Electrophilic Aromatic Substitution. Part 35.[1] Chlorination of 1,3-Dinitrobenzene, 1-Chloro-2,4-dinitrobenzene, and 2,4-Dinitrotoluene with Nitric Acid and Hydrogen Chloride or Chlorine in Sulphuric Acid or Oleum

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Solutions of sulphuric acid or oleum containing HCl or Cl_2 and nitric acid have been found both to chlorinate and nitrate deactivated aromatic compounds. The kinetics and products of the chlorination of 1,3-dinitrobenzene and 1-chloro-2,4-dinitrobenzene in sulphuric acid or oleum containing HCl and nitric acid at 130 °C, and the kinetics and products of the chlorination of 2,4-dinitrotoluene at 90 °C in sulphuric acid or oleum containing Cl_2 and nitric acid, are reported. 1,3-Dinitrobenzene and 1-chloro-2,4-dinitrobenzene were predominantly chlorinated. 2,4-Dinitrotoluene gave approximately equal amounts of 6-chloro-2,4-dinitrotoluene and 2,4,6-trinitrotoluene. The results show that under these conditions, chlorination and nitration are competing electrophilic reactions, and that chlorination is less selective than nitration. Possible mechanisms for chlorination are discussed.

We previously reported that 1-chloro-2,4-dinitrobenzene,[1] 2-chloro-1,3-dinitrobenzene,[1] and 1,3,5-trichloro-2,4-dinitrobenzene[2] gave products of chlorination as well as of nitration when treated with nitric acid in sulphuric acid or oleum. A mechanism was proposed in which hydrochloric acid, released in the decomposition of some of the aromatic substrate, is oxidised by nitric acid to an electrophilic chlorinating agent and this competes with nitronium ion for the remaining aromatic.

We now report a study in which hydrochloric acid or chlorine was added deliberately to the initial reaction mixture. For each of the title substrates, significant chlorination ensued.

Previous studies of aromatic chlorination have been restricted in the main to activated aromatic compounds. Chlorination of strongly deactivated aromatic compounds like those in the present study has not to our knowledge been reported.

Experimental

Materials.—Sulphuric acid and oleum solutions were prepared and analysed, and nitric acid purified, as previously.[2] Cylinders of HCl or Cl_2 were used. The gases were bubbled through 98% H_2SO_4 to remove moisture before use.

1-Chloro-2-nitrobenzene (m.p. 31–32 °C from EtOH–H_2O), 1-chloro-3-nitrobenzene (m.p. 45–46 °C from EtOH–H_2O), 1-chloro-4-nitrobenzene (m.p. 83.5 °C from EtOH–H_2O), 1-chloro-2,4-dinitrobenene (m.p. 50 °C from Et_2O), 2-chloro-1,3-dinitrobenzene (m.p. 87.5 °C from EtOH), 2-chloro-1,3,5-trinitrobenzene (m.p. 82 °C from EtOH), 1,2-dichloro-3-nitrobenzene (m.p. 61 °C from EtOH), 1,2-dichloro-4-nitrobenzene (m.p. 41 °C from MeOH), 1,4-dichloro-2-nitrobenzene (m.p. 55–56 °C from EtOH), 1,2-dinitrobenzene (m.p. 118 °C from EtOH), 1,3-dinitrobenzene (m.p. 90 °C from EtOH), 1,4-dinitrobenzene (m.p. 175 °C from AcOH), 1-nitronaphthalene (m.p. 59–60 °C from EtOH), 1,2,4-trichloro-3-nitrobenzene (m.p. 87–88 °C from EtOH), 1,3,5-trinitrobenzene (m.p. 122.5 °C from EtOH), and 2,4-dinitrotoluene (m.p. 70–70.5 °C from MeOH) were obtained by recrystallisation of the commercial material. AnalaR nitrobenzene was fractionally distilled, the fraction b.p. 208 °C was collected. Pure 2,4,6-trinitrotoluene (m.p. 82 °C) was supplied by the Ministry of Defence (PERME).

1,3-Dichloro-2-nitrobenzene (m.p. 70–70.5 °C from EtOH–H_2O),[3] 1,2-dichloro-3,5-dinitrobenzene (m.p. 56.5 °C from 100–120 °C light petroleum),[4] 1,3-dichloro-2,4-dinitrobenzene (m.p. 68 °C from EtOH),[1] 1,2,4-trichloro-3,5-dinitrobenzene (m.p. 103–104 °C from EtOH),[5] 2,3,4-trichloro-1,5-dinitrobenzene (m.p. 93–94 °C from EtOH),[5] 1,2,3,5-tetrachloro-4,6-dinitrobenzene (m.p. 164–165 °C from AcOH),[6] 1-chloro-3,5-dinitrobenzene (m.p. 52.5–53 °C from MeOH),[7] 2,5-dichloro-1,3-dinitrobenzene (m.p. 104.5 °C from hexane),[8] 6-chloro-2,4-dinitrotoluene (m.p. 47 °C, vacuum sublimation),[8] and 6-bromo-2,4-dinitrotoluene (m.p. 57 °C from EtOH),[9] were prepared as described or by a similar procedure.

