Nucleophilic Displacement Reactions in Aromatic Systems. Part IV. Kinetics of the Reactions of* o- *and* p-*Halogenonitrobenzenes with Piperidine and with Morpholine.*

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Arrhenius parameters have been determined for the second-order reactions in ethanol of all the *o*- and *p*-halogenonitrobenzenes with piperidine, and for the reactions of the fluoro- and bromo-compounds with morpholine. The reactions of the fluoro-compounds obey a rate law, $dx/dt = k(b-x)(a-nx)$ where $1<n<2$, and a method for determining k is developed. It is shown that a possible concurrent ethanolysis of the halogeno-compounds is of little importance and does not vitiate the results. For *para*-compounds the order of reactivity, $F \gg Cl \sim Br > I$, is shown to be mainly due to a diminution in E for the fluoro-compound of ~ 4 kcal. which, as solvation of the transition state of the reactions of this fluoro-compound is not apparently accentuated, is ascribed to diminished repulsion energy in formation of the transition state. The behaviour of the other *para*-compounds is also briefly discussed. The reactions of the *ortho*- are faster than those of the *para*-compounds at all temperatures at which the reactions have significant speed. Only a tentative discussion of the Arrhenius parameters is possible.

Although the kinetics of the reactions of *o*- and *p*-halogenonitrobenzenes with amines have been studied previously, *e.g.* by Holleman, de Mooy, and ter Weel (*Rec. Trav. chim.*, 1915, **35**, 1), and by Miller *et al.*, (*J.*, 1952, 3550; 1953, 1475), there had been no systematic investigation over the whole range of *o*- and *p*-halogenomononitrobenzenes when this investigation was begun in 1949. A preliminary account of this work has appeared (*Chem. and Ind.*, 1951, 148). Brieux and Deulofeu (*ibid.*, 1951, p. 971; *Anal. Asoc. Quím. Argentina*, 1951, **39**, 189) reported the results of a kinetic investigation of similar reactions with piperidine in benzene, but they did not investigate the reactions of the fluoro-compounds. The present paper records an investigation of the reactions in ethanol of all the *o*- and *p*-halogenonitrobenzenes with piperidine and of some with morpholine under conditions such that the order of reaction can be established. Several investigations of the solvolysis by piperidine of some of the compounds studied are on record (*e.g.* Berliner and Monack, *J. Amer. Chem. Soc.*, 1952, **74**, 1574). Non-kinetic quantitative investigations (*e.g.* Franzen and Bockhacker, *Ber.*, 1920, **53**, 1174; Brewin and Turner, *J.*, 1928, 332) are also available. The kinetics of the reactions in ethanol of *p*-halogenonitrobenzenes with ethoxide ions have recently been investigated by Bevan (*J.*, 1951, 2340), and the field has been reviewed by Bunnett and Zahler (*Chem. Reviews*, 1951, **49**, 273). The present investigation provides Arrhenius parameters for all the reactions in question, with a view to elucidation first of the influence of the halogen on reactivity and, secondly, of the fact that the rates of the reactions of the *ortho*-compounds with amines are greater than those for the *para*-compounds in the ranges of temperature so far investigated.

Experimental

Materials.—*o*- and *p*-Chloro- and -bromo-nitrobenzene and *p*-iodonitrobenzene (from British Drug Houses, Ltd.) were recrystallised from ethanol to constant m. p.; or from 1 : 1 aqueous nitric acid (Brand, *J.*, 1950, 1000) and then from ethanol. The different samples showed no significant differences in kinetic experiments. *o*-Iodonitrobenzene was prepared from *o*-nitroaniline and recrystallised from light petroleum (b. p. 60—80°). *p*-Fluoronitrobenzene was prepared by Bradlow and VanderWerf's method (*J. Amer. Chem. Soc.*, 1948, **70**, 654), fractionated at 15 mm. (50 × 1·5 cm. column packed with Fenske helices), and crystallised from ethanol between room temperature and $\sim -80°$ to a constant m. p. of 26·7—28·0°. *o*-Fluoronitrobenzene was prepared by Swarts's method (*Bull. Acad. roy. Belg.*, 1914, 178), being separated from the *p*-isomer by repeated fractional distillation (60 × 1·5 cm. column, Fenske helices),

* Part III, *J.*, 1954, 1190.

and had m. p. −5·8° to −5·5°, b. p. 221·6—221·7°/760 mm. (corr.), d_4^{16} 1·3382, d_4^{3} 1·3227, n_D^{14} 1·5349, and n_D^{20} 1·5321.

