

The Yield of Hydroxyl Radical from the Decomposition of Peroxynitrous Acid

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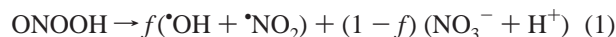
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Mechanistic predictions, based upon the assumption that free $\bullet\text{OH}$ and $\bullet\text{NO}_2$ radicals are formed as intermediates during the ONOOH decay, were tested using inorganic radical scavengers. Both the rates and the yields of $\text{Fe}(\text{CN})_6^{4-}$ and IrCl_6^{3-} oxidation by ONOOH were independent of their concentrations in submillimolar range. A $55 \pm 7\%$ $\text{Fe}(\text{CN})_6^{3-}$ yield and $25 \pm 3\%$ IrCl_6^{2-} were measured at pH 5.7, 22 °C. A yields ratio close to 2 is expected, because, of the two radicals produced, only $\bullet\text{OH}$ can rapidly oxidize IrCl_6^{3-} . The competition kinetic studies demonstrated that the relative reactivities of the oxidizing intermediate generated by ONOOH toward IrCl_6^{3-} and NO_2^- were identical with the reactivities of the “authentic” $\bullet\text{OH}$ radical generated by pulse radiolysis. It is concluded that ONOOH decomposes via its peroxy bond homolysis producing a pair of discrete $\bullet\text{OH}$ and $\bullet\text{NO}_2$ radicals with $28 \pm 4\%$ yield. A bimolecular reaction between ONOOH and $\text{Fe}(\text{CN})_6^{4-}$ with the rate constant $(8.2 \pm 0.4) \text{ M}^{-1} \text{ s}^{-1}$ significantly increases both oxidation yield and rate at high $[\text{Fe}(\text{CN})_6^{4-}]$.

Introduction

The reactivities of peroxynitrite (ONOO^-) and its conjugate acid (ONOOH) have been extensively investigated in recent years because of their potential roles in cellular defense against infection, pathophysiology, and environmental and radioactive waste chemistries.¹ The anion is fairly stable, but the peroxynitrous acid decomposes within seconds, quantitatively producing nitrate. Decomposition of ONOOH proceeds through rate-limiting formation of strongly oxidizing intermediates whose yields are always lower than limits based upon stoichiometric consumption of ONOOH.^{2–15} This indicates the existence of more than one route from ONOOH to NO_3^- .

In an early paper, Halfpenny and Robinson² explained the reactivity of ONOOH by its homolytic dissociation producing a pair of $\bullet\text{OH}$ and $\bullet\text{NO}_2$ radicals



where $0 \leq f \leq 1$ is the fraction of ONOOH which underwent homolysis. Later, using competition between H_2O_2 and NO_2^- for the $\bullet\text{OH}$ radical, Mahoney³ provided the first evidence for this pathway. Since then, numerous studies that used radical scavengers, including spin traps, produced both results that were consistent with participation of $\bullet\text{OH}$ radical^{4,14–18} and results that were inconsistent with it.^{11,19–22}

An estimate²³ and a measurement²⁴ of the free energy of ONOOH formation by Merenyi and Lind showed that a significant fraction ($f \geq 0.1$) of ONOOH should decompose to radicals. However, Koppenol et al.^{25,26} obtained lower estimates for this free energy and concluded that the ONOOH homolysis is unlikely. A model invoking formation of some activated form of ONOOH with OH radical-like reactivity was introduced as an alternative to reaction 1.^{8–11,25,27–29}

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Not only the nature but also the yield of the reactive intermediates is in dispute; the reported values range from less than 1 to about 40%.^{3–6,10–16} Many of these measurements are difficult to interpret unambiguously because they are based on the end products analyses from organic radical scavengers, when secondary reactions, particularly with oxygen, of the organic radicals and other intermediates derived from them are often ill-defined. Compounding the problem is the presence of fairly readily oxidizable NO_2^- and ONOO^- in these systems; many scavengers that were employed are rapidly oxidized by both $\cdot\text{OH}$ and $\cdot\text{NO}_2$.

