Kinetics and Mechanism of Reaction of Aryl Oxiranes with Dinitrogen Pentoxide in Dichloromethane

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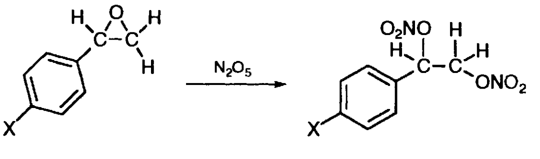
4-X-Phenyloxiranes (X = H, Cl, CF_3, NO_2) in dichloromethane react with N_2O_5 to give 1-(4-X-phenyl)ethane-1,2-diol dinitrates and with HNO_3 to give 2-(4-X-phenyl)-2-nitroethanols. Both reactions give quantitative yields. Kinetics of both reactions, mostly at reduced temperatures, have been investigated. The former reaction is second order in N_2O_5 and the latter reaction is between second and third order in HNO_3. Both reactions are retarded strongly by electron-withdrawing substituents and show large and negative entropies of activation. Mechanisms are discussed.

The recently reported reaction of oxiranes with N_2O_5 in dichloromethane to give dinitrates provides a convenient route to some explosive compounds.[1] The mechanism of this important reaction has not been investigated previously. In view of the known ready dissociation of N_2O_5 into nitronium and nitrate ions and into NO_2 and NO_3 radicals,[2] ionic, radical or concerted processes could be envisaged.

The reactions of octyl and phenyl oxiranes were first investigated but found to be rather too rapid for kinetic study. We then sought to measure reactivities relative to an aromatic reference compound by competition experiments, but in the reaction of mixtures of mesitylene and phenyl oxirane with a deficiency of N_2O_5 there was evidence for mixing control which thwarted any mechanistic investigation by this procedure. By using oxiranes derived from styrenes bearing electron-withdrawing substituents however it was possible to make observations of the kinetics, and we report on these studies here. In this work water has been rigorously excluded but because water is a likely contaminant of such solutions under preparative conditions, converting N_2O_5 immediately to nitric acid, the reactions of the same oxiranes with nitric acid were also studied.

Results

Reactions with N_2O_5.—The reactions of the oxiranes derived from styrene, 4-chlorostyrene, 4-(trifluoromethyl)styrene, and 4-nitrostyrene (referred to below as styrene oxides) with an excess of N_2O_5 in dry dichloromethane gave in each case the corresponding dinitrate (Scheme 1). No other products were detected and in no case was there observed any nitration in the aromatic ring.



X = NO_2, CF_3, Cl, H

Scheme 1

The reactions of styrene oxide and 4-chlorostyrene oxide were too fast for kinetic observation but with 4-(trifluoromethyl)styrene oxide and 4-nitrostyrene oxide it was possible to follow the reaction at reduced temperatures. For most of this work samples of the dichloromethane solution were taken by syringe at time intervals from the cold solution (which had been subasealed in a glove box) and analysed after quenching by GC.

Table 1 First[a] and third-order rate constants for the reactions of 4-nitrostyrene oxide and 4-(trifluoromethyl)styrene oxide with N_2O_5 in dichloromethane[b]

T/°C	$[N_2O_5]$/mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}	k_3/mol^{-2} dm^6 s^{-1}
4-Nitrostyrene oxide			
0	0.299	19	0.022
0	0.228	11	0.020
0	0.196	9.3	0.024
0	0.182	6.8	0.020
0	0.148	4.0	0.018
0	0.126	3.3	0.020
0	0.095	1.5	0.017
0	0.075	1.2	0.021
−20	0.347	13	0.011
−20	0.192	2.5	0.010
−20	0.142	2.4	0.012
4-(Trifluoromethyl)styrene oxide			
0	0.151	78	0.34[c]
0	0.121	45	0.31[c]
0	0.063	8.7	0.22[c]
−20	0.131	27	0.16
−20	0.127	16	0.10
−20	0.119	16	0.11
−20	0.099	10	0.10
−20	0.084	9.4	0.13
−20	0.054	3.5	0.12
−40	0.186	40	0.12[c]
−40	0.139	16	0.082[c]
−40	0.093	8.4	0.098[c]

[a] Observed first-order rate constant. [b] Runs analysed by GC of quenched aliquots unless otherwise noted. [c] Runs followed directly by NMR spectroscopy and solvent was [$^2H_2$]dichloromethane.

