The Reactivity of Dinitrogen Trioxide and of Nitrosyl Thiocyanate

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The reactions of dinitrogen trioxide as an electrophilic nitrosating agent with the azide ion and with *m*-chlorophenylhydrazine occur at rates close to the encounter limit. From the temperature variation of features in the kinetics of the reaction with azide ion it is calculated that ΔH for the formation of N_2O_3(aq) from $2HNO_2$(aq) is close to zero. Arguments are advanced to suggest that nitrosyl thiocyanate reacts with the azide ion and not with hydrazoic acid.

Dinitrogen trioxide is an important intermediate in many reactions of nitrous acid, usually functioning as an electrophilic nitrosating agent. On theoretical grounds it has been predicted [1] to be less reactive than other common nitrosating agents such as nitrosyl chloride or nitrosyl bromide, both of which can react with aromatic amines at close to the encounter rate.[2] A recent determination of the equilibrium constant for reaction (1) gave a value some two powers of ten less than previous measurements,[3] and this suggested that the rate constant for reaction (2)

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad (1)$$

$$PhNH_2 + N_2O_3 \longrightarrow \text{products} \qquad (2)$$

was *ca.* 7 × 10⁸ mol⁻¹ dm³ s⁻¹ at 25 °C, much closer to the encounter rate than had previously been realised. In this paper we report reactivities of N_2O_3 towards two powerful nucleophiles, the azide ion and *m*-chlorophenylhydrazine, which are even closer to the encounter rate, confirming the foregoing view. We also report activation energy data on the formation of N_2O_3 in reaction (1), a quantity which is of interest[4] in environmental calculations of the interaction of NO + NO_2 with water droplets.

Reaction of m-*Chlorophenylhydrazine with Dinitrogen Trioxide*.—In the course of a study of the reaction between ring-substituted arylhydrazines and an excess of nitrous acid at low acidity, it was found that reaction (3) involves at least two consecutive stages, and repeated u.v. scans of reaction mixtures showed that these stages overlap substantially. We did not succeed in finding conditions where the first reaction could be studied with its latter stages free from interference by the next stage.

$$ArNHNH_3^+ + 2HNO_2 \longrightarrow ArN_2^+ + N_2O + 3H_2O \qquad (3)$$

In order to study the first reaction free from interference, we measured the initial rate of increase of absorbance (A) at 280 nm by stopped-flow spectrophotometry. The value of $(dA/dt)_0$ is related to the chemical initial rate v_0 (mol dm⁻³ s⁻¹) by the factor $(\varepsilon_p - \varepsilon_r)d$, where ε_p and ε_r are the extinction coefficients of the products and reactants involved in the first stage, and d is the path length. Provided that $(\varepsilon_p - \varepsilon_r)$ is constant over the range of conditions studied, the kinetic order of reaction may be deduced from the variation of $(dA/dt)_0$ with concentration. The results, summarised in Table 1, show that the initial rates fit equation (4). This is precisely the form of rate equation

$$v_0 = k_1\,[HNO_2]^2[ArNHNH_3^+]/[H^+] \qquad (4)$$

originally observed by Schmid *et al.*[5] for the nitrosation of aniline, and the interpretation of (4) in terms of mechanism is similar to that postulated for Schmid's results, a rate-determining electrophilic attack by dinitrogen trioxide upon the free base form of the arylhydrazine. There are two nitrogen atoms which might be attacked. Interaction of the lone pair with the π shell of the aromatic ring would be expected to make the NH group less basic than the terminal NH_2. This is

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad \text{fast} \quad K \qquad (5)$$

$$N_2O_3 + ArNHNH_2 \longrightarrow ArNHNHNO + HNO_2 \qquad \text{slow} \quad k_2 \qquad (6)$$

confirmed by the fact that i.r. spectra show[6] that the phenylhydrazine is protonated almost exclusively on the terminal nitrogen, and also by the work of Condon *et al.*[7]

We assume that the electrophilic nitrosation reaction (6) involves essentially exclusive attack on the more basic, terminal nitrogen, forming ArNHNHNO. In more acidic conditions and with low values of $[HNO_2]$ where the electrophile is NO^+ and the concentration of the free base is reduced, reaction occurs with $ArNHNH_3^+$, and the nitrosation product is the isomer ArN(NO)NH_2 (or its conjugate acid). The rates in Table 1 in absorbance units were converted into rates in mol dm⁻³ s⁻¹ using an extinction coefficient for ArNHNHNO (obtained under other conditions) of 5 625 mol⁻¹ dm³ cm⁻¹. Taking the pK_a of *m*-$ClC_6H_4NHNH_3^+$ to be 4.92, and K for reaction (5) to be 3 × 10⁻³ mol⁻¹ dm³, then k_2 is 1.6 × 10⁹ mol⁻¹ dm³ s⁻¹.

