

Direct Determination of the Gibbs' Energy of Formation of Peroxynitrous Acid

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The kinetics of decomposition of peroxynitrous acid (ONOOH) was investigated in the presence of 0.1–0.75 M HClO₄ and at a constant ionic strength. The decay rate of ONOOH decreased in the presence of H₂O₂, approaching a limiting value well below 75 mM H₂O₂. It also decreased in the presence of relatively low [HNO₂] but did not approach a lower limiting value, since ONOOH reacts directly with HNO₂. The latter reaction corresponds to a HNO₂- and H⁺-catalyzed isomerization of ONOOH to nitrate, and its third-order rate constant was determined to be 520 ± 30 M⁻² s⁻¹. The mechanism of formation of O₂NOOH from ONOOH in the presence of H₂O₂ was also scrutinized. The results demonstrated that in the presence of 0.1–0.75 M HClO₄ and 75 mM H₂O₂ the formation of O₂NOOH is insignificant. The most important finding in this work is the reversibility of the reaction ONOOH + H₂O ⇌ HNO₂ + H₂O₂, and its equilibrium constant was determined to be (7.5 ± 0.4) × 10⁻⁴ M. Using this value, the Gibbs' energy of formation of ONOOH was calculated to be 7.1 ± 0.2 kcal/mol. This figure is in good agreement with the value determined previously from kinetic data using parameters for radicals formed during homolysis of peroxynitrite.

Introduction

Peroxynitrite (ONOOH/ONOO⁻) is a powerful oxidant that can form in biological systems in the reaction of nitric oxide with superoxide radicals.^{1,2} Peroxynitrite is well-known for its deleterious effects,^{3–5} which oftentimes derive from the formation of free radicals during its decomposition.⁶ Accurate knowledge of thermodynamical data for peroxynitrite is necessary for quantitative assessment of its chemistry. An important parameter is the Gibbs' energy of ONOOH, which has previously been determined to be 7.5 ± 0.4 kcal/mol.^{7,8} However, this determination has involved parameters

for free radicals formed via homolysis of peroxynitrite, and such parameters may not always be as accurately known as those of nonradical species. Therefore, a direct determination of the Gibbs' energy of ONOOH avoiding free radicals should be of value.

It has been known for some time that, in acidic media, the decomposition of ONOOH is proton-catalyzed, and it has been assumed that this reaction, just like the uncatalyzed consumption of ONOOH, yields nitrate as the sole product.^{9–12} In the present work, we shall scrutinize the acidic decomposition of ONOOH, which will lead to an accurate value for the Gibbs' energy of formation of ONOOH.

Experimental Section

Materials. All chemicals were of analytical grade and were used as received. Solutions were prepared with deionized water that was distilled and purified using a Milli-Q water purification system.

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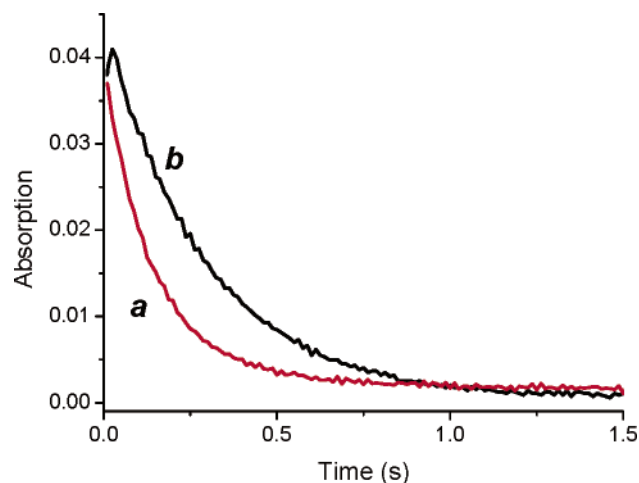


Figure 1. Decay of 0.22 mM ONOOH in the presence of residual H_2O_2 and HNO_2 (ca. 15 μM each) (a) and added 50 mM H_2O_2 (b). All solutions contained 0.5 M HClO_4 and 0.25 M NaClO_4 at 25 °C. The trace in the presence of added H_2O_2 was corrected against a blank without ONOOH.

