**, 2455 (1966). (b) Part II: P. Haake and P. S. Ossip, *Tetrahedron*, **24**, 565 (1968).

(2) Alfred P. Sloan Research Fellow, 1964–67. Inquiries should be addressed to P. H. at Wesleyan University.

(3) P. S. Ossip, Ph.D. Thesis, UCLA, 1968.

(4) We use the following conventions. In the tables, intensities are below the *m/e* values. In the text, intensities are given in parentheses following the *m/e* value. Radical ions are given as $[X]^+$ in contrast to spin-paired ions which have a charge on a given atom. Pathways for which metastables have been observed are marked with an asterisk.

(5) (a) C. E. Diebert, Ph.D. Thesis, UCLA, 1966; (b) R. D. Cook, Ph.D. Thesis, UCLA, 1967.

(6) Deuteration studies have been used in a study of triphenylphosphine oxide: D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, **90**, 966 (1968).