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# Kinetic and Thermodynamic Properties of the Aminoxyl ($NH_2O^\bullet$) Radical

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The product of one-electron oxidation of (or H-atom abstraction from) hydroxylamine is the $H_2NO^\bullet$ radical. $H_2NO^\bullet$ is a weak acid and deprotonates to form $HNO^{-\bullet}$; the $pK_a(H_2NO^\bullet)$ value is $12.6 \pm 0.3$. Irrespective of the protonation state, the second-order recombination of the aminoxyl radical yields $N_2$ as the sole nitrogen-containing product. The following rate constants were determined: $k_r(2H_2NO^\bullet) = 1.4 \times 10^8$ $M^{-1}$ $s^{-1}$, $k_r(H_2NO^\bullet + HNO^{-\bullet}) = 2.5 \times 10^9$ $M^{-1}$ $s^{-1}$, and $k_r(2HNO^{-\bullet}) = 4.5 \times 10^8$ $M^{-1}$ $s^{-1}$. The $HNO^{-\bullet}$ radical reacts with $O_2$ in an electron-transfer reaction to yield nitroxyl (HNO) and superoxide ($O_2^{-\bullet}$), with a rate constant of $k_e(HNO^{-\bullet} + O_2 \rightarrow HNO + O_2^{-\bullet}) = 2.2 \times 10^8$ $M^{-1}$ $s^{-1}$. Both $O_2$ and $O_2^{-\bullet}$ seem to react with deprotonated hydroxylamine ($H_2NO^-$) to set up an autoxidative chain reaction. However, closer analysis indicates that these reactions might not occur directly but are probably mediated by transition-metal ions, even in the presence of chelators, such as ethylenediamine tetraacetic acid (EDTA) or diethylenetriamine pentaacetic acid (DTPA). The following standard aqueous reduction potentials were derived: $E°(H_2NO^\bullet,2H^+/H_3NOH^+) = 1.25 \pm 0.01$ V; $E°(H_2NO^\bullet,H^+/H_2NOH) = 0.90 \pm 0.01$ V; and $E°(H_2NO^\bullet/H_2NO^-) = 0.09 \pm 0.01$ V. In addition, we estimate the following: $E°(H_2NOH^{+\bullet}/H_2NOH) = 1.3 \pm 0.1$ V, $E°(HNO, H^+/H_2NO^\bullet) = 0.52 \pm 0.05$ V, and $E°(HNO/HNO^{-\bullet}) = -0.22 \pm 0.05$ V. From the data, we also estimate the gaseous O−H and N−H bond dissociation enthalpy (BDE) values in $H_2NOH$, with BDE($H_2NO$−H) = 75−77 kcal/mol and BDE(H−NHOH) = 81−82 kcal/mol. These values are in good agreement with quantum chemical computations.

## Introduction

Hydroxylamine ($H_2NOH$) is a well-known reductant, which, upon oxidation, may yield several products, such as $N_2$, $N_2O$, $NO_2^-$, or $NO_3^-$, depending on the exact reaction conditions.[1] When the oxidation is initiated by a one-electron oxidant or a H-atom abstractor, an intermediate of the oxidation number N(0) is formed, which may be $H_2NO^\bullet$ or its isomer, $^\bullet NHOH$. In the gas phase, the aminoxyl radical $H_2NO^\bullet$ has a certain role in ozone destruction and other processes.[2−4] Its isomer, $^\bullet NHOH$,[5] is thermodynamically less stable. Indeed, several quantum chemical calculations,[6,7] including the most recent one,[8] predict $^\bullet NHOH$ to be higher in energy than $H_2NO^\bullet$, by ca. 6 kcal/mol. This stability order should remain the same in water, even though the $^\bullet NHOH$ species is likely to be somewhat stabilized by hydration, relative to $H_2NO^\bullet$.[9] In agreement with this expectation, electron paramagnetic resonance (EPR) investigation of the radical that formed upon one-electron oxidation of hydroxylamine by $Ce^{4+}$ revealed $H_2NO^\bullet$ as the sole species, and no evidence for the presence of the $^\bullet NHOH$ isomer could be obtained.[10−13] This establishes the $H_2NO^\bullet$ radical as the stable isomer in aqueous solutions as well. In two pulse-radiolytic publications,[14,15] it was suggested that the product of hydrogen abstraction from $H_2NOH$ by the $^\bullet OH$ radical is, in fact, the $^\bullet NHOH$ species. This conclusion was based on the similarity between the ultraviolet (UV) spectra obtained from $H_2NOH$ and $H_2NOCH_3$, given that, in the latter case, the production of $^\bullet NHOCH_3$ was ascertained. However, in view of the fact that nitroxide radicals ($R_2NO^\bullet$) absorb similarly to, e.g., $^\bullet NHOCH_3$ in the UV range,[16] the aforementioned conclusion cannot be upheld in the face of the EPR data. Actually, the immediate product of hydrogen abstraction from $H_2NOH$ might very well be the $^\bullet NHOH$ species. This is because, due to solvation by way of hydrogen bonding, the $H_2O$ solvent shields the OH group of $H_2NOH$ much better than the $H_2N$ group from attack by the $^\bullet OH$ radical.[17] However, in view of the well-documented and extremely fast *1,2*-hydrogen shift, which causes an interconversion between the isoelectronic isomers $CH_3O^\bullet$ and $^\bullet CH_2OH$ by means of solvent catalysis in protic solvents (such as $H_2O$ and alcohols),[18−20] a similarly rapid equilibration is almost certainly bound to convert the initial $^\bullet NHOH$ species to the thermodynamically stable $H_2NO^\bullet$ isomer. Hence, the less-stable $^\bullet NHOH$ is expected to survive only in very small amounts. It is an experimental fact that radicals obtained through hydrogen abstraction from the parent are more acidic than the parent itself. Consequently, given that $pK_a(H_2NOH) = 13.74$,[21] one would expect the $H_2NO^\bullet$ radical to deprotonate well below pH 14. It has been known for some time that the recombination of the $H_2NO^\bullet$ radical yields exclusively $N_2$ as the nitrogen-containing end product.[15,22] However, it is not known what the products are in very basic solutions, where the radical may be in its deprotonated form. Furthermore, until now, no thermodynamic data have been forthcoming for the $H_2NO^\bullet$ radical. The present work intends to investigate, in detail, the kinetic as well as redox and acid−base properties of the $H_2NO^\bullet$ radical in aqueous solution. Such knowledge is all the more relevant, because the $H_2NO^\bullet/HNO^{-\bullet}$ radical is the intermediate redox form between hydroxylamine and the biologically important nitroxyl (HNO).[23]

