Electrophilic Aromatic Substitution. Part 33.[1] Kinetics and Products of Aromatic Nitrations in Solutions of Dinitrogen Pentaoxide in Nitric Acid

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The kinetics and/or products of reaction, in nitric acid containing 0—5 mol dm^{-3} of dinitrogen pentaoxide, of phenyltrimethylammonium perchlorate, 1,2-dichloro-4-nitrobenzene, 2,4-dinitrotoluene, 1,4-dichloro-2-nitrobenzene, 1,2,4-trichloro-5-nitrobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichloro-2-nitrobenzene, 1,2-dichloro-3-nitrobenzene, 1,2,3,4-tetrachlorobenzene, and 1,3-dichloro-2-nitrobenzene, have been studied. For each substrate investigated kinetically, rate coefficients for nitration in solutions containing more than *ca.* 2 mol dm^{-3} dinitrogen pentaoxide increase more quickly than the concentration of nitronium ion. In the cases of 1,2,4,5-tetrachlorobenzene, 1,4-dichloro-2-nitrobenzene, and 1,2,4-trichloro-5-nitrobenzene, but not with the other substrates, there was evidence for the formation of, in addition to expected aromatic nitroproducts, unstable cyclohexadiene products. Those from 1,2,4-trichloro-5-nitrobenzene were identified as a diastereoisomeric pair of 3,5,6-trichloro-2,4-dinitrocyclohexa-2,5-dienyl nitrates. A mechanism for the formation of these products is proposed.

The kinetics and mechanism of aromatic nitration in solutions of dinitrogen pentaoxide in nitric acid (N_2O_5–HNO_3) have received little previous study, perhaps in part because of the difficulties of preparing and handling N_2O_5, a chemical of limited stability.[2] Recent improvements in the electrochemical production[3] of N_2O_5–HNO_3 make such solutions of interest for large-scale preparative nitrations. One previous study[4] reports kinetic data for nitration of 1-chloro-4-nitrobenzene at −21 °C and of 2,4-dinitrotoluene at 30 °C. Kinetic orders in N_2O_5 of 1.0 and 1.75 respectively were reported.

We report the kinetics and products of nitration of several aromatic substrates in N_2O_5–HNO_3. Phenyltrimethylammonium perchlorate (PTMAP) was studied because its rate of nitration could be investigated by u.v. spectroscopy. The chloronitro aromatics were investigated because they more closely resemble deactivated aromatics which are industrially nitrated on a large scale. For these it was necessary to use the less accurate n.m.r. method for kinetic studies.

Results

Nitration of PTMAP.—First-order rate coefficients k_1 for nitration are in Table 1 and Figure 1. The rate coefficient for pure nitric acid at 25 °C is in good agreement with a literature value.[5] Arrhenius parameters derived from second-order rate coefficients (which were obtained by dividing first-order rate coefficients by the concentration[5,6] of nitronium ion in pure nitric acid at the temperature in question) are in the footnotes to Table 1 and are similar to those reported for nitration in sulphuric acid.[7]

The concentration of nitrous acid was measured for a number of solutions of N_2O_5–HNO_3, and was found to vary between 0.006 and 0.03 mol dm^{-3}. However there was no correlation between the rate of nitration of PTMAP and the concentration of nitrous acid.

The ^1H n.m.r. spectrum of the products of nitration of PTMAP in N_2O_5–HNO_3 showed the *meta* isomer to be dominant, as it is when nitration is effected in sulphuric acid.[8]

Nitration of 1,2-Dichloro-4-nitrobenzene.—Values of k_1 at 32 °C are in Table 2. The products were shown by ^1H n.m.r. spectroscopy to be 1,2-dichloro-4,5- and 1,2-dichloro-3,5-dinitrobenzene, formed in *ca.* equivalent amounts. The overall yield was shown, by the inclusion of 1,3,5-trinitrobenzene as reference, to be quantitative within experimental error. No other products were detected.

