

Peroxynitrous Acid Decomposes via Homolysis: Evidence from High-Pressure Pulse Radiolysis

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The effect of pressure on the decomposition rate of peroxynitrous acid was studied using the pulse radiolysis technique. Peroxynitrous acid was produced at pH 4.1 by irradiation of (i) aerated solution containing 0.15 M formate and 3 mM nitrite and (ii) deaerated solutions containing 3 mM nitrate and 4 mM phosphate. The volume of activation for the decomposition of ONOOH in these systems was determined to be $10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. The activation volume at pH 5.6 using the second system was found to be $10.5 \pm 1.1 \text{ cm}^3 \text{ mol}^{-1}$. The activation volume changes upon increasing the pH as pressure affects the pK_a values of ONOOH and H_2PO_4^- , which equal 6.6 and 7.2 ($I = 0$) at ambient pressure, respectively. We therefore conclude that the decomposition of ONOOH at pH 4.1 is characterized by a significant positive volume of activation, $\Delta V^\ddagger = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$, suggesting a bond breakage process that is not accompanied by charge creation, namely, homolysis of ONOOH into $\cdot\text{NO}_2$ and $\cdot\text{OH}$. The volume of the ionization of ONOOH has been determined from the dependence of ΔV^\ddagger on the pH to be $-7.2 \pm 2.1 \text{ cm}^3 \text{ mol}^{-1}$.

Introduction

The rate of decomposition of peroxynitrite (ONOOH/ONOO⁻) is highly pH-dependent and complex.^{1,2} Peroxynitrite ion is rather stable in alkaline solutions, but peroxynitrous acid isomerizes rapidly into nitrate with $k_o = 1.2 \text{ s}^{-1}$ at 25 °C.² The $pK_a(\text{ONOOH}) = 6.6 \pm 0.1$ has been determined in the presence of low concentrations of phosphate buffer using kinetic^{2,3} and absorption^{3,4} measurements.

During the isomerization of ONOOH into nitrate, a highly reactive intermediate is formed that oxidizes a large variety of substrates.⁵ Initially,^{6–8} this intermediate was believed to be the hydroxyl radical formed along with $\cdot\text{NO}_2$ via homolysis of ONOOH. Later, the mechanism for the decomposition of peroxynitrite became controversial.^{5,9–15} In our opinion, this controversy is now resolved in its major points, and most of the available data support a homolytic bond cleavage mechanism.^{14,16–19} The activation parameters for the decomposition of ONOOH were determined to be $E_a = 21 \pm 1.0 \text{ kcal mol}^{-1}$ and $A = (1.4–18) \times 10^{15} \text{ s}^{-1}$,^{18–23} the latter value being of the same order of magnitude as for the homolysis of peroxides in the gas phase and in nonpolar organic solvents.²⁴ The decomposition of ONOOH is also characterized by a significantly positive activation volume, $\Delta V^\ddagger = 9.6 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$, which we determined using the pulse radiolysis technique,²⁵ and is in favor of a bond breakage process. However, this value was criticized by Koppenol and Kissner,¹⁵ who reported an activation volume of $1.7 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ determined using the high-pressure stopped-flow technique.² They claimed that our value

was based on rate constants measured only at one pH and at two pressures, viz., 0.1 and 150 MPa at pH 4.1, and therefore, it is less reliable than their value, which they determined by measuring the rate of peroxynitrite decomposition at both pH 5.6 and pH 6.2 and at several pressures between 0.1 and 150 MPa. They concluded that the small positive volume of activation is not compatible with homolysis.^{2,15}

These controversial findings have led to speculative discussions in the literature regarding the validity of the data.^{15,26–28} It was therefore our goal to resolve this apparent discrepancy in the volume of activation data and to find possible reasons for its origin. This is of major importance, since the correct value could support or contradict the other observations in favor of homolysis of ONOOH.^{16–19,21}

Experimental Section

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

Methods. Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator delivering 5 MeV electron pulses of 1.5 μs and 200 mA. Repetitive pulsing was used to increase the yield of the radicals. The high-pressure setup was described in detail elsewhere.²⁹ Briefly, a small pillbox optical cell made of Suprasil (optical path length = 0.8 cm) is placed with its flat surface against the thin stainless steel window of the high-pressure cell so that the high-energy electrons would have a minimal path through the surrounding water-pressurizing medium. A 150 W Xe lamp produced the analyzing light, and appropriate filters were used to minimize photochemistry. The decomposition of ONOOH at pH 4.1 was followed at 280 nm and that of ONOOH/ONOO⁻ at higher pH's at 302 nm. The pressure experiments were performed up to 150 MPa at room temperature (18–19 °C).