## Experimental Section

All chemicals of the purest grade available (Lancaster and Aldrich) were used as supplied. The pulse radiolysis equipment consisted of a linear accelerator that delivered 3-MeV electrons and a computerized optical detection system.[24] The durations

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of the pulses were 10−30 ns, delivering doses of 6−18 Gy. For dosimetry, a $N_2O$-saturated $10^{-2}$ M KSCN solution was used.[25] The G$\epsilon$-value of $(SCN)_2^{\bullet}$ was taken to be $4.78 \times 10^{-4}$ $m^2/J$ at 500 nm. Superoxide ($O_2^{-\bullet}$) was produced at pH 13 by irradiation in a $\gamma$-source of air-saturated aqueous solutions containing 1 mM 2-propanol. The concentration of $O_2^{-\bullet}$ was checked spectrophotometrically at 250 nm. At this pH, and in the presence of DTPA, $O_2^{-\bullet}$ decayed in a second-order process with a rate constant of $2k_{exp} \approx 70$ $M^{-1}$ $s^{-1}$, which is significantly higher than the smallest reported[26] literature value of ca. 10 $M^{-1}$ $s^{-1}$. The kinetics of the autoxidation of hydroxylamine at high pH was monitored on a spectrophotometer either at 302 nm (the $\lambda_{max}$ of peroxynitrite)[27] or at 250 nm (the $\lambda_{max}$ of $O_2^{-\bullet}$).[26]

## Results and Discussion

**The Rate Constant of $O^{-\bullet}$ versus $NH_2OH/NH_2O^-$.** Most of the present experiments were performed in alkaline media in the presence of oxygen. The primary oxidative radical, $O^{-\bullet}$, reacts with oxygen to form $O_3^{-\bullet}$,[28] in competition with abstracting hydrogen from hydroxylamine. We studied this competition by monitoring the 400-nm absorbance of $O_3^{-\bullet}$. More specifically, from a plot of the inverse of the 400-nm absorbance against the ratio $[NH_2OH]/[O_2]$, we obtained $k(O^{-\bullet} + H_2NOH)/k(O^{-\bullet} + O_2) = 0.28 \pm 0.05$. Then, utilizing $k(O^{-\bullet} + O_2) = 3.8 \times 10^9$ $M^{-1}$ $s^{-1}$,[29] we determined the rate constant $k(O^{-\bullet} + H_2NOH)$ at pH 13.7 to be $1 \times 10^9$ $M^{-1}$ $s^{-1}$. The pH value of 13.7 is the p$K_a$ of hydroxylamine; therefore, we cannot decide whether $O^{-\bullet}$ reacts with the acid, the base, or both.