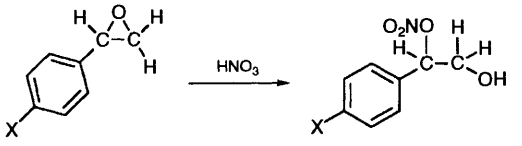
In some cases direct observations of the kinetics were made by ^1H NMR spectroscopy, and for these reactions deuteriated dichloromethane solvent was used. Results by the two methods were consistent. With N_2O_5 in excess the reactions had a first-order form. A plot of the logarithm of the observed first-order rate constant, k_{obs}, against the logarithm of the concentration of N_2O_5 revealed unexpectedly that the reaction was second order in N_2O_5, making the reaction third order overall [eqn. (1)].

$$-d[S]/dt = k_{obs}[S] = k_3[S][N_2O_5]^2 \qquad (1)$$

Values of k_{obs} and k_3 are in Table 1. The use of low temperatures reduced but did not eliminate problems associated with the instability and slow decomposition of N_2O_5 which accounts for the scatter in the results (Table 1) but the kinetic form is clearly established ([S] Is the concentration of the styrene oxide).

Activation parameters, derived from consideration of the variation of log (k_3/mol^{-2} dm^6 s^{-1}) with $1/T$ where T is the thermodynamic temperature, are in Table 2.

Reactions with HNO_3.—Styrene oxides were shown to react with nitric acid in dichloromethane to give the corresponding 2-aryl-2-nitratoethanol, Scheme 2. ^{15}N–^1H Coupling (doublet not triplet) confirmed the position of the nitrato group. Yields were quantitative by HPLC; there was no dinitrate formation.



X = NO_2, CF_3, Cl, H

Scheme 2

The kinetics of the reactions of 4-nitro- and 4-(trifluoromethyl)-styrene oxides, with nitric acid in excess, were investigated by GC analysis of quenched samples. The reactions again exhibited a first-order kinetic form. The observed first-order rate constants showed a slightly higher than second-order dependence on the concentration of nitric acid and were analysed according to eqn. (2). Values of k_3' and k_4', derived by

$$-\mathrm{d}[S]/\mathrm{d}t = k_{obs}[S] = k_3'[S][HNO_3]^2 + k_4'[S][HNO_3]^3 \quad (2)$$

least-squares regression of $k_{obs}/[HNO_3]^2$ on $[HNO_3]$, are in Table 3.

Table 2 Activation enthalpies and enthalpies for reaction of substituted styrene oxides with N_2O_5

Substituent	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}
4-Nitro	16 ± 2	−220 ± 20
4-(Trifluoromethyl)	12 ± 2	−214 ± 20

The reaction of 4-chlorostyrene oxide with an excess of HNO_3 was too quick to study, but by reducing the nitric acid concentration to only 2.5 fold in excess of the substrate and using a temperature of −40 °C, under which conditions the reaction was just slow enough to follow kinetically and exhibited a third-order kinetic form, a third-order rate constant could be derived for comparison with the values of k_3' for the other two substrates (Table 3).

Reaction with N_2O_5–HNO_3 *Mixtures.*—In order to investigate the effect which adventitious water might have on the N_2O_5 reaction, the kinetics of reaction of 4-nitrostyrene oxide with an excess of N_2O_5 and added nitric acid were investigated. The reactions, which gave exclusively the dinitrate, were again of first-order form. Values of k_{obs} are in Table 4. These are much larger than the values estimated for reaction with the same concentration of N_2O_5 in the absence of HNO_3 (first figures in parentheses) plus the values estimated for reaction with the same concentration of HNO_3 in the absence of N_2O_5 (second figures in parentheses). The latter reaction would initially give the mononitrate but this would react rapidly with N_2O_5 to give the dinitrate.[1] The small contribution of this pathway, was estimated using eqn. (2) with values of k_3' and k_4' at 0 °C calculated assuming the activation enthalpy to be the same as for the 4-(trifluoromethyl) compound (Table 3). It is clear that the values of k_{obs} in Table 4 are much greater than the estimated sum of contributions from independent reactions with N_2O_5 and HNO_3.

