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Article

Nitrous Acid as a Source of NO and NO_2 in the Reaction with a Macrocyclic Superoxorhodium(III) Complex

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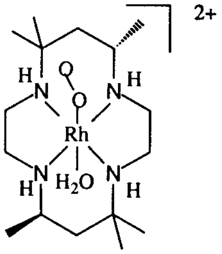
The title reaction takes place according to the stoichiometry $2L^2RhOO^{2+} + 3HNO_2 + H_2O \rightarrow 2L^2Rh(OH_2)^{3+} + 3NO_3^- + H^+$ (L^2 = *meso*-Me_6-[14]ane-N_4). The kinetics are second order in HNO_2 and independent of the concentration of L^2RhOO^{2+}, rate = $(k_1 + k_2[H^+])[HNO_2]^2$, where $k_1 = 10.9$ M^{-1} s^{-1} and $k_2 = 175$ M^{-2} s^{-1} at 25 °C and 0.10 M ionic strength. The reaction produces two observable intermediates, the nitrato ($L^2RhONO_2^{2+}$) and hydroperoxo (L^2RhOOH^{2+}) complexes. The product analysis and kinetics are indicative of the initial rate-controlling formation of NO and NO_2, both of which react rapidly with L^2RhOO^{2+} in subsequent steps. The reaction with NO produces mainly $L^2RhONO_2^{2+}$, which hydrolyzes to $L^2Rh(OH_2)^{3+}$ and NO_3^-. Another minor pathway generates the hydroperoxo complex, which was detected by its known reaction with Fe_{aq}^{2+}. The reaction of NO_2 with L^2RhOO^{2+} requires an additional equivalent of HNO_2 and produces $L^2Rh(OH_2)^{3+}$ and NO_3^- via a proposed peroxynitrato complex $L^2RhOONO_2^{2+}$. This work provides strong evidence for the long-debated reaction between HNO_2 and $H_2NO_2^+$ to generate N_2O_3.

Introduction

Recently we studied the reaction of NO with two superoxometal complexes, $Cr_{aq}OO^{2+}$ [1] and L^2RhOO^{2+} [2] (L^2 = *meso*-Me_6-[14]ane-N_4). The reasonable stability of these complexes toward metal−O_2 bond homolysis, combined with the substitutional inertness of both metals in the 3+ oxidation state, allowed us to detect several intermediates and gain a good mechanistic insight into both reactions. Our results, combined with the literature data on the reactions of NO with some oxyheme centers,[3−5] are summarized in Scheme 1, where ML represents a metal complex.



L^2RhOO^{2+}

According to this scheme, the initially formed peroxynitrito complex dissociates to NO_2 and the metal−oxo species LMO. The two fragments react with each other both inside and outside of the solvent cage to produce nitrate, either as a free ion or as a nitratometal complex $LMONO_2$, which has been observed for LM = Cr_{aq} and L^2Rh.

All but the purest samples of NO contain some level of HNO_2, which can itself serve as a source of NO. Despite that, the issue of HNO_2 interference in NO chemistry has been addressed in only a handful of cases.[6,7] Admittedly, the reactions of NO are usually much faster than those of HNO_2, but the interference from HNO_2 can still become severe, especially in experiments designed for product analysis, where HNO_2 and the substrate may be in contact for extended periods of time.

As a complement to our previous work on the NO/LMOO reactions,[1,2] we have now carried out a kinetic study of the reaction of L^2RhOO^{2+} with nitrous acid. In addition to the kinetics and mechanistic details of this reaction, we also report some novel findings pertaining to the mechanism of nitrosation reactions.

