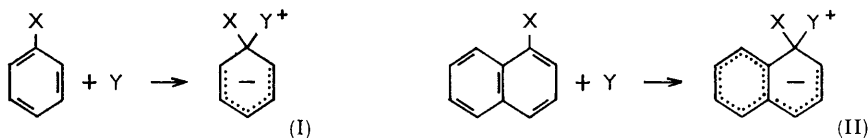**505.** *The Mechanism of Displacement Reactions. Part II.*[1] *Kinetics of the Reactions of the Four* 1-*Halogeno-2,4-dinitronaphthalenes,* 2,4-*Dinitro*-1-*naphthyl Toluene*-p-*sulphonate and* 1-*Chloro-2,4,5-trinitro-naphthalene with Aniline in Ethanol.*

By D. H. D. ELIAS and R. E. PARKER.

Rate constants at three temperatures, and Arrhenius parameters, have been determined for the reactions of the four 1-halogeno-2,4-dinitro-naphthalenes, 2,4-dinitro-1-naphthyl toluene-*p*-sulphonate, and 1-chloro-2,4,5-trinitronaphthalene with aniline in ethanol. The reactions are all of second order, and the ease of displacement of the five groups from the 1-substituted-2,4-dinitronaphthalenes follows the sequence *p*-Me·C_6H_4·SO_3 > F ≫ Br > Cl > I. The results for 1-chloro-2,4,5-trinitronaphthalene provide a measure of the transmission of electronic effects from one ring to the other in naphthalene.

The mechanism of the reactions is discussed and a two-stage mechanism is preferred.

ALTHOUGH a great many kinetic measurements have been made of the nucleophilic displacement of various groups from substituted benzenes (especially of halogens from nitrophenyl halides),[2,3] very little quantitative work has been done on corresponding reactions in the naphthalene series. In view of the doubt that still exists as to whether reactions of this kind take place by a one-stage or a two-stage mechanism,[1] studies of naphthalene systems might be expected to be particularly interesting, since the inter-mediate postulated in the two-stage mechanism should be considerably more stable in the naphthalene than in the benzene series. Dewar has calculated[4] that, whereas form-

ation of the benzene intermediate (I) involves a loss of resonance energy of 10 kcal. mole^{-1}, the formation of the corresponding naphthalene intermediate (II) involves a loss of only 2 kcal. mole^{-1}. Such a considerable increase in stability of the intermediate (relative to that of the initial state) might well be large enough to produce a situation where the decomposition of the intermediate to products becomes at least partially rate-determining. If this is so, stretching of the carbon–halogen bond will become more important and, consequently, the fluorine : chlorine ratio[1] will be smaller for the reactions of the naphthalene compounds than for the same reactions of the corresponding benzene compounds.

The results available in the literature for corresponding pairs of benzene and naphtha-lene compounds are collected in Table 1. The rate constants have been recalculated for 25° where necessary. Although no fluorine compounds have been studied in the naphtha-lene series, the orders of ease of halogen displacement shown in reactions 1, 2, and 3 (I > Br > Cl) and in reactions 6 and 7 (Br > Cl) suggest that some carbon–halogen bond stretching is involved in the rate-determining stages of these reactions. This could be accommodated either by a one-stage mechanism involving a partially bonded transition state or by a two-stage mechanism in which the decomposition of the intermediate is at

[1] Part I, Parker and Read, *J.*, 1962, 9.
[2] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[3] Bunnett, *Quart. Rev.*, 1958, **12**, 1.
[4] Dewar, " The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 177.

least partially rate-determining. However, the solvents in these reactions are non-hydroxylic and it cannot be assumed that the mechanisms are necessarily similar to those obtaining in hydroxylic solvents.

The close similarity of rate constants and Arrhenius parameters for analogous benzene and naphthalene compounds in reactions 1, 2, and 3 suggests that structures such as (I) and (II) are not much involved in the rate-determining stages and favours a one-stage mechanism with a partially bonded transition state. These reactions, and also reactions 6 and 7, may well be of a higher order than one in piperidine (because of the necessity for proton-transfer to piperidine in the transition state).

TABLE 1.

