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On the Chemical and Electrochemical One-Electron Reduction of Peroxynitrous Acid

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Peroxynitrous acid was reduced by cathodic linear sweep voltammetry at a gold electrode and by iodide at pH 3.2 and 5.6. The cathodic reduction wave was identified by measuring its decay in time, which was the same as observed by optical spectroscopy. The iodide oxidation was followed by optical measurement of the triiodide formation. Both reductions show one-electron stoichiometry, with the product $n_\alpha\alpha = 0.23 \pm 0.04$ from the electrochemical experiments, in which α is the transfer coefficient and n_α the number of electrons transferred, and an diiodine yield of ca. 0.5 equiv per equivalent of peroxynitrous acid. The voltammetric reduction was irreversible up to scan rates of 80 V s^{-1}. Both reductions were pH independent in the range studied. The voltammetric reduction is most likely an irreversible elemental reaction followed by a chemical decay that cannot be observed directly. Because of the pH independence, we conclude that both reductions have a common short-lived intermediate, namely $[HOONO]^{\bullet-}$. We estimate the electrode potential of the likely $ONOOH/ONOOH^{\bullet-}$ couple to be larger than 1 V. The commonly used electrode potential $E°(ONOOH, H^+/NO_2^\bullet, H_2O)$ does not describe the chemistry of peroxynitrous acid.

Introduction

Micromolar concentrations of both nitrogen monoxide and superoxide[1] are produced by activated macrophages during the immune response. Given the diffusion-controlled rate of 1.6×10^{10} M^{-1} s^{-1},[2] this is likely to lead to formation of peroxynitrite. Because the pK_a of peroxynitrous acid is ca. 6.8, depending on temperature, buffer composition, and concentration,[3−5] both peroxynitrous acid and peroxynitrite can be involved in deleterious reactions. Thus, peroxynitrous acid and/or its deprotonated form oxidize thiols,[5−8] nitrate tyrosines,[9−14] and tryptophan,[15,16] and initiate lipid peroxidation.[17,18] Both one-electron oxidations and oxygen-transfer reactions have been reported.[19−21]

The one-electron electrode potential of peroxynitrous acid is a crucial parameter to predict whether peroxynitrous acid can oxidize a compound specifically in a one-electron step, a process that potentially could yield free radicals. Values of 2.14 and 2.0 V were published by Merényi and Lind[22] and Koppenol and Kissner,[3] respectively, and refer to standard conditions. These values are based on determinations and estimates of the standard Gibbs energy of formation of peroxynitrous acid. To our knowledge, no direct electrochemical investigation of peroxynitrous acid has been reported.

The oxidation of the peroxynitrite anion has been studied electrochemically and an $E°'$ value of 0.51 ± 0.02 V has been reported for the $ONOO^\bullet/ONOO^-$ couple.[23]

Experimental Section

Reagents. Na_2HPO_4, NaH_2PO_4, $NaNO_2$ (Fluka/Buchs, Switzerland), H_3PO_4, NaOH (Siegfried/Zofingen, Switzerland), NaI (Merck/Darmstadt, Germany), and KO_2 (Sigma-Aldrich/St. Louis, MO) were analytical grade or better. $NO^\bullet$ (Linde/Unterschleissheim, Germany) was of 99.95% purity. Peroxynitrite was synthesized according to Koppenol et al.[24] and Bohle et al.[25] The concentration of the peroxynitrite solution was determined by measuring the absorbance at 302 nm ($\epsilon_{302} = 1705$ M^{-1} cm^{-1}).[25] Deionized water was purified further by a Millipore Milli-Q unit (Millipore/Bedford, MA). Buffers were prepared from the reagents above.

