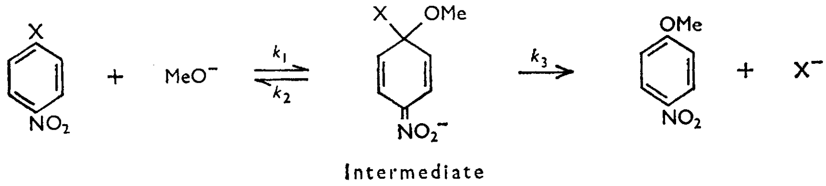
2. *The Mechanism of Displacement Reactions. Part I. Kinetics of the Reactions of the Four Picryl Halides,* 1,2,3,5-*Tetranitrobenzene, and* 1,2,4-*Trinitrobenzene with Aniline in Ethanol.*

By R. E. PARKER and T. O. READ.

Rate constants at two or three temperatures and Arrhenius parameters have been determined for the reactions of the four picryl halides, 1,2,3,5-tetranitrobenzene, and 1,2,4-trinitrobenzene with aniline in ethanol. The reactions all show second-order kinetics and the ease of displacement of X from the 1-X-2,4,6-trinitrobenzenes follows the sequence $NO_2 > F \gg Br > Cl > I$. This sequence is compared with that found for the reactions of the 1-X-2,4-dinitrobenzenes with aniline in ethanol, and a one-stage mechanism is preferred.

IT is well established that, in hydroxylic solvents, fluorine undergoes nucleophilic displacement from activated aryl halides much more readily than do the other halogens. The only exceptions are reactions involving particularly bulky reagents such as *N*-methylaniline[1] or iodide ion.[2] On the other hand, the order of ease of displacement of chlorine, bromine, and iodine varies considerably and appears to depend on the reagent. Thus, the order $F \gg Cl > Br > I$ is found for the reactions of *o*- and *p*-nitrophenyl halides and the 2,4-dinitrophenyl halides with sodium methoxide in methanol,[3,4,5] *p*-nitrophenyl halides with sodium ethoxide in ethanol,[6] and 2,4-dinitrophenyl halides with ammonia in methanol;[7] but the reactions of *o*- and *p*-nitrophenyl halides with piperidine in ethanol,[8] and of 2,4-dinitrophenyl halides with piperidine in methanol[9] and with aniline in ethanol,[10] all give the order $F \gg Br > Cl > I$; and the reactions of 2,4-dinitrophenyl halides with sodium thiophenoxide in methanol[11] give the order $F \gg Br > I > Cl$.



(1)

These reactions are usually explained on the basis of a two-stage mechanism such as (1). With the assumption of a stationary concentration for the intermediate, it follows that the rate of formation of products is given by:

$$d[\text{Products}]/dt = k_1k_3[\text{ArX}][\text{MeO}^-]/(k_2 + k_3). \qquad (2)$$

It can also be assumed, at least for reactions taking place under basic conditions in hydroxylic solvents, that the intermediate will lose halide ion much more easily than it will lose methoxide ion, *i.e.*, that $k_3 \gg k_2$, and therefore the observed rate constant becomes equal to k_1 and the formation of the intermediate is rate-determining. In these circumstances, the order of ease of halogen displacement to be expected will be governed by the size of the positive charge on the carbon end of the carbon-halogen bond in the nitroaryl halide (the larger this charge, the easier the approach of the nucleophile). These charges will depend on the electronegativities of the halogens and will decrease in the order

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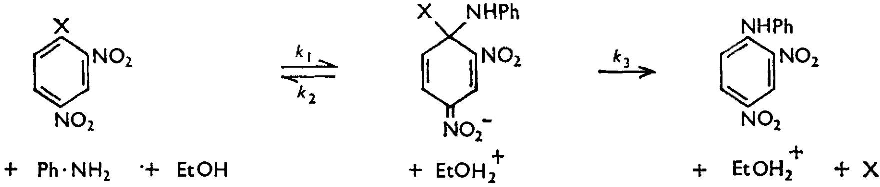
[1] Hammond and Parks, *J. Amer. Chem. Soc.*, 1955, **77**, 340.
[2] Fierens and Halleux, *Bull. Soc. chim. belges*, 1955, **64**, 717.
[3] Bolto, Miller, and Williams, *J.*, 1955, 2926.
[4] Briner, Miller, Liveris, and Lutz, *J.*, 1954, 1265.
[5] Beckwith, Miller, and Leahy, *J.*, 1952, 3552; Bevan and Bye, *J.*, 1954, 3091.
[6] Bevan, *J.*, 1951, 2340.
[7] Reinheimer, Taylor, and Rohrbaugh, *J. Amer. Chem. Soc.*, 1961, **83**, 835.
[8] Chapman, Parker, and Soanes, *J.*, 1954, 2109.
[9] Bunnett, Garbisch, and Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385.
[10] Chapman and Parker, *J.*, 1951, 3301.
[11] Bunnett and Merritt, *J. Amer. Chem. Soc.*, 1957, **79**, 5967.

