Mechanism of Decomposition of Peroxynitric Ion (O_2NOO^-): Evidence for the Formation of $O_2^{\bullet -}$ and $^{\bullet}NO_2$ Radicals

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The rate constant of the self-decomposition of O_2NOO^- was determined to be 1.35 ± 0.03 s^{-1} at 25 °C. The decomposition rate constant of O_2NOO^- in the presence of $C(NO_2)_4$, $CuSO_4$, SOD, and $Fe(CN)_6{}^{4-}$ was found to be 2.4 ± 0.2 s^{-1}, independent of the concentration of these substrates. The oxidation yields of $C(NO_2)_3{}^-$ and ferricyanide were measured to be 47 ± 5 and 83 ± 9% of added peroxynitrate, respectively, where the latter decreased to 54 ± 6% in the presence of SOD. We therefore suggest that ca. 50% of O_2NOO^- homolyses into $O_2^{\bullet -}$ and $^{\bullet}NO_2$ ($k = 1.05 \pm 0.23$ s^{-1}). The equilibrium constant of the homolysis of O_2NOO^- into $^{\bullet}NO_2$ and $O_2^{\bullet -}$ and the reduction potential of the couple $O_2NOOH,H^+/NO_3^-$ were calculated to be 2.3×10^{-10} M and 1.83 V, respectively.

Introduction

Peroxynitric acid ($pK_a = 5.9 \pm 0.1$)[1,2] is a relatively stable species in aqueous solutions ($\tau_{1/2} = 17-70$ min)[1,3,4] whereas the anion decomposes relatively quickly ($k = 1.0 \pm 0.2$ s^{-1})[1,2] to yield at pH > 5 nitrite and oxygen.[5] It was shown that peroxynitrate (O_2NOOH/O_2NOO^-) is formed in aqueous solution through the very fast recombination of $HO_2^{\bullet}/O_2^{\bullet -}$ with $^{\bullet}NO_2$.[1,2] O_2NOOH was also prepared in aqueous solution by the reaction of HNO_2 with a greater than 2-fold excess of H_2O_2 in strong acid at or below 0 °C.[3,4] Peroxynitric acid is a powerful oxidant that can oxidize the substrates directly as in the case of iodide[2−4] or indirectly through intermediates that are formed during its decomposition as in the case of ferrocyanide and β-nicotinamide adenine dinucleotide, reduced (NADH).[2] We have determined the rate constant of the oxidation of NADH and ferrocyanide by O_2NOOH to be 0.05 ± 0.005 s^{-1} and the stoichiometry of the reaction to be $[Fe(CN)_6{}^{3-}]/[O_2NOOH] = 2$.[2] These results are in agreement with the radical mechanism (reactions 1−3), which has been suggested earlier for the decomposition of O_2NOOH,[5,6] as both $^{\bullet}NO_2$ and $HO_2^{\bullet}$ radicals are capable of oxidizing ferrocyanide and NADH.[7]

$$O_2NOOH \rightleftharpoons HO_2^{\bullet} + {}^{\bullet}NO_2 \qquad (1)$$
$$k_1 = 0.05\ s^{-1\,(2)},\ k_{-1} = 1.8 \times 10^9\ M^{-1}\ s^{-1\,(1)}$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \qquad (2)$$
$$k_2 = 8.3 \times 10^5\ M^{-1}\ s^{-1\,(7)}$$

$$2{}^{\bullet}NO_2 + H_2O \rightarrow HNO_2 + NO_3^- + H^+ \qquad (3)$$
$$k_3 = 6.5 \times 10^7\ M^{-1}\ s^{-1\,(7)}$$

However, it was reported that in the presence of excess of H_2O_2 over O_2NOOH, $\Delta[H_2O_2]/\Delta[O_2NOOH] = 1$ in diluted reaction mixture,[1] and 0.64 in undiluted reaction mixture.[3] These results do not support the radical mechanism as reactions 1−3 produce equal amounts of HNO_2 and H_2O_2 that react together to yield ONOOH, which subsequently isomerizes fast to nitrate.[8]

