Nitration of styrenes by dinitrogen pentoxide in dichloromethane

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The reaction of 4-R-substituted styrenes (R = H, Me, Cl, CF_3, NO_2) with N_2O_5 in dichloromethane gives several products including 1-aryl-2-nitroethyl nitrate 1, 1,2-dinitro-1-arylethane 2, 1,2-dinitrato-1-arylethane 3 and 2-aryl-2-nitroethyl nitrate 4. When R = CF_3 or NO_2, 1–4 are the only products and 1 predominates at low temperature and/or high concentrations of N_2O_5. All are formed in part by radical pathways, as is shown by ^{15}N CIDNP effects. Evidence for ionic pathways is also presented. The kinetics of formation of 1 from 4-nitrostyrene at −45 °C are of high order in N_2O_5.

Introduction

In a previous paper[1] we reported on the kinetics and mechanism of the reaction of dinitrogen pentoxide, N_2O_5, with oxiranes, a reaction known[2] to provide a convenient route to some explosive compounds. Reactions of N_2O_5 with alkenes are also of interest because oxirane containing polymers, which are treated with N_2O_5 in the preparation of explosive materials, include double bonds in the polymer backbone[2] which might also react.

The reaction of N_2O_5 with alkenes is complex and gives rise to a variety of products prominent amongst which is the nitro nitrate product of addition across the double bond.[3] There is evidence that under certain circumstances and in the presence of excess nitrate, added to suppress the concentration of nitronium ion, *cis*-addition occurs.[3] Similarly, the reaction of styrene with acetyl nitrate is reported to give, amongst other products, the β-nitroacetate formed by *cis*-addition.[4]

However the variety of products which are observed both with acetyl nitrate and with dinitrogen pentoxide reacting with alkenes, argues against any single mechanism.

We report here on a study of the reactions of substituted styrenes. The effects of concentration, additives and temperature on relative yields have also been explored.

Results

Products from the reaction of *para*-substituted styrenes with N_2O_5

Examination by ^1H NMR spectroscopy of the products of the reaction of 4-nitrostyrene with N_2O_5 in dichloromethane at room temperature revealed signals consistent with four addition compounds (Table 1). Similar signals were observed for all the substituted styrenes. It will be shown below that the compounds responsible for these signals have structures **1–4**. These will be referred to as the β-nitro nitrate, the dinitro, the dinitrate and the α-nitro nitrate respectively.

The isolation and identity of **1** came from the low temperature reaction of 4-nitrostyrene with N_2O_5 in which only one product was observed. The mass spectrum, infrared spectrum and elemental analysis were consistent with a nitro nitrate addition product. The preparation was repeated with an ^{15}N enriched HNO_3–N_2O_5 mixture, and the proton coupled ^{15}N NMR spectrum of the product showed couplings only consistent with structure **1**, the β-nitro nitrate.

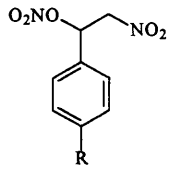
Compound **2** was isolated as a white solid when the products of reaction of 4-nitrostyrene with nitrogen dioxide were treated with chloroform. Mass, infrared, ^1H and natural abundance ^{15}N NMR spectra, and elemental analysis were consistent with the dinitro structure shown.

It has been reported previously[1] that substituted styrene oxides give rise to 1,2-dinitrato-1-arylethanes when treated with N_2O_5. The ^1N NMR and ^{15}N NMR spectra of the product of reaction of 4-nitrostyrene oxide with N_2O_5 were identical to that of compound **3** in the mixture formed by treating 4-nitrostyrene with N_2O_5 which identified **3** as the dinitrate.

Compound **4** was characterised by proton–carbon heteronuclear multiple quantum correlation NMR of the mixture of four compounds obtained from the reaction of 4-nitrostyrene with N_2O_5. The chemical shift of the CH carbon of **4** was closest to that of the corresponding carbon of the dinitro compound, and the chemical shift of the CH_2 carbon was closest to that of the dinitrate compound, indicating a nitro nitrate addition product but with the nitro and nitrate groups reversed compared with **1**. This was further substantiated by preparing the same mixture of products using 100% ^{15}N-labelled N_2O_5. The chemical

Table 1 ^1H NMR data for compounds **1–4** formed from 4-nitrostyrene

Compound	Chemical shifts	Coupling constants/Hz
1	7.63m dd, (H_a)	J_{ab} 5.95
	4.94, dd, (H_b)	J_{bc} 9.31
	4.80, dd, (H_c)	J_{ac} 2.19
2	6.42, dd, (H_d)	J_{de} 6.72
	5.67, dd, (H_e)	J_{ef} 10.15
	4.93, dd, (H_f)	J_{df} 2.00
3	6.28, q, (H_g)	J_{gh} 7.20
	4.85, m, (H_h)	
4	5.97, dd, (H_i)	J_{ij} 6.00
	5.45, dd, (H_j)	J_{ik} 8.00
	5.00, dd, (H_k)	J_{jk} 2.25



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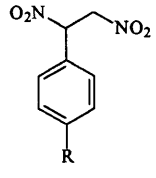

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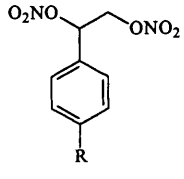