Chlorination Studies Using HCl.—Dry hydrogen chloride gas was bubbled through concentrated sulphuric acid or oleum to effect saturation, and then a weighed amount of pure nitric acid was added; this caused a yellowish green colouration. (If the nitric acid were added too rapidly the solution became hot, and a gas was evolved which gave positive tests for chlorine.[10])

A known amount of aromatic substrate in solution in acetic acid (50 mm^3) was placed in one closed limb of a vessel consisting of two open and two closed tubes joined in an X-shape. Solvent was removed under reduced pressure. The mixed acid prepared as above was transferred to the other closed limb. A condenser and $CaCl_2$ guard tube were fitted. The limb containing mixed acid was then placed in a thermostat at 130 (±0.2) °C for 10 min. During this time bubbles of gas were released from the surface of the solution. The limb containing the aromatic was immersed in the final minute of the warm-up period. The contents of the two limbs were thoroughly mixed, producing an aromatic concentration of, typically, 1×10^{-3} mol dm^{-3}. For kinetic studies, samples were taken at time intervals as previously,[1] placed in pre-weighed stoppered flasks, cooled, weighed, then quenched and extracted with dichloromethane after the addition of the g.c. reference standard. The dichloromethane extract was concentrated and analysed as previously;[1] g.c. conditions are in Table 1. First-order rate coefficients were calculated from the amount of unchanged aromatic substrate using a computer program. For product studies the same procedure was used. The products from the reaction of 1,3,-dinitrobenzene contained both 1,3,5-trinitrobenzene and 1,2-dichloro-3,5-dinitrobenzene which we were unable to resolve by g.c. These were analysed by the following procedure.

The m.s. response factor was calculated using mixtures of the two products, now called A and B [equation (1)].

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

Substrate	Component	Response factor[b]	Retention time(s)
1-Chloro-2,4-dinitrobenzene[c]	1-Chloro-2,4-dinitrobenzene	0.802	355
	1,2-Dichloro-3,5-dinitrobenzene	0.904	458
	2-Chloro-1,3,5-trinitrobenzene	*d*	568
	1,2,4-Trichloro-3,5-dinitrobenzene	0.981	575
	2,3,4-Trichloro-1,5-dinitrobenzene	0.889	683
	1,2,3,5-Tetrachloro-4,6-dinitrobenzene[e]		731
1-Chloro-2-nitrobenzene[f]	1-Chloro-2-nitrobenzene		110
	1,4-Dichloro-2-nitrobenzene		144
	1,2-Dichloro-3-nitrobenzene		177
	1,3-Dinitrobenzene[e]		377
	1-Chloro-2,4-dinitrobenzene	0.979	592
	2-Chloro-1,3-dinitrobenzene	1.026	684
1-Chloro-4-nitrobenzene[g]	1-Chloro-4-nitrobenzene		162
	1,2-Dichloro-4-nitrobenzene	1.070	263
	1,3-Dinitrobenzene[e]		397
	1-Chloro-2,4-dinitrobenzene	0.953	580
1,3-Dichloro-2-nitrobenzene[f]	1,3-Dichloro-2-nitrobenzene		150
	1,2,4-Trichloro-3-nitrobenzene		215
	1-Nitronaphthalene[e]		438
	1,3-Dichloro-2,4-dinitrobenzene	0.601	736
1,3-Dinitrobenzene[c]	1,3-Dinitrobenzene	0.861	256
	1-Chloro-3,5-dinitrobenzene	0.916	310
	1-Chloro-2,4-dinitrobenzene	0.717	348
	2,5-Dichloro-1,3-dinitrobenzene	0.851	405
	1,2-Dichloro-3,5-dinitrobenzene–1,3,5-Trinitrobenzene mixtures[h]	0.814	457
	1,2,4-Trichloro-3,5-dinitrobenzene	0.981	565
	2,3,4-Trichloro-1,5-dinitrobenzene	0.889	676
	1,2,3,5-Tetrachloro-4,6-dinitrobenzene[c]		733
Nitrobenzene[c]	Nitrobenzene		
	1-Chloro-3-nitrobenzene		338
	1,4-Dinitrobenzene		622
	1,3-Dinitrobenzene	1.012	671
	1,2-Dinitrobenzene		726
	1-Chloro-2,4-dinitrobenzene[e]		806
2,4-Dinitrotoluene[c]	2,4-Dinitrotoluene	1.019	326
	6-Chloro-2,4-dinitrotoluene	1.052	407
	2,4,6-Trinitrotoluene	0.989	492
	6-Bromo-2,4-dinitrotoluene	0.936	547
	1,2,3,5-Tetrachloro-4,6-dinitrotoluene[e]		731

