# Mechanism of the Acid Catalysed Pathway for the Nitrosation of Hydroxylamine

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The profile of rate constant *versus* $[H^+]$ for the acid catalysed pathway of the nitrous acid reaction with the hydroxyammonium ion can be quantitatively interpreted in terms of a reversible $O$-nitrosation, followed by an $O$ to $N$ migration of the nitroso group in the conjugate base species $NH_2ONO$. There is no need to assume a non-steady-state mechanism involving $NO^+$, as has been proposed previously.

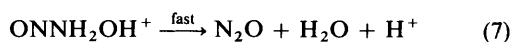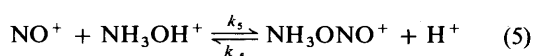Although the details of the mechanism of reaction between hydroxyammonium ion and nitrous acid [eqn. (1)] at low

$$HNO_2 + NH_3OH^+ \longrightarrow N_2O + 2H_2O + H^+ \quad (1)$$
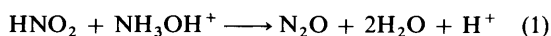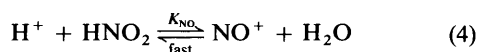
acidities are well understood there is a long standing problem concerning the reaction at higher acidities, above $[H^+] = 0.01$ mol dm$^{-3}$. At low acidities [1,2] reaction involves an $N$-nitrosation by neutral reagents ONX (X = Cl, Br, SCN, NO$_2$) reacting with the free base $NH_2OH$. The rate law, $v = k[NH_3OH^+]$ $[HNO_2][X^-]$, shows that the rate is independent of acidity. At higher acidities there is an acid catalysed reaction which involves the nitrosonium ion as the electrophile reacting with $NH_3OH^+$. A comparison of the reactivity patterns for $NH_3OH^+$, $NH_2MeOH^+$, $NH_3OMe^+$ and $NH_2MeOMe^+$ with nitrous acid showed [2] that the acid catalysed pathway occurs in those compounds where there is an hydroxy group; this has been confirmed [3] in other systems of the type $NH_2ROH^+$ and $NH_3OR^+$. It appears that in these cases there is an initial $O$-nitrosation to form a nitrito species $NH_3ONO^+$, followed by an $O$ to $N$ migration of the nitroso group. The reaction follows second-order kinetics [eqn. (2)] and the unresolved problem

$$-d[HNO_2]/dt = k_2[NH_3OH^+][HNO_2] \quad (2)$$
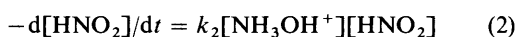
concerns the acidity dependence of $k_2$. Typical profiles of $k_2$ *versus* [HX] where HX is HClO$_4$ and H$_2$SO$_4$ are shown in Fig. 1. Around pH1–2 the rate law is given by [eqn. (3)], but as the

$$-d[HNO_2]/dt = k_3[H^+][HNO_2][NH_3OH^+] \quad (3)$$
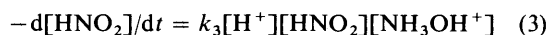
acidity rises $k_2$ increases steeply, reaches a sharp maximum close to [HX] = 2 mol dm$^{-3}$ and then decreases slowly towards higher acidities. The mechanism proposed originally is shown in eqns. (4)–(7). Bonner et al.[4] have shown by isotopic labelling

$$H^+ + HNO_2 \underset{\text{fast}}{\overset{K_{NO}}{\rightleftharpoons}} NO^+ + H_2O \quad (4)$$

$$NO^+ + NH_3OH^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} NH_3ONO^+ + H^+ \quad (5)$$

$$NH_3ONO^+ \overset{k_6}{\longrightarrow} ONNH_2OH^+ \quad (6)$$

$$ONNH_2OH^+ \overset{\text{fast}}{\longrightarrow} N_2O + H_2O + H^+ \quad (7)$$

