The Effect of Added Halide and Thiocyanate Ions on the Nitroamine–Nitrous Acid Reaction. The Oxidation of Nitroamine by Halogens

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The nitrous acid–nitroamine reaction is catalysed by added thiocyanate ion or chloride ion, with a rate law $-d(HNO_2)/dt = k_3[HNO_2][NH_2NO_2][X^-]$, where $X^- = SCN^-$ or Cl^-, which may be re-expressed as $-d(HNO_2)/dt = k_5[NOX][NHNO_2^-]$. This rate law corresponds to a rate-determining attack of the covalent nitrosyl compound upon the deprotonated nitroamine molecule: for thiocyanate, $k_5 = 1.3 \times 10^4$ dm^3 mol^{-1} s^{-1} at $I = 0.25$ mol dm^{-3} and 0 °C. The addition of bromide results in a small catalytic effect, but after an induction period there is rapid increase in the rate of loss of nitrous acid, with a change in stoicheiometry. It is suggested that the reaction is initiated by the attack of bromine or bromine atoms (formed by decomposition of nitrosyl bromide) on nitroamine to give a species that reacts with nitrous acid.

Nitroamine and nitrous acid react [1] in aqueous perchloric acid solution to give nitrate and dinitrogen, with a rate law given by equation (1) where $k_4 = 2.8 \times 10^{-3}$ and $k_5 = 1.6 \times 10^3$

$$\text{Rate} = (k_4[NH_2NO_2] + k_5[NHNO_2^-])[H^+][HNO_2] \quad (1)$$

dm^6 mol^{-2} s^{-1} at 0 °C. The two terms in the rate law correspond to attack of the nitrosating agent upon the neutral and deprotonated nitroamine molecules. We now report upon the catalysis of the nitroamine–nitrous acid reaction by added chloride, bromide, and thiocyanate and also, arising from this, on the reaction between nitroamine and halogens.

Experimental

Nitroamine was prepared by the sulphamic acid–nitric acid reaction as described earlier.[1] All other reagents were the best grade available. Kinetic runs on the catalysis of the nitroamine–nitrous acid reaction were initiated by adding a known volume of sodium nitrite solution to a solution of the remaining components at an appropriate temperature. The runs were followed by withdrawing samples at various time intervals and analysing them for nitrite by the standard colorimetric method using sulphanilic acid and β-naphthol. Runs were usually carried out at $I = 0.250$ mol dm^{-3}, maintained by sodium perchlorate, and with an excess of nitroamine over nitrous acid.

Spectroscopic measurements were carried out on Unicam SP 500 and SP 800 instruments using silica cells. Nitrate was determined as described earlier.[1]

Results

Studies on the reaction catalysed by chloride or thiocyanate ions show the stoicheiometry of the reaction to be represented by equation (2).

$$NH_2NO_2 + HNO_2 \longrightarrow N_2 + HNO_3 + H_2O \quad (2)$$

Addition of bromide affects the stoicheiometry and will be discussed later.

Catalysis by Thiocyanate Ion.—The addition of thiocyanate ion results in a significant increase in the rate of the nitroamine–nitrous acid reaction. First-order rate constants for the reaction ($k_{obs.}$) were obtained from plots of log (optical density) against time, and show the reaction to be first order in nitrous acid. First-order rate constants for the thiocyanate-catalysed reaction are given by $k_1 = (k_{obs.} - k_0)$, where k_0 is the measured first-order rate constant for the kinetic run without added thiocyanate. The dependence of the rate of the thiocyanate-catalysed reaction upon $[NH_2NO_2]$, $[H^+]$, and $[SCN^-]$ was found by observing the effect of change in the concentration of these species on values of k_1. Rate constants k_2 and k_3 are given by $k_2 = k_1/[NH_2NO_2]$ and $k_3 = k_2/[SCN^-]$. Values of rate constants $k_{obs.}$, k_1, k_2, and k_3 are shown in Table 1. Values of k_0 at constant conditions vary slightly with each batch of nitroamine, as noted earlier,[1] and were remeasured at the start of each set of runs.

Constancy of values of k_2 and k_3 over a range of $[NH_2NO_2]$ and $[SCN^-]$ respectively confirms the thiocyanate-catalysed reaction to be of first order in both nitroamine and thiocyanate. Values of k_1 are independent of $[H^+]$, so the final rate law is given by equation (3), which may be rewritten as equations (4) and (5). Rate law (5) may be interpreted in terms of a rate-determining attack of nitrosyl thiocyanate on the

$$-d(HNO_2)/dt = k_3[HNO_2][NH_2NO_2][SCN^-] \quad (3)$$

$$-d(HNO_2)/dt = k_4[H^+][HNO_2][SCN^-][NHNO_2^-] \quad (4)$$

$$-d(HNO_2)/dt = k_5[NOSCN][NHNO_2^-] \quad (5)$$

deprotonated nitroamine molecule. Rate constant $k_4 = k_3/K_a$ (where K_a is the acid dissociation constant for nitroamine) and rate constant $k_5 = k_4/K_{NOSCN}$, where K_{NOSCN} is the formation constant for nitrosyl thiocyanate. A value for K_a is known [2] (2.55×10^{-7} mol dm^{-3}, measured at 0 °C and over a nitroamine concentration range 0.01—0.001 mol dm^{-3}), while the thermodynamic constant K_{NOSCN} has been determined at 0 °C (46 dm^6 mol^{-2}). Using literature values for activity coefficients [3,4] the value at 0.25 mol dm^{-3} ionic strength has been calculated to be 27.5 dm^6 mol^{-2}. The mean value of k_5 was calculated to be 1.3×10^4 dm^3 mol^{-1} s^{-1}.