Discussion

Reactions with N_2O_5.—The most important observations with regard to the mechanism of this reaction are (*i*) the rate constants are very sensitive to the aryl ring substituent, (*ii*) the reaction is second order in N_2O_5 (Table 1), and

Table 3 First,[a] third[b] and fourth[b] order rate constants for the reactions of 4-nitrostyrene oxide and 4-(trifluoromethyl)styrene oxide with HNO_3 in dichloromethane

Temp /°C	$[HNO_3]$ /mol dm^{-3}	k_{obs} /10^{-4} s^{-1}	k_3' /10^{-3} mol^{-2} dm^6 s^{-1}	k_4' /mol^{-3} dm^9 s^{-1}
4-Nitrostyrene oxide				
25	0.266	19	5.2 ± 3.3	0.071 ± 0.025
25	0.133	2.4		
25	0.133	2.2		
25	0.119	1.2		
25	0.0839	1.3		
25	0.0794	0.42		
25	0.0666	0.64		
25	0.0398	0.12		
4-(Trifluoromethyl)styrene oxide				
25	0.0765	30	330[c] ± 55	2.1[d] ± 1.1
25	0.0574	13		
25	0.0383	6.3		
25	0.0287	3.6		
25	0.0191	1.2		
2.4	0.110	50	230[c] ± 15	1.5[d] ± 0.2
2.4	0.066	14		
2.4	0.0409	5.1		
4-Chlorostyrene oxide				
−40.0	−0.0593	[e]	14 400	

[a] Observed first-order rate constant. [b] Third- and fourth-order rate constants, k_3' and k_4', with their standard errors, derived by least-squares analysis; see eqn. (2). [c] Approximate values for the activation enthalpy and entropy derived from these are 10 kJ mol^{-1} and −220 J K^{-1} mol^{-1}, respectively. [d] Approximate values for the activation enthalpy and entropy derived from these two values are 8 kJ mol^{-1} and −210 J K^{-1} mol^{-1}, respectively. [e] Third-order rate constant measured directly; see text.

Table 4 First[a]-order rate constants for the reactions of 4-nitrostyrene oxide with N_2O_5 and HNO_3 in dichloromethane at 0 °C

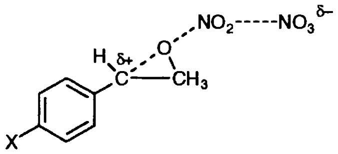
$[N_2O_5]$/mol dm^{-3}	$[HNO_3]$/mol dm^{-3}	$10^4\,k_{obs}$/s^{-1} [b]
0.141	0.0528	29 (4.0 + 0.2)
0.134	0.0495	18 (3.7 + 0.2)
0.113	0.0422	12 (2.6 + 0.1)
0.0895	0.0330	5.7 (1.6 + 0.1)
0.0887	0.0330	5.3 (1.6 + 0.1)

[a] Observed first-order rate constant. [b] The first value in parentheses is the value that would be observed in the absence of the nitric acid and the second value in parentheses is that which it is estimated would be observed in the absence of the N_2O_5.

(*iii*) the entropies of reaction are large and negative (Table 2).

A reliable Hammett ρ-value cannot be estimated because only the two substrates with the most electron-withdrawing substituents reacted slowly enough for kinetic study, but these indicate a value of about −5.0. This suggests that the transition state is polar, with a considerable positive charge on the alpha carbon. A radical reaction cannot be ruled out completely because both the NO_2 and the NO_3 radicals are thought to be rather electrophilic, but our failure to observe any ^{15}N nuclear polarization in the product when 4-(trifluoromethyl)styrene oxide was treated with ^{15}N enriched N_2O_5 (see Experimental), under conditions similar to those used clearly to demonstrate from the observed ^{15}N nuclear polarization the radical nature of the reaction of NO_2 with alkenes,[3] is an indication that the present reaction is not a radical one.

The substituent effect at first suggests a transition state like **I** formed by heterolysis of the α-carbon–oxygen bond of a complex formed by nitronium ion attachment to the epoxide oxygen.



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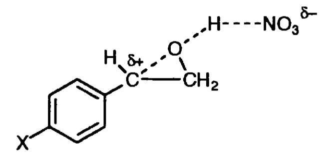

II

This picture is incomplete however, because the reaction is second order in N_2O_5, and a second molecule of N_2O_5 must additionally be present. Its role does not appear to be to initiate nitrate attack at the α-position[4] because this would lead to retention of configuration, whereas the nitration of *R*-styrene oxide by N_2O_5 gives an enantiomeric excess of only 4% in favour of the product with retention of configuration. The product is virtually racemic (see Experimental). A more likely role for the second molecule of N_2O_5 is to provide solvation for the developing nitrate ion. The termolecular nature of the reaction, and the polar nature of the transition state, account for the observed highly negative entropy of activation.

A practical consequence of the very small enthalpy of activation is that from the preparative point of view low temperatures may well be beneficial to yields. It is likely that the reaction will then compete best with side reactions.