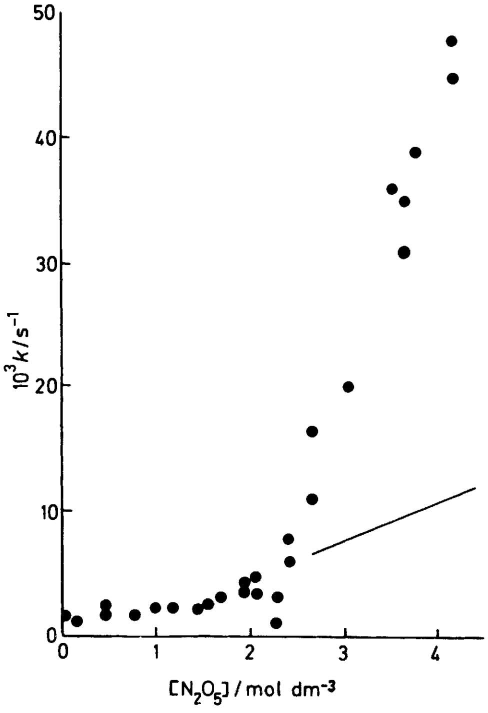


Figure 1. Rate profile for the nitration of PTMAP in N_2O_5–HNO_3 at 1.1 °C

Nitration of 2,4-Dinitrotoluene.—Values of k_1 are in Table 3. The only product was shown by ^1H n.m.r. spectroscopy to be 2,4,6-trinitrotoluene, formed in quantitative yield.

Nitration of 1,4-Dichloro-2-nitrobenzene.—Values of k_1 are in Table 4. For this and the preceding two substrates the rate

Table 1. First-order rate coefficients for the nitration of PTMAP in pure nitric acid and in N_2O_5–HNO_3 at 1.1 °C unless otherwise stated

$[N_2O_5]$/mol dm^{-3}	0	0	0	0	0	0	
10^3k/s^{-1}	1.0^{a,b}	1.2^{a,c}	1.3^{a,d}	1.4^{a,e}	1.7^{a,f}	2.3^{a,g}	
$[N_2O_5]$/mol dm^{-3}		0	0	0		0.02	
10^3k/s^{-1}		3.6^{a,h}	5.3^{a,i}	5.8^{a,j}		1.3	
$[N_2O_5]$/mol dm^{-3}	0.17	0.46^{k}	0.86	1.0	1.2	1.4	1.5
10^3k/s^{-1}	0.97	1.7	1.7	2.2	2.2	2.2	2.5
$[N_2O_5]$/mol dm^{-3}	1.7	1.9^{k}	2.0^{k}	2.3^{k}	2.4^{k}	2.6^{k}	3.0
10^3k/s^{-1}	3.0	3.9	3.9	3.2	6.8	14	20
$[N_2O_5]$/mol dm^{-3}	3.5	3.6^{k}	4.1^{k}	4.5	5.5		
10^3k/s^{-1}	36	33	45	67	59		

[a] Arrhenius parameters from these results and reported[5,6] concentrations of nitronium ion (see text) are $E_a = 66$ kJ mol^{-1}, $\log_{10}(A/\text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}) = 10.0$. [b] 0.3 °C. [c] 0.8 °C. [d] 1.5 °C. [e] 5.0 °C. [f] 5.1 °C. [g] 10.0 °C. [h] 15.2 °C. [i] 21.0 °C. [j] 25.0 °C. [k] Mean of two determinations.

Table 2. First-order rate coefficients for the nitration of 1,2-dichloro-4-nitrobenzene in N_2O_5–HNO_3 at 32 °C

$[N_2O_5]$/mol dm^{-3}	0	0.21	0.42	0.94	1.3	1.4
10^3k/s^{-1}	2.9	10.0	5.0	6.0	9.0	16.0
$[N_2O_5]$/mol dm^{-3}	2.2	2.4	2.8	2.8	3.0	3.2
10^3k/s^{-1}	26	29	9	20	42	60
$[N_2O_5]$/mol dm^{-3}	3.4	3.5	3.7	4.2	4.5	
10^3k/s^{-1}	43	76	82	73	94	

Table 3. First-order rate coefficients for the nitration of 2,4-dinitrotoluene in N_2O_5–HNO_3 at 32 °C

$[N_2O_5]$mol dm^{-3}	0	3.4	3.7	4.3	5.1	5.4	5.5
10^5k_1/s^{-1}	0.028	1.0	0.32	1.1	1.7	1.6	2.6

Table 4. First-order rate coefficients for the nitration of 1,4-dichloro-2-nitrobenzene in N_2O_5–HNO_3 at 32 °C

$[N_2O_5]$/mol dm^{-3}	0	0.42	0.94	1.3	1.4	2.8	3.2	3.3
10^5k_1/s^{-1}	0.29	0.22	0.80	1.4	2.2	1.3	1.8	2.9
$[N_2O_5]$/mol dm^{-3}	3.4	3.7	4.2	4.5	5.4			
10^4k_1/s^{-1}	5.6	4.2	8.3	25	21			

profiles were very scattered, and the data should be considered as only semi-quantitative, at least in part because considerable decomposition of N_2O_5 occurs during these slow reactions.