Rate constants at 25° and Arrhenius parameters for corresponding benzene and naphthalene compounds. (k and A in sec.$^{-1}$ for reactions 1—3, and in l. mole^{-1} sec.$^{-1}$ for reactions 4—10; E in kcal. mole^{-1}.)

No.		Reagent	Solvent	Benzene			Naphthalene		
				k	E	$\log_{10} A$	k	E	$\log_{10} A$
1	1-Chloro [5]	Piperidine	Piperidine	3.2×10^{-15}	26.8	5.2	3.6×10^{-14}	25.4	5.2
2	1-Bromo [5,6]	Piperidine	Piperidine	3.2×10^{-13}	24.1	5.2	2.1×10^{-13}	25.0	5.7
							3.5×10^{-13}	24.9	5.8
3	1-Iodo [6]	Piperidine	Piperidine	7.8×10^{-13}	23.6	5.2	1.8×10^{-12}	23.1	5.2
4	1,2-Dinitro [7,8]	NaOMe	MeOH	3.5×10^{-5}			3.58×10^{-3}	18.2	10.9
5	1,4-Dinitro [8,9]	NaOMe	MeOH	8.4×10^{-5}	22.4	12.4	1.00×10^{-3}	19.0	11.0
6	1-Chloro-4-nitro [10,11]	Piperidine	C_6H_6	1.81×10^{-8}	13.7	2.3	2.72×10^{-8}	14.9	3.4
7	1-Bromo-4-nitro [10,11]	Piperidine	C_6H_6	4.33×10^{-8}	13.6	2.6	1.16×10^{-7}	15.0	4.0
8	1-Chloro-2,4-dinitro [12,13]	NaOMe	MeOH	2.50×10^{-2}	17.0	10.9	3.40×10^{-1}	11.6	8.0
				2.96×10^{-2}	17.4	11.3			
9	1-Chloro-2,4-dinitro [12]	NaOEt	EtOH	8.25×10^{-2}	16.4	10.9	7.37×10^{-1}	9.9	7.1
10	1-Chloro-2,4-dinitro [14,15]	Ph·NH$_2$	EtOH	6.15×10^{-5}	11.2	4.0	2.18×10^{-2}		

As far as reactions in hydroxylic solvents are concerned, the considerably lower energies of activation for the naphthalene compounds than for their benzene analogues in reactions 5, 8, and 9 suggest that structures such as (I) and (II) are important in these reactions (and, by analogy, in reactions 4 and 10 also), either as intermediates in a two-stage mechanism or as major contributors to the structure of the transition state in a one-stage mechanism.

The present investigation was designed to provide further evidence relating to the mechanism of the reactions of activated naphthyl halides in hydroxylic solvents, particularly by a comparison of the ease of displacement of the four halogens from the 1-halogeno-2,4-dinitronaphthalenes. 2,4-Dinitro-1-naphthyl toluene-*p*-sulphonate was included to extend the range of displaceable groups and 1-chloro-2,4,5-trinitronaphthalene was studied as an example of a compound containing an activating group in the second ring of naphthalene.

[5] Richardson, Brower, and Amstutz, *J. Org. Chem.*, 1956, **21**, 890.
[6] Berliner, Quinn, and Edgerton, *J. Amer. Chem. Soc.*, 1950, **72**, 5305.
[7] Lobry de Bruyn and Steger, *Rec. Trav. chim.*, 1899, **18**, 41 (quoted by Bevan and Bye, *J.*, 1956, 469).
[8] Bamford, Ph.D. Thesis, London, 1960.
[9] Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74.
[10] Brieux and Deulofeu, *Chem. and Ind.*, 1951, 971.
[11] Simonetta and Beltrame, *Gazzetta*, 1958, **88**, 769.
[12] Talen, *Rec. Trav. chim.*, 1928, **47**, 329.
[13] Beckwith, Miller, and Leahy, *J.*, 1952, 3552.
[14] Singh and Peacock, *J. Phys. Chem.*, 1936, **40**, 669.
[15] van Opstall, *Rec. Trav. chim.*, 1933, **52**, 901.