Recent examination of oxygen evolution from decomposing peroxyxynitrite revealed a peculiar pattern that could only be explained by invoking $\cdot\text{OH}$ generation.¹⁵ The objective of the present study was to investigate the existence and to determine the yield of a homolytic decomposition pathway for ONOOH using well-defined, purely inorganic systems. Our approach was to study oxidation of a one-electron reductant that: (i) rapidly reacts only with $\cdot\text{OH}$, but not with $\cdot\text{NO}_2$ and (ii) forms an easily detectable nonradical product that is stable toward reduction by NO_2^- and ONOO^- . These requirements are, obviously, conflicting. Any species with the redox potential above $E(\cdot\text{NO}_2/\text{NO}_2^-) = 1.04 \text{ V}^{30}$ is expected to oxidize NO_2^- , and a species with the potential below this value should be oxidizable by $\cdot\text{NO}_2$. Consequently, we have taken some pain to identify this reductant. Hexachloroiridate(III), IrCl_6^{3-} , has been selected because its undesired reactions are sufficiently retarded kinetically. An unselective radical scavenger, $\text{Fe}(\text{CN})_6^{4-}$, was also used for comparison. In this study we use competition kinetics to show that the strongly oxidizing intermediate derived from ONOOH has reactivity which is identical to that of radiolytically generated $\cdot\text{OH}$ radical. The yield of 0.28 ± 0.04 for the radicals in reaction 1 was measured.

Experimental Section

Materials. Solutions of peroxyxynitrite were prepared from NaNO_2 (taken in 10% stoichiometric excess) and H_2O_2 acidified by HClO_4 in a tandem quench-flow mixing apparatus³¹ and stored at -70°C . The product solution typically contained 130–160 mM peroxyxynitrite, as determined spectrophotometrically ($\epsilon_{302} = 1670 \text{ M}^{-1} \text{ cm}^{-1}$),³² 40–50 mM residual nitrite, 0.1 M NaOH, and 0.3 M NaClO_4 . $\text{Na}_3\text{IrCl}_6 \cdot \text{H}_2\text{O}$ was synthesized by reducing $\text{Na}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ (Strem) with the excess of NaNO_2 in hot ethanol.³³ The precipitate was washed with ethanol 10 times and vacuum-dried. The UV-vis spectrum of the product was identical to previously reported spectra.³³ Ion chromatography (Dionex 2010i chromatograph, HPIC AS-3 column, conductivity detector with ion suppression; eluent, 2.8 mM NaHCO_3 and 2.2 mM Na_2CO_3) revealed the presence of $\sim 0.5 \text{ mol } \%$ residual nitrite. The purity of the iridium complex was further tested by oxidizing it with an excess of $\text{Ce}(\text{IV})$ in 0.1 M H_2SO_4 ; the extinction coefficient of the resultant IrCl_6^{2-} coincided within 1% with the reported³³ value $\epsilon_{488} = 4050 \text{ M}^{-1} \text{ cm}^{-1}$. All experiments were performed within 15–20 min after dissolving $\text{Na}_3\text{IrCl}_6 \cdot \text{H}_2\text{O}$, because solutions aged for several hours showed noticeable decreases in oxidation yields when reacted with ONOOH . This was, most probably, due to partial hydrolysis of IrCl_6^{3-} , the first step of which occurs with $t_{1/2} \approx 19 \text{ h}$ at room temperature.³³ The solutions were prepared using Milli-Q purified water. Low-carbonate NaOH (Baker) was used to adjust the pHs of phosphate buffers. All other chemicals were of analytical-grade and used as received.

Measurements. Stopped-flow experiments were done using an Applied Photophysics DX17-MV instrument. Pulse radiolysis was performed with a 2 MeV electron beam from a Van de Graaff