The overall yield of the aromatic products of nitration in solutions of dinitrogen pentaoxide in nitric acid was measured by g.c. (Table 5). All three possible dinitro products were formed, the proportions being measured by g.c. and by n.m.r. (Table 6). The decrease in overall yield and concomitant change in absolute yield for the three isomers, obtained by combining and smoothing the data in Tables 5 and 6, are shown in Figure 2.

An interesting feature of this reaction which helps to explain the departure from a quantitative overall yield is that the ^1H n.m.r. spectrum of the product mixture contained not only peaks due to the three aromatic dichlorodinitro products but also peaks in the region δ 5.9—6.9 suggesting the formation of dienes.[9] The intensity of these peaks increased during the initial stages of reaction, but was never as great as that of the aromatic products. The 'diene' peaks subsequently decayed and had disappeared completely 1 h after the start of the reaction, without detectable increase in the intensity of the aromatic product peaks. The 'diene' peaks were most prominent in solutions containing high concentrations of dinitrogen pentaoxide. Their pattern was complex and because of their low intensity and transient nature a high-resolution spectrum could not be recorded. Similar observations relating to the next substrate (see below) were investigated in more detail.

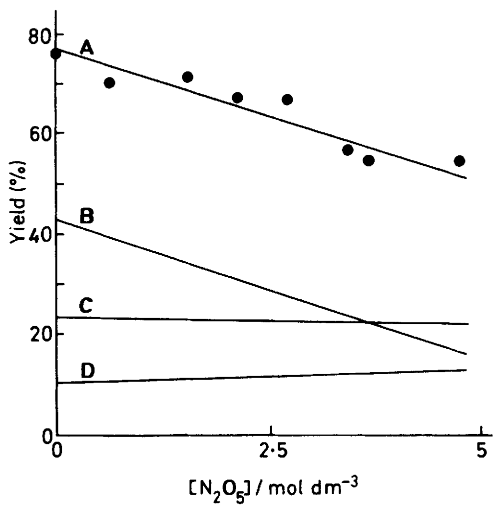
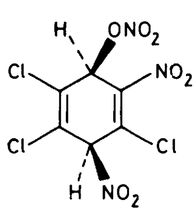


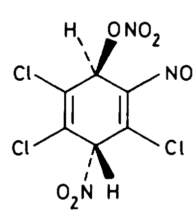
Figure 2. Product yields in the nitration of 1,4-dichloro-2-nitrobenzene in N_2O_5–HNO_3 at 35 °C. **A**; total yield of aromatic product. **B**; 2,5-dichloro-1,3-dinitrobenzene. **C**; 1,4-dichloro-2,5-dinitrobenzene. **D**; 1,4-dichloro-2,3-dinitrobenzene

Nitration of 1,2,4-*Trichloro*-5-*nitrobenzene*.—Kinetic data were not recorded for this substrate. The only aromatic product was 1,2,4-trichloro-3,5-dinitrobenzene, the yield of which decreased with increasing concentration of dinitrogen pentaoxide (Table 7).

The ^1H n.m.r. spectra of the products of nitration in solutions containing high concentrations of N_2O_5 showed, in addition to peaks due to the starting material and to the aromatic product, a set of four peaks in the region δ 5.96—6.09 and a set of three peaks in the region δ 6.86—6.93. These peaks decayed very slowly, still being discernible for hours after the start of reaction. When the products were freed from HNO_3–N_2O_5 under vacuum, the peaks survived in the n.m.r. spectrum of the residual red oil. Attempts to separate this mixture chromatographically were unsuccessful. Decoupling experiments* established that the first set of peaks were two doublets centred on δ 5.97 and 6.06 and the second set were two overlapping doublets centred on δ 6.87 and 6.90. These chemical shifts[8] and coupling constants[10] (2 Hz between δ 5.97 and 6.87, and 4 Hz between δ 6.06 and 6.90) are consistent with the presence in the reaction mixture of the diastereoisomeric pair (**1**) and (**2**), in roughly equivalent proportions.



