Nucleophilic Aromatic Substitution of the Nitro-group

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The reaction of piperidine with 1,2,4-trinitrobenzene or with *o*-dinitrobenzene in benzene affords 2,4-dinitro-1-piperidinobenzene or 2-nitro-1-piperidinobenzene, respectively, in quantitative yield. Neither reaction undergoes base catalysis and overall second-order kinetics (first-order with respect to each reagent) were observed for a wide range of piperidine concentrations in benzene. Acid catalysis does not occur either as added *p*-methoxyphenol fails to affect appreciably the kinetics of the reaction of the trinitrobenzene. Comparison with the reaction of piperidine with 1-fluoro-2,4-dinitrobenzene in benzene, where pronounced catalysis by both piperidine and *p*-methoxyphenol has been observed, allows an interpretation of the reaction in terms of an addition–elimination mechanism with rapid expulsion of the nitro-group from the intermediate. Why the expulsion of the nitro-group from the intermediate should occur so easily is not clear, however. The recent literature concerning the nucleophilic aromatic substitution of the nitro-group is reviewed.

It has been long recognized that a nitro-group which is *ortho* or *para* to an activating (electron attracting) group in an aromatic compound can be easily replaced by nucleophilic reagents.[1] In addition to such typical nucleophilic aromatic substitution reactions, which are thought to occur by an addition–elimination mechanism,[2] non-activated aromatic nitro-groups are also sometimes replaced by a variety of reagents. Thus, replacement of a nitro-group by chlorine by treatment of various nitrohalogenobenzenes with ammonium chloride or phosphorus pentachloride is not a typical nucleophilic aromatic substitution as it is not accelerated by electron-attracting *ortho* or *para* substituents.[1a] Similarly reaction of elemental sulphur with 1-nitronaphthalene gives 1,1′-dinaphthyl sulphide and 1,1′-dinaphthyl polysulphides [3] for which a radical mechanism has been suggested.[3] Other cases of replacement of an aromatic nitro-group by nucleophiles have been rationalized in terms of an addition–elimination mechanism.[2] Some of these cases have been examined only from a preparative standpoint.[4] Kinetic investigations of reaction of

[1] (*a*) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, 1951, **49**, 273; (*b*) R. G. Shepherd and J. L. Fedrick, in 'Advances in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York and London, vol. 4, 1965.
[2] F. Pietra, *Quart. Rev.*, 1969, **23**, 504.
[3] J. A. Elix and G. C. Morris, *Tetrahedron Letters*, 1969, 671.
[4] J. H. Gorvin, *Chem. and Ind.*, 1967, 1525; S. Pietra and G. Casiraghi, *Gazzetta*, 1970, **100**, 119; S. Pietra, G. Casiraghi, and F. Rolla, *ibid.*, 1969, **99**, 665; R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc.* (*C*), 1968, 2221.

piperidine with 1,2,4-trinitrobenzene in methanol (replacement of the 1-nitro-group) [5a] and with 1,4-dinitrobenzene in dimethyl sulphoxide,[5b] the reaction of aniline with 1,2,3-trinitrobenzene in ethanol (replacement of the 2-nitro-group),[5c] with 1,2,4-trinitrobenzene (replacement of the 1-nitro-group,[5d] and with 1,2,3,5-tetranitrobenzene (replacement of the 2-nitro-group),[5d] and the reaction of sodium thiophenoxide with 1,2,4-trinitrobenzene (replacement of the 1-nitro-group) [5e] have been reported. In all these cases, comparison with the replacement of other leaving groups by the same reagent has been made.[5] In these reactions the nitro-group is replaced as easily as fluorine (in some cases a little easier,[5d,e] and in some others a little more difficult [5b]) which is usually one of the groups most easily replaced.* The lack of such an ' element effect ' [5a] is good evidence in favour of an addition–elimination mechanism.[2]

More complex processes have also been examined. Thus, triethyl phosphite displaces a nitro-group from *o*-dinitrobenzene to give diethyl *o*-nitrophenylphosphonate and ethyl nitrite.[7] This has been interpreted [7] in terms of a nucleophilic aromatic substitution occurring *via* an addition–elimination mechanism [2] (the *o*-nitro-group has an anchimeric role since *p*-dinitrobenzene is unreactive under the same conditions) followed by dealkylation by the nitrite ion.

