# Interactions of 1,2,3,5- and 1,2,4,5-Tetranitrobenzene with Some Nucleophiles in Protic Solvents

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In the presence of hydroxide ion or sulphite ion in water, or ethoxide ion in ethanol, 1,2,3,5-tetranitrobenzene gives red complexes which are shown, from <sup>1</sup>H n.m.r. measurements, to result from covalent addition of the nucleophile at a hydrogen-carrying ring carbon. The equilibrium constant for the formation of the hydroxide adduct has the value  $2 \cdot 4 \times 10^4$  l. mole<sup>-1</sup>. The solutions are not stable and replacement of the nitro-group at C-2 occurs quickly. The rate constants have been measured. In contrast 1,2,4,5-tetranitrobenzene reacts with hydroxide to give 2,4,5-trinitrophenol without the production of colour. With ethoxide or sulphite ions coloured species are produced whose structures are discussed.

THE highly coloured Meisenheimer complexes formed from aromatic di- and tri-nitro-compounds by the covalent addition of nucleophiles are well known.<sup>1</sup> For example 1,3,5-trinitrobenzene forms adducts (I) which have characteristic visible and <sup>1</sup>H n.m.r. spectra.



We report here on the interactions of 1,2,3,5- and 1,2,4,5-tetranitrobenzene (TNB) with certain nucleophiles in protic solvents. Our main purpose was to investigate and compare the structures and stabilities of the species formed from the two isomers. In addition, in view of our interest<sup>2</sup> in the carbon basicities<sup>3</sup> (thermodynamic affinity for carbon) of nucleophiles it was hoped that the presence of a fourth nitro-group might render these compounds susceptible to complex formation with nucleophiles too unreactive to form adducts with other nitro-compounds.

Previously Murto <sup>4</sup> has shown that 1,2,3,5-tetranitrobenzene gives in the presence of aqueous sodium hydroxide or ethanolic sodium ethoxide, a red colour, which he attributed to the formation of a charge-transfer species



(II). In the former case he found that the colour faded quickly to give picric acid, the rate of decomposition being independent of hydroxide concentration at 0.001-0.005 M.

#### EXPERIMENTAL

1,2,3,5-Tetranitrobenzene was prepared from picramide by the method of Holleman <sup>5</sup> and recrystallised from chloroform to constant m.p. 127°. 1,2,4,5-Tetranitrobenzene was prepared by basically the same method as Borsche and Feske.<sup>6</sup> 1,3-Dichloro-4,6-dinitrobenzene was converted via the diphenoxy-compound to 1,3-dihydroxylamino-4,6-dinitrobenzene which on oxidation with nitric acid (D = 1.5) gave 1,2,4,5-tetranitrobenzene. The product was recrystallised from chloroform to m.p. 188°. Aqueous buffer solutions were prepared from borax and sodium hydroxide and the acidities checked with a pH meter.

<sup>1</sup>H N.m.r. spectra were recorded either at  $31^{\circ}$  with a Perkin-Elmer R10 spectrometer at 60 Mc./sec. or at 0° with a Varian A56/60 instrument. Solutions (concentration *ca*. 0·2M) were prepared by the injection of a concentrated solution of nitro-compound in dioxan into aqueous or ethanolic alkali. Spectra were recorded within two minutes of mixing and subsequent changes in spectra were noted.

Visible spectra were recorded with Unicam SP 800 and SP 500 instruments; the latter which was used for the accurate determination of optical densities was fitted with a thermostatted cell compartment. All kinetic and equilibrium measurements were carried out at  $22 \pm 0.2^{\circ}$ . Test solutions were prepared by the injection from a microsyringe of exactly 20 µl. of nitro-compounds in dioxan (ca. 0·1M) into 20 ml. of stock solution previously brought to 22°.