EXPERIMENTAL

Materials.—1-*Fluoro*-2,4-*dinitronaphthalene.*   5,6,7,8-Tetrahydro-1-naphthylamine   was prepared from 1-naphthylamine by reduction with sodium and " isopentanol " (mainly 3-methyl-butan-1-ol) according to Bamberger and Althausse's method [16] and had b. p. 144—146°/13 mm.

Freshly distilled 5,6,7,8-tetrahydro-1-naphthylamine (53·5 g.) was mixed with concentrated hydrochloric acid (107 ml.) and water (134 ml.) and diazotised between −10° and 0° by the addition of a concentrated solution of sodium nitrite (27 g.) in water. The filtered solution was added to a concentrated solution of sodium tetrafluoroborate (150 g.) in water, both solutions being at 0°. The precipitated diazonium tetrafluoroborate, after successive washing with ice-cold water, ethanol, and ether, and drying, was thermally decomposed and the distillate was extracted with ether. The ethereal extract was washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid, and water, dried and distilled, to give 5-*fluoro*-1,2,3,4-*tetrahydronaphthalene*, b. p. 82°/11 mm., n_D^{19} 1·5211 (Found: C, 80·0; H, 7·5; F, 13·0. $C_{10}H_{11}F$ requires C, 80·0; H, 7·4; F, 12·7%). Gas-chromatographic analysis of this material on a column of Silicone resin supported on Celite showed only one peak.

5-Fluoro-1,2,3,4-tetrahydronaphthalene (15 g.) was added dropwise to nitric acid (45 ml.; *d* 1·5) between 6° and 14°. Then the solution was stirred for a further 30 min. without cooling and poured on ice. Repeated crystallisation of the precipitate from ethanol gave 5-*fluoro*-1,2,3,4-*tetrahydro*-6,8-*dinitronaphthalene*, m. p. 60—62° (Found: C, 50·6; H, 4·0; F, 8·0; N, 11·5. $C_{10}H_9FN_2O_4$ requires C, 50·0; H, 3·8; F, 7·9; N, 11·7%).

The fluoro-dinitro-compound (10 g.) was heated to 100° under a reflux condenser, and bromine (14 g.) added dropwise down the condenser. The temperature was kept at 100° until no more hydrogen bromide was evolved. The mixture was then heated to 170—180° and kept at this temperature until no more acid was evolved. After cooling, the dark mixture was extracted with several portions of hot benzene and the combined extracts were treated with charcoal and evaporated. Repeated crystallisation of the orange residue from light petroleum (b. p. 60—80°)–benzene gave pale yellow 1-*fluoro*-2,4-*dinitronaphthalene*, m. p. 144—145° (Found: C, 51·5; H, 2·4; F, 8·1; N, 11·1. $C_{10}H_5FN_2O_4$ requires C, 50·9; H, 2·1; F, 8·1; N, 11·9%). In spite of the poor analysis for nitrogen, there can be little doubt that the material obtained is as stated since qualitative analysis shows it to contain no halogen other than fluorine and determination of the amount of reaction with aniline in ethanol gives 100·4% reaction after " infinite " time (see below). Also, it is possible to isolate a high yield of *N*-phenyl-2,4-dinitro-1-naphthylamine from the reaction with aniline.

1-*Chloro*-2,4-*dinitronaphthalene.*   2,4-Dinitro-1-naphthol was heated with diethylaniline and toluene-*p*-sulphonyl chloride according to Ullmann and Bruck's method [17] and the product was purified by crystallisation from benzene and by chromatography on an alumina column. The pure material had m. p. 146·5°.

1-*Bromo*-2,4-*dinitronaphthalene.*   2,4-Dinitro-1-naphthylamine was diazotised and converted into 1-bromo-2,4-dinitronaphthalene by Hodgson and Walker's method.[18] Purification as for 1-chloro-2,4-dinitronaphthalene gave material of m. p. 160°.

1-*Iodo*-2,4-*dinitronaphthalene.*   The crude product obtained from 2,4-dinitro-1-naphthylamine by Hodgson and Walker's method [18] was repeatedly crystallised from 2-ethoxyethanol and finally chromatographed on alumina. The pure material had m. p. 182—183°.

