Electrophilic Aromatic Substitution. Part 34.[1] Nitration of 1-Chloro-4-nitrobenzene, 1,3-Dichloro-2-nitrobenzene, 1,3-Dinitrobenzene, 1-Chloro-2,4-dinitrobenzene, and 2-Chloro-1,3-dinitrobenzene in Sulphuric Acid and Oleum

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Yields of the expected nitro products from 1-chloro-4-nitrobenzene and 1,3-dichloro-2-nitrobenzene nitrated at 25 °C in sulphuric acid or oleum containing 1 mol dm^{-3} nitric acid were quantitative. The rate profile for nitration of 1,3-dichloro-2-nitrobenzene is normal, but sulphonation is a competing process when the concentration of nitric acid is low. Kinetics of nitration of 1,3-dinitrobenzene at 150 °C are reported; yields of 1,3,5-trinitrobenzene, the only detected aromatic product, are low. The title chlorodinitrobenzenes each give, on nitration at 130 °C, a dichlorodinitrobenzene as well as a chlorotrinitrobenzene. The kinetics and yields of the two products from 1-chloro-2,4-dinitrobenzene under a variety of conditions are reported and discussed in relation to a previously proposed mechanism.

In a previous paper[2] the nitration of 1,3,5-trichloro-2,4-dinitrobenzene, which gave considerable amounts of 1,2,3,5-tetrachloro-4,6-dinitrobenzene as well as the expected 1,3,5-trichloro-2,4,6-trinitrobenzene, was examined and a mechanism proposed. Here we report a study of some related aromatic substrates in an attempt to establish the structural features which lead to the formation of chlorinated as well as nitrated products from chloronitrobenzenes, and to see whether the results support the mechanism previously proposed.

Previous work concerning the nitration of the title substrates is sparse. Several early studies of 1,3-dinitrobenzene established that yields are generally low,[3] and more recently[4] nitration in 11% oleum at 130 °C was reported to give 40—44% 1,3,5-trinitrobenzene with a rate constant of 6.6×10^{-3} mol^{-1} dm^3 s^{-1}. For nitration by nitronium tetrafluoroborate at 95 °C, a yield[5] of 62% and a rate constant[6] of 2.5×10^{-7} mol^{-1} dm^3 s^{-1} has been reported. No other aromatic products have been found. The kinetics of nitration of 1-chloro-4-nitrobenzene have been studied in some detail,[7] but yields have not been quantitatively established. For the nitration of 1-chloro-2,4-dinitro- and 2-chloro-1,3-dinitro-benzene in 11% oleum at 130 °C, yields of the expected nitro product of 45% and 75%, respectively, have been obtained and the rate constants reported were 3×10^{-5} and 7×10^{-4} mol^{-1} dm^3 s^{-1}, respectively; no other aromatic products were identified.[4]

Experimental

Materials.—Sulphuric acid and oleum solutions were prepared, and nitric acid purified, as previously.[2]

1,3-Dinitrobenzene (m.p. 90—90.5 °C from EtOH), 1,3,5-trinitrobenzene (m.p. 122—123 °C from EtOH), 1-chloro-4-nitrobenzene (m.p. 83.5 °C from EtOH–H_2O), 2-chloro-1,3-dinitrobenzene (m.p. 86—87 °C from EtOH), 1-chloro-2,4-dinitrobenzene (m.p. 49—50 °C from Et_2O), 2-chloro-1,3,5-trinitrobenzene (m.p. 82 °C from EtOH), and 1-nitronaphthalene (m.p. 59—60 °C from EtOH), were recrystallised from commercially available materials.

[1-^{2}H]-3,5-Dinitrobenzene was prepared[8] by diazotisation of 3,5-dinitroaniline followed by reduction with [^{2}H]hypophosphorous acid. Mass spectroscopy showed there to be 55% deuterium incorporation.