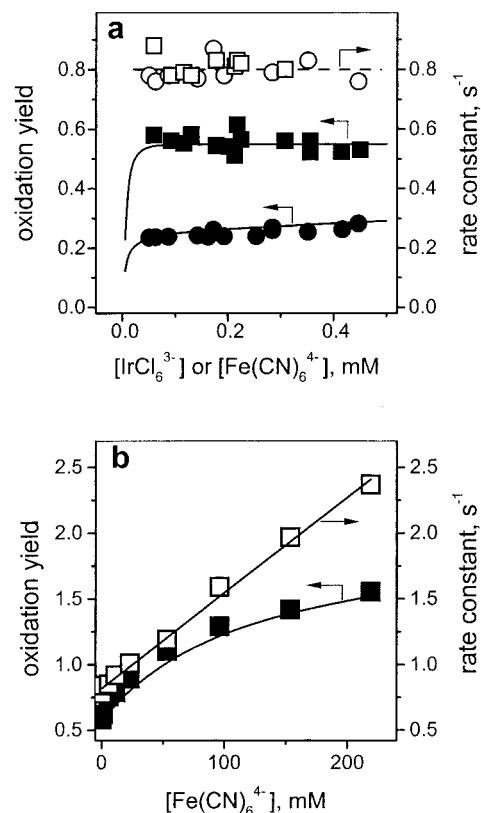
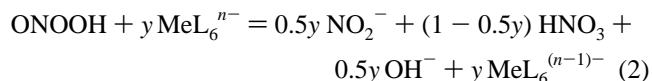


Figure 1. Concentration dependence of the yields (closed symbols) and rate constants (open symbols) for IrCl_6^{3-} (●, ○) and $\text{Fe}(\text{CN})_6^{4-}$ (■, □) oxidation by ONOOH . Conditions: $[\text{ONOOH}] + [\text{ONOO}^-] = (20\text{--}24) \mu\text{M}$. The yields were measured 10 s after the reaction initiation when product formation was more than 99% complete. Solid lines in panel A show numerical simulations for the corresponding mechanisms (see Discussion and Supporting Information); the dashed line corresponds to a rate constant of 0.8 s^{-1} for peroxyxynitrite decay without added complexes. The straight line in panel B gives a linear fit to the rate data; the curve shows yield dependence predicted by eq 12.

accelerator (50–800 ns pulse width) using optical detection (6.1 cm optical path). N_2O -saturated 10 mM KSCN was used for dosimetry: $G\epsilon_{472} = 4.84 \times 10^4 (\text{radicals}/100 \text{ eV})\text{M}^{-1} \text{ cm}^{-1}$. The oxidation of IrCl_6^{3-} was monitored at 488 nm, where the extinction coefficients for IrCl_6^{3-} and IrCl_6^{2-} are 4050 and $18 \text{ M}^{-1} \text{ cm}^{-1}$, respectively.³³ Formation of $\text{Fe}(\text{CN})_6^{3-}$ was monitored at 420 nm, $\epsilon_{420} = 1000 \text{ M}^{-1} \text{ cm}^{-1}$.³⁴ Decomposition of ONOOH was followed at 270 nm. All experiments were done in 62.5 mM phosphate, pH 5.70, 22°C .

Results

Oxidation of IrCl_6^{3-} and $\text{Fe}(\text{CN})_6^{4-}$ by ONOOH . These experiments were done at pH 5.7 where about 90% of peroxyxynitrite is protonated ($\text{p}K_a(\text{ONOOH}) = 6.6$).³⁵ When ONOOH decomposed in the presence of IrCl_6^{3-} or $\text{Fe}(\text{CN})_6^{4-}$, the complexes were oxidized, as was determined from the optical spectra of product solutions, i.e., the reaction stoichiometry



where MeL_6^{n-} stands for IrCl_6^{3-} or $\text{Fe}(\text{CN})_6^{4-}$, and $0 \leq y \leq 2$ is the oxidation yield. The yields were calculated from the stopped-flow transient absorbance data as the molar ratios of the product formed to the peroxyxynitrite introduced. The results are presented in Figure 1a together with the apparent first-order

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Table 1. Temperature Dependencies of the Rate Constants and the Yields of IrCl₆³⁻ and Fe(CN)₆⁴⁻ Oxidation by ONOOH^a

temp, °C	Fe(CN) ₆ ⁴⁻		IrCl ₆ ³⁻	
	Fe(CN) ₆ ³⁻ yield, %	k, s ⁻¹	IrCl ₆ ²⁻ yield, %	k, s ⁻¹
7	46 ± 3 ^b	0.11 ± 0.04	22 ± 4	0.12 ± 0.01
22	55 ± 7	0.81 ± 0.03	25 ± 3	0.79 ± 0.04
37	59 ± 3	5.0 ± 0.2	27 ± 3	4.74 ± 0.2

