# The Stabilities of Meisenheimer Complexes. Part 17.[1] The Reactions of 1-X-2,4,6-Trinitrobenzenes with Hydroxide Ions in Water

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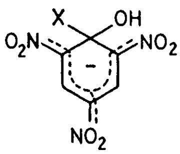
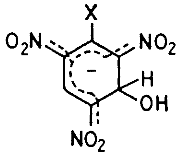
Kinetic, equilibrium, and spectroscopic data are reported for the reactions of 1-X-2,4,6-trinitrobenzenes (X = $NO_2$, Cl, OMe, or $O^-$) with hydroxide ions in water at 25 °C. In each case an initial fast reaction gives the 3-hydroxy-adduct and it is shown that ionisation of the added hydroxy-group occurs. Base addition at the 1-position of the substrate leading to nucleophilic displacement of X is about an order of magnitude slower than at the 3-position. There is evidence for nucleophilic displacement of the substituent X by hydroxide within the 3-hydroxy-complexes.

The reaction of aqueous sodium hydroxide with 1-X-2,4,6-trinitrobenzenes may result in the formation of stable σ-adducts when X is a poor leaving group [2-4] or in nucleophilic substitution when X is labile. In the latter case reaction is likely to proceed by an addition–elimination mechanism [5,6] *via* the intermediate (1).



(1)



(2)

In a kinetic study of the alkaline hydrolyses of picryl chloride and 2,4,6-trinitroanisole Gaboriaud and Schaal observed [7] transient coloured species which were taken to be the intermediates (1). However this interpretation requires loss of hydroxide ion from (1) to be a considerably faster process than loss of chloride or methoxide ions.[8,9] This is unlikely in view of known leaving group tendencies. The alternative possibility that the coloured species actually observed during the reaction are the 3-hydroxy-adducts (2) has received support from $^1H$ n.m.r. measurements on these systems.[10-12]

We report here kinetic studies by stopped-flow spectrophotometry of the reactions of several 1-X-2,4,6-trinitrobenzenes (X = $NO_2$, OMe, Cl, or $O^-$) with aqueous sodium hydroxide. Our results allow comparison of the relative rates of base addition at the 1- and 3-positions. They provide further evidence for the previously noted [13] ionisation of added hydroxy-groups, and provide kinetic evidence for nucleophilic substitution of X by hydroxide within the 3-hydroxy-complexes (2).

## RESULTS AND DISCUSSION

We have worked at sodium hydroxide concentrations up to 1M where activity coefficients will deviate from unity. Two possible approaches are (i) to relate the basicity of the medium to an acidity function [14] (the $J_-$ function would be appropriate here) or (ii) to work at constant ionic strength. We chose the latter alternative using sodium chloride as compensating electrolyte.

Previous work [15,16] indicates that addition of sodium chloride in water slightly lowers the values of rate coefficients for both forward and reverse reactions of σ-complex formation. To measure this effect in a situation similar to that used in our systems we determined the rate coefficients for reaction of sodium hydroxide with 1-chloro-2,4-dinitrobenzene which quantitatively yields 2,4-dinitrophenol. In this reaction no coloured intermediate is observed and hydroxide attack at the 1-position will be rate determining. The data in Table 1 indicate a small differential salt effect at base concentrations >0.5M.

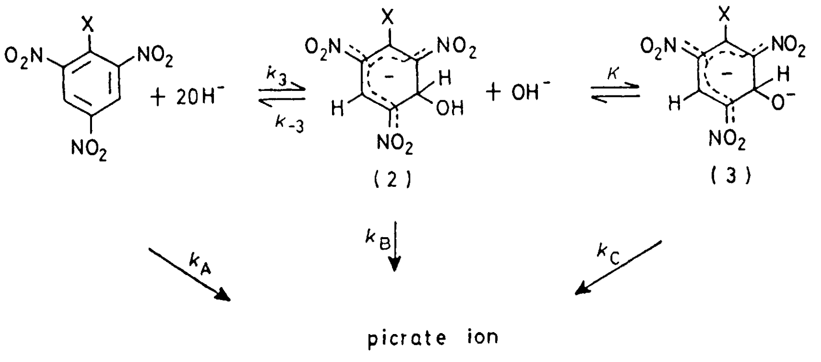
Table 1

Rate data for reaction of 1-chloro-2,4-dinitrobenzene with sodium hydroxide in water at 25 °C with $I$ = 2M

