607. *The Mechanism of Displacement Reactions. Part III.** *Kinetics of the Reactions of the Four* 2-*Halogeno*-1,3-*dinitrobenzenes and* 1,2,3-*Trinitrobenzene with Aniline in Ethanol.*

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

Rate constants at three temperatures and Arrhenius parameters have been determined for the reactions of the four 2-halogeno-1,3-dinitrobenzenes and 1,2,3-trinitrobenzene with aniline in ethanol. The reactions are all of the second order and the ease of displacement of the five groups is in the sequence: $NO_2 > F \gg Br > Cl > I$. These reactions of the four halides are slower than those of the corresponding 2,4-dinitrophenyl halides. The reaction of 1,2,3-trinitrobenzene is, however, faster than that of 1,2,4-trinitrobenzene and this is attributed to steric acceleration.

The mechanism of the reactions is discussed, a one-stage mechanism being preferred.

MANY kinetic measurements have been made of the displacement of halogens and of other groups from 4-substituted *m*-dinitrobenzenes,[1,2] but the corresponding reactions of 2-substituted *m*-dinitrobenzenes have received almost no attention. In the latter series the only kinetic results reported are for the reactions of 2-chloro-1,3-dinitrobenzene with sodium methoxide in methanol at several temperatures[3] and with sodium ethoxide in ethanol at one temperature.[4] From the results collected in Table 1 it can be seen that the lower reactivity towards sodium methoxide of *o*- than of *p*-chloronitrobenzene is preserved on the addition of a further *o*-nitro-group, but that the difference becomes much greater. Thus, at 25°, the *para*/*ortho* ratio is 3·1 : 1 in the mononitro-series and 41 : 1 in the dinitro-series, the larger ratio in the latter series being due almost entirely to the fact that the energy of activation is 2·4 kcal. mole^{-1} higher for 2-chloro-1,3- than for 1-chloro-2,4-dinitrobenzene.

On the other hand, it is well known that, towards amines, the *o*-nitrophenyl halides are more reactive than their *para*-isomers[5] (*para*/*ortho* ratio for reactions with piperidine in ethanol at 25° about 0·3 : 1 for all four halides), and it would be interesting to know whether this difference is preserved in the dinitro-series. Also the presence of the two *o*-nitro-groups, coupled with the use of a relatively large reagent, might be expected to produce a steric effect in the reactions of 2,6-dinitrophenyl compounds with amines and possibly, therefore, to alter the order of ease of displacement of the different leaving groups.

TABLE 1.

Rate constants at 25° and Arrhenius parameters for reactions with sodium methoxide in methanol (k_2 and A in l. mole^{-1} sec.$^{-1}$; E in kcal. mole^{-1}).[3]

	10^5k_2	E	$\log_{10} A$
p-Chloronitrobenzene	0·0363	24·0	11·1
o-Chloronitrobenzene	0·0117	23·5	10·3
1-Chloro-2,4-dinitrobenzene..................	3020	17·4	11·3
2-Chloro-1,3-dinitrobenzene..................	74·1	19·8	11·4

The present paper reports the results of a kinetic investigation of the reactions of the four 2-halogeno-1,3-dinitrobenzenes and 1,2,3-trinitrobenzene with aniline in ethanol.

---

* Part II, *J.*, 1962, 2616.

[1] Parker and Read, *J.*, 1962, 9.

[2] (*a*) Chapman and Parker, *J.*, 1951, 3301; (*b*) Bunnett *et al.*, *J. Amer. Chem. Soc.*, 1957, **79**, 385, 5967; 1958, **80**, 6020; Beckwith, Miller, and Leahy, *J.*, 1952, 3552; Bevan and Bye, *J.*, 1954, 3091; Reinheimer, Taylor, and Rohrbaugh, *J. Amer. Chem. Soc.*, 1961, **83**, 835.

[3] Miller, *J.*, 1952, 3550.

[4] Bevan, *J.*, 1960, 1347.

[5] Chapman, Parker, and Soanes, *J.*, 1954, 2109.