The replacement of an aromatic nitro-group by a nucleophile may compete with the formation of a Meinsenheimer adduct [2] at an unsubstituted ring position. This is the case in the interaction of methoxide ion with 1,3,5-trinitrobenzene where 3,5-dinitroanisole is the predominant product. A kinetic study suggests that the free reagents are responsible for 3,5-dinitroanisole formation whereas the Meisenheimer adduct does not lie along the path of this reaction.[8a] Other studies of this reaction have been reported.[8b] Such competitive processes may be rather common.[8c-e] Kinetic studies have also been reported for the replacement of a nitro-group by the methoxy-group [9a] or by ethylenediamine [9b] for *p*- or *o*-dinitrobenzene.

Some photonucleophilic aromatic substitutions [2,10] of the nitro-group have also been discovered. These are the reaction of *p*-nitroanisole with ammonia [10] or with pyridine,[11] the reaction of 4-nitropyridine *N*-oxide with piperidine,[12] the reaction of *p*-nitrophenylphosphate with pyridine,[13] and the reaction of hydroxide ion with some nitronaphthalenes [14a] or with 1,3,5-trinitrobenzene.[14b] The last example is peculiar because, in contrast with all other photochemical reactions in which intermediate formation of an excited state of the substrate along the reaction path has been postulated, the light absorbing species here is the Meisenheimer adduct formed from the substrate and hydroxide ion.[14b] This process is thought to be followed by nitro-group replacement by another hydroxide ion.[14b]

The reaction of *sym*-trichlorotrinitrobenzene with sodium borohydride [15] leads to the replacement of one or two nitro-groups by the hydride ion.[15] The reaction course has been rationalized [15] on the basis of a nucleophilic aromatic substitution by hydride ion *via* an addition–elimination mechanism,[2] although a kinetic investigation would be highly desirable to provide support for this mechanism. Lack of activation of chlorine replacement has been attributed to the nitro-groups being considerably rotated out of the plane of the benzene ring in the substrate.[15a] A similar course was observed on treatment of *sym*-trichlorotrinitrobenzene with lithium chloride where chloride replaces a nitro-group.[15b] Here, however, chloride exchange would pass undetected and the reference to the work of Ueda's *et al.*[15c] (where the change in the extent of coplanarity of the nitro-groups on going from the substrate to the Meisenheimer adduct refers to nitro-groups in the *ortho*-position to the reaction centre) is clearly unjustified. Replacement of a nitro-group by chloride has also been observed on treatment of aromatic diazonium salts with hydrogen chloride.[15d] However, the most interesting results in this connection were obtained with *sym*-trinitrotrimethoxybenzene. Here, on treatment with ethoxide it is a methoxy-group which is replaced.[15e]

The unusual suggestion that replacement of an *o*-nitro-group by hydroxide ion for 2,4,6-trinitro-*N*-t-butylbenzamide occurs *via* rate-limiting heterolysis of the aromatic carbon–nitrogen bond has been made.[16b] It has been correctly pointed out, however, that such an interpretation is not supported by the experimental results [16b] and a review on the unimolecular mechanism

* It must be warned, however, that comparison of the leaving group mobilities with that of fluorine may not be straightforward. It has been proved, that the very easy replaceability of aromatic fluorine by nucleophiles is at least in some cases due to the intervention of intramolecular catalytic processes which are usually not needed for replacement of most other groups.[6]

[5] (*a*) J. F. Bunnett, E. W. Garbish, jun., and K. M. Pruitt, *J. Amer. Chem. Soc.*, 1957, **79**, 385; (*b*) H. Suhr, *Chem. Ber.*, 1964, **97**, 3268; (*c*) R. E. Parker and T. O. Read, *J. Chem. Soc.*, 1962, 3149; (*d*) *ibid.*, p. 9; (*e*) J. F. Bunnett and W. D. Merritt, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 5967.

[6] F. Pietra and F. Del Cima, *Tetrahedron Letters*, 1967, 4573.

[7] J. I. G. Cadogan and D. T. Eastlick, *J. Chem. Soc.* (*B*), 1970, 1314, and preceding papers.