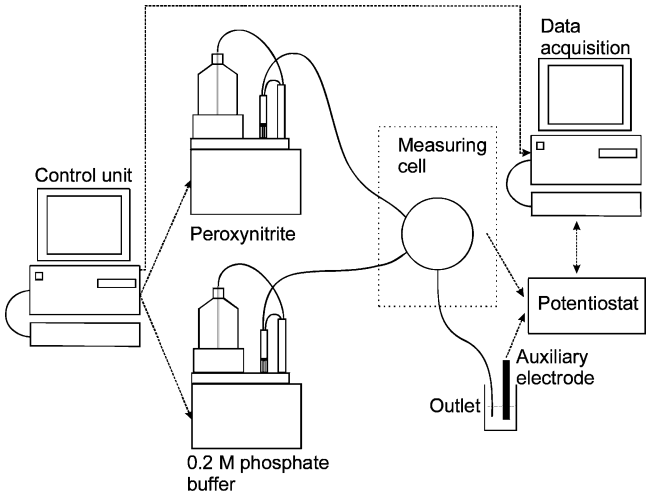

Figure 1. The equipment for stopped-flow electrochemistry consists of two pumps, controlled by computer, an electrochemical cell, a potentiostat, and a computer for the collection and evaluation of the data.

Cyclic Voltammetry. Cyclic voltammograms were measured by a stopped-flow technique. The apparatus setup is shown in Figure 1. One pump (Dosimat 665 titration unit from Metrohm/Herisau, Switzerland) was filled with a 0.2 M NaH_2PO_4 solution and the second one with peroxynitrite solution in 0.01 M NaOH. The pump units were activated simultaneously by a computer.

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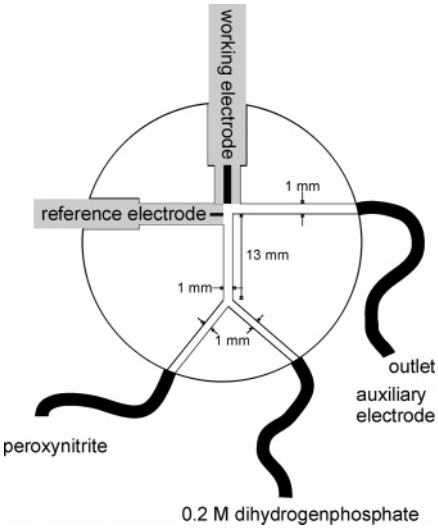

Figure 2. Details of the measuring cell.

The titration devices were both set to a flow of 20 mL/min, and the measuring cell (Figure 2) was flushed with 20 times its volume. The measurements were started by a trigger signal sent by the pump control unit to the measuring computer. The measuring equipment consisted of a computer with a 60 kHz 12 bit analog to digital converter, an AMEL 2049 potentiostat, and an AMEL 586 function generator (Amel/Milan, Italy). The working electrode was a planar gold disk from Metrohm (Herisau, Switzerland) with an active surface of 1.2 mm^2.[26] The reference electrode was an Ag/AgCl electrode from Methrom (Herisau, Switzerland) filled with 0.1 M KCl and 0.1 M $NaNO_3$ as bridge electrolyte, with a electrode potential of 0.270 V vs normal hydrogen electrode (25 °C). The auxiliary electrode was a glassy carbon electrode from Metrohm (Herisau, Switzerland).

Stopped-Flow Spectrophotometrie Studies. Kinetics experiments were carried out at 25 °C and ambient pressure with an Applied Photophysics SX 17MV (Leatherhead, Surrey, UK) stopped-flow spectrophotometer operated in the symmetric mixing mode. The reaction was initiated by mixing 10, 50, or 100 μM peroxynitrite in 0.01 M sodium hydroxide with various sodium iodide concentrations (200 μM to 40 mM) in 0.2 M phosphate buffer at pH 5.8 and at pH 3.2. The changes in absorbance were followed at 350 nm and the pH of the mixture was determined at the outlet of the stopped-flow apparatus with a glass electrode. The equilibrium constant of the triiodide formation $I_2 + I^- \leftrightarrows I_3^-$ was determined to be 930 M^{-1} in the phosphate buffer system used, somewhat different from the 710 M^{-1} found in the literature,[27] which is a value obtained by extrapolation to zero ionic strength. The extinction coefficient of I_3^- at 350 nm was 28 100 M^{-1} cm^{-1}, in good agreement with the literature.[27]