### RESULTS

1,2,3,5-Tetranitrobenzene and Hydroxide Ion.-We have extended Murto's measurements to solutions containing a smaller concentration of hydroxide ion by the use of borax buffers (pH = 9.2 to 10.6). In these solutions as in dilute sodium hydroxide solutions a red colour is formed very quickly and fades with production of picric acid. The visible spectrum of the red species is shown in Figure 1. In the range pH 9.2—12 the shape of the visible spectrum does not vary, which indicates the presence of a single complex. Measurements of optical density were made at 5000 Å where the product, picric acid, had negligible absorption and in all cases the rate of fading was found to be first order in concentration of the red species. Extrapolation of logarithmic plots to zero time gave the optical density at the time of mixing  $(D_0)$ . Two such plots are shown in Figure 2. The values of initial optical density and rate constants for the fading reaction at various hydroxide concentrations are in Table 1. The results show that the initial extent of conversion of 1,2,3,5-tetranitrobenzene to the red species, which we shall call A, increases with [OH<sup>-</sup>] concentration. However in solutions containing ca. 10<sup>-3</sup>M-hydroxide ion,

- <sup>3</sup> A. J. Parker, Proc. Chem. Soc., 1961, 371.
- <sup>4</sup> J. Murto, Suomen Kem., 1965, B38, 251.
- <sup>5</sup> A. F. Holleman, Rec. Trav. chim., 1930, 49, 112.
- <sup>6</sup> W. Borsche and E. Feske, Ber., 1926, 59B, 683.

<sup>&</sup>lt;sup>1</sup> (a) M. R. Crampton, Adv. Phys. Org. Chem., 1969, 7, 211; (b) R. Foster and C. A. Fyfe, Rev. Pure Appl. Chem., 1966, 16, 61; (c) E. Buncel, A. R. Norris, and K. E. Russell, Quart. Rev., 1968, 22, 123.

<sup>&</sup>lt;sup>2</sup> M. R. Crampton, J. Chem. Soc. (B), 1968, 1208.

conversion to complex is nearly complete. Assuming that the complex results from a l:l interaction, values of the



FIGURE 1 Absorption spectra at 0° of 1,2,3,5-tetranitrobenzene (ca.  $1 \times 10^{-4}$ M in water containing A,  $5 \times 10^{-3}$ M- and B, 0.2M sodium hydroxide



FIGURE 2 Illustration of the first-order fading reaction of the red complex formed from 1,2,3,5-tetranitrobenzene in aqueous buffers at pH A, 9-6 and B, 10-6. Measurements at 5000 Å

Table 1

1,2,3,5-Tetranitrobenzene.<sup>a</sup> Initial optical densities  $(D_0)$  at 5000 Å and rate constants  $(k_{obs})$  for the destruction of complex in aqueous buffers at 22°.

				10 <sup>-2</sup> k. °	
10 <sup>5</sup> [OH~]		$10^{3}k_{obs}$	$10^{-4} K$ (calc.)	(l. mole <sup>-1</sup>	
(M)	D0 <sup>b</sup>	(sec1)	(l. mole <sup>-1</sup> )	sec. <sup>-1</sup> )	
1.7	0.28	$3.5\pm0.5$	2.4	2.5	
2.7	0.39	4.6	2.5	2.5	
3.9	0.48	5.0	2.5	$2 \cdot 3$	
$5 \cdot 1$	0.54	5.4	2.5	$2 \cdot 2$	
10	0.68	6.0	2.4	$2 \cdot 0$	
17	0.77	6.8	$2 \cdot 3$	$2 \cdot 0$	
<b>23</b>	0.81	6.9	$2 \cdot 2$	$2 \cdot 0$	
40	0.88	7.2	$2 \cdot 4$	$1 \cdot 9$	
200	0.96	7.4		1.8	
500	0.92	7.5		1.8	

<sup>a</sup> The rate constant  $k_{\rm w}$  for the neutral hydrolysis of 1,2,3,5-tetranitrobenzene has the value  $6.3 \times 10^{-4}$  sec.<sup>-1</sup> (measured from the rate of formation of picric acid in water at pH 3). <sup>b</sup> For [1,2,3,5-TNB] =  $6.7 \times 10^{-5}$ M. <sup>c</sup> Calculated from expression (iii).

equilibrium constant for its formation K (= [A]/TNB][OH<sup>-</sup>]), were calculated. These values are given in column 4 of Table 1 and indicate a value for K of  $(2.4 \pm 0.2) \times 10^{4}$  l. mole<sup>-1</sup>.

Increasing the concentration of sodium hydroxide in the range 0.01 to 0.2M caused a shift in the maximum to longer wavelength in the visible spectrum of 1,2,3,5-tetranitrobenzene (see Figure 1). This may indicate the formation of a higher, probably 1:2, complex.