**p$K_a$ of the $NH_2O^{\bullet}$ Radical.** The peak absorbance of the $H_2NO^{\bullet}$ radical is observed at 217 nm. Our instrument is not designed to measure below 250 nm; therefore, the methyl viologen radical cation ($MV^{\bullet+}$) was used as a monitor. $N_2O$-saturated solutions containing 1 mM $H_2NOH$ and 0.2 mM methyl viologen ($MV^{2+}$) were pulse-irradiated. Under these conditions, a competition exists between $N_2O$ and $MV^{2+}$ for the solvated electron. Furthermore, the H atom reacts only with $MV^{2+}$. As a result, ca. 14% of the radicals formed are $MV^{\bullet+}$, with the remainder being essentially $NH_2O^{\bullet}$. The absorbance of $MV^{\bullet+}$ was measured at 405 nm. The decay of $MV^{\bullet+}$ followed second-order kinetics. At each pH, the traces were fitted to the two reactions given below:

$$2NH_2O^{\bullet} \rightarrow \text{products} \qquad (k_{obs})$$

$$NH_2O^{\bullet} + MV^{\bullet+} \rightarrow \text{products} \qquad (k_m)$$

The $k_m$ values were determined to be rather insensitive toward the pH; they remained essentially constant above pH 13. Below pH 11, all traces yielded identical $k_m$ and $k_{obs}$ values, thus resulting in very accurate values for $k_1$ and $k_4$. In this pH interval, the only major error source was the uncertainty in the delivered dose. In Figure 1, the $k_{obs}$ values are plotted against the pH. The line in Figure 1 was calculated using the rate constants of the reactions collected in Scheme 1.

**Reaction with Oxygen; Formation of Peroxynitrite.** The rate constant for the oxygen-dependent reaction ($k_6$) was obtained at pH 13 by measuring, at 250 nm, the rate of formation of $O_2^{-\bullet}$ in a pulse-irradiated 1 mM $H_2NOH$ solution containing $N_2O$ and various amounts of $O_2$. The results are presented in Figure 2. From the line in Figure 2 and by utilizing p$K_a$ = 12.6, a rate constant of $k_6 = 2.2 \times 10^8$ $M^{-1}$ $s^{-1}$ was obtained. Pulse irradiation of alkaline $N_2O/O_2$ saturated solutions containing 1mM $H_2NOH$ shows the buildup of a stable absorbance at 302 nm, which we ascribe to the peroxynitrite anion, $ONOO^-$.

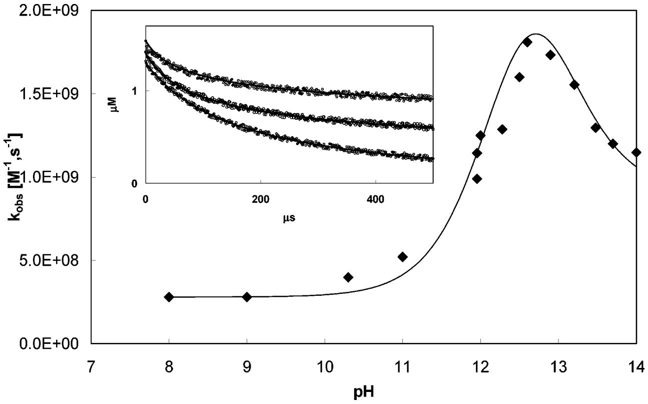

**Figure 1.** Observed rate constant of recombination of $NH_2O^{\bullet}$ versus pH. Conditions: $N_2O$-saturated solution containing 1 mM $H_2NOH$ and 0.2 mM methyl viologen. Between pH 8−10.5, phosphate, borate, and carbonate buffers were used to adjust the pH, whereas, at pH >10.5, the pH was adjusted by $OH^-$ addition. Dose/pulse = 17 Gy. The line is a fit of Scheme 1 to the experimental points. Inset shows time traces at pH 8 (bottom), pH 12.6 (top), and pH 14 (middle). All traces started at the same point, but, for clarity, the traces at pH 8 and pH 12.6 have been shifted. The full lines are the fits that have been obtained.

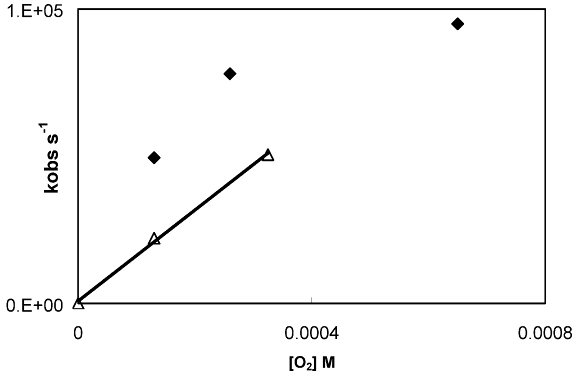

**Figure 2.** Plots of (△) the observed rate constant of $O_2^{-\bullet}$ formation at 250 nm versus oxygen concentration (conditions: pH 13, 1 mM $H_2NOH$) and (◆) the observed rate constant of peroxynitrite buildup at 302 nm versus oxygen concentration (conditions: pH 14.3, 1 mM $H_2NOH$).

