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Spontaneous Reactions and Reduction by Iodide of Peroxynitrite and Peroxynitrate: Mechanistic Insight from Activation Parameters

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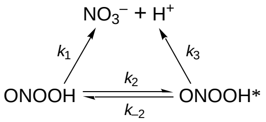
Thermal and pressure activation parameters are reported for the decomposition of peroxynitrate, isomerization of peroxynitrite, and their reduction by iodide in aqueous solutions. The spontaneous decomposition reactions are characterized by activation enthalpies of ca. 16 kcal/mol, activation entropies close to zero, and significantly positive activation volumes between 7 and 10 cm^3/mol. These parameters suggest that the rearrangement of both peroxo species, leading to intermediates of increased partial molar volume, must include partial bond cleavage. The iodide-induced reduction reactions are characterized by significantly smaller activation enthalpies, negative activation entropies between −19 and −23 cal/(mol·K), and negative activation volumes between −6 and −11 cm^3/mol. These parameters suggest that bond formation between the redox partners occurs before electron transfer and favors an inner-sphere mechanism. The results are discussed regarding mechanisms based on ambient kinetic data suggested in the literature.

Introduction

Peroxynitrite (ONOOH/ONOO$^-$) has a pK_a of 6.8 and is stable in alkaline solutions.[1] The acid form isomerizes to nitrate[2,3] with $k = 1.3$ s^{-1} at 25 °C.[1,4,5] Recently, Goldstein et al.[4] proposed that the decomposition of ONOOH involves a direct isomerization to nitrate and in parallel the formation of a yet unidentified intermediate, ONOOH*, which subsequently isomerizes to nitrate. The mechanism of the decomposition of ONOOH is described in Scheme 1,

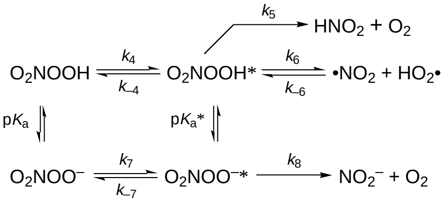
Scheme 1



where $k_1 = 1.0$ s^{-1}, $k_2 = 0.65$ s^{-1}, $k_{-2} \sim k_3$ and $10 \leq k_3 \leq 2 \times 10^5$ s^{-1} at 25 °C.[4] Arguments against the formation of hydroxyl radicals through the homolysis of ONOOH were given and discussed in detail elsewhere.[4] These arguments include thermodynamic calculations,[5] the effect of viscosity on the rate of the self-decomposition rate of peroxynitrite,[1,6] and the effect of scavengers on the oxidation yields of the indirect oxidation of various substrates by peroxynitrite.[4]

Peroxynitrate (O_2NOOH/O_2NOO^-) has a pK_a of 5.9,[7,8] and it is relatively stable in acid solutions ($\tau_{1/2} \sim 30$ min).[7−10] It has been suggested that peroxynitrate decomposes mainly through a unimolecular dissociation of the anion into nitrite and oxygen,[7−10] and that the decomposition of O_2NOOH takes place either through its dissociation into $HO_2^{\bullet}$ and $^{\bullet}NO_2$[9,10] or into HNO_2 and O_2.[7] The half-life of the anion is ca. 1 s.[7,8] We have shown, using the pulse radiolysis technique, that both suggestions do not agree with the kinetics and the yields of the indirect oxidation of ferrocyanide and NADH by peroxynitrate.[8] We have suggested that the decomposition of peroxynitrate takes place via the formation of yet unidentified intermediates (O_2NOOH^*, O_2NOO^{-*}) through the following mechanism:[8]

Scheme 2



The goal of this study was to measure the thermal and pressure activation parameters for the spontaneous decomposition of peroxynitrite and peroxynitrate in order to obtain further insight into our earlier suggested mechanisms, which were based on kinetics and oxidation yields in the presence of various substrates under ambient conditions.[8,11] The activation parameters were also determined for the direct oxidation of iodide by ONOOH and O_2NOOH,[8,11] to gain more information on the nature of the oxidation mechanism.

