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Electron Transfer. 119. Reductions of Rhodium-Bound Superoxide[1]

Sanchita Purohit Ghosh,* E. Gelerinter, Gloria Pyrka, and E. S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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Treatment of $(Rh^{II})_2^{4+}(aq)$ with O_2 in 3 M $HClO_4$ yields a violet (ϵ^{560}_{max} = 620 M^{-1} cm^{-1}) superoxo complex, the properties of which are in accord with the assigned formula $[(H_2O)_4(OH)Rh^{III}(O_2)Rh^{III}(OH)(H_2O)_4]^{3+}$. This cation is reduced, in 1:1 reactions with V(II), Eu(II), Ti(III), and Fe(II), or in 2:1 reactions with ascorbic acid and hydroquinone, to a $1e^-$ reduction product, the corresponding peroxo complex. The latter regenerates the superoxo derivative, together with the bridged cation, $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$, on standing. The yield of superoxo complex reformed in this disproportionation approaches the theoretical 67% with the Eu(II) reaction, but falls between 45 and 57% with the other reductants. Reductions of the superoxo complex utilize parallel pathways, at different protonation levels. In most cases, an inverse-$[H^+]$ route competes with an $[H^+]$-independent path; with Ti(III) and V(III), kinetic components are proportional to $[H^+]^{-1}$ and $[H^+]^{-2}$. The high rate of reduction by V(II) insures that this reaction proceeds without ligand bridging and, in conjunction with the model of Marcus, allows us to estimate a self-exchange rate of $10^{-3.2}$ M^{-1} s^{-1} for the $(Rh^{III})_2$-bound superoxo–peroxo couple. Analogous consideration of the Fe(II) reduction, however, points to a predominant inner-sphere path in this instance. The regeneration of the superoxo from the peroxo complex exhibits first-order kinetics with a rate constant 2.1×10^{-3} s^{-1} (23 °C, μ = 2.0 M) independent of the reductant at hand or the acidity of the medium, suggesting a rate-determining heterolysis of the peroxy function. The $2e^-$ reagents, Sn(II), U(IV), and $(Mo_2O_4)^{2+}$ also react with equimolar quantities of the superoxo complex. The product here is ESR-silent at room temperature and, unlike the $1e^-$ product, does not regenerate the parent superoxo species on standing.

The intervention of superoxide, O_2^-, in life processes[2] is responsible, in large part, for continued experimental activity dealing with the reactions of this anion and its derivatives. Superoxide has been implicated as an intermediate in some autoxidations[3] and as a metabolic byproduct from aerobic organisms.[4] Its existence in biosystems is generally short-lived, for it suffers rapid disproportionation into O_2 and H_2O_2, a transformation effectively catalyzed by superoxide dismutases.[5] These bimetalloproteins are presumed to protect the organism from superoxide toxicity, the exact nature of which has not yet been determined.[5,6]

A variety of metal complexes of superoxide can be examined by conventional methods in the absence of facile paths for decomposition. Supplementing an array of derivatives of substitution-inert metal centers,[7] several less-robust superoxo adducts of d^0 and d^9 ions have been studied in solution.[8] Binuclear (μ-coordinated) superoxo complexes may often be isolated as crystalline solids and are thus particularly well suited to quantitative studies. The reductions of $(Co^{III})_2$-bound superoxide, both by metal ion centers[9] and by nonmetallic donors,[10] have been examined in some detail. Reductions with organic thiols are of import because of the role assumed by RSH/R_2S_2 systems in mediating redox potentials at biological sites,[11] whereas reactions with ascorbic acid deserve attention in view of the action of this molecule as an antioxidant[12] and as a hydroxylase cofactor[13] in biosystems. In a number of instances these reactions, which are favored thermodynamically, are slow but are dramatically catalyzed by dissolved copper, even at the 10^{-7} M level.[10bc]

The present study pertains to redox reactions of the dinuclear rhodium(III)-bound superoxo cation I. Our incursion into

$$[(H_2O)_4(OH)Rh^{III}(O_2)Rh^{III}(OH)(OH_2)_4]^{3+}$$

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rhodium systems was prompted, in part, by the recent quickening of interest in compounds of this element,[14] both as catalysts in a wide variety of organic reactions,[15] and as chemotherapeutic agents.[16] Additional significance is attached to the oxidant