Experimental Section

Perchloric acid, sodium perchlorate, sodium hydroxide, zinc metal, mercury(II) chloride (all Fisher), sodium nitrite, 4-aminoben-

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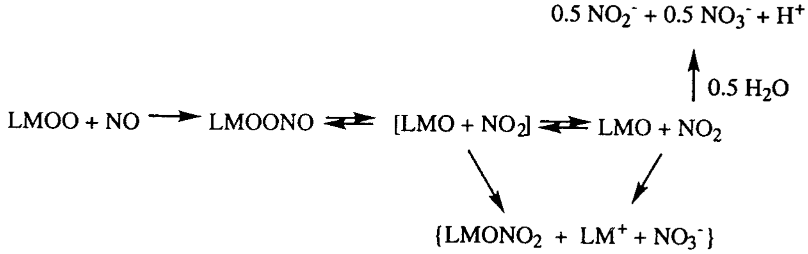
Scheme 1



zoic acid, 1-naphthol, and hexaammineruthenium(III) chloride (all Aldrich) were reagent grade or better and were used as received. Solutions of Fe_{aq}^{2+} and $Ru(NH_3)_6^{2+}$ were prepared by a Zn/Hg reduction of the respective 3+ ions under anaerobic conditions. Deionized water was further purified by passage through a Millipore Milli-Q water purification system.

Oxygen-saturated solutions of L^2RhOO^{2+} were prepared as described previously[8] and standardized spectrophotometrically, $\epsilon_{271}\{L^2RhOO^{2+}\} = 1.0 \times 10^4$ M^{-1} cm^{-1} (pH = 1−4) and $\epsilon_{265}\{L^2Rh(OH)OO^+\} = 1.1 \times 10^4$ M^{-1} cm^{-1} (pH = 11−12). For work under anaerobic conditions, the solutions were purged with argon. Because of the much faster homolysis of the superoxo complex in acidic solutions,[2] the purging time was 20 min at pH = 1−4 (40% decomposition) and 40 min at pH = 11−12 (10% decomposition). The decomposition products had no effect on the L^2RhOO^{2+}/HNO_2 reaction. This was confirmed by reacidifying a degassed alkaline solution, where the extent of the decay was only minimal, and carrying out the reaction with NO. Once the difference in the initial concentrations of L^2RhOO^{2+} was taken into account, the products and kinetics were identical to those obtained with a heavily decomposed solution that had been degassed at pH 1. L^2RhOOH^{2+} was prepared by the reduction of L^2RhOO^{2+} with a stoichiometric amount of $Ru(NH_3)_6^{2+}$ under argon. Under our experimental conditions, L^2RhOOH^{2+} showed less than 5% decomposition in 5 h.

NO stock solutions were prepared by saturating 20 mL of degassed water with the purified NO gas (Matheson), as described previously.[2] A typical stock solution contained 1.7 mM NO and 0.2 mM nitrite. Nitrite analyses were carried out as described previously.[2]

Kinetic runs were initiated by injecting a neutral solution of sodium nitrite into a spectrophotometric cell containing all the other components. Stock solutions of nitrous acid were not used to avoid potential problems with the decomposition of HNO_2 over longer periods of time.

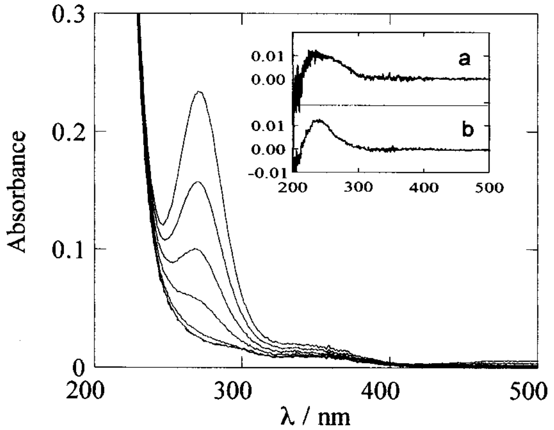


Figure 1. Spectral changes in the reaction between 30 μM L^2RhOO^{2+} and 105 μM HNO_2 at pH = 3.3 and 25 °C at times 0 (top), 3, 6, 9, 12, and 120 min after mixing. Inset shows (a) difference between the spectra at 12 and 120 min, and (b) difference between the spectra at 12 and 120 min for the reaction of 29 μM L^2RhOO^{2+} with an excess (50 μM) of NO at pH = 3.3. Path length: 1 cm.