| [NaOH]/M | $k_{obs}{}^a/s^{-1}$ | $10^4k_{obs.}/[NaOH]/ l\ mol^{-1}\ s^{-1}$ |
|---|---|---|
| 0.05 | $5.68 \times 10^{-6}$ | 1.14 |
| 0.10 | $1.17 \times 10^{-5}$ | 1.17 |
| 0.30 | $3.57 \times 10^{-5}$ | 1.19 |
| 0.60 | $8.14 \times 10^{-5}$ | 1.36 |
| 1.00 | $1.54 \times 10^{-4}$ | 1.55 |

[a] Measured by following the increase in absorption due to 2,4-dinitrophenol at 360 nm.

*General Formulation.*—We interpret our data according to the Scheme. For each of the three parent 1-X-



Scheme

2,4,6-trinitrobenzenes (X = $NO_2$, Cl, or OMe) a rapid colour-forming reaction was observable giving the 3-hydroxy-adduct. The first-order rate coefficient, $k_{\text{fast}}$, for this process is related to the base concentration by equation (1) and the measured equilibrium constant is given by equation (2). Proton transfer from the added hydroxy-group, (2) + $OH^- \longrightarrow$ (3), will be very rapid and will not be observable as a separate process on the stopped-flow timescale.

$$k_{\text{fast}} = k_3[\text{NaOH}] + \frac{k_{-3}}{1 + K[\text{NaOH}]} \quad (1)$$

$$K_c = K_3(1 + K[\text{NaOH}] \quad (2)$$

The reaction product was in each case picric acid. If we assume that nucleophilic attack occurs only on the neutral parent then the rate coefficient for this process, $k_{\text{slow}}$, is given by equation (3). If we also allow nucleophilic substitution by hydroxide attack on the 1-position of the 3-hydroxy-adduct (2) and its anion (3) then equation (4) results.

$$k_{\text{slow}} = \frac{k_A[\text{NaOH}]}{1 + K_3[\text{NaOH}] + KK_3[\text{NaOH}]^2} \quad (3)$$

$$k_{\text{slow}} = \frac{k_A[\text{NaOH}] + k_BK_3[\text{NaOH}]^2 + k_CKK_3[\text{NaOH}]^3}{1 + K_3[\text{NaOH}] + KK_3[\text{NaOH}]^2} \quad (4)$$

1,2,4,6-*Tetranitrobenzene*.—There is $^1H$ n.m.r. evidence [10] that the complex initially produced results from hydroxide addition at the 3-position. Because of the four nitro-groups present there is extensive conversion into complex in very dilute base or in aqueous alkaline buffers. The values of the rate constants were found to be $k_3$ 2 900 l mol$^{-1}$ s$^{-1}$ and $k_{-3}$ 0.2 s$^{-1}$ leading to a value for $K_3$ of $1.45 \times 10^4$ l mol$^{-1}$.

The published spectra [10] show that in dilute base ($5 \times 10^{-3}$M) maxima are at 420 and 500 nm while in more concentrated base the maximum shifts to longer wavelength and intensifies. If this spectral change was associated with the formation of a 1 : 2 adduct by covalent base addition at a second ring position then this process should be separately observable by stopped-flow spectrophotometry. However careful examination of the system showed only a single rate process associated with the initial colour formation. It thus seems probable that the observed spectral change results from ionisation of the added hydroxy-group (2) $\longrightarrow$ (3). Measurements of the optical density at 450 nm after completion of the initial colour forming processes are in Table 2 and give a value for $K$ of 24 l mol$^{-1}$.

