

Electrophilic Aromatic Substitution. Part 32.¹ The Nitration of 1,3,5-Trichloro-2-nitrobenzene, 1,3,5-Trichloro-2,6-dinitrobenzene, and 1,2,3,5-Tetrachloro-4,6-dinitrobenzene in Sulphuric Acid and in Oleum

Roy B. Moodie,* Malcolm A. Payne, and Kenneth Schofield
The Department of Chemistry, The University of Exeter, Exeter EX4 4QD

The kinetics of nitration of 1,3,5-trichloro-2-nitrobenzene (TCNB) in sulphuric acid and in oleum at 25, 50, and 75 °C, and of 1,3,5-trichloro-2,4-dinitrobenzene (TCDNB) in oleum at 150 °C have been measured. 1,2,3,5-Tetrachloro-4,6-dinitrobenzene (TetCDNB) reacts with nitric acid in sulphuric acid and in oleum at 150 °C; the rate profile for the reaction shows a nitration process to be occurring. From TCNB in sulphuric acid the yield of TCDNB was not quite quantitative and at 25 °C in oleum a small amount of 1,2,3,5-tetrachloro-4-nitrobenzene was also formed. TCDNB gave a mixture of TCTNB (the major product) and TetCDNB in proportions which varied with acidity; lower acidities were more favourable to the formation of TetCDNB. The total amount of chlorine present in the TCDNB, TCTNB, and TetCDNB was equal to that present in the TCDNB at the start of the reaction. The nitration of TetCDNB in sulphuric acid at 150 °C gave carbon dioxide and hydrogen chloride, and some sulphur dioxide and nitric oxide or nitrogen dioxide. In the nitration of TCDNB this compound produces the chlorinating agent and reacts with it to give TetCDNB. The chlorinating agent can chlorinate added 1,3-dinitrobenzene. The use of H¹⁵N₂O₃ in the nitration of TCDNB leads to ¹⁵N-incorporation in it and in the TetCDNB produced. Separate nitration of TetCDNB causes only slight ¹⁵N-incorporation into it. It is suggested that in addition to the main route of nitration leading to TCTNB, the nitration of TCDNB gives an *ipso*-Wheland intermediate by attack of nitronium ion at a nitrated position; this intermediate may either return to starting material or give a diene by nucleophilic capture. Decomposition of the diene gives hydrogen chloride or chloride anion which is oxidised by nitric acid to an electrophilic chlorinating agent.

1,3,5-Trichloro-2,4,6-trinitrobenzene (TCTNB) is an intermediate in the manufacture of 1,3,5-triamino-2,4,6-trinitrobenzene, an important explosive. It is normally prepared by nitration of 1,3,5-trichlorobenzene in oleum. Yields are 80–83%, the major by-product being 1,2,3,5-tetrachloro-4,6-dinitrobenzene.² A study of the kinetics and mechanism of the reactions involved is reported in this paper. Of the three stages of nitration, only the first, mononitration of 1,3,5-trichlorobenzene, has been studied previously.³ We therefore concentrated our attention on the second and third nitration stages, *viz.*, mononitrations of 1,3,5-trichloro-2-nitrobenzene and 1,3,5-trichloro-2,4-dinitrobenzene. It also proved necessary to study the reaction of 1,2,3,5-tetrachloro-4,6-dinitrobenzene with nitric acid in sulphuric acid and oleum; these results also are described.

The following abbreviations will be used throughout the text: TCB for 1,3,5-trichlorobenzene, TCNB for 1,3,5-trichloro-2-nitrobenzene, TCDNB for 1,3,5-trichloro-2,4-dinitrobenzene, TCTNB for 1,3,5-trichloro-2,4,6-trinitrobenzene, TetCDNB for 1,2,3,5-tetrachloro-4,6-dinitrobenzene.

Experimental

Materials.—TCB (m.p. 63–64 °C from EtOH) and 1,3-dinitrobenzene (m.p. 90 °C from EtOH) were recrystallised from commercially available material. TCNB (m.p. 70–72 °C from EtOH) was prepared as described,⁴ except that the reaction mixture was poured onto crushed ice immediately after dissolution of TCB had occurred. TCDNB⁴ (m.p. 129–130 °C from EtOH), TetCDNB⁴ [m.p. 164–165 °C from AcOH; ¹³C n.m.r. in the presence of Cr(acac)₃ δ 117.9, 128.8, 134.7, and 147.5 p.p.m.] and 1,2,3,5-tetrachloro-4-nitrobenzene⁵ (m.p. 38–39 °C from EtOH) were prepared as described. TCTNB of 90% purity was supplied to us by the Ministry of Defence. A

sample was purified by preparative t.l.c. as follows. TCTNB (150 mg) was dissolved in dichloromethane (*ca.* 1 cm³) and put on a 20 cm × 20 cm plate of Kieselgel 60 PF. The plate was run twice with 90% n-hexane–10% toluene. The sample recovered from the plate was *ca.* 98% pure. The purity of all the above compounds was checked by g.l.c.

Sulphuric acid was AnalaR grade; concentrations of the diluted acid were determined by density measurements. Oleum was prepared by vacuum distillation of sulphur trioxide from commercial oleum into AnalaR sulphuric acid.⁶ The concentration of sulphur trioxide was determined by titration with water as described.⁷ Nitric acid was prepared from fuming nitric acid by vacuum distillation from sulphuric acid, and stored in the dark at –10 °C.

Kinetics.—For the nitrations at 25 °C, a volumetric flask (500 cm³) containing H₂SO₄ was thermally equilibrated together with a flask containing an acetic acid solution (10 cm³) of the aromatic substrate in the required concentration (*ca.* 5 × 10^{–2} M). Known amounts of nitric acid and aromatic solution (typically 1 cm³) were then added to the H₂SO₄, so that the nitric acid concentration was at least 10 times that of the aromatic. At the requisite times, samples (100 cm³) were withdrawn and quenched in ice-cold water (*ca.* 1 000 cm³).