Kinetic and spectral measurements utilized a Shimadzu 3101 PC spectrophotometer equipped with a thermostated cell compartment. All of the kinetic runs were conducted at 25 ± 0.5 °C and 0.10 M ionic strength, maintained with $HClO_4$ and $NaClO_4$. Nonlinear least-squares fittings of the data to the first- and second-order rate equations, eqs 1 and 2, were performed with the use of the program Kaleidagraph 3.0. The symbols Abs_0, Abs_t, and Abs_∞ represent the absorbance readings at times zero, t, and infinity, respectively, k is the observed rate constant, and $[A]_0$ is the initial concentration of the reactant A. Kinetic simulations were carried out with the use of Chemical Kinetics Simulator v1.01 software for PC.

$$Abs_t = Abs_\infty + (Abs_0 - Abs_\infty)\,e^{-kt} \qquad (1)$$

$$Abs_t = Abs_\infty + \frac{Abs_0 - Abs_\infty}{1 + [A]_0 kt} \qquad (2)$$

Results

General Observations. Upon mixing of a solution of L^2RhOO^{2+} (20−83 μM) with an excess of nitrous acid at acidic pH, the absorption maximum of L^2RhOO^{2+} at 271 nm disappeared in several minutes. The rate increased with $[HNO_2]$ and decreased with pH. No reaction was observed in alkaline solutions.

The reaction generated an intermediate which subsequently decayed, causing a decrease in absorbance at 240 nm. Figure 1 shows repetitive spectral scans for a solution initially containing 30 μM L^2RhOO^{2+} and 105 μM HNO_2 at pH = 3.3, and a difference spectrum for the intermediate decay. Also shown is the difference spectrum obtained in the reaction of the same concentration of L^2RhOO^{2+} with excess NO.

After completion of the reaction at pH 3.3, the solution was made alkaline by the addition of NaOH and the decompositon of the intermediate was monitored at pH 11.8 and an ionic strength of 0.016 M. The rate constant obtained, $k = 2.0 \times 10^{-3}$ s^{-1}, was identical to our reported[2] value for the hydrolysis of the nitrato complex $L^2RhONO_2^{2+}$, eq 3.

$$L^2RhONO_2^{2+} + H_2O \rightarrow L^2Rh(OH_2)^{3+} + NO_3^- \qquad (3)$$

Under the experimental conditions in Figure 1, it takes 12 min for all the L^2RhOO^{2+} to react. The decay of $L^2RhONO_2^{2+}$ according to eq 3 continues until completion at 120 min. From the absorbance change for the latter

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process, and using $\Delta\epsilon_{240} = 1.6 \times 10^3$ M^{-1} cm^{-1},[2] we calculated the amount of $L^2RhONO_2^{2+}$ that was present in solution 12 min after the mixing of the reagents. The amount found was 8 μM, i.e., 27% of the initial concentration of L^2RhOO^{2+}.

In addition to $L^2RhONO_2^{2+}$, the reaction generates another intermediate, which was identified as L^2RhOOH^{2+} by its reaction with Fe_{aq}^{2+}, as follows. After the disappearance of L^2RhOO^{2+} in the reaction with HNO_2, an excess of Fe_{aq}^{2+} (0.33−1.0 mM) was added and the absorbance monitored at 240 nm. The observed absorbance increase was biphasic, consistent with the oxidation of Fe_{aq}^{2+} in two parallel reactions. The faster step was first order in both $[Fe^{2+}]$ and the oxidant with $k = 23 \pm 4$ M^{-1} s^{-1}, in reasonable agreement with $k = 28 \pm 2$ M^{-1} s^{-1} determined earlier[2] for the $Fe_{aq}^{2+}/L^2RhOOH^{2+}$ reaction, eq 4. The kinetics of the slower step matched precisely those for the reaction of Fe_{aq}^{2+} with HNO_2.[2] Identical observations were made in the L^2RhOO^{2+}/NO reaction,[2] except that the yield of L^2RhOOH^{2+} in the present work, 6%, was smaller than the 10% found in the NO reaction. The yields are based on $\Delta\epsilon_{240} = 1.0 \times 10^4$ M^{-1} cm^{-1} for reaction 4.