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Table I. Stoichiometries of the Reductions of $(Rh^{III})_2$-Bound Superoxide[a]

reductant (red)	10^4 [ox], M	10^4 [red], M	[H^+], M	waiting period, min	Δ[red]/Δ[ox] initial	Δ[red]/Δ[ox] overall[b]
ascorbic acid	2.8	0.5–1.0	1.0	0.5	0.47 ± 0.02	1.22 ± 0.02
hydroquinone	2.2	0.5–1.0	1.0	1.0	0.49 ± 0.01	1.15 ± 0.05
Fe(II)	2.8	0.7–2.0	0.32	5.0	0.94 ± 0.02	2.5 ± 0.1
U(IV)	7.1	1.9–7.6	1.0	5–20	1.08 ± 0.02	*c*
Ti(III)	7.6	2.0–6.0	0.80	2.0	0.93 ± 0.05	2.4 ± 0.1
$(Mo^V)_2$	7.5	2.0–6.0	0.75	25–55	1.06 ± 0.02	*c*
Eu(II)	3.0	1.5–3.0	1.0	0.2	1.08 ± 0.02	2.9 ± 0.1
V(II)	7.3	1.0–6.0	0.75	0.5–1.4	0.95 ± 0.03	2.1 ± 0.1
V(III)[d]	15.0	5.0–10.0	1.2	130–250	1.01 ± 0.03	*c*
Sn(II)	7.5	0.9–6.2	1.0	3–6	0.91 ± 0.05	*c*

[a] Reactions of $[(H_2O)_4(OH)Rh^{III}(O_2)Rh^{III}(OH)(OH_2)_4]^{3+}$ (I) at 25 °C; λ = 560 nm. [b] Ratio includes reduction of superoxo complex taken and regenerated superoxide (see Experimental Section). [c] Regeneration of superoxide not observed with these reductants. [d] Reaction was carried out at 45 °C.

chosen because of an increasing body of evidence[17] that many, but not all,[18] compounds previously thought to be Rh(IV) species are instead Rh(III)-superoxo derivatives.

Experimental Section

Materials. Ascorbic acid and L-cysteine (Aldrich Chemicals) and hydroquinone (Eastman Kodak) were used as received. Solutions of $Fe(ClO_4)_2$,[19] $TiCl_3$,[20] $Eu(ClO_4)_2$,[21] U(IV) in $HClO_4$,[22] $VO(ClO_4)_2$,[23] $V(ClO_4)_2$,[24ab] $V(ClO_4)_3$,[24c] $Mo_2O_4(H_2O)_6(ClO_4)_2$,[25] and $NaClO_4$ (used as a supporting electrolyte in kinetic experiments)[10b] were prepared as described.

The rhodium-superoxo complex I was prepared using a modification of the method of Moszner.[26] A solution of hydrated rhodium(III) chloride (Aldrich) (0.40 g, 1.9 mmol) was treated with silver perchlorate ("$AgClO_4{\cdot}xH_2O$", 1.32 g) at 65 °C for 20 min. The preparation was filtered, and the filtrate was made 1.0 M in $HClO_4$ and then sparged with N_2 for 60 min. The Rh(III) was then reduced to $(Rh^{II})_2{}^{4+}$ by addition of 2.8 mmol of $Cr(ClO_4)_2$,[27] and the resulting solution was subjected to cation-exchange chromatography under N_2, using Dowex 50W-X2 (200 mesh, H^+ form). Elution with 1.0 M $HClO_4$ removed $Cr(H_2O)_5Cl^{2+}$, and elution with 2.0 M $HClO_4$ removed $Cr(H_2O)_6{}^{3+}$. A third compact (green) band was eluted with 3.0 M $HClO_4$ and exhibited the spectrum reported[26] for $(Rh^{II})_2{}^{4+}$. The latter cation was converted to the violet superoxo complex I, by passing O_2 through the eluted solution for 60 min (progress of this oxidation was monitored spectrophotometrically). The oxidized mixture was diluted with an equal volume of water and chromatographed on Dowex 50W-X2 (H^+). The desired violet cation was removed with 3.0 M $HClO_4$, leaving behind a smaller yellow band, which was not eluted. The superoxo complex is stable in 1–3 M $HClO_4$, but decomposes slowly at pH > 1 to a dark blue species. The ESR spectrum of the violet superoxo complex[28] in 1 M $HClO_4$ exhibited a single peak; $g = 2.040$ (reported[26] 2.0414).