Peroxynitrite and peroxynitrate were synthesized through the reaction of nitrite with acidified H_2O_2 using a quenched-flow with a computerized syringe pump (World Precision Instruments model SP 230IW) as described elsewhere.^{12,13} Briefly, peroxynitrite was synthesized by mixing 0.60 M H_2O_2 in 0.7 M HClO_4 with 0.63 or 0.60 M nitrite, and the mixture was quenched with 3 M NaOH at room temperature. The stock solutions contained ca. 0.12 M peroxynitrite. Starting with 0.63 M nitrite, the stock solution ended up containing about 3% residual H_2O_2 and 12% residual nitrite. When 0.60 M nitrite was used, the amounts of H_2O_2 and nitrite remaining were about 7% each.¹² The yield of peroxynitrite was determined from its absorption at 302 nm using $\epsilon = 1670 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁴ Peroxynitric acid was prepared by mixing nitrite with excess H_2O_2 in HClO_4 at room temperature, and its concentration was determined through its reaction with iodide at pH 4.4.¹³ The concentration of H_2O_2 was determined using the Fricke method.

Methods. Stopped-flow kinetic measurements were carried out using the Bio SX-17MV sequential stopped-flow from Applied Photophysics with a 1-cm optical path. Peroxynitrite in 0.01 M NaOH was mixed with HClO_4 solutions at a 1:1 ratio. In some experiments, the acidic solution also contained H_2O_2 , while in others the alkaline peroxynitrite solutions contained nitrite. In another set of experiments, equal volumes of acidified H_2O_2 and nitrite were mixed. A constant ionic strength of 0.75 M was maintained in all experiments using NaClO_4 in addition to HClO_4 . The formation and decomposition of ONOOH was followed at 290 nm, where all other species absorb negligibly. All experiments were carried out at 25 °C.

Simulations were carried using the GLINT global analysis package (Applied Photophysics), and a noncommercial program INTKIN written by Dr. H. A. Schwarz.

Results and Discussions

Effect of H_2O_2 on the Decay of ONOOH. The decay rate of ONOOH in the presence of 0.1–0.75 M H^+ was found to decrease with increasing $[\text{H}_2\text{O}_2]$, and to approach a limiting lower value. For instance, at 0.5 M H^+ , the limiting rate was reached above 20 mM H_2O_2 . Typical kinetic traces

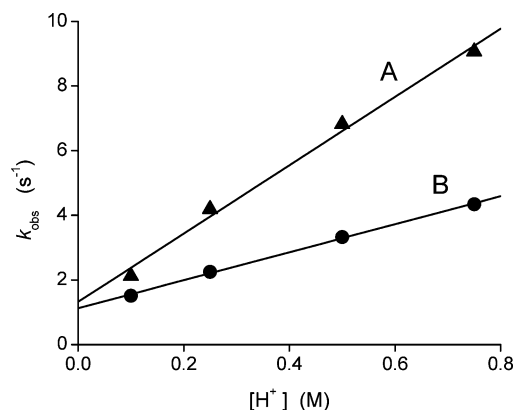
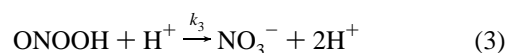
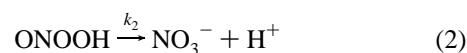
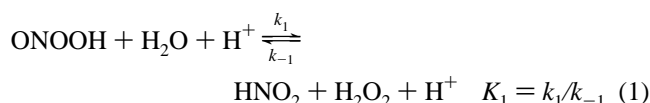


Figure 2. Observed decay rate constant of 0.21 mM ONOOH in the presence of residual H_2O_2 and HNO_2 (A) and 50 mM added H_2O_2 (B) at $I = 0.75 \text{ M}$ and 25 °C.

at 0.5 M H^+ without and with 50 mM added H_2O_2 are given in Figure 1. The decay of ONOOH in the presence of residual HNO_2 and H_2O_2 could not be fitted to a single exponential decay, but to two consecutive first-order reactions, where the contribution of the second reaction was less than 8%. These observations will be discussed in following paragraphs. In the presence of 50 mM H_2O_2 added, a small fast build-up of the absorption was observed, which subsequently decayed via a first-order reaction. The small build-up of the absorption is attributed to the formation of ONOOH via the reaction of H_2O_2 with the residual HNO_2 ,^{9–12} which is present in all preparations. Figure 2 displays the observed first-order decay rate constant of ONOOH as a function of $[\text{H}^+]$ in the presence of residual H_2O_2 and HNO_2 as well as with 50 mM H_2O_2 added. These findings can be rationalized in terms of reactions 1–3.