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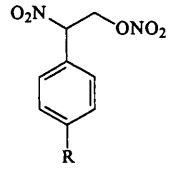

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Table 2 Effect of temperature: yields[a] of compounds of types **1–4** at various temperatures from 4-R-styrenes (0.1 M) and N_2O_5 (0.4 M) in dichloromethane

	R = Trifluoromethyl			
T/°C	**1**	**2**	**3**	**4**
40	19	18	33	30
30	32	18	27	24
20	56	11	20	13
10	69	7	15	9
0	91	1	6	1
−10	99	0	1	0
−20	100	0	0	0
	R = Nitro			
35	31	15	24	21
25	33	10	30	22
15	39	9	30	22
5	49	6	21	16
−5	91	0	9	0
−15	99	0	1	0
−25	100	0	0	0

[a] Yields are percentages based on the integrated α-CH proton signal compared to the total α-CH proton signal.

Table 3 Effect of concentration of N_2O_5 and of added nitric acid: yields[a] of compounds of types **1–4** at 20 °C from 4-R-styrenes (0.1 M) and N_2O_5 (0.1–2.0 M) in dichloromethane

	R = Trifluoromethyl				R = Nitro			
$[N_2O_5]$/mol dm^{-3}	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
0.1	27	26	24	23	14	24	30	32
0.1 (0.02)[b]	37	23	20	21	26	25	24	24
0.4	56	11	20	13	36	10	31	23
0.4 (0.04)[b]	56	11	19	14	49	10	24	18
0.04 (0.08)[b]	79	4	12	6	74	3	15	18
0.5	48	12	23	16	32	13	31	24
1.0	58	5	23	16	48	6	25	21
1.5	87	0	13	0	80	0	14	6
2.0	99	0	1	0	84	0	11	5

[a] See footnote to Table 2. [b] Concentration of added nitric acid/mol dm^{-3}. Where this figure is absent no nitric acid was added.

Table 4 Effect of additives: yields[a] of compounds of types **1–4** in the presence of added tetrabutylammonium nitrate (TBAN) (0.2 M) or nitrogen dioxide (0.2 M) at 20 °C from 4-R-Styrenes (0.1 M) and N_2O_5 (0.4 M) in dichloromethane

	R = Trifluoromethyl				R = Nitro			
Additive	**1**	**2**	**3**	**4**	**1**	**2**	**3**	**4**
None	56	11	20	13	36	10	31	23
TBAN	0	5	95	0	0	5	95	0
NO_2	51	38	7	4	50	39	6	5

[a] See footnote to Table 2.

shifts of the two peaks associated with compound **4** in the ^{15}N NMR were consistent with a nitro nitrate and had proton couplings consistent with the α-nitro nitrate structure **4**. Compounds **3** and **4** were thus identified in the mixtures; attempts to separate them chromatographically were unsuccessful.

Compounds with structures **1–4** were identified in the product mixtures from all the substituted styrenes by ^1H NMR spectroscopy as is now described.

Styrene. The nitration products (N_2O_5, 20 °C) were obtained as a yellow oil in which HPLC revealed at least 10 different compounds. Some of the peaks could be assigned to compounds of type **1–4**, and the aromatic region revealed clear evidence of concomitant aromatic nitration. Attempts to separate the mixture were unsuccessful. Varying the temperature had little effect on the number or ratio of products formed. The reaction was not investigated further.

4-Methylstyrene. The nitration products (N_2O_5, 20 °C) were obtained as a yellow oil in which HPLC and ^1H NMR spectroscopy revealed compounds of type **1–4** and at least three unknown compounds in small amounts with similar splitting patterns. There was evidence of aromatic nitration as well as alkene nitration. The number of products was reduced when the reaction temperature was lowered; at −60 °C the predominant product was the β-nitro nitrate **1** with additionally only compounds of types **2** and **3**, in small amount. The reaction was too fast to follow even at this temperature, the lowest attainable because of solvent freezing.

4-Chlorostyrene. At least nine products were present in the yellow oil obtained when the reaction temperature was 20 °C. At −60 °C reaction was too fast to follow but there were only four products and these were of types **1–4**, with **1** predominant.

4-(Trifluoromethyl)styrene and 4-nitrostyrene. These two substrates gave rise to compounds of type **1–4** only. No other products were observed and the overall yield appeared to be quantitative. Accordingly, a detailed investigation of the effects of concentration, temperature and additives on the relative yields of the four compounds was made and it was found that both substrates responded entirely similarly to these changes in conditions. In what follows, yields quoted are based on the integrated signal for the α-proton as a percentage of the total integrated α-proton signal.

Effect of temperature on relative yields.—The data are shown in Table 2. With both substrates there was a marked trend towards compound **1** as the temperature was reduced; at the lowest temperatures this was the only product and the yield appeared quantitative.

Effect of the concentration of N_2O_5 *on relative yields.*—The data are in Table 3. With both substrates there was a marked trend towards compound **1** as the concentration of N_2O_5 was increased.