The colour produced initially fades slowly to give picric acid. Rate measurements were made at 450 nm in the thermostatted cell compartment of a Unicam SP 500 spectrophotometer. The data in Table 2 show that the first-order rate coefficients, $k_{\text{slow}}$, increase with increasing base concentration. If we assume that nucleophilic substitution can occur only by attack on the substrate, then as the parent is converted into its 3-hydroxy-adduct (2) and the dianion (3) it is predicted that the rate coefficient should decrease [equation (3), penultimate column in Table 2]. If nucleophilic attack is allowed to occur on (2) and (3) then good agreement can be obtained between the experimental data and that calculated (final column in Table 2) from equation (4) with $k_A$ 140 l mol$^{-1}$ s$^{-1}$, $k_B$ 0.2 l mol$^{-1}$ s$^{-1}$, and $k_C$ 0.03 l mol$^{-1}$ s$^{-1}$.

This is very strong evidence for nucleophilic substitution in the 3-hydroxy-complex and its anion.

2,4,6-*Trinitroanisole*.—Two processes are observable by stopped-flow spectrophotometry, a rapid colour-forming reaction, and a slower decomposition to picric acid. The visible spectra initially produced in solutions containing 0.1M-base without added salt and 0.96M-base with $I$ = 2M are given in the Figure. They show a distinct change in spectral shape as the base concentration is increased, the maximum shifting to longer wavelength. No new relaxation time was observable

TABLE 2

Rate and equilibrium data for reaction of 1,2,4,6-tetranitrobenzene with hydroxide ions in water at 25 °C

| $[HO^-]$ [a] / M | O.D. (450 nm) [b] | O.D. (calc.) [c] | $k_{\text{fast}}$ / s$^{-1}$ | $k_{\text{fast}}$(calc.) [d] / s$^{-1}$ | $10^3k_{\text{slow}}$ / s$^{-1}$ | $10^3k_{\text{slow}}$(calc.) [e] / s$^{-1}$ | $10^3k_{\text{slow}}$(calc.) [f] / s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $2 \times 10^{-6}$ | | | 0.21 | 0.21 | | | |
| $5 \times 10^{-6}$ | | | 0.21 | 0.21 | | | |
| $1.3 \times 10^{-5}$ | | | 0.24 | 0.24 | | | |
| $5 \times 10^{-5}$ | | | 0.34 | 0.34 | | | |
| $1.1 \times 10^{-4}$ | | | 0.54 | 0.52 | | | |
| $1.0 \times 10^{-3}$ | 0.51 | 0.52 | 2.6 | 2.9 | 8.8 | 8.8 | 9.0 |
| $5.0 \times 10^{-3}$ | 0.58 | 0.58 | 15 | 14.5 | 10.1 | 8.5 | 9.4 |
| $1.0 \times 10^{-2}$ | 0.62 | 0.61 | 30.2 | 29.0 | 9.7 | 7.7 | 9.4 |
| $2.0 \times 10^{-2}$ | 0.63 | 0.66 | 57.3 | 58.0 | 9.0 | 6.4 | 9.4 |
| $4.0 \times 10^{-2}$ | 0.72 | 0.72 | | | 9.2 | 4.8 | 9.5 |
| $7.0 \times 10^{-2}$ | 0.77 | 0.77 | | | 10.8 | 3.5 | 9.9 |
| 0.10 | 0.81 | 0.80 | | | 14.0 | 2.8 | 11.0 |
| 0.20 | 0.84 | 0.84 | | | 14.4 | 1.6 | 13.5 |
| 0.40 | 0.85 | 0.87 | | | 20.3 | 0.9 | 19.4 |
| 0.70 | 0.89 | 0.88 | | | 27.4 | 0.5 | 29.2 |