$F \gg Cl > Br > I$. When the reagent is a neutral molecule (*e.g.*, ammonia or an amine), rather than an anion, a proton-transfer is usually involved and the situation may be slightly different. In a hydroxylic solvent, however, a proton-transfer from nitrogen to the oxygen atom of a solvent molecule will be very fast and will probably take place simultaneously with the formation of the intermediate, which will therefore become a termolecular process:



(3)

If this is so, the same equations will hold as for reactions with anions, and the same order of ease of halogen displacement is to be expected, *i.e.*, $F \gg Cl > Br > I$.

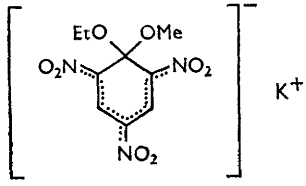
The fact that this order is shown by only five of the ten series of reactions listed above is not easy to accommodate on the basis of the two-stage mechanism. To do so, it is necessary to assume either that the stationary-state approximation is incorrect or, if it is correct, that k_3 is not large compared with k_2. Both these assumptions seem very unlikely. An alternative explanation, suggested by Bunnett,[12] is that, with highly polarisable reagents such as thiophenoxide ion, there is an accelerative London-force interaction between the reagent and the displaced group. Since the polarisability of the halogens increases in the order $F < Cl < Br < I$, this effect, combined with the effect of the electronegativity of the halogen, could in general give rise to any resultant order of ease of halogen displacement. Another and much simpler alternative is to assume that the reactions take place by a one-stage mechanism, in which the formation of the transition state involves some carbon–halogen bond stretching.

The ten series of reactions referred to above all involve mono- or di-nitroaryl halides and it seemed of interest to extend these investigations to the reactions of the picryl halides. If the two-stage mechanism is correct and an intermediate is involved in these reactions, the rate of formation of the intermediate should be considerably increased, and its rate of decomposition considerably decreased, by the introduction of a third nitro-group. This effect might well be large enough to give rise to a situation where the stationary-state assumption is no longer valid and where the decomposition of the intermediate is rate-determining. If this happened and if $k_2 \gg k_3$, the rate of formation of products would be given by:

$$\mathrm{d}[\text{Products}]/\mathrm{d}t = Kk_3[\text{ArX}][\text{Reagent}], \qquad (4)$$

where K is the equilibrium constant for the formation of the intermediate ($=k_1/k_2$), and [ArX] and [Reagent] denote the actual concentrations (corrected for the presence of the intermediate). The rate constant k_3 for the decomposition of the intermediate would depend on the ease of breaking of the carbon–halogen bonds and should increase in the order $F \ll Cl < Br < I$. The variation of the equilibrium constant K with change of halogen is less easy to predict, but it seems likely to be small, so that changes in the observed rate constant ($=Kk_3$) would be governed largely by changes in k_3. An unusual order of ease of halogen displacement might therefore be expected. In support of these expectations there was the isolation by Meisenheimer [13] of the complex (I) and the order $Cl < Br < I$ found by Rheinlander [14]

(I)



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[12] Bunnett, *J. Amer. Chem. Soc.*, 1957, **79**, 5969.

[13] Meisenheimer, *Annalen*, 1902, **323**, 205.

[14] Rheinlander, *J.*, 1923, 3099.

for the ease of displacement of halogen from the picryl halides by *N*-methylaniline in ethanol.

We have accordingly studied the kinetics of the reactions of the four picryl halides with aniline in ethanol and, to extend the range of displaceable groups, we have included 1,2,3,5-tetranitrobenzene. To make possible a complete comparison between 2,4,6-trinitrophenyl compounds and 2,4-dinitrophenyl compounds, we have also included 1,2,4-trinitrobenzene. For this study we prepared picryl fluoride by the nitration of 1-fluoro-2,4-dinitrobenzene and found that our product has properties different from those reported in the literature (see Experimental).