To check the molar absorbance of the superoxo complex, an aliquot was decomposed by heating at 80 °C with concd HCl for 30 min. Rhodium was then estimated by treatment with $SnCl_2$ as described,[29a] using $\epsilon_{470} = 3.90 \times 10^3\ M^{-1}\ cm^{-1}$).[29b] Four determinations yielded $\epsilon_{560} = 620 \pm 8$, $\epsilon_{420} = 400$ [illegible] 5, and $\epsilon_{235} = (1.10 \pm 0.01) \times 10^4\ M^{-1}\ cm^{-1}$ (per dimer) for the superoxo complex, values about 30% greater than those reported by Moszner.[26] Use of the latter values in our stoichiometry experiments (see below) led to apparently nonintegral and chemically unreasonable stoichiometric ratios with all reductants.

Stoichiometric Experiments. Stoichiometries of the reductions of the $(Rh^{III})_2$–superoxide complex were measured at 560 nm. These determinations were, in some cases, complicated by the slow partial regeneration of the superoxide after it had been consumed (see below), but this complication could be minimized by adding deficient quantitites of the reductant to a known excess of the superoxo complex. Decreases in absorbance were then measured immediately after reaction had ceased, and these changes were compared to those resulting from an addition of an excess of the reductant. In those instances when regeneration was apparent, an "overall stoichiometry" was also estimated by spectrophotometric titrations of successively smaller increments of the regenerated superoxide until the latter no longer appeared. Results of both types of determination are summarized in Table I

Kinetic Measurements. Rates of reduction of the superoxo complex were estimated from absorbance changes at 560 nm by using a Beckman Model 5260 recording spectrophotometer or a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. All experiments were carried out under N_2. Acidity was regulated by adding perchloric acid, and ionic strength was generally maintained at 1.0 M using $NaClO_4$. Reactions were generally carried out with the reductant in excess, and, except for the fastest reactions, concentrations were adjusted so that less than 10% of the reductant was consumed during a run. Kinetic curves generated with the reductant in large excess were exponential, and rate constants were obtained from logarithmic plots of absorbance differences against reaction time. For reactions of this type, specific rates from replicate runs agreed to better than 5%. Reactions were first order in both redox partners.

Reactions of the superoxo complex with Cr^{2+} were too rapid to follow, even under second-order conditions using the stopped-flow technique, whereas reactions with Cu^+ were too rapid to follow using conventional mixing.[30] Reductions with the protonated forms of hydrazine ($N_2H_5{}^+$) and hydroxylamine (NH_3OH^+) were slow and yielded profiles suggesting autocatalysis; these reactions are being examined in more detail. Reductions with 2-aminoethanethiol, $HSCH_2CH_2NH_3{}^+$, were complicated by precipitation. Unlike reactions of $(Co^{III})_2$–superoxo complexes,[10bc] reductions with ascorbate and cysteine exhibited no catalysis by Cu^{2+}.

The regeneration of the $(Rh^{III})_2$–superoxo complex was best observed by treating this oxidant with an equimolar quantity of Fe^{II}, Eu^{II}, Ti^{III}, or V^{II} or with a half-molar quantity of ascorbate or hydroquinone, whereupon the initial quick disappearance of the violet cation was followed by a much slower exponential growth of 45–64% of the superoxo derivative originally taken. The rate constant for this "follow-up" step ($2.1 \times 10^{-3}\ s^{-1}$, 23 °C, $\mu = 2.0$ M) was independent of the reductant chosen and of

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acidity in the range 0.24–1.0 M H^+. This rise was not observed if the mixture resulting from action of any of the indicated reductants was treated with H_2O_2, nor was it seen if the initial reduction was carried out using Sn^{II}, U^{IV}, or $(Mo^V)_2$.