$$2Fe_{aq}^{2+} + L^2RhOOH^{2+}\ (+3H^+) \rightarrow 2Fe_{aq}^{3+} + L^2Rh(OH_2)^{3+} + H_2O \qquad (4)$$

The overall stoichiometry of the L^2RhOO^{2+}/HNO_2 reaction was determined in two sets of experiments utilizing either HNO_2 or L^2RhOO^{2+} in excess and quantitating the unreacted amounts at the end of the reaction. The stoichiometric ratio varied somewhat with the initial concentrations. The average value was $[HNO_2]/[L^2RhOO^{2+}] = 1.55 \pm 0.15$, which agrees with a formal net reaction in eq 5.

$$2L^2RhOO^{2+} + 3HNO_2 + H_2O \rightarrow 2L^2Rh(OH_2)^{3+} + 3NO_3^- + H^+ \qquad (5)$$

The kinetics of disappearance of L^2RhOO^{2+} were monitored at its 271 nm maximum. Under conditions of excess L^2RhOO^{2+}, the reaction could be followed to completion, Figure 2. Excellent fits of such traces to the integrated rate law of eq 2 established unequivocally the second-order dependence on $[HNO_2]$. There was no dependence on $[L^2RhOO^{2+}]$, eq 6.

When an excess of HNO_2 was employed, a sudden break in the kinetic trace identified the moment when all the L^2RhOO^{2+} was consumed, Figure 2. Clearly, superoxorhodium served only as a scavenger for the reactive intermediates produced from HNO_2. Under these conditions, the kinetic determinations utilized initial rates from the first 2−3% of the reaction. The kinetics were again second order in $[HNO_2]$ and zero order in $[L^2RhOO^{2+}]$, eq 7.

$$-d[HNO_2]/dt = k_{obs}[HNO_2]^2 = 3k[HNO_2]^2 \qquad (6)$$

$$(rate)_i = -d[L^2RhOO^{2+}]/dt = 2k[HNO_2]^2 \qquad (7)$$

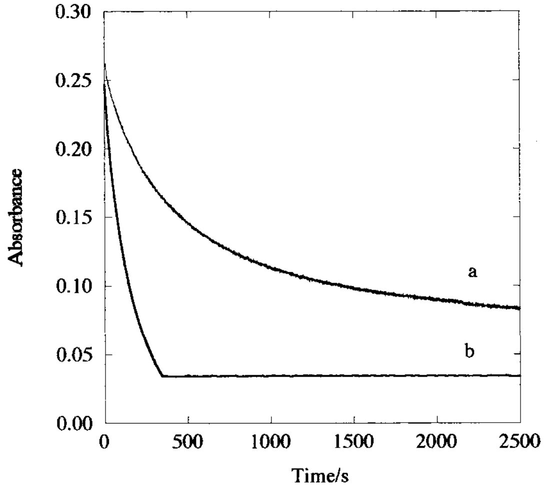

Figure 2. Kinetic traces at 271 nm for the reaction of 27 μM L^2RhOO^{2+} with HNO_2 at pH 1 and 25 °C: (a) $[HNO_2] = 33$ μM; (b) $[HNO_2] = 67$ μM. Path length: 1 cm.