Experimental Section

Materials. All chemicals were of analytical grade and were used as received. The pH was adjusted with 1 mM acetate or phosphate buffers.

Methods. Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator with 5 MeV electrons pulses of 0.4−1.5 μs and 200 mA current. The dose per pulse was 10−29 Gy, respectively, and was determined with the 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.[12] In some of the systems, repetitive pulsing was used to increase

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the yield of the radicals. A 150 W Xe lamp produced the analyzing light, and appropriate filters were used to minimize photochemistry. Irradiations at ambient pressure were carried out in a 4-cm long Spectrosil cell using three light passes.

The high-pressure setup, consisting of a 1.5 cm pillbox optical cell, made of Suprasil, was placed near the thin stainless steel window[13] of the modified high-pressure cell so that the high-energy electrons would have a minimal path through the surrounding water-pressurizing medium. Repetitive pulsing was used for the pressure experiments, which were performed up to 1500 atm at room temperature (20 °C).

Formation of Peroxynitrite and Peroxynitrate. Peroxynitrite and peroxynitrate were produced by irradiation of air-saturated solutions containing formate and nitrite or nitrate, respectively. At pH ≥ 3, the following reactions take place:

$$H_2O \rightarrow e^-_{aq}\ (2.6),\ {}^{\bullet}OH\ (2.7),\ H^{\bullet}\ (0.6),\ H_2\ (0.45),\ H_2O_2\ (0.7),\ H_3O^+\ (2.6) \quad (9)$$

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

The solute concentrations were such that $^{\bullet}OH$ is scavenged by formate to produce superoxide via reactions 10−12

$$^{\bullet}OH + HCO_2^- \rightarrow H_2O + CO_2^{\bullet -} \qquad k_{10} = 3.5 \times 10^9\ M^{-1}\ s^{-1\,(14)} \quad (10)$$

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \qquad k_{11} = 3.5 \times 10^9\ M^{-1}\ s^{-1\,(14)} \quad (11)$$

$$H^+ + O_2^{\bullet -} \rightleftharpoons HO_2^{\bullet} \qquad pK_a = 4.8^{(15)} \quad (12)$$

and the solvated electrons are scavenged by O_2 and nitrite to produce peroxynitrite:

$$e_{aq}^- + O_2 \rightarrow O_2^{\bullet -} \qquad k_{13} = 2 \times 10^{10}\ M^{-1}\ s^{-1\,(14)} \quad (13)$$

$$e_{aq}^- + NO_2^- \rightarrow NO_2^{2-} \qquad k_{14} = 4.1 \times 10^9\ M^{-1}\ s^{-1\,(14)} \quad (14)$$

$$NO_2^{2-} + H_2O \rightarrow {}^{\bullet}NO + 2OH^- \qquad k_{15} = 4.3 \times 10^4\ M^{-1}\ s^{-1\,(14)} \quad (15)$$

$$O_2^{\bullet -} + {}^{\bullet}NO \rightarrow ONOO^- \qquad k_{16} = 4.3 \times 10^9\ M^{-1}\ s^{-1\,(16)} \quad (16)$$

$$^{\bullet}NO + HO_2^{\bullet} \rightarrow ONOOH \qquad k_{17} = 3.2 \times 10^9\ M^{-1}\ s^{-1\,(15)} \quad (17)$$

In the presence of high concentrations of nitrate, the solvated electrons are scavenged by nitrate

$$e_{aq}^- + NO_3^- \rightarrow NO_3^{2-} \qquad k_{18} = 9.7 \times 10^9\ M^{-1}\ s^{-1\,(14)} \quad (18)$$

$$NO_3^{2-} + H_2O \rightarrow {}^{\bullet}NO_2 + 2OH^- \qquad k_{19} = 5.5 \times 10^4\ s^{-1\,(14)} \quad (19)$$