1,3-Dichloro-2-nitrobenzene (m.p. 70—70.5 °C from EtOH–H_2O)[9] and 1,2-dichloro-3,5-dinitrobenzene [m.p. 56.5 °C from light petroleum (b.p. 100—120 °C)][10] were prepared as described. 1,3-Dichloro-2,4-dinitrobenzene (m.p. 68 °C from EtOH) was prepared from 1,3-dichloro-2-nitrobenzene using a method similar to that described for the nitration of trichlorobenzenes.[11] The crude product was recrystallised from H_2SO_4 (98%) and then from EtOH (m.p. 68 °C).

Kinetics.—With 1,3-dichloro-2-nitrobenzene, an aliquot, typically 20 μl, of an acetic acid solution of the substrate was added to a 4 cm path length u.v. cuvette containing the sulphuric acid or oleum and nitric acid ($1—9 \times 10^{-2}$ mol dm^{-3}) at 25.0 ± 0.1 °C. The change with time of the absorbance at 310 nm was monitored using a Pye–Unicam SP1800 spectrophotometer and a micro-computer as previously.[12]

With 1,3-dinitrobenzene, an aliquot, typically 200 μl, of an acetic acid solution of the substrate was added to a volumetric flask containing nitric acid in sulphuric acid or oleum. Samples were transferred to glass tubes, sealed, and placed in an oil-bath at 150 ± 0.2 °C. It was subsequently discovered that at 150 °C in sulphuric acid or oleum, acetic acid reduces nitric acid to nitrous acid (two moles per mol of acetic acid). Some of the runs were therefore repeated in the absence of acetic acid. No significant difference was found provided that the concentration of nitric acid was corrected for this loss in the calculation of second-order rate coefficients. This correction has been made in the results reported. A tube was cooled and opened and a known amount of 1,3,5-trichloro-2,4-dinitrobenzene added as reference for g.c. analysis. The contents were poured into iced water and extracted with dichloromethane, which was dried ($MgSO_4$) and fractionally distilled (20 cm column packed with glass helices). The column was rinsed with a small volume of dichloromethane to give a concentrated sample, which was analysed by g.c. (Table 1).

On opening some of the tubes it was apparent that considerable internal pressure had developed. For safety some of the later runs were performed using an opening system similar to that described below for 1-chloro-2,4-dinitrobenzene; this gave results comparable to those using sealed tubes.

With 1-chloro-2,4-dinitrobenzene, a solution of the substrate in diethyl ether (160 μl) was placed in one limb of an X-shaped tube. Solvent was removed under reduced pressure. Sulphuric acid or oleum and nitric acid were placed in another limb. A

Table 1. Gas chromatography data for products and standards[a]

Substrate	Component	Response factor[b]	Retention time/s	Column and conditions
1-Chloro-4-nitrobenzene	1-Chloro-4-nitrobenzene	—	—	15% SE30 on Chromasorb W AW-DCMS, 3 m glass column, nitrogen flow rate 40 ml min^{-1}, oven temp. 195 °C
	1,3-Dinitrobenzene[c]	—	351	
	1-Chloro-2,4-dinitrobenzene	0.942	498	
1-Chloro-2,4-dinitrobenzene	1-Chloro-2,4-dinitrobenzene	0.802	338	As above, but oven temp. 220 °C
	1,2-Dichloro-3,5-dinitrobenzene	0.904	444	
	2-Chloro-1,3,5-trinitrobenzene	*d*	534	
	1,2,3,5-Tetrachloro-4,6-dinitrobenzene[c]	—	—	
1,3-Dichloro-2-nitrobenzene	1,3-Dichloro-2-nitrobenzene	—	—	3% OV225 on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 40 ml min^{-1}, oven temp. 175 °C
	1-Nitronaphthalene[c]	—	418	
	1,3-Dichloro-2,4-dinitrobenzene	0.546	697	
1,3-Dinitrobenzene	1,3-Dinitrobenzene	0.933	210	3% OV 225 on Chromasorb WHP, 7 ft glass column, nitrogen flow rate 35 ml min^{-1}, oven temp. 180 °C
	1,3,5-Trichloro-2,4-dinitrobenzene[c]	—	300	
	1,3,5-Trinitrobenzene	0.875	1 040	
	1,3-Dinitrobenzene	—	230	10% SE30 on Chromasorb W AW-DCMS, 5 ft glass column, nitrogen flow rate 40 ml min^{-1}, oven temp. 180 °C
	2,4-Dinitrotoluene[c]	—	300	
	1,3,5-Trinitrobenzene	0.748	450	
2-Chloro-1,3-dinitrobenzene	2-Chloro-1,3-dinitrobenzene	0.848	325	15% SE30 on Chromasorb W AW DCMS, 3 m glass column nitrogen flow rate 40 ml min^{-1}, oven temp. 220 °C
	1,4-Dichloro-2,6-dinitrobenzene	0.851	375	
	2-Chloro-1,3,5-trinitrobenzene	0.325	521	
	1,2,3,5-Tetrachloro-4,6-dinitrobenzene[c]	—	687	