### SCHEME 1

$$NH_2O^{\cdot} \leftrightarrow HNO^{\cdot -} + H^+ \qquad pK_a = 12.6 \pm 0.3$$

$$2\ NH_2O^{\cdot} \rightarrow N_2 + 2\ H_2O \qquad 2k_1 = (2.8 \pm 0.5)\times 10^8\ M^{-1}s^{-1} \qquad (1)$$

$$NH_2O^{\cdot} + HNO^{\cdot -} \rightarrow N_2 + H_2O + OH^- \qquad 2k_2 = (5 \pm 1)\times 10^9 \pm M^{-1}\ s^{-1} \qquad (2)$$

$$2\ HNO^{\cdot -} \rightarrow N_2 + 2\ OH^- \qquad 2k_3 = (9 \pm 3)\times 10^8\ M^{-1}\ s^{-1} \qquad (3)$$

$$NH_2O^{\cdot} + MV^{\cdot +} \rightarrow \text{products}^- \qquad k_4 = (5.8 \pm 0.5)\times 10^8\ M^{-1}\ s^{-1} \qquad (4)$$

$$HNO^{\cdot -} + MV^{\cdot +} \rightarrow \text{products} \qquad k_5 = (7.8 \pm 0.5)\times 10^8\ M^{-1}\ s^{-1} \qquad (5)$$

Reaction 1 is known to form $N_2$ as the only nitrogen-containing product and, hence, proceed by way of combination.[15,22] Because reaction 2 has not been studied before, we checked it with respect to the possible formation of HNO, which is the expected product of dismutation. HNO deprotonates slowly to yield $NO^-$ with $k(OH^- + HNO \rightarrow NO^- + H_2O) = 5 \times 10^4$ $M^{-1}$ $s^{-1}$.[30] $NO^-$ reduces $MV^{2+}$ in a diffusion-controlled reaction.[31] At pH values in the range of 12.5−14, where most $NH_2O^{\bullet}$ is removed through reactions 2 and 3, no absorbance buildup related to the formation of $NO^-$ could be observed. Thus, we conclude that reaction 2 proceeds mainly by way of combination, eventually forming $N_2$, while dismutation accounts for <5% or so.

The rate of buildup of $ONOO^-$ increases as the hydroxide concentration increases (Figure 3). Furthermore, it is independent of the $O_2$ concentration at pH <13.5. The rate constant that is extracted from Figure 3 is equal to $5.1 \times 10^4$ $M^{-1}$ $s^{-1}$,

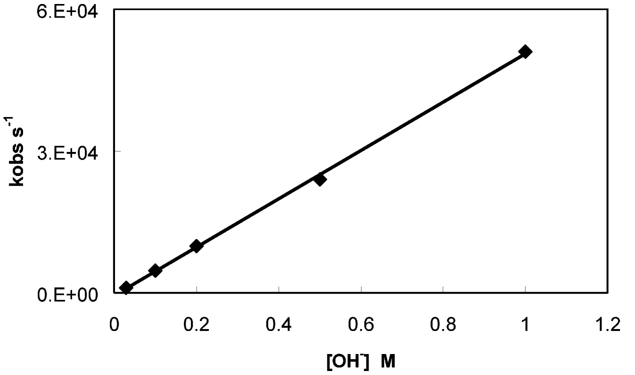

**Figure 3.** Variation with hydroxide concentration of the measured rate constant for peroxynitrite buildup at 302 nm. Conditions: 1 mM $H_2NOH$, saturated with a 1/1 mixture of $N_2O/O_2$; dose = 15 Gy.

which is in excellent agreement with the value of $4.9 \times 10^4$ $M^{-1}$ $s^{-1}$, which is the previously measured value for the deprotonation of HNO.[30] The following reactions are involved in the formation of $ONOO^-$:

$$HNO^{-\bullet} + O_2 \rightarrow HNO + O_2^{-\bullet} \tag{6}$$

$$HNO + OH^- \rightarrow NO^- + H_2O \tag{7}$$

$$NO^- + O_2 \rightarrow ONOO^- \tag{8}$$

Figure 2 also includes the measured rates of $ONOO^-$ buildup in 2 M NaOH versus the $O_2$ concentration (denoted as $[O_2]$). These latter data show that the rate varies with $O_2$. However, because the two consecutive reactions 6 and 7 have similar rates, the rate of $ONOO^-$ buildup is not strictly proportional to $[O_2]$. Under the present conditions, reaction 8 (with $k_8 = 2.7 \times 10^9$ $M^{-1}$ $s^{-1}$)[30] is sufficiently fast not to interfere with the rate-determining steps. Experiments at pH 7−9 showed no reaction between the neutral $H_2NO^\bullet$ radical and $O_2$. From this observation, an upper limit of $10^7$ $M^{-1}$ $s^{-1}$ is calculated for the rate constant of the reaction of $H_2NO^\bullet$ with $O_2$. At pH 7−9, a rate constant of $k_9 = 2 \times 10^9$ $M^{-1}$ $s^{-1}$ was measured.

