Nitration and Oxidation of Substituted Benzaldehydes in Solutions of Dinitrogen Pentaoxide or Nitronium Trifluoromethanesulfonate in Nitric Acid

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The competition between oxidation to the corresponding benzoic acid and nitration in the aromatic ring of some substituted benzaldehydes has been probed by kinetic and product studies. Nitrodeformylation was not detected. 4-Carboxybenzaldehyde is nitrated but nitro- and dinitro-substituted benzaldehydes are predominantly oxidised. Rapid reversible *gem*-dinitrate formation occurs in concentrated solutions of dinitrogen pentaoxide in nitric acid, and the equilibrium extent of formation of dinitrato-(4-nitrophenyl)methane from 4-nitrobenzaldehyde is reported. Both species are oxidised in processes in which α-hydrogen loss is at least partially rate determining, as shown by kinetic hydrogen isotope effects. There is evidence for the intrusion of radical mechanisms in concentrated solutions of dinitrogen pentaoxide.

We previously reported on the kinetics[1] and products[2] of nitration of some aromatic compounds in the title media. In that work it was established that solutions of dinitrogen pentaoxide, but not of nitronium trifluoromethanesulfonate, could give rise to a radical mechanism in competition with the normal nitronium ion mechanism of nitration. We now report on the reactions of substituted benzaldehydes in the same media, with which substrates there is competition between oxidation and nitration. Nitrodeformylation,[3] which might have been expected in view of our observation of nitrodecarboxylation as a side reaction of some substituted benzoic acids,[2] has not been observed. The following substrates were chosen for investigation: 2-, 3- and 4-nitro, 2,4- and 2,6-dinitro, and 4-carboxybenzaldehyde. Of these 4-nitrobenzaldehyde was selected for detailed study. A feature of some interest is the formation, in relatively concentrated solutions of dinitrogen pentaoxide in nitric acid, of the *gem*-dinitrate ester, dinitrato-(4-nitrophenyl)methane, in rapid and mobile equilibrium with the parent aldehyde. Such *gem*-dinitrate formation has been reported previously only in the cases of acetaldehyde and trifluoroacetaldehyde reacting with dinitrogen pentaoxide in the absence of solvent.[4]

Results

The Kinetics of Nitration and Oxidation of Substituted Benzaldehydes.—4-Nitrobenzaldehyde. There was no detectable reaction when 4-nitrobenzaldehyde was kept for 17 h at 36 °C in pure nitric acid. Reaction occurred at convenient rates in solutions of nitronium trifluoromethanesulfonate or dinitrogen pentaoxide in nitric acid and kinetics were followed by monitoring the disappearance of the aldehydic ^{1}H NMR signal. Where this was obscured because of coalescence with the *gem*-dinitrate at the reaction temperature (*vide infra*), it was necessary, for each reading, to cool the NMR tube to −33 °C at which temperature the solution was still liquid and the exchange was slow enough for the peak to reappear. Observed first-order rate constants are given in Table 1.

2- and 3-Nitrobenzaldehydes. Kinetics of the disappearance of aldehyde in nitronium trifluoromethanesulfonate solutions were investigated and rate constants are given in Table 1.

4-Carboxybenzaldehyde. At ambient temperature this substrate reacted inconveniently quickly for kinetic study. The following observed first-order rate constants were determined for its reaction in 2 mol dm⁻³ dinitrogen pentaoxide solution at lower temperatures: 3.5×10^{-4} s⁻¹ at −2.5 °C and 8.7×10^{-4} s⁻¹ at 5 °C.

2,6-Dinitrobenzaldehyde. Kinetic results for this compound

are given in Table 1. Because the reaction was extremely slow in nitronium trifluoromethanesulfonate solution only one rate constant was determined. In concentrated solutions of dinitrogen pentaoxide however rate constants approached those observed for 4-nitrobenzaldehyde.

2,4-Dinitrobenzaldehyde. This substrate reacted very slowly indeed and kinetic information is restricted to the observation that after 12 h at 42 °C in a solution containing 3.5 mol dm⁻³ nitronium trifluoromethanesulfonate, there had been 28% reaction. The rate constant deduced from this single observation is in Table 1. In 4.0 mol dm⁻³ dinitrogen pentaoxide solution N_2O_5 decomposition was comparable in rate to the reaction under study and precluded kinetic investigation.

