54. *Studies in Aromatic Nucleophilic Substitution. Part IV.* Relative Nucleophilic Powers of Common Reagents.*

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Relative reactivities of a series of reagents of widely differing nucleophilic power towards an aromatic carbon atom have been measured in absolute methanol. Arrhenius parameters are recorded. The results show the necessity for the analysis of products in any attempt to correlate such relative rates. The reactivity of the thiophenoxide ion is discussed.

The original statement by Hughes, Ingold, and Patel [1] that for replacement reactions, $Y + R{-}X \longrightarrow Y{-}R + X$, basicity is a sufficient indication of the nucleophilic power of Y was a close enough approximation to develop the theory of such replacement reactions. Later, numerous experimental results have shown that relative nucleophilic powers towards Lewis acids and protons do not normally follow the same sequence. Swain and Scott [2] and Edwards [3] have set up equations designed to correlate rates of nucleophilic displacements and equilibrium data. On the matter of displacements at an aromatic carbon atom, the data are limited: an approximate order of nucleophilic powers was drawn up by Bunnett and Zahler [4] and supplemented by Bunnett and Davis.[5] The results to be discussed are an attempt to document such relative reactivities under standard conditions.

* Parts I—III, *J.*, 1951, 2340; 1953, 655; 1954, 3091.

[1] Hughes, Ingold, and Patel, *J.*, 1933, 526.
[2] Swain and Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.
[3] Edwards, *ibid.*, 1954, **76**, 1540.
[4] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[5] Bunnett and Davis, *J. Amer. Chem. Soc.*, 1954, **76**, 3011.

Since a number of reactions have been studied in methanol or ethanol the solvent used was absolute methanol. A preliminary account has been given.[6] Results are assembled in Tables 1 and 4.

TABLE 1. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *for reaction of* p-*fluoronitrobenzene with* X *in absolute methanol.*

X	SPh$^-$			$C_6H_5\cdot NH_2$		
Temp.	35·07°	49·72°	60·08°	149·5°	158·6°	168·4°
k_2	$5{\cdot}01 \times 10^{-4}$	$2{\cdot}17 \times 10^{-3}$	$5{\cdot}67 \times 10^{-3}$	$1{\cdot}28 \times 10^{-5}$	$1{\cdot}82 \times 10^{-5}$	$2{\cdot}55 \times 10^{-6}$

TABLE 2. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *for reaction of picryl chloride with* X *in absolute methanol.*

X	$C_6H_5\cdot NH_2$			m-$NO_2\cdot C_6H_4\cdot NH_2$		
Temp.	−22·04°	−16·71°	−10·80°	4·00	25·06°	35·12°
k_2	$5{\cdot}65 \times 10^{-2}$	$7{\cdot}72 \times 10^{-2}$	$1{\cdot}11 \times 10^{-1}$	$5{\cdot}54 \times 10^{-4}$	$2{\cdot}29 \times 10^{-3}$	$4{\cdot}15 \times 10^{-3}$
X	Cl$^-$			MeOH		
Temp.	34·52°	49·86°	59·99°	35·06°	49·76°	67·70°
k_2	$2{\cdot}42 \times 10^{-5}$	$1{\cdot}31 \times 10^{-4}$	$4{\cdot}02 \times 10^{-4}$	$6{\cdot}39 \times 10^{-7}$	$2{\cdot}47 \times 10^{-6}$	$1{\cdot}08 \times 10^{-5}$

TABLE 3. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *at* 25° *and Arrhenius parameters* ($k_2 = Be^{-E/RT}$).

Reaction of X with :	*p*-fluoronitrobenzene				picryl chloride			
X	OMe$^-$ [a]	SPh$^-$	OPh$^-$ [b]	$C_6H_5\cdot NH_2$	$C_6H_5\cdot NH_2$	m-$NO_2\cdot C_6H_4\cdot NH_2$	Cl$^-$	MeOH
k_2	1·80 ×10^{-4}	1·68 ×10^{-4}	~10^{-6}	$1{\cdot}56 \times 10^{-8}$	$6{\cdot}77 \times 10^{0}$	$2{\cdot}27 \times 10^{-3}$	7·40 ×10^{-6}	7·55 ×10^{-9}
log B	11·0	10·7	—	2·11	5·59	5·34	11·5	6·64
E	20·1	19·8	—	13·5	7·86	10·9	22·7	18·1

(*a*) Bevan and Bye, *J.*, 1954, 3091; (*b*) England, *Chem. and Ind.*, 1954, 1145.