EXPERIMENTAL

Materials.—Picryl fluoride. A mixture of 1-fluoro-2,4-dinitrobenzene (55·8 g., 0·3 mole), 100% sulphuric acid (450 g.), and 100% nitric acid (75 g.) was heated at 130° for 18 hr. in a flask fitted with a reflux condenser and protected from atmospheric moisture by a silica gel guard tube. After cooling, the mixture was poured on ice, and water (*ca* 4 l.) was added. The blue oil which separated gradually solidified and became yellow. After filtration, the product was washed several times with water, dried, and crystallised repeatedly from dry light petroleum (b. p. 60—80°)–benzene to constant m. p. 130—131·5° (Found: C, 32·1; H, 1·2; N, 18·3; F, 7·9. Calc. for $C_6H_2FN_3O_6$: C, 31·2; H, 0·9; N, 18·2; F, 8·2%).

The product is extremely reactive to nucleophiles, including water, and quickly changes to picric acid unless moisture is rigorously excluded. Reaction with aniline was shown to give 2,4,6-trinitrodiphenylamine (m. p. and mixed m. p.) in almost theoretical yield. Reaction with dimethylamine gave the 2,4,6-trinitrophenyl-derivative which was similarly characterised, in at least 80% yield.

Of the two preparations of picryl fluoride reported in the literature, the product of m. p. 35° prepared by Oláh and his co-workers [15] by a method similar to ours has subsequently been shown to undergo a sharp increase of m. p. on repeated crystallisation,[16] finally to 130°. The material of m. p. 35°, which gave a satisfactory analysis, is presumably either an impure picryl fluoride or, possibly, a different crystalline form. We were not able to repeat Leonard's preparation [17] and his brownish-yellow compound of m. p. 150—160° is almost certainly a mixture, containing little, if any, picryl fluoride.

Picryl chloride. The commercial material (from British Drug Houses, Ltd.) was crystallised from chloroform to a constant m. p. 81—82°.

Picryl bromide. Bromobenzene was nitrated by Sugden and Willis's method [18] and the product was crystallised from ethanol to constant m. p. 122—124°.

Picryl iodide. Picryl chloride was treated with potassium iodide according to Hepp's method.[19] However, Hepp gives no details and it was found necessary to follow the method given below fairly closely. The preparation was unsuccessful if the ethanol was too dry or if methanol was used as the solvent, and the use of sodium iodide in dry acetone gave 1,3,5-trinitrobenzene as the only isolated product.

Picryl chloride (16 g.) was added to dried, powdered potassium iodide (52·8 g.) in commercial absolute ethanol (800 ml.). The mixture was well shaken, heated under reflux for 1·75 hr., cooled quickly, and poured into water (3 l.). The precipitate which was formed on stirring was separated, washed with water, dried, and crystallised from benzene to constant m. p. 168·5—170°.

1,2,3,5-*Tetranitrobenzene.* Ethyl picrate, prepared from ammonium picrate by Müller and Stenhouse's method,[20] was converted into 2,4,6-trinitrophenylhydroxylamine and thence into 1,2,3,5-tetranitrobenzene by Borsche's method.[21] The crude product was crystallised from chloroform between room temperature and $-50°$ to constant m. p. 127·5—129°.

[15] Oláh, Pavláth, Kuhn, and Varsányi, *Acta Chim. Hung.*, 1955, **7**, 431.
[16] Oláh, personal communication.
[17] Leonard, B.P. 537,010.
[18] Sugden and Willis, *J.*, 1951, 1360.
[19] Hepp, *Annalen*, 1882, **215**, 361.
[20] Müller and Stenhouse, *J.*, 1866, 235.
[21] Borsche, *Ber.*, 1923, **56**, 1496, 1500.

1,2,4-*Trinitrobenzene.* 2,4-Dinitrophenylhydroxylamine was prepared from 2,4-dinitroanisole and oxidised to 1,2,4-trinitrobenzene according to Borsche's method.[21] The yellow solid did not crystallise from very dilute aqueous methanol, as stated by Borsche, or from other organic solvents. It crystallised, however, from 1 : 1 nitric acid to constant m. p. 58·5—60·5°.

2,4-*Dinitrodiphenylamine.* 1-Chloro-2,4-dinitrobenzene and aniline were allowed to react according to Davis and Ashdown's method [22] and the product was crystallised from ethanol to constant m. p. 155—157°.

2,4,6-*Trinitrodiphenylamine.* Solutions of picryl chloride and of aniline in ethanol were mixed according to Le Fèvre's method [23] and the red crystals which separated were crystallised from much ethanol and had m. p. 177·5—179°.

Aniline. Acetanilide was crystallised from aqueous acetic acid and then hydrolysed with 24% hydrochloric acid. The product, isolated in the usual way and fractionally distilled *in vacuo* from zinc dust, had b. p. 75°/15 mm., n_D^{25} 1·5839. The pure aniline was stored under nitrogen and samples were occasionally submitted to gas chromatography on a column of silicone resin supported on Celite. The fact that only one peak was obtained showed the absence of detectable amounts of impurities.