Results

Voltammetry. Electrochemical reduction of peroxynitrous acid at a polycrystalline gold electrode with a linear sweep yielded a cathodic wave that could be assigned unambiguously to peroxynitrous acid, since the peak current at a given scan rate decreased with the time between the formation of the acid by mixing peroxynitrite with dihydrogen phosphate/phosphoric acid and the onset of the voltammetric scan. The rate constant for the first-order decrease in peak current was (1.1 ± 0.1) s^{-1} at pH 5.6 and (1.5 ± 0.1) s^{-1} at pH 3.2, quite typical for peroxynitrous acid isomerization at room temperature.[4] The reduction wave of peroxynitrous acid was followed by further

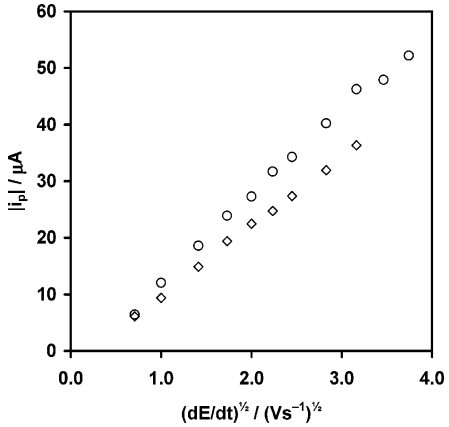

Figure 3. Peak currents vs square root of the scan rate: 1 mM peroxynitrite with 0.1 M phosphoric acid/phosphate buffers, gold electrode; circles, pH 3.2; diamonds, pH 5.6.

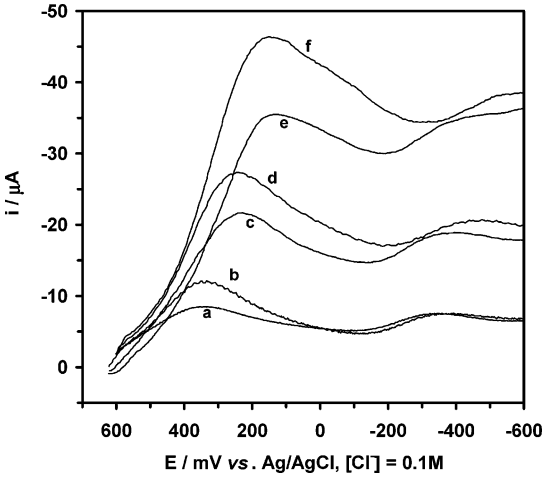

Figure 4. Reduction waves of peroxynitrous acid at pH 3.2 and 5.6 and several scan rates: 1 mM peroxynitrous acid, 0.1 M phosphoric acid/phosphate buffers; (a) pH 5.6, 1 V s^{-1}; (b) pH 3.2, 1 V s^{-1}; (c) pH 5.6, 4 V s^{-1}; (d) pH 3.2, 4 V s^{-1}; (e) pH 5.6, 10 V s^{-1}; (f) pH 3.2, 10 V s^{-1}.

reduction waves at more negative potential. These waves are most probably caused by the reduction of decomposition products, possibly nitrogen dioxide and dinitrogen tetraoxide. Nitrite was ruled out, because it yielded no cathodic wave under the same conditions. Cyclic scans up to 80 V s^{-1} showed no reoxidation wave. The negative peak potential shift for a 10-fold increase in scan rate from 1 to 10 V s^{-1} was 190 mV at pH 3.2 and 210 mV at pH 5.6. The peak currents were always directly proportional to the initial peroxynitrous acid concentration and to the square root of the scan rate at both pH values (Figure 3). The peak current−scan rate relation indicates that the reductions observed were caused by species under diffusion control and not adsorbed to the electrode surface. The current peaks at pH 3.2 were higher than at pH 5.6 (Figure 4) for the same peroxynitrous acid concentrations and scan rates, but hardly shifted by the different pH. The variation of maximum current strength with pH was caused by a change in ohmic resistance of the metal−solution interface, which depends on the buffer composition. At pH 5.6, there is a considerable concentration of monohydrogen phosphate present, while at pH 3.2, dihydrogen phosphate is the only anionic species.