When the concentration of ONOOH is initially well below 1 mM and only residual H_2O_2 and HNO_2 are present, reaction –1 is negligible, and the rate law for the decay of ONOOH simplifies to:

$$-d[\text{ONOOH}]/dt = (k_1[\text{H}^+] + k_2 + k_3[\text{H}^+])[\text{ONOOH}] \quad (4)$$

At high $[\text{H}_2\text{O}_2]$, reaction 1 is quenched; i.e., equilibrium 1 is completely shifted to the left, and therefore eq 4 reduces to eq 5:

$$-d[\text{ONOOH}]/dt = (k_2 + k_3[\text{H}^+])[\text{ONOOH}] \quad (5)$$

We obtained $k_2 = 1.3 \pm 0.3 \text{ s}^{-1}$ and $(k_1 + k_3) = 10.6 \pm 0.6 \text{ M}^{-1} \text{ s}^{-1}$ from the intercept and slope of line A in Figure 2, and from line B in Figure 2, $k_2 = 1.1 \pm 0.1 \text{ s}^{-1}$ and $k_3 = 4.3 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$. Both intercepts agree with the well-known

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Table 1. Summary of All the Rate Constants Derived from the Present Study at $I = 0.75 \text{ M}$

no.	reaction	k
1	$\text{ONOOH} + \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{HNO}_2 + \text{H}^+$	$6.3 \pm 0.7 \text{ M}^{-1} \text{ s}^{-1}$
-1	$\text{H}_2\text{O}_2 + \text{HNO}_2 + \text{H}^+ \rightarrow \text{ONOOH} + \text{H}^+$	$(9.6 \pm 1.0) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$
2	$\text{ONOOH} \rightarrow \text{NO}_3^- + \text{H}^+$	$1.2 \pm 0.2 \text{ s}^{-1}$
3	$\text{ONOOH} + \text{H}^+ \rightarrow \text{NO}_3^- + 2\text{H}^+$	$4.3 \pm 0.1 \text{ M}^{-1} \text{ s}^{-1}$
9	$\text{ONOOH} + \text{HNO}_2 + \text{H}^+ \rightarrow \text{HNO}_2 + \text{NO}_3^- + 2\text{H}^+$	$520 \pm 30 \text{ M}^{-2} \text{ s}^{-1}$

Table 2. Observed Formation (k_f) and Decay (k_d) Rate Constants of ONOOH under Limiting Concentrations of HNO_2 or H_2O_2 in the Presence of 0.5 M HClO_4 and 0.25 M NaClO_4

$[\text{H}_2\text{O}_2]$, mM	$[\text{HNO}_2]$, mM	k_f , s^{-1}	k_d , s^{-1}
75	1	310 ± 20	3.5 ± 0.1
50	1	210 ± 10	3.5 ± 0.1
50	2.25	210 ± 10	3.5 ± 0.1
20	1	104 ± 2	3.4 ± 0.1
10	1	58 ± 1	3.3 ± 0.1
5	1	b	3.1 ± 0.1
1	5	b	4.4 ± 0.1
1	10	56 ± 1	6.3 ± 0.1
1	20	104 ± 3	9.5 ± 0.1
1	50	210 ± 16	16.7 ± 0.2

^a The decay of the absorption followed first-order kinetics, and k_d was determined. The formation of the absorption could not be well separated from its decay, and therefore, k_f was determined by fitting the kinetic trace to two consecutive first-order reactions, where the rate constant for the second reaction was fixed to the observed k_d . ^b Non-pseudo-first-order conditions.