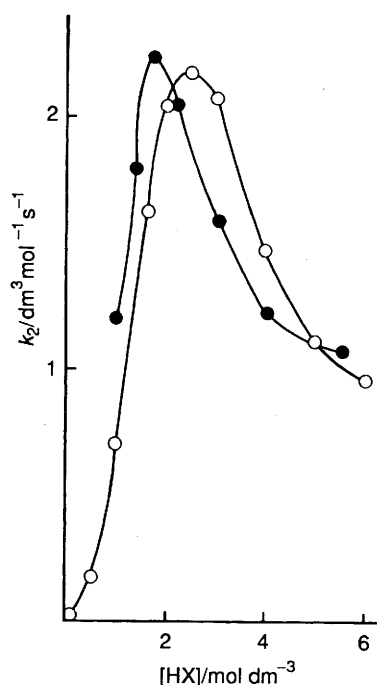that a symmetrical intermediate is involved in the formation of



Fig. 1 Variation of the second-order rate constant $k_2$ with concentration of mineral acid at 0 °C: ●, H$_2$SO$_4$: ○, HClO$_4$

$N_2O$ at all acidities up to 5 mol dm$^{-3}$ perchloric acid, and *cis*-hyponitrous acid, HON=NOH, may be an intermediate in eqn. (7). The levelling off in rate at higher acidities was ascribed [2] to the term $k_{-5}[H^+]$ becoming much greater than $k_6$ so that effectively eqn. (5) becomes an equilibrium. The fact that $k_2$ decreases with increase in acidity beyond the maximum was ascribed to a medium effect on $k_6$, the decrease being less marked in a mixture of HClO$_4$ + NaClO$_4$ of constant ionic strength.

A much more quantitative treatment of the shape of the $k_2/[H^+]$ profile was devised by Bennett et al.[5] who studied the reaction in solutions of constant ionic strength LiNO$_3$ + HNO$_3$. They fitted their data by a non-linear least-squares procedure to an expression of the type shown in eqn. (8), using

$$k_2 = \frac{aa_H}{1 + da_H + fa_H^2} \quad (8)$$

calculated values of the hydrogen ion activity $a_H$. Under their conditions $a_H$ is calculated to be almost proportional to the molar concentration of nitric acid. They comment that the value of the parameter $d$ is extremely sensitive around the maximum,
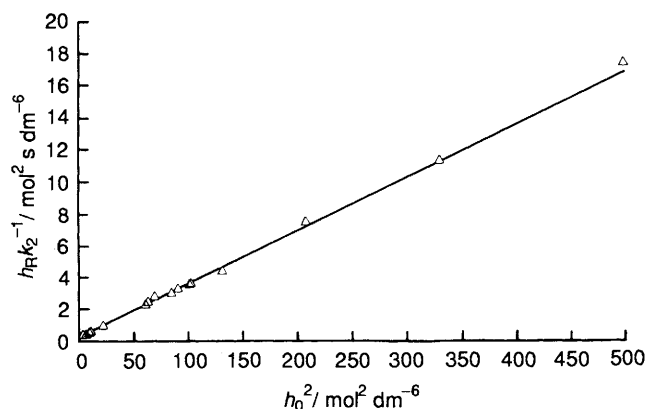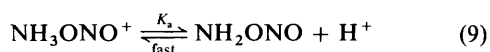
**Fig. 2** Treatment of kinetic data for reaction in sulfuric acid at 25 °C by use of acidity functions

and that as the data set is limited the value of $d$ may be close to zero. They were only able to predict an equation of the form of eqn. (8) from the mechanism of eqns. (4)–(7) by assuming that $NO^+$ is not at a steady-state distribution. This assumption is not reasonable. The formation constant $K_{NO}$ for $NO^+$, and the rate constant for its formation from $H^+ + HNO_2$ are known, and Ridd has estimated [6] that the rate constant for the reverse reaction in eqn. (4), the rehydration of $NO^+$, is ca. $2 \times 10^9$ s$^{-1}$. This gives a rate that is many orders of magnitude greater than the rate of any other reaction in which $NO^+$ is consumed in this system. Were the non steady-state explanation to be correct it would be in complete contrast to a great amount of published work on the kinetics and mechanism of diazotisation, deamination and nitrosation reactions. In fairness to Bennett *et al.* it must be noted that they explicitly stated there were problems, and recognised the possibility of there being additional steps in the mechanism.