This value is less than that (7.4 × 10⁹ mol⁻¹ dm³ s⁻¹) expected[8] for an encounter-controlled process, but is not much below it. The high reactivity of *m*-$ClC_6H_4NHNH_2$ is probably due to the α-effect, and presumably N_2H_4 would be even more reactive. However, the much higher pK_a for $NH_2NH_3^+$ (8.01) means that the concentration of the free base is too low for the mechanism to be easily observable. Our attempts to observe the nitrosation of hydrazine by N_2O_3 by raising the nitrite concentration and reducing the acidity through the use of HNO_2–$NaNO_2$ buffers were unsuccessful.

Reaction of Azide Ion with Dinitrogen Trioxide.—The reaction (7) between nitrous acid and hydrazoic acid has been

$$HNO_2 + HN_3 \longrightarrow N_3NO + H_2O \longrightarrow N_2 + N_2O + H_2O \qquad (7)$$

shown[9] to involve nitrosyl azide as an intermediate by ^{15}N tracer experiments. The kinetics of reaction at 0 °C obey[10] equation (8) below $[H^+]$ = 0.04 mol dm⁻³ and (9) above

$$\text{rate} = k_4[HNO_2]^2 + k_5[H^+][HNO_2][HN_3] \qquad (8)$$

$$\text{rate} = k_5[H^+][HNO_2][HN_3] \qquad (9)$$

$[H^+]$ = 0.1 mol dm⁻³. The transition between these two equations appears as a point of inflection on a plot of rate

Table 1. Initial rates of reaction between *m*-chlorophenylhydrazine and nitrous acid, measured at 280 nm; I = 0.2 mol dm^{-3}; 25 °C[a]

$10^4[ArNHNH_3^+]$ mol dm^{-3}	$10^3[HNO_2]$ mol dm^{-3}	$10^3[H^+]$ mol dm^{-3}	$10^2(dA/dt)_0$/s^{-1}	k_1/mol dm^{-3} s^{-1}
2.0	5.0	5.0	13.6	44.4
1.0	5.0	5.0	6.50	42.5
0.5	5.0	5.0	3.28	42.9
0.2	5.0	5.0	1.34	43.8
1.0	10.0	5.0	23.0	40.7
1.0	2.0	5.0	1.03	39.8
1.0	1.0	5.0	0.30	45.3
1.0	5.0	10.0	5.09	49.5
1.0	5.0	2.5	8.04	41.6
1.0	5.0	1.0	9.67	43.5

[a] All concentrations are stoicheiometric values. In calculating k_1 corrections must be applied to allow for the ionisation of nitrous acid using pK_a 2.84 (I = 0.2 mol dm^{-3}).

Table 2. Activation energy for the formation of dinitrogen trioxide

T/°C	12	15	25	30	35	40	45
k_4/mol^{-1} dm^3 s^{-1} [a]		4.15	12.2	17.7	28.5	41.9	58.6
k_4/mol^{-1} dm^3 s^{-1} [b]	3.43	4.69	11.74		27.2		

[a] Nitrite–azide reactions: $[HNO_2]$ = 0.03 mol dm^{-3}, $[NaNO_2]$ = 0.03 mol dm^{-3}, $[HN_3]$ = 0.01 mol dm^{-3}. [b] Nitrite–thiosulphate reaction: $[HNO_2]$ = 0.025 mol dm^{-3}, $[NaNO_2]$ = 0.025 mol dm^{-3}, $[Na_2S_2O_3]$ = 0.002 mol dm^{-3}.