Ethanol. Commercial absolute ethanol was dried by Lund and Bjerrum's method [24] and fractionally distilled through a 50 × 1·5 cm. column packed with Fenske helices. The water content was determined by Karl Fischer titration [25] and was adjusted to 0·20% w/w by addition of distilled water. The advantages of this solvent are that it has a known water content and is less hygroscopic than more anhydrous ethanol. It was used for all the kinetic measurements except those involving picryl fluoride or 1,2,3,5-tetranitrobenzene. For the reactions of these two compounds a mixture of very dry ethanol (~99·96% w/w) and ethyl acetate was used (see below).

Ethyl acetate. " AnalaR " ethyl acetate (from British Drug Houses, Ltd.) was shaken with saturated aqueous sodium hydrogen carbonate solution, dried ($CaCl_2$) and fractionated (b. p. 77°/760 mm.).

Thermostats. For the temperature range 20—35° conventional thermostats were used, the temperature control in all cases being better than ±0·03°. For reactions at 0° a stirred mixture of ice and water, suitably insulated, was used. It was found that the temperature, which was always between 0·00° and 0·05°, remained constant throughout a run. For the temperature range −20° to −70° a " Townson and Mercer Minus Seventy Thermostat Bath " was used. This had a temperature control of ±0·05°.

Kinetic Procedure.—Reactions of picryl chloride. bromide, and iodide, and of 1,2,4-*trinitrobenzene.* Standard solutions of each reactant in 99·80% ethanol were prepared at the temperature of the thermostat and the reaction was started by mixing appropriate quantities of these solutions in a 50 ml. graduated flask. At known intervals aliquot parts (5 ml.) were withdrawn and added to about 40 ml. of 0·05N-sulphuric acid in 90% aqueous ethanol in a 50 ml. graduated flask. This quenching solution was prepared by diluting 100 ml. of 0·5N-aqueous sulphuric acid to 1 l. with absolute ethanol and addition to it effectively stopped the reaction by converting all the free aniline into anilium ion. When all the withdrawals had been made for a particular run, the resulting solutions were each diluted to 50 ml. with quenching solution and the optical densities at appropriate wavelengths were determined with a Unicam S.P. 600 spectrophotometer, the quenching solution being used as a blank.

The solutions from the reactions of the picryl compounds were measured at two wavelengths, so that the absorption due to the product, 2,4,6-trinitrodiphenylamine, could be separated from that due to the picryl halides themselves. 1,2,4-Trinitrobenzene does not absorb appreciably in the visible region of the spectrum and it was only necessary to measure the solutions resulting from the reaction of this compound at one wavelength. The wavelengths used and the extinction coefficients are shown in Table 1.

Reactions of picryl fluoride and 1,2,3,5-*tetranitrobenzene.* The speed of these reactions was such that it was necessary to follow them at temperatures down to −65° and, under these conditions, it was impracticable to withdraw aliquot parts by pipette, because the rise in temperature of the solution in the pipette would have introduced considerable error. To overcome

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[22] Davis and Ashdown, *J. Amer. Chem. Soc.*, 1924, **46**, 1051.

[23] le Fèvre, *J.*, 1931, 813.

[24] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[25] Smith, Bryant, and Mitchell, *J. Amer. Chem. Soc.*, 1939, **61**, 2407.

this difficulty, three-limbed reaction vessels of the type illustrated (Fig. 1) were used. Limbs A and B could hold ~4 ml. of liquid each and limb C could hold 6 ml. Since both picryl fluoride and 1,2,3,5-tetranitrobenzene react with water to form picric acid and with ethanol to form ethyl picrate, it was not possible to prepare stock solutions of these compounds in 99·80% ethanol, nor was it possible to use an aqueous quenching solution to stop the reactions. The reactions were therefore started by mixing a solution of picryl fluoride or tetranitrobenzene in dry ethyl acetate with a solution of aniline in dry ethanol (~99·96% w/w) and were stopped by addition to a solution of toluene-*p*-sulphonic acid in dry ethyl acetate. In these circumstances there is no formation of ethyl picrate or picric acid, since the reaction with aniline is very much faster than reaction with ethanol or water.

TABLE 1.

Wavelengths and molar extinction coefficients.