TABLE 4. k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *at* 25° *for reaction of* p-*fluoronitrobenzene with* X.

X	OMe$^-$	SPh$^-$	OPh$^-$	$C_6H_5\cdot NH_2$	m-$NO_2\cdot C_6H_4\cdot NH_2$	Cl$^-$	MeOH
k_2	$1{\cdot}80 \times 10^{-4}$	$1{\cdot}68 \times 10^{-4}$	~10^{-6}	$1{\cdot}56 \times 10^{-8}$	$5{\cdot}23 \times 10^{-12}$	$1{\cdot}71 \times 10^{-14}$	$1{\cdot}74 \times 10^{-17}$

DISCUSSION

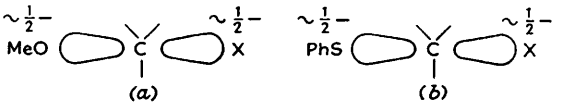
In Table 4 are shown rate constants for the reaction of various nucleophiles X with *p*-fluoronitrobenzene, calculated on the assumption that the relative rates for aniline with the latter and with picryl chloride are preserved for other nucleophiles X. It is probable that in the latter case the steric requirements of the two *o*-nitro-groups in initial and transition states are such as to make the last three values of Table 4 only approximations to the actual value of k_2 for the reaction of *p*-fluoronitrobenzene with X. However, it is unlikely that such effects will invalidate the calculated order of reactivity, which corresponds closely to that set up approximately by Bunnett and Zahler [4] with one important exception. The thiophenoxide ion, from our data, has a reactivity very close to that of the methoxide ion, contrary to experience of their relative reactivities at an aliphatic carbon atom; cf. references in Bevan and Hirst,[6] where the difference is ~10^3 in favour of the thiophenoxide ion. The closeness of the figures for OMe$^-$ and for SPh$^-$ suggested the possibility that the equilibrium

$$Ph\cdot SH + MeO^- \rightleftharpoons Ph\cdot S^- + MeOH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

lies well to the left. However, rate constants determined by following decrease in concentration of sulphide ion, and separately of alkalinity, corresponded exactly and the reaction product was almost pure 4-nitrodiphenyl sulphide. Further, Hammett [7] gives the autoprotolysis constant of methanol at 25° as pK = 16·7, and Hine and Brader [8] give for the

[6] Bevan and Hirst, *Chem. and Ind.*, 1954, 1422.
[7] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, p. 256.
[8] Hine and Brader, *J. Amer. Chem. Soc.*, 1953, **75**, 3964.

thiophenol in methanol a value of $pK_a = 11{\cdot}6$. From these figures it can be shown that in (1), under the conditions used, Ph·SH is more than 97% converted into PhS^-. This means that MeO^- is a considerably stronger base than PhS^-. The transition states for attack by these two ions may be represented by (*a*) and (*b*). Evidently in (*b*) the negative charge



can be moved further away by resonance in the benzene ring, with a consequent lowering of transition-state energy (cf. Swain and Scott [2]). However, if this were the only factor involved then the phenoxide ion should be more reactive than the methoxide ion, and the *p*-nitrophenoxide ion even more so: but this is not found experimentally. A conflicting factor is the availability at the attacking centre of the electron pair involved in partial-bond formation, balanced against the internuclear repulsion term. Thus $\geqslant C{-}S^-$, being more polarisable than $\geqslant C{-}O^-$, can form a partial bond at greater internuclear distance than the latter, with a consequent lowering of transition-state energy, accounting for the greater reactivity observed for the aliphatic ion.

However, in the transition state of aromatic substitution, in which it is fairly generally agreed that the reactive carbon atom is approximately tetrahedral, in order to form partial bonds both $\geqslant C{-}O^-$ and $\geqslant C{-}S^-$ must approach close to the tetrahedral bond distance; thus the latter loses its advantage of being able to form a partial bond at relatively greater internuclear distance. The driving force of the weaker S–C partial bond is less than that of the O–C bond, with a consequent levelling in the reactivities of the two ions.