[a] Either a Pye 104, a Pye GCD, or a Pye PU4900 instrument fitted with a flame ionisation detector and Laboratory Data Control 308 computing integrator. [b] Response factor = [Area ratio (Aromatic/Reference standard)]/[Mole ratio (Aromatic/Reference standard)]. [c] Reference standard. [d] Values were obtained from a calibration graph of response factor *vs.* area ratio.

Table 2. Yields of 1-chloro-2,4-dinitrobenzene from the nitration of 1-chloro-4-nitrobenzene,[a,b] and of 1,3-dichloro-2,4-dinitrobenzene from the nitration of 1,3-dichloro-2-nitrobenzene[a,c] in sulphuric acid and oleum[d] at 25.0 ± 0.1 °C

Substrate: 1-chloro-4-nitrobenzene

Oleum (%)	Yield (%)[e]
8.0	100
13.0	101
19.8	101

Substrate: 1,3-dichloro-2-nitrobenzene

H_2SO_4 (%)	
88.4	100
91.8	100, 102
Oleum (%)	
8.0	103
13.1	101, 102
18.6	101
25.2	87, 88
29.7	80
34.6	61
42.9	46, 104[f]

[a] Initial substrate concentration 1×10^{-4} mol dm^{-3}. [b] [HNO_3] 1.0 mol dm^{-3}. [c] [HNO_3] 0.05 mol dm^{-3} unless stated. [d] Oleum strength is expressed as weight percent of 'excess' sulphur trioxide. [e] Yields after 10 half-lives for reaction. [f] [HNO_3] 0.94 mol dm^{-3}.

condenser and drying tube were fitted and the limb containing acid was immersed in an oil-bath at 130 ± 0.2 °C for 10 min. The limb containing aromatic was immersed for the final minute of the warm-up period. The contents of the two limbs were then thoroughly mixed. Samples (*ca.* 5 ml) were withdrawn through the condenser using an elongated pipette, the tip of which had been removed to facilitate quick delivery. The sample was cooled, weighed, and quenched in chilled water (500 ml). The extraction with dichloromethane was as described above. G.c. conditions are in Table 1. First-order rate coefficients were calculated from the amount of unchanged substrate, using a computer program.

[1-^{2}H]-3,5-Dinitrobenzene was shown by g.c.m.s. not to undergo hydrogen exchange under the conditions of a nitration experiment. Products from runs using $H^{15}NO_3$ were also analysed by g.c.m.s. (V.G. Micromass 16F single-focussing magnetic sector mass spectrometer fitted with a Pye 104 oven). Enrichment was calculated as previously.[2]

Results

1-Chloro-4-nitrobenzene.—The yields of 1-chloro-2,4-dinitrobenzene were quantitative (Table 2). Kinetics for this substrate were not reinvestigated.[7]

1,3-Dichloro-2-nitrobenzene.—The yields of 1,3-dichloro-2,4-dinitrobenzene (Table 2) were quantitative except in concentrated oleum solutions containing low concentrations of nitric acid. Kinetic investigation revealed that the departure from quantitative yield was entirely due to competing sulphonation. Second-order rate coefficients for nitration are in Table 3. Where sulphonation was competitive, second-order rate coefficients for nitration were obtained from slopes, and first-order rate coefficients for sulphonation from intercepts, of plots of observed first-order rate coefficients against the concentration of nitric acid (Table 3 and footnotes).