The technique employed for the experiments at 50 °C was essentially the same as that used at 25 °C, except that the reference standard, 1,3-dinitrobenzene, was added at the start of the reaction, so removing the necessity for accurate sample volumes. Samples were withdrawn from the reaction flask using a 50 cm³ bulb pipette from which the tip had been removed to facilitate a quick delivery.

For the nitrations at 75 °C, sealed tubes were used instead of volumetric flasks because of possible losses due to evaporation and expansion of the contents. A solution of the aromatic substrate and 1,3-dinitrobenzene in H₂SO₄ (*ca.* 8 cm³) was

Table 1. Conditions for gas chromatographic analysis

Substrate	Component	Response factor ^a	Retention time(s)	Column	Temp.(°C)
1,3,5-Trichloro-2-nitrobenzene	1,3,5-Trichloro-2-nitrobenzene	1.28	130	3% OV225 on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 35 ml min ⁻¹ ^b	140
	1,3-Dinitrobenzene ^c		350		
	1,3,5-Trichloro-2,4-dinitrobenzene	1.19	595		
1,3,5-Trichloro-2-nitrobenzene	1,3,5-Trichloro-2-nitrobenzene	1.195	200	3% OV225 on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 40 ml min ⁻¹ ^b	170
	1,2,3,5-Tetrachloro-4-nitrobenzene		230		
	1,3-Dinitrobenzene ^c		260		
	1,3,5-Trichloro-2,4-dinitrobenzene		380		
1,3,5-Trichloro-2,4-dinitrobenzene	1,3,5-Trichloro-2,4-dinitrobenzene	1.052 ^d	210	3% OV225 on Chromasorb W HP, 7 ft glass column, nitrogen flow rate 35 ml min ⁻¹ ^b	180
	1,3-Dinitrobenzene ^c		300		
	1,2,3,5-Tetrachloro-4,6-dinitrobenzene	1.027	410		
	1,3,5-Trichloro-2,4,6-trinitrobenzene	0.828	560		
1,2,3,5-Tetrachloro-4,6-dinitrobenzene	Carbon dioxide		250	Spherocarb, 9 ft stainless steel column, helium flow rate 60 ml min ⁻¹ ^e	150
	Nitrogen dioxide		360		

^a Response factor = area ratio (product/reference)/mole ratio (product/reference). ^b Pye 104 instrument fitted with a flame ionisation detector and LDC 308 computing integrator. ^c Reference standard. ^d An average value. The actual value used in each case was calculated from the expression $y = -0.037x^4 + 0.126x^3 - 0.168x^2 + 1.018x - 0.002$ where x = area ratio, y = mole ratio. ^e Pye 104 instrument with a katharometer detector; detector sensitivity 186 mA.

weighed into a 2 cm × ca. 18 cm glass tube, and a solution of nitric acid in H₂SO₄ (ca. 2 cm³) was weighed into a 1 cm × ca. 9 cm glass tube. One end of the smaller tube had previously been sealed by blowing a thin glass bubble which could easily be broken, the other end was sealed by drawing it out to a fine point which was then bent over. After placing the smaller tube inside, the large tube was also sealed. Several tubes were prepared in this manner and were placed in a bath thermostatted at 75 °C. After having been left to equilibrate for 30 min, they were shaken in order to break both ends of the smaller tube, so mixing the contents to give a homogeneous solution. The reaction was stopped at the required time by removing the tube from the bath and immersing it in ice-cold water.

For the nitrations at 150 °C, the sealed tube method was found to be unsuitable because the build-up of gaseous by-products created excessive pressure. An open system was used, which had been found previously to give results consistent with the sealed tube method in a study of the nitration of 1,3-dinitrobenzene.⁸ In this method the reaction vessel was a glass tube (in later runs two tubes joined in an X arrangement) fitted with a condenser, T-piece, and drying tube. The aromatic compound was introduced as a solution in acetic acid, and the solvent removed under vacuum, because it was found that acetic acid reacts with nitric acid at 150 °C under the conditions. The nitrating mixture was introduced, into the other limb if the X tube was used, and the mixture brought to 150 °C in a thermostat. The X tube was tipped to allow the nitrating mixture to run into the limb containing the aromatic. Samples were taken by elongated pipette, against a current of dry nitrogen, introduced through the T piece during this operation, and weighed.

Analysis of Samples from Kinetic Runs.—This was by g.l.c., using a Pye 104 instrument fitted with a flame ionisation detector and Laboratory Data Control 308 computing integrator. Peak areas were compared with those of the reference standard, the relative response factors having previously been determined. Details of g.l.c. conditions are in Table 1.

Calculation of Second-order Rate Coefficients.—These were calculated by dividing the observed first-order coefficients by the stoichiometric concentration of nitric acid, except for the runs at 75 °C where nitric acid was insufficiently in excess of aromatic for this method to be used, and the integrated form of the second-order rate equation was therefore employed.

Stability Experiments.—These were performed and analysed in the same way as the kinetic experiments, except that no nitric acid was used in the cases of TCNB and TCDNB.

Analysis of Gaseous Products formed from TetCDNB.—Two methods were used. In the first the gases were swept into a cold trap by a stream of helium and were later analysed by g.l.c. In the second, the gases were bubbled through sodium hydroxide solution *via* a sintered bubbler. Nitrogen was used as the flushing gas in this method.

The alkaline solution containing the dissolved gases was analysed for anions. Chloride was determined by the Volhard method.⁹ Carbonate was determined by titration with dilute hydrochloric acid, using the difference between the end-points obtained first with phenolphthalein and then with Bromophenol Blue indicators. The presence of sulphite was indicated by the evolution of a small quantity of sulphur dioxide on acidification of the scrubbing solution. Therefore as sulphite interferes with the carbonate determination, some experiments were performed in which an acidified potassium dichromate scrubbing solution was included before the sodium hydroxide solution to remove any sulphur dioxide from the gas stream.