Recently, Régimbal and Mozurkewich[4] found that $\Delta[H_2O_2]/\Delta[O_2NOOH] = 0.25 \pm 0.25$, and that the stoichiometric ratio reduced to zero in the presence of 1 mM ethylendiaminetetraacetic acid (EDTA). They have shown that the measured change in $[H_2O_2]$ in undiluted solutions was due to regeneration of O_2NOOH via the reaction of ONOOH with excess of H_2O_2, and in diluted solutions due to the reaction of O_2NOOH with added HNO_2 during mixing ($O_2NOOH + HNO_2 \rightarrow 2H^+ + 2NO_3^-$). They concluded that the decay of O_2NOOH takes place via reactions 1−3 and determined $k_1 = (0.026 \pm 0.002)$ s^{-1} in the presence of $CuSO_4$,[4] which is in fair agreement with our value which was determined in the presence of ferrocyanide and NADH using the pulse radiolysis technique.[2]

In our earlier study[2] we have suggested that the mechanism of the decomposition of O_2NOO^- takes place via the formation of an oxidizing intermediate, O_2NOO^{-}*, which is capable of oxidizing ferrocyanide and NADH. We were unable to identify

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this intermediate and to determine the oxidation yields as the concentrations of these substrates could not be raised above 1 mM using the pulse radiolysis technique.[2] In this study, we used both the pulse radiolysis and stopped-flow techniques and identified $O_2NOO^{-}*$ as the couple $^{\bullet}NO_2$ and $O_2^{\bullet-}$.

Experimental Section

Chemicals. All chemicals were of analytical grade and were used as received. Tetranitromethane (TNM) was dissolved in ethanol and diluted in water. Solutions were prepared with deionized water that was distilled and purified using a Milli-Q water purification system. The concentration of H_2O_2 was determined using the iodide method.[9]

Apparatus. Stopped-flow kinetic measurements were carried out using the Bio SX-17MV sequential stopped-flow apparatus from Applied Photophysics with a mixing time of less than 2 ms and a 1-cm long mixing cell. Peroxynitric acid at pH 2 was mixed in a 1:1 ratio with iodide, TNM, and ferrocyanide in appropriate buffers (0.2 M acetate, 0.2 M phosphate, or 0.1 M borate). The reaction of peroxynitrate with I^-, TNM, and $Fe(CN)_6^{4-}$ was followed at 351 nm ($\epsilon(I_3^-) = 25\,800$ M^{-1} cm^{-1}),[9] 350 nm ($\epsilon(C(NO_2)_3^-) = 14\,400$ M^{-1} cm^{-1}),[10] and 420 nm ($\epsilon(Fe(CN)_63^-) = 1000$ M^{-1} cm^{-1}), respectively. The pH of the mixture was measured at the outlet of the flow system. The kinetic measurements were carried out at 25 °C.

Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator with 5 MeV electron pulses of 0.3−1.5 μs and 200 mA current as previously described in detail.[2] The kinetic measurements were carried out at 18 °C.

O_2NOOH Synthesis. (i) Pulse radiolysis was used to generate O_2NOO^- in aerated solutions containing 30 mM nitrate, 0.4 M formate, and 50 μM EDTA at pH > 7 as previously described in detail.[2] (ii) O_2NOOH was prepared through a modification of the synthesis described by Appelman and Gosztola.[3] A syringe pump (World Precision Instruments model SP 230IW) with a flow rate of 45 mL/min was used to mix nitrite with excess of H_2O_2 in $HClO_4$ at room temperature. The pump drove four syringes filled with nitrite (two syringes) and acidified H_2O_2 (two syringes), and the solutions were mixed by pushing the solutions through four tangential inlets of a mixing chamber. The combined solution was collected in an ice bath, immediately diluted with 0.01 M ice-cold $HClO_4$, which in some cases contained 0.1 mM EDTA, and transferred into the stopped flow. We added EDTA to the reaction mixture to avoid catalysis of O_2NOOH decomposition by traces of metal impurities.[4]