EXPERIMENTAL

Materials.—*2-Fluoro-*1,3-*dinitrobenzene.* 2-Chloro-1,3-dinitrobenzene (10·1 g.), anhydrous, finely powdered potassium fluoride (6 g.), and freshly distilled nitrobenzene (10·1 g.) were heated at 190—195° for 5 hr. with stirring. After cooling, the mixture was filtered and the solid was washed with hot toluene (100 ml.). The combined filtrate and washings were dried (Na_2SO_4) and fractionated under reduced pressure. The third fraction solidified and was crystallised repeatedly from ethanol between room temperature and $-78°$ and finally from light petroleum (b. p. 60—80°)-benzene, to give *2-fluoro-*1,3-*dinitrobenzene,* m. p. 60—63° (Found: C, 39·0; H, 1·6; F, 10·7; N, 14·9. $C_6H_3FN_2O_4$ requires C, 38·7; H, 1·6; F, 10·2; N, 15·1%). This synthesis is similar to that of 1-fluoro-2,4-dinitrobenzene by Cook and Saunders.[6]

2-*Chloro-*1,3-*dinitrobenzene.* 2,6-Dinitroaniline was prepared and diazotised by Gunstone and Tucker's method,[7] and the diazonium solution treated with cuprous chloride in hydrochloric acid. The product was crystallised from light petroleum (b. p. 60—80°)-benzene to constant m. p. 87·5—89°.

An attempted preparation of 2-chloro-1,3-dinitrobenzene from 2,6-dinitrophenol by Kubota's method [8] gave only a small yield.

2-*Bromo-*1,3-*dinitrobenzene.* Diazotised 2,6-dinitroaniline was treated with cuprous bromide in hydrobromic acid, and the product crystallised from ethanol to constant m. p. 104·5—106·5°.

2-*Iodo-*1,3-*dinitrobenzene.* Diazotised 2,6-dinitroaniline was treated with a solution of potassium iodide, and the product crystallised from ethanol to constant m. p. 115—117°.

1,2,3-*Trinitrobenzene.* 2,6-Dinitrophenylhydroxylamine was prepared from 2-chloro-1,3-dinitrobenzene and oxidised to 1,2,3-trinitrobenzene by Borsche's method.[9] The product crystallised from ethanol to constant m. p. 121—122·5°.

2,6-*Dinitrodiphenylamine.* An ethanolic solution of 2-chloro-1,3-dinitrobenzene, aniline, and sodium acetate was heated under reflux according to the method of Borsche and Rantscheff,[10] and the product crystallised from ethanol to constant m. p. 106—108°.

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.[1] This 99·80% w/w ethanol was used as solvent for all the kinetic measurements.

Kinetic Procedure.—The reactions were followed in the same way as that of picryl chloride in Part I,[2] 0·05N-sulphuric acid in 90% aqueous ethanol being used as the quenching solution. The optical densities of the final solutions were measured at 420 mμ with a Unicam S.P. 600 spectrophotometer, the molar extinction coefficient of 2,6-dinitrodiphenylamine at this wavelength being 5400. 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.

Results.—The reactions of aniline with 2-fluoro- and 2-chloro-1,3-dinitrobenzene were each carried out at three different initial concentrations and, by application of the differential method of determining reaction orders,[11] were shown to be of the first order with respect to each reactant. The results are shown 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

TABLE 2.

Orders of reaction.

Reactant	Temp.	Order with respect to nitro-compound	Order with respect to aniline
2-Fluoro-1,3-dinitrobenzene	35°	0·99	1·01
2-Chloro-1,3-dinitrobenzene	50	1·00	1·04

---

[6] Cook and Saunders, *Biochem. J.*, 1947, **41**, 558.

[7] Gunstone and Tucker, *J. Appl. Chem.*, 1952, **2**, 204.

[8] Kubota, *J. Chem. Soc. Japan.*, 1932, **53**, 404.

[9] Borsche, *Ber.*, 1923, **56**, 1494.

[10] Borsche and Rantscheff, *Annalen*, 1911, **379**, 167.

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

were also of the first order with respect to each reactant, since they all obeyed appropriate second-order rate laws.

Numerous determinations of the extent of reaction at " infinite " time (at least 30 times the half-life) showed that the reactions all go to completion. For the reasons given in Part I,[1] the reactions of 2-fluoro-1,3-dinitrobenzene and 1,2,3-trinitrobenzene were represented by the equation:

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

where a and b are the initial concentrations of aniline and nitro-compound, respectively. Values of the second-order rate constant, k_2, were determined graphically by plotting $\log_{10}$ $[(a-x)/(b-x)]$ against t. The reactions of the chloride, bromide, and iodide were represented by the equation:

$$t = \frac{2{\cdot}303}{2k_2(\frac{1}{2}a-b)} \log_{10} \frac{b}{\frac{1}{2}a} + \frac{2{\cdot}303}{2k_2(\frac{1}{2}a-b)} \log_{10} \frac{\frac{1}{2}a-x}{b-x}$$

and the values of k_2 were determined by plotting $\log_{10}$ $[(\frac{1}{2}a-x)/(b-x)]$ against t.