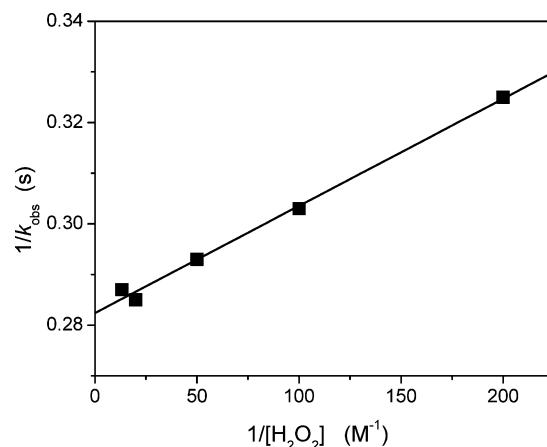
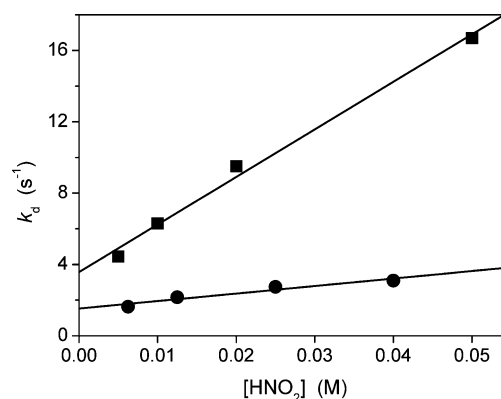
rate constant of neutral decomposition of ONOOH at 25°C .^{2,8} The difference between the two limiting rate constants, calculated from the slopes at high and residual H_2O_2 , yields $k_1 = 6.3 \pm 0.7 \text{ M}^{-1} \text{ s}^{-1}$. All the rate constants obtained in the present study are compiled in Table 1.

Reaction of HNO_2 with H_2O_2 . Upon mixing HNO_2 at constant $[\text{H}^+]$ with varying amounts of excess H_2O_2 , or vice versa, the rapid build-up of the absorption at 290 nm is followed by a slower decay. The data are presented in Table 2. The rate of formation of ONOOH was first order with respect to $[\text{HNO}_2]$ and $[\text{H}_2\text{O}_2]$, as long as the latter was kept well below ca. 0.25 M . This behavior is in agreement with earlier observations.⁹⁻¹² In the presence of a sufficiently large excess of H_2O_2 over HNO_2 or vice versa, the rate of reaction -1 becomes so much faster than that of reaction 1 that only the former can be observed. Under these conditions, the rate of formation of ONOOH is given by eq 6:

$$d[\text{ONOOH}]/dt = k_{-1}[\text{H}^+][\text{H}_2\text{O}_2][\text{HNO}_2] \quad (6)$$

From the data in Table 2, one obtains $k_{-1}[\text{H}^+] = (4.8 \pm 0.5) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, and hence, $k_{-1} = (9.6 \pm 1.0) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$. We determined above $k_1 = 6.3 \pm 0.7 \text{ M}^{-1} \text{ s}^{-1}$ in an independent kinetic measurement, and hence, k_1/k_{-1} yields the equilibrium constant $K_1 = (6.6 \pm 1.5) \times 10^{-4} \text{ M}$.

Although it has been reported previously that the rate of decay of ONOOH is independent of $[\text{H}_2\text{O}_2]$,¹² closer inspection of the data in Table 2 reveals that it increases slightly but systematically as $[\text{H}_2\text{O}_2]$ varies from 5 to 50 mM. From this variation, the equilibrium constant K_1 can be determined directly as follows. At high $[\text{H}_2\text{O}_2]$, the establishment of equilibrium 1 is much more rapid than the decay of the equilibrated mixture of HNO_2 and ONOOH. This means that

**Figure 3.** Double reciprocal plot of the dependence of the observed rate constant of the decay of ONOOH on $[\text{H}_2\text{O}_2]$. The data were taken from Table 1.**Figure 4.** Observed decay rate constant of ONOOH vs $[\text{HNO}_2]$ under limiting concentrations of H_2O_2 in the presence of 0.1 M HClO_4 (●) and 0.5 M HClO_4 (■). The ionic strength was 0.75 M .

$(k_1 + k_{-1}[\text{H}_2\text{O}_2])[\text{H}^+] \gg (k_2 + k_3[\text{H}^+])$, and hence, eq 7 is obtained:

$$-d([\text{HNO}_2] + [\text{ONOOH}])/dt = (k_2 + k_3[\text{H}^+])[\text{ONOOH}] \quad (7)$$

These are equilibrium conditions, which imply that $[\text{HNO}_2] = K_1[\text{ONOOH}]/[\text{H}_2\text{O}_2]$. Consequently, eq 8 is obtained:

$$-d[\text{ONOOH}]/dt = (k_2 + k_3[\text{H}^+])([\text{H}_2\text{O}_2]/(K_1 + [\text{H}_2\text{O}_2]))[\text{ONOOH}] \quad (8)$$

An inverse plot of k_{obs} versus $[\text{H}_2\text{O}_2]$ yields $1/\text{intercept} = (k_2 + k_3[\text{H}^+]) = 3.5 \pm 0.1 \text{ s}^{-1}$ and $\text{slope}/\text{intercept} = K_1 = (7.5 \pm 0.4) \times 10^{-4} \text{ M}$ (Figure 3). The former value is virtually identical to the one obtained from Figure 2B. Most importantly, the quantitative agreement between the directly and indirectly determined K_1 firmly settles its value.