[a] Either 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] 15% SE30 on Chromasorb W AWDCMS, 9 ft glass column, nitrogen flow rate 40 cm^3 min^{-1} oven temp. 175 °C. [d] Values were obtained from a calibration graph of response factor *versus* area ratio. [e] Reference standard. [f] 3% OV225 on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 40 cm^3 min^{-1}, oven temp. 175 °C. [g] 10% Dexsil 400GC on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 40 cm^3 min^{-1}, oven temp. 195 °C. [h] See Experimental section.

m.s. response factor =

$$\frac{\text{area ratio molecular ion (A/B)}}{\text{mole ratio (A/B)}} \qquad (1)$$

The g.c. response factor was calculated using mixtures of A, B and the reference standard R (Table 1) [equation (2)]

$$\text{g.c. response factor} = \frac{\text{area ratio (A + B)/R}}{\text{mole ratio (A + B)/R}} \qquad (2)$$

This varied linearly with changes in A/B. Using these calibrations, compositions were determined by g.c.m.s. and yields by g.c.

Chlorination Studies Using Cl_2.—Dry chlorine gas was bubbled through concentrated sulphuric acid or oleum to effect saturation. Nitric acid was added and did not cause effervescence. The procedure was as above. In the study of the chlorination of 2,4-dinitrotoluene, the effect of a controlled atmosphere above the solution was investigated using the apparatus shown in Figure 1. In experiments 1–3, 10 cm^3 of the mixed acid solution saturated with chlorine were placed in the apparatus together with the aromatic. The reaction vessel was placed in a thermostat bath at 90 °C, with the stopcock open, and magnetically stirred. The contents of the apparatus were cooled, quenched and analysed as previously after 2 h.

In experiment 4, the apparatus containing the mixed acid and aromatic (5.2×10^{-2} mol dm^{-3}) was assembled, flushed with Cl_2 for 5 min (a small bore p.v.c. tube was passed down the p.v.c. vent tube through the stopcock into the reaction vessel) and sealed by closing the stopcock. The reaction vessel was immersed in a thermostat bath at 90 °C and magnetically stirred for 2 h. The contents were quenched, cooled, and analysed. In experiments 5 and 6 the aromatic concentration was the same as in experiment 4. The apparatus was flushed with Cl_2 for 5 min. The stopcock was closed and the reaction vessel cooled to *ca.* − 80 °C. This solidified the reaction mixture and liquified the Cl_2. A measured volume of Cl_2 from a gas syringe, equivalent to the head-space volume, was injected through a silicone–PTFE septum. The contents of the reaction vessel were

Table 2. The observed first-order rate coefficients for chlorination of 1,3-dinitrobenzene and 1-chloro-2,4-dinitrobenzene in sulphuric acid or oleum, containing HCl and nitric acid, at 130.0 ± 0.2 °C.

Acid	$[HNO_3]$/mol dm^{-3}	$10^5 k_2$(obs)/s^{-1}
1,3-Dinitrobenzene[a]		
H_2SO_4 (%)		
91.8	1.00	7.6
98.0	1.00	37
Oleum (%)		
1.2	0.50	48
1.2	1.00	47
6.0	1.00	58
10.3	1.00	60
11.9	1.00	58
1-Chloro-2,4-dinitrobenzene[a]		
Oleum (%)		
1.1	1.0	48
4.0	1.0	44
8.9	1.0	96

[a] Initial concentration 1.0 × 10^{-3} mol dm^{-3}.

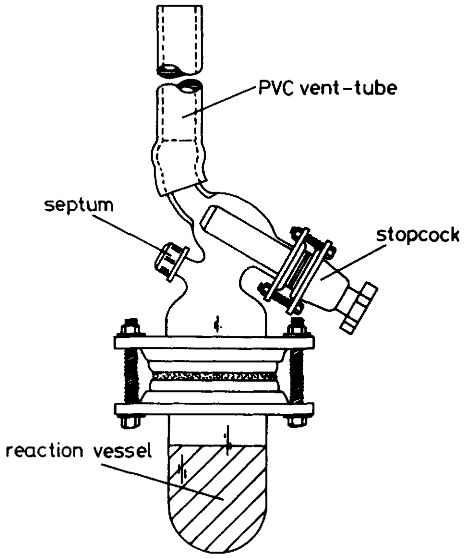


Figure 1. Apparatus for chlorinations under pressure.