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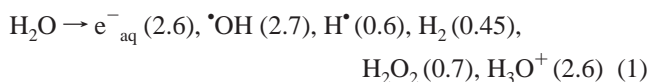
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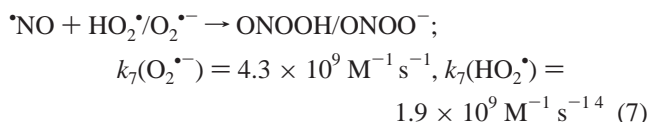
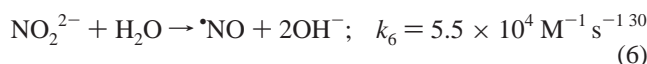
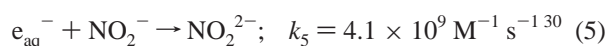
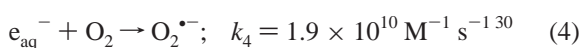
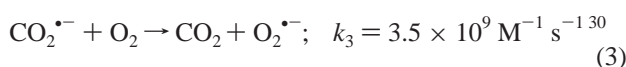
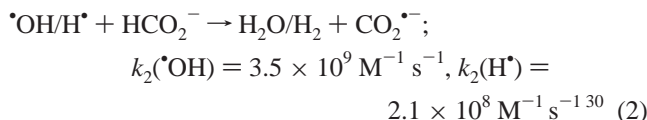
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Results

Peroxyntous acid was produced by irradiation of (i) air-saturated solutions containing 0.15 M formate and 3 mM nitrite^{4,25} and (ii) He-saturated solutions containing 3 mM nitrate and 4 or 100 mM phosphate buffer.^{3,19} In the first system, peroxyntite is formed via reactions 1–7:

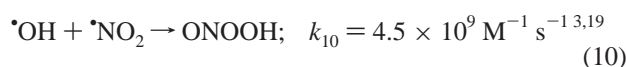
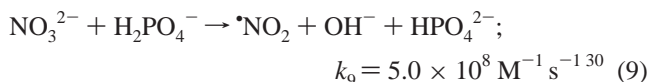
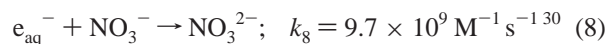


(the numbers in parentheses are *G* values, which represent the number of molecules formed per 100 eV energy absorbed by pure water),



Under these conditions superoxide, which has a pH-dependent half-life,³⁰ is produced in excess over $\cdot\text{NO}$. Therefore, during the decomposition of ONOOH, where $\cdot\text{NO}_2$ is formed as an intermediate,^{16–19} peroxyntite ($\text{O}_2\text{NOOH}/\text{O}_2\text{NOO}^-$, $\text{p}K_a = 5.9 \pm 0.1$) is formed to some extent.^{31,32} Peroxyntic acid (O_2NOOH) is relatively stable in acidic solution, whereas O_2NOO^- decomposes with a rate similar to that of ONOOH into nitrite and dioxygen. In addition, O_2NOO^- has an absorption similar to that of ONOO^- .^{4,31,32} Therefore, the formation of peroxyntite interferes with the measurements at $\text{pH} > 5$, and the formate/nitrite system is suitable only at $\text{pH} < 5$.

In the second system peroxyntite is formed via reactions 1 and 8–10, and this system can be used for measurements at all pH's.