Product	Wavelength (mμ)	Molar extinction coeff.
2,4,6-Trinitrodiphenylamine	360	12,100
	390	11,900
2,4-Dinitrodiphenylamine	359	17,100

A solution of picryl fluoride or tetranitrobenzene in dry ethyl acetate (1 ml.) was placed in limb A of the reaction vessel, a solution of aniline in dry ethanol (3 ml.) in limb B and a 0·006N-solution of toluene-*p*-sulphonic acid in dry ethyl acetate (5 ml.) in limb C. The vessel was completely immersed in the thermostat liquid and, after the solutions had cooled to the temperature of the thermostat (about 1 hr.), the vessel was shaken, while still immersed, in such a way that the reactant solutions in limbs A and B were mixed. After a suitable interval (usually a few minutes), the vessel was shaken in such a way that the reaction solution was mixed with the quenching solution. After the reaction had been stopped in this way, the vessel was removed from the thermostat. The contents were allowed to warm to room temperature, quantitatively transferred to a graduated flask, and made up to 25 ml. with quenching solution. The optical density of this solution was determined as before and the whole procedure was repeated for several different time intervals.

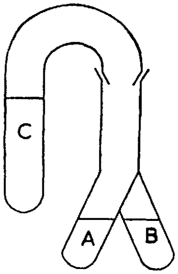

FIG. 1.

RESULTS

The reactions of aniline with picryl fluoride, picryl iodide and 1,2,3,5-tetranitrobenzene were each carried out at three different initial concentrations and, by application of the differential method of determining reaction orders,[26] were shown to be of the first order with respect to each reactant. The results are collected in Table 2 and each result is the mean of at least five determinations. It was assumed that the reactions of the remaining compounds with aniline were also of the first order with respect to each reactant, since they all obeyed appropriate second-order rate laws.

TABLE 2.

Orders of reaction.

Reactant	Temp.	Order with respect to nitro-compound	Order with respect to aniline
Picryl fluoride	−25°	0·91	1·03
Picryl iodide	+20	1·03	1·07
1,2,3,5-Tetranitrobenzene	−65	1·01	1·08

All the reactions can be represented by the equations:

$$\mathrm{ArX + Ph{\cdot}NH_2 \xrightarrow{Slow} Ar{\cdot}NHPh + HX} \qquad (5)$$

$$\mathrm{HX + Ph{\cdot}NH_2 \overset{Fast}{\rightleftharpoons} Ph{\cdot}NH_3^+ + X^-} \qquad (6)$$

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[26] Laidler, "Chemical Kinetics," McGraw-Hill, New York, 1950, p. 14.

That reaction (5) goes to completion has been shown by numerous determinations of the extent of reaction at " infinite " time (at least 30 times the half-life); this was invariably between 96% and 104%. Where X = Cl, Br, or I, reaction (6) also goes to completion and the reactions of these compounds obeyed the rate law:

$$\mathrm{d}x/\mathrm{d}t = k_2(a - 2x)(b - x), \tag{7}$$

giving

$$t = \frac{2{\cdot}303}{2k_2(a/2 - b)} \log_{10} \frac{b}{a/2} + \frac{2{\cdot}303}{2k_2(a/2 - b)} \log_{10} \frac{a/2 - x}{b - x}, \tag{8}$$

where a is the initial concentration of aniline and b is the initial concentration of nitro-compound. Values of the second-order rate constant, k_2, were determined graphically by plotting $\log_{10}[(a/2 - x)/(b - x)]$ against t.

Where X = F, it has previously been shown [10] that the equilibrium (6) lies almost completely on the left. The following rate law was therefore used for the reaction of picryl fluoride:

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)(b - x), \tag{9}$$

giving

$$t = \frac{2{\cdot}303}{k_2(a - b)} \log_{10} \frac{b}{a} + \frac{2{\cdot}303}{k_2(a - b)} \log_{10} \frac{a - x}{b - x}. \tag{10}$$

Since nitrous acid is an even weaker acid than hydrogen fluoride (at least in aqueous solution), equations (9) and (10) have also been applied to the reactions where X = NO_2. For the reaction of 1,2,4-trinitrobenzene, values of k_2 were determined graphically by plotting $\log_{10}[(a - x)/(b - x)]$ against t. For the reactions of picryl fluoride and 1,2,3,5-tetranitrobenzene, a value of k_2 was calculated from equation (10) for each optical-density determination made and the mean of these values taken.

In every case a good proportion of the reaction was followed, usually 15—75%, and all the runs were done in duplicate. The measured rate constants are shown in Table 3 and the rate constants interpolated or extrapolated to 25°, together with the Arrhenius parameters and heats and entropies of activation, are collected in Table 4. For the reactions of picryl chloride,

TABLE 3.