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 at 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 ±3%, E and $\Delta H^{\ddagger}$ to ±0·5 kcal. mole^{-1}, $\log_{10}A$ to ±0·4, and $\Delta S^{\ddagger}$ to ±1·8 cal. mole^{-1} deg.$^{-1}$.

DISCUSSION

Whereas the *o*-nitrophenyl halides are more reactive than their *para*-isomers towards piperidine in ethanol[5] (by a factor of 2—3 at 25°), it is evident from Table 5 that the 2-halides are less reactive than their isomers towards aniline in ethanol (by a factor of 2—3 at 25° and by a rather smaller factor at 50°). If we make the reasonable assumption that piperidine and aniline are too similar for this difference to be attributable to the use of different reagents, we have the situation that, for reaction with amines in hydroxylic solvents, the movement of a nitro-group from a *para*- to an *ortho*-position has an accelerating effect in the mononitro-series and a decelerating effect in the dinitro-series. There is an

TABLE 3.

Measured rate constants in 99·80% ethanol.

Compound	Temp.	10^5k_2 (l. mole^{-1} sec.$^{-1}$)	Compound	Temp.	10^5k_2 (l. mole^{-1} sec.$^{-1}$)
1,2,3-Trinitrobenzene	0·02°	2,410	2-Bromo-1,3-dinitrobenzene	25·02°	5·33
	24·10	9,270		35·00	11·1
	35·04	15,600		48·87	31·8
2-Fluoro-1,3-dinitrobenzene	25·05	237	2-Iodo-1,3-dinitrobenzene ...	25·02	1·32
	35·17	394		35·07	2·89
	48·94	788		48·99	8·20
2-Chloro-1,3-dinitrobenzene	25·04	2·95			
	39·45	8·99			
	49·00	17·6			

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	10^5k_2 at 25°	E	$\log_{10} A$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
1,2,3-Trinitrobenzene	9600	9·0	5·6	8·4	−34·8
2-Fluoro-1,3-dinitrobenzene	235	9·4	4·3	8·8	−40·9
2-Chloro-1,3-dinitrobenzene	2·94	14·2	5·9	13·6	−33·6
2-Bromo-1,3-dinitrobenzene	5·33	14·1	6·1	13·5	−32·7
2-Iodo-1,3-dinitrobenzene	1·32	14·9	6·0	14·3	−33·2

increase in the energy of activation in both series, but, whereas this increase in the mononitro-series (1·0—1·6 kcal. mole^{-1}) is more than compensated for by an increase in $\log_{10}A$ (1·1—1·7 units), the greater increase in the dinitro-series (2·9—3·0 kcal. mole^{-1}) is not compensated by the increase in $\log_{10}A$ (1·7—1·9 units).

There can be little doubt that the higher entropies of activation observed in the reactions of compounds o-$NO_2{\cdot}C_6H_4X$ and 1,3,2-$(NO_2)_2C_6H_3X$ are correctly interpreted by Bunnett and Morath's suggestion of "built-in solvation,"[12] whereby 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. This is supported by the high entropies of activation found for the reactions of the picryl halides with aniline (Table 5) and by the results obtained for reactions with methoxide ion (Table 1), where the movement of a nitro-group from a *para*- to an *ortho*-position does not increase the entropy of activation (since built-in solvation is not possible with negative reagents).

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}).

	2-X-1,3-dinitrobenzene			1-X-2,4-dinitrobenzene [1, 2a]			Picryl [1]		
Group X	10^4k_2	E	$\log_{10} A$	10^4k_2	E	$\log_{10} A$	$10k_2$	E	$\log_{10} A$
NO_2	3260	9·0	5·6	2110	7·8	4·6	42,100	4·4	6·6
F	87·7	9·4	4·3	168	6·4	2·6	3,340	4·4	5·5
Cl	1·98	14·2	5·9	2·69	11·2	4·0	33·4	7·8	5·8
Br	3·66	14·1	6·1	4·05	11·2	4·2	47·9	8·9	6·7
I	0·832	14·9	6·0	1·31			9·40	9·8	6·6

The increased energies of activation are more difficult to interpret. The fact that, for reactions with amines, the movement of a nitro-group from a *para*- to an *ortho*-position produces about twice as big an increase in energy in the dinitro- as in the mononitro-series suggests that a primary steric effect is operating, for such more-than-linear increases of energy with increasing substitution near the reaction site are much more characteristic of steric than of electronic effects. Such an interpretation is supported by the observation that, for reaction with the small methoxide ion, the change from *p*- to *o*-chloronitrobenzene produces no increase in energy of activation (Table 1).