The volume of activation for the decomposition of ONOOH was determined at pH 4.1 upon repetitive pulsing of both systems i and ii to be 10.7 ± 1.9 and $10.0 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$, respectively (Figure 1). These values are in excellent agreement with our earlier reported value of $9.6 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$.²⁵ Though pH 4.1 is ideal for the determination of the volume of activation

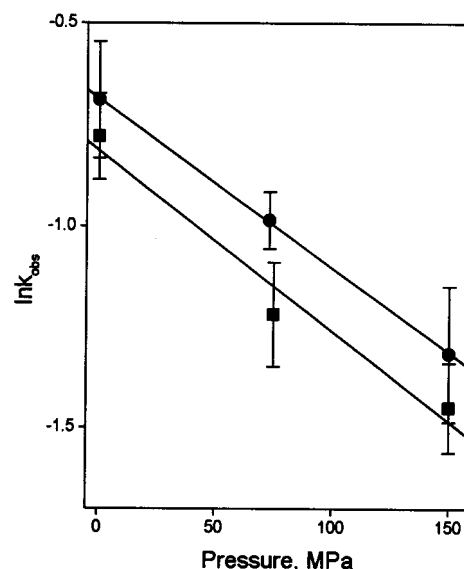


Figure 1. Pressure dependence of the decomposition rate constant of ONOOH at pH 4.1, which was generated in (■) aerated solutions containing 0.15 M formate and 3 mM nitrite at 18 °C and (●) He-saturated solutions containing 3 mM nitrate at 19 °C.

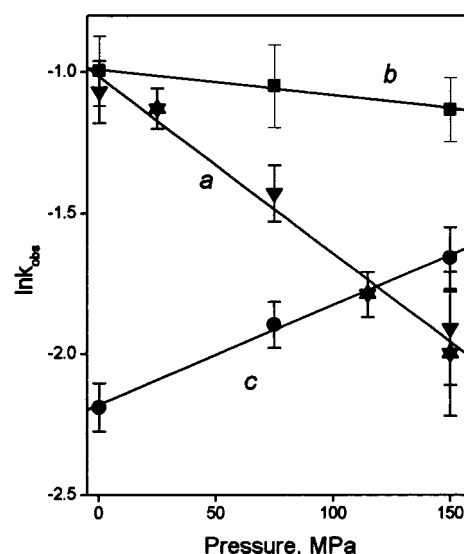


Figure 2. Pressure dependence on the rate of peroxyntite decomposition generated in He-saturated solutions containing 3 mM nitrate at 18 °C: (a) pH 6.2 and 4 mM phosphate buffer, where the pressure was increased from 0.1 to 150 MPa (▼) and then decreased back to ambient pressure (★); (b) (■) pH 6.2, 100 mM phosphate buffer; (c) (●) pH 7.2, 4 mM phosphate.

for the decomposition of ONOOH, since it is far away from the $\text{p}K_a(\text{ONOOH}) = 6.6$, it was decided to measure the effect of pressure also at pH 5.6 and 6.2, where a value of $1.7 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ had been reported.²

The effect of pressure on the decomposition rate constant of peroxyntite at $\text{pH} > 5$ was studied upon repetitive pulsing of system ii in the presence of 4 or 100 mM phosphate buffer. The activation volume in the presence of 4 mM phosphate buffer was found to be 10.5 ± 1.1 and $15.0 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ at pH 5.6 and 6.2 (Figure 2), respectively. However, in the presence of 100 mM phosphate buffer there was hardly any effect of pressure on the decomposition rate, i.e., $\Delta V^\ddagger = 1.0 \pm 0.5$ and $2.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ at pH 5.6 and 6.2 (Figure 2), respectively. The activation volume was also determined at pH 7.2 in the

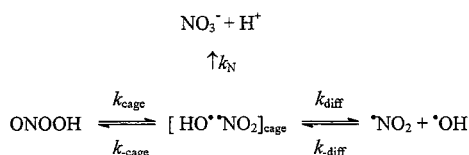
presence of 4 mM phosphate buffer to be $-8.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ (Figure 2).