[a] Data with $[OH^-] < 10^{-3}$M were determined using 0.013M borax buffers. Data with $[OH^-] \geqslant 10^{-3}$M were at $I$ 1M with NaCl. [b] For $4 \times 10^{-5}$M parent. [c] Taking a value for $K$ of 24 l mol$^{-1}$ and values of 0.55 and 0.90 respectively for complete conversion of substrate into hydroxy-adduct, (2), and its anion, (3). [d] Calculated from equation (1) with $k_3$ 2 900 l mol$^{-1}$ s$^{-1}$, $k_{-3}$ 0.2 s$^{-1}$, and $K$ 24 l mol$^{-1}$. [e] Calculated from equation (3) with $k_A$ 140 l mol$^{-1}$ s$^{-1}$, $K$ 24 l mol$^{-1}$, and $K_3$ $1.45 \times 10^4$ l mol$^{-1}$. [f] Calculated from equation (4) with $k_A$ 140 l mol$^{-1}$ s$^{-1}$, $k_B$ 0.2 l mol$^{-1}$ s$^{-1}$, $k_C$ 0.03 l mol$^{-1}$ s$^{-1}$, $K$ 24 l mol$^{-1}$, and $K_3$ $1.45 \times 10^4$ l mol$^{-1}$.

TABLE 3

Rate and equilibrium data for reaction of 2,4,6-trinitroanisole with sodium hydroxide in water at 25 °C with $I$ 2M

| [NaOH] / M | $k_{\text{fast}}$ / $s^{-1}$ | $k_{\text{fast}}$(calc.)[a] / $s^{-1}$ | O.D. (480 nm)[b] | $K_c$ / l $mol^{-1}$ | $K_c$(calc.)[c] / l $mol^{-1}$ | $k_{\text{slow}}$ / $s^{-1}$ | $k_{\text{slow}}$(calc.)[d] / $s^{-1}$ | $k_{\text{slow}}$(calc.)[e] / $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.01 | 8.1 ± 0.2 | 8.0 | 0.0015 | 1.25 | 1.3 | | | |
| 0.02 | 7.9 | 7.7 | 0.0031 | 1.3 | 1.35 | 0.026 | 0.027 | 0.027 |
| 0.05 | 6.7 | 7.0 | 0.0075 | 1.35 | 1.55 | 0.064 | 0.064 | 0.066 |
| 0.10 | 6.3 | 6.4 | 0.0175 | 1.7 | 1.9 | 0.131 | 0.115 | 0.125 |
| 0.20 | 6.3 | 6.2 | 0.038 | 2.3 | 2.6 | 0.202 | 0.175 | 0.205 |
| 0.40 | 7.0 | 7.2 | 0.079 | 4.8 | 4.1 | 0.26 | 0.19 | 0.27 |
| 0.50 | 7.2 | 8.0 | 0.090 | 6.0 | 4.8 | 0.30 | 0.19 | 0.30 |
| 0.60 | 9.5 | 9.0 | | | | 0.31 | 0.17 | 0.29 |
| 0.70 | 9.9 | 10.0 | 0.093 | 5.0 | 6.0 | 0.31 | 0.16 | 0.30 |
| 0.80 | 10.3 | 11.0 | | | | 0.29 | 0.15 | 0.30 |
| 1.0 | | | 0.105 | | | 0.30 | 0.13 | 0.31 |
| 1.5 | | | 0.115 | | | | | |
| 2.0 | | | 0.12 | | | | | |

[a] Calculated from equation (1) with $k_3$ 12 l $mol^{-1}$ $s^{-1}$, $k_{-3}$ 8.4 $s^{-1}$, and $K$ 6 l $mol^{-1}$. [b] Corresponds to O.D. after completion of the fast colour forming reactions. Measured by stopped-flow spectrophotometry. Values quoted are for 1 × $10^{-5}$M-parent and 1-cm cell. [c] Calculated from equation (2) with $K_3$ 1.2 l $mol^{-1}$ and $K$ 6 l $mol^{-1}$. [d] Calculated from equation (3) with $k_A$ 1.4 l $mol^{-1}$ $s^{-1}$, $K_3$ 1.4 l $mol^{-1}$, and $K$ 6 l $mol^{-1}$. [e] Calculated from equation (4) with $k_A$ 1.4 l $mol^{-1}$ $s^{-1}$, $k_B$ 0.8 and $k_C$ 0.1 l $mol^{-1}$ $s^{-1}$, $K_3$ 1.4 l $mol^{-1}$ and $K$ 6 l $mol^{-1}$.