Effect of the concentration of added HNO_3 *on relative yields.*—Nitric acid is a possible contaminant through hydrolysis of N_2O_5 by adventitious water and although every effort was made to keep the system as dry as possible it was of interest to see what the effect of such contamination might be. The results are in Table 2 and it is seen that added nitric acid causes a small increase in the relative yield of **1**. The effect is modest and encourages the belief that any small adventitious amounts of water not removed despite our precautions would not seriously have affected the results.

We have also studied in detail the reactions of the same substrates with nitric acid in the absence of N_2O_5; these results will be described in a subsequent publication.

Effect of added nitrogen dioxide on relative yields.—In this context the term nitrogen dioxide embraces also its dimer, N_2O_4, and no distinction is implied. Added nitrogen dioxide significantly enhances the relative yields of **1** and **2**, at the expense of **3** and **4** (Table 4).

Effect of added tetrabutylammonium nitrate (TBAN) on relative yields.—The formation of **1** and **4** was completely suppressed, and **3** was formed in near quantitative yield along with a small amount of **2** (Table 4). The same additive suppressed reaction at −45 °C completely.

Kinetics of the reaction of 4-nitrostyrene with N_2O_5

The reactions described are for the most part too fast for kinetic study. Only with 4-nitrostyrene, at −45 °C, with at least a 10 fold excess of N_2O_5 and using the minimum concentration of the substrate consistent with NMR investigation of the progress of reaction, was it found possible to obtain information about the kinetics. Under these conditions the reaction, which

Table 5 Observed first-order rate constants, k_{obs}, in the reaction of 4-nitrostyrene (0.02 M) with N_2O_5 in CD_2Cl_2 at −45 °C

$[N_2O_5]$/mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
0.196	37
0.196	24
0.176	20
0.162	13
0.152	8.2
0.152	7.2

proceeds to form **1** quantitatively and exclusively, had a first-order form over at least two half-lives. Observed first-order rate constants are in Table 5. The difficulty of obtaining good reproducibility at this low temperature and low substrate concentration is apparent from the results. Nevertheless they do show that the order in N_2O_5 is very high. This reduced the range of concentrations over which the measurements could be made and limited further the accuracy of the determination of reaction order. The order in N_2O_5 derived from the results is 5 ± 2.

Part of the object of this work was to compare the reactivity of alkenes and oxiranes towards N_2O_5. These results make possible for the first time the direct kinetic comparison of 4-nitrostyrene with 4-nitrostyrene oxide. The reported [1] activation parameters for the latter reaction, which is approximately second-order in N_2O_5, make possible the estimation of the first-order rate constant for reaction of 4-nitrostyrene oxide to form **3** in 0.2 M N_2O_5 at −45 °C of 1.3 × 10^{-4} s^{-1}, about 20 times slower than the reaction of 4-nitrostyrene under those conditions (Table 5). Of course the conclusion cannot be drawn that alkenes always react faster than oxiranes with N_2O_5 because the comparison is temperature, concentration and substituent sensitive.

^{15}N Chemically induced dynamic nuclear polarisation (CIDNP) effects

The reaction of 4-nitrostyrene with N_2O_5 containing 10% isotope excess of ^{15}N was monitored by ^{15}N NMR spectroscopy. Large CIDNP effects, indicative of radical processes, were observed during the first six minutes of reaction. Emission signals were seen at $\delta = 0.08$ and $\delta = -0.67$, and enhanced absorption signals at $\delta = -7.15$ and $\delta = -7.49$, all relative to external nitromethane. These signals disappeared completely after 6 min. Accumulation of the ^{15}N spectrum at the end of reaction showed that these four peaks were present at normal intensity and were attributable respectively to the α-nitro group of **4**, the α-nitro group of **2**, the β-nitro group of **1** and the β-nitro group of **2**. The experiment was repeated using 100% isotopically enriched $^{15}N_2O_5$. The same four CIDNP signals were seen but this time additionally two small transient enhanced emission signals were apparent at $\delta = -45.96$ and $\delta = -47.37$ relative to external nitromethane. These two signals disappeared after 4 min. The chemical shifts correspond to those of the two nitrato groups of the dinitrate **3**.

Discussion

Compounds of types **1**–**4** feature amongst the products of the reactions of all the styrenes with N_2O_5 and are the only products from 4-trifluoromethylstyrene and 4-nitrostyrene, with **1** predominating as the temperature is lowered. The reaction is too quick for convenient kinetic study and only 4-nitrostyrene, at the lowest practicable temperature and concentration, could be investigated in this way revealing that the reaction producing **1** is of high order in N_2O_5. All other information has to be gleaned from the effects of temperature, concentration and additives on relative yields. The dominance of **1** at low temperature suggests that its formation has a lower activation energy and correspondingly more negative entropy of activation than the reactions producing **2**–**4**. This observation is consistent with the molecular mechanism proposed by Stevens and co-workers.[3] However, the high order in N_2O_5 is not consistent with the molecular concerted addition, a mechanism which would be expected to be first-order in N_2O_5. Added tetrabutyl ammonium nitrate prevented reaction at low temperature, and favoured the dinitrate product **3** at room temperature. This suggests that the nitronium ion may be the reagent in the formation of **1**, its concentration being suppressed by the addition of nitrate [reaction (1)]. The high

$$NO_2^+ + NO_3^- \rightleftharpoons N_2O_5 \rightleftharpoons NO_2 + NO_3 \qquad (1)$$