$$O_2^{-\bullet} + NH_2O^\bullet \rightarrow \text{products} \tag{9}$$

**The Reaction between $O_2^{-\bullet}$ and $H_2NOH/H_2NO^-$.** In aerated solutions of $H_2NOH$ at pH 13, a slow formation of peroxynitrite (PN) after an induction period is observed at 302 nm. When $O_2^{-\bullet}$ is deliberately added (pH 13), a rapid formation of PN and a simultaneous decay of $O_2^{-\bullet}$ can be observed at 250 nm (see inset in Figure 4). After $O_2^{-\bullet}$ has decayed, d[PN]/d*t* is identical to that found in aerated solutions at the end of the induction period. Here, we used values of $\epsilon_{250}(O_2^{-\bullet}) = 2250$ $M^{-1}$ $cm^{-1}$ and $\epsilon_{302}(ONOO^-) = 1680$ $M^{-1}$ $s^{-1}$. The $O_2^{-\bullet}$ traces were corrected for the PN absorbance at 250 nm and converted to concentrations. To obtain good second-order fits, we had to allow for the final concentration of $O_2^{-\bullet}$ to be ca. $4 \times 10^{-7}$ M. Because of the smallness of the signal, we cannot decide with certainty whether this finding corresponds to a steady-state concentration having been attained by $O_2^{-\bullet}$. The extracted 2*k* values are presented in Figure 4. Because reactions 10 and 6 constitute a $O_2^{-\bullet}$-mediated chain reaction, we need a termination reaction for $O_2^{-\bullet}$. Obviously, this must occur by way of combination between $O_2^{-\bullet}$ and the aminoxyl radical ($H_2NO^\bullet$/$HNO^{-\bullet}$) in reaction 11, which probably produces $NO_2^-$ as the end product:

$$O_2^{-\bullet} + H_2NOH \rightarrow HO_2^- + H_2NO^{\bullet}* \tag{10}$$

$$O_2 + H_2NO^{\bullet}* \rightarrow O_2^{-\bullet} + HNO \rightarrow PN \tag{6}$$

$$O_2^{-\bullet} + H_2NO^{\bullet}* \rightarrow \text{products} \tag{11}$$

Here, $H_2NO^\bullet*$ signifies the sum of $H_2NO^\bullet$ and $HNO^{-\bullet}$ at the actual pH.

We obtain the following:

$$-\frac{d[O_2^{-\bullet}]}{dt} = 2k_{11}[H_2NO^{\bullet}*][O_2^{-\bullet}] \tag{12}$$

Applying the steady-state approximation to the propagation steps 6 and 10, we obtain

$$-\frac{d[O_2^{-\bullet}]}{dt} = \{2k_{11}k_{10}/(k_6[O_2] + k_{11}[O_2^{-\bullet}])\}[H_2NOH][O_2^{-\bullet}]^2 \tag{13}$$

However, given that, under our conditions, $k_6[O_2] \gg k_{11}[O_2^{-\bullet}]$, expression 13 simplifies to eq 14:

$$-\frac{d[O_2^{-\bullet}]}{dt} = \left(\frac{2k_{11}k_{10}}{k_6[O_2]}\right)[H_2NOH][O_2^{-\bullet}]^2 \tag{14}$$

Expression 14 contains the first-order dependence in $[H_2NOH]$, as well as the second-order dependence in $[O_2^{-\bullet}]$ and, therefore, rationalizes the plot of Figure 4.

Because every $H_2NO^\bullet*$ radical that reacts with oxygen yields PN, we also get

$$\frac{d[PN]}{dt} = k_6[O_2][H_2NO^{\bullet}*] \tag{15}$$

and

$$\frac{d[PN]}{d[O_2^{-\bullet}]} = -\frac{k_6[O_2]}{2k_{11}[O_2^{-\bullet}]} \tag{16}$$

A plot of the relative yield $-\Delta[PN]/\Delta[O_2^{-\bullet}]$ versus $1/[O_2^{-\bullet}]$ is given in Figure 4. The slope of the line yields $k_6[O_2]/2k_{11} = 3.6 \times 10^{-6}$ M. Inserting the experimental value of an air-saturated solution at pH 13 of $k_6[O_2] = 3.9 \times 10^4$ $s^{-1}$, we obtain $2k_{11} = 1 \times 10^{10}$ $M^{-1}$ $s^{-1}$. By combining the slopes of the main plot and the inset, we obtain $k_{10} = 9.5$ $M^{-1}$ $s^{-1}$. At pH 13, 70% of the hydroxylamine radical is in its deprotonated form ($HNO^{-\bullet}$). Recall that our measured rate constant for the neutral radical is $k_9 = 2 \times 10^9$; thus, the extracted value for $k_{11} = 5 \times 10^9$ at pH 13 seems unreasonably high, considering the charges involved. Clearly, the derived value of $k_{11}$ is dependent on the $k_6$ value that is used. However, our measured value of $k_6$ should be accurate within 25%. Any other competing reactions, such as

$$HNO + O_2^{-\bullet} \rightarrow NO^\bullet + HO_2^- \tag{17}$$

$$HNO^{-\bullet} + O_2 \rightarrow NO^\bullet + O_2^{-\bullet} + H^+ \tag{18}$$

can be excluded, based on the following grounds. First, to have any influence on the rate of reaction 11 and the ratio of $\Delta[PN]/$