TABLE 4

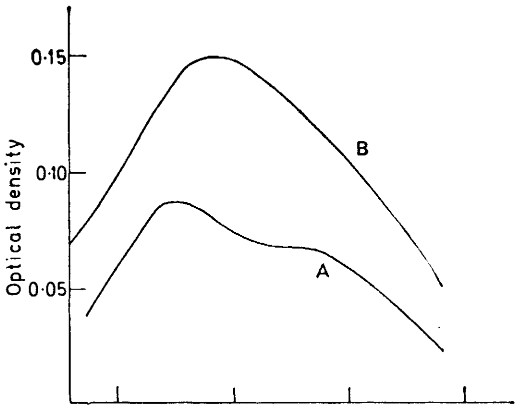
Rate and equilibrium data for reaction of picryl chloride with sodium hydroxide in water at 25 °C with $I$ 2M

| [NaOH] / M | $k_{\text{fast}}$ / $s^{-1}$ | $k_{\text{fast}}$(calc.)[a] / $s^{-1}$ | O.D. (440 nm)[b] | $K_c$[c] / l $mol^{-1}$ | $K_c$(calc.)[d] / l $mol^{-1}$ | $10^2k_{\text{slow}}$ / $s^{-1}$ | $10^2k_{\text{slow}}$(calc.)[e] / $s^{-1}$ | $10^2k_{\text{slow}}$(calc.)[f] / $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 0.01 | 12.4 | 12.3 | 0.0012 | 0.78 | 0.70 | | | |
| 0.02 | 11.8 | 11.1 | 0.0023 | 0.76 | 0.78 | 1.01 | 0.79 | 0.79 |
| 0.05 | 8.9 | 8.6 | 0.0071 | 0.96 | 1.05 | 1.76 | 1.85 | 1.88 |
| 0.10 | 7.0 | 6.8 | 0.0195 | 1.45 | 1.5 | 3.27 | 3.3 | 3.4 |
| 0.20 | 5.7 | 5.9 | 0.0485 | 2.3 | 2.4 | 5.00 | 4.8 | 5.4 |
| 0.40 | 6.2 | 6.8 | 0.0975 | 4.3 | 4.2 | 6.8 | 4.8 | 6.3 |
| 0.60 | 7.8 | 8.6 | 0.126 | 7.2 | 6.0 | 6.0 | 4.0 | 6.4 |
| 0.80 | 10.5 | 10.7 | 0.132 | 7.2 | 7.8 | 6.0 | 3.3 | 6.4 |
| 1.0 | 14.0 | 13.0 | 0.141 | | | 6.9 | 2.7 | 6.4 |

[a] Calculated from equation (1) with $k_3$ 12 l $mol^{-1}$ $s^{-1}$, $k_{-3}$ 14 $s^{-1}$, and $K$ 15 l $mol^{-1}$. [b] After completion of fast colour-forming processes. Corrected for absorption by parent. Values quoted are for 1 × $10^{-4}$M parent in 1-cm cell. [c] Taking an O.D. value of 0.155 for complete conversion. [d] Calculated from equation (2) with $K_3$ 0.6 l $mol^{-1}$ and $K$ 15 l $mol^{-1}$. [e] Calculated from equation (3) with $k_A$ 0.4 l $mol^{-1}$ $s^{-1}$, $K_3$ 0.85 l $mol^{-1}$, and $K$ 15 l $mol^{-1}$. [f] Calculated from equation (4) with $k_A$ 0.4, $k_B$ 0.2, $k_C$ 0.03 l $mol^{-1}$ $s^{-1}$, and $K_3$ 0.85, $K$ 15 l $mol^{-1}$.

corresponding to this change which is thus attributed to ionisation of the 3-hydroxy-adduct, (2)→(3).