In order to examine the n.m.r. spectrum of species A, measurements were made in aqueous solutions containing equal concentrations of 1,2,3,5-tetranitrobenzene and sodium hydroxide. The spectrum recorded at 0° to slow down the rate of decomposition showed two sets of doublets (*J ca.* 1.5 Hz) at -8.3 and -6.15 p.p.m. relative to tetramethylsilane. With time these bands decreased in intensity and a new band at -8.75 p.p.m. attributed to picric acid grew at their expense. We have not so far succeeded in obtaining interpretable spectra in solutions containing excess of sodium hydroxide.

1,2,3,5-Tetranitrobenzene and Sulphite Ion.—Sodium sulphite solutions were prepared in buffers of pH 8 to inhibit interaction of tetranitrobenzene with hydroxide ions produced by hydrolysis of the sulphite. In solutions containing ca. 0.001M-sodium sulphite and  $1 \times 10^{-4}$ M-tetranitrobenzene a strong red colour is produced. The visible spectrum recorded at 0° shows two distinct absorption maxima at 4430 and 5300 Å and is similar, but shifted to longer wavelength, to that of the hydroxide complex (A). However the colour is not stable but fades very quickly. The product of reaction has little absorption above 3000 Å and probably results from replacement of the 2-nitro-group by sulphite.

An attempt was made to determine the equilibrium constant for formation of the coloured species, by the same method as for the hydroxide complex. In this case measurements of optical were made at 5300 Å. Logarithmic plots of optical density against time were again linear which showed the fading reaction to be first order in the coloured species. Extrapolation to zero time showed that in solutions containing  $1 \times 10^{-4}$  M-TNB and  $2 \times 10^{-4}$  M-sulphite, complex formation was virtually complete and in a solution  $1\, imes\,10^{-4}$ M-sulphite about 90% of the tetranitrobenzene was converted to complex. This latter result indicates that the complex cannot have greater than 1 sulphite: 1 tetranitrobenzene stoicheiometry, and gives a value for the equilibrium constant for formation of a 1 : 1 complex of  $1 \times 10^{6}$  l. mole<sup>-1</sup>. However due to the instability of sulphite in dilute solution this is probably a minimum value. The first-order rate constant for the fading reaction, which is independent of sulphite concentration in these solutions where most of the tetranitrobenzene is in the form of complex, has the value of 8  $\times$  10<sup>-2</sup> sec.<sup>-1</sup>.

1,2,3,5-Tetranitrobenzene and Ethoxide Ion.—Murto<sup>4</sup> found that in dilute solutions a red species with maxima at 4100 and 4900 Å was initially produced and that this gradually decomposed to produce 2,4,6-trinitrophenetole which exists in alkaline solutions as the complex (III), which has a very similar absorption spectrum. We add to this that in solutions containing  $1 \times 10^{-4}$ M-tetranitrobenzene and  $1 \times 10^{-4}$ M-sodium ethoxide conversion to the initially produced complex is nearly complete. This indicates a very large (>10<sup>6</sup> 1. mole<sup>-1</sup>) value for the equilibrium constant for complex formation.

In order to examine the nature of the initially produced species we have taken <sup>1</sup>H n.m.r. spectra. 1,2,3,5-Tetranitrobenzene in ethanol shows a single sharp peak at -9.4 p.p.m. relative to tetramethylsilane. A solution containing one equivalent of sodium ethoxide shows initially two doublets (*J ca.* 1.5 Hz) at -8.60 and -6.30 p.p.m. These bands gradually decrease in intensity and new bands at -8.85 p.p.m., attributed to the adduct (III), and -8.80 p.p.m., attributed to picric acid, grow at their expense. The production of picric acid probably results from the presence of traces of water in the solvent. However in



the presence of excess of tetranitrobenzene a considerable amount of picric acid is formed. It is possible that an electron-transfer mechanism may operate, perhaps with transfer occurring between the complex and unchanged tetranitrobenzene.<sup>7</sup> There is however no doubt with respect to the spectrum of the initially produced species which shows two doublets, as noted.