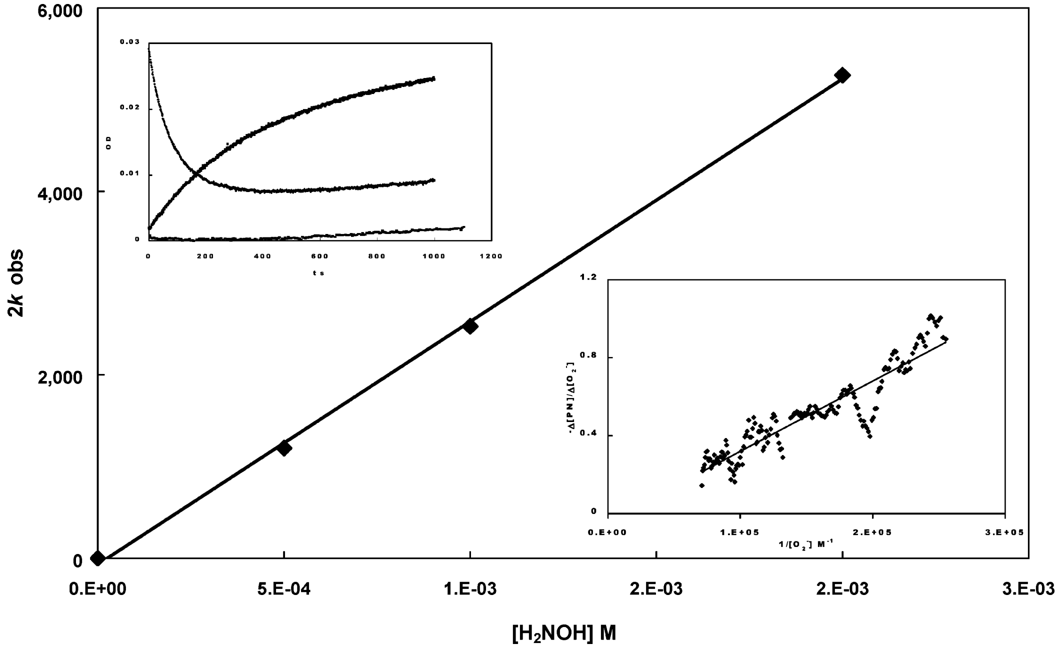

**Figure 4.** Plot of the observed second-order rate constant of $O_2^-$ decay versus $H_2NOH$ concentration in air saturated solutions at pH 13. Insets: upper left shows the decay of superoxide at 250 nm and the simultaneous buildup of PN at 302 nm. The lower trace show the buildup of PN when no superoxide is added. Lower right shows a plot of $-[PN]/\Delta[O_2^{-\bullet}]$ versus $1/[O_2^{-\bullet}]$.

$\Delta[O_2^{-\bullet}]$, at least 50% of the superoxide should react in one of the above reactions. In the pulse radiolysis experiments, the rate of buildup of PN follows the rate of deprotonation of HNO. Any production of $NO^\bullet$ through reaction 17 or 18 would have been manifested as a pH-independent rate, especially at pH ~12, which could not be observed. The improbably high value of the derived $k_{11}$ value suggests that the autoxidation of hydroxylamine is more complex than implied by the aforementioned model. It would seem that this process is mediated by transition-metal ion impurities, probably Fe(III)/FeII) and/or Cu(II)/Cu(I), even in the presence of chelators such as EDTA or DTPA. The initiation reaction is also probably mediated by metal ions and, hence, may not be a simple reaction between $H_2NO^-$ and molecular oxygen. In support of this view, the length of the induction period varies from day to day in a seemingly erratic fashion, independent of the presence and nature of the chelator. In an early study[32]of the autoxidation of hydroxylamine, the intermediacy of HNO was demonstrated. However, the process was thought to be a simple stoichiometric reaction between $H_2NO^-$ and molecular oxygen, and neither the chain character of the process nor the vital role of the superoxide was recognized.

**Thermodynamics of $H_2NO^\bullet/HNO^{-\bullet}$.** Previously, several papers[1,33−40] that involve the one-electron oxidation of hydroxylamine have been published. Two of these[35,36] will be scrutized below, because they are relevant for the thermochemistry of the $H_2NO^\bullet$ radical. In both of these studies, the rate expressions were analyzed in detail during oxidation of $H_3NOH^+$ by either Pu(IV)[36] or Fe(III)[35] in very acidic solutions. Similar rate expressions were reported in both studies, namely

$$-\frac{d[H_3NOH^+]}{dt}=\frac{k[H_3NOH^+]^2[ox]^2}{[red]^2[H^+]^4}$$

Here, $k$ is a formal rate constant and “ox” signifies the oxidized form of the metal ion ($Pu^{4+}$ or $Fe^{3+}$), whereas “red” is the corresponding reduced form ($Pu^{3+}$ or $Fe^{2+}$). With $Pu^{4+}$, the experimental value of $k$ can be calculated to be $0.029/(0.33)^2 = 0.266\ M^3\ s^{-1}$, whereas with $Fe^{3+}$, $k$ was reported to be $1.85 \times 10^{-9}\ M^3\ s^{-1}$. In both studies, the intermediacy of free radicals was demonstrated. Furthermore, as long as the value of the term $[H_3NOH^+]/[ox]$ was not too small, the exclusive end-product of the oxidation was determined to be molecular nitrogen. These findings can be rationalized by the following simple scheme.