Results

Reaction of Peroxynitrate with Iodide. We have previously shown using the pulse radiolysis technique that O_2NOOH oxidizes directly iodide with $k = 840 \pm 50$ M^{-1} s^{-1} and that $[I_3^-]_T = [O_2NOOH]_0$, where $[I_3^-]_T = [I_2] + [I_3^-]$.[2]

$$O_2NOOH + 2I^- + H^+ \rightarrow H_2O + NO_3^- + I_2 \qquad (4)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K_5 = 714\ M^{-1\,(9)} \qquad (5)$$

The rate constant of the reaction of O_2NOOH with I^- was determined in the presence of excess of iodide by plotting k_{obs} of the formation of I_3^- as a function of $[I^-]$ at various pH's.[2] At that time, we did not pay any attention to the intercept of the line obtained at pH 6.8, which was higher than the rate constant of the self-decomposition of peroxynitrate at that pH (Figure 2 in ref 2). In this study we repeated these experiments at higher pH's.

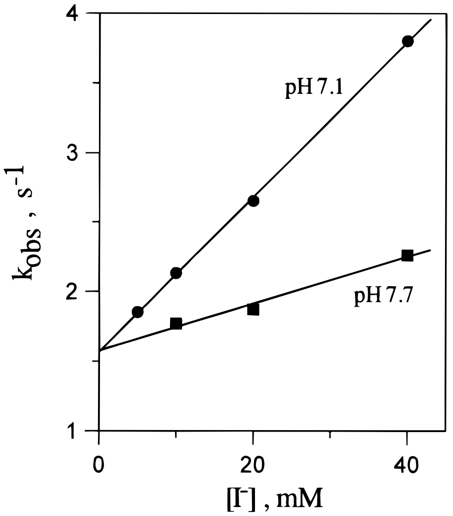

Figure 1. Observed rate constant of the formation of I_3^- as a function of $[I^-]$. The irradiated solutions contained 30 mM nitrate, 0.4 M formate, and 50 μM EDTA at pH 7.1 and 7.7 (1 mM phosphate buffer) and were air-saturated.

When aerated solutions containing 30 mM nitrate, 0.4 M formate, and 50 μM EDTA at pH 7.1 and 7.8 (1 mM phosphate buffer) were irradiated, the formation and decay of O_2NOO^- were followed at 325 nm. The rate constant of the decomposition of O_2NOO^- at these pH values was found to be 0.67 ± 0.03 s^{-1} (18 °C). In the presence of excess of iodide over peroxynitrate, the rate of the formation of I_3^- was first-order. The observed first-order rate constant was linearly dependent on $[I^-]$ at both pH's, yielding the same intercept, 1.55 ± 0.05 s^{-1} (Figure 1). From the slopes of these lines we determined the rate constant of the direct reaction of peroxynitrate with iodide to be 56 and 17 M^{-1} s^{-1} at pH 7.1 and 7.7, respectively. The rate constant decreased with increasing the pH as O_2NOOH is the reacting species, in agreement with $k = 840 \pm 50$ M^{-1} s^{-1} and $pK_a(O_2NOOH) = 5.9 \pm 0.1$.[2]

The oxidation of iodide by O_2NOOH was used to determine the yield of O_2NOOH obtained through the reaction of NO_2^- with excess of acidified H_2O_2. The mixture was immediately diluted 2500 or 5000 times in ice-cold 0.01 M $HClO_4$ containing 0.1 mM EDTA and was transferred into the stopped-flow apparatus where it was mixed with equal volume of 0.2 M NaI in 0.2 M acetate buffer at pH 4.4. Using this method, the relatively high residual H_2O_2 in the final mixtures does not interfere with the determination of $[O_2NOOH]$ because the rate of the oxidation of iodide by H_2O_2 is slower than that by O_2NOOH, and the two processes are well separated. The rate constant of the formation of I_3^- in the presence of 0.1 M iodide was found to be 860 ± 20 M^{-1} s^{-1}, independent of the composition of the mixture, and in excellent agreement with $k = 840 \pm 50$ M^{-1} s^{-1}, which was determined using the pulse radiolysis technique.[2] The yield of O_2NOOH increased with increasing $[H_2O_2]$ and $[H^+]$, and reached ca. 74% of the initial nitrite ($[NO_2^-] = 0.06-0.30$ M) when reacting with 5.5 M H_2O_2 in the presence of 1.65 M $HClO_4$. As O_2NOOH is most probably formed via the reaction of NO_2^+ with H_2O_2,[3,4] ca. 26%

