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Nitrosation of Ammonia

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The kinetics of the nitrosation of the ammonia in acid solution show a first-order dependence on $[NH_4^+]$ and $[HNO_2]$, and a zero-order dependence upon $[H^+]$. Reaction is very strongly catalysed by both Br^- and SCN^-. These facts are consistent with a mechanism in which BrNO or ONSCN reacts with the free base form of ammonia in the rate-limiting step, to give initially a *N*-nitroso ion which breaks down rapidly to give nitrogen. Kinetic analysis yields values of 2.6×10^7 and 0.11×10^7 l mol^{-1} s^{-1} for the second-order rate constants for attack of BrNO and ONSCN respectively. Similarly values of 2.3×10^7 and 1.7×10^7 l mol^{-1} s^{-1} were obtained for the corresponding reactions of the more basic dimethylamine. These results for BrNO, and others in the literature strongly suggest that for these and other very basic aliphatic amines, the reaction is encounter-controlled, although the rate constants are $\sim 10^2$ smaller than the calculated value. The more limited results available for the thiocyanate catalysed reactions show that ONSCN is always less reactive than BrNO, but as with the most basic amines such as dimethylamine, it too probably reacts at the encounter rate. Differences between aliphatic and aromatic amine reactions are discussed.

The thermal decomposition of solutions containing the ammonium and nitrite ions is a well known laboratory preparation of nitrogen [equation (1)]. The usual procedure is

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O \quad (1)$$

to mix aqueous ammonium chloride and sodium nitrite; nitrogen is evolved upon warming the solution. The reaction has been examined mechanistically to some extent, and the reaction is thought to involve nitrosation of the free base form of ammonia present in low concentration [equation (2)].

$$NH_3 + HNO_2 + H^+ \xrightarrow{\text{slow}} ON\overset{+}{N}H_3 \xrightarrow{\text{fast}} HN_2^+ + H_2O \xrightarrow{\text{fast}} N_2 + H^+ \quad (2)$$

Ammonia seems to behave in the same way as primary and secondary amines (aliphatic and aromatic), at least as far as all reactions appear to involve rate-limiting *N*-nitrosation. Ammonia can thus be regarded as the parent primary aliphatic amine. The outline mechanism given in (2) has recently been confirmed by Olah and co-workers[1] using a ^{15}N-labelling technique. They used $^{15}NO^+BF_4^-$ as the nitrosating agent, and obtained $^{14}N{-}^{15}N$, consistent with the intermediacy of the parent diazonium ion HN_2^+ (protonated dinitrogen).

Reaction with nitrous acid in aqueous acid is very slow for ammonia. This makes the determination of accurate rate constants difficult because the decomposition rate of nitrous acid is now significant compared to the nitrosation rate. Further, early workers[2] used a method based on measurement of the gas evolved, and again this is likely to be in error because of gaseous decomposition products of nitrous acid. Catalysis by chloride and bromide ion has been reported[3] as expected for the nitrosation of an amine-like substrate. However the second-order rate constants for ClNO and BrNO attack are given as 3.0×10^9 and 1.9×10^9 l mol^{-1} s^{-1} respectively at 25 °C. These values are much closer to the values reported for aniline and some aniline derivatives[4] (and also to that calculated for an encounter-controlled process) than to those determined for the more basic aliphatic amines[5] (typically $\sim 2 \times 10^7$ l mol^{-1} s^{-1}).

The object of the present work is to determine second-order rate constants for attack of ammonia by nitrosating agents in order to establish whether ammonia (pK_a 9.5) behaves as a typical aliphatic amine, *e.g.* dimethylamine (pK_a 10.9), or whether for some reason ammonia behaves more like the aniline derivatives. A further point of interest here is to investigate the question of encounter-controlled rates in the reactions of ammonia with suitable nitrosating agent. We report results for the bromide and thiocyanate ion catalysed reactions. The corresponding chloride ion reactions were inconveniently slow for accurate rate measurements and catalysis by thiourea (one of the most efficient catalysts[6]) proved difficult to measure accurately since the decomposition of the *S*-nitrosothiourea intermediate was more rapid than its reaction with ammonia. We have determined also the data for the nitrosation of dimethylamine (DMA) under the same conditions, for comparison purposes.