A third modification of the scrubbing method was used in one case where the gases were bubbled through a solution of silver nitrate (0.1 mol dm⁻³) acidified with nitric acid (1 mol dm⁻³). This was done in order to determine whether the chloride anion originated from hydrogen chloride or chlorine.

¹⁵N-Enrichment Studies.—Samples of TCDNB and TetCDNB, extracted during their nitration with H¹⁵NO₃, were analysed by g.c.-m.s. The degree of ¹⁵N incorporation was estimated by comparing the molecular ion peak (*M*) and the

($M + 1$) peak with those from unenriched samples. Comparisons were based on peak areas calculated by a process of triangulation, as it was apparent that this was more accurate than a simple comparison of peak heights. The percentage

% incorporation =

$$\left[\frac{(M + 1)'}{M' + (M + 1)'} - \frac{(M + 1)}{M + (M + 1)} \right] \times 100 \quad (1)$$

incorporation was calculated using equation (1) where M' = area of molecular ion peak in sample and M = area of molecular ion peak in unenriched sample. In order to obtain greater accuracy in peak measurements, the mass range studied was restricted to *ca.* 10 mass units.

Results

Kinetics.—Good first-order kinetics for the nitration of TCNB in H_2SO_4 and oleum were observed at all of the temperatures studied. The second-order rate coefficients are listed in Table 2. The rate profile for the nitrations of TCNB at 25 °C is in Figure 1.

The Arrhenius parameters for the nitration of TCNB in the temperature range 25–75 °C have been calculated from the second-order rate coefficients and are listed in Table 3.

Second-order rate coefficients for the nitration of TCDNB in oleum at 150 °C are given in Table 2. The rate profile is plotted in Figure 2 together with that for the nitration of 1,3-dinitrobenzene for comparison.⁸ Good first-order kinetics were obtained over the acidity range studied, but at acidities lower than 6% oleum there were deviations from first-order kinetics, presumably because of the increasing extent of chlorination. If the nitration was carried out in oleum containing sulphur dioxide the rate was unaffected.

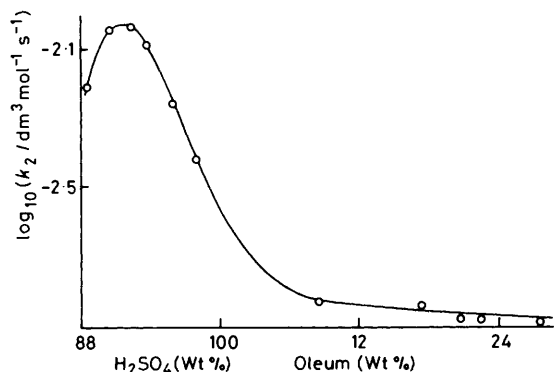


Figure 1. Rate profile for nitration of TCNB in aqueous H_2SO_4 and oleum at 25 °C

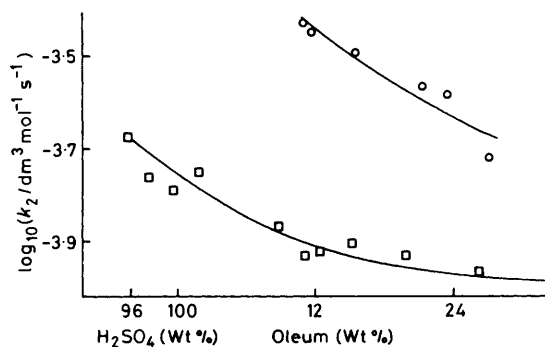


Figure 2. Rate profiles for nitration of TCDNB (circles) and *m*-dinitrobenzene (squares) in aqueous H_2SO_4 and oleum at 150 °C

An experiment was performed in which TCDNB was nitrated in 11.1% oleum with 0.970 mol dm^{-3} nitric acid at 150 °C in the presence of TCTNB (TCDNB and TCTNB were in approximately equimolar quantities, *ca.* 6×10^{-4} mol dm^{-3}). A value of 3.78×10^{-4} dm^3 mol $^{-1}$ s $^{-1}$ was obtained for the second-order rate coefficient which within experimental error is the same as that obtained without added TCTNB. (The product distributions were also identical when account was taken of the added TCTNB.)

Table 2. Second-order rate coefficients for the nitration of TCNB, TCDNB, and TetDCNB