Amines.—Piperidine and morpholine were purified as described in Part III (*loc. cit.*) and had b. p. 106·4/760 mm., n_D^{20} 1·4532, and b. p. 128·0°/760 mm., n_D^{20} 1·4549, respectively.

Solvent.—This was prepared as described in Part I (*J.*, 1952, 437).

Reaction Products.—The *N-o*-nitrophenyl and *N-p*-nitrophenyl derivatives of piperidine and morpholine were isolated from solutions used in kinetic experiments and had m. p.s in agreement with those in the literature. The very hygroscopic *piperidine hydrofluoride* was prepared by Neusser's method (*Z. anorg. Chem.*, 1940, **244**, 13), the crude solid product being crystallised from benzene, and the material carefully protected from the atmosphere during all operations (Found: $C_5H_{11}N$, 79·3; F, 17·4. $C_5H_{11}N$,HF requires $C_5H_{11}N$, 81·0; F, 18·1%). As the product decomposed on desiccation at 15 mm., no effort was made to purify it further. The low analytical figures are probably due to adhering benzene. *Morpholine hydrofluoride monohydrate*, a deliquescent crystalline solid, was similarly prepared and crystallised from benzene containing a little ethanol (Found: C_4H_9ON, 69·7; F, 15·1. C_4H_9ON,HF,H_2O requires C_4H_9ON, 69·6; F, 15·2%).

Procedure.—For the fluoro-compounds sealed bulbs were used for the slower reactions: for the faster reactions stoppered calibrated flasks were used. The reaction was arrested by adding the reaction mixture to 20 c.c. of 1 : 1 or (for *ortho*-compounds) 1 : 7 hydrochloric acid and extracting unchanged fluoro-compound with benzene. After the solution had been made strongly alkaline and a little sodium dithionite added to destroy *N-o-* or *-p*-nitrophenylpiperidine, which are steam-volatile and interfere with the final titration, the solution was steam-distilled (100—150 c.c. of distillate for piperidine, 300 c.c. for morpholine) and the unchanged piperidine or morpholine in the distillate was determined acidimetrically (bromophenol-blue). The time of the first analysis was taken as zero, thus eliminating initial errors. Blank determinations showed that this procedure was satisfactory for piperidine and morpholine under the reaction conditions. For the other halogeno-compounds the method of sealed bulbs was used, and, as the reactions were carried out at 70—90°, cooling and addition of dilute sulphuric acid adequately arrested the reaction. Halide ions were determined potentiometrically in the diluted solution with a silver indicator electrode and a lead amalgam–lead sulphate (in saturated magnesium sulphate solution) half-cell. When 0·08N-silver nitrate was used, potential increases of 10, 2·5, and 0·7 v/ml. were obtained at the end-point for iodides, bromides, and chlorides respectively. E.M.F. readings were stable to 2 mv. some 5 sec. after addition of reagent (cf. Edwards, *Trans. Faraday Soc.*, 1937, **33**, 1294); it was desirable to shield the titration cell from direct light. Blank experiments showed that none of the other substances present in kinetic experiments vitiated the determination of halogens by this method.

Results

Detailed values for some of the reactions are given in Table 1, and all the results are summarised in Table 2.

For the reactions of all save the fluoro-compounds, it was confirmed that two moles of amine are consumed per mole of halogeno-compound, since, for example, piperidine hydrobromide reacted negligibly slowly with *o*- and *p*-bromonitrobenzene in ethanol at 90°, and for the reaction of *p*-bromonitrobenzene with piperidine in ethanol at 90° piperidine determinations gave the same rate coefficients as bromide-ion determinations. Thus

$$k = \frac{1}{2t(0{\cdot}5a - b)} \cdot 2{\cdot}303 \log_{10} \frac{b}{0{\cdot}5a} \cdot \frac{0{\cdot}5a - x}{b - x}$$

Halide determinations at " infinite " time (at least thirty times the half-life of the reaction) gave values of 99·7—100·2% reaction for the *ortho*-compounds. For the *para*-compounds the value was 98·7—99·7%. We ascribe this deficit to the intervention of a reductive side reaction. From these observations we conclude that reversibility of the reactions may be neglected and that the reagents and analytical procedure were satisfactory. The reactions were shown to be of the second order within experimental error by the half-life method.