Additional Observations. Solutions obtained by rapid reductions of the superoxo complex I (using Eu^{II} or Ti^{III}) exhibited, prior to significant superoxo regeneration, a shoulder at 312 nm ($\epsilon = 1.9 \times 10^3$ M^{-1} cm^{-1} per Rh). After all regenerated superoxide had been consumed, maxima were observed at 408 ($\epsilon = 95$ M^{-1} cm^{-1}) and 242 nm ($\epsilon = 1750$ M^{-1} cm^{-1}) (per Rh), corresponding to the spectrum reported[31] for the dinuclear bridged complex, $[(H_2O)_4Rh(\mu\text{-}OH)_2Rh(OH_2)_4]^{4+}$. Reduction of I with the $2e^-$ reagents, Sn^{II}, U^{IV}, and $(Mo_2O_4)^{2+}$, yielded a pale yellow product, ESR-silent at room temperature, with a shoulder at 375 nm ($\epsilon = 290$ M^{-1} cm^{-1}).

Cyclic voltammograms of the superoxo complex (3.5×10^{-3} M in 3.0 M $HClO_4$), carried out in an attempt to estimate a formal potential for the peroxo/superoxo couple, indicated a quasireversible reduction near 700 mV (vs NHE). Reaction of I with an equimolar concentration of $IrCl_6^{3-}$ resulted in a very slow, but nearly complete (greater that 95%) conversion to $IrCl_6^{2-}$.[32]

Results and Discussion

The violet cationic complex examined in this work has been generated in a solution having (aside from superoxide) only H_2O and OH^- as ligating species. Its reported[26] net charge (3+), its ESR spectrum,[26] the ease with which it undergoes $1e^-$ reductions, and the mode of its preparation are in accord with the assigned[26] dinuclear structure I (analogous to other μ-superoxo bridged $(Rh^{III})_2$ complexes of known structure)[33] featuring in this instance two hydroxo and eight aqua groups.

Reactions of this oxidant with the rapid $1e^-$ reductants, Eu^{II}, V^{II}, Ti^{III}, and Fe^{II}, are seen (Table I) to consume nearly equimolar quantities of the redox partners, pointing to conversion to the corresponding μ-peroxo complex (eq 1).

$$Rh^{III}(O_2^-)Rh^{III} + M^{2+} \rightarrow Rh^{III}(O_2^{2-})Rh^{III} + M^{3+} \quad (1)$$

Reductions by ascorbic acid and by hydroquinone, which exhibit 1:2 stoichiometry, also yield this product. Although these organics may be considered 2e reagents, both have been found to undergo oxidation, in many cases, via successive 1e steps.[34]

The regeneration of the superoxo from the peroxo complex at low pH has been noted in the $(NH_3)_4Rh^{III}$ series by Springborg and Zehnder[33c] and has been described as a disproportionation (eq 2)

$$3Rh^{III}(O_2^{2-})Rh^{III} + 4H^+ \rightarrow 2Rh^{III}(O_2^-)Rh^{III} + 2(H_2O)Rh^{III} \quad (2)$$

However, these authors have pointed out that the yield of rhodium appearing in the superoxo derivative which is produced falls well below the 67% value calculated on the basis of eq 2. We find similarly incomplete reconversions when the superoxo cation I is reformed in solutions resulting from reductions by ascorbic acid, hydroquinone, V^{II}, Ti^{III}, or Fe^{II}, each of which regenerates this oxidant in 45–57% yield. Only with reductions by Eu^{II} does the recovery of superoxide (64%) approach the value implied by eq 2.[35] Action of the remaining $1e^-$ reductants appears to proceed, in minor part, through an alternate path, although the "overall product", a μ-$(OH)_2$ cation, is the same for all.