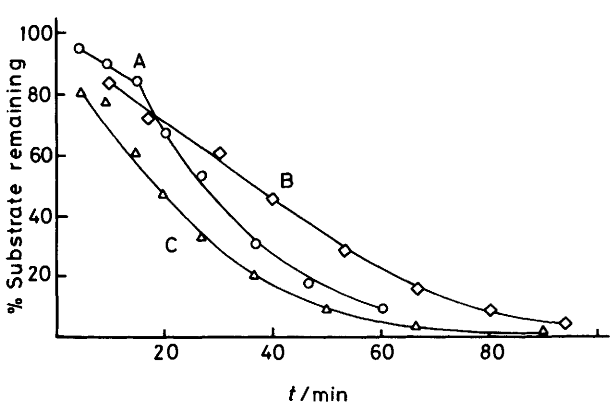


Figure 2. Percentage substrate as a function of time during chlorinations in oleum at 130 °C containing nitric acid (1.0 mol dm^{-3}) and HCl or Cl_2. Curve A (circles): 1,3-dinitrobenzene, 17.5% oleum, HCl. Curve B (diamonds): 1-chloro-2,4-dinitrobenzene, 15.5% oleum, HCl. Curve C (triangles): 1-chloro-2,4-dinitrobenzene, 15.5% oleum, Cl_2.

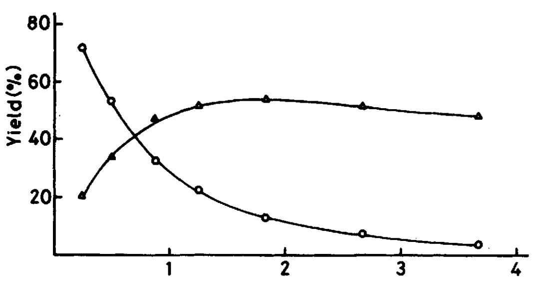


Figure 3. The chlorination of 1,3-dinitrobenzene in 98% H_2SO_4 at 130 °C containing nitric acid (1.0 mol dm^{-3}) an HCl. Circles; 1,3-dinitrobenzene. Triangles; 1-chloro-3,5-dinitrobenzene.

warmed slowly to 90 °C, stirred for 2 h, then cooled, quenched and analysed as previously.

Results

Chlorination of 1,3-*Dinitrobenzene*.—Observed first-order rate coefficients for chlorination in 91.8% sulphuric acid–11.9% oleum, containing HCl and 1.0 mol dm^{-3} nitric acid, are in Table 2. Under these conditions, substrate disappearance followed good first-order kinetics over 3–4 half-lives. In more concentrated oleum solutions, departures from first-order kinetics became increasingly pronounced; a typical run is illustrated in Figure 2, curve A.

Yields of products from reactions quenched after approximately 70% of the substrate had been consumed are in Table 3. The major product was 1-chloro-3,5-dinitrobenzene, the yield of which decreased with long reaction times (Figure 3) due to further chlorination (Table 4).

Neither substrate nor product underwent chlorination when treated with acid containing HCl but no nitric acid (Table 5).

Chlorination of 1-*Chloro*-2,4-*dinitrobenzene*.—First-order kinetics were observed for reaction in 1.1–8.9% oleum containing HCl and nitric acid; rate coefficients are in Table 2. The major product was 1,2-dichloro-3,5-dinitrobenzene (Table 6). Departures from first-order kinetics were again apparent in more concentrated oleum solutions. The use of Cl_2 in place of HCl led to the reappearance of first-order kinetics (Figure 2; compare curves B and C) with little change in product proportions (Table 6; compare last two rows).

Attempted Chlorination of Mildly Deactivated Compounds.—The products of reaction at 25 °C of nitrobenzene, 1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene and 1,3-dichloro-2-nitrobenzene, each in 98.0% H_2SO_4 containing HCl or Cl_2 and nitric acid at 25 °C, were mainly those of nitration (Table 7). Small amounts of chlorinated products were detected.

Chlorination of 2,4-*Dinitrotoluene*.—With this substrate, chlorine was used in place of HCl throughout. Substrate disappearance followed a first-order kinetic form and rate coefficients are in Table 8.

The variation of product yields with time is illustrated by data for reactions in 92.2% sulphuric acid and 5.1% oleum in Tables 9 and 10 respectively. The major products were 2,4,6-trinitrotoluene and 6-chloro-2,4-dinitrotoluene.

A third product, which appeared at the start of reaction and then showed no further increase in concentration with time, was identified by g.c.m.s. as 6-bromo-2,4-dinitrotoluene. This is attributed to the presence of bromine in the commercial grade chlorine gas used. In a separate experiment, bromine was shown to react much more quickly than chlorine under similar

Table 3. Products of chlorination of 1,3-dinitrobenzene[a] in sulphuric acid or oleum, containing HCl and nitric acid[b] at 130.0 ± 0.2 °C.