2,4-*Dinitro*-1-*naphthyl* toluene-p-*sulphonate.*   Treatment of 2,4-dinitro-1-naphthol with diethylaniline and toluene-*p*-sulphonyl chloride at room temperature [17] and repeated crystallisation of the product from glacial acetic acid gave material of m. p. 158°.

1-*Chloro*-2,4,5-*trinitronaphthalene.*   1-Chloro-2,4-dinitronaphthalene was nitrated by Rindl's method [19] and the product crystallised from glacial acetic acid to a constant m. p. 144°.

N-*Phenyl*-2,4-*dinitro*-1-*naphthylamine.*   1-Chloro-2,4-dinitronaphthalene was refluxed with an excess of aniline in ethanol. The product, which separated on cooling, was crystallised from ethanol to constant m. p. 181°.

N-*Phenyl*-2,4,5-*trinitro*-1-*naphthylamine.*   1-Chloro-2,4,5-trinitronaphthalene was refluxed with an excess of aniline in ethanol and the product was crystallised from ethanol to constant m. p. 221°

[16] Bamberger and Althausse, *Ber.*, 1888, **21**, 1786; Bamberger and Müller, *ibid.*, p. 847.
[17] Ullmann and Bruck, *Ber.*, 1908, **41**, 3932.
[18] Hodgson and Walker, *J.*, 1933, 1620.
[19] Rindl, *J.*, 1913, **103**, 1911.

Aniline. Aniline was purified and stored as in Part I.[1]

Ethanol. Commercial absolute ethanol was dried and the water content adjusted to 0·20% w/w as in Part I. This 99·80% w/w ethanol was used as solvent for all the kinetic measurements except those involving 1-fluoro-2,4-dinitronaphthalene. For this a mixture of very dry ethanol (~99·96% w/w) and benzene was used (see below).

Kinetic Procedure.—Reactions of all compounds except 1-fluoro-2,4-dinitronaphthalene. These reactions were followed in the same way as the reaction of picryl chloride in Part I,[1] except that 0·05N-sulphuric acid in 50% aqueous ethanol was used as the quenching solution. This solution was prepared by diluting 500 ml. of 0·5N-aqueous sulphuric acid to 1 l. with absolute ethanol. The optical densities of the final solutions were measured at 410 mμ with a Hilger " Uvispek " H700-302 spectrophotometer, the molar extinction coefficients at this wavelength being 12,500 for N-phenyl-2,4-dinitro-1-naphthylamine and 11,910 for the 2,4,5-trinitro-amine. None of the reactants absorbs appreciably in the visible region of the spectrum and it was, therefore, only necessary to measure the solutions at one wavelength.

Reactions of 1-fluoro-2,4-dinitronaphthalene. This compound does not dissolve readily in ethanol and attempts to prepare a solution by warming led to some ethanolysis. Consequently, the reaction was started by mixing appropriate quantities of a solution of 1-fluoro-2,4-dinitronaphthalene in dry benzene with a solution of aniline in dry ethanol (~99·96% w/w). The amount of benzene in the solution was always 4% v/v. The subsequent procedure was the same as for the reactions of the other compounds.

RESULTS

The reactions of aniline with 1-fluoro-2,4-dinitronaphthalene, 1-iodo-2,4-dinitronaphthalene, and 2,4-dinitro-1-naphthyl toluene-*p*-sulphonate were each carried out at three different initial concentrations and, by application of the differential method of determining reaction orders,[20] were shown to be of the first order with respect to each reactant. The results are collected in Table 2; each result is the mean of at least four determinations.
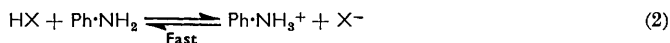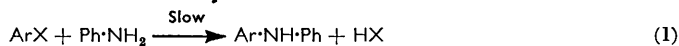
TABLE 2.

Orders of reaction.

Reactant	Temp.	Order with respect to naphthalene compound	Order with respect to aniline
1-Fluoro-2,4-dinitronaphthalene *	20·6°	1·00	1·01
	39·6	1·01	1·02
1-Iodo-2,4-dinitronaphthalene..................	40·0	0·99	1·03
2,4-Dinitro-1-naphthyl toluene-*p*-sulphonate	20·6	0·98	1·01
	39·6	0·97	1·01

* In 96 : 4 v/v ethanol–benzene.