Reactions with Nitric Acid.—The products of these reactions are 2-nitrato-2-arylethanols (Scheme 2). The Hammett ρ-value, based on k_3' values at 25 °C with that for 4-chlorostyrene oxide being calculated from the value for −40 °C assuming an activation energy as for the trifluoromethyl compound, is −5.9. This suggests a transition state like **II** formed by α carbon–oxygen heterolysis following or accompanying oxygen protonation.

However, again the order in nitric acid [slightly higher than two and analysed for convenience in terms of second and third order contributions, eqn. (2) and Table 3] argues against such a simple picture. Again the need for solvation of the developed or developing nitrate ion and/or incipient nitrate ion attack at the α-carbon[4] may account for the additional one or two molecules of nitric acid necessary to form the transition states. The high polarity and molecularity account for the negative activation entropies (footnotes to Table 3).

Reaction with N_2O_5–HNO_3 *Mixtures*.—The reaction produces the dinitrate at a rate greater than the sum of the rates for reactions with N_2O_5 and HNO_3 independently (Table 4). The kinetic form of this substantial catalysis has not yet been established and it is hoped to investigate this point more thoroughly. The result would again be difficult to rationalize if the reaction were a radical one, but is consistent with the solvation requirements of a developing polar transition state.

From the practical point of view it is interesting to note that, had the nitric acid arisen from partial hydrolysis in an incompletely dried medium of a higher concentration of N_2O_5 added originally, then the reaction would still give the dinitrate and proceed more quickly than if that higher concentration of N_2O_5 had been added to a completely dry system. In other words the presence of small amounts of water can actually be beneficial.

Experimental

Materials.—Dichloromethane was dried by distillation from calcium hydride. Anhydrous nitric acid and dinitrogen pentoxide were prepared as described previously.[5] ^{15}N Dinitrogen pentoxide was prepared by dehydration of ^{15}N nitric acid by phosphorus pentoxide under a stream of ozonised oxygen.[6]

4-*Nitrostyrene oxide*. This was prepared from 4-nitrobenzaldehyde and trimethylsulfonium iodide as described.[7] Mp(EtOH) 80–82 °C; δ_H(250 MHz, $CDCl_3$) 8.12 (2 H, d, *J* 11.8 Hz, arom), 7.42 (2 H, d, *J* 11.8 Hz, arom), 3.93 (1 H, q, CH, C-1), 3.18 (1 H, q, *J* 5 Hz, CH, C-2) and 2.74 (1 H, q, *J* 5 Hz, CH, C-2); δ_C(62.9 MHz; $CDCl_3$) 147.86, 145.38 (C arom), 126.25, 123.72 (CH, arom), 51.59 (CH_2) and 51.40 (CH); ν/cm^{-1} 3066, 3001, 2928 (arom C–H str.), 1524 (asym arom N–O str.), 1348 (C–O str.), 1319 (sym arom N–O str.) 906 and 851 (*p*-substituted aromatic C–H def); λ_{max}(MeCN–H_2O 70:30)/nm 274.

4-(*Trifluoromethyl*)*styrene oxide*. This was prepared similarly, and purified by distillation. Colourless oil, b.p. 96–98 °C/6 mmHg; δ_H(300 MHz; $CDCl_3$) 7.58 (2 H, d, *J* 8 Hz, arom), 7.36 (2 H, d, *J* 8 Hz, arom), 3.87 (1 H, q, *J* 3.5 Hz, CH, C-1), 3.13 (1 H, q, *J* 5.5 Hz, CH, C-2) and 2.74 (1 H, q, *J* 5.5 Hz, CH, C-2); δ_C(75.5 MHz; $CDCl_3$) 142.0 (C, arom, J_{CCCCCF} 1 Hz), 130.03 (C, arom, m, J_{CCF} 32 Hz), 125.70 (CH, arom, J_{CCCCF} 0 Hz), 125.40 (CH, arom, q, J_{CCCF} 4 Hz), 129.51, 126.70, 122.30, 118.30 (CF_3, J_{CF} 272 Hz), 51.52 (CH) and 51.15 (CH_2); ν/cm^{-1} 3060 (C–H, str. arom), 1254 (C–O, str.) and 822 (*p*-substituted aromatic C–H def).

4-*Chlorostyrene oxide*. This was prepared similarly and purified by distillation. Colourless oil, b.p. 120 °C/22 mmHg; δ_H(300 MHz; $CDCl_3$) 7.35 (2 H, d, *J* 9.5 Hz, arom), 7.24 (2 H, d, *J* 9.5 Hz, arom), 3.91 (1 H, q, *J* 2.5 Hz, CH), 3.15 (1 H, dd, *J* 5.5

Hz, J' 4.0 Hz, CH) and 2.84 (1 H, dd, J 5.5 Hz, J' 2.6 Hz, CH); δ_C(75.5 MHz, $CDCl_3$) 136.21 (C arom), 133.94 (C, arom), 128.73 (CH, arom), 126.84 (CH, arom), 51.75 (CH) and 51.16 (CH_2); ν/cm^{-1} 3059 (C–H str. arom), 1253 (C–O str.) and 830 (*p*-substituted aromatic C–H def).