Stopped-Flow. Peroxynitrous acid oxidizes iodide to diiodine like other peroxides.[28,29] However, unlike other peracids, it cannot be determined quantitatively by iodometric titration, since the relative yield of the reaction depends on the concentrations

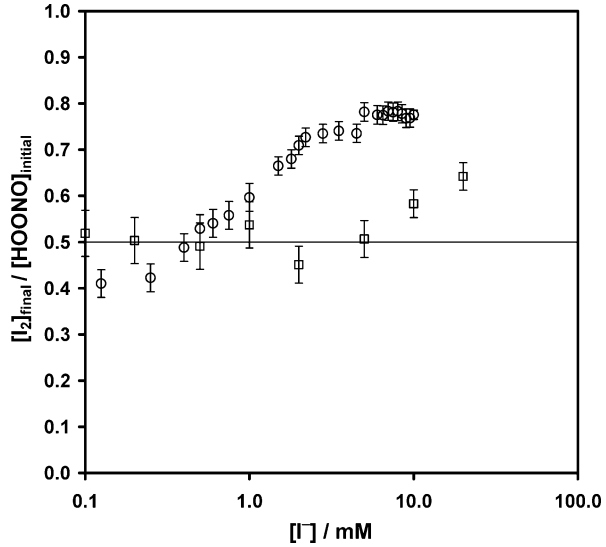

Figure 5. Relative yields of diiodine from the oxidation of iodide by peroxynitrous acid vs total iodide concentration: 0.1 M phosphoric acid/phosphate buffers.; circles, $[HOONO]_{initial} = 25\ \mu M$; squares, $[HOONO]_{initial} = 5\ \mu M$.

involved. With iodide concentrations below 1 mM, but in at least 5-fold excess over peroxynitrous acid, precisely 0.5 equiv of diiodine was produced. Only with iodide concentrations below 100 μM did the isomerization of the peroxynitrous acid compete with the iodide oxidation, and the diiodine yield dropped below 0.5 equiv. At iodide concentrations above 1 mM, the diiodine yield rose above 0.5 equiv and approached, but never reached, 1 equiv (Figure 5). The rate law of the reaction was first order in both iodide and peroxynitrous acid, which means that only these molecules are involved in the rate-determining step. The second-order rate constant at pH 3.2 was $(2.8 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$, based on the rate of formation of diiodine, which was obtained by converting the I_3^- absorbance vs time trace with the law of mass action of the equilibrium $I_2 + I^- \leftrightarrows I_3^-$ into the diiodine concentration vs time. The reaction rate increased somewhat from pH 5.6 to 3.2, and this small change can be attributed to the fact that at pH 5.6 about 10% of the peroxynitrite is in the less reactive $ONOO^-$ form.

Discussion

The complete lack of reoxidation wave and the linear dependence of the peak current on the square root of the scan rate rule out a quasireversible electrochemical reaction.[30] The remaining conceivable mechanisms are (a) an irreversible electrochemical reaction E_i, (b) an irreversible electrochemical reaction E_i preceded by a chemical equilibrium, C_rE_i, or (c) a reversible electrochemical reaction followed by an irreversible chemical process, E_rC_i. Process c would show no reoxidation wave only if the kinetic parameter $\lambda = (k_c/\upsilon)(RT/nF)$, in which k_c is the chemical rate constant based on mole fractions and υ the scan rate, were larger than 0.1.[31] The shift of the negative peak potential with a 10-fold increase in υ should be 29.6 mV/n for a truly reversible electrode reaction. In the case of a quasireversible reduction, the shift should not exceed 59.1 mV/n.[32] The experimentally determined shift of about 200 mV is far too high to account for any reduction of type c. The huge peak potential shift suggests $n_\alpha = 1$ for the rate-determining electrochemical step and an α smaller than 0.5. Processes a and b remain. As regards possibility b, a preceding equilibrium could be the hydronation of peroxynitrous acid, eq 1,