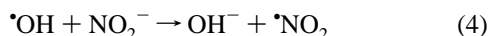
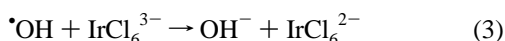
^a Conditions: [ONOOH] + [ONOO⁻] = 24 μM; [IrCl₆³⁻] and [Fe(CN)₆⁴⁻] were varied within the 0.2 – 1.0 mM range at each temperature. ^b The errors are reported as twice standard deviations for the multiple measurements.

rate constants for the product accumulation kinetics, which were always purely exponential. The data show that the rate constants and the oxidation yields were independent of the reductant concentration in the submillimolar range for both Fe(CN)₆⁴⁻ and IrCl₆³⁻; the average yields at the plateau regions in Figure 1a were (55 ± 7) and (25 ± 3)%, respectively, i.e., within the uncertainty, the yield ratio was 2.

The reaction rate constants were identical to that of peroxy-nitrite decomposition without added complexes and strongly temperature-dependent; 21.4 kcal/mol activation energy estimated from the data in Table 1 is within the range of 20.2 – 22.0 kcal/mol of the reported values.^{36–38} In contrast, the oxidation yields for both IrCl₆³⁻ and Fe(CN)₆⁴⁻ were only weakly dependent on temperature (Table 1). These facts were interpreted in terms of monomolecular, rate-limiting, activated formation from ONOOH of equimolar amounts of two different oxidizing species with about 28% yield; they both oxidized Fe(CN)₆⁴⁻, but only one of them oxidized IrCl₆³⁻.

In parallel with this monomolecular pathway, there exists a bimolecular pathway, as shown in Figure 1b by the linear concentration dependence of the apparent oxidation rate constant at high [Fe(CN)₆⁴⁻]. The oxidation yield also grew with [Fe(CN)₆⁴⁻] showing the onset of saturation. Notably, even at the high end of [Fe(CN)₆⁴⁻] in Figure 1a, contributions from this pathway to the yield and the rate are unmeasurably small.

Competition Kinetics. To identify the stronger oxidizing intermediate generated by ONOOH, we compared its relative reactivities toward IrCl₆³⁻ and NO₂⁻ with the reactivities of the •OH radical generated by pulse radiolysis in N₂O-saturated buffer. When both IrCl₆³⁻ and NO₂⁻ are present, they are oxidized in competing reactions:



If all •OH is scavenged in these reactions, the yield of IrCl₆²⁻, Y, is determined by the relative •OH reactivity

$$\frac{Y_0}{Y} - 1 = \frac{k_4}{k_3} \frac{[\text{NO}_2^-]}{[\text{IrCl}_6^{3-}]} \quad (5)$$

where Y₀ is the yield in the absence of added nitrite. As shown in Figure 2, a linear dependence upon the [NO₂⁻]/[IrCl₆³⁻] ratio

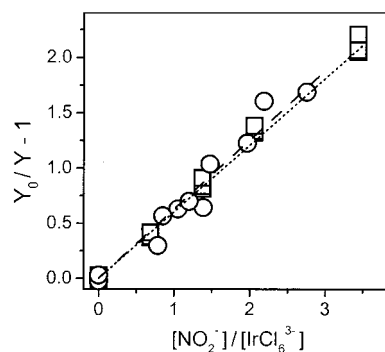


Figure 2. Dependence of the IrCl₆²⁻ yield on the [NO₂⁻]/[IrCl₆³⁻] ratio in reaction with radiolytically generated •OH (□ and dotted line) and in reaction with ONOOH (○ and dashed line). The lines give linear fits to the data points. In the pulse radiolysis experiment: [IrCl₆³⁻] = 0.21 mM, added [NO₂⁻] was varied from 0 to 0.74 mM, and about 0.9 μM of •OH was generated by a typical pulse. In the reaction with ONOOH (stopped-flow data): [ONOOH] + [ONOO⁻] = 19.4 μM, [IrCl₆³⁻] was varied from 0.15 to 0.38 mM, and added [NO₂⁻] was varied from 0 to 0.60 mM.

with a slope $k_4/k_3 = 0.61 \pm 0.01$ was, indeed, observed. From the IrCl₆³⁻ accumulation kinetics, we determined $k_3 = (1.2 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (data not shown; other workers^{39,40} reported 1.3×10^{10} and 8.9×10^9). The rate constant $k_4 = (7.3 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ calculated from our k_3 and the slope in Figure 2 falls within the range of known values,⁴¹ i.e., $(7-12) \times 10^9$.