A much more satisfactory interpretation [4,7] is to assume that the O to N migration of the nitrosyl group can only occur in the free base form of the $O$-nitrosated species, where there is a free lone pair on the nitrogen to accept the nitrosonium ion. Zollinger has independently recently made [8] a similar suggestion. If eqn. (6) is replaced by eqns. (9) and (10), then a steady

$$NH_3ONO^+ \underset{fast}{\overset{K_a}{\rightleftharpoons}} NH_2ONO + H^+ \qquad (9)$$

$$NH_2ONO \xrightarrow{k_7} ONNHOH \qquad (10)$$

state treatment assuming the acid–base equilibrium (9) to be maintained gives rate eqn. (11), writing concentrations of $H^+$

$$k_2 = \frac{k_5 k_7 K_{NO} K_a [H^+]}{k_{-5}[H^+]^2 + k_7 K_a} \qquad (11)$$

rather than activities. This is exactly the form found by Bennett *et al.* with the coefficient $d = 0$. It also fits the data [9] for $HClO_4 + NaClO_4$ of constant ionic strength of 3 mol dm$^{-3}$. At low acidities eqn. (11) simplifies to $k_2 = k_5 K_{NO}[H^+]$, and $k_5$ is calculated to be $6 \times 10^6$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C. This is much lower than the figure of $2 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ which can be calculated [10] for the reaction of $NO^+$ with $NH_3NH_2^+$, presumably due to the lower nucleophilic character of the hydroxyl compared to the amino group.

In their study of the nitrosation of another cationic species by $NO^+$, the anilinium ion, Challis and Ridd showed [11] the importance of working at constant ionic strength. This may not always be practicable. In the present work we had occasion to check the detailed acidity dependence of $k_2$ in sulfuric acid at

25 °C, where partial ionisation to sulfate and hydrogensulfate ions occurs. We attempted to allow for activity coefficient effects by use of acidity functions. The $NO^+$–$HNO_2$ equilibrium has been reported to follow the $H_R$ acidity function, and we assumed that the reverse reaction of eqn. (5) and equilibrium (9) would both follow $H_0$. Substituting $h_R$ and $h_0$ for the appropriate $[H^+]$ terms in the numerator and denominator of eqn. (11), leads to eqn. (12). If this expression is rearranged, a plot of $h_R/k_2$ versus

$$k_2 = \frac{k_5 k_7 K_{NO} K_a h_R}{k_{-5} h_0^2 + k_7 K_a} \qquad (12)$$

$h_0^2$ should be linear. Kinetic data for reaction in sulfuric acid from 0.92 to 2.94 mol dm$^{-3}$ are shown in Fig. 2, with a slope of $0.0339 \pm 0.005$ s and an intercept of $0.30 \pm 0.09$ mol$^2$ s dm$^{-6}$. Above 2.94 mol dm$^{-3}$ sulfuric acid there were deviations. Bennett *et al.* comment that for their system the acidity function approach did not work as well as their method of calculating a value of $a_H$. There is a wide range of acidity functions with different dependences upon mineral acid concentration, depending on the type of neutral indicator base used, and our choice of $H_0$, although successful, was rather arbitrary. We do not claim general validity for our approach. At sufficiently high acidities it has been found that for some mineral acids $H_R = 2H_0$. For conditions where $k_{-5}h_0^2 \gg k_7 K_a$ this would lead to a value of $k_2$ of $k_5 k_7 K_{NO} K_a/k_{-5}$, essentially independent of acidity, as is observed. We do not see any way at present of obtaining values for $k_7$, $K_a$ and $k_{-5}$. However, some information about reaction (10) may be obtained from the solvent isotope effect. The value for higher concentrations of $H_2SO_4/D_2SO_4$ was measured [2] to be $k_2(H)/k_2(D) \approx 6.9$. If reaction (5) is essentially a rapid equilibrium then eqns. (4) and (5) may be written as eqn. (13). From Schowen's approximate treatment [12] the solvent

$$NH_3OH^+ + HONO \rightleftharpoons NH_3ONO^+ + H_2O \qquad (13)$$
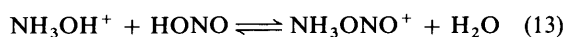
isotope effect on this equilibrium should be close to unity. Thus $6.9 = K_a(H)k_7(H)/K_a(D)k_7(D)$. For a wide range of acids $K_a(H)/K_a(D)$ comes to within $\pm 20\%$ of 3.4. Assuming the value to be a reasonable estimate for $NH_3ONO^+$, then $k_7(H)/k_7(D) \approx 2$, suggesting a modest degree of stretching of the bonds to hydrogen for the transition state of reaction (10).

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