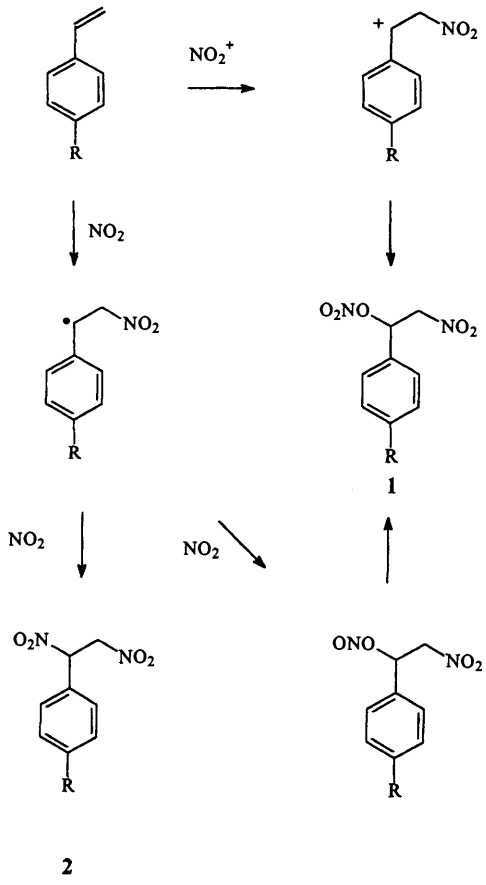
order in N_2O_5 may then reflect the need for dipolar solvation of ions in this non-polar medium. The enhanced yield of **1** on addition of nitric acid can be explained in the same way. The ionic route to **1** *via* nitronium then nitrate ion addition, though clearly indicated by the evidence described, cannot be the only one however. The CIDNP signals indicate that **1** is formed in part also by a radical pathway to which we return in a moment.

The reaction producing **2** appears to be a radical process and the CIDNP signals are consistent with the sequential addition of two NO_2 groups, first at the β-position and then, in the step which produces the nuclear polarisation and is responsible for the enhanced absorption from the β-nitro and the enhanced emission from the α-nitro, at the α-carbon. The addition of NO_2 to alkenes has been suggested to occur in this way and it has been shown that the observations are in accord with Kaptein's rules.[5] The radical route to **1** can be explained similarly, because the second addition of the NO_2 can occur through the oxygen to generate nitrite or the nitrogen. The β-nitro nitrite was not observed but would be expected to be oxidised rapidly to the β-nitro nitrate under the conditions. If the nuclear polarisation is carried over to the product, the polarisation observed is consistent with Kaptein's rules.[5]

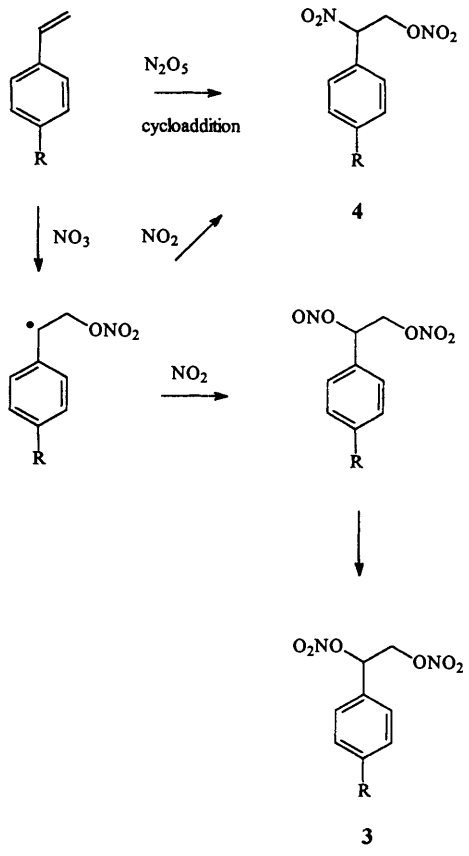
The addition of NO_2 enhances the yield of both **1** and **2** (Table 4) which is in agreement with this interpretation. The alternative, in which the initially formed β-nitro radical reacts at the α-position with the NO_3 radical in the polarisation-producing step to give **1** directly, may not be involved at all and certainly cannot be the only radical path to **1** because the concentration of NO_3 would be rendered extremely small by the presence of the added NO_2 [reaction (1)]. The mechanisms we propose for the formation of **1** and **2** are summarised in Scheme 1.

Formation of the dinitrate **3** and the α-nitro nitrate **4** are more difficult to explain. Both show CIDNP effects as described above so both are formed at least in part by radical processes. In a subsequent paper concerned with the reaction of the same set of substituted styrenes with nitric acid, in the absence of N_2O_5, we shall show that compounds **1**–**3** are again formed (along with another product) but **4** is absent even when NO_2 is added. This rules out any route to **3** or **4** based on initial attack of NO_2 on the alkene through its oxygen (with subsequent oxidation of nitrito group to nitrato group) and shows that the activated process of addition of NO_2 to the double bond can only occur through nitrogen. The ambident nature of the NO_2 radical appears to be manifested only in unactivated, radical combination, processes.