The addition of NO₂⁻ also decreased the IrCl₆²⁻ yield in the reaction with ONOOH in a manner consistent with eq 5 (Figure 2). The slope of the dependence was 0.63 ± 0.05 , i.e., within the uncertainty, equal to the slope obtained from the pulse radiolysis experiment. Thus, this analysis identifies the stronger oxidizing intermediate derived from ONOOH during its decomposition as a free •OH radical; the weaker oxidant must, then, be the •NO₂ radical.

Direct comparison of the IrCl₆²⁻ yield with that of Fe(CN)₆³⁻ (reactions 3 and 9) in the pulse radiolysis experiments under identical conditions (0.21 mM of either IrCl₆³⁻ or Fe(CN)₆⁴⁻ in N₂O-saturated 62.5 mM phosphate, pH 5.7) gave the yield ratio $Y_0(\text{IrCl}_6^{2-})/Y_0(\text{Fe}(\text{CN})_6^{3-}) = 0.92 \pm 0.02$ (Supporting Information). The less-than-unity ratio could be due to (a) uncertainties of the extinction coefficients used for calculations or (b) a real effect demonstrating an additional pathway for reaction 3. It has been suggested,³⁹ that IrCl₆³⁻ oxidation by •OH proceeds, at least in part, via an adduct $\{(\text{Cl})_5\text{Ir}\cdots\text{Cl}\cdots\text{OH}\}^{3-}$. If so, the additional pathway may be the adduct decay to $\text{Cl}^- + (\text{Cl})_5\text{Ir}(\text{OH})^{2-}$. Whatever the case, the interpretation of the competition experiments (Figure 2) is not affected, because the decrease in yield should be the same, regardless of the •OH origin. However, the absolute yields of IrCl₆²⁻ in Figure 1a should be less than half of the Fe(CN)₆³⁻ yield by a factor of 0.92, a 25% yield is expected, which is exactly as observed. A corresponding correction was also applied to the simulation of the lower curve in Figure 1a (Discussion and Supporting Information).

Reactions of IrCl₆^{3-/2-} with •NO₂, NO₂⁻, and ONOO⁻. These reactions were briefly examined to determine whether they could be a source of complications in the experiments described above. No reactions of IrCl₆³⁻ with NO₂⁻ or ONOO⁻

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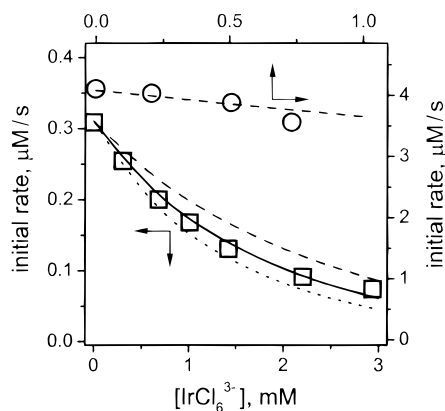
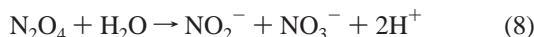
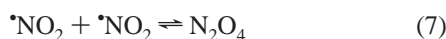


Figure 3. Dependence of the initial rate of IrCl_6^{2-} reduction by NO_2^- upon added IrCl_6^{3-} . Conditions: lower data set (\square) – $[\text{Na}_2\text{IrCl}_6] = 50 \mu\text{M}$, $[\text{NaNO}_2] = 0.5 \text{ mM}$; upper data set (\circ) – $[\text{Na}_2\text{IrCl}_6] = 6 \mu\text{M}$, $[\text{NaNO}_2] = 47.5 \text{ mM}$. The curves were numerically simulated for $k_{-6} = 3 \times 10^3$ (dashed line), 4×10^3 (solid line), and $5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (dotted line). (See Supporting Information for simulation details.)

were detected. The oxidation of nitrite by IrCl_6^{2-} has been reported:^{42,43}