1,3-Dinitrobenzene.—Nitration in sulphuric acid and oleum at 150 °C gave rise to the yields of 1,3,5-trinitrobenzene in Table 4. The only other detected products were gaseous and included carbon dioxide and oxides of nitrogen. It was established in separate experiments (Table 5) that both 1,3-dinitrobenzene in the absence of nitric acid and 1,3,5-trinitrobenzene in the presence of nitric acid are stable and can be recovered quantitatively after the duration of a nitration experiment.

Kinetics of disappearance of substrate were first-order. Division of the first-order rate coefficients by the nitric acid

Table 3. Second-order rate coefficients for nitration of 1,3-dichloro-2-nitrobenzene[a] at 25.0 ± 0.1 °C

H_2SO_4 (%)	10^2 [HNO_3]/mol dm^{-3}	10^2 k_2/dm^3 mol^{-1} s^{-2}
88.4	4.04	6.98
88.4	4.64	7.09
90.6	4.13	10.9
92.9	6.58	10.6
92.9	4.83	10.7
93.5	5.03	9.74
95.0	4.49	9.20
95.0	4.78	8.37
97.5	5.40	6.09
98.0	5.88	3.98
98.1	4.90	3.99
Oleum (%)		
4.5	5.39	2.67
6.0	5.39	2.60
7.2	5.21	2.62
13.3	5.79	2.46
13.6	4.68	2.31
13.6	6.28	2.45
18.9[b]	(1—9)	2.74
25.9[b]	(1—9)	3.05
38.5[b]	(1—9)	3.29

[a] Initial substrate concentration 4 × 10^{-5} mol dm^{-3}. [b] First-order rate coefficients for sulphonation: 9 × 10^{-5} s^{-1} (18.9% oleum); 3.7 × 10^{-4} s^{-1} (25.9% oleum);. and 1.7 × 10^{-3} s^{-1} (38.5% oleum).

Table 4. Yields of 1,3,5-trinitrobenzene[a] from the nitration of 1,3-dinitrobenzene[b] at 150.0 ± 0.2 °C in sulphuric acid and oleum

H_2SO_4 (%)	[HNO_3]/mol dm^{-3}	Yield (%)
92.4	1.00	42
94.9	1.02	42
96.0	1.01	39
98.0	0.36	22
98.0	0.58	25
98.0	0.75	30
98.0	1.00	35
98.0	2.02	40
Oleum (%)		
11.9	0.99	30
22.9	0.26	37
22.9	1.04	38
39.1	1.00	40

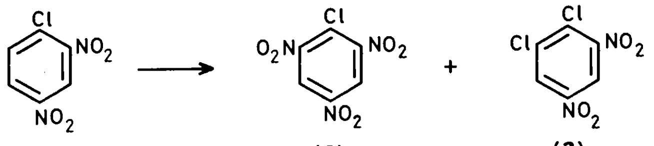
[a] After > 10 half-lives for reaction. [b] Initial substrate concentration 1—7 × 10^{-3} mol dm^{-3}.

concentration gave the second-order rate coefficients in Table 6. The discrepancies between these values in a given medium can in large part be accounted for by the water released when the nitric acid is ionised to nitronium ion.

The kinetics of reaction of [1-^{2}H]-3,5-dinitrobenzene (Table 6), despite an isotopic purity of only 55%, show clearly that the kinetic hydrogen isotope effect, k_H/k_D, is close to unity. Calculations show that an isotope effect of two would have given a detectably curved first-order plot of considerably lower slope than that observed.[13]

Incorporation of ^{15}N into substrate during nitration was sought but not found (Table 7).