[8] (*a*) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1962; (*b*) I. R. Bellobono, *Ricerca sci.*, 1969, **39**, 358, 365; (*c*) R. C. Farmer, *J. Chem. Soc.*, 1959, 3433; (*d*) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1697; (*e*) C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 129.

[9] (*a*) R. Schaal and J. C. Latour, *Bull. Soc. chim. France*, 1964, 2177; (*b*) R. Schaal and C. Vermesse-Jacquinot, *Compt. rend.*, 1964, 258; (*c*), *ibid.*, p. 2334.

[10] E. Havinga, *Pure Appl. Chem.*, 1968, **16**, 137.

[11] R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Amer. Chem. Soc.*, 1965, **87**, 2945.

[12] R. M. Johnson and C. W. Rees, *J. Chem. Soc.* (*B*), 1967, 15.

[13] R. L. Letsinger and O. B. Ramsay, *J. Amer. Chem. Soc.*, 1964, **86**, 1447.

[14] (*a*) G. M. J. Beijersberger van Henegouwen, *Rec. Trav. chim.*, 1970, **89**, 907; (*b*) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1964, 1717.

[15] (*a*) L. A. Kaplan, *J. Amer. Chem. Soc.*, 1964, **86**, 740; (*b*) P. H. Gore, S. D. Hammond, and D. F. C. Morris, *Tetrahedron Letters*, 1970, 2747; (*c*) H. Ueda, N. Sakabe, J. Tanaka, and A. Furusaki, *Nature*, 1967, **215**, 956; (*d*) B. Anderson and B. Lamm, *Acta Chem. Scand.*, 1969, **23**, 2983; (*e*) S. S. Gitis, A. I. Glaz, and A. Sch. Glaz, *Z. org. Chim.*, 1967, **3**, 1620.

[16] (*a*) P. J. Hutchinson and R. J. L. Martin, *Austral. J. Chem.*, 1965, **18**, 699; (*b*) B. Capon, M. J. Perkins, and C. W. Rees, ' Organic Reaction Mechanisms,' Interscience, 1965, p. 146.

for nucleophilic aromatic substitution in which this example [16a] has no place has appeared.[2]

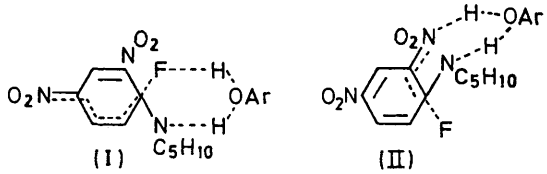
In contrast with the ease of replacement of an aromatic nitro-group by nucleophiles *via* an addition–elimination mechanism the nitro-group is not a good leaving group for the formation of arynes [2] in benzenoid substrates.[17a] Consistent with this and with the difficulty of generating arynes in five-membered rings [2] (see, however ref. 17b) is the replacement, with rearrangement (*cine* substitution [2]) of a nitro-group of 3,4-dinitrothiophen by thiophenoxide ion to give 2-(4-nitro)thienyl phenyl sulphide which was suggested [17c] to occur *via* an anomalous addition–elimination mechanism rather than *via* an aryne mechanism.[2] It is also noteworthy that the direct replacement of the nitro-group of 5-nitro-1,2,4-triazole by trimethylamine has been reported.[17d] Replacement of a nitro- by a chloro-group has also been observed on treatment of aza-activated nitro-aromatic compounds with thionyl chloride or phosphoryl chloride.[1b]

The success of these reactions and the easy replacement of the nitro-group of 2-methyl-6-nitropyridine-3-carboxylic acid by methanolic hydrogen chloride or by concentrated hydrogen chloride,[18] have led to the suggestion that ' the nitro-group seems to be especially susceptible to acid catalysis.'[19]

Electrophilic catalysis, by the cation of the nucleophile, of the removal of the nitro-group has also been suggested for the reaction of sodium thiophenoxide with 2-bromo-5-nitro-1,3,4-thiadiazole to give 2-bromo-5-phenylthio-1,3,4-thiadiazole as the sole monosubstitution product.[20]