Although the equilibrium constant $K_6 = 3.15 \times 10^{-3}$ derived from redox potentials ($E(\text{IrCl}_6^{2-}/\text{IrCl}_6^{3-}) = 0.892 \text{ V}^{44}$ and $E(\bullet\text{NO}_2/\text{NO}_2^-) = 1.04 \text{ V}^{30}$) is small, the oxidation goes to completion owing to hydrolysis of the $\bullet\text{NO}_2$ radical, that is,



for which $k_7 = 4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-7} = 6.9 \times 10^3 \text{ s}^{-1}$, and $k_8 = 1 \times 10^3 \text{ s}^{-1}$ have been measured.⁴⁵ We determined the value of $k_6 = (13.1 \pm 0.4) \text{ M}^{-1} \text{ s}^{-1}$ at $22 \text{ }^\circ\text{C}$ and $I \approx 0.075 \text{ M}$ from the kinetics of IrCl_6^{2-} decay⁴⁶ at different concentrations of NO_2^- added in excess (Supporting Information). Because k_6 is small, reactions 6–8 could not interfere with the IrCl_6^{2-} yield measurements presented in Figures 1 and 2 for solutions with less than 0.8 mM NO_2^- content. IrCl_6^{2-} that was produced persisted for minutes, i.e., much longer than ONOOH decay time $t_{1/2} \approx 1 \text{ s}$.

To obtain an estimate for the rate of the reverse reaction 6, we examined the kinetics of IrCl_6^{2-} reduction by NO_2^- with large amounts of added IrCl_6^{3-} . As expected, a deceleration due to IrCl_6^{3-} reoxidation by $\bullet\text{NO}_2$ was observed (Figure 3, lower data set). With known k_6 , k_7 , k_{-7} , and k_8 , these data were modeled using k_{-6} as the only adjustable parameter; the value $k_{-6} = 4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was derived (see Supporting Information for details). From our k_6 and k_{-6} we obtained $K_6 = 3.28 \times 10^{-3}$, which is within 5% of the thermodynamic estimate. Because the $\bullet\text{NO}_2$ decay is second-order in the radical, the contribution of reverse reaction 6 to reoxidation of the iridium

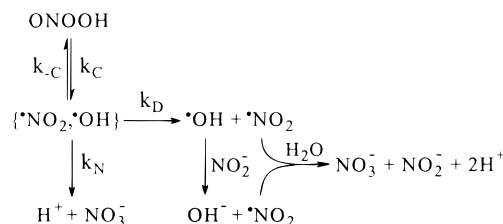
complex depends on the steady-state radical concentration, which, in turn, is controlled by the rate of its formation. For the upper data set in Figure 3, we adjusted conditions so that the rate of the $\bullet\text{NO}_2$ radical formation by reaction 6 ($\sim 4 \mu\text{M/s}$) approximated the rate of its generation from the ONOOH decomposition for the data in Figure 1a. Only small deceleration was observed at $[\text{IrCl}_6^{3-}]$ below 0.5 mM , indicating that most of $\bullet\text{NO}_2$ hydrolyzed. The value of k_{-6} is, thus, sufficiently low, so that the $\text{IrCl}_6^{3-} + \bullet\text{NO}_2$ reaction contributes little to the IrCl_6^{2-} yield in Figure 1a. More accurate, but less direct, analysis using numerical simulations confirmed this conclusion (Discussion and Supporting Information).

In alkaline solution, IrCl_6^{2-} oxidized ONOO^- with the rate constant $550 \text{ M}^{-1} \text{ s}^{-1}$, as measured from the dependence of IrCl_6^{2-} decay rate upon $[\text{ONOO}^-]$ (Supporting Information). Because in all experiments that are described above $[\text{ONOO}^-]$ was less than $5 \mu\text{M}$, this reaction would proceed on the time scale of minutes and can be ignored in our analysis.