H_2SO_4 (%)	$[HNO_3]/mol\ dm^{-3}$	$k_2/dm^3\ mol^{-1}\ s^{-1}$
TCNB, ^a 25.0 (±0.1) °C		
88.6	5.0×10^{-2}	6.2×10^{-3}
90.6	5.0×10^{-2}	9.0×10^{-3}
92.4	5.0×10^{-2}	9.2×10^{-3}
93.8	5.0×10^{-2}	8.2×10^{-3}
96.0	5.0×10^{-2}	5.5×10^{-3}
98.0	5.0×10^{-2}	3.2×10^{-3}
8.6% oleum ^b	6.9×10^{-2}	1.47×10^{-3}
17.6% oleum ^b	8.1×10^{-2}	1.45×10^{-3}
20.8% oleum ^b	7.9×10^{-2}	1.35×10^{-3}
22.6% oleum ^b	7.9×10^{-2}	1.34×10^{-3}
27.9% oleum ^b	8.0×10^{-2}	1.33×10^{-3}
TCNB, ^a 50.0 (±0.1) °C		
88.2	5.5×10^{-3}	3.2×10^{-2}
90.6	5.7×10^{-3}	8.1×10^{-2}
92.4	5.9×10^{-3}	8.9×10^{-2}
93.8	5.1×10^{-3}	8.1×10^{-2}
96.0	5.6×10^{-3}	6.0×10^{-2}
98.0	5.9×10^{-3}	3.4×10^{-2}
TCNB, ^a 75.0 (±0.1) °C		
88.2	2.9×10^{-3}	0.154 ^c
90.6	3.2×10^{-3}	0.43 ^c
92.4	2.9×10^{-3}	0.55 ^c
93.8	2.9×10^{-3}	0.46 ^c
96.0	2.5×10^{-3}	0.38 ^c
98.0	3.0×10^{-3}	0.26 ^c
TCDNB, ^d 150.0 (±0.2) °C		
6.2% oleum ^b	0.98	8.4×10^{-4}
11.1% oleum ^b	0.76	3.7×10^{-4}
11.9% oleum ^b	0.99	3.5×10^{-4}
15.6% oleum ^b	0.75	3.1×10^{-4}
21.3% oleum ^b	0.77	2.6×10^{-4}
22.1% oleum ^b	0.93	2.6×10^{-4}
23.5% oleum ^b	0.98	2.5×10^{-4}
26.9% oleum ^b	0.76	1.86×10^{-4}
TetDCNB, ^e 150.0 (±0.2) °C		
80.6	0.40	5.7×10^{-5}
85.2	0.25	3.2×10^{-4}
87.2	0.20	5.1×10^{-4}
90.6	0.053	3.0×10^{-3}
98.0	0.103	3.4×10^{-4}
98.0	0.20	3.5×10^{-4}
15.6% oleum ^b	0.48	6.7×10^{-5}
21.3% oleum ^b	0.50	8.4×10^{-5}
29.1% oleum ^b	0.50	7.1×10^{-5}

^a Initial concentration $1-4 \times 10^{-4}$ mol dm^{-3} . ^b Oleum strength is expressed as weight percent of 'excess' of sulphur trioxide. ^c Approximate concentrations are given as each value of k_2 is the mean of four experiments using slightly different concentrations. ^d Initial concentration 6×10^{-4} mol dm^{-3} . ^e Initial concentration 5×10^{-4} mol dm^{-3} .

Table 3. Arrhenius parameters for the nitration of TCNB determined over the temperature range 25.0–75.0 °C

H ₂ SO ₄ (%)	E _a /kJ mol ⁻¹	log ₁₀ (A/dm ³ mol ⁻¹ s ⁻¹)
88.2	58.3 ± 1.2	8.0
90.6	66.7 ± 2.8	9.6
92.4	71.9 ± 1.3	10.5
93.8	71.0 ± 3.0	10.3
96.0	73.3 ± 3.3	10.5
98.0	75.9 ± 1.1	10.8

Table 4. Yields of TCDNB from the nitration of TCNB or TCB

Temp. (°C)	H ₂ SO ₄ (%)	Yield (%) ^a
25.0 (±0.1)	90.6	97.5 ^b
25.0 (±0.1)	98.0	97.0 ^c
50.0 (±0.1)	96.0	98.5 ^b
50.0 (±0.1)	96.0	96.4 ^b
75.0 (±0.1)	93.8	100.6 ^b
75.0 (±0.1)	98.0	93.3 ^b
120.0 (±0.2)	98.0	88.2 ^{c,d}
120.0 (±0.2)	98.0	87.1 ^{c,d}
120.0 (±0.2)	98.0	86.8 ^{c,d}
120.0 (±0.2)	98.0	98.5 ^{c,e}
120.0 (±0.2)	98.0	97.7 ^{c,e}
120.0 (±0.2)	98.0	91.6 ^{c,f}
120.0 (±0.2)	98.0	97.7 ^{c,f}
120.0 (±0.2)	98.0	94.2 ^b
120.0 (±0.2)	98.0	97.4 ^b
120.0 (±0.2)	98.0	95.7 ^b
120.0 (±0.2)	98.0	96.0 ^b

^a After at least 10 half-lives for nitration. ^b Starting material was TCNB. ^c Starting material was TCB. ^d H₂SO₄ solution of TCB kept separate from the nitric acid until the temperature had equilibrated. ^e Nitric acid present with the TCB in the H₂SO₄ solution.

The instability of TetCDNB in solutions of nitric acid in sulphuric acid–oleum at 150 °C is due to a nitration process. This can be seen from the rate profile which has the characteristic shape of a nitration rate profile, with the maximum rate coefficient occurring at ca. 91% H₂SO₄. The reaction is first order in nitric acid. The second-order rate coefficients for this nitration are listed in Table 2.

Product Studies.—The only product detected from the nitration of TCNB in H₂SO₄ was TCDNB, the yield of which was slightly less than quantitative. These yields are shown in Table 4. Nitration at 25 °C in oleum gave also a very small amount (<4%) of 1,2,3,5-tetrachloro-4-nitrobenzene. This was identified by g.c.–m.s. followed by comparison with an authentic sample.

At 25, 50, and 75 °C the yield of TCDNB was independent of whether the starting material was TCB or TCNB, but at 120 °C there was a distinct reduction in yield when TCB was used, if it was present in the H₂SO₄ solution without any nitric acid during the warm-up period. This was shown to be due to sulphonation.⁸ If the H₂SO₄ solution containing the aromatic were mixed with the nitric acid when cold, so allowing nitration to occur during the warm-up period, or alternatively if the aromatic were isolated from both acids until the temperature had equilibrated, then the yield was essentially the same as when the starting material was TCNB.

The nitration of TCDNB gives a mixture of TCTNB and TetCDNB. The proportions vary with acidity, lower acidities favouring the production of TetCDNB. Yields are in Table 5, but particularly in the dilute oleums they are probably low due to decomposition of TetCDNB. The variation of product distribution with time at two acidities is illustrated in Figures 3 and 4.

Table 5. Acidity dependence of formation of TetCDNB in the nitration of TCDNB^a at 150.0 (±0.2) °C

Oleum (%)	Yield of TetCDNB (%) ^b
5.9	11.7
8.9	6.3
11.9	7.8
16.4	7.9
22.9	4.9

^a [TCDNB] ca. 3 × 10⁻⁴ mol dm⁻³. ^b Yield after one half-life of nitration of TCDNB.