For the fluoro-compounds the stoicheiometry of the reactions is more complicated. The amine hydrofluorides react more or less rapidly under the conditions employed in kinetic experiments with the fluoronitrobenzenes. However the same rate law as above was used for calculation of the velocity coefficients, subject to considerations explained on p. 2111. Determinations at infinite time showed 100 ± 1·5% reaction. The order of the reactions was determined by the differential method (Laidler, " Chemical Kinetics," McGraw-Hill, New York, 1950, p. 14).

TABLE 1.

Reactions of Piperidine.

p-*Fluoronitrobenzene at* 40·0°. $a = 0{\cdot}3867$M, $b = 0{\cdot}0956$M.*

Time (min.)	81	156·5	301	425	553	1216	∞
Decompn. (%)	16·4	28·8	47·4	57·9	65·8	86·7	99·1
10^5k	9·67	9·86	10·35	10·30	10·20	9·93	—

Mean $k = 10{\cdot}05 \pm 0{\cdot}23 \times 10^{-5}$ *; after correction for solvent expansion, $10{\cdot}33 \pm 0{\cdot}24 \times 10^{-5}$. Order with respect to amine 1·06; with respect to *p*-fluoronitrobenzene 1·00.

o-*Bromonitrobenzene at* 79·7°. $a = 0{\cdot}4$M, $b = 0{\cdot}1$M.

Time (hr.)	4·22	6·93	14·55	19·63	27·02	45·20	62·50	92·33
Decompn. (%)	13·4	20·7	37·6	45·9	55·5	71·7	80·2	89·7
10^5k	2·45	2·44	2·49	2·48	2·47	2·49	2·44	2·50

Mean $k = 2{\cdot}64 \pm 0{\cdot}02 \times 10^{-5}$ after correction for solvent expansion.

p-*Bromonitrobenzene at* 79·9°. $a = 0{\cdot}4$M, $b = 0{\cdot}1$M.

Time (hr.)	15·97	25·00	47·33	64·42	88·42	113·23	145·37	184·6	304·7
Decompn. (%)	13·8	20·8	35·6	44·4	54·3	62·3	70·2	76·8	89·2
10^6k	6·70	6·85	7·15	7·23	7·32	7·39	7·45	7·36	7·49

Mean $k = 7{\cdot}22 \pm 0{\cdot}21 \times 10^{-6}$. After extrapolation to zero time (see p. 2112) and correction for solvent expansion $k = 6{\cdot}96 \times 10^{-6}$.

Reactions of Morpholine.

o-*Fluoronitrobenzene at* 40·0°. $a = 0{\cdot}3929$M, $b = 0{\cdot}0968$M.

Time (min.)	200·5	420·5	661	1403	1910	∞
Decompn. (%)	21·4	39·8	52·5	74·0	83·9	99·9
10^5k	5·25	5·60	5·47	5·18	5·52	—

Mean $k = 5{\cdot}40 \pm 0{\cdot}15 \times 10^{-5}$; after correction for solvent expansion $5{\cdot}55 \pm 0{\cdot}15 \times 10^{-5}$. Order with respect to amine 1·02, with respect to *o*-fluoronitrobenzene 1·06.

o-*Bromonitrobenzene at* 90·6°. $a = 0{\cdot}4176$M, $b = 0{\cdot}2012$M.

Time (hr.)	7·45	17·00	32·47	45·17	83·17	145·17	212·50
Decompn. (%)	10·3	21·2	35·5	44·6	63·7	80·1	89·0
10^6k	9·99	9·85	9·90	9·89	9·99	9·98	9·96

Mean $k = 9{\cdot}94 \pm 0{\cdot}05 \times 10^{-6}$; after correction for solvent expansion $10{\cdot}74 \pm 0{\cdot}06 \times 10^{-6}$.

p-*Bromonitrobenzene at* 90·0°. $a = 0{\cdot}4170$M, $b = 0{\cdot}2034$M.