1-(4-*Nitrophenyl*)*ethane*-1,2-*diol dinitrate*. Dinitrogen pentoxide in dry dichloromethane (43 cm^3) was prepared, in a 50 cm^3 graduated flask, in a dry glove box at 0 °C. To this solution, a cold solution of 4-nitrostyrene oxide in dry dichloromethane (5 cm^3) was added quickly and the solution quickly made up to the mark with cold dry dichloromethane. The initial concentrations of N_2O_5 and 4-nitrostyrene oxide were 0.113 and 0.0071 mol dm^{-3}, respectively. This solution was then left for 1 h. After this time the reaction was quenched with a saturated sodium hydrogen carbonate solution and stirred for 5 min. The organic layer was then separated from the aqueous layer and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a yellow oil. The dinitrate was purified by silica gel column chromatography, from base line impurity, using dichloromethane as eluent. The dinitrate was isolated as a yellow oil; yield 86%; δ_H(300 MHz, $CDCl_3$) 8.29 (2 H, d, J 8.5 Hz, arom), 7.64 (2 H, d, J 8.5 Hz, arom), 6.24 (1 H, q, J 7 Hz, CH) and 4.79 (2 H, m, CH_2); δ_C(75.5 MHz; $CDCl_3$) 148.85, 139.71 (C, arom), 127.71, 124.53 (CH, arom), 79.24 (CH, C-1) and 70.61 (CH_2, C-2); ν/cm^{-1} 1655 (asym, NO_2, str.), 1531 (arom, N–O asym), 1310 (arom, N–O sym), 1285 (sym, NO_2, str.) and 1095 (C–O str.).

1-(4-*Trifluoromethyl*)*phenylethane*-1,2-*diol dinitrate*. This was prepared in an identical manner. After column chromatography using dichloromethane as eluent the product was isolated as a pale-green oil; yield 99%; δ_H(300 MHz; $CDCl_3$) 7.74 (2 H, d, J 8 Hz, arom), 7.58 (2 H, d, J 8 Hz, arom), 6.18 (1 H, t, J 6 Hz, C-1) and 4.76 (2 H, m, C-2); δ_C(75.5 MHz; $CDCl_3$) 136.78 (C, arom, J_{CCCCCF} 1 Hz), 132.06 (C, arom, q, J_{CCF} 32.8 Hz), 127.06 (CH, arom, J_{CCCCF} 0 Hz), 126.42 (CH, arom, J_{CCCF} 4.0 Hz), 128.99, 125.38, 121.77, 118.16 (CF_3), 79.69 (CH, C-1) and 70.85 (CH_2, C-2); ν/cm^{-1} 1655 (NO_2, asym, str.) 1276 (NO_2, sym, str.) and 1066 (C–O, str.).

1-*Phenylethane*-1,2-*diol dinitrate*. This was prepared in a similar manner. The dinitrate was purified by silica gel column chromatography using the solvent system 5% ethyl acetate–petroleum spirit (b.p. 60–80 °C). The dinitrate was isolated as a pale-yellow oil; yield 99%; δ_H(250 MHz; $CDCl_3$) 7.37 (5 H, m, arom), 6.14 (1 H, m, C-2), 4.75 (2 H, m, C-1); δ_C(62.9 MHz; $CDCl_3$) 132.81 (C, arom), 130.17, 129.36, 126.72 (CH, arom), 80.69 (C-2) and 71.37 (C-1). ν/cm^{-1} 1649 (NO_2 asym, str.), 1285 (NO_2 sym, str.), 908 (C–O str.) and 735 (NO_2 wagging) (M^+, 228.03731. $C_8H_8N_2O_6$ requires M, 228.03824).

Nitration of (R)-*Styrene Oxide by Dinitrogen Pentoxide*.—The nitration of (R)-styrene oxide (0.3 g; 2.5 mmol) as described above gave 1-phenylethane-1,2-diol dinitrate; $[\alpha]_D^{24} = -3.1$ (9.3 g in 100 cm^3 dichloromethane).