1-*Chloro*-2,4-*dinitrobenzene* (**1**).—Reaction with nitric acid in sulphuric acid and in oleum at 130 °C gave the expected nitro product 2-chloro-1,3,5-trinitrobenzene (**2**), and also the chlorination product, 1,2-dichloro-3,5-dinitrobenzene (**3**) (Scheme 1).



Scheme 1.

Data are in Table 8. Yields of (**2**) and (**3**) are expressed as a percentage of (**1**) consumed at the stated time. In each case three values have been selected for times corresponding most closely to 40, 60, and 80% consumption of (**1**). This represents only part of the data obtained. A typical run is illustrated in the Figure, and shows yields based on initial reactant, not on reactant consumed as in Table 8.

Separate stability tests were made (Table 5) and show that (**1**) is stable in the absence and (**2**) in the presence of nitric acid under the reaction conditions. Some reaction of (**3**) with nitric acid is evident and accounts in part for the diminishing yields of (**3**) with time at low acid concentration (Table 8).

The kinetics of the reaction are difficult to present. Reaction in 4% oleum is not first-order; substrate disappearance shows an induction period. First-order behaviour was found however for reaction in 98% H_2SO_4, and in ⩾14% oleum. First-order rate coefficients are in Table 9. Those for 98% H_2SO_4 are clearly not proportional to the concentration of nitric acid which deterred us from deriving second-order rate coefficients.

Incorporation of ^{15}N into (**1**) during nitration was sought but not found. However, the chlorinated product (**3**) was enriched in ^{15}N and this label was not acquired subsequent to its formation (Table 10 and footnotes).

2-*Chloro*-1,3-*dinitrobenzene*.—A solution initially containing 1 × 10^{-3} mol dm^{-3} of this substrate and 1 mol dm^{-3} nitric acid in 6% oleum was analysed after 40 min at 130 ± 0.2 °C. There remained 11% of the substrate. 2-Chloro-1,3,5-trinitrobenzene, 1,4-dichloro-2,6-dinitrobenzene, and an unidentified product with an intermediate g.c. retention time, had been formed. The yields (based on substrate consumed, and in the case of the unidentified product assuming a g.c. response factor of unity) were 74, 3, and 1%, respectively. No further investigations of this substrate were made.

Discussion

1-*Chloro*-4-*nitrobenzene and* 1,3-*Dichloro*-2-*nitrobenzene*.—The products of nitration of these two substrates are entirely normal (Table 2). Except where sulphonation is competitive (*viz.* concentrated oleum solutions containing relatively low concentrations of nitric acid) quantitative nitration to the expected product occurs. No products of chlorination could be detected, and the trace of 1,2,3,5-tetrachloro-4-nitrobenzene observed in the nitration of 1,3,5-trichloro-4-nitrobenzene[2] remains the only example of this type of behaviour amongst chloromononitrobenzenes. The contrasting behaviour of chlorodinitrobenzenes is discussed below.

The rate profile for 1,3-dichloro-2-nitrobenzene is also normal. The ratio of rate coefficients for this substrate and 1,3,5-trichloro-2-nitrobenzene[2] is almost constant (*ca.* 12) between 88—98% H_2SO_4. In oleum the ratio increases (*ca.* 22 in 25% oleum). The reason for this is not clear but the effect is small.

1,3-*Dinitrobenzene*.—It seemed possible that with this and other highly deactivated substrates, the Wheland intermediate might be so unstable that it is bypassed in an S_E3-type transition state in which nitronium ion attack and proton abstraction are

Table 5. Stability tests on reactants and products

Substrate	T/°C	Medium	$[HNO_3]$/mol dm^{-3}	Duration	Recovery
1,3-Dinitrobenzene	150	98% H_2SO_4	0	24 h	97
		11% Oleum	0	127 min	99
1,3,5-Trinitrobenzene	150	98% H_2SO_4	0.84	19 h	100
1-Chloro-2,4-dinitrobenzene	130	92% H_2SO_4 [a]	0	5 h	100
		6% Oleum [a]	0	40 min	103
2-Chloro-1,3,5-trinitrobenzene	130	1% Oleum	1.0	2 h	98
1,2-Dichloro-3,5-dinitrobenzene	130	1% Oleum	1.0	2 h	88 [b]

[a] In connection with experiments to be reported later, these solutions were saturated with HCl. [b] 2,3,4-Trichloro-1,5-dinitrobenzene (1%) and 1,2,4-trichloro-3,5-dinitrobenzene (trace) were also detected.