Table II. Representative Kinetic Data for the Reductions of $[(H_2O)_4(OH)Rh(O_2)Rh(OH)(OH_2)_4]^{3+}$ by Ascorbic Acid and by Ti(III)[a]

ascorbic acid reductions			Ti(III) reactions		
[red], mM	$[H^+]$, M	k, s^{-1} [b]	[red], mM	$[H^+]$, M	k, s^{-1} [b]
0.63	0.50	1.42 (1.47)	1.25	1.00	0.50 (0.49)
1.00	0.50	2.2 (2.3)	2.5	1.00	0.97 (0.98)
2.0	0.50	4.5 (4.6)	3.5	1.00	1.41 (1.38)
3.5	0.50	7.4 (8.1)	5.0	1.00	1.95 (1.96)
5.0	0.50	11.8 (11.6)	8.0	1.00	3.1 (3.1)
7.5	0.50	17.7 (17.5)	10.0	1.00	3.9 (3.9)
1.00	1.00	1.62 (1.50)	2.5	0.75	1.28 (1.35)
1.00	0.75	1.80 (1.78)	2.5	0.62	1.60 (1.69)
1.00	0.40	3.0 (2.7)	2.5	0.50	2.3 (2.2)
1.00	0.30	3.6 (3.4)	2.5	0.35	3.7 (3.4)
1.00	0.21	4.8 (4.6)	2.5	0.25	5.5 (5.2)
			2.5	0.20	6.8 (7.0)
			2.5	0.125	13.7 (13.9)

[a] Reactions were carried out at 20.5 ± 0.5 °C; $\mu = 1.0$ M ($NaClO_4$); [ox] = 1.25×10^{-4} M throughout. [b] Pseudo-first-order rate constants; parenthetical values were calculated using rate laws and kinetic parameters in Table III.

Representative kinetic data, pertaining to reductions of the superoxo complex by ascorbic acid and by Ti(III), are found in Table II. Reactions are first order in reductant and in superoxide and are retarded by increases in H^+. The acidity dependence is less marked for the ascorbic acid reductions, which conform to eq 4, than for the

$$(k)_{obsd} = [HAsc](k_o + k'[H^+]^{-1}) \quad (4)$$

Ti(III) reductions, which are in accord with eq 5.

$$(k)_{obsd} = [Ti^{III}](k'[H^+]^{-1} + k''[H^+]^{-2}) \quad (5)$$

Rates calculated using eqs 4 and 5 are compared to observed values in this table.

Rate laws and kinetic parameters for several of the other reductants are summarized in Table III. Note that rate constants for the very rapid reactions of Eu(II) and V(II) could be estimated in 1.0 M H^+, but not at lower acidities.

Each of the reductants except hydroquinone is seen to operate through two parallel pathways at different protonation levels. For ascorbic acid, cysteine, and Fe(II), an $[H^+]$-independent route competes with an inverse-H^+ route featuring the redox pair from which a single H^+ has been lost, whereas with Ti(III) and V(III) the two components require loss of one and two protons. Since both of these tripositive reducing centers are known to favor deprotonated paths, even in strongly acidic aqueous media,[20,36] it is reasonable in these instances to ascribe the $[H^+]^{-1}$-proportional term, k', to deprotonation of the reductant, and the $[H^+]^{-2}$ term, k'', to deprotonation of both partners. With the remaining two-term reductions, for which the ratio k_o/k' varies only slightly, k_o pertains to the redox partners as such, whereas k' most likely reflects H^+-loss from the superoxo complex.

Although the presence of a hydroxo ligand is known to offer a facile inner-sphere route for reductions of transition-metal based

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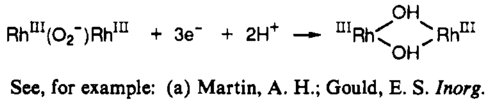
(35) This difference is in accord with the approach to 3:1 overall stoichiometry observed with Eu(II), but not with the other reductants (Table I). In the absence of side reactions, 3 equiv of reducing agent are consumed when superoxide I is converted completely to the μ-$(OH)_2$ product.



$$Rh^{III}(O_2^-)Rh^{III} + 3e^- + 2H^+ \rightarrow {}^{III}Rh(\mu\text{-}OH)_2Rh^{III}$$

(3)

(36) See, for example: (a) Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1975**, *14*, 873. (b) Ram, M. S.; Martin, A. H.; Gould, E. S. *Inorg. Chem.* **1983**, *22*, 1103. (c) Furman, S. C.; Garner, C. S. *J. Am. Chem. Soc.* **1952**, *74*, 2333. (d) Ghosh, M. C.; Gould, E. S. *J. Am. Chem. Soc.* **1993**, *115*, 3167.