against $[H^+]$. The $k_4[HNO_2]^2$ term corresponds to the mechanism (10)—(13) with k_6 as a rate-determining step at low

$$2HNO_2 \longrightarrow N_2O_3 + H_2O \qquad k_6 \qquad (10)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \qquad k_7 \qquad (11)$$

$$N_2O_3 + N_3^- \longrightarrow N_3NO + NO_2^- \qquad k_8 \qquad (12)$$

$$N_3NO \longrightarrow N_2 + N_2O \qquad \text{fast} \qquad (13)$$

acidities. As $[H^+]$ increases so $[N_3^-]$ decreases, and the disappearance of the k_4 term in (8) is due to there being too low a concentration of azide ion to compete effectively with water for the dinitrogen trioxide. The mid-point of the transition corresponds to $k_7[N_2O_3] = k_8[N_2O_3][N_3^-]$. The value of k_7 is shown[11] at 20 °C from pulse-radiolysis work to be 530 s^{-1}, so if the transition from (8) to (9) were observable at 20 °C a value of k_8 could be calculated.

The earlier measurements[10] at 0 °C were extended to 20 °C using $[HN_3]_0 = [HNO_2]_0$ = 0.0004 mol dm^{-3}, and the mid-point of the transition (8)—(9) was determined to be at $[H^+]$ = 0.02 mol dm^{-3}. Taking[12] the pK_a for hydrazoic acid at 20 °C to be 4.70 and k_7 to be 530 s^{-1} we calculate k_8 to be 2.1×10^9 mol^{-1} dm^3 s^{-1}, again a value not far below the encounter limit. If we assume the activation energy for k_8 to be 21.0 kJ mol^{-1}, the value for an encounter reaction,[8] then we can calculate k_8 at 0 °C to be 1.1×10^9 mol^{-1} dm^3 s^{-1}, and taking a pK_a for HN_3 of 4.96 enables one to calculate k_7 to be *ca.* 62 s^{-1} at 0 °C. This gives an activation energy for (11) of 71 kJ mol^{-1}. It is difficult to estimate an error for these values. If the acidity at the mid-point of the transition is estimated to ±10%, this gives an error in the activation energy of ±6 kJ mol^{-1}.

Measurements of the Activation Energy for the Formation of Dinitrogen Trioxide.—To provide a reliable value for the activation energy of reaction (10), reaction (8) was investigated using hydrazoic acid with a large excess of HNO_2–$NaNO_2$ buffer. The relatively low acidity and high value of $[HNO_2]$ ensured that the k_4 terms completely swamped the k_5 term in (8) and that only the former was observed.

The disappearance of nitrous acid was followed spectrophotometrically, and as there was a large excess of nitrite buffer and the rate of reaction was independent of the azide concentration, individual runs yielded zero-order kinetics. The rate data, summarised in Table 2, gave an activation energy of 67.3 ± 2.0 kJ mol^{-1}. To confirm these results we have also examined the reaction (14) of thiosulphate with nitrous acid.

$$S_2O_3^{2-} + HNO_2 + H^+ \longrightarrow O_3SSNO^- + H_2O \qquad (14)$$

The product is the yellow-coloured nitroso derivative of the thiosulphate ion, its colour arising from the S–N=O grouping. This reaction can also proceed by a rate-determining formation of dinitrogen trioxide,[13] and can be followed by monitoring the growth in absorbance at 420 nm due to the product. The results are summarised in Table 2 and give an activation energy of 65.6 ± 0.6 kJ mol^{-1}. The close agreement between the activation energies for the forward and the back reaction in (1) implies that ΔH is not far from zero. In a detailed survey of the thermochemistry of equilibria involving oxides of nitrogen, Schwartz and White suggest ΔH = 35.5 kJ mol^{-1} for reaction

$$2HNO_2(aq) \longrightarrow N_2O_3(g) + H_2O(l) \qquad (15)$$

(15). The difference between this value and zero implies considerable solvation for N_2O_3 in aqueous solution.