The Products of Reaction of Substituted Benzaldehydes.— These were studied with a view to investigating the competition between nitration and oxidation, and to establishing whether any nitrodeformylation was occurring.

2-Nitrobenzaldehyde. The oxidation/nitration ratio determined from the NMR spectra recorded during the kinetic runs was *ca.* 4:1. The overall yield was quantitative to the limits of NMR accuracy.

3-Nitrobenzaldehyde. The formal product of nitrodeformylation, 1,3-dinitrobenzene was detected by GC analysis following the reaction of this substrate in a solution containing 5.2 mol dm⁻³ dinitrogen pentaoxide in nitric acid. However the proportions of the products and the time of the reaction were consistent with this having been formed following oxidation to 3-nitrobenzoic acid, which is known to undergo some nitrodecarboxylation under the conditions.[2] There was no evidence of direct nitrodeformylation.

The oxidation/nitration ratio in the kinetic runs was *ca.* 3:2, and the overall yield, by NMR spectroscopy, was quantitative.

4-Nitrobenzaldehyde. Products are listed in Table 2. Bearing in mind the fact that 2,4-dinitrobenzoic acid is the product of oxidation followed by nitration, not nitration followed by oxidation, (the extent of oxidation of 2,4-dinitrobenzaldehyde during the time of the experiment would be negligible) it is clear that oxidation is the predominant reaction. In solutions of nitronium trifluoromethanesulfonate the overall yield is close to quantitative and oxidation accounts for at least 91% of the primary reaction. Nitration becomes more important when reaction is effected in dinitrogen pentaoxide solutions, and the overall yield of determined products is much diminished.

4-Carboxybenzaldehyde. NMR data indicated that this substrate underwent quantitative nitration, only, under the conditions of the kinetic experiments.

Table 1 Observed first-order rate constants k for the disappearance of substituted benzaldehydes from solutions of nitronium trifluoromethanesulfonate (stoichiometric concentrations S) or dinitrogen pentaoxide (stoichiometric concentration P) in nitric acid at 35 (± 0.5) °C[a]

2-Nitrobenzaldehyde		3-Nitrobenzaldehyde		4-Nitrobenzaldehyde				2,6-Dinitrobenzaldehyde				2,4-Dinitrobenzaldehyde	
S/mol dm^{-3}	k/10^{-5} s^{-1}	S/mol dm^{-3}	k/10^{-5} s^{-1}	S/mol dm^{-3}	k/10^{-5} s^{-1}	P/mol dm^{-3}	k/10^{-5} s^{-1}	S/mol dm^{-3}	k/10^{-5} s^{-1}	P/mol dm^{-3}	k/10^{-5} s^{-1}	S/mol dm^{-1}	k/10^{-5} s^{-1}
2.1	13	3.3	6.8	2.1	4.6	2.0	3.5	4.1	1.0	2.0	1.8	3.5[e]	0.76
2.6	15	3.7	7.8	2.6	5.6	3.8	28			2.9	7.4		
				3.4	9.1	3.8[c]	17			4.0	24		
				3.7	11.0	4.4	33			5.2	59		
				4.1	10.7	4.9	32, 40			5.2[d]	20		
				3.1[b]	31	4.9[c]	14, 21						
				3.1[b,c]	19	5.2	42						
						5.2[d]	17						

[a] Unless otherwise stated. [b] 45 (± 0.5) °C. [c] Substrate was α-deuterio-4-nitrobenzaldehyde. [d] 25 (± 0.5) °C. [e] 42 (± 0.5) °C. Rate constant determined from a single measurement (see text).

Table 2 Yields[a] from reaction of 4-nitrobenzaldehyde in solutions of nitronium trifluoromethanesulfonate (stoichiometric concentration S) or dinitrogen pentaoxide (stoichiometric concentration P) in nitric acid at 35 (± 0.2) °C

	S/mol dm^{-3}	P/mol dm^{-3}			
Product	3.3	3.8	4.9	3.8[b]	4.9[b]
4-Nitrobenzoic acid	82	49	43	56[b]	43[b]
2,4-Dinitrobenzoic acid	9	2	6	b	b
2,4-Dinitrobenzaldehyde	c	3	6	4[b]	8[b]
Overall yield	91[d]	53	55	60[b]	51[b]

[a] Yields expressed as a percentage of the amount of reacted substrate at the time of analysis. Reaction time was ca. two half-lives. Yields were determined by GC unless otherwise stated. [b] Substrate was α-deuterio-4-nitrobenzaldehyde and yields were by NMR. The yields of 2,4-dinitrobenzaldehyde and of 2,4-dinitrobenzoic acid could not be determined separately by NMR. The combined yield is given against the aldehyde. [c] Trace amount evident. [d] This yield was determined by GC but by NMR it appeared to be quantitative.