Measured rate constants in 99·80% ethanol.

Compound	Temp.	10^2k_2 (l. mole^{-1} sec.$^{-1}$)	Compound	Temp.	10^2k_2 (l. mole^{-1} sec.$^{-1}$)
1,2,3,5-Tetranitro-benzene *	−59·7°	10,400	Picryl bromide	0·00°	40·8
	−24·6	45,700		19·28	114
Picryl fluoride *	−59·0	1,190		34·30	254
	−24·3	4,990	Picryl iodide	0·00	6·28
Picryl chloride	0·02	32·2		19·26	20·2
	19·37	85·7		34·30	46·3
	35·46	168	1,2,4-Trinitrobenzene	0·03	2·61
				25·28	7·99
				35·11	11·8

* In 75% ethanol–25% ethyl acetate (v/v).

TABLE 4.

Rate constants at 25°, Arrhenius parameters, and heats and entropies of activation (k_2 and A in l. mole^{-1} sec.$^{-1}$; E and $\Delta H^\ddagger$ in kcal. mole^{-1}; $\Delta S^\ddagger$ in cal. mole^{-1} deg.$^{-1}$).

Compound	10^2k_2 at 25°	E	$\log_{10} A$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
1,2,3,5-Tetranitrobenzene *	200,000	4·4	6·6	3·9	−34·6
Picryl fluoride *	21,000	4·4	5·5	3·9	−40·4
Picryl chloride	108	7·8	5·8	7·2	−39·3
Picryl bromide	156	8·9	6·7	8·3	−34·6
Picryl iodide	27·8	9·8	6·6	9·2	−35·1
1,2,4-Trinitrobenzene	7·89	7·8	4·6	7·2	−45·7

* In 75% ethanol–25% ethyl acetate (v/v).

bromide, and iodide and 1,2,4-trinitrobenzene, the rate constants are accurate to better than $\pm 3\%$, E and $\Delta H^{\ddagger}$ to $\pm 0{\cdot}3$ kcal. mole^{-1}, $\log_{10} A$ to $\pm 0{\cdot}2$, and $\Delta S^{\ddagger}$ to $\pm 1{\cdot}0$ cal. mole^{-1} deg.$^{-1}$. For the very fast reactions of picryl fluoride and 1,2,3,5-tetranitrobenzene, the rate constants are accurate only to about $\pm 6\%$, E and $\Delta H^{\ddagger}$ to $\pm 0{\cdot}4$ kcal. mole^{-1}, $\log_{10} A$ to $\pm 0{\cdot}3$, and $\Delta S^{\ddagger}$ to $\pm 1{\cdot}5$ cal. mole^{-1} deg.$^{-1}$.

DISCUSSION

It is immediately obvious from Table 4 that no unusual order of ease of halogen displacement is observed in the reactions of the picryl halides with aniline in ethanol. The order found, $F \gg Br > Cl > I$, is the same as that for the reactions of *o*- and *p*-nitrophenyl halides with piperidine in ethanol [8] and of 2,4-dinitrophenyl halides with piperidine in methanol [9] and with aniline in ethanol,[10] and it is clearly determined largely by the polarisation of the carbon–halogen bonds. This dependence on the polarisation of the bond between carbon and the displaceable group (which is assumed to be determined mainly by the inductive effect of the group) is borne out by the high rate for the reaction of 1,2,3,5-tetranitrobenzene, since the nitro-group is more electron-withdrawing than any of the halogens (as shown, for example, by the values of the inductive substituent constants, σ', which decrease in the order [27] $NO_2 > F > Cl > Br > I$). A two-stage mechanism, in which the decomposition of the intermediate has become rate-determining, is therefore ruled out for these reactions of the picryl halides. The remaining possibilities are a two-stage mechanism in which the formation of the intermediate is still largely rate-determining, or a one-stage mechanism.

Even though a two-stage mechanism, in which the decomposition of the intermediate is rate-determining, appears to be ruled out by the above considerations, the additional stabilisation of the intermediate by the third nitro-group in going from the reactions of the 2,4-dinitrophenyl compounds to those of the picryl compounds might be expected to produce a change in such a direction that decomposition of the intermediate becomes more nearly rate-determining. This would imply an increase in the relative importance of carbon–halogen bond stretching; and, since the strengths of the carbon–halogen bonds are in the order $F \gg Cl > Br > I$, it should produce a tendency towards a reactivity order, $F \ll Cl < Br < I$. It follows that, if we define, for example, a fluorine–chlorine ratio as the ratio of the rate constant of a fluoride to that of the analogous chloride for reaction with the same reagent under the same conditions of solvent and temperature, this ratio should be smaller for picryl than for 2,4-dinitrophenyl compounds. However, a comparison of the rate constants collected in Table 5 shows that this is not so. At 50° the fluorine–chlorine ratio *increases* from 62 to 100 * in going from the 2,4-dinitrophenyl to the picryl series. The chlorine–bromine ratio and the bromine–iodine ratio also increase from 0·64 to 0·70 and from 3·2 to 5·1, respectively.