Discussion

In general, an increase in pressure favors ionization of weak acids and bases; i.e., pressure affects the buffer equilibria and the pK_a value of ONOOH. The volume of activation for the dissociation of H_2PO_4^- is $\Delta V(K_b) = -26 \text{ cm}^3 \text{ mol}^{-1}$.³³ Thus, the pH of the solution will decrease with increasing pressure, and this will cause an increase in the rate of peroxynitrite decomposition, since ONOOH is the unstable form. Therefore, the effect of pressure on the decomposition rate of ONOOH should be studied in acidic solution, as far as possible away from $pK_a(\text{ONOOH}) = 6.6$, where small changes in the pH will have no effect on the decomposition rate of ONOOH. This restriction already excludes the use of phosphate buffer, since $pK_b(\text{H}_2\text{PO}_4^-) = 7.2$ ($I = 0$).³⁴ Since our measurements were done at pH 4.1 and in two different systems, we conclude that the decomposition of ONOOH is characterized by a significant positive volume of activation, $\Delta V^\ddagger = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$.

The direct isomerization of ONOOH to nitrate does not occur in a single step as it has been well established that many substrates are oxidized by ONOOH via intermediates that are formed during its decomposition.⁵ In addition, direct isomerization into nitrate is expected to exhibit a significantly negative ΔV^\ddagger as a result of charge creation ($\text{ONOOH} \rightarrow \text{NO}_3^- + \text{H}^+$).³⁰ Since the isomerization of ONOOH into nitrate is characterized by a significantly positive $\Delta V^\ddagger = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$, it must involve the formation of an intermediate that is accompanied by a volume increase. Bond breakage could account for the observed ΔV^\ddagger value only when it is not accompanied by charge creation.

SCHEME 1



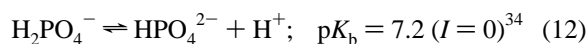
The detailed mechanism for the homolysis of ONOOH has been suggested previously (Scheme 1).^{12,14,19} Applying the steady-state approximation to the short-lived cage and assuming that the highly reactive and unselective $\cdot\text{OH}$ radical would react predominantly with nitrite, formate, the buffer, or impurities, i.e., $k_{\text{diff}} \approx 0$, one obtains eq 11.

$$k_o = k_{\text{cage}}(k_{\text{diff}} + k_N)/(k_{\text{diff}} + k_{\text{cage}} + k_N) \quad (11)$$

Since $k_N/k_{\text{diff}} \approx 2$ (ca. 30–40% oxidation yield)⁵ and $k_N/k_{\text{cage}} \approx 1$ (the combination reaction of $\cdot\text{NO}_2 + \cdot\text{OH}$ yields directly approximately equal amounts of ONOOH and $\text{NO}_3^- + \text{H}^+$)¹⁹ and since k_{diff} , k_{cage} , and k_N are diffusion-controlled rate constants that are not affected by pressure in water over the selected pressure range, we conclude that $\Delta V^\ddagger(k_o) = \Delta V^\ddagger(k_{\text{cage}}) = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. This value supports the formation of $\cdot\text{OH}$ and $\cdot\text{NO}_2$ in a solvent cage without any charge creation, since many reactions that involve bond breakage or homolysis have volumes of activation between 5 and $10 \text{ cm}^3 \text{ mol}^{-1}$.³³

An increase of ca. $5 \text{ cm}^3 \text{ mol}^{-1}$ in ΔV^\ddagger was observed when the pH was raised to 6.2, and a dramatic decrease to a significantly negative value, $\Delta V^\ddagger = -8.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$, was observed at pH 7.2, both in the presence of 4 mM phosphate buffer (Figure 2). These observations can be accounted for as

follows. Consider the equations



$$k_{\text{obs}} = k_o[\text{H}^+]/(K_a + [\text{H}^+]) \quad (15)$$

At pH 4.1, where $[\text{H}^+] \gg K_a$, one obtains from eq 15 that $k_{\text{obs}} = k_o$, and therefore, $\Delta V_{\text{exp}}^\ddagger = \Delta V^\ddagger(k_o) = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$.

At pH 6.2 (4 mM phosphate), k_{obs} is given by eq 15 and $\ln k_{\text{obs}} = \ln k_o - \ln(K_a/[\text{H}^+] + 1)$. Hence, $\Delta V_{\text{exp}}^\ddagger = \Delta V^\ddagger(k_o) + RT \partial \ln(K_a/[\text{H}^+] + 1)/\partial P = \Delta V^\ddagger(k_o) - (<\Delta V(K_a)) = 15.0 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$, and an upper limit of ca. $-5 \text{ cm}^3 \text{ mol}^{-1}$ can be set for $\Delta V(K_a)$.