$$H_3NOH^+ + ox \leftrightarrow H_2NO^\bullet + 2H^+ + red \qquad (K_{eq})$$

$$2H_2NO^\bullet \rightarrow N_2 + 2H_2O \qquad (2k_1)$$

According to this model, $k = (K_{eq}^2) \times (2k_1)$.

Utilizing our experimental value of $2k_1 = 2.8 \times 10^8\ M^{-1}\ s^{-1}$, we obtain $K_{eq} = 3.1 \times 10^{-5}\ M^2$ for $Pu^{4+}/Pu^{3+}$ and $K_{eq} = 2.6 \times 10^{-9}\ M^2$ for $Fe^{3+}/Fe^{2+}$. The experiments were performed at an ionic strength of ca. 1 M, and the ionic medium was composed mainly of $HClO_4$ and $NaClO_4$. In such media, the following formal potentials ($E_f$) apply:

$$E_f(Pu^{4+}/Pu^{3+}) = 0.982\ V \qquad \text{(from ref 41)}$$

and

$$E_f(Fe^{3+}/Fe^{2+}) = 0.738\ V \qquad \text{(from ref 42)}$$

Using these potentials coupled to the aforementioned $K_{eq}$ values, we can calculate the $E_f$ value for the redox reaction:

$$H_2NO^\bullet + 2H^+ + e^- \leftrightarrow H_3NOH^+$$

The calculated potential is 1.249 V with Pu and 1.246 V with Fe. The excellent agreement of these two values derived from completely independent experiments is ample proof of the aforementioned model being adequate. It also shows that the derived potential is probably accurate within 10 mV. Now, in 1 M ionic media, the activity coefficient of $H^+$ is ca. 0.85,[9] and we assume approximately the same value for $H_3NOH^+$, with it having a single positive charge as well. Therefore, the standard redox potential ($E°$) should be higher than $E_f$ merely by −59.16

$\times$ log(0.85) = 4 mV. Hence, we adopt

$$E^\circ(\mathrm{H_2NO^\bullet, 2H^+/H_3NOH^+}) = 1.25 \pm 0.01\ \mathrm{V}$$

Using p$K_a$($H_3NOH^+$) = 5.96,[43] we obtain

$$E^\circ(\mathrm{H_2NO^\bullet, H^+/H_2NOH}) = 0.90 \pm 0.01\ \mathrm{V}$$

From the finding that the experimental rate of consumption of $H_3NOH^+$ is inversely proportional to the fourth power in [$H^+$], even at such high acidities as 1 M $H^+$ or higher, we can conclude that the $H_2NO^\bullet$ radical remains unprotonated down to and below pH 0, i.e., p$K_a$($H_2NOH^{+\bullet}$) < 0. This is in clear contradiction to the reported value of p$K_a$($H_2NOH^{+\bullet}$) = 4.2 ± 0.1.[14,15] However, we believe the latter value to bear on a kinetic artifact, deriving from the fact that the rate of the $^\bullet$OH radical reacting with hydroxylamine is dramatically reduced at pH values below p$K_a$($H_3NOH^+$) = 5.96. Actually, in an EPR work,[44] alkylated nitroxide radicals, such as TEMPO, were shown to be protonated on the oxygen only in very concentrated $H_2SO_4$ solutions, and the p$K_a$ of the protonated radicals were estimated to be −5.5 ± 1.[44] Given that the $H_2NO^\bullet$ radical is a somewhat weaker base than, e.g., TEMPO, we extrapolate p$K_a$($H_2NOH^{+\bullet}$) = −7 ± 2. From this value, we estimate

$$E^\circ(\mathrm{H_2NOH^{+\bullet}/H_2NOH}) = 1.3 \pm 0.1\ \mathrm{V}$$

This potential is quite reasonable, given that it is close to the reported reduction potentials of secondary alkyl aminyl radical cations.[45]

Because p$K_a$($H_2NOH$) = 13.74,[21] we immediately derive

$$E^\circ(\mathrm{H_2NO^\bullet/H_2NO^-}) = 0.09 \pm 0.01\ \mathrm{V}$$

From $E^\circ$ = −1.87 V for the reaction

$$\mathrm{N_2(g) + 2H_2O + 4H^+ + 2e^- \leftrightarrow 2NH_3OH^+}$$

we obtain $\Delta G_f^\circ(\mathrm{NH_3OH^+})$ = −13.5 kcal/mol.[46] Then, by use of p$K_a$($H_3NOH^+$)[43] and p$K_a$($NH_2OH$),[21] we calculate $\Delta G_f^\circ(\mathrm{NH_2OH})$ = −5.4 kcal/mol and $\Delta G_f^\circ(\mathrm{NH_2O^-})$ = 13.4 kcal/mol. By means of the aforementioned reduction potentials, we then obtain $\Delta G_f^\circ(\mathrm{NH_2O^\bullet})$ = 15.4 kcal/mol for the $NH_2O^\bullet$ radical.