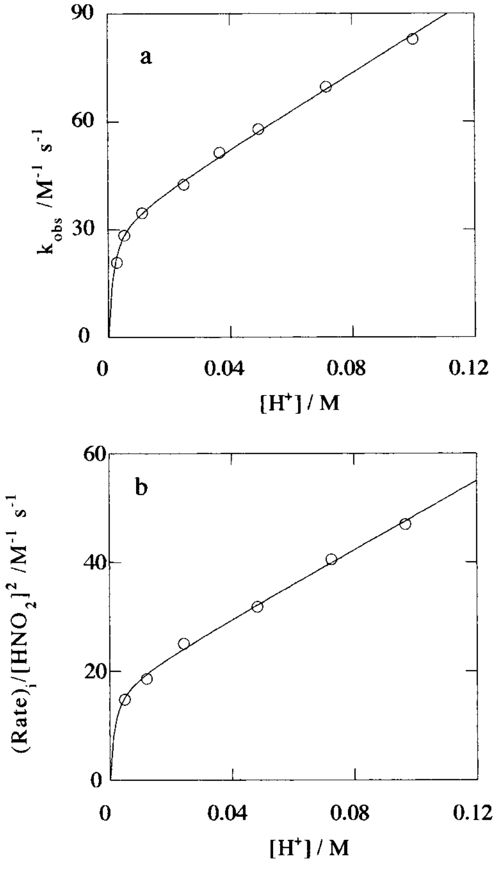

Figure 3. (a) Plot of k_{obs} vs $[H^+]$ for the reaction between 27 μM L^2RhOO^{2+} and 50 μM HNO_2. (b) Plot of $v_i/[HNO_2]^2$ vs $[H^+]$ for the reaction between 57 μM L^2RhOO^{2+} and 8 μM HNO_2. The solid lines represent nonlinear least-squares fits to eq 8. $T = 25$ °C.

The different multipliers for k, 2 vs 3, in eqs 6 and 7 follow directly from the stoichiometry of eq 5. The *rate constants,* obtained by fitting the data to the second-order rate law, yield information on the disappearance of HNO_2, eq 6. The *initial rate* measurements pertain to the disappearance of L^2RhOO^{2+}, eq 7.

The kinetics are pH dependent. Figure 3 shows a plot of the observed second-order rate constants (eq 6) and the initial rates (eq 7) vs $[H^+]$ at 0.10 M ionic strength. To allow for an easy comparison of the two sets of data, the quantity plotted on the *y*-axis in Figure 3b is an apparent second-order rate constant $(\mathrm{rate})_i/[\mathrm{HNO_2}]^2$ and has units $\mathrm{M^{-1}\ s^{-1}}$.

The acid dependence is consistent with HNO_2 as the reactive form, participating in an acid-independent and an acid-catalyzed reaction, as described in eqs 8 and 9, where $[\mathrm{HNO_2}]_{\mathrm{tot}} = [\mathrm{HNO_2}] + [\mathrm{NO_2^-}]$, and $K_a = 6.3 \times 10^{-4}$ M.[9] The fit of all the data in Figure 3 to eq 8 yields $k_1 = 10.9 \pm 1.0\ \mathrm{M^{-1}\ s^{-1}}$ and $k_2 = 175 \pm 17\ \mathrm{M^{-2}\ s^{-1}}$.

$$\frac{-\mathrm{d}[\mathrm{HNO_2}]}{\mathrm{d}t} = \frac{-3\ \mathrm{d}[\mathrm{L^2RhOO^{2+}}]}{2\ \mathrm{d}t} = 3(k_1 + k_2[\mathrm{H^+}])\left([\mathrm{HNO_2}]_{\mathrm{tot}}\frac{[\mathrm{H^+}]}{K_a + [\mathrm{H^+}]}\right) \quad (8)$$

$$\mathrm{HNO_2} \rightleftarrows \mathrm{H^+} + \mathrm{NO_2^-} \qquad K_a \quad (9)$$

Another set of experiments was carried out at 1.0 M H^+. A series of runs at different nitrous acid concentrations gave a second-order rate constant of $552 \pm 11\ \mathrm{M^{-1}\ s^{-1}}$. This value is within 1% of that calculated from the parameters at 0.10 M ionic strength, see above. The lack of ionic strength dependence is expected for a reaction with a charge product of zero for the dominant forms of the reactants, HNO_2 and L^2RhOO^{2+}.

Discussion

The pH dependence of the HNO_2/L^2RhOO^{2+} reaction indicates the occurrence of two parallel pathways, one acid-independent and the other acid-catalyzed. The additional decrease in reactivity at higher pH is caused by the deprotonation of HNO_2, $K_a = 6.3 \times 10^{-4}$ M, which increases the proportion of the unreactive NO_2^- ion. We consider it much less likely that the deprotonation of L^2RhOO^{2+} had a major effect on the rate at the acidities studied (pH < 4). The pK_a of the coordinated water is probably >6, similar to that of the related cobalt complex $L^2(H_2O)CoOO^{2+}$,[10] and there would be no significant depletion of the reactive form at pH < 4.