(R)-1-*Phenylethane*-1,2-*diol dinitrate*. To (R)-phenylethane-1,2-diol (0.25 g; 2.1 mmol) in dichloromethane, in an ice bath, N_2O_5 in dichloromethane was added in small portions, until no substrate OH signal could be observed by ^{1}H NMR spectroscopy. The reaction was then quenched in water and worked-up as described above. Yield after chromatography 85%. This material was shown by ^{1}H NMR studies and GC retention to be 1-phenylethane-1,2-diol dinitrate; $[\alpha]_D^{25} = -63.6$ (0.69 g in 100 cm^3 dichloromethane).

2-(4-*Nitrophenyl*)-2-*nitratoethanol*. To nitric acid (0.8119 g; 0.0129 mol) in dichloromethane, 4-nitrostyrene oxide (47 mg; 2.89 × 10^{-4} mol) in dichloromethane, was added quickly and the reaction left at 25 °C for 10 min. After this time the reaction was quenched with water and the organic layer separated and dried over $MgSO_4$. The solvent was then removed and the product purified by silica gel column chromatography using ethyl acetate as eluent. The product was isolated as a yellow-orange oil (yield 85%). HPLC analyses before column chromatography showed the yield to be quantitative; δ_H(300 MHz, [$^2H_6$]acetone) 8.36 (2 H, d, J 7 Hz, arom), 7.81 (2 H, d, J 7 Hz, arom), 6.28 (1 H, t, J 4.5 Hz, CH), 4.82 (1 H, br s, OH, exch. D_2O) and 4.09 (2 H, br t, CH_2); δ_C(75.5 MHz, [$^2H_6$]acetone) 149.15, 143.80 (2 × C, arom), 128.92, 124.53 (2 × CH, arom), 86.01 (CH) and 63.67 (CH_2); ν/cm^{-1} 3370 (bonded OH str. very broad), 1661 (asym, NO_2, str.), 1522 (arom, N–O, asym, str.), 1352 (coupled C–O and O–H, str.; primary OH), 1209 (arom, N–O, sym, str.), 1284 (sym, NO_2, str.), 1194 and 1110 (coupled C–O and O–H str.).

2-(4-*Chlorophenyl*)-2-*nitratoethanol*. This material was prepared similarly, as a yellow oil, in quantitative yield; δ_H(300 MHz; $CDCl_3$) 7.34 (4 H, dd, J 9 Hz, arom), 6.91 (1 H, q, J 4 Hz, CH, C-1), 3.92 (1 H, dd, J 13 Hz, J' 8 Hz, CH, C-2), 3.81 (1 H, dd, J 13 Hz, J' 4 Hz, CH, C-2) and 3.71 (1 H, br s, OH); δ_C(75.5 MHz; $CDCl_3$) 135.33 (C, arom), 133.06 (C, arom), 129.20 (CH, arom), 128.15 (CH, arom, 85.21 (CH, C-1) and 63.49 (CH_2, C-2); ν/cm^{-1} 3379 (bonded O–H str. br), 1643 (asym, NO_2, str.), 1309 (coupled C–O str. and O–H def.; primary OH), 1275 (sym, NO_2, str.), 1092, 1047 (coupled C–O str. and O–H def.) and 852 (O–N str.).

2-*Phenyl*-2-*nitratoethanol*. The compound was prepared similarly. After column chromatography using 5% ethyl acetate–light petroleum mixture as eluent, the yield was 98% (pale-green oil); δ_H(250 MHz; $CDCl_3$) 7.58–7.21 (5 H, m, arom), 5.97 (1 H, dd, CH, C-2), 3.97 (1 H, dd, CH, C-1), 3.85 (1 H, dd, CH, C-1) and 3.60 (1 H, br s, OH); δ_C(62.9 MHz; $CDCl_3$) 134.642 (C, arom), 129.24, 128.997, 126.74 (3 × CH, arom), 88.103 (CH, C-2) and 63.773 (CH_2, C-1); ν/cm^{-1} 3411 (bonded OH str. br), 1641 (asym, NO_2, str.), 1276 (sym, NO_2, str.), 906 (N–O, str.) and 740 (NO_2, wagging).