Table 3 Equilibrium ratios K of α-deuteriodinitrato-(4-nitrophenyl)-methane- to α-deuterio-4-nitrobenzaldehyde at $-33.0(\pm 0.5)$ °C in solutions of dinitrogen pentaoxide (stoichiometric concentration P^a) in nitric acid

| P/mol dm^{-3}	K
3.8	0.45
4.4	1.44
4.9	4.26

[a] As determined at room temperature before cooling for the NMR measurement.

2,4- and 2,6-Dinitrobenzaldehydes. GC and NMR data point to quantitative oxidation to the respective benzoic acids in both media.

gem-Dinitrate Formation in Concentrated Solutions of Dinitrogen Pentaoxide in Nitric Acid.—The ^{1}H and ^{13}C NMR spectra (Figs. 1 and 2) are consistent with the formation of dinitrato-(4-nitrophenyl)methane (the gem-dinitrate of 4-nitrobenzaldehyde) in equilibrium with the parent aldehyde [eqn. (1)]. Interconversion is sufficiently rapid to give coalesced signals at room temperature, but the separate resonances are apparent when solutions are cooled to -33 °C. The ^{15}N NMR spectrum of a solution of the substrate in ^{15}N-enriched solvent (Fig. 3) showed a doublet in the correct region for organic
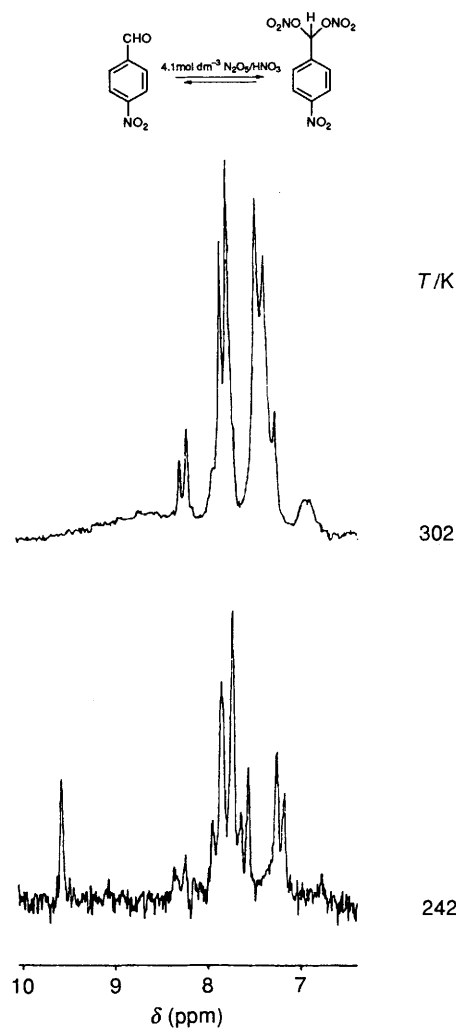
Fig. 1 ^{1}H NMR spectra of 4-nitrobenzaldehyde in 4.1 mol dm^{-3} N_2O_5/HNO_3 at the temperatures shown

nitrates and the $^3J_{NH}$ coupling constant (3.7 Hz) is similar to that previously observed in cyclohexadienyl nitrates.[2]

