Reactivity of Peroxynitric Acid (O_2NOOH): A Pulse Radiolysis Study

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Peroxynitrate (O_2NOOH/O_2NOO^-) is formed within less than 2 ms after pulse irradiation of aerated solutions containing relatively low concentrations of formate and nitrate. The pK_a for peroxynitric acid was determined to be 5.9 ± 0.1 both from the pH-dependent absorbance of the anion at 310 nm and from the dependence of the decay kinetics on pH. An absorption spectrum was measured for the anion giving $\epsilon_{max}(290) = 1500 \pm 100$ M^{-1} cm^{-1}. This method of generation of peroxynitrate is very useful for studying the mechanism of the oxidation of various substrates by peroxynitrate. The oxidation by peroxynitrate can take place either directly or indirectly. In the direct oxidation pathway, the reaction is first order in peroxynitrate and first order in the substrate, whereas in the indirect oxidation pathway, the reaction is zero order in the substrate. In both cases, the observed rate constants are highly pH-dependent. The results show that the direct oxidation pathway takes place through O_2NOOH. We suggest that the indirect oxidation takes place through reactive intermediates that are formed during the decomposition of peroxynitrate. In the presence of sufficient concentrations of the substrates, the oxidation yields approach 100% through the direct and indirect oxidation pathways.

Introduction

Peroxynitric acid, O_2NOOH, is formed in the gas phase by the recombination of $HO_2^•$ and $^•NO_2$ radicals.[1−3] In the gas phase, at ordinary temperatures, the compound is in equilibrium with its precursors, and it decays slowly due to the dismutation of $HO_2^•$.[4,5] In aqueous solutions, peroxynitrate (O_2NOOH/O_2NOO^-) decomposes mainly through a unimolecular dissociation of the anion into nitrite and oxygen.[6−8] It has been suggested that the decomposition of O_2NOOH takes place through its dissociation into $HO_2^•$ and $^•NO_2$, but recently it was argued that O_2NOOH decomposes directly into HNO_2 and O_2.[8]

Peroxynitric acid is a strong oxidizing agent, reacting rapidly with I^-, Br^-, Cl^-, VO^{2+}, and benzene.[7,9] The oxidation mechanism has not been investigated, as it is very difficult to prepare O_2NOOH in aqueous solutions. The reported methods for its preparation are as follows: (i) 90% H_2O_2 and 70% HNO_3;[6] (ii) 90% H_2O_2 and NO_2BF_4;[6] (iii) HNO_2 and excess H_2O_2;[9] (iv) pulse radiolysis of O_2-saturated nitrite/nitrate solutions.[8]

Nitrogen dioxide is one of the most important toxic components of photochemical smog,[10] and thus, understanding the reactions that $^•NO_2$ undergoes in the lungs exposed to smoggy air is of considerable importance. Peroxynitrate may be formed in the lungs through the reaction of superoxide with $^•NO_2$,[8] and therefore the mechanism of its formation and decomposition as well as its redox chemistry is of great importance. In this study, we used the pulse radiolysis technique to study the mechanism of the oxidation of various substrates by peroxynitrate. This method seems to be the best for this purpose because it does not require extreme conditions.

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Experimental Section

Materials. All chemicals were of analytical grade and were used as received. β-Nicotinamide adenine dinucleotide, reduced (NADH) from Grade III yeast was obtained from Sigma. Solutions of NADH were prepared immediately before use, and the concentration of NADH was determined using $\epsilon_{340} = 6200$ M^{-1} cm^{-1}. Solutions were prepared with deionized water that was distilled and purified using a Milli-Q water purification system, and unless otherwise stated, they contained 100 μM EDTA. The pH was adjusted with the use of 1 mM acetate, phosphate, or borate buffers. All experiments were carried out at 22 °C.

Methods. Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator using 5 MeV electron pulses of 0.1−1.5 μs and a 200 mA current. The dose per pulse was 3−29 Gy, respectively, and was determined with a hexacyanoferrate(II) dosimeter (5 mM $K_4Fe(CN)_6$ in N_2O-saturated water) using $G\epsilon(Fe(CN)_6^{3-}) = 6.7 \times 10^3$ M^{-1} cm^{-1} at 420 nm.[11] A 150 W Xe or a 200 W Xe−Hg lamp produced the analyzing light. Appropriate filters were used to minimize photochemistry. Irradiations were carried out in 1- or 4-cm-long Spectrosil cells using one or three light passes.

Results

Formation of O_2NOOH/O_2NOO^-. Logager and Sehested[8] produced peroxynitrate by irradiating O_2-saturated solutions containing nitrite or nitrate. We modified this method somewhat and irradiated air-saturated solutions containing nitrate and formate. Under these conditions, the following reactions take place:

$$H_2O \xrightarrow{\gamma} e_{aq}^- \ (2.6),\ ^•OH\ (2.7),\ H^•\ (0.6),\ H_2\ (0.45),\ H_2O_2\ (0.7),\ H_3O^+\ (2.6) \qquad (1)$$

The numbers in parentheses are G values, which represent the

(11) Buxton, G. V.; Stuart, C. R. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 279.

number of molecules formed per 100 eV of energy absorbed by pure water.