Catalysis by Chloride Ion.—Added chloride ion has only a small effect on the rate of the nitroamine–nitrous acid reaction. The observed rate law is identical to that found for catalysis by thiocyanate. Values of k_3, as defined above for catalysis by the thiocyanate ion, lie in the range (1.20—1.60) ×

Table 1. Catalysis of the nitrous acid–nitroamine reaction by thiocyanate ion at 0 °C, $[HNO_2] = 1 \times 10^{-3}$ mol dm^{-3}, and $I = 0.25$ mol dm^{-3}

$[H^+]$/ mol dm^{-3}	$[NH_2NO_2]$/ mol dm^{-3}	$[SCN^-]$/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	10^4k_1/s^{-1}	10^3k_2/ dm^3 mol^{-1} s^{-1}	10^2k_3/ dm^6 mol^{-2} s^{-1}
0.05	0.0258	0.000	0.200			
0.05	0.0258	0.100	2.36	2.16	8.57	8.57
0.05	0.0258	0.150	3.95	3.75	14.5	9.69
0.05	0.0258	0.200	4.78	4.58	17.8	8.90
0.05	0.0200	0.000	0.274			
0·05	0.0200	0.010	0.450	0.176	0.880	8.80
0.05	0.0200	0.040	0.955	0.681	3.41	8.53
0.05	0.0200	0.100	2.18	1.90	9.50	9.50
0.10	0.0129	0.000	0.137			
0.10	0.0129	0.025	0.432	0.295	2.28	9.12
0.10	0.0129	0.050	0.703	0.566	4.39	8.78
0.10	0.0129	0.050	0.716	0.579	4.49	8.98
0.10	0.0129	0.075	0.944	0.807	6.25	8.33
0.10	0.0129	0.100	1.33	1.19	9.25	9.25
0.10	0.020	0.000	0.340			
0.10	0.020	0.010	0.537	0.197	0.985	9.85
0.10	0.020	0.025	0.830	0.490	2.45	9.80
0.10	0.020	0.100	2.32	1.98	9.90	9.90
0.10	0.040	0.000	0.528			
0.10	0.040	0.020	1.230	0.702	1.76	8.80
0.10	0.050	0.000	0.516			
0.10	0.050	0.040	2.36	1.84	3.68	9.20
0.10	0.075	0.020	2.52	1.44	19.2	9.60
0.10	0.100	0.020	2.42	2.00	20.0	10.0
0.21	0.020	0.000	0.322			
0.21	0.020	0.040	1.01	0.688	3.44	8.60

Table 2. Catalysis of the nitrous acid–nitroamine reaction by chloride ion at 0 °C, $[HNO_2] = 1 \times 10^{-3}$ mol dm^{-3}, and $I = 0.25$ mol dm^{-3}

$[H^+]$/ mol dm^{-3}	$[NH_2NO_2]$/ mol dm^{-3}	$[Cl^-]$/ mol dm^{-3}	$10^5k_{obs.}$/s^{-1}	10^5k_1/s^{-1}	10^3k_2/ dm^3 mol^{-1} s^{-1}	10^3k_3/ dm^6 mol^{-2} s^{-1}
0.05	0.050	0.000	3.87			
0.05	0.050	0.150	4.94	1.07	0.214	1.43
0.05	0.050	0.200	5.10	1.23	0.246	1.23
0.15	0.050	0.000	3.40			
0.15	0.050	0.025	3.60	0.20	0.04	1.60
0.15	0.042	0.050	3.65	0.25	0.060	1.20

10^{-3} dm^6 mol^{-2} s^{-1}. The scatter in value results from the fact that the first-order rate constant for the catalysed reaction is given by a small difference between $k_{obs.}$ and k_0, where $k_{obs.}$ and k_0 are the measured first-order rate constants for the reaction in the presence and absence of chloride ion respectively. Because of this scatter in values of k_3 the kinetic data are not presented in full. Some data are presented in Table 2.