$$NO_2C_6H_4CHO + N_2O_5 \rightleftharpoons NO_2C_6H_4CH(ONO_2)_2 \quad (1)$$
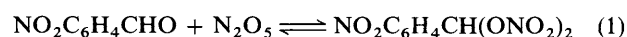
For determination of the equilibrium ratio of gem-dinitrate to parent aldehyde, it was convenient to use the α-deuteriocompound to avoid interference from the signal for the methane proton of the gem-dinitrate. Values of this ratio are in Table 3.
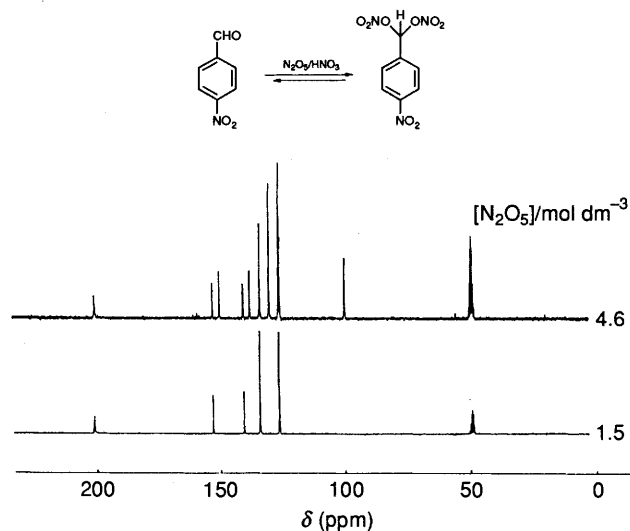
Fig. 2 ^{13}C NMR spectra of 4-nitrobenzaldehyde at 240 K in dinitrogen pentaoxide solutions for the concentrations shown
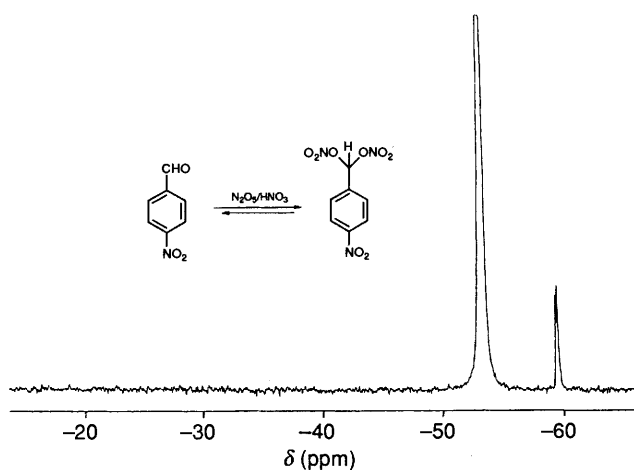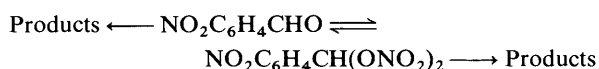

Fig. 3 ^{15}N NMR spectrum of 4-nitrobenzaldehyde in ^{15}N-labelled 4.6 mol dm^{-3} dinitrogen pentaoxide solution, showing the peaks due to the nitrate groups in the gem-dinitrate at δ ca. -59 ppm

A curious feature, and one which we are unable to explain, is the extraordinarily steep dependence of this ratio on the stoichiometric concentration of dinitrogen pentaoxide. Solutions at this lower temperature were, by visual inspection, homogeneous and liquid, and gave sharp NMR spectra.

2,6-Dinitrobenzaldehyde did not form detectable quantities of gem-dinitrate even in concentrated solutions of dinitrogen pentaoxide. Both 4-carboxy- and 2,4-dinitro-benzaldehydes showed evidence of gem-dinitrate formation. This point was not investigated with the other substrates.

Discussion

Comparison of the kinetics of reaction of 4-nitrobenzaldehyde in dinitrogen pentaoxide and nitronium trifluoromethane-sulfonate solutions (Fig. 4) reveals that substantial conversion to the gem-dinitrate (Table 3) leads to enhanced rates, and this suggests the following outline mechanism. The aldehyde and the

$$\text{Products} \longleftarrow \text{NO}_2\text{C}_6\text{H}_4\text{CHO} \rightleftharpoons$$
$$\text{NO}_2\text{C}_6\text{H}_4\text{CH(ONO}_2)_2 \longrightarrow \text{Products}$$

gem-dinitrate both undergo concurrent nitration and oxidation. Nitration is the minor reaction under all conditions, as the yield
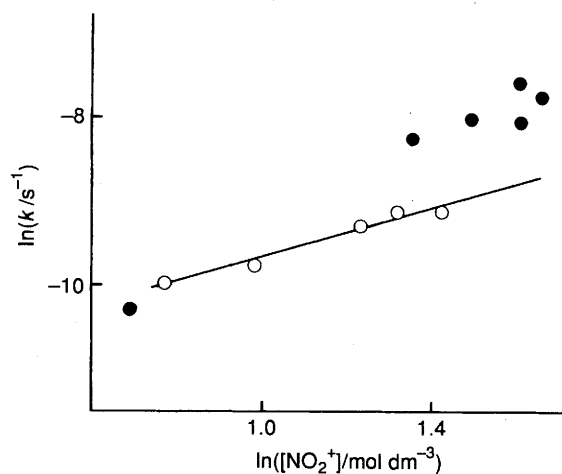