(**1**)



(**2**)

The ^{13}C and ^{15}N n.m.r. spectra of the product mixture were also consistent with the presence of (**1**) and (**2**). The ^{13}C n.m.r. spectrum had in addition to peaks due to starting material and aromatic product four peaks in the range δ 73—78 p.p.m. each

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* We thank A. J. Sanderson for these measurements.

Table 5. Total yield of aromatic products from the nitration of 1,4-dichloro-2-nitrobenzene in N_2O_5–HNO_3 at 35 °C

$[N_2O_5]$/mol dm^{-3}	0	0.61	1.6	2.1	2.7	3.4	3.7	4.8
Yield (%)	77	70	71	66	67	56	54	54

Table 6. Relative yields of 2,5-dichloro-1,3-dinitrobenzene (**A**), 1,4-dichloro-2,5-dinitrobenzene (**B**), and 1,4-dichloro-2,3-dinitrobenzene (**C**) from the nitration of 1,4-dichloro-2-nitrobenzene in N_2O_5–HNO_3 at 32 °C

$\frac{[N_2O_5]}{\text{mol dm}^{-3}}$	Relative yields (%)		
	(**A**)	(**B**)	(**C**)
0	54	32	14
0.42	46	41	13
0.94	45	38	17
1.3	47	34	19
1.4	52	30	18
2.8	44	37	19
2.8	44	31	25
3.2	39	40	21
3.3	41	37	22
3.4	42	32	26
3.7	42	35	23
4.2	31	45	24
4.5	28	39	22
5.4	26	49	25

Table 7. Yield of 1,2,4-trichloro-3,5-dinitrobenzene from the nitration of 1,2,4-trichloro-5-nitrobenzene in N_2O_5–HNO_3 at 35 °C

$[N_2O_5]$/mol dm^{-3}	0	0.86	1.8	2.3	2.6
Yield (%)	80	65	62	60	55

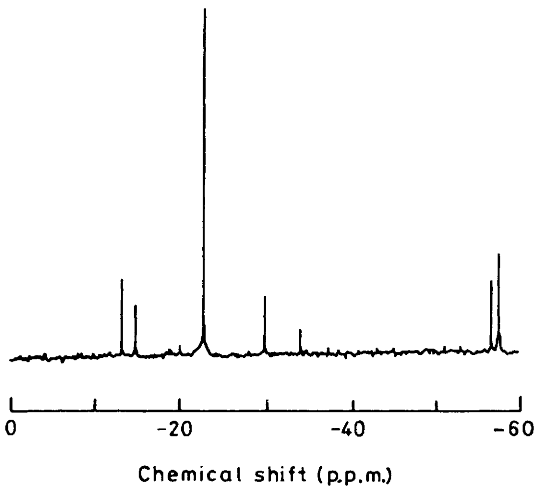


Figure 3. ^{15}N N.m.r. spectrum of product mixture from the nitration of 1,2,4-trichloro-5-nitrobenzene in ^{15}N-enriched N_2O_5–HNO_3

of which gave a doublet in the off-resonance decoupled spectrum. These peaks are attributed to the tetrahedral carbons of (**1**) and (**2**). There were eight peaks in the range δ 123—133 p.p.m., which were not split in the off-resonance decoupled spectrum, consistent with the trigonal carbons of (**1**) and (**2**). There was one unassigned peak at δ 168.8 p.p.m.

The ^{15}N n.m.r. spectrum of the products of nitration using ^{15}N-enriched N_2O_5–HNO_3 is shown in Figure 3. The two peaks at δ −56.6 and −57.4 p.p.m. are consistent with covalently bonded nitrates. (These peaks disappear when the sample is exposed to the atmosphere and a new broad peak at δ −47 p.p.m. is observed which is attributed to the nitric acid formed by hydrolysis of the nitrate esters.) Of the remaining peaks, the largest, δ −22.7 p.p.m., is due to the aromatic product. There remain, in addition to a small unassigned peak at δ −19.9, two pairs of peaks. One pair (it is not certain which) is attributed to the nitro groups attached to tetrahedral carbon in (**1**) and (**2**). The other pair may be due to the nitro groups attached to trigonal carbon in (**1**) and (**2**). This implies that exchange has occurred, a point which is taken up in the Discussion section.

Nitration of Other Species.—The following substrates underwent nitration in saturated solutions of dinitrogen pentaoxide in nitric acid at 32—35 °C. Reactions were followed and products investigated by ^1H n.m.r. spectroscopy. (*a*) 1,2,4,5-Tetrachlorobenzene was nitrated to give 2,3,5,6-tetrachloronitrobenzene. Peaks were also observed in the 'diene' region of the spectrum. The starting material dissolved far less readily than the nitroaromatics studied though once dissolved the reaction was rapid, being complete in under 15 min.