Experimental

All materials used were of the highest purity available. Solutions of sodium nitrite were prepared daily. Rate measurements were carried out in the cell of a recording spectrophotometer, noting the disappearance of the nitrous acid absorbance at 370 nm (for the ammonia reactions) and the appearance of the nitrosamine absorbance at 332 nm (for the dimethylamine reactions). Most of the reactions were quite slow and the spontaneous decomposition of nitrous acid a significant factor. Therefore the initial rate method was used throughout, and in all cases the corresponding rate of decomposition of nitrous acid was also measured, and an appropriate correction made. The experimental error is thus larger than we would like (typically 5—10% for duplicate experiments). Further, for the ammonia reaction, measurements were complicated by the formation of bubbles (on the cell walls) which were periodically removed. In spite of these difficulties, agreement between rate constants deduced from (a) variation with $[H^+]$ and (b) variation with [substrate], was reasonable. The quoted first-order rate constants k_0 are the mean values of three separate determinations. Experiments at different $[HNO_2]$ gave the same k_0 values, confirming the first-order dependence upon $[HNO_2]$.

Results and Discussion

Some rate measurements were obtained for the reaction of nitrous acid with ammonia in acid solution in the absence of a nucleophilic catalyst. Reaction was very slow even with a high

Table 1. Variation of k_0 with $(NH_4)_2SO_4$.[a]

[NaBr] = 0.4M		[NaSCN] = 2 × 10^{-2}M	
$[(NH_4)_2SO_4]$/M	10^4k_0/s^{-1}	$[(NH_4)_2SO_4]$/M	10^4k_0/s^{-1}
0.38	0.6 ± 0.1	0.38	0.9 ± 0.2
0.75	1.5 ± 0.1	0.75	1.7 ± 0.3
1.50	2.8 ± 0.2	1.25	3.0 ± 0.4
		1.50	3.5 ± 0.4

[a] $[HClO_4]$ 0.1M; $[NaNO_2]$ 3.8 × 10^{-3}M

Table 2. Variation of k_0 with $[Br^-]$ and $[SCN^-]$ for the nitrosation of $(NH_4)_2SO_4$.[a]

[NaBr]/M	10^4k_0/s^{-1}	10^2[NaSCN]/M	10^4k_0/s^{-1}
0.2	1.0 ± 0.04	1.0	1.5 ± 0.2
0.4	2.9 ± 0.2	2.0	3.1 ± 0.3
0.6	2.9 ± 0.2	4.0	6.4 ± 0.1
0.8	5.3 ± 0.1	6.0	9.9 ± 0.3
1.0	6.0 ± 0.5	8.0	11.5 ± 0.1

[a] $[(NH_4)_2SO_4]$ 0.75M; $[HClO_4]$ 0.1M; $[NaNO_2]$ 3.8 × 10^{-3}M.

Table 3. Dependence of k_0 upon $[H^+]$.[a]

$[H^+]$/M	10^4k_0/s^{-1}
0.05	2.1 ± 0.2
0.10	2.4 ± 0.2
0.15	2.3 ± 0.2
0.20	2.7 ± 0.2

[a] $[(NH_4)_2SO_4]$ 0.355M; [NaSCN] 2.5 × 10^{-2}M; $[NaNO_2]$ 4 × 10^{-3}M.

Table 4. Values of k_1 (l mol^{-1} s^{-1}) for the reaction of NH_3 with XNO and of Me_2NH with XNO.

	(a) NH_3 reaction	
	(i) From $[X^-]$ dependence	(ii) From $[NH_4^+]$ dependence
BrNO	2.4 × 10^7	2.9 × 10^7
ONSCN	1.0 × 10^6	1.1 × 10^6
	(b) Me_2NH reaction	
	(i) From $[X^-]$ dependence	(ii) From [amine] dependence
BrNO	2.3 × 10^7	—
ONSCN	1.7 × 10^7	1.9 × 10^7

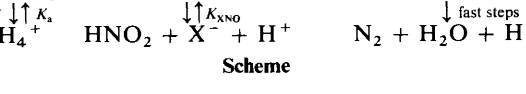
concentration of NH_4^+, and the decomposition of nitrous acid was a serious interference. Nevertheless it was possible to show that under these conditions (3M-acid) reaction was first-order in $[HNO_2]$ so that the likely reagent is $H_2NO_2^+$ or NO^+ and not N_2O_3.

(a) *Reactions with* NH_4^+. For the Br^- and SCN^- catalysed reactions gas evolution (nitrogen) made absorbance measurements difficult in the middle and later stages of the kinetic experiments, so the initial rate method was used, making the correction for nitrous acid decomposition. In all experiments $[NH_4^+] \gg [HNO_2]$. Reaction was first-order in $[NH_4^+]$ for both Br^- and SCN^- reactions as shown in Table 1, both sets of results give acceptable straight lines through the origin.