	Yield (%)						
Acid	13DNB[c]	IC35DNB[d]	1C24DNB[e]	12DC35DNB[f]	25DC13DNB[g]	135TNB[h]	Aggregate yield (%)
H_2SO_4 (%)							
91.8	32.3	22.8	0.7	0.0	0.5	15.1	71.4
98.0	25.5	54.9	2.2	0.6	5.8	3.0	91.9
Oleum (%)							
1.2[i]	34.8	47.6	2.4	0.5	3.5	0.5	89.3
1.2	29.9	55.6	2.4	0.6	5.3	1.2	95.0
6.0	26.5	59.3	2.8	1.0	6.3	0.8	96.8
10.3	35.2	53.4	2.7	0.6	4.6	0.8	97.3
11.9	37.9	52.3	2.7	0.6	4.1	0.6	98.2

[a] [1,3-Dinitrobenzene] 1.0 × 10^{-3} mol dm^{-3}. [b] [HNO_3] 1.0 mol dm^{-3} unless otherwise noted. [c] Recovered 1,3-dinitrobenzene. [d] 1-Chloro-3,5-dinitrobenzene. [e] 1-Chloro-2,4-dinitrobenzene. [f] 1,2-Dichloro-3,5-dinitrobenzene. [g] 2,5-Dichloro-1,3-dinitrobenzene. [h] 1,3,5-Trinitrobenzene. [i] [HNO_3] 0.5 mol dm^{-3}.

Table 4. Tests of the stability of the initial products from the chlorination of 1,3-dinitrobenzene in oleum containing HCl and 1.0 mol dm^{-3} nitric acid at 130.0 ± 0.2 °C.

Oleum (%)	Substrate[a]	Product or recovered substrate	Yield (%)
1.1	2-Chloro-1,3,5-trinitrobenzene[b]	2-Chloro-1,3,5-trinitrobenzene	99.1
1.1	1,2-Dichloro-3,5-dinitrobenzene[b]	1,2-Dichloro-3,5-dinitrobenzene	82.2
		1,2,4-Trichloro-3,5-dinitrobenzene	0.5
		2,3,4-Trichloro-1,5-dinitrobenzene	1.9
6.0	1-Chloro-2,4-dinitrobenzene[c]	1-Chloro-2,4-dinitrobenzene	67.7
		1,2-Dichloro-3,5-dinitrobenzene	29.0
6.0	1-Chloro-3,5-dinitrobenzene[c]	1-Chloro-3,5-dinitrobenzene	85.9
		1,2-Dichloro-3,5-dinitrobenzene	2.7
		2,5-Dichloro-1,3-dinitrobenzene	1.1

[a] [Substrate] = 1.0 × 10^{-3} mol dm^{-3}. Products analysed after 40 min. [b] Products analysed after 2 h. [c] Products analysed after 40 min.

Table 5. The stability of selected aromatic compounds in sulphuric acid or oleum, containing HCl, at 130.0 ± 0.2 °C.

Substrate[a]	Recovery (%) in 91.8% H_2SO_4	Recovery (%) in 6.0% oleum
1-Chloro-2,4-dinitrobenzene	100.1	102.9
1-Chloro-3,5-dinitrobenzene	86.9	84.5
1,2-Dichloro-3,5-dinitrobenzene	97.7	100.0
1,4-Dichloro-2,6-dinitrobenzene	83.5	99.8
1,3-Dinitrobenzene	100.6	101.2
1,3,5-Trinitrobenzene	98.4	99.2

[a] [Substrate] = 1.0 × 10^{-3} mol dm^{-3}. Solutions analysed after two half-lives.

conditions. Thus in 10 min at 90 °C, 2,4-dinitrotoluene in 98% H_2SO_4 containing Br_2 and 0.5 mol dm^{-3} nitric acid gave 6-bromo-2,4-dinitrotoluene (94.7%) and 2,4,6-trinitrotoluene (0.4%). An identical experiment using Cl_2 in place of Br_2 gave 6-chloro-2,4-dinitrotoluene (12.1%), 2,4,6-trinitrotoluene (2.7%), and unchanged 2,4-dinitrotoluene (81.8%). The reaction of bromine is to be investigated.[11] However, with regard to chlorination, the side reaction due to the bromine impurity was small in extent and is not considered further here.

An investigation was made of the effect of varying the aromatic concentration and the partial pressure of chlorine above the solution on the relative yields of chlorinated and nitrated products. The six experiments are described in detail in the experimental section; the yields of the products are in Table 11.

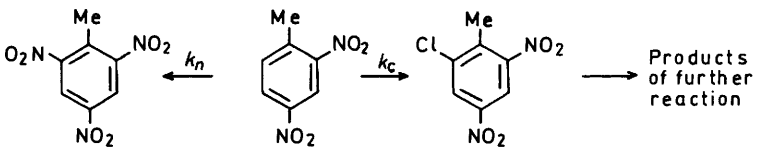
2,4,6-Trinitrotoluene in sulphuric acid containing Cl_2 and nitric acid, and 2,4-dinitrotoluene in sulphuric acid containing Cl_2, were completely stable at 90 °C and could be recovered quantitatively. There was some decomposition of 6-chloro-2,4-dinitrotoluene under the experimental conditions (Table 12); products were not established.

Attempted Chlorination of 1,3,5-*Trinitrobenzene*.—For the attempted chlorination of 1,3,5-trinitrobenzene in 98.0% sulphuric acid containing Cl_2 and 1.0 mol dm^{-3} nitric acid at 180 °C, no products were detected and 81.9% of the initial charge of 1,3,5-trinitrobenzene was recovered. Following reaction at 230 °C no products were detected and no 1,3,5-trinitrobenzene was recovered.