Table 6. Second-order rate coefficients for nitration for 1,3-dinitrobenzene[a] at 150.0 ± 0.2 °C in sulphuric acid and in oleum

H_2SO_4 (%)	$[HNO_3]$/mol dm^{-3}	$10^4\ k_2$/dm^3 mol^{-1} s^{-1}
96.0	0.81	2.1
98.0	0.81	1.7
98.0[b]	0.81[b]	1.6[b]
100.0	0.81	1.6
Oleum (%)		
2.1	0.79	1.8
9.0	0.81	1.4
11.1	0.80	1.2
11.1[b]	0.80[b]	1.2[b]
12.5	0.81	1.2
15.3	0.79	1.2
20.0	0.80	1.2
26.0	0.80	1.1
0.1	1.54	2.0
5.4	1.54, 1.61[c]	1.7, 1.8[c]
11.0	1.53, 1.52[c]	1.4, 1.5[c]
18.1	1.54	1.2
25.8	1.54	1.2
26.0	1.54	1.2
25.0	2.31	1.3
35.2	2.32	1.4

[a] Initial substrate concentration 6×10^{-4} mol dm^{-3}. Rate coefficients ± 10%. [b] ([1-^{2}H]-3,5-Dinitrobenzene) 6×10^{-4} mol dm^{-3}. [c] Open system, rather than sealed tubes, used. See Experimental section.

Table 7. ^{15}N Incorporation[a] during the nitration of 1,3-dinitrobenzene with 0.57 mol dm^{-3} $H^{15}NO_3$ in 25.7% oleum at 150 ± 0.2 °C

Time/min[a]	Incorporation (%)[b]
60	1
150	1
240	1
330	1
420	1
510	1

[a] Estimated half-life under the conditions is 185 min. [b] Error estimated to be ±1%.

concurrent. The absence of a primary kinetic hydrogen isotope effect shows that this does not occur, and the S_E3 mechanism is discounted for this and the two substrates discussed below.

Although chlorination products are not possible with this substrate, a study of the yields and kinetics of reaction is reported for comparison. As has been found previously for nitration in a variety of media (see Introduction) yields of 1,3,5-trinitrobenzene, the only aromatic nitro product observed, are rather low. The stability tests (Table 5) shows that this is not due to sulphonation.

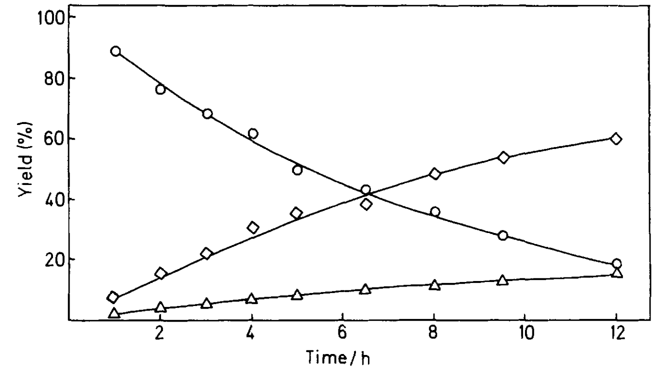


Figure. Formation of 2-chloro-1,3,5-trinitrobenzene (**2**) (diamonds) and 1,2-dichloro-3,5-dinitrobenzene (**3**) (triangles) in the nitration of 1-chloro-2,4-dinitrobenzene (**1**) (circles) in 14.8% oleum containing 1.0 mol dm^{-3} HNO_3 at 130 ± 0.2 °C. Yields are based on initial reactant