Time (hr.)	32·33	61·62	94·87	144·0	211·6	331·9	412·1	662·5
Decompn. (%)	12·5	22·1	31·5	43·1	55·2	70·0	76·4	88·3
10^6k	2·84	2·87	2·90	2·96	3·00	3·07	3·08	3·10

Mean $k = 2{\cdot}98 \pm 0{\cdot}09 \times 10^{-6}$; after extrapolation to zero time and correction for solvent expansion $k = 3{\cdot}00 \pm 0{\cdot}09 \times 10^{-6}$.

* a is the initial amine concentration and b that of the halogeno-compound. All values of k, the velocity coefficient, are in l. mole^{-1} sec.$^{-1}$

TABLE 2.

Nitrobenzene derivative	Amine	10^6k 70·0°	10^6k 80·0°	10^6k 90·0°	E (kcal. mole^{-1})	$\log_{10} A$
o-Fluoro- *	Piperidine	108	252	536	14·8	7·0
	Morpholine	12·3	27·4	55·4	13·8	5·4
o-Chloro-	Piperidine	6·86	14·7	29·8	18·1	6·4
o-Bromo-	Piperidine	12·8	27·0	56·0	18·3	6·8
	Morpholine	2·48	5·17	10·3	17·7	5·6
o-Iodo-	Piperidine	5·00	11·0	23·2	19·2	6·9
p-Fluoro- *	Piperidine	24·7	50·8	105	13·2	5·3
	Morpholine	2·22	4·57	9·11	12·9	4·0
p-Chloro-	Piperidine	2·64	5·55	10·8	17·1	5·3
p-Bromo-	Piperidine	3·59	7·10	13·9	16·8	5·2
	Morpholine	0·63	1·30	2·57	17·7	5·1
p-Iodo-	Piperidine	—	—	4·0	18·0	5·5

k's are accurate to ± 3%. Usually some 80—90% of the reaction was studied. E's are accurate to ± 0·5 kcal. mole^{-1}, and values of $\log_{10} A$ to ± 0·5 unit. * 50° lower.

DISCUSSION

The stoicheiometry of the reactions of the fluoro-compounds corresponds to a rate law $dx/dt = k(b - x)(a - nx)$ where $1 < n < 2$. The necessary correction, which will be greater for the weaker base, to k calculated with $n = 2$ may be determined as follows. From experiments with morpholine k is determined by assuming $n = 2$, and from the slope of

x–t curves for experiments with morpholine hydrofluoride, and $(b - x)$ at time t, and the approximate value of k, a value of [free morpholine] is obtained. From this and other experimentally determined magnitudes the equilibrium constant K for the dissociation of morpholine hydrofluoride is determined. K is then used to correct the value of the morpholine concentration in the expression $dx/dt = k$[fluoro-compound][morpholine] for reactions of morpholine itself, whence a corrected value of k is obtained by determining dx/dt from the slope of an appropriate x—t curve. If necessary k may be obtained more exactly by repeating the process. However, the maximum correction to k that we have determined is ~2% so that we have neglected this correction throughout and determined k's by using the above rate law with $n = 2$. For reactions of piperidine the correction is ~0·1%.

In these reactions, of all those so far studied, the intervention of ethanolysis (cf. Part II, *J.*, 1953, 3394) is the most acute. However, the value of the relative rate of ethanolysis at x% " apparent reaction ", α_x, may be evaluated from the relation $\alpha_x = \{c[R_2H_2N^+]\}^{-1}$, where $c = k_4/k_2K_b$ (cf. Part II, p. 3394, and *Chem. and Ind.*, 1953, 1266). For the reaction of *p*-chloronitrobenzene with piperidine at 90°, where α_x is largest, the use of Bevan's value of k_2 (*J.*, 1951, 2340) gives $\alpha_x = 0{\cdot}1x^{-1}$. The correction to be applied to the mean rate coefficient will nevertheless be only ~3%, since after ~30% reaction α_x is negligible. Such corrections have not been applied to the values in Table 2, as they are of the same order as the experimental error, but the slight reduction of the k's should be borne in mind in what follows. As morpholine is a weaker base than piperidine by a factor of $\sim 10^3$ in water at 25°, it is probable that corrections for ethanolysis are unimportant for its reactions.