(*b*) Pentachlorobenzene dissolved slowly in the nitrating solution, giving a solution whose spectrum contained no peaks. It seems likely that reaction to give pentachloronitrobenzene was rapid.

(*c*) The nitration of 1,2,3-trichlorobenzene was complete in under 2 min. The spectrum at this stage showed a singlet due to 2,3,4-trichloro-1,5-dinitrobenzene and a pair of doublets, assumed due to 1,2,3-trichloro-4-nitrobenzene. After 11 min only the singlet remained.

(*d*) 1,3,5-Trichloro-2-nitrobenzene was nitrated to give 1,3,5-trichloro-2,4-dinitrobenzene. After 2 min the spectrum contained only one singlet which was shown by comparison with the spectrum of an authentic sample to be due to the product.

(*e*) 1,2-Dichloro-3-nitrobenzene was nitrated. After 2 min the spectrum of the reaction mixture contained only a pair of doublets (assumed due to 1,2-dichloro-3,4-dinitrobenzene) and two singlets (assumed due to 1,2-dichloro-3,5-dinitrobenzene).

(*f*) 1,2,3,4-Tetrachlorobenzene was nitrated to give 1,2,3,4-tetrachloro-5-nitrobenzene. The reaction was complete in *ca.* 90 min and no 'diene' peaks were observed.

(*g*) 1,3-Dichloro-2-nitrobenzene was completely converted into 1,3-dichloro-2,4-dinitrobenzene in under 4 min. No 'diene' peaks were observed.

Discussion

Rates of Nitration.—Solutions of N_2O_5 in nitric acid provide an unusually effective medium for nitration. This is illustrated in Table 8. It is seen that nitration in 4—5 mol dm^{-3} N_2O_5 in HNO_3 is 15—30 times faster than in aqueous sulphuric acid of optimum[11] composition (90—92%) containing 1 mol dm^{-3} nitric acid. These rate enhancements cannot solely be due to higher concentrations of nitronium ion. The solid line in Figure 1 indicates the rate profile which would obtain if N_2O_5 were completely dissociated to NO_2^+ and NO_3^- in the absence of medium effects. Two possible causes can be considered for the rather dramatic increase in rate at high concentrations of N_2O_5, which was observed with each of the substrates investigated. One is a change in mechanism, the other is a medium effect. If there is a change in mechanism it is unlikely to be due to a change of electrophile, because it is difficult to imagine a more potent nitrating agent than nitronium ion which is known to be effective at lower concentrations. We note here also that the increase in rate is not associated with the formation of dienes because it is found with substrates which undergo quantitative aromatic nitration with no diene formation. Nitrous acid catalysis can be discounted because there was no discernible

Table 8. Comparison of first-order rate coefficients for nitration, $10^4 k_1/s^{-1}$, under various conditions, of (**A**) phenyltrimethylammonium perchlorate, (**B**) 1,2-dichloro-4-nitrobenzene, and (**C**) 1,4-dichloro-2-nitrobenzene

	Substrate (temperature)		
Conditions	(**A**) (1.1 °C)	(**B**) (32 °C)	(**C**) (32 °C)
HNO_3 (1M) in H_2SO_4 (stated %)	27[a] (90.6%)	0.62 (90.7%)	1.2 (91.8%)
HNO_3 (100%)	14	0.29	0.30
HNO_3 Containing N_2O_5 (stated concentration)	720 (5.51M)	9.4 (4.45M)	21 (5.39M)

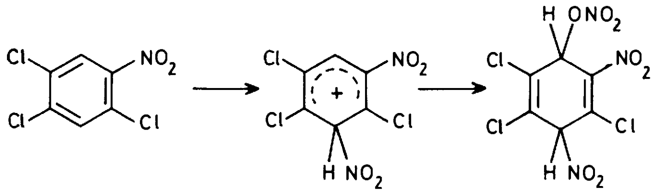
[a] Estimated from data given in ref. 6.

dependence of rate coefficients on the concentration of nitrous acid. The intrusion of a radical mechanism such as has been suggested[4] cannot be ruled out, but is rendered less likely by our failure to observe a CIDNP effect in the ^{15}N n.m.r. spectral peak of the aromatic product following nitration of 1,2,4-trichloro-5-nitrobenzene in ^{15}N-enriched N_2O_5–HNO_3.