A key intermediate in the formation of **3** and **4** may well be the β-nitrato radical $RC_6H_4\dot{C}HCH_2ONO_2$, the formation of which we return to below. Reaction of this radical with either NO_3 or NO_2 could be the step producing the nuclear polarisation. Formation of **3** by α-addition of NO_3 would not account for the observed CIDNP signals for **3** because MOPAC calculations, for which we thank Dr J. P. B. Sandall, indicate



Scheme 1



Scheme 2

that the hyperfine coupling constants at the nitrogen atoms of these two radicals are both negative; thus according to Kaptein's rules, whatever the relative magnitudes of the *g* values, their combination would cause one signal to be in emission and the other in absorption, rather than both in emission as observed. However α-addition of NO_2 [the hyperfine coupling constant of which is positive and the *g* value (2.000 [7]) almost certainly lower than that of β-nitrato radical] would be consistent with Kaptein's rules with regard to the formation of both **3** and **4**. Addition through nitrogen would lead to **4** with the nitro group signal in emission as observed and addition of the NO_2 through oxygen followed by rapid oxidation of the first formed nitrito nitrate to the dinitrate should give both nitrato signals of **3** in emission, again as observed. The routes from the β-nitrato radical to **3** and **4** which would produce the observed polarisations are shown in Scheme 2.

The β-nitrato radical might be formed directly by combination of NO_3 with the alkene as shown in Scheme 2. Added NO_2 reduces the relative yields of **3** and **4** (Table 4) which on this hypothesis would be expected [see reaction (1)].

There remain some of our observations that are unexplained. These are: the failure of NO_2 to eliminate formation of **3** and **4** completely, the predominance of **3** but not **4** in the presence of added tetrabutylammonium nitrate and the increasing importance of **4** as the concentration of N_2O_5 decreases (Table 3). It is likely therefore that the processes shown are not the only mechanisms leading to the formation of either **3** or **4**. The last mentioned observation may mean that **4** is formed in part by the cycloaddition of N_2O_5 (Scheme 2). This reaction would be first-order in N_2O_5 and, because the competing reactions are of higher order, be more important at low concentrations of N_2O_5 as observed (Table 3). This is the mechanism previously postulated to explain the observations of *cis*-addition.[3]

Experimental

Materials

Nitrogen dioxide, sodium hydroxide, ethanol, magnesium sulfate, light petroleum, sodium chloride, 2-(*p*-nitrophenyl)-ethyl bromide, styrene oxide, styrene, 4-chlorostyrene, 4-methylstyrene, 4-(trifluoromethyl)styrene, phosphorus pentoxide, dimethyldichlorosilane and carbon tetrachloride were used without further purification. Dichloromethane was dried by continuous distillation from calcium hydride directly before use. Deuteriated dichloromethane and deuteriated chloroform for kinetic NMR experiments were dried by continuous distillation from phosphorus pentoxide in silanised glassware.[7]

4-Nitrostyrene

Sodium hydroxide pellets (13.71 g, 0.34 mol) were added to ethanol (200 ml), the solution was warmed to 40 °C and stirred for 2 h. To this solution 2-(4-nitrophenyl)ethyl bromide (10.00 g, 0.043 mol) was added and the stirring continued for a further 30 min, maintaining the temperature at 40 °C. The mixture was then poured into a saturated salt solution (40.00 g, 0.068 mol NaCl, in 200 ml of water) and the organic layer taken up in diethyl ether and dried over anhydrous $MgSO_4$. The 4-nitrostyrene was purified by column chromatography on flash silica, using 100% light petroleum (bp 60–80 °C) as the eluting solvent. The crude material was then recrystallised from light petroleum, giving 3.89 g of the compound (60%), mp 27 °C (lit.,[8] 28 °C); δ_H(250 MHz; $CDCl_3$) 8.15 (2 H, d, aromatic), 7.50 (2 H, d, aromatic), 6.75 (1 H, dd, CH), 5.87 (1 H, d, CH_2), 5.75 (1 H, d, CH_2).

Preparation of dinitrogen pentoxide

Dinitrogen pentoxide was prepared by the gas phase reaction of nitrogen dioxide and ozone.[1] The nitrogen dioxide was stored in a cooled reservoir containing phosphorus pentoxide. Upon warming it was combined with ozone as a 5–10% mixture with oxygen, which had been dried by passing it through phosphorus

pentoxide. The disappearance of the brown nitrogen dioxide gas indicated the formation of N_2O_5, which was passed through two drying tubes containing phosphorus pentoxide. The N_2O_5 was then collected as a white solid in a silanised[7] volumetric flask which was cooled in a dry ice–acetone bath. Immediately after the collection flask, a sulfuric acid bubbler was fitted to prevent the contamination of the collected N_2O_5. After collection the N_2O_5 was immediately placed in a dry glove box ready for use.