It appears therefore that, if the two-stage mechanism operates here at all, it must do so in such a way that the decomposition of the intermediate does not enter at all into the rate-determining step. If this is true for the reactions of the picryl compounds with aniline in ethanol, it must also be true, *a fortiori*, for the similar reactions of the 2,4-dinitrophenyl compounds.

Before accepting the two-stage mechanism, it is still necessary to explain why the order of ease of halogen displacement is $F \gg Br > Cl > I$, and not $F \gg Cl > Br > I$. The greater reactivity of the bromide than of the chloride cannot be due to bond-strength effects, since the decomposition of the intermediate does not enter into the rate-determining step. The only reasonable explanation is that of Bunnett,[12] who has postulated

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* The increase in the fluorine-chlorine ratio should really be greater than this, because the reaction of picryl fluoride was studied in 3 : 1 ethanol–ethyl acetate and it would certainly be rather faster in pure ethanol.

[27] Taft, " Steric Effects in Organic Chemistry," ed. M. S. Newman, John Wiley, New York, 1956, p. 595.

an accelerative London-force interaction between the reagent and the displaced group. This will be greater for bromine than for the less polarisable chlorine.

The final choice is between (*a*) a two-stage mechanism in which the formation of the intermediate is fully rate-determining and to which must be added the polarisability effect of Bunnett, or (*b*) a simple one-stage mechanism in which a small amount of bond stretching has taken place in the formation of the transition state. These two possibilities correspond to the energy diagrams of Figs. 2 and 3, respectively, and, although it is not possible to decide between them on the evidence now available, we prefer to accept the simpler one-stage mechanism for the two series of reactions of Table 5 and believe that this can be extended to all reactions of nitroaryl compounds with amines in hydroxylic solvents (although not necessarily to reactions with other reagents or in non-hydroxylic solvents).

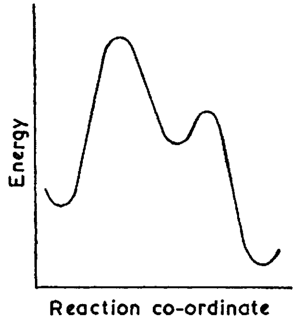

FIG. 2. Energy profile for two-stage mechanism.

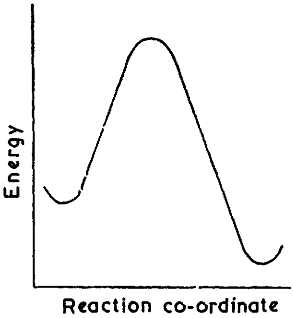

FIG. 3. Energy profile for one-stage mechanism.

TABLE 5.

Rate constants at 50° and Arrhenius parameters for reactions with aniline in ethanol (k_2 and A in l. mole^{-1} sec.$^{-1}$; E in kcal. mole^{-1}).

Displaced group	2,4-Dinitrophenyl compounds 10^4k_2	E	$\log_{10} A$	Picryl compounds $10k_2$	E	$\log_{10} A$
NO_2	2,110	7·8	4·6	42,100	4·4	6·6
F	168	6·4	2·6 [10]	3,340	4·4	5·5
Cl	2·70	11·2	4·0 [10]	33·4	7·8	5·8
Br	4·20	11·2	4·2 [10]	47·9	8·9	6·7
I	1·31 [10]	—	—	9·40	9·8	6·6

On the basis of the one-stage mechanism, structures (II—V) will contribute to the transition state and, in particular, the amount of C–X bond stretching which has taken place will be determined by the contribution of structure (II). Although it has been objected that such structures violate the Pauli exclusion principle, these objections can be overcome if the carbon atom attacked can use a 3*d*-orbital as in one of the arrangements suggested by Gillespie.[28] The inclusion of structures such as (II), because they involve C–X bond stretching, make any order of ease of halogen displacement possible and the results of Table 5 can be explained by assuming that structure (II) makes a small contribution to the transition state for the reactions of the picryl compounds and that an analogous structure makes a greater (but still small) contribution to the transition state for the reactions of the 2,4-dinitrophenyl compounds. Further, the partial CN and CX bonds of structures such as (II) are longer than the corresponding full bonds of structures such as (III), (IV), and (V), and structures such as (II) will therefore be relatively more important contributors if the reagent is a bulky molecule which cannot so easily form the fully bonded structures. It is significant that, in the reactions quoted above, the small reagents

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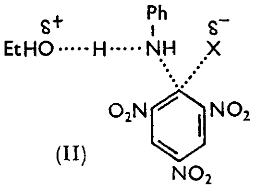
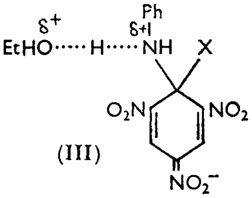
[28] Gillespie, *J.*, 1952, 1002.