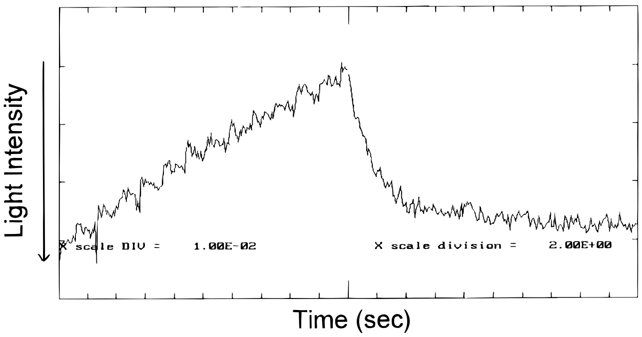


Figure 1. Kinetic trace obtained at 280 nm when 15 pulses of 1.5 μs are delivered into the solution at 1500 atm and ambient temperature. Air-saturated solution contained 0.15 M formate and 3 mM nitrite at pH 4.1 ($I_o = -1060$ mV, $\Delta V_1 = 57$ mV, $\Delta V_2 = 48$ mV).

TABLE 1: k_{obs} of the Decomposition of O_2NOO^- and of the Reactions of ONOOH and O_2NOOH with Iodide at Various Temperatures

temp, °C	k_{obs}, s^{-1} (self-decay of O_2NOO^-) (pH 8.3)	k_{obs}, s^{-1} (ONOOH + I^-) (pH 4.4)	k_{obs}, s^{-1} (OONOH + I^-) (pH 3.3)
0.8			0.34
1.1	0.12		
6.2	0.20		
6.6			0.46
11.9	0.33		
14.1			0.64
18.3		19.8	
20.5	0.75		
23.8			1.08
28.9	1.71		
30.5		27.6	
36.2			1.96
37.3	3.93		
47.9		47.8	

which reacts fast with superoxide to produce peroxynitrate:

$$^{\bullet}NO_2 + O_2^{\bullet -} \rightarrow O_2NOO^- \qquad k_{20} = 4.5 \times 10^9\ M^{-1}\ s^{-1\,(7)} \quad (20)$$

$$^{\bullet}NO_2 + HO_2^{\bullet} \rightarrow O_2NOOH \qquad k_{21} = 1.8 \times 10^9\ M^{-1}\ s^{-1\,(7)} \quad (21)$$

Results

The volume of activation of the spontaneous decomposition of ONOOH was determined upon repetitive pulsing of air-saturated solutions containing 0.15 M formate and 3 mM nitrite at pH 4.1. Under these conditions, ONOOH is formed via reactions 12−17, and its decomposition was followed at 280 nm. When the pressure was increased from 1 to 1500 atm, the observed first-order decomposition rate constant decreased from 0.74 ± 0.07 to 0.41 ± 0.08 s^{-1}, respectively, which corresponds to $\Delta V^* = 9.6 \pm 1.0$ cm^3/mol. A typical trace for 1500 atm is given in Figure 1. Thermal activation parameters for the spontaneous decomposition of ONOOH were reported to be $\Delta H^* = 171$ kcal/mol and $\Delta S^* = 32$ cal/(mol·K).[5]

When the same solutions were irradiated in the presence of 1 mM iodide, the formation of I_3^- was followed at 380 nm in the temperature range 1.2−47.9 °C. The kinetic results are summarized in Table 1. The observed first-order rate constant in the presence of 1.3 mM iodide increased with increasing pressure (Table 2). The resulting activation parameters are given in Table 3.

TABLE 2: k_{obs} (s^{-1}) as a Function of Pressure in the Absence and Presence of Iodide at 20 °C

P, atm	$ONOOH \rightarrow NO_3^- + H^+$ [a]	$ONOOH + 3I^- \rightarrow I_3^- + NO_2^- + OH^-$ [b]	$O_2NOO^- \rightarrow NO_2^- + O_2$ [c]	$O_2NOOH + 3I^- + H^+ \rightarrow I_3^- + NO_3^- + H_2O$ [d]
1	0.74 ± 0.07	28.7 ± 3.1	1.24 ± 0.08	0.97 ± 0.1
750				1.40 ± 0.13
1500	0.41 ± 0.08	42.0 ± 3.8	0.82 ± 0.06	2.00 ± 0.09

[a] pH 4.1. [b] pH 4.4 and 1.3 mM iodide. [c] pH 8.3. [d] pH 3.5 and 1.05 mM iodide.