Table III. Kinetic Parameters for Reductions of $[(H_2O)_4(OH)Rh(O_2)Rh(OH)(OH_2)_4]^{3+}$.[a]

$$\text{Rate} = [\text{ox}][\text{red}](k_o + k'[H^+]^{-1} + k''[H^+]^{-2})$$

reductant	k_o, M^{-1} s^{-1}	k', s^{-1}	k'', M s^{-1}	
ascorbic acid	$(6.7 \pm 1.2) \times 10^2$	$(8.3 \pm 0.6) \times 10^2$		
hydroquinone	$(6.5 \pm 0.1) \times 10^2$			
L-cysteine	0.116 ± 0.037	0.35 ± 0.02		
Ti(III)		$(3.5 \pm 0.1) \times 10^2$	44 ± 3	
Fe(II)	$(1.92 \pm 0.32) \times 10^2$	$(1.59 \pm 0.16) \times 10^2$		
V(III)		$(9.9 \pm 0.8) \times 10^{-2}$	$(6.3 \pm 0.5) \times 10^{-2}$	
Eu(II)[b]				k_{obs} $(2.8 \pm 0.4) \times 10^5$ (1 M H^+)
V(II)[b]				k_{obs} $(1.4 \pm 0.1) \times 10^6$ (1 M H^+)

[a] Reactions were carried out at 20.5 ± 0.5 °C; $\mu = 1.0$ M ($NaClO_4$); [ox] = $(0.6–0.2) \times 10^{-4}$ M; [red] = $(0.6–0.8) \times 10^{-3}$ M; $[H^+]$ = 0.20–1.0 M. Rate law describes $-d(\ln[\text{ox}])/dt$. [b] Rapid reactions, for which rate constants (listed in M^{-1} s^{-1}) were determined only in 1.0 M $HClO_4$.

Table IV. Estimated Self-Exchange Rates and Contributing Parameters for Reductions of $[(H_2O)_4(OH)Rh(O_2)Rh(OH)(OH_2)_4]^{3+}$ (20.5 °C, $\mu = 1.0$ M)

reductant	$(E_o)_{ox}$ V	$(E_o)_{red}$ V[a]	log k_{22}[b]	log K_{12}[c]	k_{12}, M^{-1} s^{-1}	log k_{11}[d]
V^{2+}	1.02[e]	−0.255	−2.52	21.7	7×10^5[f]	−3.2
Eu^{2+}	1.02[e]	−0.38	−4.5	23.8	1.4×10^5[f]	−4.1
Fe^{2+}	1.02[e]	+0.74	+0.60	4.8	1.9×10^4[g]	−0.66

[a] Bard, A. J., Parsons, R., Jordan, J., Eds. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985. [b] Estimated self-exchange rate for the reductant (ref 39). [c] Estimated as $\Delta E_o/0.059$. [d] Self-exchange rate for oxidant, estimated using eq 6 in text. [e] Calculated from estimated 95% completion of oxidation of $IrCl_6^{3-}$ (E_o 0.87 V) in a 1:1 reaction with the superoxo oxidant. [f] $[H^+]$-independent rate constant (k_o), taken as $0.5 \times (k)_{obsd}$ in 1.0 M H^+ (Table III). [g] Value of k_o (Table III).

oxidants,[37] a hydroxo-bridged path obviously cannot extend to all of the present reductants. The structures of ascorbate and cysteine do not allow them to enter into bridging of this type. Moreover, the rate for V^{2+} is far in excess of the limit (near 10^2 M^{-1} s^{-1}) on inner-sphere reductions imposed by ligand substitution on this center.[38]

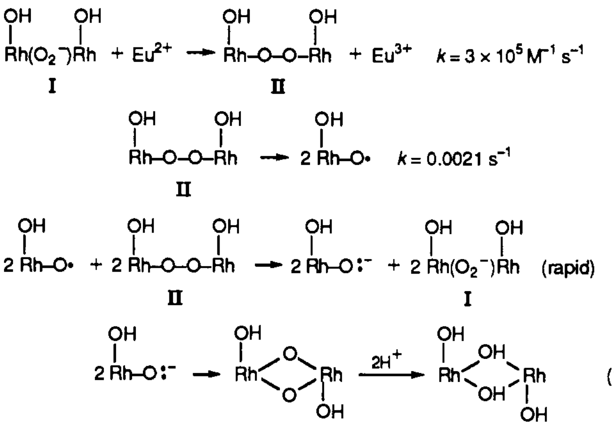
Since the V^{2+} reduction is preponderantly outer-sphere, its rate may be used, in conjunction with eq 6,[39] (which is based on the model of Marcus) to estimate the self-exchange rate for the $(Rh^{III})_2$-bound superoxo–peroxo couple.