At pH 7.2 (4 mM phosphate), where $[\text{H}^+] \approx K_b < K_a$, one obtains from eq 15 that $k_{\text{obs}} \approx k_o[\text{H}^+]/K_a \approx k_o K_b/K_a$, and hence, $\Delta V_{\text{exp}}^\ddagger = \Delta V^\ddagger(k_o) + \Delta V(K_b) - \Delta V(K_a) = -8.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$. Since $\Delta V(K_b) = -26 \text{ cm}^3 \text{ mol}^{-1}$ ³³ and $\Delta V^\ddagger(k_o) = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$, one calculates $\Delta V(K_a) = -7.2 \pm 2.1 \text{ cm}^3 \text{ mol}^{-1}$, which agrees well with the estimated value at pH 6.2. This value is quite reasonable, since it is of the same magnitude as those reported for the dissociation of two weak acids, viz., $\Delta V(K_a) = -6 \text{ cm}^3 \text{ mol}^{-1}$ for HCOOH ³⁰ and $\Delta V(K_a) = -7.6 \text{ cm}^3 \text{ mol}^{-1}$ for HN_3 .³⁵

Kissner et al.² used the high-pressure stopped-flow technique and determined in the presence of 100 mM phosphate buffer activation volumes of 1.8 ± 1.1 and $1.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ at pH 5.6 and 6.2, respectively. We repeated their experiments using the pulse radiolysis technique and found that the activation volumes at these pH's decreased from 10.5 ± 1.1 and $15.0 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ in 4 mM phosphate buffer to 1.0 ± 0.5 and $2.2 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ in 100 mM phosphate buffer, respectively, as shown in Figure 2 for pH 6.2. Note that when the pulse radiolysis procedure is used, relatively low concentrations of peroxynitrite are formed in situ, and only low concentrations of phosphate buffer are required. This is not the case with the stopped-flow procedure, where relatively high concentration of the buffer is required when peroxynitrite, which is stored in alkaline solutions, is mixed with the buffer. Kissner et al.² found that the apparent pK_a of ONOOH depends on the type of buffer used (phosphate, ammonia, and borate) and its concentration, and they ascribed this to general acid catalysis. However, this has not been proven, since, although ammonia and borate have the same pK_a values, borate was found to be a much more efficient catalyst. They also suggested that the mechanism involves the formation of an adduct between the peroxy moiety and the Lewis acid. However, it is difficult to envisage the formation of such adducts in the case of NH_4^+ and H_2PO_4^- , and therefore, the mechanism for the accelerated decay of peroxynitrite by borate may differ from that for ammonia and phosphate.

At ambient pressure, the decomposition rate constants of peroxynitrite at pH 4.1, 5.6, and 6.2 are not affected upon increasing the concentration of phosphate from 4 to 100 mM. However, increasing the pressure to 150 MPa in the presence of 100 mM phosphate, which causes at most a 5-fold increase in the rate constant, cancels the effect measured in the presence of 4 mM phosphate. We have no explanation for these observations, although they must be related to a catalytic effect of H_2PO_4^- on the decomposition of ONOOH that is accelerated by pressure. This uncertainty, however, has no effect on the conclusion reached in this study, since we determined ΔV^\ddagger at pH 4.1 (in two systems and in the absence and presence of 4

mM phosphate) as well as at pH 5.6 (4 mM phosphate) and found the same activation volume for the different experiments, $\Delta V^\ddagger = 10.3 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$. The latter value is in agreement with our earlier one, $9.6 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$, which was based on rate constants measured only at 0.1 and 150 MPa at pH 4.1.²² The activation volume of ca. $10 \text{ cm}^3 \text{ mol}^{-1}$ and the relatively high activation entropy ($A = 1.4 \times 10^{15}$ to $1.8 \times 10^{16} \text{ s}^{-1}$, $\Delta S^\ddagger = 7.4\text{--}13 \text{ eu}$)¹⁸⁻²² supports a homolytic bond cleavage mechanism, namely, homolysis of ONOOH into $\cdot\text{NO}_2$ and $\cdot\text{OH}$. The results of this study demonstrate the complications caused by high buffer concentrations and the selected pH in studying the effect of pressure on such decomposition reactions.

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