For the sake of completeness we have prepared 2,4,6-trinitrophenetole and taken its n.m.r. spectrum in ethanol and in the presence of sodium ethoxide. The neutral molecule shows a sharp band at  $-9\cdot0$  p.p.m. which shifts to  $-8\cdot85$ p.p.m. on addition of alkali and indicates formation of the adduct (III). No other bands were observed between  $-9\cdot0$ and  $-6\cdot0$  p.p.m. This result precludes the possibility that the doublets we have observed in solutions of 1,2,3,5tetranitrobenzene in ethanolic ethoxide result from the adduct (IV), which could be produced in these solutions *via* 2,4,6-trinitrophenetole. (*cf.* Servis,<sup>8</sup> Crampton and Gold <sup>9</sup>).

1,2,3,5-Tetranitrobenzene and other Nucleophiles.—The interactions in water of 1,2,3,5-tetranitrobenzene with a variety of nucleophiles, including azide, hypochlorite, iodide, phenoxide, thiocyanate, and thiosulphate ions, were examined. In no case was there evidence of the production of complexes with absorption maxima above 4000 Å.

1,2,4,5-*Tetranitrobenzene and Hydroxide Ion.*—In borax buffers (pH 9·2—10) or dilute sodium hydroxide solutions in water, a yellow species,  $\lambda_{max}$ . 3750 Å,  $\varepsilon$  1·45 × 10<sup>4</sup>, is gradually formed. The product was isolated and found to have m.p. 94° which showed it to be the expected 2,4,5-trinitrophenol. The rate of formation of trinitrophenol, followed by measurement of optical density at 3700 Å, was found to be first order in tetranitrobenzene. Rate constants in buffers of varying pH are given below.

105 [ОН-] (м)	1.8	$2 \cdot 6$	4.8	6.8	10.7
$10^3 k (sec.^{-1})$	1.15	1.73	2.7	<b>4</b> ·0	5.8

A plot of k versus [OH<sup>-</sup>] was linear showing the reaction to be first order in hydroxide ion. The slope gave the bimolecular rate constant for the reaction of tetranitrobenzene with hydroxide ion as 50 l. mole<sup>-1</sup> sec.<sup>-1</sup>.

The hydrolysis proceeds in this case without the production of any coloured intermediate. Visible spectra recorded at pH 11 at  $0^{\circ}$  showed no absorption in the visible region other than that due to 2,4,5-trinitrophenol. Assuming that any complex formed would have an extinction

<sup>7</sup> G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, 1964, **86**, 1807.

coefficient in the region of  $1 \times 10^4$  somewhere in the visible spectrum, this allows a maximum value to be put on the equilibrium constant for formation of such a complex. An initial absorption of 0.05 would be detectable, showing that the equilibrium constant for formation of a 1:1 complex must have a value less than 50 l. mole<sup>-1</sup>.

1,2,4,5-Tetranitrobenzene and other Nucleophiles.—Addition of 1,2,4,5-tetranitrobenzene, dissolved in dioxan or ethanol, to dilute solutions of sodium ethoxide in ethanol results in the formation of a transitory purple colour. This fades within one second no doubt due to a nucleophilic substitution reaction which destroys the parent nitro-compound. This colour was apparent in solutions containing  $10^{-1}$ ,  $10^{-2}$ , or  $10^{-3}$  M-sodium ethoxide and  $1 \times 10^{-4}$ -TNB. In the absence of quantitative measurements we can say little about the equilibrium constant for formation of the coloured species. However the observation of colour in a solution containing  $10^{-3}$ M-ethoxide suggests that  $K \ge 10^2$  1. mole<sup>-1</sup>.

Solutions containing  $1 \times 10^{-4}$ M-tetranitrobenzene and  $1 \times 10^{-2}$ M-sodium sulphite in water showed a transient blue colour. Colour formation was greater in solutions containing dimethyl sulphoxide. By making measurements at 0° it was possible to determine the absorption maximum which was found to be at 6500 Å. In solutions in water containing  $10^{-1}$ M-sodium sulphite a pink colour,  $\lambda_{max}$ . 4900 Å, was initially produced though this quickly faded.