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-} \qquad (2)$$

$$k_2 = 1.9 \times 10^{10}\ M^{-1}\ s^{-1}$$ [12]

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} \qquad (3)$$

$$k_3 = 9.7 \times 10^9\ M^{-1}\ s^{-1}$$ [12]

$$e_{aq}^- + H^+ \rightarrow H^\bullet \qquad (4)$$

$$k_4 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$$ [12]

$$NO_3^{2-} + H_2O \rightarrow {}^\bullet NO_2 + 2OH^- \qquad (5)$$

$$k_5 = 5.5 \times 10^4\ s^{-1}$$ [12]

$$NO_3^{2-} + H^+ \rightarrow {}^\bullet NO_2 + OH \qquad (6)$$

$$k_6 = 2 \times 10^{10}\ M^{-1}\ s^{-1}$$ [12]

$$NO_3^{2-} + O_2 \rightarrow NO_3^- + O_2^{\bullet-} \qquad (7)$$

$$k_7/k_5 = 576\ M^{-1} \quad \text{(see below)}$$

$$H^\bullet + O_2 \rightarrow HO_2^\bullet \qquad (8)$$

$$k_8 = 2 \times 10^{10}\ M^{-1}\ s^{-1}$$ [12]

$$^\bullet OH/H^\bullet + HCO_2^- \rightarrow H_2O/H_2 + CO_2^{\bullet-} \qquad (9)$$

$$k_{OH} = 3.5 \times 10^9\ M^{-1}\ s^{-1} \text{ [12]} \qquad k_H = 2.1 \times 10^8\ M^{-1}\ s^{-1} \text{ [12]}$$

$$CO_2^{\bullet-} + O_2 \rightarrow CO_2 + O_2^\bullet \qquad (10)$$

$$k_{10} = 2.4 \times 10^9\ M^{-1}\ s^{-1}$$ [12]

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

$$pK_a = 4.8$$ [13]

Under our experimental conditions ([KNO_3] = 0.375−40 mM, [$NaHCO_2$] = 0.01−0.4 M, pH > 3), all the primary free radicals formed by the radiation are converted into $^\bullet NO_2$ and $HO_2^\bullet/O_2^{\bullet-}$, which subsequently yield O_2NOOH/O_2NOO^- through reactions 12 and 13.

$$^\bullet NO_2 + O_2^{\bullet-} \rightarrow O_2NOO^- \qquad (12)$$

$$k_{12} = 4.5 \times 10^9\ M^{-1}\ s^{-1}$$ [8]

$$^\bullet NO_2 + HO_2^\bullet \rightarrow O_2NOOH \qquad (13)$$

$$k_{13} = 1.8 \times 10^9\ M^{-1}\ s^{-1}$$ [8]

$$O_2NOOH \rightleftharpoons H^+ + O_2NOO^- \qquad (14)$$

$$pK_a = 5.85$$ [8]

The change in the absorbance with time was monitored at 250 nm, where $\epsilon_{250}(O_2^{\bullet-})$ = 2250 M^{-1} cm^{-1}.[13] When $O_2^{\bullet-}$ was generated in excess over $^\bullet NO_2$ at pH >6.8, a fast first-order decay of $O_2^{\bullet-}$ followed by a slower second-order decay was observed. During the fast decay observed at 250 nm, a transient was formed with maximum absorbance around 290 nm (Figure 1). The yield of the transient as measured at 310 (where superoxide does not absorb) decreased with the decrease in pH with an apparent $pK_a = 5.8 \pm 0.1$ (Figure 2), assuming that O_2NOOH does not absorb at 310 nm.[8]

The total yield of peroxynitrate, $G(O_2NOOH)_T$, equals $G(^\bullet NO_2)$ because under our experimental conditions there is always an excess of superoxide over $^\bullet NO_2$. The yield is given by

$$G(O_2NOOH)_T = \frac{k_3[NO_3^-]}{k_3[NO_3^-] + k_2[O_2] + k_4[H^+]}\ \frac{k_5 + k_6[H^+]}{k_5 + k_6[H^+] + k_7[O_2]}G_e = \frac{k_5 + k_6[H^+]}{k_5 + k_6[H^+] + k_7[O_2]}\alpha G_e \qquad (15)$$

$$G(O_2^-)_T = G_{OH} + G_H + G_e - G(O_2NOOH)_T \qquad (16)$$

As predicted by eq 15, the yield of peroxynitrate at pH 6.8 decreased with the increase in [O_2] (Table 1). A plot of α/OD_{320} versus [O_2] yields a straight line with slope/intercept = k_7/k_5 = 576 M^{-1}. Forni et al.[14] determined $k_7/k_5 = 1.5 \times 10^3\ M^{-1}$ at pH 6 ($k_5 = 5.5 \times 10^4\ s^{-1}$, $k_7 = 8.5 \times 10^7\ M^{-1}\ s^{-1}$) in aqueous solutions containing 0.5 mM ABTS (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid), 1 M *tert*-butyl alcohol, and 0.5 M nitrate. In their study,[14] the yield of $ABTS^+$ decreased with the increase in [O_2], and the [$ABTS^{\bullet+}$]/[e_{aq}^-] values were 0.81 and 0.51 in air/N_2 and O_2/N_2, respectively. From their results we calculated that k_7/k_5 = 772 M^{-1}, which is closer to our value. We were unable to determine how they calculated their reported value.