$$HOONO + H^+ \leftrightarrows [H_2OONO]^+ \quad (1)$$

which is supported by the slightly increased isomerization rate of peroxynitrous acid at pH <3.[33] An estimated pK_a of about 2 for equilibrium 1 is compatible with this observation. The hydronation equilibrium would be reached much faster than the electrochemical reduction, and therefore the hydronation equilibrium should shift the peak potential position by

$$\Delta E = (RT/\alpha n_\alpha F)\ln(K/K+1) \quad (2)$$

with $K = X_{H_2OONO^+}/X_{HOONO}$

from the value without a preequilibrium. K is the equilibrium constant for a given buffer pH and p$K_a = 2$. With the assumption of $\alpha = 0.5$, the peak potential at pH 3.2 should differ by about 200 mV from that at 5.6 with $n_\alpha = 1$, or by 100 mV with $n_\alpha = 2$, at the same scan rates. Experimentally this was not found: the peaks appeared at nearly identical potentials at both pH values (Figure 4). The peak potential difference was only 15 mV at 10 V s^{-1} and smaller at lower scan rates. The lack of a significant pH-dependent peak shift rules out a hydronation equilibrium. Another preceding equilibrium could be the homolysis of peroxynitrous acid, which is claimed to take place at a rate of one-third of the isomerization rate:[34,35]

$$HOONO \leftrightarrows NO_2^\bullet + OH^\bullet \quad (3)$$

The rate of this reaction would be almost pH independent below the pK_a of peroxynitrous acid. It is, however, rather unlikely that the cathodic current measured was caused by the reduction of hydroxyl radicals, when one considers that their steady-state concentration would be very low due to fast recombination reactions that result in nitric acid, peroxynitrous acid, dinitrogen tetraoxide, and hydrogen peroxide. The shape of the cathodic peak and its potential shift with scan rate imply a kinetically inhibited reduction, which is not what one expects for hydroxyl radicals. Since there were no other reactants present, a purely irreversible mechanism of type a is consistent with the data obtained. Linear sweep peaks of reaction type a can be analyzed for αn_α by means of the relation $|E_p - E_{p/2}| = 1.857RT/\alpha n_\alpha F$.[36] The average of αn_α, in which α is the transfer coefficient and n_α the number of electrons transferred, for 11 peaks recorded at pH 3.2 yields $\alpha n_\alpha = 0.26 \pm 0.06$, and for 9 peaks at pH 5.6, $\alpha n_\alpha = 0.27 \pm 0.03$. Plots of $\ln(i_p)$ vs E_p have slopes with $\alpha n_\alpha = 0.21 \pm 0.01$ for pH 5.6 and $\alpha n_\alpha = 0.22 \pm 0.02$ for pH 3.2, in good agreement with the values derived from $|E_p - E_{p/2}|$. An α of 0.5 implies a perfectly symmetric activation barrier and is representative for most reversible electrochemical reactions. An α below 0.4 is typical for irreversible reactions, and an α below 0.2 is rarely observed. From the experimentally observed product $\alpha n_\alpha = 0.26$ we conclude that n_α equals 1. The rate-determining step in the electrochemical reduction of peroxynitrous acid is obviously the transfer of an electron to the molecule. If the electron transfer would yield a moderately stable product, the transfer would be at least quasireversible; since this is not the case it must be followed by a very fast and irreversible decay, eqs 4−6,

$$HOONO + e^- \leftrightarrows [HOONO]^{\bullet -} \quad (4)$$

$$[HOONO]^{\bullet -} \rightarrow OH^- + NO_2^\bullet \quad (5)$$

$$[HOONO]^{\bullet -} + H^+ \rightarrow H_2O + NO_2^\bullet \quad (6)$$

so that no quasireversible signal can be observed with ordinary

voltammetry equipment. The formation of $[HOONO]^{\bullet -}$, otherwise named (hydridodioxido)oxonitrate(•1−), as an intermediate is not that farfetched: it has been shown that $NO_2^{\bullet 2-}$ can be produced from nitrite and hydrated electrons.[37−43]