Table 6. Analysis of sodium hydroxide scrubber used to collect gaseous products from the nitration of TetCDNB at 150.0 (±0.2) °C

H ₂ SO ₄ (%)	[HNO ₃]/mol dm ⁻³	No. of equivalents ^a of Cl ⁻	No. of equivalents ^a of CO ₃ ²⁻ + SO ₃ ²⁻
90.7	~0.25	1.3	3.0
98.0	~0.5	1.7	8.4
98.0	~0.5	1.7	5.6
98.0 ^b	~0.5	—	3.7
98.0 ^b	~0.5	—	3.7

^a With respect to the amount of TetCDNB used. ^b Potassium dichromate scrubber included.

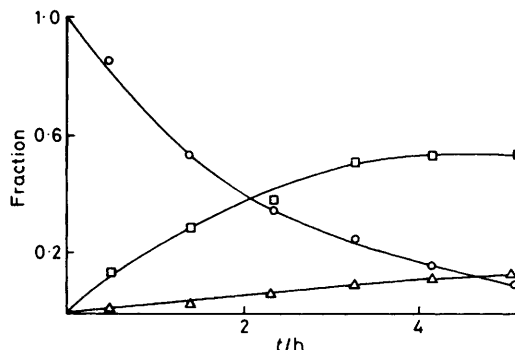
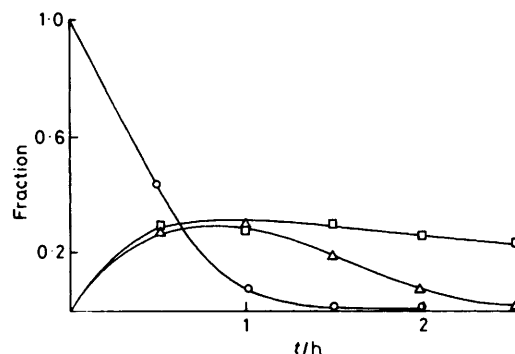
**Figure 3.** Nitration of TCDNB in 98% H₂SO₄ containing 0.49 mol dm⁻³ HNO₃ at 150 °C. Variation with time of the concentrations of TCDNB (circles), TetCDNB (triangles), and TCTNB (squares) expressed as fractions of the starting concentration of TCDNB**Figure 4.** Nitration of TCDNB in 21% oleum containing 0.48 mol dm⁻³ HNO₃ at 150 °C. Variation with time of the concentrations of TCDNB (circles), TetCDNB (triangles), and TCTNB (squares) expressed as fractions of the starting concentration of TCDNB

Table 7. Stability of TCTNB^a in oleum containing nitric acid at 150.0 (±0.2) °C

Oleum (%) ^b	[HNO ₃]/ mol dm ⁻³	Recovery (%) of TCTNB after 1 h	Recovery (%) of TCTNB after 3 h
98% H ₂ SO ₄	0.80	80.3	60.7
5.3	0.80	82.7	81.2
13.5	0.80	107.9	101.7
21.8	0.80	94.0	91.6
23.1	0.83	94.5	84.1
27.0	0.85	84.5	86.4
29.9	0.84	98.2	100.2
13.5	2.43	58.2	34.1
21.8	2.39	91.0	68.3
29.9	2.41	84.7	81.2

^a [TCTNB] ~ 4.9 × 10⁻⁴ mol cm⁻³.**Table 8.** Chlorine balance^a at the end of the reaction for the nitration of TCDNB at 150.0 (±0.2) °C

Oleum (%) ^b	Chlorine balance
6.2	0.65
11.1	1.01
11.1	0.99
11.9	0.93
15.6	0.97
15.7	1.00
19.0	1.00
21.3	1.04
21.3	1.05
23.5	0.99
23.5	1.08

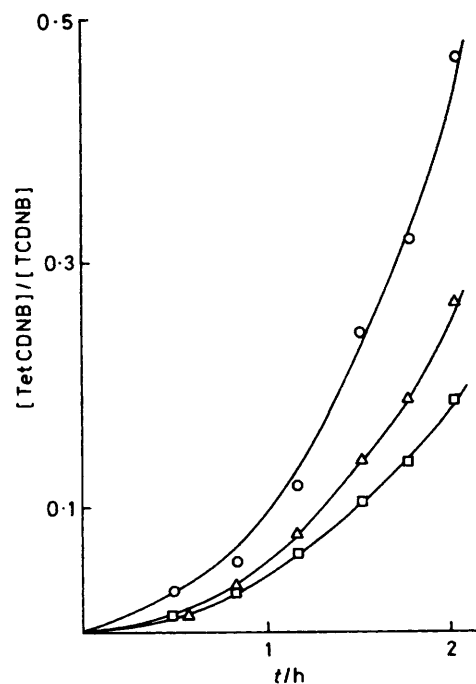
^a 1.0 is 100% balance. ^b Oleum strength is expressed as weight percent of 'excess' of sulphur trioxide.

The only detected products from the nitration of TetCDNB in H₂SO₄ at 150 °C were gaseous. The results from the experiments in which these were absorbed in sodium hydroxide solution are given in Table 6. When an acidified potassium dichromate scrubber was included to absorb any sulphur dioxide, as expected, the results from the carbonate analysis were lower owing to the absence of the interfering sulphite anion.

Mass spectrometric analysis of the gases collected in the cold trap clearly indicated the presence of carbon dioxide (ca. 4 mol. equiv. with respect to the amount of TetCDNB), together with a small amount (ca. 5% of the amount of carbon dioxide) of a product with an *m/e* value of 30. This molecular mass corresponds with that of nitric oxide, but it could also be due to nitrogen dioxide as this compound gives only a very weak molecular ion.