2-(4-*Trifluoromethyl*)*phenyl*-2-*nitratoethanol*. This was prepared similarly, except that ^{15}N nitric acid was used and the eluent for column chromatography was dichloromethane; δ_H(300 MHz; $CDCl_3$) 7.68 (2 H, d, J 8 Hz, arom), 7.51 (2 H, d, J 8 Hz, arom), 5.97 (1 H, q, CH), 3.96 (1 H, dd, J 8 Hz, CH), 3.88 (1 H, dd, J 4.5 Hz, CH), 3.70 (1 H, br s, OH); δ_C(75.5 MHz; $CDCl_3$) 138.52 (C, arom, J_{CCCCCF} 1 Hz), 131.60 (C, arom, m, J_{CCF} 33 Hz), 127.11 (CH, arom, s, J_{CCCCF} 0 Hz), 126.01 (CH, arom, q, J_{CCCF} 3.8 Hz), 129.12, 125.42, 121.89 and 118.29 (CH_3, J_{CF} 272 Hz); ν_{max}/cm^{-1} 3389 (bonded O–H str. br) 1611 (asym, NO_2, str.), 1329 (coupled C–O str. and O–H def.; primary OH), 1266 (sym, NO_2, str.), 1169, 1126 (coupled C–O str. and O–H def.), 1068 (C–O, str., C–O–N) and 838 (O–N, str.).

^{15}N *NMR Details and GC Conditions*. These are in Tables 5 and 6, respectively.

Typical Kinetic Experiments (*Dinitrogen Pentoxide*).—For the majority of these studies, kinetics were studied by aliquot extraction and the subsequent analysis of the isolated reaction mixture by GC.

Freshly prepared dinitrogen pentoxide in a dry silanized, volumetric flask (in a dry glove box) was sealed by a silicone rubber subaseal. Dry dichloromethane (*ca.* 45 cm^3) was then added by syringe, at the required temperature to overcome heat loss due to the thermal capacity of the cold flask, and be at the desired temperature for the reaction. To this, a solution of the substituted styrene oxide containing a reference standard in dry dichloromethane (5 cm^3), at the required temperature was added by syringe through the subaseal and the solution quickly made up to the mark. Initial concentrations of dinitrogen pentoxide, substituted styrene oxide and reference standard were typically 0.05–0.2, 5–10 × 10^{-3} and 7 × 10^{-3} mol dm^{-3}, respectively.

Aliquots (10 cm^3) of the reaction solution were removed, by

Table 5 ^{15}N NMR data

Substrate	Primary nitrate[a]	$^{3}J_{NH}$/Hz	Secondary nitrate[a]	$^{3}J_{NH}$/Hz
1-Phenylethane-1,2-diol dinitrate	−46.83 (t)	3.6	−48.27 (d)	2.5
1-(4-Nitrophenyl)ethane-1,2-diol dinitrate[b]	−46.21 (t)	1.9	−48.46 (d)	1.4
1-(4-Trifluoromethylphenyl)ethane-1,2-diol dinitrate	−48.26 (t)	3.6	−50.39 (d)	2.6
2-Phenyl-2-nitratoethanol	—	—	−44.70 (d)	2.3
1-(4-Nitrophenyl)-2-nitratoethanol	—	—	−47.58 (d)	2.7

[a] Chemical shifts relative to external nitromethane. [b] Singlet at δ −12.85 aromatic nitro group.

Table 6 GC conditions for the analysis of the reaction of *p*-substituted styrene oxides and nitric acid

Compound	Response factor	Retention time/min	GC conditions
4-Nitrostyrene oxide	0.689	8.76	Column Dextril 400
Methyl-4-nitrobenzoate	—[a]	6.52	$T_{injector}$ = 225 °C; T_{column} = 195 °C; $T_{detector}$ = 250 °C
Mononitrate[b]	0.1918	4.78	N_2 flow rate 40 cm^3 min^{-1}
4-(Trifluoromethyl)styrene oxide	1.3235	4.24	Column OV 225
Mononitrate[c]	0.1902	6.57	$T_{injector}$ = 170 °C; T_{column} = 115 °C; $T_{detector}$ = 182 °C
2-Nitrofluorobenzene		8.58	N_2 flow rate 40 cm^3 min^{-1}
4-Chlorostyrene oxide	4.1688	9.95	Column Dextril 400
Mononitrate[d]	—	—	$T_{injector}$ = 210 °C; T_{column} = 150 °C; $T_{detector}$ = 220 °C
3-Fluoronitrobenzene	—[a]	3.92	N_2 flow rate 40 cm^3 min^{-1}
4-Nitrostyrene oxide	0.689	8.89	Column Textril 400
Methyl-4-nitrobenzoate[a]	—	6.52	$T_{injector}$ = 225 °C; T_{column} = 195 °C; $T_{detector}$ = 250 °C
Dinitrate[e]	—	4.85	N_2 flow rate 40 cm^3 min^{-1}
4-Trifluoromethylstyrene oxide	1.3235	4.24	Column OV 225
2-Nitrofluorobenzene[a]	—	8.58	$T_{injector}$ = 170 °C; T_{column} = 115 °C; $T_{detector}$ = 182 °C
Dinitrate[f]	—	—	N_2 flow rate 40 cm^3 min^{-1}