(NH_3, OMe^-, and OEt^-) give the order of ease of displacement $F \gg Cl > Br > I$, the larger reagents (piperidine and aniline) give the order $F \gg Br > Cl > I$, the still larger thiophenoxide ion gives the order $F \gg Br > I > Cl$, and the very bulky reagents, iodide ion and *N*-methylaniline, give the order $F < Cl$.

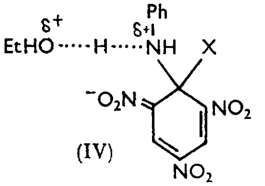
A comparison of the results in Table 5 shows that, for reactions with aniline in ethanol, the introduction of a third nitro-group into the 2,4-dinitrophenyl compounds increases the rate constants at 50° by 7000—20,000 times, and that this is due to a decrease of 2—3 kcal. mole^{-1} in E, reinforced by an increase of 2—3 units in $\log_{10} A$. The decrease in the energy of activation is, of course, expected. Of the two main energy factors involved in the formation of the transition state,[29] the repulsion energy (energy necessary to bring the reagent from infinity to its transition-state distance) will be very much greater than the bond-stretching energy (energy necessary to stretch the C–X bond from its initial to its transition-state length), and the additional nitro-group, by increasing the positive charge on the attacked carbon atom, will lower the repulsion energy. The increase in the entropy of activation was, however, unexpected. It cannot be due to a more loosely bound transition state, since this would imply a greater contribution from the partially bonded structure and hence an increase in the importance of C–X bond stretching and would be reflected in a lower fluorine–chlorine ratio. Nor is it likely to be due to an increase in the freedom of rotation of the additional *o*-nitro-group in the transition state, for, although the *o*-nitro-groups will be much more nearly coplanar with the benzene ring in the transition state than in the initial state, their positions will probably be fixed almost as rigidly in the transition state as in the initial state. The most likely explanation for the increased entropies is provided by " built-in solvation," suggested by Bunnett and Morath.[30] Electrostatic interaction in the transition state between the positively charged amino-nitrogen atom and the adjacent negatively charged oxygen atoms of the *o*-nitro-groups reduces the need for external solvation of these charges. Since the solvent molecules involved in external solvation exchange translational and rotational degrees for freedom for vibrational degrees of freedom, the entropy of the system is decreased, and any lessening of the need for external solvation will therefore result in an increase of entropy (or, at least, in a smaller decrease). This effect will be greater for the picryl compounds with two *o*-nitro-groups than for the 2,4-dinitrophenyl compounds with only one *o*-nitro-group. A study of the reactions of the 2,6-dinitrophenyl compounds with aniline in ethanol, to be reported later, shows that these reactions also have higher entropies of activation than the reactions of the 2,4-dinitrophenyl compounds.



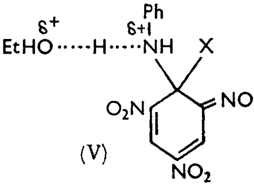
(II)



(III)



(IV)



(V)

The especially low values of the energy and entropy of activation for the reaction of

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[29] Hinshelwood, Laidler, and Timm, *J.*, 1938, 848.

[30] Bunnett and Morath, *J. Amer. Chem. Soc.*, 1955, **77**, 5051, 5165; Bunnett, Morath, and Okamoto, *ibid.*, p. 5055.

the fluoride in the 2,4-dinitrophenyl series (Table 5), which have been ascribed to the very high solvation of the incipient fluoride ion in the transition state,[10] are very much less marked in the picryl series. This is consistent with the smaller contribution of the partially bonded structure to the transition state in the picryl series and the correspondingly smaller negative charge on fluorine.

Grateful acknowledgment is made to Monsanto Chemicals Limited for a Research Scholarship (to T. O. R.), and to Professor J. C. Tatlow for fluorine analyses.

THE UNIVERSITY, SOUTHAMPTON.

[*Received, July* 13*th*, 1961.]