To summarise, it appears that the decomposition resulting from the nitration of TetCDNB produces ca. 4 mol. equiv. carbon dioxide, ca. 2 mol. equiv. hydrogen chloride, and small amounts of sulphur dioxide and nitric oxide or nitrogen dioxide.

Capture experiments, in which TCDNB was nitrated in the presence of DNB, resulted in a reduction in the proportion of TetCDNB produced, with larger quantities of DNB producing a greater reduction. This is illustrated by the plots shown in Figure 5 where the ratio of TetCDNB to TCDNB is plotted against time. As the acidity and nitric acid concentration were the same in each case, these graphs are directly comparable with each other. G.c. analysis of the reaction mixture showed there to be a product present, which was shown by g.c.-m.s. to have a molecular weight corresponding to dinitrochlorobenzene, pre-

**Figure 5.** Nitration of TCDNB in 11% oleum containing 0 (circles), 1 (triangles), or 2 (squares) molar equivalents of *m*-dinitrobenzene. Variation with time of the ratio of concentrations, [TetCDNB]/[TCDNB]

sumably the 3,5-isomer [*m/e* 205(3%), 204(35), 203(5), 202(100), 188(3), 186(11), 168(10), 158(13), and 156(38)].

Stabilities of the Aromatic Compounds.—TCTNB, TCDNB, TCTNB, and TetCDNB are stable under the conditions of the experiments, in the absence of nitric acid. In the presence of nitric acid, TetCDNB is nitrated, as previously described, and TCTNB shows signs of decomposition in H₂SO₄ and in low concentrations of oleum, but at a much slower rate than TetCDNB (Table 7).

Chlorine Balance.—The total amount of chlorine present in the three aromatic compounds TCDNB, TetCDNB, and TCTNB towards the end of the nitration of TCDNB can be compared with that present in TCDNB at the beginning of the reaction. This can be done by taking the sum of the amounts of the three compounds, in the case of TetCDNB multiplying the amount by 4/3 to take into account the four chlorine substituents. It is found that towards the end of the reaction a good chlorine balance is obtained, that is to say that the total amount of chlorine in the three aromatic compounds is equal to that present in the TCDNB at the start of the reaction. This is not true at low acidities because of the decomposition of TetCDNB.

The chlorine balances observed at several acidities are shown in Table 8.

H¹⁵N₃ Studies.—Following the nitrations of TCDNB using ¹⁵N-labelled nitric acid, the degree of ¹⁵N-incorporation in both the TCDNB and TetCDNB produced was determined from the mass spectra which were obtained by g.c.-m.s. studies (Table 9). The same method was used for the ¹⁵N-incorporation experiments in which TetCDNB was itself nitrated using ¹⁵N-labelled nitric acid.

Table 9. ^{15}N -Incorporation during the nitration of TCDNB with labelled nitric acid at $150.0 (\pm 0.2)^\circ\text{C}$

Oleum (%)	t/min	% Incorporation in TCDNB	% Incorporation in TetCDNB
2.8 ^a	20	0.5	
	40	0.3	3.2
	60	0.9	3.6
	80	0.8	3.4
	100	0.4	4.6
18.7 ^b	121	0.9	4.4
	45	0.6	
	91	1.4	2.7
	134	2.9	4.2
	180	4.7	4.2
28.0 ^c	226	5.1	5.7
	278	6.1	6.0
	55	0.8	6.0
	101	1.6	6.0
	156	4.0	5.8
	198	5.0	
	253	5.5	5.7
	302	6.3	6.6

^a $[\text{H}^{15}\text{NO}_3]$ 0.29 mol dm⁻³. ^b $[\text{H}^{15}\text{NO}_3]$ 0.43 mol dm⁻³. ^c $[\text{H}^{15}\text{NO}_3]$ 0.47 mol dm⁻³.

Table 10. ^{15}N -Incorporation during the nitration of TetCDNB with labelled nitric acid at $150.0 \pm 0.2^\circ\text{C}$

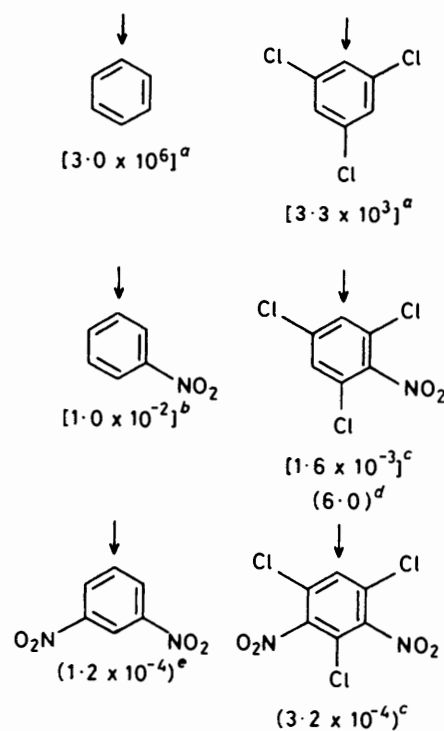
Acidity	t/min	% Incorporation in TetCDNB
97.5% H_2SO_4 ^a	33	1.1
	89	0.5
	150	1.2
	210	1.7
25.5% oleum ^b	93	1.4
	177	1.9
	279	2.8
	354	2.2

^a $[\text{H}^{15}\text{NO}_3]$ 0.186 mol dm⁻³. ^b $[\text{H}^{15}\text{NO}_3]$ 0.56 mol dm⁻³.