In the exchange reaction of chloride ion with picryl chloride it was found that methanolysis occurs slowly and that the final product is picric acid. The concentration of chloride ion produced by the reaction

$$C_6H_2(NO_2)_3Cl + CH_3{\cdot}OH \longrightarrow C_6H_4(NO_2)_3{\cdot}O{\cdot}CH_3 + Cl^- + H^+$$

rises to a maximum and then falls rapidly to zero. This is evidently due to cleavage of the 2 : 4 : 6-trinitroanisole by chloride ion: $C_6H_2(NO_2)_3{\cdot}O{\cdot}CH_3 + Cl^- + H^+ \longrightarrow C_6H_2(NO_2)_3{\cdot}OH + CH_3Cl$. Initial rates for the exchange reaction were measured while methanolysis had not occurred to more than a few units %.

The results in Tables 3 and 4 show that, although the parallel between nucleophilic power and basicity is overall a useful guide, the application of this principle within a fairly narrow range of relative reactivity requires detailed consideration of the various transition states involved.

Experimental

Materials.—p-*Fluoronitrobenzene.* This was prepared from fluorobenzene by Swarts's method [9] and separated from the *ortho*-isomer by fractionation at 20 mm.; it had m. p. 21—21·5° (labile form).

Picryl chloride. This was prepared by the method of Boyer *et al.*; [10] it had m. p. 83·5°.

Aniline. A commercial sample, shaken with zinc dust and distilled at 16 mm., had b. p. 76° (uncorr.).

m-*Nitroaniline.* A commercial sample, recrystallised from benzene, had m. p. 114·5—115° (uncorr.).

Thiophenol. A commercial sample was distilled, and the middle fraction used.

Methanol. Magnesium (10 g.) and iodine (0·5 g.) were dissolved in " AnalaR " methanol (2 l.), which was then refluxed for ½ hr. and distilled.

Kinetic Measurements.—Thermostat temperatures below 100° were steady to within ±0·02°; those above 100° to within ±0·05°.

(1) *Reaction of methoxide ion with* p-*fluoronitrobenzene.* Bevan's procedure [11] was used

[9] Swarts, *Rec. Trav. chim.*, 1913, **33**, 263.
[10] Boyer, Spencer, and Wright, *Canad. J. Res.*, 1946, **24**, *B*, 202.
[11] Bevan, *J.*, 1953, 655.

except that the indicator was bromocresol-green–methyl-red. For the reaction at 49·66°, $k_2 = 2{\cdot}38 \times 10^{-3}$ l. sec.$^{-1}$ mole^{-1}; Bevan and Bye [12] gave for this temperature $k_2 = 2{\cdot}39 \times 10^{-3}$ l. sec.$^{-1}$ mole^{-1}.

(2) *Reaction of thiophenoxide ion with* p-*fluoronitrobenzene.* The reaction was followed by two methods: measurements of (*a*) the reduction in alkalinity, by acid titration; (*b*) the disappearance of thiophenoxide ion, by reaction with iodine.

Initially, in (*b*) the constants obtained were 10—11% higher than in (*a*) and the infinity titre corresponded to more thiophenoxide consumed than was required by theory. This was attributed to oxidation of thiophenoxide ion to disulphide and was eliminated by conducting the reaction in an atmosphere of nitrogen.

Thiophenol was weighed into a flask, and the flask flushed with oxygen-free nitrogen. Sodium methoxide solution was added, leaving a 5% excess of thiophenol. The reaction tubes were flushed with nitrogen, and aliquot portions of a standard solution of *p*-fluoronitrobenzene in methyl alcohol added. The tubes were cooled in ice, nitrogen bubbled through for a further 20 sec. to remove dissolved air, and aliquot parts of thiophenoxide solution added. The tubes were sealed and placed in the thermostat. The reaction was stopped by plunging the tubes into ice-water. In method (*a*), the contents of the tubes were added to an excess of standard hydrochloric acid plus 10 c.c. of benzene, and the excess of acid back-titrated with sodium hydroxide (methyl-red–bromocresol-green indicator). In (*b*), the contents of a tube were added to 25 c.c. of N-hydrochloric acid, solid potassium iodide was added followed by a known volume of standard potassium iodate solution, and the excess of iodine titrated with sodium thiosulphate. The light green colour which developed in "infinity" tubes was probably due to the formation of a trace of nitroso-compound. Results are given below.