## DISCUSSION

The <sup>1</sup>H n.m.r. spectra observed in solutions containing equal concentrations of 1,2,3,5-tetranitrobenzene and either sodium hydroxide or sodium ethoxide show that the red species produced have structure (V; R = H, Et). The spin-coupled bands at *ca.* -8.5 and -6.2 p.p.m. are attributed respectively to the ring hydrogens at C-6 and C-4, the large high-field shift, relative to the parent compound, of the latter band being consistent with a covalency charge at this position. The spectra are not consistent with structure (II) or with an adduct (VI)



formed by base addition at C-2, where the ring hydrogens would be more nearly if not completely equivalent. It seems unlikely that the mode of interaction will change with concentration so that the visible spectra produced in more dilute solutions are also attributed to structure (V). By analogy the red species produced in dilute aqueous sodium sulphite solutions will result from sulphite addition at C-4. Spectral data for these adducts are collected in Table 2.

The red species initially produced are not, however, stable and nucleophilic displacement of the nitro-group at C-2 occurs rapidly. Measurements of the rate of

- <sup>8</sup> K. L. Servis, J. Amer. Chem. Soc., 1967, 89, 1508.
- <sup>9</sup> M. R. Crampton and V. Gold, J. Chem. Soc. (B), 1966, 893.

# TABLE 2

Spectral data for 1:1 adducts a formed from 1,2,3,5-tetranitrobenzene with nucleophiles

		<sup>1</sup> H n.m.r.	spectrum
	Visible spectrum	Chem. shi	ts of ring
Nucleophile	$\lambda_{max}$ (Å)	protons <sup>b</sup>	(p.p.m.)
он-	4180, 4960	8.30	-6.12
OEt-	4100, 4860	-8.60	6.30
SO3 <sup>2-</sup>	4430, 5300	not me	asured
<ul> <li>Addition</li> </ul>	n at C-4. <sup>b</sup> Each bar	nd is a doublet (	I ca. 1.5 Hz)

fading in aqueous alkaline buffers show that the velocity is first order in the concentration of complex. However, it seems unlikely that the adduct with structure (V; R = H) can decompose directly to picric acid, and more likely reaction paths involve direct nucleophilic substitution of the nitro-group at C-2 by hydroxide ion or water. The former path would involve the intermediate (VI; R = H). The variation with hydroxide concentration of the rate of fading of the red species, which we denote by A, can be rationalised in the following way.10

The rate of formation of the product, picric acid, is given by

$$d[P]/dt = k_2[TNB][OH^-] + k_w[TNB]$$

where  $k_2$  is the rate constant for the reaction of 1,2,3,5tetranitrobenzene with hydroxide ion. However tetranitrobenzene and the adduct (A) are in equilibrium, K =[A]/[TNB][OH<sup>-</sup>].

Therefore 
$$d[P]/dt = k_2[A]/K + k_w[A]/K[OH^-]$$
 (i)

The n.m.r. spectra show that no appreciable concentration of the intermediate (VI), is produced. Thus for material balance

$$d[P]/dt = -d([A] + [TNB])/dt$$
  
= -d([A] + [A]/K[OH<sup>-</sup>])/dt (ii)

Equating the rates of production of picric acid given by (i) and (ii) and using  $k_{obs} = -dln[A]/dt$  gives

$$k_2/K + k_w/K[OH^-] = k_{obs}(1 + 1/K[OH^-])$$
 (iii)

in which the only non-observable quantity is  $k_2$ . Values calculated from this expression are in Table 1. It is not expected that the value of  $k_2$  would vary with base concentration and the drift in calculated values is probably not significant.

In solutions containing ca.  $1 \times 10^{-3}$ M-hydroxide, conversion of 1,2,3,5-tetranitrobenzene to adduct is virtually complete, also the contribution to the overall rate of decomposition from the neutral hydrolysis will be negligible. Whence it is easily shown that  $k_{obs} =$  $k_2/K$ . Now  $k_2$  and K will not be expected to vary greatly with base concentration, thus explaining the constancy of  $k_{\rm obs}$ , the rate of fading of adduct, in these solutions.<sup>4</sup> Similar reasoning explains why the rates of decomposi-

tion of the ethoxide or sulphite adducts are independent of nucleophile concentrations.

In aqueous solutions of 1,2,4,5-tetranitrobenzene and hydroxide there is no evidence for complex formation. With ethanolic ethoxide or dilute aqueous sodium sulphite, blue colours are formed which may be due to adducts of structure (VII;  $Nu = OEt \text{ or } SO_3^{-}$ ). The



visible absorption is at high wavelength as would be expected for such complexes (cf. Pollitt and Saunders <sup>11</sup>). The pink colour produced in more concentrated sulphite solutions could then be attributed to a di-adduct or to a decomposition product. However the blue colour may result from charge-transfer interaction. In the absence of n.m.r. spectra we can make no firm assignment.