Discussion

The results show that substantial chlorination of highly deactivated aromatic compounds can be achieved using solutions of nitric acid in sulphuric acid or oleum containing dissolved HCl or Cl_2. It seems likely that the chlorinating agent is the same whichever gas is used because there is evidence (see Experimental section) that HCl is oxidised to Cl_2 under the conditions and because a comparison of the two gases (Table 6, last two rows) shows that both give similar results with regard to primary and secondary products. Such differences as there are arise from different solubilities and additional reactions (oxidation to chlorine and formation of chlorosulphonic acid[12]) which occur with HCl but not with Cl_2. The reactions with Cl_2 are therefore simpler to interpret and are discussed first.

Chlorination of 2,4-*Dinitrotoluene* (24*DNT*) using Cl_2.—The reaction gives rise to 2,4,6-trinitrotoluene (246TNT) and 2-chloro-4,6-dinitrotoluene (2C46DNT). The latter decomposes



Scheme 1.

Table 6. Products of chlorination of 1-chloro-2,4-dinitrobenzene[a] in oleum containing HCl and 1.0 mol dm^{-3} nitric acid at 130.0 ± 0.2 °C.

Oleum (%)	Yield (%)				Aggregate yield (%)
	1C24DNB[b]	12DC35DNB[c]	2C1135TNB[d]	234TC15DNB[e]	
1.1	10.2	74.3	8.6	1.0	94.2
4.0	14.0	71.6	5.6	1.5	92.7
8.9	13.9	77.4	4.4	1.4	97.1
15.5	9.0	78.2	2.9	1.4	91.5
15.5[f]	8.9	67.2	3.5	1.5	81.1

[a] [1-Chloro-2,4-dinitrobenzene] = 1.0 × 10^{-3} mol dm^{-3}. Products analysed after approximately 3 half-lives. [b] Recovered 1-chloro-2,4-dinitrobenzene. [c] 1,2-Dichloro-3,5-dinitrobenzene. [d] 2-Chloro-1,3,5-trinitrobenzene. [e] 2,3,4-Trichloro-1,5-dinitrobenzene. [f] Cl_2 used in place of HCl.

Table 7. Products of the chlorination[a] of mildly deactivated aromatic compounds in 98.0% sulphuric acid containing HCl and nitric acid[b] at 25.0 ± 0.1 °C.

Substrate	Product	Yield (%)
1-Chloro-2-nitrobenzene	1-Chloro-2,4-dinitrobenzene	94.8
	2-Chloro-1,3-dinitrobenzene	6.7
	1,2-Dichloro-3-nitrobenzene	0.2
	1,4-Dichloro-2-nitrobenzene	0.3
1-Chloro-4-nitrobenzene[c]	1-Chloro-2,4-dinitrobenzene	95.3 (97.8)
	1,2-Dichloro-4-nitrobenzene	4.2 (2.4)
1,3-Dichloro-2-nitrobenzene	1,3-Dichloro-2,4-dinitrobenzene	101.5
	1,2,4-Trichloro-3-nitrobenzene	0.3
Nitrobenzene	1-Chloro-3-nitrobenzene	1.2
	1,2-Dinitrobenzene	1.3
	1,3-Dinitrobenzene	96.4
	1,4-Dinitrobenzene	1.0

[a] After 15–20 half lives for reaction. [b] $[HNO_3]$ 1.0 mol dm^{-3}. [c] Figures in parentheses are those obtained when Cl_2 was used instead of HCl and the nitric acid concentration was 0.1 mol dm^{-3}.

Table 8. The observed first-order rate coefficients for the chlorination of 2,4-dinitrotoluene[a] in sulphuric acid or oleum, containing Cl_2 and nitric acid, at 90.0 ± 0.2 °C

Media	$[HNO_3]$/mol dm^{-3}	$10^5\,k_1$(obs)/s^{-1}
H_2SO_4 (%)		
85.9	0.20	3.6
85.9	0.30	8.2
85.9	0.50	10
85.9	1.00	15
88.2	0.50	46
92.2	0.25	41
92.2	0.50	80
92.2	0.75	89
96.2	0.50	58
98.0	0.10	9.6
98.0	0.50	31
98.0	1.00	57
Oleum (%)		
5.1	0.50	12
15.5	0.50	6.8
15.5	0.99	17
15.5	1.00	18

[a] [2,4-Dinitrotoluene] = 1.0 × 10^{-3} mol dm^{-3}.

to some extent during reaction (Scheme 1). Consequently the first-order rate coefficients for chlorination and nitration, k_c and k_n respectively were derived using equations (3)–(5).

$$[\mathrm{DNT}] = [DNT]_0 \exp(-k_{\mathrm{obs}}t) \qquad (3)$$

$$k_n = ([\mathrm{TNT}]/[\mathrm{DNT}])(k_{\mathrm{obs}}/[\exp(k_{\mathrm{obs}}t) - 1]) \qquad (4)$$

$$k_c = k_{\mathrm{obs}} - k_n \qquad (5)$$

Values of k_n and k_c are in Table 13. The second-order rate coefficients for nitration, obtained by dividing k_n by the concentration of nitric acid, are in satisfactory agreement with literature values[13] so, despite the presence of chlorine, nitration is effected by nitronium ion in the usual way.