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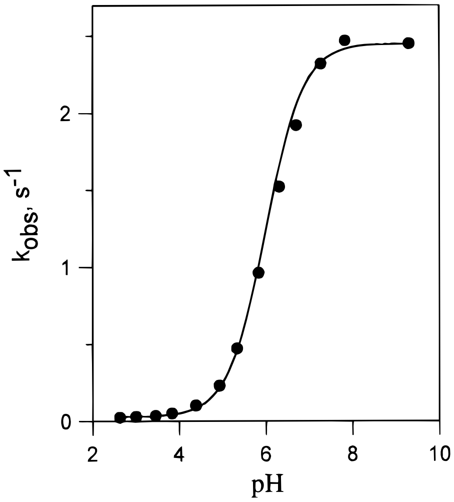

Figure 2. Observed rate constant of the formation of *NF*$^-$ as a function of pH. All solutions contained 45 ± 5 μM peroxynitrate, 0.139 mM TNM, and 0.1 M acetate or phosphate buffer. The solid curve was calculated using $k_f = 2.45$ s^{-1} (alkaline), $k_f = 0.026$ s^{-1} (acid), and $pK_a = 6.0$.

of the initial nitrite is converted into NO_3^- due to the hydrolysis of NO_2^+ which competes with the reaction of NO_2^+ with H_2O_2.

Spectrum and Decay Rate of O_2NOO^-. The spectrum of O_2NOO^- was measured by diluting 0.116 ± 0.012 M O_2NOOH 676 times in 0.01 M $HClO_4$ containing 0.1 mM EDTA and mixing it with appropriate buffers (0.2 M phosphate or 0.1 M borate buffers) in a 1:1 ratio. The maximum extinction coefficient of 1550 ± 150 $M^{-1}cm^{-1}$ at 285 nm was measured, and is in excellent agreement with the values determined previously using the pulse radiolysis technique.[1,2] The decay of O_2NOO^- was found to be first order and the rate constant was determined to be $k_d = 1.35 \pm 0.03$ s^{-1} at pH 7.7–9.3.

Reaction of O_2NOO^- with TNM. Stock solution of 0.116 ± 0.012 M O_2NOOH was diluted 2500 times and mixed in a 1:1 ratio with an appropriate buffer containing TNM. We observed the buildup of the characteristic absorption of $C(NO_2)_3^-$ (*NF*$^-$), which is known to be formed via reaction 6.

$$C(NO_2)_4 + O_2^{\bullet -} \rightarrow C(NO_2)_3^- + {}^{\bullet}NO_2 + O_2 \qquad (6)$$
$$k_6 = 2.0 \times 10^9\ M^{-1}\ s^{-1\ (7)}$$

The formation of *NF*$^-$ was first-order in [peroxynitrate], zero-order in [TNM], and k_{obs} decreased with decreasing the pH (Figure 2). The yield of *NF*$^-$ was independent of [TNM], $[NF^-]/[O_2NOO^-]_0 = 0.47 \pm 0.02$ at pH 6.7–9.3 and $[NF^-]/[O_2NOOH]_0 = 0.87 \pm 0.09$ at pH 3–3.5. As O_2NOOH decomposes via reaction 1 to $HO_2^{\bullet}$, and k_6 is relatively high, TNM at concentrations exceeding 0.1 mM is sufficient to quantitatively intercept superoxide and also to completely block radical recombination at pH 3, and therefore one expects 100% yield of *NF*$^-$ at pH 3. As the yield of *NF*$^-$ was halved at pH 6.7–9.3, we conclude that about 50% of O_2NOO^- decomposes into $O_2^{\bullet -}$ and ${}^{\bullet}NO_2$:

$$O_2NOO^- \rightleftharpoons O_2^{\bullet -} + {}^{\bullet}NO_2 \qquad (7)$$

Thus, by looking at the build-up rate and the yield of *NF*$^-$ as a function of pH, one should obtain both the total rate constant of the decomposition as well as the yield of homolysis of O_2NOOH/O_2NOO^-. Figure 2 demonstrates an increase from 0.026 ± 0.003 s^{-1} at pH 3 to 2.45 ± 0.05 s^{-1} at pH > 7, while the yield of homolysis is essentially halved. The apparent $pK_a(O_2NOOH) = 6.0 \pm 0.1$ resulting from Figure 2 is in agreement with 5.9 ± 0.1 determined earlier using the pulse radiolysis technique.[1,2] The rate constant of the homolysis of O_2NOOH extracted from Figure 2, $k_1 = 0.026 \pm 0.003$ s^{-1}, is in excellent agreement with that determined in the presence of copper ions,[4] and in fair agreement with that determined in the presence of ferrocyanide and NADH using the pulse radiolysis technique, $k_1 = 0.05 \pm 0.005$ s^{-1}.[2]

Table 1. Rate Constants of the Formation (k_f) and Yields of Ferricyanide Obtained via the Reaction of 86–480 μM O_2NOO^- with Ferrocyanide under Various Conditions at pH 7.7

$[Fe(CN)_6^{4-}]$, mM	k_f, s^{-1}	$[Fe(CN)_6^{3-}]/[O_2NOO^-]_0$	k_f,[b] s^{-1}	$[Fe(CN)_6^{3-}]/[O_2NOO^-]_0$[b]
∞	2.28[a]	0.83[a]		
50	2.39	0.80	2.45	0.53
25	2.05	0.71	2.30	0.54
12.5	1.80	0.58		
4.2	1.62	0.41	2.33	0.54
2.1			2.28	0.56
1.4	1.48	0.29		

[a] Determined via extrapolation by plotting $1/(k_f - k_d)$ and $[O_2NOO^-]_0/[Fe(CN)_6^{3-}]$ vs $1/[Fe(CN)_6^{4-}]$. [b] [SOD] = 2 μM.

Reaction of O_2NOO^- with $CuSO_4$ and Superoxide Dismutase (SOD). The decay of O_2NOO^- was followed in the presence of $CuSO_4$ and SOD as both compounds are known to be efficient catalysts of superoxide dismutation.[7] EDTA was omitted from the reaction mixture in the case of $CuSO_4$. The observed rate constant of the decay of 86 ± 6 μM O_2NOO^- was found to be 2.43 ± 0.15 s^{-1} at pH 7.8, independent of 20–500 μM $CuSO_4$, and 2.35 ± 0.05 s^{-1} in the presence of 3.1 and 6.2 μM SOD at pH 8.6. These rate constants are within experimental error identical to those obtained for the formation of *NF*$^-$ at pH > 7.

Reaction of O_2NOO^- with Ferrocyanide. The decomposition of peroxynitrate in the presence of ferrocyanide also supports the homolysis O_2NOO^- into ${}^{\bullet}NO_2$ and $O_2^{\bullet -}$. When O_2NOOH at pH 2 was mixed with ferrocyanide in 0.2 M phosphate buffer, the formation of ferricyanide was observed, and the buildup of the absorption at 420 nm was described by a single exponential. The observed first-order rate constant of the formation of ferricyanide and its yield decreased with decreasing $[Fe(CN)_6^{4-}]$ (Table 1). Ferrocyanide is oxidized by both ${}^{\bullet}NO_2$ and $HO_2^{\bullet}$, and though $O_2^{\bullet -}$ is capable of reducing ferricyanide, it is expected that at pH 7.7 and in the presence of high $[Fe(CN)_6^{4-}]$, both radicals will oxidize ferrocyanide.