Using our value for k_7/k_5 = 576 M^{-1}, eqs 15 and 16, and the experimental conditions of Figure 1, we calculated that $[O_2^{\bullet-}]_0$ = 10.3 μM and $[^\bullet NO_2]_0 = [O_2NOO^-]_T$ = 6.07 μM. The residual spectrum of peroxynitrate was corrected for excess $O_2^{\bullet-}$ (Figure 1), resulting in $\epsilon_{290}^{max}(O_2NOO^-) = 1500 \pm 150\ M^{-1}\ cm^{-1}$, assuming that O_2NOOH does not absorb at 290 nm and its pK_a equals 5.85.[8]

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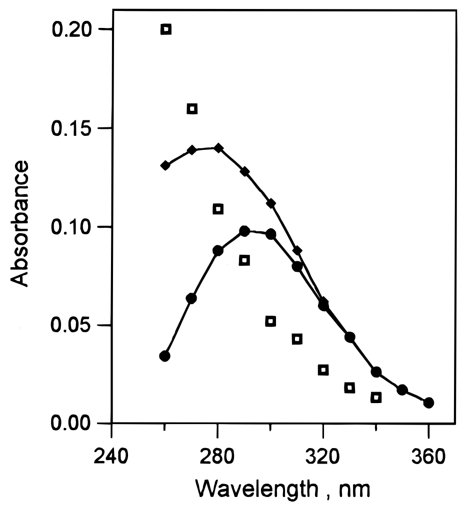

Figure 1. Absorbances of a pulse-irradiated air-saturated solution containing 0.01 M formate,11.25 mM nitrate, and 100 μM EDTA at pH 6.8 (1 mM phosphate buffer): absorbance measured 40 μs after the pulse (□); absorbance measured 1 ms after the pulse (♦); residual absorbance corrected for excess $O_2^{\bullet -}$ (if all $^{\bullet}NO_2$ radicals react with $O_2^{\bullet -}$, $[O_2^{\bullet -}]_0 = 10.2$ μM and $[^{\bullet}NO_2]_0 = [O_2NOO^-]_T = 6.07$ μM) (●). The optical path length was 12.1 cm, and the dose was 27.6 Gy.

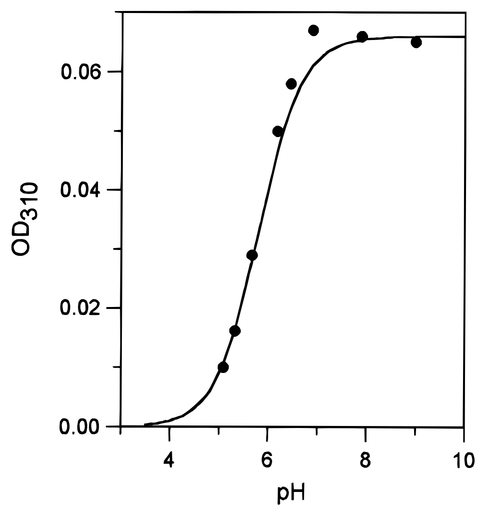

Figure 2. Absorbance measured at 310 nm 1−2 ms after the end of the pulse as a function of pH. All solutions were air-saturated and contained 0.01 M formate, 100 μM EDTA, and 11.25 mM nitrate. The optical path length was 12.1 cm, and the dose was 20.6 Gy. The solid curve was calculated using $pK_a = 5.8$, $OD_{310}(O_2NOO^-) = 0.066$, and $OD_{310}(O_2NOOH) = 0$.

Table 1. Yield of O_2NOO^- as a Function of $[O_2]$

$[O_2]$, M	OD_{320}	$G(NO_3^{2-}) = \alpha G_e$	α/OD_{320}
2.4×10^{-4}	0.069	$0.985G_e$	14.27
4.5×10^{-4}	0.061	$0.971G_e$	15.92
7.5×10^{-4}	0.051	$0.953G_e$	18.68
1.2×10^{-3}	0.046	$0.927G_e$	21.22

[a] All solutions contained 10 mM formate and 30 mM nitrate at pH 6.8. The dose was 27.6 Gy, and the optical path length was 12.1 cm.

The decay of O_2NOOH/O_2NOO^- was studied at pH 3.8−10. Below pH 5 repetitive pulsing was used to produce detectable amounts of O_2NOOH at 264 nm. The decay rate was first order and decreased with the decrease in pH (Figure 3), indicating that O_2NOOH is relatively stable as compared to O_2NOO^-. We determined the rate constant of the decay of O_2NOO^- to be 1.0 ± 0.1 s^{-1}. The best fit to the experimental data given in Figure 3 was obtained for $k_d = 1.0$ s^{-1} (alkali), $k_d = 7 \times 10^{-4}$−4.6×10^{-3} s^{-1} (acid),[7,8] and $pK_a = 5.9 \pm 0.1$.