A possible reason for the low yield might be that initial attack of nitronium ion occurs not only at C-5 but also at C-1, *i.e. ipso* to nitro, followed by nucleophilic capture and decomposition of the diene to give gaseous products [Scheme 2, X = Y = H, steps (a)—(d) only] as proposed previously[2] for 1,3,5-trichloro-2,4-dinitrobenzene (Scheme 2, X = Y = Cl). In contrast to the latter case, there was no ^{15}N exchange of substrate during nitration (Table 7). If the mechanism of Scheme 2 is correct for 1,3-dinitrobenzene, then step (b) is irreversible, perhaps because nitronium ion loss from the *ipso*-Wheland intermediate is not in this case sterically assisted. However, positive evidence for the operation of this mechanism is lacking.

1-*Chloro*-2,4-*dinitrobenzene* (**1**) *and* 2-*Chloro*-1,3-*dinitrobenzene*.—Both give rise to chlorination as well as nitration products, as with 1,3,5-trichloro-2,4-dinitrobenzene.[2] Since the mononitro compounds we have studied (*vide supra*) do not give such products, either high temperatures or highly deactivated aromatic compounds or both are necessary for this type of reaction to occur. The case of 2-chloro-1,3-dinitrobenzene was not studied in detail; what follows relates to 1-chloro-2,4-dinitrobenzene (**1**).

It appears that the mechanism of Scheme 2 (X = Cl, Y = H) can explain some but not all of the observations. The formation of the chlorinated product, (**3**), the fact that it is the isomer expected from an electrophilic chlorination, and that it is partially enriched in ^{15}N when labelled nitric acid is used, are satisfactorily explained, as previously.[2] The lack of concurrent ^{15}N-enrichment of the substrate can be accounted for as for 1,3-dinitrobenzene above. Observations which are less readily accommodated relate to 98% H_2SO_4 and 4% oleum only, and are considered in the following two paragraphs.

The increase in the yield of the normal nitro product (**2**) with the concentration of nitric acid in 98% H_2SO_4 (Table 8, first three rows) can only be accounted for if amongst steps (c)—(h)

Table 8. Yields of (**2**) and (**3**), expressed as a percentage of the reactant consumed, at times corresponding to consumption of approximately 40, 60, and 80% of (**1**)[a] in sulphuric acid or oleum containing nitric acid[b] at 130 ± 0.2 °C

			Yield (%)	
Medium	Time/min	Reactant (**1**) consumed (%)	(**2**)	(**3**)
98% H_2SO_4[c]	60, 120, 180	33, 65, 81	—, 11, 12	24, 20, 16
98% H_2SO_4	50, 80, 140	40, 59, 78	27, 31, 31	25, 22, 19
98% H_2SO_4[d]	30, 60, 90	44, 69, 82	48, 41, 42	16, 12, 9
4.0% Oleum	45, 70, 102	40, 65, 83	23, 18, 18	22, 16, 11
14.8% Oleum	180, 410, 720	32, 57, 82	67, 68, 74	17, 16, 18
15.5% Oleum	240, 410, 720	40, 57, 78	73, 70, 71	10, 10, 10
15.5% Oleum	240, 410, 720	44, 58, 79	56, 58, 67	8, 9, 11
25.7% Oleum	240, 480, 720	37, 62, 79	61, 60, 54	8, 10, 8

[a] Initial substrate concentration 1 × 10^{-3} mol dm^{-3}. [b] Nitric acid concentration 1 mol dm^{-3} unless stated. [c] Nitric acid concentration 0.5 mol dm^{-3}. [d] Nitric acid concentration 2 mol dm^{-3}.