Fig. 4 Rate profiles for the disappearance of 4-nitrobenzaldehyde in solutions of nitronium trifluoromethanesulfonate ($\bigcirc$) and of dinitrogen pentaoxide ($\bullet$) at 35 °C

of 2,4-dinitrobenzaldehyde indicates (Table 2). It is likely that it is effected entirely by the normal nitronium ion mechanism, except possibly at high concentrations of N$_2$O$_5$. Here a small contribution from a radical mechanism with cyclohexadiene formation similar to that previously[2] observed may be indicated by the observation of weak emission signals (not eventually evident in absorption) in both the aliphatic and aromatic nitro regions of the ^{15}N NMR spectrum when labelled, saturated N$_2$O$_5$ solution was used.

Oxidation, the major reaction, involves removal of α-hydrogen from either the aldehyde or the gem-dinitrate in steps which, the kinetic hydrogen isotope effects (Table 1) demonstrate are at least partially rate-determining. The rate profile (Fig. 4) indicates that the reaction of the gem-dinitrate is the more facile. Whatever process is responsible for the loss of yield at high concentrations of dinitrogen pentaoxide probably also involves at least partially rate-determining α-hydrogen removal from the gem-dinitrate, because the loss of yield is similar with labelled and unlabelled substrate. It seems possible that the reaction of the gem-dinitrate starts with α-hydrogen atom abstraction by a radical species. The reaction of the aldehyde on the other hand could be one of hydride ion abstraction by nitronium ion. Such a reaction would be strongly inhibited by electron withdrawing substituents, and an indication that this is the case comes from a comparison of the reactivity of 2-nitro and 2,4-dinitrobenzaldehydes in nitronium trifluoromethanesulfonate solutions (Table 2); both substrates are predominantly oxidised and despite differences in temperature and nitronium ion concentration it is clear that the introduction of the 4-nitro group is severely deactivating, perhaps by 100-fold.

It is not necessarily the case that the hydride ion is abstracted from the aldehyde directly, as that would lead to the formation of a benzoyl cation bearing electron withdrawing substituents which would be a very high energy intermediate. It is possible that there is present an undetectably small concentration of the mono-nitrate ester of the gem-diol, which would be formed by the formal addition of nitric acid, and that this is the species from which hydride ion abstraction occurs. Hydride removal from complexes formed from the gem-diol has been suggested for aldehyde oxidations with other reagents.[5]

2,6-Dinitrobenzaldehyde is quantitatively oxidised to the corresponding acid in both media. There is no detectable gem-dinitrate formation in N$_2$O$_5$ solutions (the extent of its formation would be expected to be smaller for steric reasons) but the steep dependence of the rate constant on [N$_2$O$_5$] (the log–log plot of rate constant against [N$_2$O$_5$] has a slope of 3.5)

and the rate enhancement over solutions of nitronium trifluoromethanesulfonate suggests that in N_2O_5 reaction occurs through a small equilibrium concentration of the *gem*-dinitrate. That the yield of the benzoic acid is quantitative may indicate that, following α-hydrogen atom removal from the *gem*-dinitrate, reactions other than elimination of NO_2 (to give the benzoyl nitrate and thence the benzoic acid) are sterically more inhibited than they are with the 4-nitro analogue.

Relative Reactivities amongst the Aldehydes.—Comparisons amongst substrates in solutions of dinitrogen pentaoxide is difficult since the extent of *gem*-dinitrate formation varies from substrate to substrate and there is also the incursion of radical mechanisms of nitration at high $[N_2O_5]$ to be considered. Results in solutions of nitronium trifluoromethanesulfonate are far easier to compare. Taking the rate of oxidation of 4-nitrobenzaldehyde to be 1, that of 3-nitrobenzaldehyde is *ca.* 0.4, that of 2-nitrobenzaldehyde *ca.* 2, that of 2,6-dinitrobenzaldehyde *ca.* 0.1, and that of 2,4-dinitrobenzaldehyde *ca.* 0.03. This pattern is similar to that for ring nitration, as might be expected if the rate determining step involves the removal of a hydride ion from the aldehyde or some other intermediate. The substituent effects on oxidation are rather less than those on nitration, hence nitration dominates in dilute N_2O_5/HNO_3 in the reaction of carboxybenzaldehyde, though, relative to 4-nitrobenzaldehyde, this substrate is probably activated to both processes.