Determination of k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *for reaction of* p-*fluoronitrobenzene with* SPh^- *in absolute methanol.*

Method (*b*). Initially, [Halide] = 0·03087N, [SPh^-] = 0·06395N. Temp. 49·72°.
Concns. in ml. of 0·01988N-$Na_2S_2O_3$ solution per 10·04 ml. sample.

t (sec.)	0	36	45	55	65	75	85	95	105	116
[Ph·SNa]	31·07	27·61	27·03	26·32	25·6	24·83	24·53	23·65	23·13	22·55
[Halide]	15·28	11·82	11·24	10·53	9·82	9·04	8·74	7·86	7·34	6·76
10^3k_2	—	2·05	1·99	1·99	2·04	2·13	2·02	2·20	2·22	2·27

Mean $k_2 = 2{\cdot}11 \times 10^{-3}$. By method (*a*), $k_2 = 2{\cdot}13 \times 10^{-3}$.

(3) *Reaction of* p-*fluoronitrobenzene with aniline.* This reaction was followed by Chapman and Parker's method.[13] The results are annexed. Corrected for solvent expansion on the assumption that the figures for methanol [14] may be extrapolated to higher temperatures, $k_2 = 2{\cdot}18 \times 10^{-5}$.

Determination of k_2 (*l. sec.*$^{-1}$ *mole*$^{-1}$) *for reaction of* p-*fluoronitrobenzene with aniline in absolute methanol.*

Initially, [Fluoride] = 0·015M, [Aniline] = 0·06M. Temp. 158·6°.
Concns. in ml. of 0·02022N-$Na_2S_2O_3$ per 5·06-ml. sample.

t (hr.)	0	43·91	57·41	59·01	60·76	67·93	73·5	83·3	93·68
[Aniline]	90·20	86·64	85·96	85·56	85·72	85·63	85·08	84·44	83·64
[Halide]	21·71	18·15	17·47	17·07	17·23	17·14	16·59	15·95	15·15
10^5k_2	—	1·93	1·80	1·94	1·81	1·66	1·75	1·78	1·86

Mean $k_2 = 1{\cdot}82 \times 10^{-5}$.

(4) *Reaction of picryl chloride with aniline.* The reaction was very rapid at −20° so the following technique was used. Portions (5 ml.) of standard methanol solutions of aniline and picryl chloride in stoppered test-tubes were brought to thermostat temperature. For "initial" readings, the contents of an aniline tube were poured into one of picryl chloride, the tube was restoppered and shaken, and the contents were quickly poured into 25 ml. of acetone and 2 ml. of concentrated nitric acid. Chloride ion liberated was titrated potentiometrically by silver nitrate. For other readings the same procedure was used on tubes which, after being shaken, were re-immersed in the thermostat for a definite time.

[12] Bevan and Bye, *J.*, 1954, 3091.
[13] Chapman and Parker, *J.*, 1951, 3301.
[14] Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950, p. 30.

In this reaction, as for the analogous reaction of *m*-nitroaniline, 2 mols. of amine are consumed per mol. of halide; hence the equation for the second-order rate constant is

$$k_2 = [2{\cdot}303/2t(0{\cdot}5a - b)]\log_{10}b(0{\cdot}5a - x)/0{\cdot}5a(b - x)$$

The results follow.

Determination of k_2 (l. sec.$^{-1}$ mole^{-1}) for reaction of picryl chloride with aniline in absolute methanol

Initially, [Picryl chloride] = 0·02702N, [Aniline] = 0·1201N. Temp. −10·86°.
Concns. in ml. of 0·0100N-$AgNO_3$ per 10-ml. sample.

t (sec.)	0	22·0	30·0	46·0	52·0	65·0	76·0
[Aniline]	56·71	50·97	49·41	46·79	46·02	44·52	42·79
[Halide]	23·70	17·96	16·40	13·78	13·01	11·51	9·78
$10k_2$	—	1·17	1·16	1·15	1·14	1·12	1·20

Mean $k_2 = 1{\cdot}16 \times 10^{-1}$; duplicate, $1{\cdot}15 \times 10^{-1}$.

(5) *Reaction of* m-*nitroaniline with picryl chloride.* Standard solutions of the two reagents in methanol were brought to thermostat temperature, and equal volumes mixed. Portions (10 ml.) were withdrawn at intervals, run into 20 c.c. of *ca.* 2N-nitric acid, and the chloride ion titrated potentiometrically with silver nitrate. The results are tabulated below.