Discussion

Mechanism. The simplest mechanism that accounts for the data presented above is shown in Scheme 1, where $\{\bullet\text{NO}_2, \bullet\text{OH}\}$

Scheme 1



represents a radical pair in a solvent cage. All reactions leading to the radicals must be reversible to accommodate the observation that a significant fraction of $\bullet\text{NO}_2$ and $\bullet\text{OH}$ radicals radiolytically generated in water recombine to produce ONOOH.^{47,48} However, any practical ONOOH solution is invariably contaminated with NO_2^- . Even at NO_2^- levels as low as $1 \mu\text{M}$, scavenging of $\bullet\text{OH}$ by NO_2^- (reaction 4) will produce the second $\bullet\text{NO}_2$ rapidly enough to make the ONOOH homolysis irreversible. Subsequent hydrolysis of the $\bullet\text{NO}_2$ radicals (reactions 7 and 8) produces NO_3^- and regenerates NO_2^- .

Ferrocyanide is rapidly oxidized by both radicals



with $k_9 = 1.1 \times 10^{10}$ and $k_{10} = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$,^{41,49} hence $55 \pm 7\%$ yield of $\text{Fe}(\text{CN})_6^{3-}$, which is twice the yield of ONOOH homolysis. The upper solid curve in Figure 1a shows agreement between the measured yields and their calculated values obtained by assigning $f = 0.28$ in reaction 1 and numerically integrating the rate laws given by reactions 1, 4, and 7–10 (see Supporting Information for simulation details).

In contrast, only $\bullet\text{OH}$ rapidly oxidizes IrCl_6^{3-} . As described in the results section, oxidation by $\bullet\text{NO}_2$ (reverse reaction 6) is slow and contributes little if the concentration of IrCl_6^{3-} is not too high. Correspondingly, only about 25% of ONOOH can be

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(46) The decay was always exponential, but dependent upon the solution ionic strength. The k_6 values of $26.9 \text{ M}^{-1} \text{ s}^{-1}$ at $I = 1.0 \text{ M}$ and 19.6 at $I = 0.1$ were also reported^{42,43} for $25 \text{ }^\circ\text{C}$.

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used for oxidation. The lower solid line in Figure 1a shows a simulation for the mechanism comprising reactions 1, 3, 4, and 6–8, for which all the rate constants are available (results section). Again, $f = 0.28$ was assumed; a correction for 92% yield of IrCl_6^{2-} in reaction 3 was applied (Supporting Information). A close correspondence between the data and the simulation is obvious; even the slight yield increase with $[\text{IrCl}_6^{3-}]$ could be reproduced.

The competition kinetics studies described here identify the species that oxidizes IrCl_6^{3-} as the •OH radical, thus providing strong support for Scheme 1. All reactions involving the {•NO₂, •OH} cage decay are not expected to be significantly activated; consequently, the observed radical yields $f = k_D/(k_D + k_N)$ are nearly temperature-independent (Table 1). In contrast, the rate constant for radical generation $fk_1 = f[(k_D + k_N)k_C/(k_{-C} + k_D + k_N)]$ is controlled by the peroxy bond breaking (k_C) and is, therefore, strongly activated (Table 1). About 1:1 partitioning between ONOOH and HNO₃ was recently measured for the •NO₂ + •OH recombination,⁴⁸ i.e., $k_{-C} \approx k_N$. Accepting that and using $f = 0.28$ and $k_1 = 0.9 \text{ s}^{-1}$ determined in this work,⁵⁰ we estimate $k_{-C}/k_D \approx k_N/k_D = 2.6$ and $k_C \approx 1.6 \text{ s}^{-1}$.

The results for a high $[\text{Fe}(\text{CN})_6^{4-}]$ in Figure 1b can be explained by a direct reaction



followed by rapid oxidation of the second $\text{Fe}(\text{CN})_6^{4-}$ via reaction 10. The rate constant $k_{11} = (8.2 \pm 0.4) \text{ M}^{-1} \text{ s}^{-1}$ was obtained from the straight line in Figure 1b.⁵⁰ Reactions 1 and 9–11 predict the oxidation yield concentration dependence that saturates at 2

$$\text{Yield} = \frac{2(fk_1 + k_{11}[\text{Fe}(\text{CN})_6^{4-}])}{k_1 + k_{11}[\text{Fe}(\text{CN})_6^{4-}]} \quad (12)$$

Because of the solubility of $\text{Fe}(\text{CN})_6^{4-}$, we could not reach the plateau. However, a curve in Figure 1b, drawn using this equation, satisfactorily describes the yield data.