In Table 3 are collected the equilibrium constants for formation of adducts from the two tetranitrobenzenes

# TABLE 3

Equilibrium constants for formation of 1:1 adducts
from polynitro-compounds with various nucleophiles

		K (l. mole <sup>-1</sup> )	
	OH-	OEt-	SO32-
1,2,3,5-Tetranitrobenzene	$2.4 imes10^4$	>106	≥106
1,2,4,5-Tetranitrobenzene	< 50	≥10²	~102
1,3,5-Trinitrobenzene	2.7 •	$(2\cdot0~ imes~10^3)$ b	$(2\cdot 5 \times 10^2)$
• Ref. 12. • R	ef. 1(c). • F	Ref. 13.	

and for comparison equivalent data for 1,3,5-trinitrobenzene. The values for 1,2,4,5-tetranitrobenzene assume that the formation of blue colour corresponds to the production of adduct; if this is not the case then the values will be smaller. Despite this uncertainty it is clear that the adducts formed from 1,2,3,5-tetranitrobenzene have considerably greater stabilities than those formed from its isomer. This adds to the increasing evidence <sup>1a, 14</sup> that the presence of a strongly electronwithdrawing group *para* to the position of addition is of great importance in the determination of the stabilities of Meisenheimer-type complexes. The very great increase in reactivity of 1,2,3,5-tetranitrobenzene relative to 1,3,5-trinitrobenzene is perhaps surprising as the fourth nitro-group is *meta* to the position of addition, so that electronic effects would not be expected to be very large. However 1,2,3,5-tetranitrobenzene contains three nitro-groups at adjacent ring positions which will cause considerable steric strain. It has previously been shown <sup>13</sup> that adducts formed by the addition at C-3 to 1-X-2,4,6-trinitrobenzenes  $(X = NH_2, NMe_2, etc.)$  have greater stability than those from 1,3,5-trinitrobenzene. This has been ascribed partly to a steric effect which makes the conformation of the molecule particularly

<sup>13</sup> M. R. Crampton, *J. Chem. Soc.*, 1967, 1341. <sup>14</sup> J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1969, 34, 689.

Cf. V. Gold and C. H. Rochester, J. Chem. Soc., 1964, 1692.
 R. J. Pollitt and B. C. Saunders, J. Chem. Soc., 1965, 4615.
 V. Gold and C. H. Rochester, J. Chem. Soc., 1964, 1710.

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attractive for addition. It may be that the greatly enhanced reactivity of 1,2,3,5-tetranitrobenzene also derives partly from steric effects.

The rate constant for the nucleophilic displacement of a nitro-group by hydroxide ion in 1,2,3,5-tetranitrobenzene  $(2 \times 10^2 \text{ l. mole}^{-1} \text{ sec.}^{-1})$  is surprisingly only slightly greater than with 1,2,4,5-tetranitrobenzene (50 l. mole<sup>-1</sup> sec.<sup>-1</sup>). Murto <sup>15</sup> has shown that for a number of picryl compounds the rate-determining step in the reaction with hydroxide ion is addition of hydroxide and that the rate of this process depends on the electron density at the reaction centre. It seems likely that an intermediate such as (VI; R = H) formed from tetranitrobenzene will lose nitrite ion rather than hydroxide so that the measured rate constants for reaction will similarly correspond to the rates of hydroxide addition. However due to the presence of the nitro-group at C-2 the electron density at this position in 1,2,3,5-tetranitrobenzene would be expected to be smaller than that at C-4. On this basis the adduct with structure (VI) should be formed more rapidly than that with structure (V). The fact that the latter adduct is in fact more quickly produced infers that base addition is faster at C-4 than at C-2, which in turn implies some steric hindrance to addition at C-2. This can perhaps be understood in terms of shielding of the reaction centre from the incoming hydroxide ion by the adjacent nitro-groups. Similar effects have been observed with other crowded nitro-compounds.<sup>8,9</sup> This effect is likely to be less important for 1,2,4,5-tetranitrobenzene, perhaps explaining the similar rates of nucleophilic displacement for the two isomers.

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<sup>15</sup> J. Murto, Acta Chem. Scand., 1966, 20, 310.