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.

All the reactions can be represented by the schemes:

$$ArX + Ph \cdot NH_2 \xrightarrow{\text{Slow}} Ar \cdot NH \cdot Ph + HX \tag{1}$$

$$HX + Ph \cdot NH_2 \underset{\text{Fast}}{\rightleftharpoons} Ph \cdot NH_3^+ + X^- \tag{2}$$

That reaction (1) 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 98% and 102%. Where X = Cl, Br, I, or *p*-Me·C₆H₄·SO₃, reaction (2) also goes to completion and the reactions of these compounds obeyed the rate law:

$$dx/dt = k_2(a - 2x)(b - x), \tag{3}$$

giving

$$t = \frac{2 \cdot 303}{2k_2(a/2 - b)} \log_{10} \frac{b}{a/2} + \frac{2 \cdot 303}{2k_2(a/2 - b)} \log_{10} \frac{a/2 - x}{b - x}, \tag{4}$$

where a is the initial concentration of aniline and b is the initial concentration of naphthalene

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

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 [21] that the equilibrium of equation (2) lies almost completely on the left. The following rate law was, therefore, used for the reaction of 1-fluoro-2,4-dinitronaphthalene:

$$dx/dt = k_2(a - x)(b - x), \tag{5}$$

giving

$$t = \frac{2 \cdot 303}{k_2(a - b)} \log_{10} \frac{b}{a} + \frac{2 \cdot 303}{k_2(a - b)} \log_{10} \frac{a - x}{b - x} \tag{6}$$

Values of k_2 were determined graphically by plotting $\log_{10} [(a - x)/(b - x)]$ against t.

In every case a good proportion of the reaction was followed, usually $10-70\%$, and all the runs were done in duplicate. By experiments at higher concentrations, it was shown that high yields of the expected product could be isolated from each reaction studied. The measured rate constants are given 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. All the rate constants are accurate to better than $\pm 3\%$, E and $\Delta H^{\ddagger}$ to $\pm 0 \cdot 6$ kcal. mole^{-1}, $\log_{10} A$ to $\pm 0 \cdot 4$, and $\Delta S^{\ddagger}$ to $\pm 1 \cdot 8$ cal. mole^{-1} deg.$^{-1}$.

DISCUSSION

To attempt to understand the mechanisms of these reactions it is helpful to compare the results with those for the reactions of the analogous benzene compounds with aniline in ethanol, and the relevant values of rate constants and Arrhenius parameters are collected in Table 5. It is assumed that the presence of 4% of benzene in the solvent for the reaction

TABLE 3.

Measured rate constants in 99·80% ethanol.

Compound	Temp.	$10^2 k_2$ (l. mole^{-1} sec.$^{-1}$)
1-Fluoro-2,4-dinitronaphthalene *	0·05°	6·60
	20·50	10·6
	30·00	13·0
1-Chloro-2,4-dinitronaphthalene	30·00	1·81
	40·20	2·83
	49·90	4·32
1-Bromo-2,4-dinitronaphthalene	30·00	2·02
	39·70	3·07
	49·70	4·73
1-Iodo-2,4-dinitronaphthalene	39·90	1·41
	49·70	2·22
	59·50	3·40
2,4-Dinitro-1-naphthyl toluene-*p*-sulphonate	20·40	11·5
	29·60	17·1
	39·50	26·5
1-Chloro-2,4,5-trinitronaphthalene	20·00	16·9
	29·50	23·1
	40·00	33·4

* In 96 : 4 v/v ethanol–benzene.

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	$10^3 k_2$ at 25°	E	$\log_{10} A$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1-Fluoro-2,4-dinitronaphthalene *	117	3·7	1·8	3·1	$-52 \cdot 3$
1-Chloro-2,4-dinitronaphthalene	14·3	8·5	4·4	7·9	$-40 \cdot 7$
1-Bromo-2,4-dinitronaphthalene	15·7	8·5	4·5	7·9	$-40 \cdot 3$
1-Iodo-2,4-dinitronaphthalene	6·68	9·3	4·6	8·7	$-39 \cdot 6$
2,4-Dinitro-1-naphthyl toluene-*p*-sulphonate	152	7·9	5·0	7·3	$-37 \cdot 9$
1-Chloro-2,4,5-trinitronaphthalene	200	6·2	3·9	5·6	$-42 \cdot 8$

* In 96 : 4 v/v ethanol–benzene.