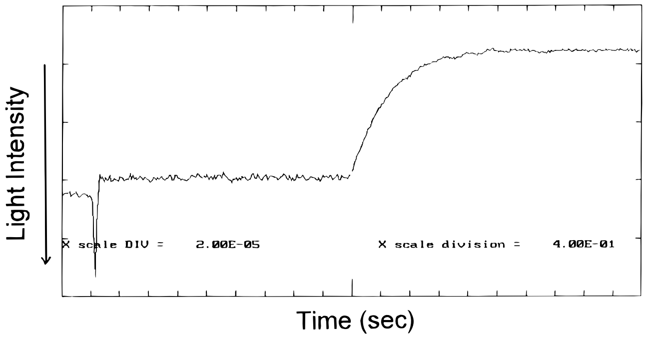


Figure 2. Kinetic trace obtained at 352 nm when air-saturated solution containing 0.1 M formate, 30 mM nitrate, and 1.05 mM iodide at pH 3.5 was pulse irradiated at 1500 atm and ambient temperature (I_o = −967 mV, ΔV_1 = 16 mV, ΔV_2 = 88 mV).

The activation parameters for the spontaneous decomposition of O_2NOO^- and for the reaction of O_2NOOH with 1.05 mM iodide were determined upon irradiation of air-saturated solutions containing 20−100 mM formate, 20−30 mM nitrate at pH 8.3 and 3.5, respectively. Under these conditions, peroxynitrite is formed via reactions 18−21. The spontaneous decomposition of O_2NOO^- was followed at 310 nm upon repetitive pulsing, and the formation of I_3^- was followed at 352 nm by delivering one pulse into the solution. A typical kinetic trace at 1500 atm is given in Figure 2. The results are summarized in Tables 1−3.

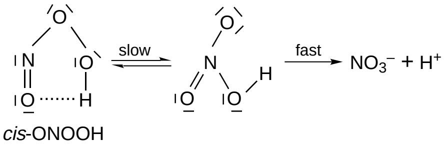
Discussion

The ONOOH System. The unusual stability of peroxynitrite in alkaline solutions is due to folding into the *cis* conformation, which cannot directly isomerize to nitrate. When protonated, peroxynitrite isomerizes rapidly to nitrate. It was suggested previously that peroxynitrite iomerizes to the *trans* conformation, which is less stable by 3−5 kcal/mol,[17,18] and is also capable of rearranging to nitrate and also forms an excited state, which can react like the hydroxyl radical and nitrogen dioxide.[19] However, most of the experimental results for the indirect oxidation of various substrates do suggest a direct isomerization of *cis*-ONOOH (~60%) and in parallel its conversion into a highly reactive intermediate (~40%) (Scheme 1*)*.[4]

According to our suggested mechanism (Scheme 1), the observed rate constant for the decomposition of ONOOH is given by eq 22:

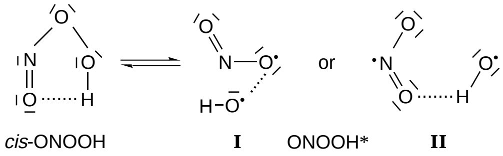
$$k_{obs} = k_1 + \frac{k_2 k_3}{k_{-2} + k_3} \sim k_1 + k_2/2 \tag{22}$$

Thus, both reactions 1 and 2 contribute to k_{obs}, and therefore they also contribute to the observed volume of activation. The direct isomerization of *cis*-ONOOH to nitrate (reaction 1) is clearly complex and requires more than one step. If this reaction would occur in one step, a significantly negative ΔV^* is expected due to charge creation ($ONOOH \rightarrow NO_3^- + H^+$).[20,21] Since we measured a significantly positive ΔV^* of 9.6 cm^3/mol, it is suggested that the direct isomerization of *cis*-ONOOH takes place through the formation of an intermediate, which is accompanied by a volume increase. This intermediate decomposes rapidly to nitrate, and the whole process is described by eq 23:



(23)

In addition, the conversion of *cis*-ONOOH to ONOOH* may also contribute to the positive value of ΔV^* if this process involves a volume increase due to bond lengthening or partial desolvation.