Experimental

Materials.—The following materials were recrystallised from commercially available reagents: 4-nitobenzaldehyde, 4-nitrobenzoic acid, 2,4-dinitrobenzaldehyde, 2,4-dinitrobenzoic acid, 2,6-dinitrobenzoic acid, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-carboxybenzaldehyde and 1,4-dinitrobenzene. 2,6-Dinitrobenzaldehyde was washed with aqueous sodium hydrogencarbonate before use. Methyl 4-nitrobenzoate, methyl 2,4-dinitrobenzoate, and methyl 2,6-dinitrobenzoate were prepared by the addition of a purified sample of the relevant acid to excess diazomethane in AR diethyl ether, and, after the removal of the solvent, were used without further purification. Anhydrous nitric acid, dinitrogen pentaoxide and nitronium trifluoromethanesulfonate were prepared as described previously.[1,6] Diazomethane was made by a standard preparation.[7]

α-Deuterio-4-nitrobenzaldehyde. The synthetic pathway for this substrate is shown in the Scheme.
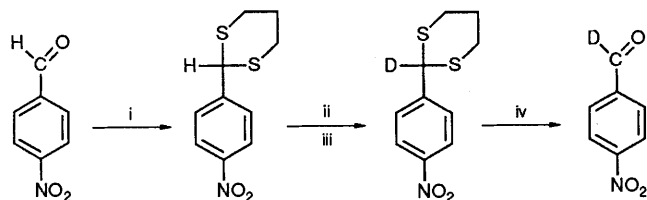
Scheme *Reagents:* i, $HS(CH_2)_3$ SH, HCl; ii, KOBu^t; iii, DCl/D_2O; iv, HNO_3

To a solution of 4-nitrobenzaldehyde (4.0 g, 26.7 mmol) in trichloromethane (30 cm^3) was added propane-1,3-dithiol (3.0 cm^3, 28.0 mmol). Dry hydrogen chloride was bubbled rapidly into the mixture until it was saturated (after *ca.* 10 min). During this time the reaction vessel was kept at *ca.* 4 °C in an ice-water bath. The solution was then washed with 10% aqueous potassium hydroxide (30 cm^3), and water (30 cm^3). Trichloromethane was removed on a rotary evaporator, and the crude 2-(4-nitrophenyl)-1,3-dithiane was recrystallised from methanol to give yellow needles of pure product (m.p. 142 °C, lit.[8] 139–140 °C).

2-(4-Nitrophenyl)-1,3-dithiane (1.0 g, 4.13 mmol) in dried tetrahydrofuran (20 cm^3) was cooled to -70 °C and treated under nitrogen with a solution of potassium *tert*-butoxide in tetrahydrofuran (7.0 cm^3, 7.0 mmol). The addition was dropwise over ten min. After having stood for a further ten min, excess deuterium oxide was added and the solution was allowed to warm to room temperature. Deuterium chloride (20%) was added and the tetrahydrofuran removed on a rotary evaporator. The resulting suspension was extracted with dichloromethane three times and the crude solid 2-deuterio-2-(4-nitrophenyl)-1,3-dithiane, was obtained from the organic phase by the removal of the dichloromethane on a rotary evaporator. The NMR spectrum indicated at least 95% incorporation of deuterium at C(2).

The deuteriated dithiane (*ca.* 0.4 g) was treated with AR nitric acid (70%) at ambient temperature. The resulting brown solution was added to chilled water (20 cm^3) and extracted with dichloromethane. The organic phase was washed with aqueous sodium hydrogencarbonate (5%) and the dichloromethane removed on a rotary evaporator. The resulting solid, α-deuterio-4-nitrobenzaldehyde (m.p. 107–109 °C) was used without further purification. The NMR spectrum showed no signal at 9.8 ppm, suggesting at least 95% deuterium incorporation.

Kinetics of Reactions in Nitric Acid Solutions.—The method employed varied depending on the reaction to be studied.