A change of mechanism would be expected to set in at different concentrations of N_2O_5 with substrates of different reactivity. The evidence on this point is far from clear because of the uncertainties in the rate coefficients determined by the n.m.r. method, and the effects of decomposition of the N_2O_5 during reaction. However, in so far as comparison can be made the increase in rate seems to set in at concentrations of N_2O_5 in the region of 1.5—2.0 mol dm^{-3} regardless of substrate.

These observations lead us at this stage tentatively to favour an explanation based on medium effects and we plan further work to test this point.

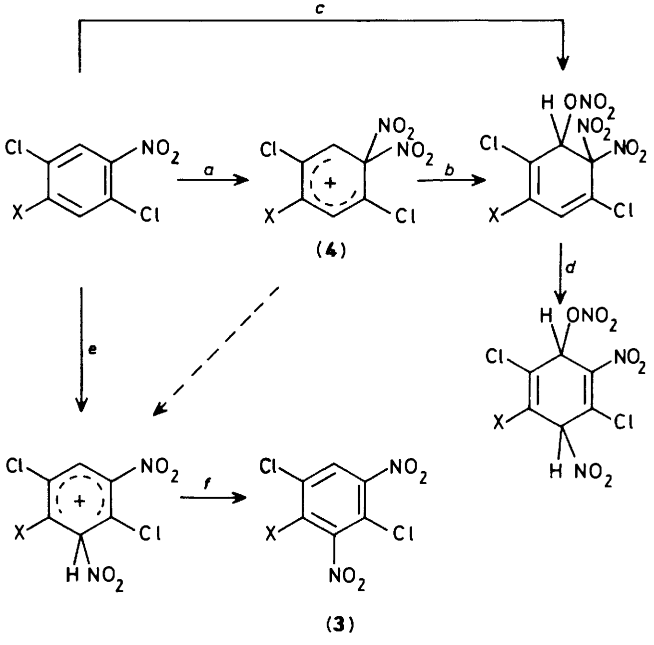
Products of Nitration.—With some substrates quantitative aromatic nitration took place, but with others there was evidence also of cyclohexadiene formation. In the case of 1,2,4-trichloro-5-nitrobenzene the dienic products were sufficiently stable to permit detailed n.m.r. investigation, and thus lead to the conclusion that they were the diastereoisomeric pair of 3,5,6-trichloro-2,4-dinitrocyclohexa-2,5-dienyl nitrates, (**1**) and (**2**). It seems extremely unlikely that these are formed by nucleophilic capture of a Wheland intermediate formed by nitronium ion attack at an unsubstituted position as in Scheme 1.



Scheme 1.

Such Wheland intermediates almost invariably* lose their highly acidic proton to give the aromatic nitro product. A more probable mechanism is one in which there is *ipso*-attack and capture.[9-12] *ipso*-Attack at nitro positions has been reported previously.[1-11] We propose, for the nitration of 1,2,4-trichloro-5-nitrobenzene, Scheme 2 (X = Cl).

Nitronium ion attack occurs at an unsubstituted position leading to the aromatic nitro product (steps *e* and *f*) and at the



Scheme 2.

nitro-substituted position (step *a*) followed if the concentration of nitrate ions is sufficiently high (that is at high stoicheiometric concentrations of N_2O_5) by nucleophilic capture (step *b*). An alternative to step *b* would be step *c* which is the synchronous, or step-wise homolytic,[13] addition of covalent N_2O_5 (which is presumably present in low equilibrium concentration). There is then a 1,3-rearrangement (step *d*) which may be a radical or sigmatropic process. (Both have been reported.[9b]) The ^{15}N n.m.r. spectra of the dienic products (Results section) can most readily be explained if there is ^{15}N-enrichment of both nitro groups. This conclusion will be checked by preparing and studying the ^{15}N-labelled substrate. In the meantime we note that Scheme 2 would explain why such enrichment occurs.