Similarly there is a first-order dependence upon $[Br^-]$ and $[SCN^-]$ at constant $[NH_4^+]$ as shown in Table 2. Plots of k_0 *vs.* $[Br^-]$ and $[SCN^-]$ are linear with a very small positive intercept common to both, which represents the uncatalysed reaction. As expected SCN^- catalysis is much more marked than is Br^- catalysis. In addition k_0 is independent of acidity, within the experimental error as shown in Table 3 for the SCN^- reaction. The data define the rate equation [equation (3)],

$$\text{Rate} = k[NH_4^+][HNO_2][Br^- \text{ or } SCN^-] \qquad (3)$$

which is consistent with the mechanistic scheme given that $[NH_4^+]$ is virtually equal to the total stoicheiometric concentration and under our conditions there is no significant



Scheme

conversion of HNO_2 to XNO (X = Br or SCN) so that the measured third-order rate constant $k = k_1K_aK_{XNO}$ (see Scheme). Values of k_1 are given in Table 4 for both Br^- and SCN^- from the rate constant variation with both $[NH_4^+]$ and with $[Br^-]$ or $[SCN^-]$. For each nucleophile, there is good agreement between the two sets of results.

(b) *Reactions with* Me_2NH. The experiments outlined in (a) were also carried out with dimethylamine, measuring the formation of the nitrosamine as a function of time. In all experiments nitrosamine formation was quantitative and reaction was first-order in $[HNO_2]$, $[Me_2NH]$ and $[Br^-]$ or $[SCN^-]$. Values of k_1 are given in Table 4, again for the SCN^- reaction there is good agreement between two sets of experimental data.

Both ammonia and dimethylamine react with BrNO with similar rate constants, 2.7 × 10^7 and 2.3 × 10^7 l mol^{-1} s^{-1} respectively. (The latter agrees reasonably with literature values[5,7] of 3.4 × 10^7 and 3.6 × 10^7 l mol^{-1} s^{-1}). This is inspite of the fact that dimethylamine is 1.5 pK_a units more basic (and presumably is more nucleophilic) than ammonia. Examination of a larger range[5] of rate constants for BrNO reactions with aliphatic amines reveals that for ten amines with a pK_a range 8.00—11.25, k_1 values mostly lie in the range 2—3 × 10^7 l mol^{-1} s^{-1}. This is convincing evidence that these reactions occur at the encounter limit and that ammonia can properly be regarded as a typical aliphatic amine. The earlier value[3] of k_1 for BrNO reaction with ammonia of 1.9 × 10^9 l mol^{-1} s^{-1} is likely to be in error, which may have arisen from the failure to account for the spontaneous decomposition of nitrous acid, which is a major factor in these relatively slow reactions.

Regarding the k_1 value for the ONSCN reaction with ammonia, since it is 20—30 times smaller than the BrNO value, it is not representing an encounter-controlled reaction. It is now well known that ONSCN is less reactive than is BrNO; this is to be expected by consideration of the relative nucleophilicities of SCN^- and Br^- and is also predicted by MO calculations using frontier orbital theory.[8] On the other hand the similarity of the k_1 values for the DMA reactions for BrNO and ONSCN suggests that here both reactions are encounter-controlled. Simple pK_a arguments would predict that (below the encounter limit) DMA is more reactive than ammonia.

The outstanding problem is that although there is very strong evidence in favour of the suggestion that aliphatic amines with $pK_a > 8$ react with BrNO at the encounter limit (and the same is true for ClNO reactions in alkaline solution[9]) the value of the rate constant is *ca.* 10^2 smaller than that predicted by the Schmoluchowski equation (7.4 × 10^9 l mol^{-1} s^{-1} for reactions in water at 25 °C).[10] The equation is based on a simple kinetic theory model and upon the Stokes–Einstein relationship.

The behaviour of aliphatic amines contrasts with that of aromatic amines where k_1 values are approximately constant (for $pK_a > 4$) for both BrNO and ClNO reactions, and the derived k_1 values do approach the calculated limit.

It has already been suggested[5] that there are perhaps two such limits, one for aliphatic and one for aromatic systems, the difference arising from the relative sizes of the two groups, or from the fact that the π-electron system confers an extra reactivity to the aromatic amines. Maybe it is fortuitous that the limiting k_1 value for the aromatic amines agrees so well with the calculated value. The answer to this problem probably lies in the need for a better theoretical model from which to calculate the limiting k_1 value, which may not be independent of the nature of the reactants.

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