[21] Chapman and Parker, *J.*, 1951, 3301.

TABLE 5.

Rate constants and Arrhenius parameters for reactions with aniline in ethanol of the 1-halogeno-2,4-dinitro-derivatives of benzene and naphthalene (k_2 and A in l. mole^{-1} sec.$^{-1}$; E in kcal. mole^{-1}).

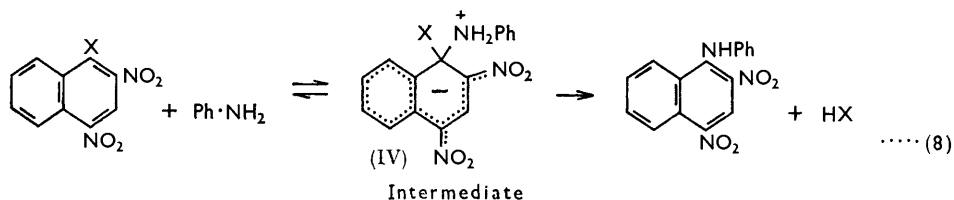|	Benzene				Naphthalene			
Halogen	k_2 at 25°	k_2 at 50°	E	$\log_{10} A$	k_2 at 25°	k_2 at 50°	E	$\log_{10} A$
F	7.20×10^{-3}	1.68×10^{-2}	6.4	2.6	1.17×10^{-1}	1.91×10^{-1}	3.7	1.8
Cl	6.72×10^{-5}	2.69×10^{-4}	11.2	4.0	1.43×10^{-2}	4.37×10^{-2}	8.5	4.4
Br	9.93×10^{-5}	4.05×10^{-4}	11.2	4.2	1.57×10^{-2}	4.79×10^{-2}	8.5	4.5
I		1.31×10^{-4}			6.68×10^{-3}	2.24×10^{-2}	9.3	4.6

of 1-fluoro-2,4-dinitronaphthalene has only a negligible effect on the rate of reaction of this compound.

The two most likely mechanisms are (*a*) a one-stage mechanism (7) in which the structure of the transition state is a resonance hybrid of the partially bonded structure (III) and the fully bonded structure (IV), and (*b*) a two-stage mechanism (8) in which the fully bonded structure (IV) is an intermediate.[1]

The facts that the reactions of the naphthalene compounds are all faster than those of the corresponding benzene compounds (Table 5), and that the energies of activation are distinctly lower for the reactions of the naphthalene compounds (2·7 kcal. mole^{-1}

..... (7)
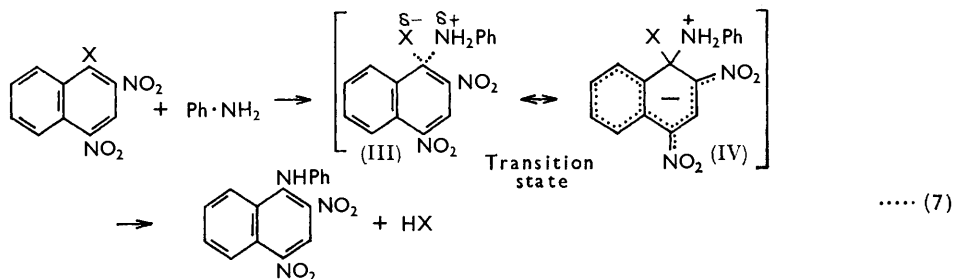
lower in each case), indicate that the fully bonded structure (IV) and the analogous benzene structure must be important in these reactions, either as intermediates in a two-stage mechanism or as major contributors to the structure of the transition state in a one-stage mechanism. This follows because structure (IV) would be expected to be considerably more stable (relative to the initial state) than its benzene analogue (8 kcal. mole^{-1} more stable if Dewar's calculation can be applied directly), whereas there is no reason to suppose that structure (III) would be any more stable (relative to the initial state) than the analogous partially bonded benzene structure.