Electrophilic catalysis of the removal of the leaving group in nucleophilic aromatic substitution is relevant to the understanding of the detailed reaction mechanism of aromatic substitution and to synthetic problems.[2] Lam and Miller reported that the removal of fluorine from 1-fluoro-2,4-dinitrobenzene by iodide or by thiocyanate ions undergoes strong electrophilic catalysis by hydrogen or by thorium ions, respectively.[21] However, a check of the thiocyanate reaction has revealed that this is by no means a simple aromatic substitution, the reaction products being bis-2,4-dinitrophenyl sulphide (67%), 2,4-dinitro-1-thiocyanatobenzene (1%), and 1-isothiocyanato-2,4-dinitrobenzene (33%).[22] The formation of the last compound was inferred from the presence of the i.r. absorption band characteristic of organic isothiocyanates but it was not isolated. The addition of thorium nitrate failed to affect either the product distribution or the rate. Therefore, the original claim [21] of the catalysis by thorium ions of the removal of fluorine was refuted.

It has been shown unequivocally, however, that in some cases the substitution of fluorine by nucleophilic reagents from aromatic substrates requires the leaving fluorine to become bound to an acid catalyst. These are examples of bifunctional catalysis. The reaction of 1-fluoro-2,4-dinitrobenzene with piperidine in benzene undergoes catalysis by *para*-substituted phenols, the catalytic coefficient being independent of the acidity of the phenol.[23] The reaction has been interpreted as proceeding through a simultaneous removal of the ammonium proton by the phenolic oxygen and of fluorine by the phenolic hydrogen from the intermediate [2] (I).[23] Bifunctional catalysis was further substantiated by the observation that the reaction is strongly catalysed by 2-pyridone.[24] The bifunctional catalyst is involved in the simultaneous removal of both the ammonium



proton and fluorine and not in the alternative situation of the removal of the ammonium proton with more or less synchronous hydrogen bonding to the *o*-nitro-group [intermediate (II)] by the fact that the reaction of 2,4-dinitrophenyl phenyl ether with piperidine in benzene undergoes base catalysis while bifunctional compounds have no rate effect.[25,26]

When a reaction of this type involves a fast decomposition of the intermediate to products, no rate acceleration by either acidic or bifunctional catalysts was found.[2,23]

We extended our studies on the incidence of electrophilic catalysis in aromatic nucleophilic substitution to the replacement of the nitro-group as previous studies did not give a clear-cut answer. We report here a kinetic investigation of the reaction of piperidine with 1,2,4-trinitrobenzene and *o*-dinitrobenzene in benzene and of the influence of added *p*-methoxyphenol.

RESULTS

The reaction of piperidine with 1,2,4-trinitrobenzene or with *o*-dinitrobenzene affords 2,4-dinitro-1-piperidinobenzene [27] or 2-nitro-1-piperidinobenzene,[27] respectively in quantitative yield. Rate data are in the Table. When *p*-methoxyphenol was present in the reaction mixture, the second-order rate coefficient was calculated by use of the stoicheiometric concentration of the substrate and the concentration of free piperidine (not associated with phenol)

[17] (*a*) P. Buck, *Angew. Chem.*, 1969, **81**, 136, 146; (*b*) R. C. Martin and D. R. Bloch, *J. Amer. Chem. Soc.*, 1971, **93**, 451; (*c*) C. Dell'Erba, D. Spinelli, and G. Leandri, *Gazzetta*, 1969, **99**, 535; (*d*) L. I. Bagal, M. S. Pevzner, and V. Ya. Samarenko, *Khim. geterotsikl. Soedinenii*, 1970, 269.

[18] R. J. Dummel and H. S. Mosher, *J. Org. Chem.*, 1959, **27**, 2644.

[19] Ref. 1*b*, p. 208.

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[21] K. B. Lam and J. Miller, *Chem. Comm.*, 1966, 643; J. Miller, ' Aromatic Nucleophilic Substitution,' Elsevier, London, 1968, p. 152, 337.

[22] D. E. Giles and A. J. Parker, *Austral. J. Chem.*, 1970, **23**, 1581.

[23] F. Pietra and D. Vitali, *J. Chem. Soc.* (*B*), 1968, 1318.

[24] F. Pietra and D. Vitali, *Tetrahedron Letters*, 1966, 5701.

[25] F. Pietra, *Tetrahedron Letters*, 1965, 2405.