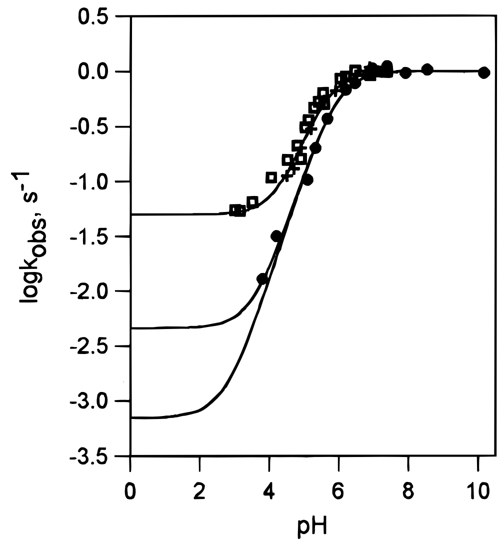

Figure 3. Decay plots: observed rate constant for the decay of peroxynitrate in the presence of 10 mM formate and 12−50 mM nitrate as a function of pH (●). The solid curves were calculated using $k_d = 1.0$ s^{-1} (alkaline) and 4.6×10^{-3} s^{-1} [7] or 7×10^{-4} s^{-1} [8] (acid) and $pK_a = 5.9$. Oxidation plots: observed rate constant for the oxidation of 0.1−1 mM $Fe(CN)_6^{4-}$ in the presence of 0.1 M formate and 30−50 mM nitrate (□) and of the oxidation of 0.1−0.275 mM NADH in the presence of 30 mM formate and nitrate (+) by peroxynitrate as a function of pH. The solid curve for the oxidation rates was calculated using $k_f = 1.0$ s^{-1} (alkaline) and 0.05 s^{-1} (acid) and $pK_a = 5.6$.

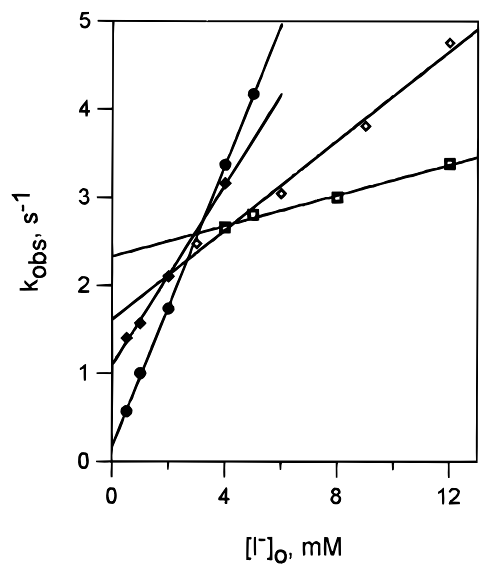

Figure 4. Observed rate constant for the formation of I_3^- in the oxidation of I^- by peroxynitrate as a function of $[I^-]$. All solutions contained 30 mM nitrate and 0.1−0.4 M formate at pH 4.9 (●), 5.9 (▼), 6.4 (◇), and 6.8 (□). The dose was 7 Gy.

Our results are is in agreement with the earlier reported values of $\epsilon_{285}^{max}(O_2NOO^-) = 1650 \pm 100$ M^{-1} cm^{-1}, $pK_a = 5.85 \pm 0.1$, and $k_d(\text{alkali}) = 1.0 \pm 0.2$ s^{-1}.[8]

In conclusion, we have shown that peroxynitrate is formed within less than 2 ms after the irradiation of aerated solutions containing relatively low concentrations of formate and nitrate. This method is very useful for studying the mechanism of the oxidation of various substrates by peroxynitrate.

Oxidation of Iodide by Peroxynitrate. When aerated solutions containing 30 mM nitrate, 0.1−0.4 M formate, and 0.5−20 mM iodide were irradiated, I_3^- was formed. The stoichiometry and the kinetics of the reaction were studied by following the formation of I_3^- at 352 nm, using $\epsilon_{352}(I_3^-) = 25\,800$ M^{-1} cm^{-1}, and 710 M^{-1} for the stability constant of

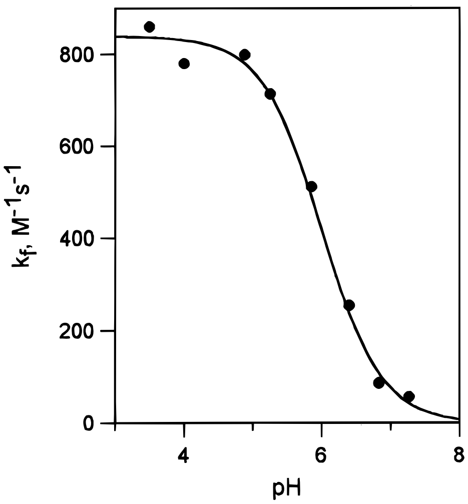

Figure 5. Observed rate constant for the oxidation of iodide by peroxynitrate as a function of pH. All solutions contained 30 mM nitrate and 0.1−0.4 M formate. The dose was 7 Gy. The solid curve was calculated with the assumption that O_2NOO^- does not oxidize iodide and by using $k(O_2NOOH + I^-) = 840\ M^{-1}\ s^{-1}$ and $pK_a = 6$.