Both $L^2RhONO_2^{2+}$ and L^2RhOOH^{2+}, involved as intermediates in this work, have also been observed earlier in the NO/L^2RhOO^{2+} reaction, but in greater yields. This observation supports the detailed mechanism for the HNO_2/L^2RhOO^{2+} reaction presented in Scheme 2.

The quadratic dependence on $[HNO_2]$ is indicative of an initial rate-controlling formation of N_2O_3, as reported for the decomposition of nitrous acid and for various nitrosation reactions.[11−16] Rate constants for reaction S1 in the range from 10 to 15 $\mathrm{M^{-1}\ s^{-1}}$ have been reported previously.[15,17,18] Our value of 10.9 $\mathrm{M^{-1}\ s^{-1}}$ for the $[H^+]$ independent term is in close agreement with these reports.

Scheme 2

	k_f[a,b]	k_r[b,c]
(S1) $2\,\mathrm{HNO_2} \rightleftarrows \mathrm{N_2O_3} + \mathrm{H_2O}$	10.9[d]	530[e]
(S2) $\mathrm{N_2O_3} \rightleftarrows \mathrm{NO} + \mathrm{NO_2}$	8×10^4 [e]	10^9 [e]
(S3) $\mathrm{NO} + \mathrm{L^2RhOO^{2+}} \rightarrow \mathrm{L^2RhOONO^{2+}}$	$>10^6$ [f]	
(S4) $\mathrm{L^2RhOONO^{2+}} \rightarrow \{\mathrm{L^2RhONO_2^{2+}} + \mathrm{L^2Rh^{3+}} + \mathrm{NO_3^-} + \mathrm{L^2RhOOH^{2+}}\}$	$>10^3$ [f]	
(S5) $\mathrm{NO_2} + \mathrm{L^2RhOO^{2+}} \rightarrow \mathrm{L^2RhOONO_2^{2+}}$	$>10^3$ [d]	
(S6) $\mathrm{L^2RhOONO_2^{2+}} + \mathrm{HNO_2} \rightarrow \mathrm{L^2Rh^{3+}} + 2\,\mathrm{NO_3^-} + \mathrm{H^+}$	>500 [d]	
(S7) $2\,\mathrm{NO_2} \rightleftarrows \mathrm{N_2O_4}$	5×10^8 [e]	7×10^3 [e]
(S8) $\mathrm{N_2O_4} + \mathrm{H_2O} \rightarrow \mathrm{HNO_2} + \mathrm{NO_3^-} + \mathrm{H^+}$	10^3 [e]	

[a] k_f = forward rate constant. [b] Units: $\mathrm{s^{-1}}$ (first-order reactions) or $\mathrm{M^{-1}\ s^{-1}}$ (second-order reactions). [c] k_r = reverse rate constant. [d] This work. [e] Reference 19. [f] Reference 2.

Almost certainly, N_2O_3 does not react with the superoxorhodium directly, but only after the homolysis to NO and NO_2, $k = 8 \times 10^4\ \mathrm{s^{-1}}$, eq S2.[19] Both fragments could then react rapidly with L^2RhOO^{2+}, eqs S3 and S5. The reaction with NO is known to be fast, $k_{S3} > 10^6\ \mathrm{M^{-1}\ s^{-1}}$, and yields $L^2RhONO_2^{2+}$ and L^2RhOOH^{2+} as intermediates.[2] The observation of the same intermediates in this work strongly supports the involvement of NO.