We recall that p$K_a$($NH_2O^\bullet$) ≈ 12.6, yielding $\Delta G_f^\circ(\mathrm{HNO^{-\bullet}})$ ≈ 32.5 kcal/mol.

Recently, based on improved experimental data in the gas phase,[47] the aqueous Gibbs energy of nitroxyl was re-estimated to be $\Delta G_f^\circ(\mathrm{HNO})$ = 27.5 ± 1 kcal/mol.[30] From this value, we calculate $E^\circ(\mathrm{HNO, H^+/H_2NO^\bullet})$ = 0.52 ± 0.05 V and $E^\circ(\mathrm{HNO/HNO^{-\bullet}})$ = −0.22 ± 0.05 V.

**O−H and N−H Bond Dissociation Enthalpies in $H_2NOH$.** On the assumption that water solvates $H_2NOH$ somewhat stronger than $H_2NO^\bullet$ and that the difference amounts to no more than ca. 2 kcal/mol,[9] we can arrive at a rather accurate estimate of the gaseous O−H bond dissociation enthalpy (BDE) of $H_2NO$−H, according to

$$\mathrm{BDE(H_2NO{-}H)} \approx 23.06 \times E^\circ(\mathrm{H_2NO^\bullet,H^+/H_2NOH}) + \Delta G^\circ_{\mathrm{g-aq}}(\mathrm{H_2NOH}) - \Delta G^\circ_{\mathrm{g-aq}}(\mathrm{H_2NO^\bullet}) + 56.4 = 75{-}77\ \mathrm{kcal/mol}$$

In this expression, $\Delta G^\circ_{\mathrm{g-aq}}$ signifies the free energy of transfer from gas to water and the constant 56.4 kcal/mol includes well-known parameters[48] for gaseous $H_2$ and $H^\bullet$, as well as a small entropy-related term, which, at room temperature, amounts to ca. −0.3 kcal/mol.

A similar, if somewhat less-accurate, estimate can be made for the gaseous N−H BDE as follows. We assume that the difference between the aqueous p$K_a$ values of $CH_3OH$ and $H_2NOH$ is approximately the same as that between the corresponding radicals $^\bullet CH_2OH$ and $^\bullet NHOH$, i.e., p$K_a$($CH_3OH$) − p$K_a$($NH_2OH$) ≈ p$K_a$($^\bullet CH_2OH$) − p$K_a$($^\bullet NHOH$):

$$15.1 - 13.7\ (\text{from ref 21}) \approx 10.7\ (\text{from refs 49 and 50}) - \mathrm{p}K_\mathrm{a}(^\bullet\mathrm{NHOH})$$

Hence, a value of p$K_a$($^\bullet NHOH$) ≈ 9.3 is predicted. This value lies ca. 3.3 units below the experimental p$K_a$($H_2NO^\bullet$) ≈ 12.6, whereas, in aqueous solutions, the $H_2NO^\bullet$ radical should be more stable than $^\bullet NHOH$ by ca. 1.36 × 3.3 = 4.5 kcal/mol. We calculate

$$\Delta G_f^\circ(^\bullet\mathrm{NHOH}) \approx 15.4 + 4.5 = 19.9\ \mathrm{kcal/mol}$$

and

$$E^\circ(^\bullet\mathrm{NHOH,H^+/H_2NOH}) \approx 1.1\ \mathrm{V}$$

Because the free energies of aqueous solvation of $NH_2OH$ and $^\bullet NHOH$ should be approximately the same, we estimate, for the gaseous N−H bond enthalpy,

$$\mathrm{BDE(N{-}H)} \approx 23.06 \times E^\circ(^\bullet\mathrm{NHOH,H^+/H_2NOH}) + 56.4 = 81{-}82\ \mathrm{kcal/mol}$$

Hence, the N−H bond would seem to be 5−7 kcal/mol stronger than the O−H bond, which is an estimate that agrees very well with most quantum chemical results.[6−8]

## Conclusions

The one-electron oxidized product of hydroxylamine ($NH_2OH$) is the aminoxyl radical ($NH_2O^\bullet$). The $NH_2O^\bullet$ radical deprotonates to yield $HNO^{\bullet-}$ with a p$K_a$ = 12.6 ± 0.3. Both acidic and basic forms of the radical recombine to yield $N_2$. $HNO^{\bullet-}$ reacts with molecular oxygen to yield nitroxyl (HNO) and superoxide ($O_2^{\bullet-}$). Several important redox potentials were evaluated, and the O−H and N−H bond strengths in hydroxylamine were estimated.

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