Scheme 2 (X = H) might well apply to the nitration of 1,4-dichloro-2-nitrobenzene (though in this case the structure of the dienic products was not established). However in order to explain why the formation of dienes at high concentrations is accompanied by the loss in yield (Figure 2) of only one of the aromatic nitro products (**3**; X = H) it is necessary to consider linking the Wheland intermediates in Scheme 2 by the dashed arrow shown. This rearrangement could be two 1,2-nitro group shifts,[12] or a sigmatropic rearrangement.[14] Either view however is not easily reconciled with previous work.[15,16] Wheland intermediate (**4**), formed from a rather unreactive aromatic, would be expected more easily to loose a nitronium ion (reverse of step *a*). The loss of yield of (**3**; X = H) in the nitration of 1,4-dichloro-2-nitrobenzene in concentrated N_2O_5–HNO_3 (Figure 2) still lacks a satisfactory explanation.

Experimental

Materials.—The following were recrystallised from available laboratory reagents: 1-chloro-4-nitrobenzene (m.p. 83—83.5 °C, EtOH–H_2O), 1,3,5-trichloro-2-nitrobenzene (m.p. 70—72 °C, EtOH), 1,2-dichloro-4-nitrobenzene (m.p. 40—40.5 °C, MeOH), 1,3-dinitrobenzene (m.p. 90—90.5 °C, EtOH), 1-naphthol (m.p. 95.5—96 °C, CCl_4), sulphanilic acid (m.p. 286—287 °C, H_2O), 1,4-dichloro-2-nitrobenzene (m.p. 55—56 °C, EtOH), 2,4-dinitrotoluene (m.p. 70—70.5 °C, EtOH), 1,3,5-trinitrobenzene (m.p. 122.5—123 °C, EtOH), 1,2,4-trichloro-5-nitrobenzene

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* The only known exceptions occur in cases where there is intramolecular nucleophilic capture.[9a]

Table 9. Details of gas chromatographic conditions

Compound	Response factor[a]	Retention time/s	Column[b]	Temp/°C
1,4-Dichloro-2-nitrobenzene	[c]	141	3% OV 225 on	165
1,3-Dinitrobenzene[d]		373	Chromasorb WHP	
2,5-Dichloro-1,3-dinitrobenzene	0.92	614	7 ft Glass	
1,4-Dichloro-2,5-dinitrobenzene	0.90	716		
1,4-Dichloro-2,3-dinitrobenzene	0.96	804		
1,3-Dinitrobenzene[d]		393	10% Dexil on	170
1,4-Dichloro-2,3-dinitrobenzene	0.96	884	Chromasorb	
			7ft Glass	
1,3-Dinitrobenzene[d]		316	3% OV 17 on	180
1,2,4-Trichloro-3,5-dinitrobenzene	0.94	787	Chromasorb WHP	
			9 ft Glass	

[a] Response factor = Area ratio (product/reference)/Mole ratio (product/reference). [b] All on a Pye 104 instrument, flame ionisation detector, LDC 308 computing integrator. Nitrogen flow rate 40 cm^3 min^{-1}. [c] Not determined. [d] Reference standard.

(m.p. 57—58.5 °C, EtOH), 1,2,4-trichloro-3,5-dinitrobenzene (m.p. 99—100.5 °C, EtOH), 1,2-dichloro-3-nitrobenzene (m.p. 61—62 °C, EtOH), 1,2,3-trichloro-4-nitrobenzene (m.p. 54.5—55 °C, EtOH), 1,3,5-trichloro-2,4-dinitrobenzene (m.p. 129—130 °C, EtOH), 1,2,3,4-tetrachloro-5-nitrobenzene (m.p. 64—66 °C, EtOH), 1,2,3,4-tetrachlorobenzene (m.p. 46.5—47 °C, EtOH), 1,2,4,5-tetrachlorobenzene (m.p. 137.5—139 °C, EtOH), 1,3-dichloro-2-nitrobenzene (m.p. 71—72 °C, EtOH), pentachlorobenzene (m.p. 84—85 °C, EtOH). A sample of 2,4,6-trinitrotoluene supplied to us by the Ministry of Defence was used without further purification. 1,4-Dichloro-2,5-dinitrobenzene (m.p. 115—117 °C, EtOH) was prepared as described.[14,17] PTMAP (m.p. 178—179 °C, H_2O) was prepared as described.[5,8]

1,4-*Dichlorodinitrobenzenes*. These were prepared by nitration of 1,4-dichlorobenzene in mixed acid, and separation of the product mixture, as described.[18—20]

Dinitrogen pentaoxide. This was prepared in a gas-flow system[21] in which oxygen containing *ca.* 3% ozone–nitrogen dioxide were mixed; the dinitrogen pentaoxide formed was condensed in a cold trap. Solutions of dinitrogen pentaoxide were prepared by the addition of pure nitric acid.