I_3^-.[15] The formation of I_3^- obeyed first-order kinetics and was faster than the self-decomposition of peroxynitrate at pH 3.45−7.3. The observed first-order rate constant was linearly dependent on $[I^-]_0$ (Figure 4) and was highly pH dependent, resulting in an apparent $pK_a = 6.0 \pm 0.1$ (Figure 5). These results show that the oxidation of iodide takes place through O_2NOOH, and that the rate constant of this reaction is $840 \pm 50\ M^{-1}\ s^{-1}$.

The stoichiometry of the reaction was determined in the presence of 0.5−2 mM iodide at pH 3.45−4.9. The total yield of I_3^- ($G(I_3^-)_T = G(I_2) + G(I_3^-)$) was obtained by using the stability constant of I_3^- or by adding 0.3 M iodide to the solution after the irradiation to convert all I_2 to I_3^-. The total yield of I_3^- obtained by both methods was found to be identical, and under various experimental conditions $G(I_3^-)_T = G(O_2NOOH)_T$.

Oxidation of Ferrocyanide by Peroxynitrate. The oxidation of ferrocyanide by peroxynitrate was followed at 420 nm ($\epsilon_{420} = 1000\ M^{-1}\ cm^{-1}$). In this system, reactions 17−19 may interfere with the determination of the stoichiometry and the kinetics.

$$Fe(CN)_6^{4-} + {}^\bullet OH \rightarrow Fe(CN)_6^{3-} + OH^- \qquad (17)$$

$$k_{17} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}\ [12]$$

$$Fe(CN)_6^{4-} + {}^\bullet NO_2 \rightarrow Fe(CN)_6^{3-} + NO_2^- \qquad (18)$$

$$k_{18} = 2.1 \times 10^{6}\ M^{-1}\ s^{-1}\ [16]$$

$$Fe(CN)_6^{4-} + HO_2^\bullet \rightarrow Fe(CN)_6^{3-} + HO_2^- \qquad (19)$$

$$k_{19} = 1.6 \times 10^{5}\ M^{-1}\ s^{-1}\ [12]$$

Under our experimental conditions where $[HCO_2^-]/[Fe(CN)_6^{3-}] > 30$, reaction 17 can be neglected. However, because of the competition of reactions 18 and 19 with reactions 12 and 13, the concentration of ferrocyanide must not exceed 1 mM at pH >4 and 0.4 mM at pH <4.

The rate of formation of ferricyanide obeyed first-order kinetics. The observed rate constant for the formation of

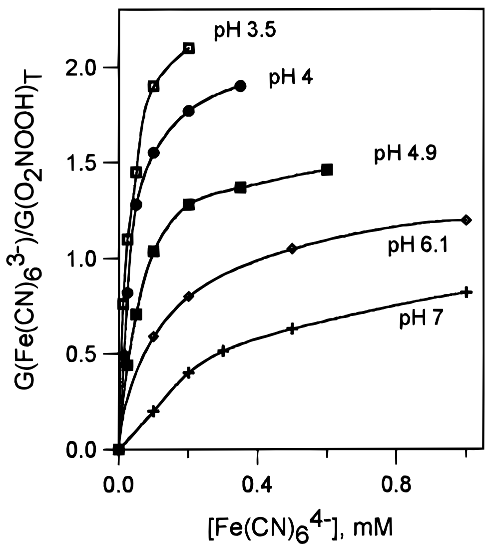

Figure 6. Oxidation yield of ferricyanide as a function of pH and ferrocyanide concentrations at various pH's. The dose was 21.5−27 Gy. The yield of peroxynitrate was calculated according to eq 15.

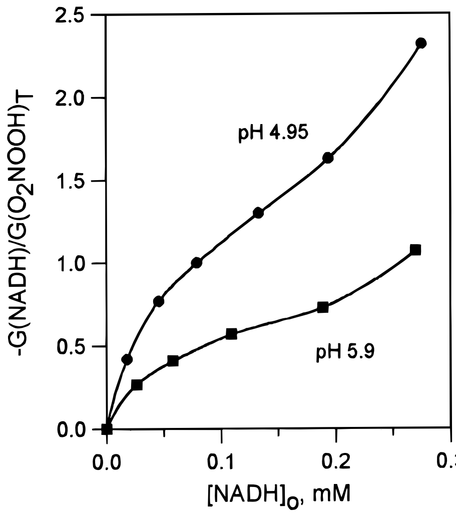

Figure 7. Oxidation yield of NADH as a function of $[NADH]_0$ at pH 4.95 and 5.9. Aerated solutions contained 30 mM formate and 30 mM formate. The dose was 27.6 Gy. The yield of peroxynitrate was calculated according to eq 15.

ferricyanide at acid pH's increases slightly with the increase in $[Fe(CN)_6^{4-}]_0$, reaching a plateau value at high yields. Under these conditions, it was found to be highly pH-dependent (Figure 3). The yields of ferricyanide were dependent on pH and $[Fe(CN)_6^{4-}]_0$ (Figure 6). The stoichiometry of the reaction was determined under acidic solutions to be $[Fe(CN)_6^{3-}]/[O_2NOOH] = 2.0 \pm 0.2$.