The similarity of the rate profiles for nitration and chlorination (Figure 4) is striking, and rules out the possibility that the chlorinating agent is formed irreversibly from Cl_2 and nitric acid, because it is inconceivable that its chlorinating ability would vary with acidity in the same way as for nitration.[14] A possible explanation is that the transition states for nitration and chlorination are as in structures (**1**) and (**2**) respectively. In the latter the nitronium ion is seen as acting as a Friedel–Crafts type catalyst for chlorination. It is possible that

Table 9. The distribution of products for the reaction of 2,4-dinitrotoluene[a] in 92.2% sulphuric acid containing Cl_2 and nitric acid[b] at 90.0 ± 0.2 °C.

Time/min	Yield (%) 24DNT[c]	6C24DNT[d]	246TNT[e]	6B24DNT[f]	Aggregate yield (%)
4	75.6	8.3	2.3	9.8	96.0
14	52.3	24.5	8.8	10.0	95.6
20	39.5	32.4	11.3	9.4	92.0
26	27.4	37.5	13.6	9.2	87.2
38	16.3	47.8	16.7	9.0	89.3
48	9.5	52.3	19.1	8.8	89.2

[a] [2,4-Dinitrotoluene] = 1.0×10^{-3} mol dm^{-3}. [b] [HNO_3] = 0.5 mol dm^{-3}. [c] Recovered 2,4-dinitrotoluene. [d] 6-Chloro-2,4-dinitrotoluene. [e] 2,4,6-Trinitrotoluene. [f] 6-Bromo-2,4-dinitrotoluene.

Table 10. The distribution of products for the reaction of 2,4-dinitrotoluene[a] in 5.1% oleum containing Cl_2 and nitric acid[b] at 90.0 ± 0.2 °C.

Time/min	Yield (%) 24DNT[c]	6C24DNT[d]	246TNT[e]	6B24DNT[f]	Aggregate yield (%)
30	78.9	5.5	7.6	3.2	95.3
110	51.4	19.1	25.6	2.9	98.9
160	34.8	25.2	33.9	2.8	96.7
210	25.0	30.2	38.3	2.9	96.3
270	15.0	34.4	44.0	2.8	96.2
330	9.7	36.4	45.3	2.8	89.2

For footnotes see Table 9.

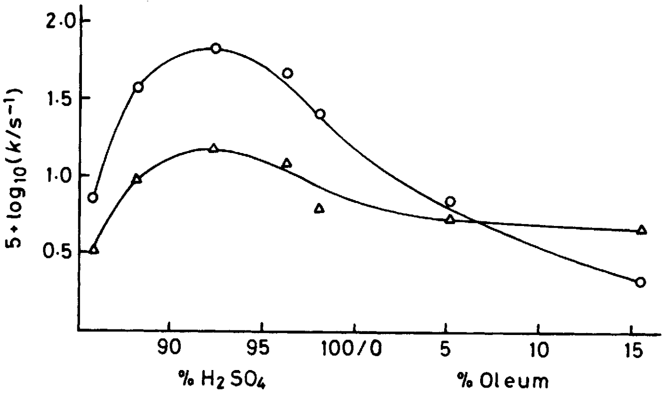
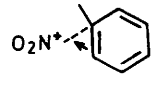
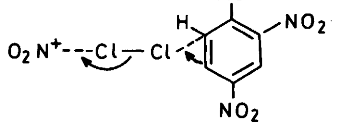


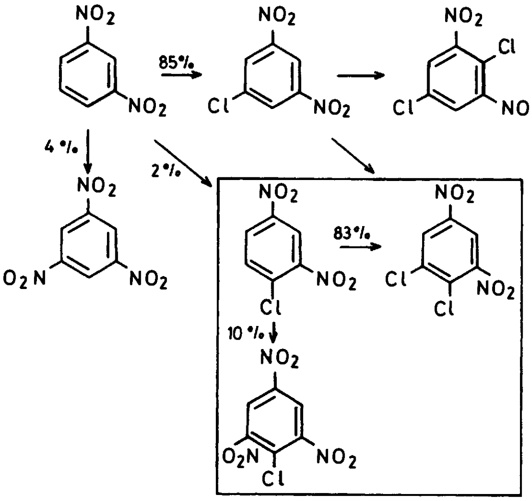
Figure 4. Rate profiles for nitration (k_n, triangles) and chlorination (k_c, circles) of 2,4-dinitrotoluene in sulphuric acid and oleum containing nitric acid (0.5 mol dm^{-3}) and Cl_2 at 90 °C.

there is substantial pre-equilibrium formation of a complex, $NO_2Cl_2^+$. This would lead to a non-linear (saturation) dependence of k_c upon the concentration of nitric acid. There is some evidence for this (Table 13) but the large cumulative errors in k_c derived by equations (3)–(5) preclude firm conclusions.