The variation with base concentration of the value of the rate coefficient of the fast process is also indicative of hydroxy-ionisation. As shown in Table 3 the data are well represented by equation (1) with $k_3$ 12 l $mol^{-1}$ $s^{-1}$, $k_{-3}$ 8.4 $s^{-1}$, and $K$ 6 l $mol^{-1}$. The optical densities at 480 nm after completion of the fast processes are also given in Table 3 and have been used to work out values of the stoicheiometric equilibrium constant, $K_c$. These are compared with values calculated using equation (2). A flaw in this treatment is that the proportions of the 3-hydroxy-adduct (2) and its anion (3) will vary in these solutions. Since we do not know the precise value of the extinction coefficient of the former species we have assumed a value identical with that of (3). The slight difference in the value of $K_3$ (1.2 l $mol^{-1}$) obtained here from that obtained by kinetic measurements (1.4 l $mol^{-1}$) is probably a consequence of this assumption.



Visible spectra initially produced from 2,4,6-trinitroanisole and sodium hydroxide. Concentrations are A, parent 4 × $10^{-5}$M, NaOH 0.1M; B, parent 1 × $10^{-5}$M, NaOH 0.96M, $I$ 2M

The rate coefficients $k_{\text{slow}}$ for the fading reaction to give picric acid are correlated better by equation (4) with $k_A$ 1.4 l $mol^{-1}$ $s^{-1}$, $k_B$ 0.8 l $mol^{-1}$ $s^{-1}$, and $k_C$ 0.1 l $mol^{-1}$ $s^{-1}$ than by equation (3). This indicates that nucleophilic substitution of methoxide by hydroxide is likely to occur in the 3-hydroxy-adduct. However the case is not so clear cut here as with 1,2,4,6-tetranitrobenzene since it would be possible to replicate the experimental data solely by allowing the value of $k_A$ to increase from 1.4 at low base to 3.3 l $mol^{-1}$ $s^{-1}$ at 1M-base. In view of the relatively small variation with base concentration in the value of the rate coefficient for nucleophilic attack by hydroxide on 1-chloro-2,4-dinitrobenzene in similar media (Table 1) we think that this alternative explanation is unlikely.

*Picryl Chloride*.—The behaviour is qualitatively similar to that of 2,4,6-trinitroanisole. Two processes only are observable by stopped-flow spectrophotometry, a fast colour-forming reaction and a slower fading reaction to yield picric acid; data are given in Table 4. The values of the rate coefficients for formation of the coloured species go through a pronounced minimum with increasing base concentration. This behaviour indicates ionisation of the added hydroxy-group and the data are represented well by equation (1) with $k_3$ 12 l mol$^{-1}$ s$^{-1}$, $k_{-3}$ 14 s$^{-1}$, and $K$ 15 l mol$^{-1}$. Values of the equilibrium constant $K_c$ increase with base concentration and accord with $K_3$ 0.6 and $K$ 15 l mol$^{-1}$. This value of $K_3$ is less reliable than that obtained kinetically since the adduct (2) and its derived anion (3) may have different extinction coefficients at 440 nm.

The rate coefficients for picric acid formation are in best accord with nucleophilic attack on both the parent and its derived adducts.

*Picrate Ion*.—Previous spectroscopic studies[2] have shown that in concentrated base a stable di-adduct is formed by hydroxide addition at both the 3- and 5-positions. By stopped-flow spectrophotometry we observe two time-dependent processes. The faster of these results in an increase in absorption at all wavelengths above 400 nm. We associate this process with hydroxide addition at one ring position to give (2; X = O$^-$). Rate and equilibrium data are in Table 5.