The reaction of L^2RhOO^{2+} with NO_2 has not been studied, but the equivalent reaction of $Cr_{aq}OO^{2+}$, whose reactivity is often comparable to that of L^2RhOO^{2+}, has $k = 2.3 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$.[1] This result supports the proposed formation of the peroxynitratorhodium complex $L^2RhOONO_2^{2+}$ in eq S5. The novel reaction of this intermediate with HNO_2, eq S6, draws support from the known oxidation of HNO_2 by peroxynitric acid, eq 10, $k_{10} = 50\ \mathrm{M^{-1}\ s^{-1}}$ [15] or $10\ \mathrm{M^{-1}\ s^{-1}}$.[20]

$$\mathrm{HOONO_2} + \mathrm{HNO_2} \rightarrow 2\mathrm{NO_3^-} + 2\mathrm{H^+} \quad (10)$$

Our kinetic simulations require $k_{S6} > 500\ \mathrm{M^{-1}\ s^{-1}}$ to account for the observed stoichiometry. This value is reasonable, considering that oxidations by peroxo species are often greatly accelerated by coordination to positively charged metal centers.[21]

Still, on the basis of kinetics and stoichiometry alone, one cannot distinguish between the two likely fates for NO_2 described by eqs S5 and S6 or eqs S7 and S8. We prefer the sequence S5−S6, however, because the dimerization/hydrolysis of eqs S7 and S8 can prevail only if the rate constant k_{S5} is smaller than $10^3\ \mathrm{M^{-1}\ s^{-1}}$, as shown by kinetic simulations. Such a small rate constant is considered unlikely,

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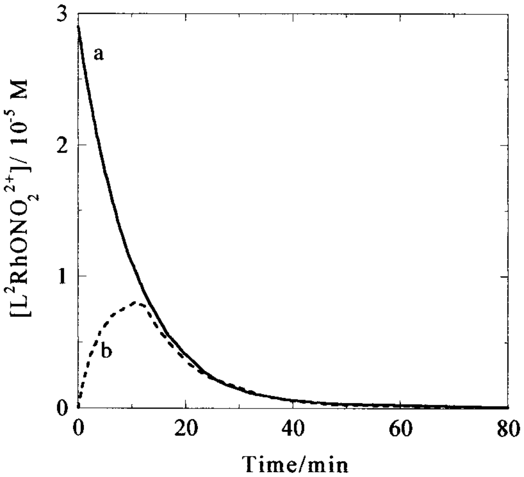

Figure 4. Simulated time profiles for the formation and decay of L^{2}RhONO$_2^{2+}$ generated in the reactions between L^{2}RhOO^2 (30 μM) and an excess of either (a) NO (50 μM) or (b) HNO$_2$ (105 μM), both at 25 °C and pH 3.3.

given that the equivalent reaction between NO$_2$ and CrOO^{2+} has $k = 2.3 \times 10^8$ M^{-1} s^{-1}.[1]

According to the mechanism depicted in Scheme 2, only 50% of L^{2}RhOO^{2+} reacts with NO as in eq S3, the rest being consumed by NO$_2$, eq S5. This analysis agrees with the experimental amount of L^{2}RhOOH^{2+}, 6%, being about half of that produced in the NO/L^{2}RhOO^{2+} reaction.[2] On the other hand, the absorbance changes for the hydrolysis of L^{2}RhONO$_2^{2+}$ produced from HNO$_2$ and NO are similar, Figure 1, and could lead one to believe that the same amount of the nitrato complex was produced in the two experiments.

In fact, the total *yields* of L^{2}RhONO$_2^{2+}$ indeed differ by a factor of ~2, but the *concentrations* of L^{2}RhONO$_2^{2+}$ in the two experiments were comparable at the moment when all the L^{2}RhOO^{2+} was consumed in the reaction with HNO$_2$, and [L^{2}RhONO$_2^{2+}$] was at the maximum, i.e., 12 min after the reagents in Figure 1 were mixed. This fortuitous result stems from the kinetics of L^{2}RhONO$_2^{2+}$ formation. The NO/L^{2}RhOO^{2+} reaction is over in mixing time, and the decomposition of L^{2}RhONO$_2^{2+}$ starts a fraction of a second after the reagents are mixed. The HNO$_2$/L^{2}RhOO^{2+} reaction is much slower, so that the formation and decomposition of L^{2}RhONO$_2^{2+}$ take place on comparable time scales, allowing a smaller fraction of L^{2}RhONO$_2^{2+}$ to decompose in the first 12 min.