The value of rate constant k_3 for the thiocyanate-catalysed reaction is *ca.* 9×10^{-2} dm^6 mol^{-2} s^{-1}, suggesting that thiocyanate catalysis is about sixty times more effective than chloride catalysis. However, this result really reflects the differing extents to which NOSCN and NOCl are formed in solution. A value [5] for $K_{NOCl} = 5.5 \times 10^{-4}$ dm^6 mol^{-2} at 0 °C has been reported, so that $K_{NOSCN}/K_{NOCl} \approx 9 \times 10^4$. Thus these results confirm the greater activity of nitrosyl chloride towards deprotonated nitroamine by a factor of 1.5×10^3, with $k_5 \approx 2 \times 10^7$ dm^3 mol^{-1} s^{-1}.

Catalysis by Bromide Ion.—This differed from that observed for chloride and thiocyanate. In reactions with added bromide there appeared to be some catalytic effect for a period of up to 1 h, which was rather greater than that found for chloride at similar concentrations. However, eventually there was a substantial increase in the rate of loss of nitrous acid, the rate increasing with time, *e.g.* successive values of $t_{\frac{1}{2}}$ (min) are 49, 11, and 7 at 0 °C, $[H^+] = 0.1$, $[NH_2NO_2] = 0.02$, $[HNO_2] = 0.001$, and $[Br^-] = 0.05$ mol dm^{-3}. The induction period decreased with increase in $[Br^-]$. It was noted that the solution became red prior to the onset of the rapid reaction, and that the intensity of this colour decreased as the reaction proceeded. The bromide-dependent reaction was suppressed by the addition of ethanol.

The immediate explanation of these results is that the nitrosyl bromide in solution decomposes to give nitrogen monoxide and bromine, and that one of these species reacts with nitroamine to give a new species that reacts rapidly with nitrous acid. An alternative view is that nitrous acid reacts with the bromine formed in solution, a reaction that occurs rapidly.[6] However, the reaction solution without nitroamine is stable with respect to decomposition of nitrous acid, so nitroamine must be involved in the decomposition pathway.

Studies on the stoicheiometry of the bromide-dependent reaction showed a decreased production of nitrate, with $\Delta[HNO_3]/\Delta[HNO_2] = 0.56$ at $[H^+] = 0.1$ mol dm^{-3}. The gaseous products under these conditions were not examined.

It was clearly of interest to examine the reactivity of nitroamine to bromine and its hydrolysis products. Reaction did not occur with hypobromite or bromate. However, nitroamine and freshly prepared bromine water reacted after an induction period of a few minutes, while addition of nitroamine to a solution of bromine that had stood for some time resulted in immediate decolourisation. Addition of ethanol prevented the nitroamine–bromine reaction taking place. Nitroamine reacted readily with an aqueous solution of iodine without an induction period.

Discussion

The results for catalysis of the nitroamine–nitrous acid reaction by thiocyanate and chloride ions may be understood readily. It is clear that the nitrosating species, the nitrosyl compound NOX, reacts with the deprotonated nitroamine molecule and not with the neutral molecule. This is in accord with the lack of reactivity of nitrosyl thiocyanate and nitrosyl chloride, compared to other nitrosating agents, in that reaction only takes place with the species with enhanced nucleophilic character, namely the nitroamine anion. It seems reasonable that the rate-determining step is that of N-nitrosation, subsequent steps being fast. In the following scheme the $NH{=}NO_2H$ form of the anion is not invoked ($X^- = Cl^-$ or NCS^-).

$$H^+ + HNO_2 + X^- \rightleftharpoons NOX + H_2O$$
$$NOX + NHNO_2^- \longrightarrow ONNHNO_2 + X^-$$
$$ONNHNO_2 \longrightarrow HONN{=}NO_2 \longrightarrow OH^- + N_2 + NO_2^+$$

Scheme.

A comparison of these results with those for other anion-catalysed nitrosations is of interest. Rate constants k_5 (using the notation of this paper) are shown below ($dm^3\ mol^{-1}\ s^{-1}$) for reaction[7] of NOX with various substrates at 0 °C.

	10^7k_5 (NOCl)	10^7k_5 (NOSCN)
NH_2OH	3.5	0.36
NH_2OCH_3	1.6	0.13
$NHNO_2^-$	*ca.* 2	0.0013

It is clear that the rate constant for the $NOCl–NHNO_2^-$ reaction is very similar to those found for other substrates, while that for the $NOSCN–NHNO_2^-$ reaction is much smaller than those found for other substrates. The reactivity of NOSCN towards the deprotonated nitroamine molecule is lower than expected by a factor of 10^2.

The reaction with added bromide cannot be explained at present and further work is probably required on the reactions between nitroamine and the halogens. However, it seems likely that it is initiated by attack of bromine (or bromine atoms in equilibrium concentration) on the nitroamine to give eventually some species that reacts with nitrous acid. A possible intermediate is the radical species $\dot{N}HNO_2$, which could dimerise to give $O_2N{\cdot}NHNH{\cdot}NO_2$. This could break down to give initially $NO_2 + N_2H_2$ and finally $N_2O_4 + N_2 + N_2H_4$. The formation of N_2O_4 (and hence $HNO_2 + HNO_3$) could account for the observed stoicheiometry for the production of nitrate, while decomposition of nitrous acid would occur *via* reaction with hydrazine.[8]

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