Preparation of 1-(4-nitrophenyl)-2-nitroethyl nitrate (1, R = NO_2)

1-(4-Nitrophenyl)-2-nitroethyl nitrate was prepared as described in the quenched method below. The concentrations of 4-nitrostyrene and N_2O_5 were 0.1 and 0.4 mol dm^{-3}, respectively, and the reaction temperature was −45 °C. The compound was obtained as a white crystalline solid in 99% yield; mp 124.9–125.6 °C; δ_H(250 MHz; $CDCl_3$) 8.3 (2 H, d, aromatic), 7.6 (2 H, d, aromatic), 6.7 (1 H, dd, CH), 4.9 (1 H, dd, CH_2), 4.6 (1 H, dd, CH_2); ν_{max}/cm^{-1} 2927 (C–H, str. aromatic), 1661 (O–NO_2 asymm. str.), 1552 (C–NO_2 asymm. str.), 1261 (O–NO_2 symm. str.); M^+ 257.0361. $C_8H_7N_3O_7$ requires 257.0284 (Found: C, 37.65; H, 2.81; N, 16.25. $C_8H_7N_3O_7$ requires C, 37.35; H, 2.72; N, 16.34%).

Preparation of 1-(4-trifluoromethylphenyl)-2-nitroethyl nitrate (1, R = CF_3)

This was prepared similarly. The compound was obtained as a yellow oil, in 98% yield; δ_H(250 MHz; $CDCl_3$) 7.75 (2 H, d, aromatic), 7.6 (2 H, d, aromatic), 6.6 (1 H, dd, CH), 4.8 (1 H, dd, CH_2), 4.7 (1 H, dd, CH_2); ν_{max}/cm^{-1} 2927 (C–H str aromatic), 1656 (O–NO_2 asymm. str.), 1563 (C–NO_2 asymm. str.), 900 (C–F str.); M^+ 280.0311. $C_9H_7F_3N_2O_5$ requires 280.1587 (Found: C, 38.39; H, 2.41; N, 9.98; F, 20.25. $C_9H_7F_3N_2O_5$ requires C, 38.57; N, 10.00; F, 20.36%).

Preparation of 1-(4-chlorophenyl)-2-nitroethyl nitrate (1, R = Cl)

This was prepared similarly except that the N_2O_5 concentration was 0.2 mol dm^{-3} and the reaction temperature was −50 °C. Analysis of the yellow oil by proton NMR spectroscopy showed that a number of products had been produced. The 1-(4-chlorophenyl)-2-nitroethyl nitrate was obtained by dissolving the reaction mixture in deuteriated chloroform from which a white solid was isolated in about 30% yield, mp 95.6–96.0 °C; δ_H(250 MHz; $CDCl_3$) 7.7 (2 H, d, aromatic), 7.6 (2 H, d, aromatic), 6.6 (1 H, dd, CH), 4.9 (1 H, dd, CH_2), 4.7 (1 H, dd, CH_2); ν_{max}/cm^{-1} 2923 (C–H str. aromatic), 1648 (O–NO_2 asymm. str.), 1268 (O–NO_2 symm. str.), 1566 (C–NO_2 asymm. str.), 713 (C–Cl str.); M^+ 246.6043. $C_8H_7ClN_2O_5$ requires 246.6043 (Found C, 38.94; H, 2.84; N, 11.36; Cl, 14.40. $C_8H_7ClN_2O_5$ requires C, 38.97; H, 2.87; N, 11.34; Cl, 14.13%).

Preparation of 1,2-dinitro-1-(4-nitrophenyl)ethane (2, R = NO_2)

4-Nitrostyrene (0.37 g, 2.5 × 10^{-3} mol) was dissolved in dry dichloromethane (25 ml). A finder Schlenk tube was then placed in a dry ice–acetone solution at −78 °C and nitrogen dioxide gas administered slowly from a gas cylinder. A white solid was formed (1.14 g, 0.24 mol). The solution of 4-nitrostyrene was then added, and the mixture allowed to warm up to room temperature (any pressure build-up was vented through the side arm) and allowed to stand for 2 h. It was noted that the initial solution was green. The reaction was then quenched in ice–water containing saturated aqueous sodium hydrogen carbonate; the organic layer was separated, dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow oil. This was analysed by NMR spectroscopy and HPLC and was shown to consist of three products. The 1,2-dinitro-1-(4-nitrophenyl)ethane was isolated as a white crystalline solid by dissolving the products in deuteriated chloroform, mp 95.9–96.2 °C; δ_H(250 MHz; $CDCl_3$) 8.36 (2 H, d, aromatic), 7.61 (2 H, dd, aromatic), 6.42 (1 H, dd, CH), 5.67 (1 H, dd, CH_2), 4.93 (1 H, dd, CH_2); $\delta_{^{15}N}$(300 MHz; [$^2H_6$]acetone) −0.831 (NO_2, primary), −4.865 (NO_2, terminal), −11.886 (NO_2, aromatic); ν_{max}/cm^{-1} 2926 (C–H str. aromatic), 1586 (C–NO_2 asymm. str. alkyl) 1517 (C–NO_2 asymm. str. aromatic), 1348 (C–NO_2 symm. str. alkyl), 1308 (C–NO_2 symm. str. aromatic); M^+ 241.05189. $C_8H_7N_3O_6$ requires 241.033485 (Found C, 40.25; H, 2.85; N, 16.53. $C_8H_7N_3O_6$ requires C, 39.84; H, 2.92; N, 17.42%).