While the decay rate of ONOOH approaches a limiting value as $[\text{H}_2\text{O}_2]$ increases, it keeps on increasing with increasing $[\text{HNO}_2]$, when the latter is in excess. This is clearly seen in Table 2 and Figure 4. The intercepts in this figure yield $(k_2 + k_3[\text{H}^+]) = 1.5 \pm 0.2$ and $3.6 \pm 0.4 \text{ s}^{-1}$ at 0.1 and 0.5 M H^+ , as expected, while the slopes correspond to the rate constants for the direct reaction between ONOOH and HNO_2 at 0.1 and 0.5 M H^+ , their values being 42 ± 8

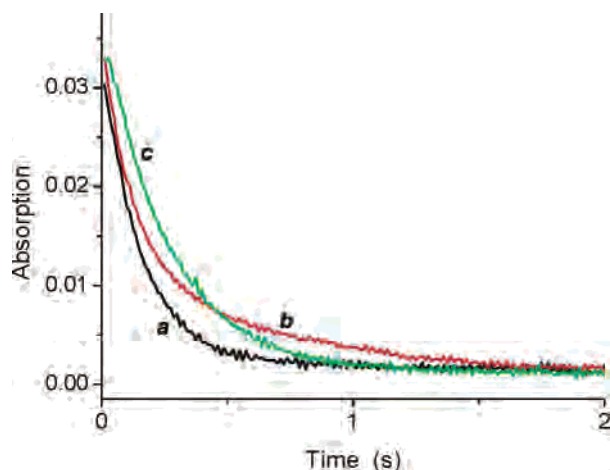
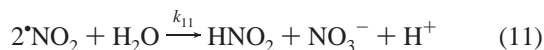
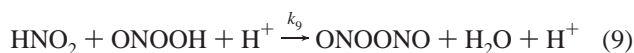


Figure 5. Decay of 0.21 mM ONOOH in the presence of residual HNO_2 and H_2O_2 (a), 0.75 mM added HNO_2 (b), and 4.4 mM added HNO_2 (c). All solutions contained 0.5 M HClO_4 and 0.25 M NaClO_4 and were at 25 °C.

and $267 \pm 16 \text{ M}^{-1} \text{ s}^{-1}$, respectively. This reaction is expected to be similar to reaction 1, as ONOOH, like H_2O_2 , is a hydroperoxide. Hence, the reaction of ONOOH with HNO_2 should form ONOONO, which decomposes fast to yield $2 \cdot \text{NO}_2$, and the latter hydrolyses to yield nitrate and HNO_2 (reactions 9–11).



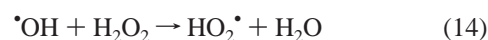
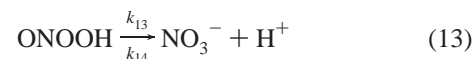
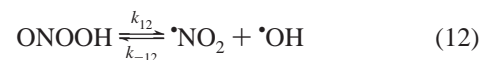
Thus, $k_9 = 520 \pm 30 \text{ M}^{-2} \text{ s}^{-1}$, and eqs 9–11 correspond to a simultaneous HNO_2 - and H^+ -catalyzed isomerization of ONOOH to nitrate.