With regard to the activation energy for the formation of dinitrogen trioxide, the usually accepted mechanism is set out as reactions (16) and (17). Some authors prefer to write the

$$H^+ + HNO_2 \rightleftharpoons NO^+ + H_2O \qquad \text{fast} \qquad K_1 \qquad (16)$$

$$NO^+ + NO_2^- \longrightarrow N_2O_3 \qquad \text{slow} \qquad k_9 \qquad (17)$$

electrophile as $H_2NO_2^+$, but this does not affect the ensuing arguments.[1] Thus the rate of reaction is given by $K_1k_9[H^+][HNO_2][NO_2^-]$. This is related to our measured value k_4 by the relationship $k_4/K_2 = K_1k_9$, where K_2 is the ionisation constant of nitrous acid. The rates of a considerable number of nitrosation reactions can be expressed in the form (18). A range

$$v_0 = k_{10}[H^+][HNO_2][X^-] \qquad (18)$$

of nucleophilic anions have very similar values of k_{10}, and similar activation energies, all close to 54 kJ mol^{-1}. Using literature values[12] for the temperature variations of K_2, we calculate that the activation energy corresponding to K_1k_{10} is 57 kJ mol^{-1}, close to the value found for other anions. When a numerical value of 3×10^{-7} is substituted for K_1 it is found that for a range of anions k_9 is close to the encounter limit for bimolecular processes.[8]

These points are relevant to a recent account[14] of the kinetics of a number of nitrosation reactions which described an investigation (among many other reactions) of the thiocyanate-ion-catalysed reaction between nitrous acid and hydrazoic acid. This was found to follow the rate law (18) with X = SCN, and the postulated mechanism is shown in (19)—(21), with the

$$\mathrm{H^+ + HNO_2 + SCN^- \longrightarrow ONSCN + H_2O} \quad k_{11} \quad (19)$$

$$\mathrm{ONSCN + H_2O \longrightarrow H^+ + HNO_2 + SCN^-} \quad k_{12} \quad (20)$$

$$\mathrm{HN_3 + ONSCN \longrightarrow products} \quad k_{13} \quad (21)$$

suggestion that $k_{13}[\mathrm{HN_3}] \gg k_{12}$. In this inequality $[\mathrm{HN_3}]$ represents total azide, not specifically hydrazoic acid. The activation energy for (18) is quoted as 54 kJ mol^{-1}, which is described as rather high for an encounter-controlled reaction. This view is not correctly expressed. The encounter-controlled process is the reaction between the electrophile and the thiocyanate ion, and this should have an activation energy of around 21 kJ mol^{-1}. The figure of 54 kJ includes a contribution for ΔH for generating the electrophile from H^+ and HNO_2, *i.e.* ΔH for (16).

In the foregoing investigation the fact that the kinetics were of zero order with respect to azide meant that there was no information about the nature of the azide species trapping the nitrosyl thiocyanate. Nitrosyl thiocyanate is known to be a markedly less reactive electrophile than dinitrogen trioxide, and this reactivity sequence is confirmed by the relative rates of hydrolysis at 20 °C of ONSCN (8 070/32 = 231 s^{-1}) and of N_2O_3 (530 s^{-1}). If the more reactive N_2O_3 reacts with azide ion then the less reactive ONSCN is also likely to do so. To settle the point, kinetic measurements need to be made under conditions where the azide trapping process determines the rate, so that the acidity dependence can show whether HN_3 or N_3^- is the nucleophile. This also needs to be done at acid concentrations sufficiently low that there are no complications due to salt effects, or the choice of an appropriate acidity function.

A further point concerns the reported catalysis[15] of the nitrosation of the arylhydrazines by Cl^-, Br^-, and SCN^-. The acidity dependence of the halide/pseudo-halide-catalysed reaction was not investigated, and it was tacitly assumed[15] that the nitrosyl halides attacked the conjugate acid form of the arylhydrazine, as was observed for nitrosation by NO^+. The similarity in reactivity between ONSCN and N_2O_3, and the fact that the latter undoubtedly nitrosates the free base form of *m*-chlorophenylhydrazine, suggests that ONSCN may also react with the free base. Thus further work on the halide-catalysed reaction of nitrous acid with arylhydrazine to establish the acidity dependence is clearly needed.

Experimental

Most kinetic measurements were carried out with a Canterbury SF3A stopped-flow instrument, with data collection and processing facilities. The measurements on the nitrosation of *m*-chlorophenylhydrazine were carried out at 280 nm, and those on the activation energy for the formation of dinitrogen trioxide at 370 nm. The kinetic studies on the transition from rate law (8) to (9) for the nitrite–azide reaction were carried out by conventional spectrophotometry at 215 nm with a Unicam SP8-200 instrument.

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