The iodide oxidation by peroxynitrous acid is hardly pH dependent in the pH range where peroxynitrite is extensively hydronated. The rate law for the iodide oxidation is $d[I_2]/dt = k[HOONO][I^-]$. This rate law, the rate constant, and the yields are in agreement with earlier observations by Goldstein and Czapski,[28] but these relative yields are not compatible with the mechanism they postulated later.[29] If the iodide oxidation were a two-electron process as suggested, a yield of 1 equiv of diiodine per equivalent of peroxynitrous should be attainable at sufficient iodide excess, which is not the case (Figure 5). Since the same rate law was found under a variety of experimental conditions, the combined observations imply that a single electron transfer to peroxynitrous acid is rate limiting, as is the case in the electrochemical reduction. Therefore, it is rather probable that the same intermediate is formed as in the electrochemical reduction, namely (hydridodioxido)oxonitrate(•1−). This unstable species decays rapidly to nitrogen dioxide and water (eqs 5 and 6). This mechanism explains why the first half-equivalent of diiodide is formed stoichiometrically, even at small iodide concentrations, while the formation of the second half-equivalent remains incomplete at high iodide excess, because eq 7

$$NO_2^{\bullet} + I^- \leftrightharpoons NO_2^- + I^{\bullet} \quad (7)$$

$$I^{\bullet} + I^- \leftrightharpoons I_2^{\bullet -} \quad (8)$$

$$2I_2^{\bullet -} \rightarrow I_3^- + I^- \quad (9)$$

is an equilibrium with a constant of about 10^{-3} [44] and nitrogen dioxide disappears rapidly through dimerization and hydrolysis, eqs 10 and 11.

$$2NO_2^{\bullet} \rightarrow N_2O_4 \quad (10)$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (11)$$

Thus, at lower iodide concentrations, the overall reaction is

$$ONOOH + I^- \rightarrow {}^1/_2NO_2^- + {}^1/_2NO_3^- + {}^1/_2I_2 + {}^1/_2H_2O \quad (12)$$

While eq 12 does describe the yield of diiodine per peroxynitrous acid well, at higher iodide concentrations there may well be additional reactions that increase the yield diiodine, such as the more quantitative formation of diiodide(•1−), which removes the iodine radical from equilibrium 7. In addition, dinitrogentetraoxide may oxidize iodide, and nitrite may do the same via the nitrosyl cation. In principle, the reaction of nitrogen dioxide with diiodide(•1−) is feasible, but kinetically unlikely. Lack of kinetic data prevents a more quantitative analysis.

The pH independence of the electrochemical reduction of peroxynitrous acid is not what one expects from the literature. Experimental determinations and theoretical estimates of the one-electron electrode potential of peroxynitrous acid assume that eq 13 applies:

$$ONOOH + H^+ + e^- \leftrightharpoons NO_2^{\bullet} + H_2O \quad (13)$$

Values of 2.14 and 2.0 V were published for the standard electrode potential by Merényi and Lind[22] and Koppenol and Kissner,[3] respectively. On the basis of the results presented here, eq 11 does not reflect the chemistry of peroxynitrous acid.

Given the irreversibility of the electrode processes, it is not possible to estimate the electrode potential of the couple ONOOH/$[ONOOH]^{\bullet -}$ strictly on the basis of the electrochemical experiments. However, the observation that iodide and hexachloroiridate(III)[45] are oxidized by peroxynitrous acid suggests that this electrode potential is larger than 1 V.

Acknowledgment. Supported by the ETH and the Schweizerische Nationalfonds.

References and Notes

(1) Systematic names: $O_2^{\bullet -}$, dioxide(•1−); $NO^{\bullet}$, oxidonitrogen(•); $ONOO^-$, oxoperoxonitrate(1−); the trivial names superoxide, nitrogen monoxide, and peroxynitrite, respectively, are allowed. $[ONOOH]^{\bullet -}$ is named (hydridodioxido)oxonitrate(•1−). Leigh, G. J. Ed. *Nomenclature of Inorganic Chemistry*; Blackwell Scientific Publications: Oxford, UK, 1990; Koppenol, W. H. *Pure Appl. Chem.* **2000**, *72*, 437−446.

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