..... (8)

The low values of $\log_{10} A$ for the reactions of the fluorides in both the benzene and the naphthalene series are most easily explained by assuming that an incipient fluoride ion is produced in the rate-determining stage and that, because of the ability of fluoride ions and incipient fluoride ions to hydrogen-bond to a hydroxylic solvent, more solvent molecules are " frozen " round these transition states than round the transition states containing incipient chloride, bromide, or iodide ions (which cannot form strong hydrogen

bonds). Such an interpretation means that some carbon–halogen bond stretching is involved in the rate-determining step and, because the value of $\log_{10} A$ for the fluoronaphthalene is lower than that for the fluorobenzene (both relative to the values for the other halides), there must be more carbon–halogen bond stretching in the transition states for the naphthalene reactions than in those for the benzene reactions. This conclusion is also supported by the lower fluorine : chlorine ratio [1] for the naphthalene reactions (8·2 at 25°) than for the benzene reactions (107 at 25°).

It is not easy to accommodate the above conclusions on the basis of a one-stage mechanism, because the greater rates for reactions of the naphthalene compounds than for those of the benzene compounds would necessitate the assumption of a greater contribution of structure (IV) to the transition state, and this is incompatible with the lower fluorine : chlorine ratio for the naphthalene compounds and with the lower value of $\log_{10} A$ for the fluoronaphthalene reaction (since a greater contribution of a fully bonded structure to a transition state implies less carbon–halogen bond stretching and, therefore, a higher fluorine : chlorine ratio).

Consequently, a two-stage mechanism is preferred for the reactions of the naphthalene compounds, and this mechanism must be such that the decomposition of the intermediate is partially (but not completely) rate-determining. It is not necessary to assume that the reactions of the benzene compounds are exactly similar, and a one-stage mechanism is still preferred for these reactions. The energy diagrams for the two series of reactions would be as depicted in Figs. 1 and 2. If the present interpretation is correct, the conclusion reached in Part I, that all activated aryl halides react with amines in hydroxylic solvents by a one-stage mechanism, requires modification for the case of reactions of activated 1-halogenonaphthalenes. Similar considerations would be expected to apply to appropriate halogen derivatives of other polycyclic hydrocarbons and the effect on the fluorine : chlorine ratio might be even more marked in some cases. For example, the stability of the intermediate (relative to that of the initial state) should be even more enhanced in the reactions of the 9-halogeno-10-nitroanthracenes and a fluorine : chlorine ratio of less than one might be expected in this case. On the other hand, the stability of the possible intermediate in the reactions of the activated 2-halogenonaphthalenes should be no greater than that in the reactions of the halogenobenzenes, and a low fluorine : chlorine ratio would not be expected for these reactions.

For the reactions of the 1-substituted 2,4-dinitronaphthalenes with aniline in ethanol, as for the similar reactions of the 1-substituted 2,4-dinitrobenzenes,[1] it is assumed that the proton-transfer to the solvent is rapid and the complete mechanism can therefore be written as (9). The transition state for the formation of the intermediate is represented by structure (V) and that for the decomposition of the intermediate to products by structure (VI). As indicated in Fig. 1, both transition states together determine the

$$\cdots\cdots (9)$$
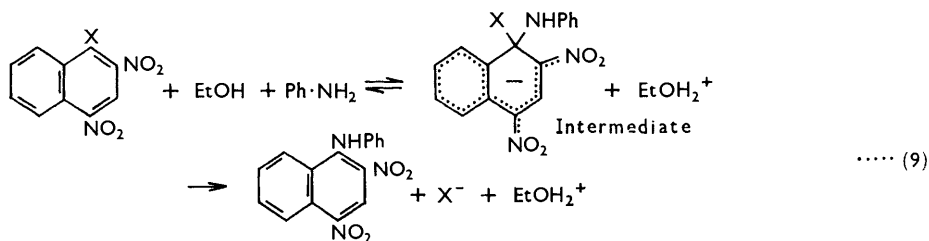
observed rate. The situation lies between the two extreme cases, in one of which (a) the formation of the intermediate is rate-determining [*i.e.*, (V) is the rate-determining transition state], and in the other (b) an equilibrium concentration of intermediate is rapidly set up and the decomposition of the intermediate is rate-determining [*i.e.*, (VI) is the rate-determining transition state].