Oxidation of NADH by Peroxynitrate. The oxidation of NADH by peroxynitrate was studied by following the decrease in the absorbance at 340 nm using a cell with a 1 cm optical path length. The concentration of NADH could not be raised above 0.2 mM, due to total absorbance of the light by the solution. In addition, the reaction could not be studied below pH 4.5 because of decomposition of NADH in acidic solutions.

When aerated solutions containing 30 mM nitrate, 30 mM formate, and 1.3×10^{-5}−2×10^{-4} M NADH were irradiated at pH 4.5−7.1; the rate of the decay of the absorbance at 340 nm was first order. The observed rate constants increased slightly with the increase in $[NADH]_0$, reaching a plateau value

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at high yields. The latter values were highly pH-dependent and within experimental error identical to the values obtained in the presence of ferrocyanide (Figure 3). The oxidation yields increased with the increase in $[NADH]_0$ and the decrease in pH, as in the case of ferrocyanide, but did not reach plateau values (Figure 7). In the presence of oxygen, a chain reaction takes place and the stoichiometry cannot be determined. ($NAD^•$, which is the product of the one-electron oxidation of NADH, reacts rapidly with oxygen to form NAD^+ and $HO_2^•$,[17] and $HO_2^•$ oxidizes another molecule of NADH to $NAD^•$.[13])

Discussion

Mechanism of Direct Oxidation by Peroxynitrate. Our results show that the oxidation of iodide takes place directly through O_2NOOH and that the stoichiometry of this process is given by eq 20. The mechanism of the oxidation of iodide by

$$O_2NOOH + 3I^- + H^+ \rightarrow I_3^- + NO_3^- + H_2O \quad (20)$$

peroxynitrate can take place through outer-sphere electron-transfer mechanisms (mechanisms I–III) or through an inner-sphere electron-transfer mechanism (mechanism IV).

mechanism I

$$O_2NOOH + I^- \rightarrow I^• + {}^•HO_2 + NO_2^- \quad (21)$$

Since the oxidation of iodide by superoxide does not compete efficiently with the dismutation of superoxide,[12,13] $G(O_2NOOH)_T/G(I_3^-)_T$ will be 0.5, in contrast to the observed value of unity. Therefore, reaction 21 cannot describe the first stage of this process.

mechanism II

$$O_2NOOH + I^- \rightarrow I^• + {}^•NO_2 + HO_2^- \quad (22)$$

$$k_{22} = 840\ M^{-1}\ s^{-1}$$

$${}^•NO_2 + I^- \rightarrow I^• + NO_2^- \quad (23)$$

$$k_{23} = 1.1 \times 10^5\ M^{-1}\ s^{-1}\ ^{12}$$

$$H_2O_2 + NO_2^- \rightarrow H_2O + NO_3^- \quad (24)$$

$$k_{24} = 4.6 \times 10^3[H^+]\ M^{-1}\ s^{-1}\ ^{18}$$

mechanism III

$$O_2NOOH + I^- \rightarrow I^• + {}^•NO_3 + OH^- \quad (25)$$

$$k_{25} = 840\ M^{-1}\ s^{-1}$$

$${}^•NO_3 + I^- \rightarrow I^• + NO_3^- \quad (26)$$

$$k_{26} > 4.0 \times 10^9\ M^{-1}\ s^{-1}\ ^{19}$$

$${}^•NO_3 + H_2O \rightarrow HNO_3 + {}^•OH \quad (27)$$

$$k_{27} = 2.9 \times 10^7\ s^{-1}\ ^{12}$$

Both mechanisms II and III are followed by reactions 28–30, and mechanism III is also followed by reactions 9 and 10.

$$I^• + I^- \rightarrow I_2^{•-} \quad (28)$$

$$k_{28} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}\ ^{12}$$

$$I_2^{•-} + I_2^{•-} \rightarrow I_3^- + I^- \quad (29)$$

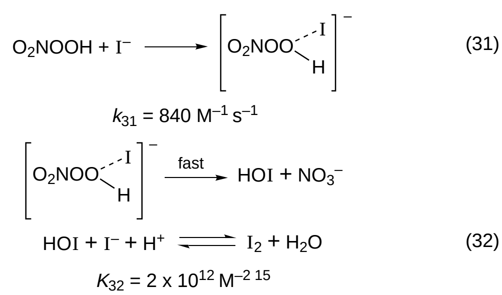
$$k_{29} = 2.3 \times 10^9\ M^{-1}\ s^{-1}\ ^{12}$$