Determination of k_2 (l. sec.$^{-1}$ mole^{-1}) for reaction of picryl chloride with m-*nitroaniline in absolute methanol.*

Initially, [Halide] = 0·02999N, [Amine] = 0·1200N. Temp. 4·00°.
Concns. in ml. of 0·009986N-$AgNO_3$ per 10-ml. sample.

t (min.)	0	72	93	113	133	153	169	191	211	267	295	331	358
[Amine]	59·06	52·07	50·40	49·25	47·86	46·65	45·90	44·84	44·04	41·94	40·76	39·75	39·07
[Halide]	29·37	22·38	20·71	19·56	18·17	16·96	16·21	15·15	14·35	12·25	11·07	10·06	9·39
10^4k_2	—	5·70	5·76	5·60	5·70	5·75	5·69	5·69	5·64	5·60	5·76	5·74	5·72

Mean $k_2 = 5{\cdot}69 \times 10^{-4}$; duplicate, $5{\cdot}62 \times 10^{-4}$.

(6) *Exchange reaction between picryl chloride and radioactive chloride ions.* An approximately 0·35N-aqueous solution of radioactive lithium chloride was evaporated to dryness, and the residue strongly heated and allowed to cool in a stream of dry air. Absolute methanol was quickly added, and the flask tightly stoppered. Two methods were used to follow the exchange reaction.

(*a*) Methanolic solutions (10 ml. each) of radioactive lithium chloride and of picryl chloride were placed in separate limbs of an " H " tube, which was then placed in a thermostat; and after attaining thermostat temperature the contents of the two limbs were mixed, the time of mixing being taken as zero, and the tube left in the thermostat for a known interval. Reaction was stopped by immersing the tube in ice-water and washing the contents into a mixture of 20 ml. of chloroform and 40 ml. of distilled water. After extraction and separation, the aqueous layer was extracted twice with 20 ml. of chloroform, the aqueous layer was evaporated to dryness, and the solid obtained dissolved in 15 ml. of distilled water; 10 ml. of the latter solution were pipetted into a counter, and the radioactivity measured by use of standard scaling equipment. The total chloride ion in a 10-ml. sample was estimated by Volhard's method.

(*b*) The two standard solutions (100 ml. of each) were mixed, and 20-ml. portions sealed in tubes and placed in the thermostat. Initial tubes were taken at zero time, and thereafter tubes were removed at known intervals. The run was stopped by plunging the tubes into ice-water, and the methanol was removed by suction. The residue was dissolved in 20 ml. of benzene and 10 ml. of water, the aqueous layer extracted with a further 20 ml. of benzene, the volume made up to 20 ml. with distilled water, and the solution evaporated to a small bulk and finally made up to 15 ml. with distilled water. The specific activity was then found as in (*a*). Blank runs with picryl chloride showed that no appreciable hydrolysis took place in either extraction technique.

If a and b are the concentrations of picryl chloride and lithium chloride, and if c and $c - x$ are the specific activities of the initial lithium chloride and the salt obtained from a reaction stopped after time t, then the second-order constant is given by the equation (cf. le Roux and Sugden [15]).

$$k_2 = [2{\cdot}303/t(a + b)] \log_{10} [1 - x(1 + b/a)/c]^{-1}$$

[15] le Roux and Sugden, *J.*, 1939, 1279.

This formula is valid when no exchange has taken place at $t = 0$, *i.e.*, as in technique (*a*). When exchange has proceeded at $t = 0$, as in (*b*), then if the specific activities at $t = 0$ and $t = t$ are x_1 and x_2, the equation becomes

$$k_2 = \frac{2{\cdot}303}{(a+b)t} \cdot \log_{10}\left\{\left[1 - \frac{x_1}{c}\left(1 + \frac{b}{a}\right)\right]\left[1 - \frac{x_2}{c}\left(1 + \frac{b}{a}\right)\right]^{-1}\right\}$$

Determination of k_2 (l. sec.$^{-1}$ mole^{-1}) for the reaction of picryl chloride with radioactive chloride ion.

Initially, [Picryl chloride] = 0·09975M, [LiCl^x] = 0·04193M. Temp., 59·99°.
Concns. in ml. of 0·03436N-NH_4CNS per 10-ml. sample.

t (min.)	0	40	60	70	80	90
[Counts/min.]	626	524·3	501·4	499·4	536·5	564·5
[Concn. of Cl^- ion]	15·4	14·18	14·10	14·36	15·64	15·44
10^4k_2	—	4·05	3·85	3·87	3·68	3·86

Mean $k_2 = 3{\cdot}86 \times 10^{-4}$.
Corrected for solvent expansion, $k_2 = 4{\cdot}02 \times 10^{-4}$.