[26] F. Pietra, D. Vitali, and S. Frediani, *J. Chem. Soc.* (*B*), 1968, 1595.

[27] F. Pietra and F. Del Cima, *J. Org. Chem.*, 1968, **33**, 1411.

calculated from available association data between *p*-methoxyphenol and piperidine in benzene.[23]

The reaction of piperidine with *p*-dinitrobenzene in benzene was also studied. The reagents were unchanged at room temperature. At 65—85° the substrate was readily consumed though, with a substrate concentration initially 6×10^{-4}M the u.v. spectrum of the reaction mixture was markedly different from that of the expected 4-nitro-1-piperidinobenzene.[27] With higher substrate concentrations (3—6×10^{-2}M) the u.v. spectrum of the reaction mixture was that expected for 4-nitro-1-piperidinobenzene at least up to 60% conversion of the substrate. This was confirmed by isolation of the reaction products. However, even under these conditions, we failed to obtain reproducible u.v. data even from samples from the same reaction batch (sealed ampoule method). Therefore no rate data are reported for this reaction.

DISCUSSION

The reactions studied here do not undergo base catalysis. For 1,2,4-trinitrobenzene this is shown by the constancy, within the limits of experimental error, of the second-order rate coefficient when the concentration of the nucleophile, which is itself a strong base in benzene, is increased by nearly 30-fold (Table, A).

This is a conclusive test of the lack of base catalysis (by an external base) of the substitution of the nitro-group by protic amines because the replacement of another leaving group, fluorine, by piperidine undergoes pronounced piperidine catalysis under otherwise identical conditions. The second-order rate coefficient for the reaction of fluoro-2,4-dinitrobenzene with piperidine in benzene at 25° increases by a factor of *ca.* 30 for the same piperidine concentration change as in the reaction of 1,2,4-trinitrobenzene (Table, A).[23]

TABLE

Rates of reaction of piperidine (pip) with 1,2,4-trinitrobenzene [with or without added *p*-methoxyphenol (mp)] and *o*-dinitrobenzene [a]

A 1,2,4-Trinitrobenzene (initial conc. $2{\cdot}5 \times 10^{-5}$M)

10^5[pip]/M	6·15	20·5	22·7	22·7 [b]	22·7 [c]	68·2	227
10^3[mp]/M				2·97	8·86		
k/l mol^{-1} s^{-1}	11·5	10·6	10·6	11·3	10·6	10·2	10·4

B *o*-Dinitrobenzene (initial concn. $3{\cdot}3 \times 10^{-4}$M)

10[pip]/M	2·11	4·62	4·66	7·03	9·33
10^4k/l mol^{-1} s^{-1}	1·03	1·29	1·29	1·44	1·64

[a] At 25° in benzene. [b] $[pip]_{free} = 1{\cdot}80 \times 10^{-4}$M. [c] $[pip]_{free} = 1{\cdot}01 \times 10^{-4}$M (calculated by use of the pseudo-equilibrium data reported in ref. 23).

For the reaction of *o*-dinitrobenzene with piperidine, which was investigated at much higher piperidine concentrations than for the corresponding reaction of 1,2,4-trinitrobenzene, a measurable increase of the second-order rate coefficient with piperidine concentration was observed (Table, B). The data fit equation (1) (pip = piperidine) with $k_0 = 8{\cdot}9 \times 10^{-5}$ l mol^{-1} s^{-1} and $k_{pip} = 8{\cdot}1 \times 10^{-5}$ l^2 mol^{-2} s^{-1}. The value of the ratio k_{pip}/k_0, which can be taken as a measure of the extent of base catalysis of this reaction, is much too small (0·91 l mol^{-1}) to indicate such catalysis. It is of the same order of magnitude already found in other reactions of this type which were clearly proved not to be subject to base catalysis.[28]

$$\text{Rate}/[C_6H_4(NO_2)_2][\text{pip}] = k_2 = k_0 + k_{pip}[\text{pip}] \quad (1)$$

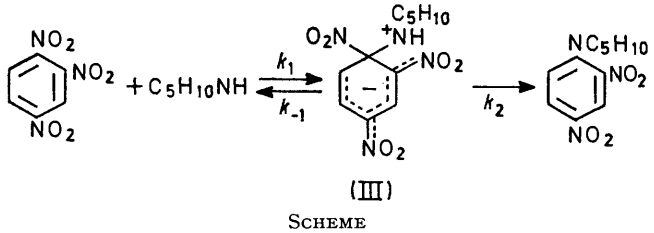
The greater sensitivity of the second-order rate coefficient for the reaction of *o*-dinitrobenzene than for the reaction of 1,2,4-trinitrobenzene (Table) may arise from the different range of amine concentrations used in the two reactions.