(24)

The transient complex **II** is that proposed recently by Houk et al.[18] in the gas phase and could be formed while the hydrogen bond existing in the *cis* conformation is retained. It is, however, difficult to envisage that either **I** or **II** will be long-lived enough to enable reactions with a variety of reducing agents.

Bond breakage could in principle account for the observed ΔV^* value, but not when it is accompanied by charge creation since this is expected to lead to a drastic increase in electrostriction and an overall volume collapse. The thermal activation parameters indicate a relatively high activation enthalpy that would favor a bond breakage process. However, the almost zero activation entropy indicates that no substantial increase in electrostriction can accompany this process. It follows that both the thermal and pressure parameters are in line with a mechanism that involves rearrangement and partial bond cleavage without a significant charge creation component.

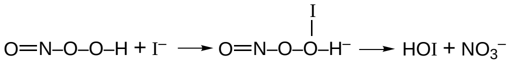
We cannot exclude the possibility of the homolysis of ONOOH on the basis of the activation volume data ($ONOOH^* \equiv {}^{\bullet}OH + {}^{\bullet}NO_2$) as it is difficult to distinguish between partial bond cleavage and homolysis in terms of volume change. Many reactions that involve bond breakage or homolysis have volumes of activation between 5 and 10 cm^3/mol.[22]

TABLE 3: Summary of Rate Constants and Activation Parameters Calculated for the Various Processes

	k (20 °C)	ΔH^*, kcal/mol	ΔS^*, cal/(mol·K)	ΔV^*, cm^3/mol
$ONOOH \rightarrow NO_3^- + H^+$	0.74 ± 0.07 s^{-1}	17 ± 1.0(5)	3 ± 2(5)	9.6 ± 1.0
$ONOOH + 3I^- \rightarrow I_3^- + NO_2^- + OH^-$	(2.3 ± 0.1) × 10^4 M^{-1} s^{-1}(11)	4.6 ± 0.4	−23 ± 1[a]	−6.2 ± 0.7
$O_2NOO^- \rightarrow NO_2^- + O_2$	1.24 ± 0.08 s^{-1}	15.6 ± 0.3	−6 ± 1	6.7 ± 0.7
$O_2NOOH + 3I^- + H^+ \rightarrow I_3^- + NO_3^- + H_2O$	840 ± 50 M^{-1} s^{-1}(8)	7.7 ± 0.3	−19 ± 1[a]	−11 ± 1.0

[a] Calculated on the basis of a second-order rate constant for this process.

In the presence of iodide, $\Delta V^* = -6.2$ cm^3/mol, which indicates that this process involves bond association. Therefore, our earlier suggested mechanism,[11] where *cis*-ONOOH oxidizes iodide directly through one- or two-electron transfer mechanisms, is probably wrong, and the following possible mechanisms are suggested for this process:



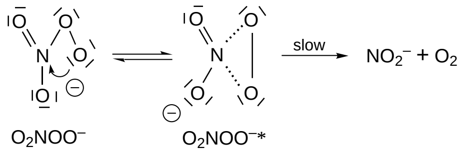
$$\mathrm{O{=}N{-}O{-}O{-}H + I^- \longrightarrow O{=}N{-}O{-}\overset{I}{\overset{|}{O}}{-}H^- \longrightarrow HOI + NO_3^-} \qquad (25)$$

$$\mathrm{HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O} \qquad K = 5 \times 10^{-13}\ \mathrm{M}^{2\,(23)} \qquad (26)$$

$$\mathrm{I_2 + I^- \rightleftharpoons I_3^-} \qquad K = 710\ \mathrm{M}^{-1\,(23)} \qquad (27)$$

The significantly negative volume of activation is accompanied by an entropy of activation that is also substantially negative and is in line with a bond formation process. The high rate constant exhibits a low activation enthalpy, which demonstrates the low barrier associated with the bond formation process in the inner-sphere electron-transfer process.