TABLE 5

Rate and equilibrium data for hydroxide addition at the 3-position of the picrate ion in water at 25 °C with $I$ 2M

| [NaOH]/ M | $k_{\text{fast}}$/ s$^{-1}$ | $k_f$(calc.)[a] | O.D. (500 nm)[b] | $K_c$/ l mol$^{-1}$ | $K_c$(calc.)[c] / l mol$^{-1}$ |
|---|---|---|---|---|---|
| 0.05 | 19.2 | 19 | 0.0035 | 0.014 | 0.0135 |
| 0.10 | 17.7 | 18.5 | 0.0070 | 0.014 | 0.014 |
| 0.20 | 17.9 | 17.2 | 0.0145 | 0.0145 | 0.015 |
| 0.40 | 15.0 | 15.1 | 0.033 | 0.0165 | 0.017 |
| 0.60 | 13.6 | 13.5 | 0.060 | 0.020 | 0.019 |
| 0.80 | 12.0 | 12.2 | 0.080 | 0.020 | 0.021 |
| 1.0 | 11.6 | 11.0 | 0.137 | 0.027 | 0.023 |

[a] Calculated from equation (1) with $k_{-3}$ 20 s$^{-1}$, $K$ 0.8 l mol$^{-1}$. [b] For 5 × 10$^{-4}$M parent in 1-cm cell. Corrected for absorption by parent. [c] Calculated from equation (2) with $K_3$ 0.013 l mol$^{-1}$ and $K$ 0.8 l mol$^{-1}$.

The fact that the rate coefficients decrease with increasing base concentration is taken as evidence for ionisation of the added hydroxy-group. The reverse rate in equation (1) is dominant and values calculated with $k_{-3}$ 20 s$^{-1}$ and $K$ 0.8 l mol$^{-1}$ give good agreement with experimental values. The extent of conversion to complex is small and there is no way of experimentally determining the value of the extinction coefficient. We have assumed a value of 1 × 10$^4$ l mol$^{-1}$ cm$^{-1}$ at 500 nm in order to calculate values of $K_c$.

The slower rate process observable by stopped-flow has small amplitude at the base concentrations used. In 1M-base there is an increase in absorption at 390 nm and a decrease at 480 nm with an associated rate coefficient of 0.15 s$^{-1}$. The process involved is likely to be formation of the di-adduct which is known to have a maximum absorption at 390 nm.

*Ionisation of Added Hydroxy-groups*.—Previously we have shown[13] that the 3-hydroxy-adduct of 2,4,6-trinitrobenzenesulphonate ion will lose a proton in aqueous base while Terrier *et al.*[17] have reported ionisation of the hydroxide adduct of 4,6-dinitrobenzofuroxan. The present work shows the generality of such ionisation, (2) + OH$^-$ $\longrightarrow$ (3).

Values of the equilibrium constant $K$ are given in Table 6. It should be noted that since reaction involves attack of hydroxide ions on negatively charged species, the values will increase with increasing ionic strength of the medium. The fact that the values of $K$ do not vary dramatically with the nature of the 1-substituent is not unexpected since there is no direct pathway for delocalisation of the resultant negative charge. However the smallest value is for the picrate ion where two negative charges are already delocalised about the ring and nitro-groups.

Ionisation of the added hydroxy-group produces dianions or, in the cases of picrate ion and 2,4,6-trinitrobenzenesulphonate ion, trianions. As we have previously noted[18] water is a particularly good solvent for the formation of multi-charged anions and, in fact, a species carrying five negative charges can be formed[2] by addition of two sulphite ions to picrate.

*Relative Rates of Addition at the* 1- *and* 3-*Positions*.—Since NO$_2^-$, Cl$^-$, and MeO$^-$ are better leaving groups than HO$^-$, nucleophilic substitution will proceed by rate-determining attack of hydroxide at the 1-position. Thus the values of $k_A$ in Table 6 are those for attack of hydroxide ion at the 1-position of the substrate. These values are smaller than those for attack at the 3-position by a factor varying between 9, in the case of trinitroanisole, and 30, in the case of picryl chloride. The inductive effect of electronegative substituents at the 1-position should favour attack at this position. However Bartoli and Todesco have argued[19] that unfavourable repulsion between entering