The reactions of the *para*-compounds, fluorides excepted, show velocity coefficients with a steady upward trend as the reaction proceeds, so these have been extrapolated to values for zero time. This observation is probably due to a salt effect of the products, but is in any case only of minor importance. The Arrhenius parameters for the reaction of *p*-iodonitrobenzene with piperidine are subject to considerably greater errors than the remainder owing to experimental factors, particularly the low solubility of the iodo-compound and the slowness of the reactions at 90° and 118°. At the higher temperature k is reliable to ± 10% only.

TABLE 3.

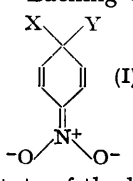
Nitrobenzene derivative	Reactions of piperidine in ethanol			Reactions of piperidine in benzene [1]			Reactions of ethoxide ions in ethanol		
	$\log_{10} A$	E (kcal. mole^{-1})	10^5k at 90°	$\log_{10} A$	E (kcal. mole^{-1})	10^5k at 90°	$\log_{10} A$	E (kcal. mole^{-1})	10^5k at 90°
o-Fluoro- ...	7·0	14·8	1230	—	—	—	11·7 [3]	20·1	4×10^4
o-Chloro- ...	6·4	18·1	2·98	3·8	13·4	5·4	10·0 [4]	22·2	39·7
o-Bromo- ...	6·8	18·3	5·60	4·6	14·1	13·9 [5]	—	—	—
o-Iodo- ...	6·9	19·2	2·32	5·0	15·3	6·2	—	—	—
p-Fluoro- ...	5·3	13·2	225	—	—	—	10·7 [2]	19·0	$2{\cdot}2 \times 10^4$
p-Chloro- ...	5·3	17·1	1·08	2·3	13·7	0·11	9·0 [2]	20·1	96·3
p-Bromo- ...	5·2	16·8	1·39	3·6 [5]	15·5 [5]	0·20 [5]	9·2 [2]	20·3	83·8
				2·6	13·6	0·26			
p-Iodo- ...	5·5	18·0	0·40	5·8	19·5	0·12	—	—	7·1 [2]

[1] Brieux and Deulofeu, *loc. cit.* [2] Bevan, *loc. cit.* [3] Bevan, *J.*, 1953, 655. [4] Riklis, *J. Gen. Chem. U.S.S.R.*, 1947, **17**, 1511. [5] P. W. Soanes, unpublished work.

In Table 3 are assembled velocity coefficients and Arrhenius parameters determined by us (ethanol) and by Brieux and Deulofeu (benzene) for reactions of piperidine, and those in the literature for ethoxide-ion reactions. We have independently confirmed Brieux and Deulofeu's values for the reaction of *o*-bromonitrobenzene, but have obtained different values for that of the *p*-isomer (Chapman and Soanes, unpublished work). Edwards (*loc. cit.*) has drawn attention to the complications attending Menschutkin-type reactions in non-polar solvents, where the salts formed are insoluble. Despite the insolubility of piperidine salts in benzene, we have observed regular kinetics as, apparently, have Brieux and Deulofeu. Nevertheless, the phenomena discussed by Edwards could only be neglected if the results of experiments having widely varied initial concentrations were available. Therefore we merely point out that when one passes from ethanol to benzene as solvent the trend in Arrhenius parameters is of the same kind as that shown by various reactions

of amines and aliphatic halides (cf. Moelwyn-Hughes, " Kinetics of Reactions in Solution," Oxford, 1947, pp. 205 *et seq.*).

Lacking compelling evidence of the intervention of stable intermediate complexes in these reactions, we assume as before a simple bimolecular mechanism (cf. Brady and Cropper, *J.*, 1950, 507, and Miller *et al.*, *loc. cit.*). While accepting in part the criticism advanced by Bunnett and Zahler (*loc. cit.*, p. 298) of previous formulations of the transition state, we believe that formula (I) represents for *para*-compounds an extreme configuration towards which the transition state tends rather than the actual transition state of the bimolecular substitution we assume to occur.