[a] Reference standard. [b] 2-(4-Nitrophenyl)-2-nitratoethanol. [c] 2-(4-(Trifluoromethyl)phenyl)-2-nitratoethanol. [d] 2-(4-Chlorophenyl)-2-nitratoethanol. [e] 1-(4-Nitrophenyl)ethane-1,2-diol dinitrate. [f] 1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diol dinitrate.

syringe, at appropriate time intervals, and quenched by injection into a subaseal flask (250 cm^3) containing cold distilled water (*ca.* 200 cm^3), which was then vigorously shaken before removal from the glove box. The organic fraction was then separated from the aqueous layer, which was then repeatedly washed with dichloromethane (3 × 10 cm^3). The organic extracts were then dried by passing through $MgSO_4$, and recombined before the solvent was carefully removed under reduced pressure, to give a concentrated solution (1–2 cm^3), which was then analysed by GC.

Reactions with the inclusion of nitric acid were undertaken in the same manner, except the nitric acid solution was added to the N_2O_5 solution prior to the start of the reaction.

Typical Kinetic Experiments (*Nitric Acid*).—To anhydrous nitric acid in dichloromethane (43 cm^3) at 25 °C, in a glove box, substituted styrene oxide and reference standard in dichloromethane (5 cm^3) was added quickly, and then the solution made up to 50 cm^3 with dichloromethane and left at the appropriate temperature for the required time. An aliquot (10 cm^3) was removed and quenched in water (*ca.* 200 cm^3) by syringing the aliquot through a subasealed flask containing the water. This flask was then shaken vigorously, and the flask then removed from the glove box. The organic layer was then separated. The aqueous layer was washed with dichloromethane (3 × 10 cm^3) and the organic fractions then combined and passed through $MgSO_4$.

The organic solvent was then removed by careful vacuum distillation, until only a small amount of solvent remained. This concentrated solution was then analysed by GC.

Kinetics by ^{1}H *NMR Spectroscopy* (*Dinitrogen Pentoxide*).—To freshly prepared N_2O_5 (typically 3.5 mmol) in a dry glove box, [$^{2}H_2$]dichloromethane (5 cm^3) was added. From this stock solution, a known volume was removed (usually between 0.25–0.1 cm^3) and this added to a known volume of [$^{2}H_2$]dichloromethane already placed in a 5 mm NMR tube, to give a total volume of 0.5 cm^3. The tube was then removed from the glove box and placed in a cardice–acetone bath until required.

To the solution of dinitrogen pentoxide a solution of the substituted styrene oxide, in [$^{2}H_2$]dichloromethane (0.25 cm^3), previously cooled in the cardice–acetone bath, containing a known amount of *meta*-dinitrobenzene (as a reference) was added and the NMR tube placed quickly within the probe, already at the desired temperature, where it was allowed to warm up to the required temperature and the reaction followed by ^{1}H NMR spectroscopy. Initial concentrations of dinitrogen pentoxide and the substituted styrene oxide were 0.1–0.2 and 0.012 mol dm^{-3}, respectively.

Kinetics by ^{1}H *NMR Spectroscopy at* −40 °C (*Nitric Acid*).—These experiments were carried out using a similar procedure. Only 4-chlorostyrene oxide was studied in this way. To nitric acid in [$^{1}H_2$]dichloromethane 4-chlorostyrene oxide in [$^{2}H_2$]dichloromethane was added. Initial concentrations were 0.059 and 0.024 mol dm^{-3}, respectively. The NMR spectra at −40 °C was recorded as quickly as possible.

CIDNP (*Chemically Induced Dynamic Nuclear Polarization*) *Experiments*.—To freshly prepared $^{15}N_2O_5$ in an 8 mm NMR tube sealed with a silicone rubber subaseal, in a dry glove box, dry dichloromethane (1 cm^3) was syringed quickly through the subaseal. The NMR tube was then removed from the glove box and cooled in a cardice–acetone bath. To this a small quantity of 4-(trifluoromethyl)styrene oxide in dichloromethane (1 cm^3), cooled previously in cardice–acetone, was syringed into the NMR tube, keeping the dinitrogen pentoxide in at least tenfold excess over the 4-trifluoromethylstyrene oxide. After transfer to the NMR probe it was allowed to warm to −40 °C. The reaction was monitored by ^{15}N NMR spectroscopy for any CIDNP effect. None was found.

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