Preparation of ^{15}N-labelled 1-(4-nitrophenyl)-2-nitroethyl nitrate

N_2O_5 (0.50 g, 4.6 × 10^{-3} mol) was weighed out into a silanised 20 ml volumetric flask and dry dichloromethane (*ca.* 15 ml) added. To this solution 10% ^{15}N-labelled anhydrous nitric acid (0.50 g, 7.0 × 10^{-3} mol) was added and the solution made up to the mark (giving an approximate ratio of 66:33 acid to N_2O_5). This solution was then added to a 30 ml volumetric flask containing 4-nitrostyrene (0.46 g, 3.14 × 10^{-3} mol) in dry dichloromethane (10 ml) giving a 4:1 ratio of nitrating agent to substrate. The flask was then placed in an insulated flask at −40 °C for 4 h. It was then quenched in ice–water containing an excess of saturated aqueous sodium hydrogen carbonate, the organic layer separated, dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a yellow solid. This was washed with aliquots (5 × 5 ml) of cold chloroform, to give the required product as a white solid in 60% yield. The ^{15}N NMR spectrum was recorded on a 300 MHz spectrometer in [$^2H_6$]acetone, with nitromethane as a reference standard; $\delta_{^{15}N}$(300 MHz, [$^2H_6$]acetone) −10.005 (NO_2, dd, $^3J_{NH}$ 4†), −52.998 (NO_3, d, $^3J_{NH}$ 3).

Preparation of ^{15}N N_2O_5

^{15}N-Labelled nitric acid (*ca.* 3 ml) was added slowly from a vented separating funnel to granulated zinc in a small three-necked flat bottomed flask to produce ^{15}N-labelled N_2O_4. A constant pressure was maintained in the reaction flask by the use of an attached syringe (20 ml). Once sufficient $^{15}N_2O_4$ had been produced, the gas was combined with ozone (as a 5–10% mixture with oxygen), and passed through phosphorus pentoxide. The N_2O_5 was then collected as described above.

Reaction of styrenes with N_2O_5

The quenched method. In all the following reactions, the amount of substrate and dry dichloromethane used were varied according to the amount of N_2O_5 produced. This avoided the need for weighing out the N_2O_5, which would increase the risk of water contamination and increase the time available for thermal decomposition. All substrate concentrations were 0.1 mol dm^{-3} and the N_2O_5 concentration was normally 0.4 mol dm^{-3}.

In a dry glove box, half the dry dichloromethane required for the reaction was injected into the flask containing the freshly prepared N_2O_5 (typically between 0.2 and 0.6 g). This was then removed from the glove box and placed in a thermally insulated temperature controlled bath at 20 °C and allowed to come to thermal equilibrium. The substrate, in the rest of the dichloromethane, was also placed in the temperature controlled bath at 20 °C prior to reaction. Once at thermal equilibrium, the solutions were taken into the glove box, mixed, the solution made up to the mark with dichloromethane and returned to the temperature controlled bath for the duration of the reaction, (typically 2 h). The reaction was then quenched in an excess of ice–water containing saturated aqueous sodium hydrogen carbonate. The mixture was shaken, the organic layer

† *J* Values are given in Hz.

separated, dried ($MgSO_4$) and the solvent removed under reduced pressure to yield the reaction products which were subsequently analysed by HPLC and NMR and IR spectroscopy.

Effect of varying temperature. The reactions were carried out in a similar manner. The reaction temperatures were varied using thermally insulated temperature controlled baths.

Effect of varying N_2O_5 concentrations. The reactions were carried out in a similar manner. The substrate concentrations were always 0.1 mol dm^{-3} and the reaction temperature was 20 °C. The concentration of the N_2O_5 was varied from 0.1 mol dm^{-3} to 2.0 mol dm^{-3}.

Effect of added nitric acid. The reactions were carried out in a similar manner. The substrate concentrations were always 0.1 mol dm^{-3}, the N_2O_5 concentration was 0.4 mol dm^{-3} and the temperature 20 °C. Nitric acid was added to the solution of N_2O_5 prior to mixing it with the substrate solution.

Effect of added nitrate salt. The reactions were carried out in a similar manner. The substrate concentrations were always 0.1 mol dm^{-3}, the N_2O_5 concentration was 0.4 mol dm^{-3}. Tetrabutylammonium nitrate was added to the solution of N_2O_5 prior to mixing it with the substrate solution. In all reactions the concentration of the tetrabutylammonium nitrate was 0.2 mol dm^{-3} and the temperature either 20 °C or −45 °C.

Effect of added nitrogen dioxide. The reactions were carried out in a similar manner. The substrate concentrations were always 0.1 mol dm^{-3}, the N_2O_5 concentration was 0.4 mol dm^{-3} and the temperature 20 °C. Nitrogen dioxide liquid was added to the solution of N_2O_5 prior to mixing it with substrate solution. In all reactions the concentration of the nitrogen dioxide was approximately 0.2 mol dm^{-3}.