$$I_2 + I^- \rightleftharpoons I_3^- \quad (30)$$

$$K_{30} = 710\ M^{-1}\ ^{15}$$

The present results rule out mechanism III because, in the presence of 0.1 M formate and 0.5 mM iodide, ${}^•NO_3$ would not be scavenged by formate ($k = 2 \times 10^5\ M^{-1}\ s^{-1}$)[12] and 0.5 mM iodide would not compete efficiently with the hydrolysis of ${}^•NO_3$ to ${}^•OH$, which in the presence of excess of formate forms superoxide. Because $HO_2^•$ does not oxidize iodide,[12] $G(O_2NOOH)_T/G(I_3^-)_T$ will not exceed 0.5, in contrast to the observed value of unity.

mechanism IV



In conclusion, the kinetics and the stoichiometry results demonstrate that the direct oxidation of iodide by peroxynitrate is consistent with either mechanism II or IV.

Mechanism of Indirect Oxidation by Peroxynitrate. The rate of the oxidation of ferrocyanide and NADH by peroxynitrate in the presence of sufficient concentrations of these substrates is zero order in the substrate concentration. The observed rate constants at pH >6 are within experimental error identical to those of the self-decay of peroxynitrate, whereas at acid solutions they are considerably higher (Figure 3). The best fit obtained for the observed oxidation rates is for $k_f = 1.0\ s^{-1}$ (alkaline), $0.05\ s^{-1}$ (acid) and $pK_a = 5.6 \pm 0.1$ (Figure 3), whereas the best fit for the rate of the self-decay of peroxynitrate is for $k_d = 1.0\ s^{-1}$ (alkaline), 7×10^{-4}–$4.6 \times 10^{-3}\ s^{-1}$ (acid)[6–8] and $pK_a = 5.9 \pm 0.1$ (Figure 3).

(17) Willson, R. L. *Chem. Commun.* **1970**, 1005.
(18) Damschen, D. E.; Martin, L. R. *Atmos. Environ.* **1983**, *17*, 2005.
(19) The rate constant of reaction 26 has not yet been determined, whereas those for reactions of ${}^•NO_3$ with chloride and bromide were determined to be 4×10^7 and $4 \times 10^9\ M^{-1}\ s^{-1}$, respectively.[12] Therefore, k_{26} is expected to be higher than the rate constant for the bromide reaction.

It was previously suggested that the decomposition of peroxynitrate takes place via the reactions[8]

$$O_2NOO^- \rightarrow NO_2^- + O_2 \qquad (33)$$

$$k_{33} = 1.0\ s^{-1}$$

$$O_2NOOH \rightarrow HNO_2 + O_2 \qquad (34)$$

$$k_{34} = 7 \times 10^{-4}\ s^{-1}$$

or via the radical mechanism[6,7]

$$O_2NOOH \rightleftharpoons {}^\bullet NO_2 + HO_2^\bullet \qquad (-13)$$

$$O_2NOO^- \rightarrow NO_2^- + O_2 \qquad (33)$$

$$HO_2^\bullet + O_2^{\bullet -} \rightarrow O_2 + HO_2^- \qquad (35)$$

$$k_{35}\ \text{pH-dependent}^{13}$$

$$2{}^\bullet NO_2 \rightleftharpoons N_2O_4 \qquad (36)$$

$$k_{36} = 4.5 \times 10^8\ M^{-1}\ s^{-1} \qquad k_{-36} = 6.9 \times 10^3\ s^{-1}\ ^{12}$$

$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad (37)$$

$$k_{37} = 1 \times 10^3\ s^{-1}\ ^{12}$$

Both mechanisms predict that the rate of the decay of peroxynitrate will be first order and pH-dependent. However, according to reactions 33 and 34, the products of the decomposition process will be oxygen and nitrite at all pH's, whereas the radical mechanism predicts the decrease in the yield of nitrite and oxygen and an increase in the yield of nitrate with a decrease in pH.

Lammel et al.[7] found that, above pH 5, the decomposition of peroxynitrate yields predominately nitrite, whereas in acidic solutions the yield of nitrite decreased to about 8%. The yield of nitrate increased with the decrease in pH, but the results are inaccurate due to nitric acid impurity.[7] This observation suggests a change in the mechanism of decomposition when the pH decreases, which supports the radical mechanism. However, Logager and Sehested[8] determined the oxidation capacity of a mixture of excess of H_2O_2 over O_2NOOH at pH 2 and found that one molecule of O_2NOOH consumed one molecule of H_2O_2. If the radical mechanism were correct, H_2O_2 would not be consumed (reactions −13, and 35−37 followed by reaction 24), whereas in the nonradical mechanism (reaction 34 followed by reaction 24), one molecule of O_2NOOH consumes one molecule of H_2O_2. However, the nonradical mechanism (reactions 33 and 34) cannot explain the decrease in the yield of nitrite with the decrease in pH, and the indirect oxidation of ferrocyanide and NADH by peroxynitrate as nitrite and oxygen does not oxidize these substrates under our experimental conditions.