(7) *Methanolysis of picryl chloride.* This reaction was followed by potentiometric measurement of the chloride ion produced in aliquot parts of standard methanolic picryl chloride immersed in a thermostat for definite periods of time. The chloride-ion concentration rose to a maximum depending on the temperature at which the run was carried out and then fell rapidly to zero. Rate constants calculated on the basis of the chloride-ion concentration produced fell off slowly with time, and that for methanolysis was taken as that determined by extrapolation of initial rate measurements to zero time.

Determination of k_1 (solvolysis) for picryl chloride in absolute methanol.

Initially, [Picryl chloride] = 0·02987M. Temp. 35·06°.
Concns. in ml. of 0·01823N-$AgNO_3$ per 9-ml. sample.

t (min.)	0	2307	2630	3090	3710	4230	5280	5280	6556
[Picryl chloride]	4·291	3·944	3·896	3·838	3·764	3·682	3·570	3·591	3·443
10^7k_1	—	6·11	6·13	6·02	5·89	6·04	5·80	5·61	5·60

Extrapolation to $t = 0$ gives pseudo-$k_1 = 6{\cdot}35 \times 10^{-7}$, duplicate $k_1 = 6{\cdot}43 \times 10^{-7}$, mean $k_1 = 6{\cdot}39 \times 10^{-7}$. k_2 = pseudo-k_1/(1000/32) = $2{\cdot}00 \times 10^{-8}$ l. sec.$^{-1}$ mole^{-1}.

Analyses of Products.—Reaction (2). Portions (50 ml. each) of 0·1199M-*p*-fluoronitrobenzene and 0·2631M-sodium thiophenoxide in absolute methanol were heated in nitrogen in a sealed ampoule for 22·5 hr. at 49·72°. The tube was chilled in ice, the contents were poured into methanolic hydrogen chloride, and the methanol was distilled off in a stream of nitrogen. The residue was extracted with ether and dilute sodium hydroxide solution; the ethereal layer was shaken four times with dilute sodium hydroxide solution, washed with water, and dried (Na_2SO_4). Distillation of the ether gave a residue which after drying over phosphoric oxide *in vacuo* had m. p. 50·8—53·5° (yield 90%) (Found: C, 62·7; H, 4·1; S, 14·0. Calc. for $C_{12}H_9O_2NS$: C, 62·3; H, 3·9; S, 13·1%). Hence the product is substantially pure 4-nitrodiphenyl sulphide. One recrystallisation from light petroleum raised the m. p. to 54·8—55·2° (Bourgevis and Huber [16] give m. p. 55°).

Oxidation with hydrogen peroxide in glacial acetic acid gave a sulphone, m. p. 144·2—144·7° (Bourgevis and Huber [16] give 143° for 4-nitrodiphenyl sulphone).

Reaction (3). At the temperature used, side reactions produce highly coloured substances. The development of colour was, however, slight over the range of times used for determining rate constants, and since Chapman and Parker [13] found the expected products in an analogous reaction at lower temperatures it is reasonable to assume that the initial consumption of amine is largely concerned in the replacement of fluoride ion. Also, consumption of amine was found to correspond with production of fluoride ion over the range of reaction followed. From a reaction mixture run at 200° for 8 days, 4-nitrodiphenylamine, m. p. 133°, was isolated together with a small quantity of (?) aniline-black.

Reactions (4) *and* (5). In both cases the addition of amine to picryl chloride gave a yellow solution and at the end of the reaction crystals separated from the solution. With aniline, the crystals had m. p. 180·8—181·4° (m. p. of 2 : 4 : 6-trinitrodiphenylamine 179°) [17]; with *m*-nitroaniline, the product had m. p. 212—213° (m. p. of 2 : 4 : 6 : 3′-tetranitrodiphenylamine 213°).[18]

[16] Bourgevis and Huber, *Bull. Soc. chim. France*, 1911, **9**, 947.
[17] Giua and Cherchi, *Gazzetta*, 1919, **49**, II, 157.
[18] Duin and Lennep, *Rev. Trav. chim.*, 1919, **38**, 368.

Reaction (7). Reaction tubes heated to 100° for 5 days were opened, and the product was evaporated to dryness on a water-bath; it had m. p. and mixed m. p. with picric acid 123—123·5°

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