(I)

Two points are noteworthy for the reactions of the *para*-compounds with piperidine in ethanol: the approximate constancy of entropy of activation, and the freedom from steric complications. There appears to be no significant accentuation of solvation of the transition state for the fluoro-compound in this series, and our previous analysis of a similar problem (Chapman and Parker, *loc. cit.*) may have over-emphasised solvation to the neglect of other factors. Of the factors thought to determine energy of activation (cf. Glasstone, Laidler, and Eyring, "Theory of Rate Processes," McGraw-Hill, New York, 1941, p. 141), the strength of the bond formed is constant throughout this series. The major variables are the strength of the bond broken and the repulsion energy. Miller *et al.* (*loc. cit.*) have dealt with a similar problem in a crudely quantitative way in terms of the difference in bond strengths and the difference in ionic resonance energies between ArX and ArI. Although they do not make it clear, it appears to us that the basis of their treatment is the assumption that differences of ionic resonance energies, taken as measuring differences in the polarity of carbon–halogen bonds, roughly measure the differences of repulsion energy themselves largely determined by the charge at the seat of substitution. Our view is that such assumptions limit the analysis of the problem to the qualitative. If we assume that the total electron-withdrawal effect of halogen at the seat of substitution is in the order F>Cl>Br>I, the repulsion energy will increase in the reverse order. Provided the transition state tends closely towards the quinonoid structure (I) the strengths of the bonds broken will probably be less important because these bonds will be little stretched in attaining the transition state, so that the order of repulsion energies determines the important features of the observed order of energies of activation. However this order, F$\ll$Cl$\sim$Br<I, can only be reproduced in detail by taking account also of the variation in bond strengths. The primary condition for nucleophilic aromatic substitution is appropriate distortion of the delocalised π-orbital by, for example, a nitro-group. The inductive effects of halogens are, on the whole, unimportant by comparison.

Reactions of the *ortho* compounds are more complex sterically. Toussaint (*Mem. Soc. Roy. Soc. Liége*, 1952, **12**, 5) has examined *o*-chloronitrobenzene by *X*-ray analysis, and in a personal communication states that " if it is assumed that the nitro-group is not deformed but simply rotated about the C–N bond, the angle of rotation would be at least 30°." If a planar configuration is assumed, the overlap between the nearer oxygen atom of the nitro-group and the halogen atom may be determined. These and similar overlaps for the transition state based on a tetrahedral model of the seat of substitution have been determined by Beckwith, Miller, and Leahy (*loc. cit.*) and by us using a coplanar fully *o*-quinonoid model of the transition state. Only qualitative conclusions may be drawn from these geometrical results because of the assumptions involved, as follows. When the reagent is small, formation of the transition state for these reactions will, on the above hypothesis, allow the nitro-group to become coplanar with the ring with diminished overlap between the nearer oxygen atom of the nitro-group and halogen in every case, the diminution being in the order F<Cl<Br<I. With a more bulky reagent it is probable that the total overlaps, including those between the nitro-oxygen atoms and atoms of the reagent, will not be much reduced. This point is difficult to determine geometrically because the position of the reagent, *e.g.*, piperidine, in the transition state is not accurately known. To compare two different reagents of similar geometry assumptions may be made with more confidence (cf. Part I, p. 444). Because of large variations in A and the complexity of the problem, the basis of the influence of halogen variation on E for these reactions remains obscure.

The increases in E observed on passing from *p*- to *o*-halogenonitrobenzenes may arise from a " net *ortho*-effect " (cf. Part I, p. 445) weakened solvation, and a relatively weak tautomeric effect of the nitro-group when in the *ortho*-position, tempered by a more powerful inductive effect and a small decrease in steric inhibition of resonance in the transition state for the *ortho*-compounds. The corresponding increase in A is probably due in part to diminished solvation, possibly because of congestion near the polar centres in the transition state for the *ortho*-compounds. The ultimate effect is that E for the *ortho*-compounds is some 1000—1500 cal. greater than for the *para*-compounds, but this is always offset by such an increase in A as to ensure faster reactions for the *ortho*-compounds.

It is noteworthy that, with piperidine and morpholine as reagents, *o*-halogenonitrobenzenes react faster than the corresponding *para*-compounds at all temperatures at which the reactions proceed with significant speed. The same is true for *o*- and *p*-fluoronitrobenzenes reacting with ethoxide ions in ethanol, but the reverse is true for *o*- and *p*-chloronitrobenzenes (cf. Table 3). Finally we may add that the reactions of morpholine reported here conform to the same broad pattern as those of piperidine.

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