Our results show that the observed rate constant of the oxidation of ferrocyanide and NADH by O_2NOOH equals 0.05 s^{-1}, which is considerably higher than the rate of the self-decomposition of peroxynitrate in acidic solutions (Figure 3).[6−8]

Considering the radical mechanism, if a scavenger ($Fe(CN)_6^{4-}$ or NADH) reacts with ${}^\bullet NO_2$ and $HO_2^\bullet$, the decay rate of O_2NOOH in the presence of sufficient concentrations of these substrates may be determined by $k_{-13} = 0.05\ s^{-1}$, and the stoichiometry will be 2. However, the dependence of the oxidation yields on pH and $[S]_0$ (S = substrate) (Figures 6 and 7) indicates that the mechanism of the indirect oxidation by peroxynitrate is not as simple as the radical mechanism. If the oxidation of a substrate takes place only through $HO_2^\bullet$ and ${}^\bullet NO_2$, the oxidation yields will decrease with the increase in pH. Under the conditions where the rates of the oxidation of S by $HO_2^\bullet$ and $NO_2^\bullet$ compete efficiently with the dismutation of superoxide and with the hydrolysis of ${}^\bullet NO_2$, the yield of S^+ will be given by eq 38. Thus, at pH > pK_a, the oxidation yields

$$\frac{G(S^+)}{G(O_2NOOH)_T} = \frac{2k_{-13}[H^+]/(K_a + [H^+])}{k_{-13}[H^+]/(K_a + [H^+]) + k_{33}K_a/(K_a + [H^+])} = \frac{2k_{-13}[H^+]}{k_{-13}[H^+] + k_{33}K_a} \qquad (38)$$

reduce to zero, independent of ferrocyanide concentrations, which is in contrast to the experimental results given in Figure 6.

We therefore suggest that peroxynitrate decomposes through the formation of O_2NOOH^* and O_2NOO^{-*} as oxidizing intermediates, where the former is in equilibrium with $HO_2^\bullet$ and ${}^\bullet NO_2$ and the latter decomposes into nitrite and oxygen (Scheme 1).

Our suggested mechanism fits the results of Lammel et al.,[7] who showed that the yield of nitrite decreased with the decrease in pH. The yield of HNO_2 in acidic solutions will depend on the relative rates of reactions 40 and 41 because $k_{-40} = 1.8 \times 10^9\ M^{-1}\ s^{-1}$,[8] and reaction −40 competes efficiently with the hydrolysis of ${}^\bullet NO_2$ and the dismutation of $HO_2^\bullet$. The contribution of reaction 41 to the decomposition process requires a detailed study on product yields (nitrite, nitrate, and oxygen) as a function of pH. Our suggested mechanism also shows that H_2O_2 is consumed by O_2NOOH, though it predicts that less than one molecule of H_2O_2 will be consumed by one molecule of O_2NOOH, which is in agreement with a recent study where only about 0.6 mol of H_2O_2 was consumed by 1 mol of O_2NOOH.[9]

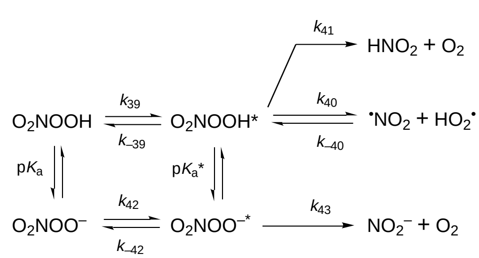
In the presence of an efficient scavenger of O_2NOOH^*, $k_{obs} = k_{39}$, and when the oxidation takes place through ${}^\bullet HO_2$ and ${}^\bullet NO_2$, $k_{obs} = k_{39}(k_{40} + k_{41})/(k_{-39} + k_{40} + k_{41})$.

Conclusions

Peroxynitrate is formed within less than 2 ms after the irradiation of aerated solutions containing formate and nitrate. This method is very useful for studying the mechanism of the oxidation by peroxynitrate.

Our suggested mechanism for the decomposition of peroxynitrate (Scheme 1) explains the following features: (i) The observed rate constant of the decay of peroxynitrate is first order and highly pH-dependent. (ii) The decomposition of peroxynitrate at pH >5 yields mainly nitrite and oxygen. The yield of nitrite decreases and that of nitrate increases in acidic

Scheme 1



solutions. (iii) Peroxynitrate may oxidize the substrates directly through O_2NOOH in a reaction that is first order in peroxynitrate and first order in the substrate, e.g., iodide. (iv) Peroxynitrate may oxidize the substrates in a reaction that is first order in peroxynitrate and zero order in the substrate, e.g., ferrocyanide and NADH. The indirect oxidation by peroxynitrate may take place through $O_2NOO^{-}*$, O_2NOOH*, $^{\bullet}NO_2$, or $HO_2^{\bullet}$, all of which are formed during the decomposition of peroxynitrate. (v) The oxidation yields at sufficient concentrations of the substrates approach 100% via the direct and indirect oxidation pathways.

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