Table 9. First-order rate coefficients for reaction of (**1**)[a] with nitric acid in sulphuric acid and oleum at 130 ± 0.2 °C

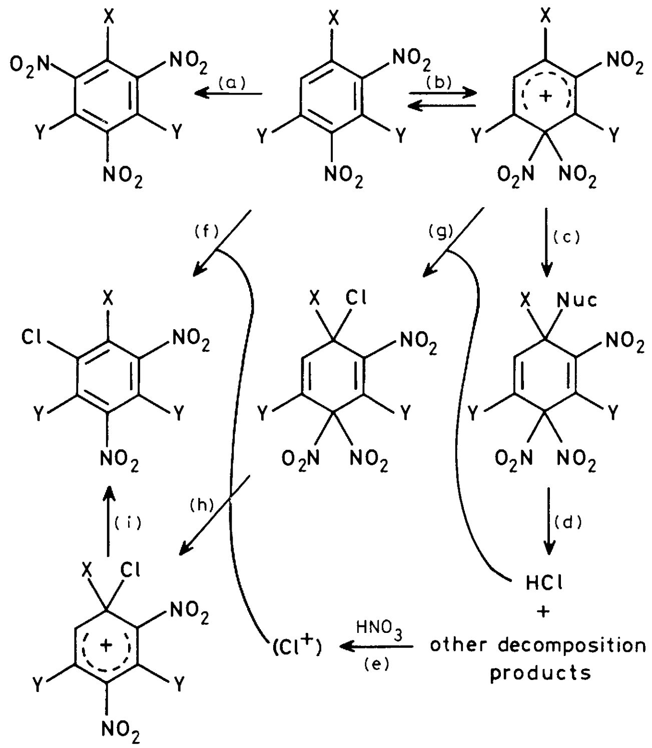
H_2SO_4 (%)	$[HNO_3]$/mol dm^{-3}	10^5 k/s^{-1}
98.0	0.5	16
98.0	1.0	19
98.0	2.0	32
Oleum (%)		
14.8	1.0	3.9
15.5	1.0	3.7, 3.8
25.7	1.0	3.6

[a] Initial substrate concentration 1 × 10^{-3} mol dm^{-3}. Rate coefficients ±10%.

Table 10. ^{15}N Incorporation[a] during the reaction of (**1**) with 1.0 mol dm^{-3} $H^{15}NO_3$ in 15.5% oleum at 130 ± 0.2 °C

	Incorporation (%)	
Time/h[b]	in (**1**)	in (**3**)
1	−1	2
2	0	3
3	−1	5
4	0	5
5	0	6 (0)[c]
6.5	1	5
8	0	5
9.5	0	6
12	0	6
28	1	9 (0)[c,d]

[a] Estimated half-life under the conditions is 5.1 h. [b] Error estimated to be ±1%. [c] In this experiment (**3**) rather than (**1**) was dissolved initially, recovered almost quantitatively at the time stated, and analysed for ^{15}N. [d] Trace amounts of 2,3,4-trichloro-1,5-dinitrobenzene and 1,2,4-trichloro-3,5-dinitrobenzene were also detected.



Scheme 2.

there is a step or steps not dependent on the concentration of nitric acid and not fast compared with (a) or (b). Increasing the nitric acid concentration then increases the consumption of (**1**) by step (a) relative to that by step (f). However, departures from a first-order form might then have been expected, and were not observed.

In 4% oleum, substrate disappearance is not first-order but shows an induction period. If this were due to a delay amongst steps (c)—(h), the yield of (**3**) (expressed as a percentage of reactant consumed, Table 8) should increase with time. The opposite is the case and this can only partly be attributed to further reaction of (**3**) (Table 5).

In summary then, we have shown that the previous observation[2] of chlorination as well as nitration products in the nitration of chloronitroaromatics is not restricted to 1,3,5-trichloro-2,4-dinitrobenzene, although it does require a highly deactivated aromatic substrate and/or high temperature. The mechanism previously proposed accounts for some but not all the observations, and is inadequate in relation to nitration in less acidic media than 14% oleum.

Acknowledgements

This work has been carried out with the support of the procurement executive of the M.O.D. We acknowledge helpful discussions with Dr. P. Golding.

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Received 5th November 1987; *Paper* 7/1962