An alternative explanation would be that an *o*-nitro-group is intrinsically less powerfully activating than a *p*-nitro-group, but this does not seem very likely. Indeed, the results for the monochloronitrobenzenes in Table 1 suggest that, as least as far as energy of activation is concerned, the reverse is the case. The lower entropy for the reaction of *o*-chloronitrobenzene, and hence the lower rate, can be explained by the additional effect of electrostatic repulsion in the transition state between the negatively charged reagent and the adjacent negatively charged nitro-group (such repulsion limiting the freedom of vibrational and rotational motion in the transition state).

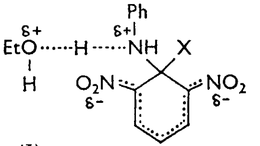
On balance, therefore, it seems to us that the most satisfactory explanation for the results of Tables 1 and 5 and of the reactions of the *o*- and *p*-nitrophenyl halides with piperidine[5] is that an *o*-nitro-group is intrinsically more powerfully activating than a *p*-nitro-group (and, therefore, since mesomeric effects are certainly not greater from the *ortho*- than the *para*-position, that a large part of the activating power of a nitro-group is due to its inductive effect), but that this greater activation by an *o*-nitro-group may be obscured by primary steric effects, especially when two *o*-nitro-groups are present.

The above discussion is equally compatible with a one-stage or with a two-stage mechanism, but we prefer a one-stage mechanism for the reasons given in Part I.[1] If it

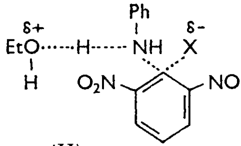
---

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

is also assumed, as in Part I, that the transfer of the proton from the amino-nitrogen atom to a molecule of solvent is fast, the transition state can be depicted as a resonance hybrid of structures (I) and (II). The lower fluorine : chlorine ratio for the reactions of these compounds (44 : 1 at 50°) than for the corresponding reactions of the 2,4-dinitrophenyl compounds (62 : 1 at 50°) implies that the contribution of structure (II) to the transition state is greater than the contribution of the analogous partially bonded structure to the transition state for the reactions of the 2,4-dinitrophenyl compounds [*i.e.*, that carbon–halogen bond stretching in the formation of the transition state is more important for compounds 1,3,2- than for compounds 2,4,1-$(NO_2)_2C_6H_3X$]. This is in line with the suggested primary steric effect for the reactions of the former compounds, since such a steric effect would de-stabilise structure (II) (with its relatively long CN and CX bonds) less than structure (I).



(I)



(II)

The reactions of the trinitro-compounds are anomalous in that 1,2,3-trinitrobenzene is more reactive than its 1,2,4-isomer, whereas all four halides 1,3,2-$(NO_2)_2C_6H_3Hal$ are less reactive than their 2,4,1-isomers. It seems likely that this anomaly is due to an abnormally high reactivity for 1,2,3-trinitrobenzene, rather than to an abnormally low reactivity for 1,2,4-trinitrobenzene; and, if so, the high reactivity of 1,2,3-trinitrobenzene is probably due to steric acceleration. All three nitro-groups in 1,2,3-trinitrobenzene must be twisted out of the plane of the benzene ring and their conjugation with the ring reduced. As far as the 1- and the 3-nitro-group are concerned, the amount of twisting is likely to be greater than for the nitro-groups in the 2-halogeno-1,3-dinitrobenzenes, not only because of the greater steric requirements of the central nitro-group in 1,2,3-trinitrobenzene than of a halogen atom, but also because of the electrostatic repulsion between the negatively charged oxygen atoms of this central nitro-group and the negatively charged oxygen atoms of the adjacent nitro-groups. The energy of the initial state for the reaction of 1,2,3-trinitrobenzene will, therefore, be raised relative to the energies of the initial states for the reactions of the 2-halogeno-1,3-dinitrobenzenes. On the other hand, the energy of the transition state is not likely to be affected, because, in this case, the attacked carbon atom will have become approximately tetrahedral and the two *o*-nitro-groups will be sandwiched between the incoming anilino-group and the outgoing displaceable group and will probably be co-planar with the ring. This type of steric acceleration is unusual in being due to a secondary steric effect (more steric inhibition of conjugation in the initial state than in the transition state). Presumably, there is superimposed on this a retarding primary steric effect, as discussed above for the reactions of the 2-halogeno-1,3-dinitrobenzenes.

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, January 15th*, 1962.]