Discussion

Reactivities.—The rate profiles for nitration (Figure 1 and 2) show the decrease in rate coefficient with increase in acidity above that represented by 92% H_2SO_4 which is normally found with nitroaromatic compounds and has been attributed to the formation of hydrogen-bonded nitroaromatic species.¹⁰ There is no evidence for substantial protonation of the substrates under the conditions of the present experiments, and basicities reported for similar compounds¹¹ make it unlikely that it occurs. Although relative reactivities are rather medium dependent, an attempt is made in Scheme 1 to make some comparisons. It is noteworthy that three chlorine substituents in a 1,3,5-arrangement deactivate benzene by a factor of 900, but nitrobenzene only by a factor of 6. In *m*-dinitrobenzene, the effect of the three chlorine substituents is *activating* by a factor of 2.5. It is likely that the bulky chlorine substituents twist the nitro group out of conjugation with the ring reducing its ($-M$) deactivating properties, and also that the activating ($+M$) property of the chlorine becomes more significant in the more deactivated rings.¹⁰ The relative importance of these two effects cannot be judged.

Products.—The fact that, under the same conditions, TCB gives the same yield of TCDNB as does TCNB confirms that the first nitration step, $\text{TCB} \rightarrow \text{TCNB}$, is quantitative. The second step, $\text{TCNB} \rightarrow \text{TCDNB}$, is almost quantitative, but



Scheme 1. Numbers below each structure are (second-order rate coefficients for nitration)/dm³ mol⁻¹ s⁻¹, divided by the number of equivalent positions for nitration as indicated. Square-bracketed numbers are for nitration in 98% H_2SO_4 at 25°C . Numbers in parentheses are for nitration in 15% oleum at 150°C . ^a Estimated using relative rate coefficients for benzene, TCB, and *p*-dichlorobenzene³ (assumed independent of acidity). ^b Ref. 12. ^c This work (Table 2). ^d Estimated using the Arrhenius parameters for 98% H_2SO_4 (Table 3). ^e Ref. 8

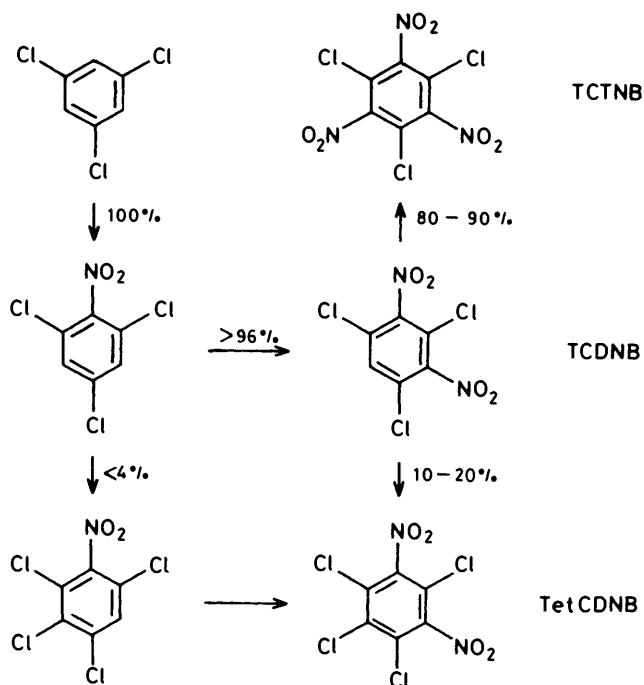
a very small amount of 1,2,3,5-tetrachloro-4-nitrobenzene has been detected under certain conditions (*vide supra*). When TCB is converted directly into TCTNB, a minor part of the TetCDNB by-product formed probably arises from nitration of 1,2,3,5-tetrachloro-4-nitrobenzene, but the major part must arise in the final nitration step, $\text{TCDNB} \rightarrow \text{TCTNB}$. This is summarised in Scheme 2.

The products of the nitration of TCDNB are TetCDNB and TCTNB, the major product being TCTNB. Both TCDNB and TCTNB could be considered as possible sources of the chlorinating agent, and both could be the species which react with the chlorinating agent, producing TetCDNB. The observation that nitration of TCDNB with TCTNB present converts the TCDNB at the same rate into the same product mixture as arises in the absence of TCTNB added initially confirms that it is TCDNB, not TCTNB, which both provides the chlorinating agent and reacts with it. The chlorinating agent may be captured, as the experiments with added 1,3-dinitrobenzene show (Figure 5). This additive reduces the yield of TetCDNB and leads to the formation of mono-, di-, and tri-chloro-derivatives of 1,3-dinitrobenzene.

All the chlorine present initially in TCDNB can be accounted for within experimental error in the TetCDNB and TCTNB produced and the small amount of TCDNB remaining towards the end of reaction (Table 8). (The deficit at the lowest acidity is due to decomposition of TetCDNB under these conditions.) It follows that each molecule of TCDNB which acts as a chlorinating source must provide all three of its chlorines in this way, each reacting subsequently with a molecule of TCDNB producing TCTNB.

The ^{15}N incorporation into TCDNB (Table 9), when H^{15}NO_3 is used for nitration, indicates the possibility of *ipso* attack at a nitro-substituted position. Consideration of all the evidence so far presented leads us tentatively to propose the mechanism shown in Scheme 3.