$$Fe(CN)_6^{4-} + {}^{\bullet}NO_2 \rightarrow Fe(CN)_6^{3-} + NO_2^- \qquad (8)$$
$$k_8 = 3.0 \times 10^6\ M^{-1}\ s^{-1\ (7)}$$

$$Fe(CN)_6^{4-} + HO_2^{\bullet} \rightarrow Fe(CN)_6^{3-} + HO_2^- \qquad (9)$$
$$k_9 = 1.4 \times 10^5\ M^{-1}\ s^{-1\ (7)}$$

$$Fe(CN)_6^{3-} + O_2^{\bullet -} \rightarrow Fe(CN)_6^{4-} + O_2 \qquad (10)$$
$$k_{10} = 6.9 \times 10^3\ M^{-1}\ s^{-1\ (7)}$$

$$HO_2^{\bullet} \rightleftharpoons H^+ + O_2^{\bullet -} \qquad (11)$$
$$pK_a = 4.8^{\ (11)}$$

The rate constant of the formation of ferricyanide (k_f) and its yield at infinite concentration of ferrocyanide were determined from the intercept of the straight lines obtained when $1/k_f$ and $[O_2NOO^-]_0/[Fe(CN)_6^{3-}]$ were plotted against $1/[Fe(CN)_6^{4-}]$ to

Table 2. Rate Constants and Yields Obtained in the Reaction of O_2NOO^- with Various Substrates

substrate (S)	$[O_2NOO^-]$, μM	pH	k^S_{obs}, s^{-1} [a]	$1 - k_d/k^S_{obs}$ [b]	$[S^+]/[O_2NOO^-]_0$
0.1−0.835 mM TNM	22 ± 2	7.7	2.52 ± 0.07	0.46 ± 0.02	0.47 ± 0.05
0.042−1 mM $CuSO_4$	86 ± 6	7.8	2.43 ± 0.15	0.44 ± 0.03	−
3.1−6.2 μM SOD	86 ± 6	8.6	2.35 ± 0.05	0.43 ± 0.03	−
4.2−50 mM $Fe(CN)_6^{4-}$	479 ± 34	7.7	2.28 ± 0.15[c]	0.40 ± 0.05	0.83 ± 0.09[c]
50 mM $Fe(CN)_6^{4-}$ (+ 4μM SOD)		7.7	2.34 ± 0.11	0.41 ± 0.04	0.54 ± 0.06

[a] k^S_{obs} is the observed rate constant of the decomposition of O_2NOO^- in the presence of the various substrates. [b] $k_d = 1.35 \pm 0.03$ s^{-1} is the observed rate constant of the self-decomposition of O_2NOO^-. [c] Determined via extrapolation by plotting $1/(k_f - k_d)$ and $[O_2NOO^-]_0/[Fe(CN)_6^{3-}]$ vs $1/[Fe(CN)_6^{4-}]$ (see Table 1).

be 2.28 ± 0.15 s^{-1} and 0.83 ± 0.09, respectively. In the presence of 2 μM SOD, the rate of the formation of ferricyanide was independent of ferrocyanide concentration and was within experimental error identical to that obtained at infinite ferrocyanide. The yield of ferricyanide in the presence of SOD was 0.54 ± 0.06, independent of ferrocyanide concentrations (Table 1).

Discussion

The observed first-order rate constant of the decay of O_2NOO^- in the presence of the various substrates and the oxidation yields in the presence of TNM and ferrocyanide are summarized in Table 2. The data shows that O_2NOO^- dissociates into ${}^\bullet NO_2$ and $O_2^{\bullet-}$ and that the contribution of this reaction to the decomposition of O_2NOO^- is ca. 50%. The yield of ferricyanide is twice the yield of NF^- as both ${}^\bullet NO_2$ and ${}^\bullet HO_2$ are capable of oxidizing ferrocyanide, whereas only $O_2^{\bullet-}$ oxidizes TNM. In the presence of SOD, the yield of ferricyanide is within experimental error identical to that of NF^- as the catalysis of superoxide dismutation by SOD competes efficiently with the oxidation of ferrocyanide by $HO_2^\bullet$.

We suggest two alternative mechanisms for the decomposition of O_2NOO^- to account for our experimental results (Table 2).