TABLE 6

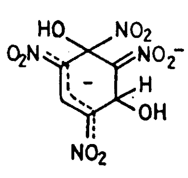
Summary of kinetic and equilibrium data

| Parent | $k_3$/l mol$^{-1}$ s$^{-1}$ | $k_{-3}$/s$^{-1}$ | $K_3$/l mol$^{-1}$ | $K$/l mol$^{-1}$ | $k_A$/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 1,2,4,6-Tetranitrobenzene[a] | 2 900 | 0.2 | 14 500 | 24 | 140 |
| Picryl chloride[b] | 12 | 14 | 0.85 | 15 | 0.4 |
| 2,4,6-Trinitroanisole[b] | 12 | 8.4 | 1.4 | 6 | 1.4 |
| 2,4,6-Trinitroanisole[a] | 12 | 8.3 | 1.4 | 2 | Not measured |
| 2,4,6-Trinitrobenzenesulphonate[c] | 0.8 | 45 | 0.018 | 32 | 0.045 |
| Picrate ion[b] | 0.26 | 20 | 0.013 | 0.8 | |

[a] $I$ 1M with NaCl. [b] $I$ 2M with NaCl. [c] Ref. 13.

and leaving groups will more than outweigh this factor. A further factor[20] which may favour addition at the 3-position is that stabilising resonance interaction between the 1-substituent and the ring is lost when addition occurs at the 1-position but not when addition occurs at the 3-position.

*Nucleophilic Substitution in the 3-Hydroxy-adducts.*—The rate data provide clear evidence in the case of tetranitrobenzene for nucleophilic displacement of nitrite by hydroxide *via* the intermediates (4) and (5). It is perhaps not surprising that these should be formed here since 1 : 2 adducts are known to be formed from both 1,3,5-trinitrobenzene[3] and picrate ion[2] at high base concentrations. However, the intermediates (4) and (5) will be unstable with respect to loss of nitrite ion and will rapidly decay to the hydroxy-adduct of picrate ion. There is no evidence for a build-up in concentration of (4) or (5) and it is likely that hydroxide attack at the 1-position will be rate determining in the overall substitution reaction. The failure to observe a complex with structure (6) indicates that in (2) hydroxide attack at the 1-position is likely to be faster or similar in rate to attack at the 5-position.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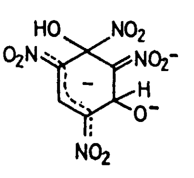
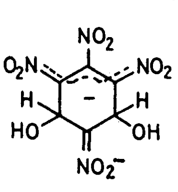

(5)


(6)

There is also evidence, though not so clear-cut, for a similar mode of nucleophilic displacement in the 3-hydroxy-complexes of picryl chloride and trinitroanisole.

## EXPERIMENTAL

1,2,4,6-Tetranitrobenzene was prepared as before[10] and recrystallised from chloroform to m.p. 124 °C (lit.,[21] 126 °C). Other nitro-compounds were recrystallised commercial specimens. Aqueous solutions of sodium hydroxide and sodium chloride were prepared from AnalaR reagents with carbon dioxide free water.

A 'Canterbury' stopped-flow spectrophotometer was used to measure rates of fast reactions and optical densities and spectral shapes of transient species. Because of the ability to measure small voltage changes (1 part in $2 \times 10^3$) small values of optical density could be determined with better accuracy than with a normal spectrophotometer. In all cases [base] $\gg$ [substrate], or the hydroxide concentration was buffered, so that first order kinetics were obtained. Rate coefficients were evaluated graphically, using the Guggenheim method where appropriate, and are accurate to ±5%. It was found that mixing water with solutions of sodium hydroxide more concentrated that 1M in the stopped-flow spectrophotometer produced turbid solutions which gave irregular traces when viewed on a time-base greater than 1 s. However, this problem was minimised by mixing solutions of similar ionic strength (*e.g.*, 2M-NaOH with 2M-NaCl).

Unicam SP 500 and SP 8000 and Beckman S 25 instruments were used to determine the spectral shapes of stable species and to measure the rates of slow reactions.

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