(1)


(2)

The experiments designed to investigate the effect of changing the concentrations of substrate and Cl_2 (Table 11) are now considered. The first three experiments show that the extent of chlorination decreases with increasing substrate concentration, indicating that the concentration of chlorine is not vastly in excess of that of substrate. (The concentration of Cl_2 in 98% H_2SO_4 at 30 °C saturated with the gas is *ca.* 4×10^{-2} mol dm^{-3}.[15])



Scheme 2.

In the fourth, fifth and sixth experiments a closed system was used with estimated partial pressures of Cl_2 of 1.25, 2.5, and 2.5 atm, respectively. The extent of chlorination increased with the pressure of chlorine.

This is consistent with the mechanism proposed and indicates that if the reaction were to be used for preparative chlorination, high pressures of chlorine would be beneficial.

Chlorination of 1,3-*Dinitrobenzene and of* 1-*Chloro*-2,4-*dinitrobenzene with* HCl.— Scheme 2 (the whole of which relates to the reaction of 1,3-dinitrobenzene and the boxed section to 1-chloro-2,4-dinitrobenzene) shows that chlorination is the predominant reaction with both substrates and that the orientation is that expected for an electrophilic substitution

Table 11. Products of the reaction of 2,4-dinitrotoluene in 98.0% sulphuric acid containing Cl_2 and nitric acid at 90.0 ± 0.2 °C.

		Yield (%)		
Exp. No.[a,b]	10^3[24DNT]/mol dm^{-3}	24DNT[c]	6C24DNT[d]	246TNT[e]
1[f]	0.2	12.8	58.6	22.6
2[f]	1.0	47.0	10.2	35.3
3[f]	5.2	55.5	4.1	38.5
4[g,h]	5.2	50.0	6.2	35.6
5[g,i]	5.0	47.9	11.4	34.6
6[g,i]	5.2	48.7	11.8	33.7

[a] Full details in experimental section. [b–e] As in Table 9. [f] Open system. [g] Closed system, head gas Cl_2 only. [h] Estimated pressure 1.25 atm. [i] Estimated pressure 2.5 atm.

Table 12. The stability of 6-chloro-2,4-dinitrotoluene[a] in sulphuric acid or oleum, containing Cl_2 and 0.5 mol dm^{-3} nitric acid at 90.0 ± 0.2 °C.

Media	Recovery (%) of 6-chloro-2,4-dinitrotoluene
H_2SO_4 (%)	
85.9	81.5
92.2	48.8
98.0	62.7
Oleum (%)	
5.1	87.1
15.5	88.2

[a] [6-Chloro-2,4-dinitrotoluene] = 1.0 × 10^{-3} mol dm^{-3}. Solutions quenched after 2 h.

Table 13. Kinetic parameters for the chlorination of 2,4-dinitrotoluene in sulphuric acid or oleum, containing Cl_2 and nitric acid at 90.0 ± 0.2 °C.

Media	[HNO_3]/mol dm^{-3}	$10^5\,k_c$/s^{-1}	$10^5\,k_n$/s^{-1}
H_2SO_4 (%)			
85.9	0.20	2.3	1.3
85.9	0.30	6.0	2.2
85.9	0.50	7.0	3.2
85.9	1.00	8.7	6.5
88.2	0.50	37	9.3
92.2	0.25	33	7.6
92.2	0.50	65	15
92.2	0.75	64	25
96.2	0.50	46	12
98.0	0.10	8.3	1.3
98.0	0.50	25	6.1
98.0	1.00	37	20
Oleum (%)			
5.1	0.50	6.7	5.3
15.5	0.50	2.1	4.7
15.5	0.99	5.9	11
15.5	1.00	5.7	12

process. The partitioning percentages depend on the conditions; those in Scheme 2 relate to reaction in 1.1–1.2% oleum containing HCl and 1.0 mol dm^{-3} nitric acid and (since yields were not quite quantitative) they do not total 100% (see Tables 3 and 6).

Chlorination only competes successfully with nitration when the aromatic is strongly deactivated. With 2,4-dinitrotoluene the two reaction are in more even competition (see above) and with less deactivated compounds (Table 7) chlorination occurs to only a very minor extent. These results show that the chlorinating agent is of lower substrate selectivity than the nitronium ion.

Uncertainties about the extent of formation of chlorosulphonic acid, the rate and extent of oxidation of HCl to Cl_2, and the extent to which HCl and/or Cl_2 are lost to the atmosphere, preclude conclusions from the kinetics about the precise nature of the chlorinating agent, but it seems likely to be the same as for 2,4-dinitrotoluene chlorination as discussed above.

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