Kinetics by ^{1}H NMR spectroscopy. From a freshly prepared sample of N_2O_5, a known amount (from 0.108 to 0.432 g depending on the required N_2O_5 concentration) was weighed out in a dry glove box, into a silanised 5 ml volumetric flask, made up to the mark with dry deuteriated dichloromethane and placed in a freezer at −60 °C until needed, to prevent N_2O_5 decomposition. 4-Nitrostyrene (0.0298 g, 2×10^{-4} mol) was weighed out into another silanised 5 ml volumetric flask and made up to the mark with deuteriated dichloromethane. Prior to the kinetic run, both flasks were placed in a temperature controlled bath at the desired reaction temperature and allowed to come to thermal equilibrium. 250 μl of each solution were then injected into a 5 mm NMR tube, shaken to ensure that the solution was homogeneous, the time noted, the sample placed in the previously cooled probe of a 250 MHz NMR spectrometer (at −45 °C) and spectra recorded at noted time intervals. The substrate concentration was always 0.02 mol dm^{-3}, the N_2O_5 concentration varied between 0.1 and 0.4 mol dm^{-3} and the reaction temperature was always −45 °C.

Reaction of 4-nitrostyrene with ^{15}N-labelled N_2O_5

In a dry glove box with a nitrogen atmosphere, 4-nitrostyrene (0.48 g, 3.24×10^{-3} mol) was dissolved in dry deuteriated dichloromethane (7.5 ml), placed in a thermally insulated temperature controlled bath at 20 °C and allowed to come to thermal equilibrium. 100% ^{15}N-labelled N_2O_5 (0.35 g, 3.24×10^{-3} mol) was dissolved in deuteriated dichloromethane (7.5 ml) and placed in the temperature controlled bath. Once at thermal equilibrium, the solutions were taken back into the glove box, mixed, the solution made up to the mark with deuteriated dichloromethane and returned to the temperature controlled bath for the duration of the reaction (3 h). The reaction was then quenched in an excess of ice–water containing saturated aqueous hydrogen carbonate. The mixture was shaken, the organic layer separated, dried ($MgSO_4$) and the solvent removed under reduced pressure to yield the reaction products which were subsequently analysed by ^{15}N and ^{1}H NMR spectroscopy.

$\delta_{^{15}N}$(400 MHz; CD_2Cl_2). *β-Nitro nitrate.*—−7.078 (β-NO_2, dd, J_{NH} 2.3, J'_{NH} 1.7), −50.194 (α-NO_3, dd, J_{NH} 2.85, J'_{NH} 0.65).

Dinitro.—−0.805 (α-NO_2, dt, J_{NH} 5.5, J'_{NH} 1.75), −7.555 (β-NO_2, q, J_{NH} complex).

Dinitrate.—−45.959 (β-NO_3, t, J_{NH} 3.6), −47.354 (α-NO_3, dd, J_{NH} 2.85, J'_{NH} 3.6).

α-Nitro nitrate.—−0.007 (α-NO_2, dt, J_{NH} 1.7, J'_{NH} 2.0), −48.311 (β-NO_3, d, J_{NH} 2.8).

These couplings were also observed in the proton NMR spectra.

δ_H(400 MHz; CD_2Cl_2). *β-Nitro nitrate.*—6.71 (α-H, complex, J_{HN} 1.7), 4.92 (β-H, ddd, J_{HN} 1.6), 4.75 (β-H, complex, J_{NH} 0.7, J'_{HN} 2.3).

Dinitro.—9.39 (α-H, ddt, J_{HN} 1.75), 5.65 (β-H, ddt, J_{HN} 1.9), 4.88 (β-H, complex, J_{HN} 2.5).

Dinitrate.—6.25 (α-H, complex, J_{HN} 2.9), 4.83 (β-Hs, complex, J_{HN} 3.6).

α-Nitro nitrate.—5.94 (α-H, ddd, J_{HN} 1.7), 5.43 (β-H, complex, J_{HN} 3.8, J'_{HN} 2.05), 4.97 (β-H, complex, J_{HN} 2.8, J'_{NH} 5.1).

Proton–carbon HMQC

Proton–carbon HMQC (heteronuclear multiple quantum correlation) spectra were obtained for the mixture of the four compounds from the reaction of 4-nitrostyrene with N_2O_5. The nature of the bonding of the carbons in the alkyl region of the styrene could be assigned (either CH or CH_2), as well assigning them to one of the four compounds; δ_C(400 MHz, CD_2Cl_2) 85.743 (CH of α-nitro nitrate), 84.312 (CH of dinitro), 79.437 (CH_2 of dinitrate), 78.426 (CH of β-nitro nitrate), 75.022 (CH_2 of β-nitro nitrate), 73.803 (CH_2 of dinitro), 70.769 (CH_2 of dinitrate), 70.341 (CH_2 of α-nitro nitrate).

Apparatus

All ^{1}H NMR spectra and kinetic runs were recorded on a 250 or a 300 MHz Bruker spectrometer. ^{15}N NMR spectra were recorded on a 400 MHz Bruker Spectrometer. HPLC chromatograms were recorded by a Waters 994 Programmable Photodiode Array Detector at 254 nm, with a 5/ODS-2 column, a flow rate of 1 ml min^{-1} and a 60:40 acetonitrile–water solvent system. Infrared spectra were recorded on a Perkin Elmer 881 Infrared Spectrophotometer.

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