Figure 4 shows simulated time profiles for the formation and decay of L^{2}RhONO$_2^{2+}$ in the reactions of L^{2}RhOO^{2+} with NO and HNO$_2$ under the conditions of Figure 1. At t = 12 min, the predicted concentrations of L^{2}RhONO$_2^{2+}$ are 30% (NO reaction) and 29% (HNO$_2$ reaction) of [L^{2}RhOO^{2+}]$_0$. The respective observed percentages were 30% and 27%, in good agreement with the prediction.

The rate law in eq 8 provides, to our knowledge, the first definitive observation of an H$^+$-catalyzed path in the formation of N$_2$O$_3$. Such a path was considered earlier, but the evidence was not convincing. In some cases the precision of the data was low,[18] and in others the acid catalysis may have been masked by complex pH dependence of the remaining chemistry. N-Nitrosation of amines[12] and diazotization of anilines,[14] for example, require the use of low [H$^+$] to prevent the protonation of the amines. Under such conditions, acid catalysis would not be observable. The formation of NO$^+$ at high [H$^+$] also presents a problem. In some reactions, such as that with *o*-chloroaniline, a kinetic term proportional to [H$^+$] and first order in [HNO$_2$] was observed, indicating the involvement of NO$^+$ or H$_2$NO$_2^+$.[16] This term, shown in eq 11[22] could easily mask the acid-dependent term observed in our study, 175[H$^+$][HNO$_2$]^2, especially because here the dependence on [HNO$_2$] is second order.

$$\mathrm{HNO_2 + H^+ \rightleftarrows H_2O + NO^+} \qquad k_f = 617[\mathrm{H^+}][\mathrm{HNO_2}] \quad (11)$$

The proposed mechanism[11] for the formation of N$_2$O$_3$ involves a nucleophilic attack of NO$_2^-$ on nitrous acidium ion H$_2$NO$_2^+$ (or NO$^+$), eq 12. Our kinetic data suggest that nitrous acid itself can also act as a nucleophile, eq 13.

$$\mathrm{H_2NO_2^+ + NO_2^- \rightarrow H_2O + N_2O_3} \qquad k_a \quad (12)$$

$$\mathrm{H_2NO_2^+ + HNO_2 \rightarrow H_3O^+ + N_2O_3} \qquad k_b \quad (13)$$

According to this proposal, the rate constants k_a and k_b are related to the rate constants k_1 and k_2 (eq 8), $k_a/k_b = k_1/K_ak_2 \sim 1 \times 10^2$. This quotient is a measure of relative kinetic nucleophilicities of NO$_2^-$ and HNO$_2$ in the reaction with H$_2$NO$_2^+$. As one would expect, the nucleophilicity of nitrite is greatly reduced upon protonation.

In view of this result, we have analyzed the published[11b] data on diazotization of aniline at low acid concentrations (0.002−0.019 M). The second-order rate constant increases with [H$^+$], and from the four data points we estimate $k_a/k_b \sim 200$, reasonably close to our result.

The clean second-order dependence on HNO$_2$ in the present work, even at 1.0 M H$^+$, clearly rules out a pathway utilizing NO$^+$, eq 11. The oxidation potential for the couple L^{2}RhOO^{2+}/L^{2}Rh^{3+}+ O$_2$ is probably near 1 V, the value reported for Cr$_{aq}$OO^{2+}/Cr$_{aq}^{3+}$ + O$_2$,[23] which makes the reaction of eq 14 thermodynamically favorable, given that

$$\mathrm{L^2RhOO^{2+} + NO^+ \rightarrow L^2Rh^{3+} + O_2 + NO} \qquad (14)$$

$E°$ for the NO$^+$/NO couple is 1.4 V.[24] The absence of this pathway apparently reflects the small self-exchange rate constants for the superoxometal complexes[23] and for the NO$^+$/NO couple.[25]

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