It is interesting that, in these reactions, the toluene-*p*-sulphonyloxy-group is displaced more easily than any of the four halogens (Table 4) and that the attack of the aniline molecule is entirely on carbon and not sulphur. A similar result was found by Bunnett,
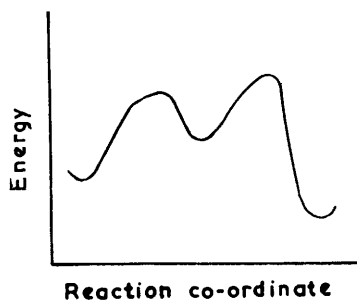

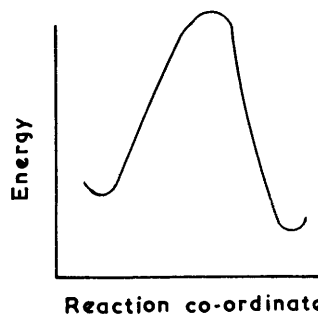FIG. 1. Energy profile for naphthalene reactions.

FIG. 2. Energy profile for benzene reactions.

Garbisch, and Pruitt [22] for the reactions of the 1-substituted 2,4-dinitrobenzenes with piperidine in methanol, where the toluene-*p*-sulphonyloxy-group is displaced more readily than chlorine, bromine, or iodine, but less readily than fluorine. It appears, therefore, that the toluene-*p*-sulphonyloxy-group is a good leaving group from highly activated positions (but not from less activated positions, because of some attack on sulphur) and, since toluene-*p*-sulphonyloxy-compounds are easily made from phenols, this may provide the preferred route to various polynitroaryl derivatives. For example, 2,4-dinitro-1-naphthyl toluene-*p*-sulphonate would be a very suitable reagent for the preparation of crystalline 2,4-dinitro-1-naphthyl derivatives of primary and secondary amines.
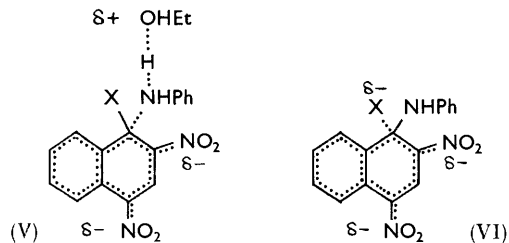
As the most important single factor determining rate in the above mechanism is the formation of the intermediate, the high reactivity of 2,4-dinitro-1-naphthyl toluene-*p*-sulphonate must be ascribed mainly to the high electronegativity of the toluene-*p*-sulphonyloxy-group and the consequent large polarisation of the carbon–oxygen bond. The high value of $\log_{10} A$ for this reaction suggests the absence of any significant amount of hydrogen bonding between the solvent and the incipient toluene-*p*-sulphonate ion and this is presumably because the negative charge in the incipient ion is dissipated over the three oxygen atoms.

Comparison of the results in Table 4 with those in Part I [1] shows that, for reactions with aniline in ethanol at 25°, whereas the introduction of a third nitro-group into 1-chloro-2,4-dinitronaphthalene (to give 1-chloro-2,4,5-trinitronaphthalene) increases the rate by a factor of only 14·0, the introduction of a third nitro-group into 1-chloro-2,4-dinitrobenzene (to give picryl chloride) increases the rate by a factor of 16,100. There are probably two reasons for the much smaller increase in the naphthalene series. First, a considerable proportion of the activating power of a nitro-group is probably due to its inductive effect

[22] Bunnett, Garbisch, and Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385.

and, since the third nitro-group in 1-chloro-2,4,5-trinitronaphthalene is further away from the site of reaction than is the third nitro-group in picryl chloride, this effect will not be felt as strongly. Secondly, the activating effect of both the 4- and the 5-nitro-group in 1-chloro-2,4,5-trinitronaphthalene is probably reduced considerably by steric inhibition of conjugation, owing to the proximity of the two groups. In this connexion, it would be interesting to study the reaction of 1-chloro-2,4,7-trinitronaphthalene where such steric inhibition of conjugation should be absent.

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