Mechanism I

$$O_2NOO^- \rightleftharpoons {}^\bullet NO_2 + O_2^{\bullet-} \qquad (7)$$

$$k_7 = 1.05 \pm 0.23\ s^{-1}, \quad k_{-7} = (4.5 \pm 1.0) \times 10^9\ M^{-1}\ s^{-1}$$ (1)

$$O_2NOO^- \rightarrow O_2 + NO_2^- \qquad (12)$$
$$k_{12} = 1.35 \pm 0.03\ s^{-1}$$

According to this mechanism, the observed rate constant of the self-decomposition of O_2NOO^- is given by $k_d = k_{12} = 1.35 \pm 0.03$ s^{-1}. In the presence of an efficient scavenger of $O_2^{\bullet-}$ and/or ${}^\bullet NO_2$ the observed rate constant of the decomposition of O_2NOO^- is given by $k^S_{obs} = k_7 + k_{12} = 2.4 \pm 0.2$ s^{-1}, and hence $[NF^-]/[O_2NOO^-]_0 = k_7/(k_7 + k_{12}) = 1 - k_d/k^S_{obs}$ and $[Fe(CN)_6^{3-}]/[O_2NOO^-]_0 = 2(1 - k_d/k^S_{obs})$. The last two entries in Table 2 show that the oxidation yields are within experimental error identical to those calculated from $(1 - k_d/k^S_{obs})$.

Mechanism II (Cage Mechanism)

$$\begin{tikzcd} & O_2 + NO_2^- & \\ O_2NOO^- \arrow[r, shift left, "k_{cage}"] & {[O_2^{\bullet-}\ {}^\bullet NO_2]_{cage}} \arrow[l, shift left, "k_{-cage}"] \arrow[u, "k_N"'] \arrow[r, shift left, "k_{diff}"] & O_2^{\bullet-} + {}^\bullet NO_2 \arrow[l, shift left, "k_{-diff}"] \end{tikzcd} \qquad (13)$$

A similar model has already been suggested by Merenyi and Lind[12] for the decomposition of ONOOH. According to this model, the observed rate constants of O_2NOO^- decomposition in the absence and presence of a radical scavenger are given by eqs 14 and 15, respectively.

$$k_d = k_{cage}k_N/(k_{-cage} + k_N) = 1.35 \pm 0.03\ s^{-1} \qquad (14)$$

$$k^S_{obs} = k_{cage}(k_N + k_{diff})/(k_{-cage} + k_N + k_{diff}) = 2.4 \pm 0.2\ s^{-1} \qquad (15)$$

The rate constant of oxygen formation from O_2NOO^- in the presence of the radical scavenger, k^{O_2}, is given by eq 16:

$$k^{O_2} = k_{cage}k_N/(k_{-cage} + k_N + k_{diff}) = k^S_{obs}k_N/(k_N + k_{diff}) \qquad (16)$$

As the oxidation yield is about 50% (Table 2), it follows that k^S_{obs} is about twice as high as k^{O_2}, and therefore $k_N \sim k_{diff}$ and $k_d/k^{O_2} = 1 + k_{diff}/(k_{-cage} + k_N) = 1 + k_N/(k_{-cage} + k_N)$. The experimental data reveal that the two rates differ by 10% at most, i.e., they are the same within experimental error. Also, the extinction coefficient of O_2NOO^-, as determined by mixing O_2NOOH with borate buffer at pH 9.3, was within experimental error identical to that determined by pulse radiolysis via the reaction of ${}^\bullet NO_2$ with $O_2^{\bullet-}$. Therefore, for the cage model to apply, we must assume that $k_{-cage}/k_N = k_{-cage}/k_{diff} \geq 10$. This is a remarkably high ratio for a radical cage, but is perhaps reasonable if singlet−triplet relaxation in the cage in competition with the other rates, e.g., electron transfer, is invoked.

Both mechanisms predict that in the absence of radical-scavenger the decomposition of O_2NOO^- yields nitrite and oxygen[5] as the reaction of ${}^\bullet NO_2$ with $O_2^{\bullet-}$ competes efficiently with the dismutation of $O_2^{\bullet-}$ and with the hydrolysis of ${}^\bullet NO_2$.[7] According to both mechanisms, $K_7 = 2.3 \times 10^{-10}$ M, and $\Delta G° = 13.2 \pm 0.2$ kcal/mol.