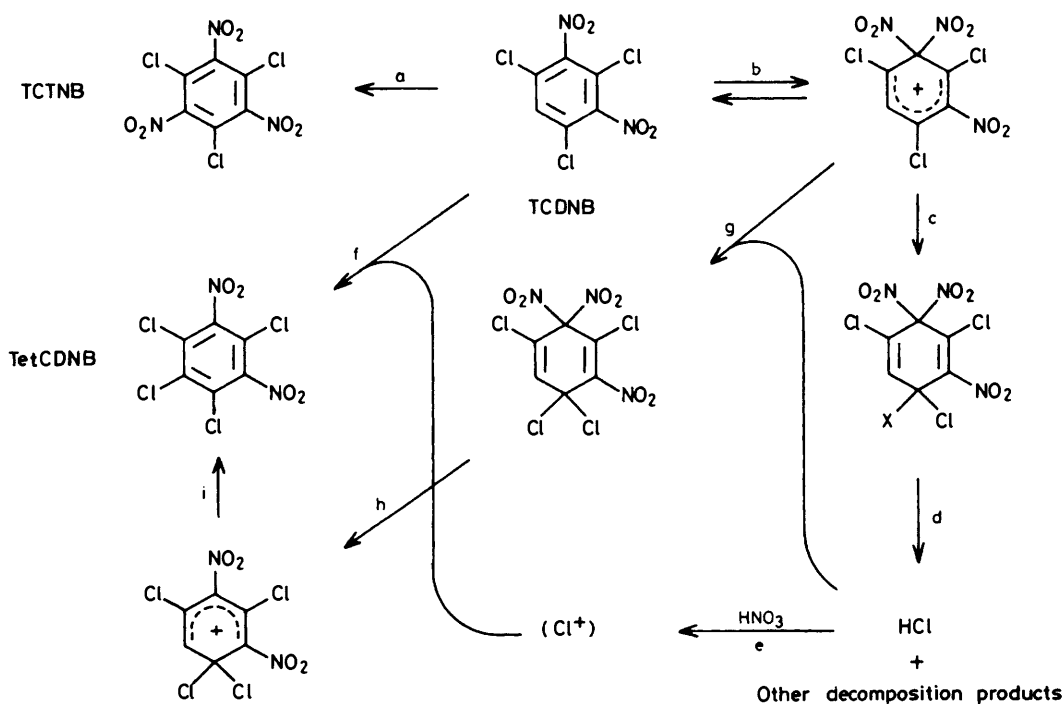
Nitration of TCDNB occurs predominantly at the unsubstituted position to give TCTNB (step a). There is also some attack by nitronium ion at the next least deactivated position,



ipso to nitro, to give a Wheland intermediate (step b). This step is to some extent reversible, giving rise when H^{15}NO_3 is used to incorporation of ^{15}N into the starting material TCDNB. The preferred fate of the Wheland intermediate is, however, nucleophilic capture (step c). The nucleophile X is unknown, perhaps hydrogen sulphate ion. The diene so formed is unstable and breaks down by an unknown sequence of steps (referred to as step d) giving up all its chlorine probably in the form of HCl. This is oxidised by nitric acid (step e) to an electrophilic chlorinating species (formally referred to as Cl^+). Reaction of this with TCDNB gives TetCDNB (step f).

Evidence in favour of the reaction proceeding largely as described by steps a—f comes not only from the fact that ^{15}N incorporation in TCDNB increases with time, but also from the variation of the extent of this incorporation with acidity (Table 9). At high acidities the concentration of nucleophilic species is relatively low, so that step c competes less effectively with the reverse of b, giving rise to relatively more ^{15}N incorporation and less TetCDNB both of which are observed.

The extent of ^{15}N -incorporation into the TetCDNB arising during the nitration of TCDNB (Table 9) is more difficult to explain; the TetCDNB is more highly labelled than TCDNB in the early stages of reaction. If the mechanism consisted only of steps a—f, TetCDNB would gain its label only in step f and the extent of labelling would always be less than that of the TCDNB remaining at the time. TetCDNB formed in the nitration of TCDNB does not gain much of its label subsequent to its formation, as is shown by the fact that in separate experiments (Table 10) on the nitration of TetCDNB itself the extent of incorporation was small. It seems that in the nitration of TCDNB there is another route to TetCDNB, additional to step f, in which TetCDNB arises from an already labelled intermediate. Such a route might be provided by steps g—i. In this sequence hydrogen chloride (or the small concentration of chloride ion in equilibrium with it) serves as an alternative nucleophile so that step g competes with step c. Acid-catalysed loss of nitrite ion¹³ (step h) and a 1,2-shift of chlorine (step i) then generates TetCDNB with some ^{15}N -incorporation.



In the proposed mechanism, it is recognised that step g is difficult to reconcile with the low concentration of HCl (deducible by difference from the data presented in Tables 3 and 4) throughout the reaction. Further investigation of this and related systems is planned.

A preliminary communication of some of this work has appeared.¹⁴

Acknowledgements

We thank the Ministry of Defence for a maintenance grant (M. A. P.), and Dr. P. Golding for helpful discussions.

References

- 1 Part 31, R. B. Moodie, K. Schofield, and A. R. Wait, *J. Chem. Soc., Perkin Trans. 2*, 1984, 921.
- 2 D. M. O'Keefe and F. T. Gurule, Report 1978, SAND-78-1001, Avail. NTIS; W. I. Quinlin, Report 1981, MHSMP-81-14, Avail. NTIS.
- 3 R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc. B*, 1970, 347.
- 4 E. H. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, 1940, **62**, 511.
- 5 V. S. F. Berckmans and A. F. Holleman, *Recl. Trav. Chim. Pays-Bas*, 1925, **44**, 851.
- 6 G. M. Bennett, J. C. D. Brand, D. M. James, T. G. Saunders, and G. Williams, *J. Chem. Soc.*, 1947, 474.
- 7 J. C. D. Brand, *J. Chem. Soc.*, 1946, 585.
- 8 M. A. Payne, Ph.D. Thesis, University of Exeter, 1982.
- 9 I. M. Kolthoff and E. B. Sandell, 'Textbook of Quantitative Inorganic Analysis,' Macmillan, London, 1964, 3rd edn.
- 10 K. Schofield, 'Aromatic Nitration,' Cambridge University Press, Cambridge, 1980.
- 11 M. Liler, 'Reaction Mechanisms in Sulphuric Acid,' Academic Press, London, 1971.
- 12 N. C. Marziano, M. Sampolini, F. Pinna, and A. Passerini, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1163.
- 13 C. Bloomfield, R. B. Moodie, and K. Schofield, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1793.
- 14 R. B. Moodie, M. A. Payne, and K. Schofield, *J. Chem. Soc., Chem. Commun.*, 1983, 233.

Received 19th November 1984; Paper 4/1958