Previous Oxidation Yield Studies. The reported yields vary widely. This is not surprising, considering that in many cases organic radical scavengers were used in neutral, or even alkaline, media where ONOOH and ONOO⁻ coexist and the mechanism of decomposition is much more complex than that depicted in Scheme 1; a number of both radical and nonradical intermediates are generated.¹⁵ Contamination by adventitious CO₂ can also interfere.³⁵ Clearly, acidic pHs are much more appropriate for determining the nature and the yields of the transients derived from ONOOH.

Although perhaps helpful for detection of the •OH presence, most organic scavengers are by no virtue suitable for the quantitative assays. This is well-illustrated by several studies

that use dimethyl sulfoxide for the oxidation assay. A yield of 24% for the •OH radical was estimated⁴ from formaldehyde production in air-saturated solution at pH 6. Pryor et al.⁷ measured only 8.2% formaldehyde yield in the same system at pH 7. Ingold et al.¹² detected no formaldehyde in an oxygen-free solution; instead, Me₂SO₂, MeSO₂H, MeSO₃H, and MeOH were found. Two techniques used to quantify the •OH yield gave 8 and 13%. The reaction conditions employed, large peroxy-nitrite concentration and high pH, are most favorable for involvement of ONOO⁻ in the oxidation.¹⁵ Yet more products from the peroxy-nitrite–DMSO reaction, namely MeONO, MeONO₂, and CH₄, were reported.⁵² The nature and multiplicity of the products clearly implicate secondary oxidations; the reactions responsible have not been identified.

Similarly discordant results were obtained for another organic radical scavenger, 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate), ABTS. Only one product, •ABTS⁺ radical, was detected, and its yields of 63, 46, and 42% at pH 5–6 and 24% at pH 7 were reported.^{6,8,51,7} ABTS reacts with both •NO₂ and •OH; the latter reaction gives •ABTS⁺ with 58% efficiency.⁵³ Correcting for this we calculate the •OH yields of 40, 29, 27, and 15%. When $\text{Fe}(\text{CN})_6^{4-}$ was used as a reductant, values corresponding to •OH yield from 48 to 29% were reported,^{10,11} but interpreted originally as oxidation via a nonradical pathway.⁵⁴ However, the yields at the higher end of this range were obtained with $[\text{Fe}(\text{CN})_6^{4-}] = 5\text{--}50 \text{ mM}$, when, as Figure 1b shows, direct reaction 11 contributes appreciably. For $[\text{Fe}(\text{CN})_6^{4-}]$ less than 3 mM, the yields were close to a 28% yield reported here.⁵⁵

In most systems it was difficult, if at all possible, to distinguish an oxidation by •OH from an electron transfer to some activated form of ONOOH. In the present report, we demonstrate for the first time by direct comparison that the reactivity of an intermediate formed during ONOOH decomposition is quantitatively identical to that of radiolytically generated •OH radical.

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Supporting Information Available: Figures showing the dependence of the rate constant for IrCl_6^{2-} reduction upon $[\text{NO}_2^-]$; the dependence of the relative yields of IrCl_6^{3-} and $\text{Fe}(\text{CN})_6^{4-}$ oxidation upon $[\text{•OH}]$; and the dependence of the rate of IrCl_6^{2-} reduction upon $[\text{ONOO}^-]$ (3 pages). Table showing the details of the numerical analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(50) A correction factor $(1 + K_a/[\text{H}^+]) = 1.12$ for the incomplete peroxy-nitrite protonation at pH 5.7 was applied to the observed rate constant for peroxy-nitrite decay (Figure 1a) and to the line slope in Figure 1b, which gives $k_1 = 0.9 \text{ s}^{-1}$ and $k_{11} = 8.2 \text{ M}^{-1} \text{ s}^{-1}$. The values of $k_{11} = 5.1\text{--}5.3$ have been reported (refs 11 and 51); since no primary data have been given, the reason for discrepancy with our value is not clear.

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(55) When revising this paper we learned that Hodges and Ingold (*J. Am. Chem. Soc.*, submitted) arrived at 27–28% ONOOH homolysis yield using an entirely different experimental approach.