Decay of ONOOH When $[\text{HNO}_2]$ or $[\text{H}_2\text{O}_2]$ Is Below a Few Millimolar. When ONOOH decayed in the presence of less than 10 mM H_2O_2 or HNO_2 , the decay obeyed two consecutive first-order reactions, where the contribution of the second reaction increased with increasing $[\text{H}_2\text{O}_2]$ or $[\text{HNO}_2]$. Such a dual decay was also observed when no extra H_2O_2 (or HNO_2) was added (see Figure 1a). These observations can now be explained. The fast decay involves the approach to equilibrium 1. Subsequently, the equilibrated mixture of ONOOH, HNO_2 , and H_2O_2 decays to nitrate, and this decay is monitored by way of the absorbance of the ONOOH fraction. Although one can obtain analytical solutions in closed form, these are not very useful, and thus, simulation of the traces is to be preferred. Some typical kinetic traces with excess $[\text{HNO}_2]$ are presented in Figure 5. These traces, as well as those with excess $[\text{H}_2\text{O}_2]$, were quantitatively simulated by means of rate constants k_1 , k_{-1} , k_2 , k_3 , and k_9 , taking into account the residual HNO_2 and H_2O_2 present in the stock solution of peroxynitrite. For example, the modeling results in the presence of 0.75 mM added HNO_2 (Figure 5b) are presented in the Supporting Information (Figure 5sup).

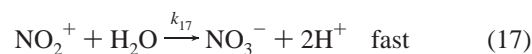
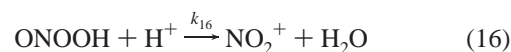
Finally, we note that, due to the reversibility of reaction 1, residual amounts of nitrite and H_2O_2 in stock solutions of peroxynitrite cannot be avoided, not even when ONOOH is synthesized from equal amounts of the reactants (see the Experimental Section).

Mechanism and Yield of Formation of O_2NOOH from ONOOH in the Presence of H_2O_2 . The most important observation in the present study was that the decay rate of ONOOH at low pH decreased with increasing $[\text{H}_2\text{O}_2]$, and we interpreted this finding in terms of the reversibility of reaction 1, where both forward and reverse rates are being catalyzed by $[\text{H}^+]$. However, it is also known that O_2NOOH is formed from ONOOH in the presence of H_2O_2 ^{13,15,16} and is relatively stable in acidic solutions. Hence, one might argue that its formation in our system could affect the kinetic interpretation. To address this point, we synthesized peroxynitrate through the reaction of nitrite with acidified H_2O_2 . The yield of O_2NOOH increased with increasing $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$. Figure 6 presents a double reciprocal plot of the yield of O_2NOOH versus $[\text{H}_2\text{O}_2]$ obtained when 0.18 M HNO_2 reacted with excess H_2O_2 in the presence of 1.65 M HClO_4 . The figure demonstrates that a yield of 100% O_2NOOH can be obtained at infinite concentrations of H_2O_2 . The present results as well as the literature data^{13,15,16} suggest that the formation of O_2NOOH from ONOOH in the presence of H_2O_2 takes place via the following mechanism.

(i) uncatalyzed pathway, where $k_{12} + k_{13} = k_2 = 1.2 \text{ s}^{-1}$ and $k_{13}/k_{12} = 2.5$:¹⁶



(ii) acid-catalyzed pathway, where $k_{16} = k_3 = 4.3 \text{ M}^{-1} \text{ s}^{-1}$:



From the slope of the line in Figure 6, we determined $k_{17}/k_{18} = 2.8 \pm 0.2 \text{ M}$. Thus, at high pH and moderate concentrations of H_2O_2 , the maximum yield of O_2NOOH does not exceed ca. 28% of the initial ONOOH,¹⁶ but it can approach 100% at low pH and very high $[\text{H}_2\text{O}_2]$. Nevertheless, under our experimental conditions, namely at 0.5 M H^+ and at the relatively low H_2O_2 concentrations of 50 – 75 mM, the acid-catalyzed pathway produces no more than

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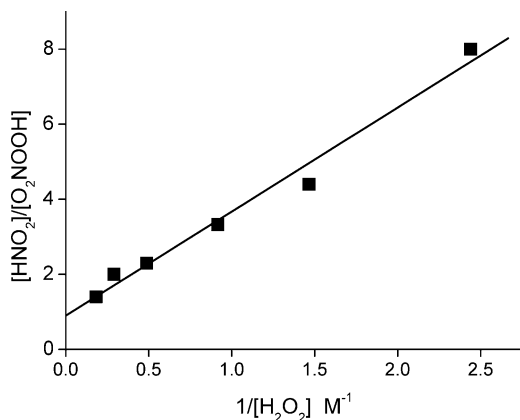
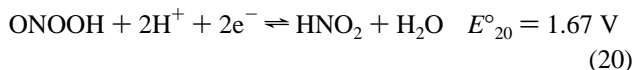
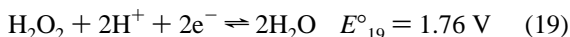


Figure 6. Dependence of the yield of O₂NOOH on [H₂O₂] at low pH. Double reciprocal plot of the yield of O₂NOOH vs [H₂O₂] obtained when 0.18 M nitrite reacted with excess of H₂O₂ in the presence of 1.65 M HClO₄ at room temperature.