Estimation of the Concentration of Solutions of Dinitrogen Pentaoxide in Nitric Acid.—In the work described in this paper, volumetric samples were analysed by titration with sodium hydroxide using a Radiometer Autoburette and titrator assembly. This method is not very accurate. Titration volumes were measured with an accuracy of $\pm 0.2\%$, but even with this precision errors in the molar concentration of ± 0.2 mol dm^{-3} accrue. Since this work was completed we have developed a method based on density measurements which is much more convenient and precise. This will be described in a later publication.

Analysis for Nitrous Acid Concentration.[22]—A sample of the solution of dinitrogen pentaoxide in nitric acid to be tested (1 cm^3) was added to a mixture of 1% sulphuric acid (1 cm^3), 1% sulphanilic acid (1 cm^3), and distilled water (10 cm^3) in a 25 cm^3 volumetric flask. The resulting solution was shaken and after 10 min 1 cm^3 of a saturated aqueous solution of 1-naphthol added. After further agitation the solution was made up to 25 cm^3 with aqueous ammonia (0.880 g cm^{-3}, *ca.* 35%). The absorbance of this solution at 523 nm was measured and the corresponding concentration of nitrous acid read from a calibration graph previously prepared by making up aqueous solutions of sodium nitrite of known concentration.

Kinetic Measurements.—For the nitration of PTMAP these were carried out by monitoring the change in u.v. absorbance at 390 nm. Reactions were started by injecting 40 μl of a solution of PTMAP in acetic acid into a thermostatted u.v. cell of 1 cm path length containing HNO_3–N_2O_5, to give an aromatic concentration of 1×10^{-3} mol dm^{-3}. Rate constants were determined as previously.[23]

Kinetic studies of the nitration of most aromatic compounds in solutions of dinitrogen pentaoxide in nitric acid could not be carried out by u.v. spectroscopy because of the strong absorption of the nitrating solutions. It was also not feasible to study these reactions by removal of samples and g.c. analysis because of the large volumes that would be involved. As a result the kinetics of most of these reactions has to be studied by n.m.r. spectroscopy.

The compound to be studied (*ca.* 0.04 g) was placed, together with an appropriate amount of reference material (1,3,5-trinitrobenzene), in the bottom of an n.m.r. tube. The reaction was commenced by the addition of a solution of dinitrogen pentaoxide in nitric acid (*ca.* 1 cm^3), the resulting mixture being shaken to promote solution before placing the tube in the thermostatically controlled probe of a JEOL JNM-HM-100 continuous-wave ^1H n.m.r. spectrometer. Spectra were recorded at appropriate time intervals and first-order rate coefficients calculated from plots of time against $-\ln(A_\infty - A_t)$, where A_t is the area of the peak relative to the area of the reference peak of time *t*.

Product Analysis.—For some reactions product analysis was carried out by identification of the product peaks in the ^1H n.m.r. spectrum of the reaction mixture. The amount of each product formed could be estimated by comparing the areas of the product peaks to the area of the reference peak.

When more accurate quantitative data were required g.c. analysis was used. Thus for 1,4-dichloro-2-nitrobenzene and 1,3,4-trichloro-5-nitrobenzene a solution of the aromatic compound in acetic acid (40 μl) was injected into 3 cm^3 of a solution of dinitrogen pentaoxide in nitric acid such that the concentration of aromatic was *ca.* 5×10^{-3} mol dm^{-3}. After being left for at least 10 half-lives of reaction the solution was quenched in water (400 cm^3), a suitable amount of reference added and the solution worked-up as described previously.[24] Products were analysed by g.c. using a Pye 104 instrument fitted with a flame ionisation detector. Peak areas were determined using a Laboratory Data Control 308 computing integrator. The detector response to the components in the reaction mixture and the reference standard was determined by a series of calibrations. Conditions of analysis are given in Table 9.

Attempted Separation of the Products of Nitration of 1,2,4-*Trichloro-*5-*nitrobenzene*.—Details of attempts to separate the diene products by various methods, none of which was successful, are given elsewhere.[25]

N.m.r. Spectroscopy.—The use of ^1H n.m.r. to study the rates of reaction has already been described. Fourier-transform ^{13}C n.m.r. spectra were recorded with a JEOL JNM-PS-100 pulse Fourier-transform spectrometer while ^{15}N spectra were recorded using a Bruker AM250 pulse Fourier-transform machine.

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