It is worthwhile to note that these mechanisms are kinetically indistinguishable. However, the former mechanism predicts on grounds of spin conservation that the main product will be ${}^1O_2$, whereas the latter mechanism predicts the formation of ${}^3O_2$.

Thermochemical and Redox Properties of O_2NOOH/O_2NOO^-. In ref 4 the equilibrium constant for reaction 1 was determined to be 1.4×10^{-11} M. Combining this value with the experimentally obtained $K_7 = 2.3 \times 10^{-10}$ M and $pK_a(HO_2^\bullet) = 4.8$, we calculate $pK_a(O_2NOOH) = 6.0$. The excellent agreement of this value with 5.9 ± 0.1, determined by means of spectrophotometric titration,[1,2] confirms the soundness of our reaction scheme. From $\Delta_f G°$ (O_2NOOH) = 1.3 kcal/mol[4] and $pK_a(O_2NOOH) = 5.9$ we immediately obtain $\Delta_f G°$ (O_2NOO^-) = 9.4 kcal/mol. Knowledge of these Gibbs free energies of formation enables us to calculate a number of standard reduction potentials, $E°$, involving O_2NOOH/O_2NOO^-. In addition, the biologically relevant reduction potential at pH 7, $E°_7$, will also

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Table 3. Reduction Potentials of Peroxynitrate (O_2NOOH/O_2NOO^-) and Peroxynitrite ($ONOOH/ONOO^-$)

reaction[a]	$E°$, V	$E°_7$, V
$O_2NOOH + 2e^- + H^+ \rightarrow NO_3^- + H_2O$	1.83	1.59
$ONOOH + 2e^- + 2H^+ \rightarrow HNO_2 + H_2O$	1.68	1.37
$O_2NOOH + e^- \rightarrow NO_3^- + {}^{\bullet}OH$	0.94	0.87
$O_2NOOH + e^- + H^+ \rightarrow NO_3^{\bullet} + H_2O$	1.22	0.74
$O_2NOOH + e^- + H^+ \rightarrow HNO_2 + HO_2^{\bullet}$	0.58	0.46
$O_2NOOH + e^- + H^+ \rightarrow {}^{\bullet}NO_2 + H_2O_2$	0.79	0.31
$ONOOH + e^- + H^+ \rightarrow {}^{\bullet}NO_2 + H_2O$	2.14	1.69

[a] All values are given in V vs NHE. $E°_7$ values were calculated by making allowance for the pK_a values of the relevant acid species.

be given. For comparative purposes, redox data[12] for $ONOOH/ONOO^-$ are compiled in Table 3 as well. Table 3 reveals that O_2NOOH is a more potent two-electron oxidant than ONOOH. This reflects, no doubt, the stability of nitrate as compared to nitrite. Thus, with respect to two-electron oxidizing power ONOOH resembles alkyl hydroperoxides,[13] while O_2NOOH is as strong an oxidant as organic peroxy acids[13] and $HOOSO_3^-$.[14] On the other hand ONOOH is seen to be a significantly more powerful one-electron oxidant than O_2NOOH. This difference suggests a much weaker O−O bond in ONOOH as compared with that in O_2NOOH. Indeed, from the values in Table 3 and utilizing $\Delta_f G°({}^{\bullet}OH) = 6.2$ kcal/mol and $\Delta_f G°({}^{\bullet}NO_3) = 29.9$ kcal/mol, we calculate the following $\Delta_f G°$-values for O−O homolysis:

$$O_2NOOH \rightarrow {}^{\bullet}NO_3 + {}^{\bullet}OH,\ \Delta_f G° = 34.8 \text{ kcal/mol} \tag{17}$$

$$ONOOH \rightarrow {}^{\bullet}NO_2 + {}^{\bullet}OH,\ \Delta_f G° = 13.6 \text{ kcal/mol} \tag{18}$$

This indicates a difference of about 20 kcal/mol between the two O−O bond strengths. An unexpected feature of O_2NOOH is its ability to produce $OH^{\bullet}$ radicals during one-electron reduction. Indeed, thermodynamically, this is the most favorable path of one-electron reduction at physiological pH. However, whether such a reaction occurs in practice with any reductant, is not known at present.

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