2% O₂NOOH. Here, the uncatalyzed pathway is the main source of O₂NOOH. However, not even this source can produce more than $\{1.2/(4.3[\text{H}^+] + 1.2)\} \times 28\% = \text{ca. } 10\%$ of ONOOH. Thus, 12% is the maximum yield that we can get. Furthermore, it should be considered that at 290 nm ONOOH ($\epsilon \approx 190 \text{ M}^{-1} \text{ cm}^{-1}$) has by far the strongest absorbance of all occurring species, including O₂NOOH ($\epsilon < 20 \text{ M}^{-1} \text{ cm}^{-1}$). Most importantly, below pH 2 O₂NOOH is a stable species on our experimental time scale, its lifetime being thousands of seconds.¹⁷ Therefore, the accumulation of no more than ca. 12% O₂NOOH during the decomposition of ONOOH in a first-order reaction has no effect whatsoever on the rate constant extracted from the signal.

Thermodynamics of ONOOH. In the present work, a very accurate value has been determined directly for the equilibrium constant of reaction 1, $K_1 = (7.5 \pm 0.4) \times 10^{-4} \text{ M}$. This allows us to determine both the standard reduction potential of ONOOH as well as the Gibbs' energy of formation of ONOOH. The standard reduction potential of H₂O₂, E°_{19} , is 1.76 V.¹⁸ By combining eqs 1 and 19, we obtain $E^\circ_{20} = 1.67 \text{ V}$.



The Gibbs' energies of formation of HNO₂ and H₂O₂ in water and that of H₂O are accurately known, with $\Delta G_f^\circ(\text{HNO}_2) = -13.3 \text{ kcal/mol}$,^{19,20,28} $\Delta G_f^\circ(\text{H}_2\text{O}_2) = -32.0 \text{ kcal/mol}$,^{18,19,29} and $\Delta G_f^\circ(\text{H}_2\text{O}) = -56.7 \text{ kcal/mol}$. By means of

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these values and K_1 , we obtain $\Delta G_f^\circ(\text{ONOOH}) = (7.1 \pm 0.2) \text{ kcal/mol}$. Using $\text{p}K_a(\text{ONOOH}) = 6.6 \pm 0.1$,²¹ we calculate $\Delta G_f^\circ(\text{ONOO}^-) = (16.1 \pm 0.3) \text{ kcal/mol}$. This is in good agreement with $(16.6 \pm 0.4) \text{ kcal/mol}$,⁷ the latter having been determined using tetranitromethane as an efficient O₂^{•-} scavenger, and employing the relevant radical parameters.

Utilizing data extracted from a number of publications,^{2,8,21–24} we can calculate a very accurate equilibrium constant for reaction 12, with $K_{12} = k_{12}/k_{-12} = (0.34 \pm 0.08)/(5 \pm 1) \times 10^9 = (7 \pm 3) \times 10^{-11} \text{ M}$. By means of the well-known value of $\Delta G_f^\circ(\text{NO}_2) = 15.1 \text{ kcal/mol}$,²⁵ we obtain $\Delta G_f^\circ(\text{OH}) = (5.9 \pm 0.3) \text{ kcal/mol}$. This figure is in excellent agreement with $\Delta G_f^\circ(\text{OH}) = (6.0 \pm 0.5) \text{ kcal/mol}$ as obtained by Schwarz and Dodson²⁶ and is only slightly lower than $6.4 \pm 0.3 \text{ kcal/mol}$, as reported by Klaening et al.²⁷

Conclusions

The reaction $\text{ONOOH} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}_2$ is reversible, and its equilibrium constant, K_1 , was determined to be $(7.5 \pm 0.4) \times 10^{-4} \text{ M}$. From K_1 , the Gibbs' energy of formation of ONOOH was calculated to be $7.1 \pm 0.2 \text{ kcal/mol}$. This value is in good agreement with the one determined using parameters for radicals formed during homolysis of peroxyxynitrite.

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Supporting Information Available: Additional figure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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