Nitrations in solutions of nitronium trifluoromethanesulfonate. For the reaction of 4-nitrobenzaldehyde the method used was that described previously.[1] The other substrates were also studied by this method, except for α-deuterio-4-nitrobenzaldehyde, when the following technique was used: Roughly measured amounts of substrate and 1-chloro-2,4-dinitrobenzene (internal reference) were placed in a 2 cm^3 volumetric flask, which was then filled to the mark with a solution of nitronium trifluoromethanesulfonate (3.05 mol dm^{-3}) in nitric acid to give a solution of *ca.* 0.1 mol dm^{-3} in substrate. The flask was placed in a constant temperature bath at 45 °C, and after thermal equilibrium had been reached, an aliquot (0.1 cm^3) was withdrawn and added directly to 5% aqueous sodium hydrogencarbonate (10 cm^3). Subsequent aliquots were taken at determined intervals over the following two hours and quenched in the same way. The quenched solutions were extracted with dichloromethane, dried over magnesium sulfate and concentrated for GC analysis. The disappearance of substrate was followed and the appearance of 2,4-dinitrobenzaldehyde noted. A duplicate experiment with unlabelled 4-nitrobenzaldehyde was performed.

Nitrations in solution of dinitrogen pentaoxide. At low, and very high, dinitrogen pentaoxide concentrations, the previous method[1] was used. When both aldehyde and *gem*-dinitrate forms were present in appreciable amounts the following method was used: roughly weighed amounts of substrate and 1,3,5-trinitrobenzene were placed in an NMR sample tube (5 mm diameter). N_2O_5 solution was added to give a solution of substrate (*ca.* 0.2 mol dm^{-3}). The mixture was immediately cooled and placed in the probe (cooled to -33 °C) of a Bruker AM250 NMR spectrometer. The ^1H spectrum of the mixture was taken and the tube was then placed in a water bath at 35 °C. Thereafter, the tube was removed from the water bath at regular intervals, cooled, and the NMR spectrum obtained, and the tube replaced. The disappearance of the high field *gem*-dinitrate peaks was followed and integrations, rather than peak heights, relative to the reference were used. The first spectra taken of the reaction of α-deuterio-4-nitrobenzaldehyde were used for the determination of the equilibrium constants in Table 3. The ratios were calculated using two groups of aromatic proton signals. The higher field (δ *ca.* 7.2) group was due to the less deshielded pair of aromatic protons in the *gem*-dinitrate.

Table 4 GC data for analysis of products from the nitration and/or oxidation of 4-nitrobenzaldehyde and 2,6-dinitrobenzaldehyde. Conditions: 3% OV225 on Chromasorb W 100–120 mesh, column temperature 225 °C, N_2 flow rate 40 cm^3 min^{-1}, glass column 9' long with 4 mm bore.

Component of product mixture	Response factor	Retention time/s
4-Nitrobenzaldehyde	1.171	139
Methyl 4-nitrobenzoate	1.243	146
1-Chloro-2,4-dinitrobenzene[a]	1.000	253
2,4-Dinitrobenzaldehyde	0.705	385
Methyl 2,4-dinitrobenzoate	1.068	445
1,4-Dinitrobenzene[a]	1.000	179
Methyl 2,6-dinitrobenzoate	1.075	531

[a] Reference standard.

The lower field (δ ca. 7.7) group was due to the four aromatic protons in the aldehyde and the two low-field aromatic protons in the gem-dinitrate. The solutions were prepared at ambient temperature and cooled as soon as the aromatics had dissolved so that the amount of nitration or oxidation of the substrate was negligible. Once cooled, the NMR tube and its contents were kept at −78 °C, until they were placed in the probe of the spectrometer where they were left for ten minutes before the spectrum was taken.

Product Studies by GC.—Analysis for aldehydes. A method similar to that employed for the kinetics of α-deuterio-4-nitrobenzaldehyde in nitronium trifluoromethanesulfonate solutions was used, except that the minimum quantity of the solutions of aldehydes and reference standard in dichloromethane were taken (and thus only a tiny proportion of these components lost).

Determination of overall yields. The dichloromethane solution containing the aldehydes and the reference was stored at −25 °C. The aqueous phase from the first extraction was acidified to ca. pH 3 and extracted three times with diethyl ether. The organic phase was treated with diazomethane as before.[2] The diethyl ether was removed on a rotary evaporator and the solid residue was dissolved in dichloromethane. This solution was combined with the aldehyde solution and the combination was dried and concentrated down for analysis. GC conditions are given in Table 4.

Product and Equilibrium Studies by NMR Spectroscopy.— These were carried out as described previously[2] in the case of the ^{15}N and ^{13}C spectra, except that, for the low temperature work, a [$^2H_6$]acetone lock was used. No lock was used for the ^1H NMR studies (and the associated kinetic runs).

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