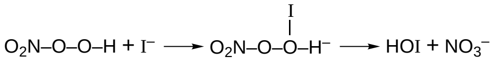
The Peroxynitrate System. Previously, we have suggested that the decomposition of O_2NOO^- to nitrite and oxygen takes place through O_2NOO^{-*} as a reactive intermediate (Scheme 2).[8] The lower pK_a of peroxynitrate as compared to peroxynitrite must be related to the higher oxidation state of N in peroxynitrate. In such a case, the negative charge on the peroxide arm interacts with the positive charge on the nitrogen-forming intermediate with a three-membered ring. This interaction weakens the N−O bond so that the formation of this intermediate leads to bond cleavage and to the formation of NO_2^- and O_2. This bond cleavage involves the reduction of N from +5 to +3 and the oxidation of O_2^{2-} to O_2, which will cause some intrinsic volume change, and could account for the less positive volume of activation as compared to that found for peroxynitrite.



(28)

The slightly smaller value of ΔV^* as compared to that for peroxynitrite is also reflected in the more negative value of ΔS^*. The latter value, however, is still close to zero and does not reflect any significant charge creation in the transition state. The activation enthalpy is very close to that found for peroxynitrite and reflects the importance of bond rearrangement and bond cleavage.

The negative activation volume in the presence of iodide, $\Delta V^* = -11$ cm^3/mol, is in favor of a bond formation process. Therefore, we suggest that the oxidation of iodide by peroxynitrate takes place through the formation of a transient complex:



$$\mathrm{O_2N{-}O{-}O{-}H + I^- \longrightarrow O_2N{-}O{-}\overset{I}{\overset{|}{O}}{-}H^- \longrightarrow HOI + NO_3^-} \qquad (29)$$

Since N is in the +3 oxidation state in peroxynitrite and in the +5 oxidation state in peroxynitrate, the peroxo group will be more positive in the case of peroxynitrate and will strengthen bond formation with I^-; thus, a more negative volume of activation will result (Table 3). Another argument would be that the partial volume of nitrite (26.2 cm^3/mol)[24] is smaller than that of nitrate (29.0 cm^3/mol),[24] so that there can be a more effective overlap of the van der Waals radii in the latter case. The negative value of ΔV^* is again accompanied by a significantly negative entropy of activation, which reflects the importance of bond formation during the electron-transfer process. The electron-transfer process itself does not involve any charge creation that could via an increase in electrostriction cause a volume collapse.[25,26] The activation enthalpy is slightly larger than that reported for the reduction of peroxynitrite and results in a decrease in the second-order rate constant.

Conclusions

The thermal and pressure activation parameters reported in this study (Table 3) contribute toward a further clarification of the intimate mechanism of the spontaneous decomposition and iodide-induced reduction reactions of peroxynitrite and peroxynitrate. The spontaneous decomposition must involve rate-determining rearrangement and partial bond cleavage that can cause an overall increase in volume in the transition state, before product formation that will involve significant charge creation in the case of peroxynitrite decomposition. The more positive ΔV^* value in this case clearly demonstrates that charge creation cannot be involved in the rate-determining step, since the spontaneous dimerization of peroxynitrate is not accompanied by charge creation and exhibits an even less positive volume of activation. The thermal activation parameters agree with this conclusion.

According to the reported activation parameters, the iodide-induced reduction of peroxynitrite and peroxynitrate must involve significant bond formation and proceed according to an inner-sphere electron-transfer mechanism. These reactions do not involve any net change in electrostriction and are not expected to exhibit major changes in electrostriction. Thus, the significantly negative ΔV^* and ΔS^* values strongly suggest direct bond formation between the redox partners and support the operation of an inner-sphere mechanism.

The results of this study have again demonstrated how an analysis of thermal and pressure activation parameters can assist the elucidation of intimate reaction mechanisms.

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