Levelling of the rate [2] for 1,2,4-trinitrobenzene could occur at the high concentration level of the nucleophile used here in the reaction of *o*-dinitrobenzene but this is unlikely because, if anything, more pronounced base catalysis is expected for the reaction of 2,4-dinitro- than of 2-nitro-activated substrates with piperidine.[6]

The reaction of 1,2,4-trinitrobenzene with piperidine does not undergo acid catalysis from the fact that *p*-methoxyphenol fails to affect the rate to any appreciable extent (Table, A). This conclusion was arrived at by calculating the second-order rate coefficient on the reasonable assumption that the fraction of piperidine not associated with phenol is the only effective nucleophile. The replacement of fluorine was shown to be subjected, under identical conditions, to pronounced catalysis by *p*-methoxyphenol [23] {already interpreted as a concerted removal of the fluorine and of the ammonium proton [intermediate (I)]}.

The kinetic effect of *p*-methoxyphenol on the reaction of *o*-dinitrobenzene with piperidine was not investigated because the association data for *p*-methoxyphenol and piperidine in benzene are available only for much lower piperidine concentrations than those used here and they cannot be safely extrapolated.[23]

The lack of both base and acid catalysis of the removal of the nitro-group by protic amines means that it is expelled from the substrate in a fast step.[2] This can be interpreted in terms of the addition–elimination mechanism in the Scheme.[2] If $k_2 \gg k_{-1}$, there is no possibility



(III)

SCHEME

of catalysis of the decomposition of the addition–intermediate (III) to products.

The exceptional lability of the nitro-group is explained by k_1 having an unusually high value and the nitro-group being expelled from the intermediate (III) in a fast step. A relatively high value for k_1 is accounted for in terms of the high electron deficiency at the C-1 in the substrate caused by the high electron-attracting power of the nitro-group.

[28] F. Pietra and F. Del Cima, *Tetrahedron Letters*, 1970, 1041.

It is more difficult to rationalise ready expulsion of the nitro-group from the intermediate (III). The only known nucleophilic replacements of a nitro-group from a saturated carbon atom occur in the case of 2-nitro-2-(*p*-nitrophenyl)propane by a variety of nucleophiles or, for purely aliphatic systems, by the lithium salts of 2-nitropropane, where a radical-ion pathway is followed.[29] However, the situation in the hypothetical intermediate (III) is very different from that at saturated carbon, in that expulsion of the nitro-group would coincide with rearomatisation of the ring thus providing the driving force in a fast, uncatalysed step. Also intramolecular electrophilic assistance by the ammonium proton might play a role. In fact, a five-centred transition state rather than a four-centred one as in fluorine displacement would be involved.*

It is somewhat surprising not to have found any competition in the removal of the ammonium proton and the nitro-group by external catalysts that have either a potential bifunctional character, like piperidine,[30] or an actual bifunctional character, like *p*-methoxyphenol.[23] However, an intramolecular process involving a moderately strained ring may be favoured over an intermolecular one and this might account for the failure to observe both piperidine and *p*-methoxyphenol catalysis in the present case.

* We are grateful to a referee for this suggestion.

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EXPERIMENTAL

U.v. spectra were taken by either a Beckmann DU or a Unicam SP 800 spectrophotometer which were also used to follow the kinetics.

1,2,4-Trinitrobenzene, m.p. 59·5—60° (lit.,[31] 60°), was prepared according to the literature. *o*- and *p*-Dinitrobenzene were commercial products and were recrystallised several times from ethanol. 2,4-Dinitro-, 2-nitro-, and 4-nitro-1-piperidinobenzene were prepared previously.[23,27] Benzene, piperidine, and *p*-methoxyphenol were purified as before.[23] The kinetic method has been already described.[27]

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