$$\log k_{12} = 0.5\{\log(k_{11}k_{22}K_{12}) + (\log K_{12})^2/[4 \log(k_{11}k_{22}/Z^2)]\} \tag{6}$$

Here, k_{12} and K_{12} are the rate and equilibrium constants for the reduction by V^{2+}, k_{11} and k_{22} are the self-exchange rates for the two redox partners, and Z is the collision frequency, 10^{11} dm^3 mol^{-1} s^{-1}. The calculated self-exchange rate, k_{11}, based upon the data for reduction by V^{2+}, is $10^{-3.2}$ M^{-1} s^{-1} (Table IV). An analogous treatment of the reduction by Eu^{2+} yields $k_{11} = 10^{-4.1}$ M^{-1} s^{-1}. Reasonable agreement (considering the approximate nature of calculations of this type) between these values points to an outer-sphere path for this reductant as well. However, further extension to the Fe^{2+} data, using the k_o kinetic component, leads to a calculated self-exchange rate 10^3–10^4 as great as that obtained from consideration of the more rapid reductants.[40] The implication is that the superoxo complex at hand utilizes a predominant inner-sphere path only in its reduction by Fe(II).

The regeneration of the superoxo complex from the peroxo product is remarkable in that it exhibits strictly first-order kinetics despite its unusual stoichiometry and its apparent nature as a disproportionation process. The observed rate constant for this reaction, 0.0021 s^{-1}, is about three times that reported[33c] for the corresponding transformation in the $[(NH_3)_4Rh^{III}]_2$ series (7.4×10^{-4} s^{-1} at 25 °C).

For the Eu(II)–superoxide system, both the kinetic picture and the observed stoichiometry are consistent with reactions 7–10 (aqua ligands are omitted). The proposed rate-determining



$$\overset{OH}{Rh}(O_2^-)\overset{OH}{Rh}\ (\mathbf{I}) + Eu^{2+} \rightarrow \overset{OH}{Rh}–O–O–\overset{OH}{Rh}\ (\mathbf{II}) + Eu^{3+} \quad k = 3 \times 10^5\ M^{-1}\ s^{-1} \tag{7}$$

$$\overset{OH}{Rh}–O–O–\overset{OH}{Rh}\ (\mathbf{II}) \rightarrow 2\ \overset{OH}{Rh}–O\bullet \quad k = 0.0021\ s^{-1} \tag{8}$$

$$2\ \overset{OH}{Rh}–O\bullet + 2\ \overset{OH}{Rh}–O–O–\overset{OH}{Rh}\ (\mathbf{II}) \rightarrow 2\ \overset{OH}{Rh}–O:^- + 2\ \overset{OH}{Rh}(O_2^-)\overset{OH}{Rh}\ (\mathbf{I}) \quad \text{(rapid)} \tag{9}$$

(10)

breakage of the O–O bond of the peroxo complex (reaction 8) brings to mind an array of free-radical reactions initiated by such a heterolysis.[41] This step appears to be favored by attachment of Rh(III) centers to both ends of the peroxy function.[42,43] The succeeding step, reaction 9, an (outer-sphere) electron transfer to electron-deficient Rh–O•, is presumably too rapid to affect the kinetic picture.

Incomplete regeneration of the superoxo complex observed with reductions by ascorbate, hydroquinone, and the d-block metal centers (Table I) must be attributed to diversion of the (OH)-RhO• intermediate rather than the peroxo complex **II**, for the rate constant pertaining to heterolysis of the latter is not influenced by changes of the reductant. With the organic reactants, a minor portion of this odd-electron fragment may be lost by reaction with the aromatic ring or by further oxidation of dehydroascorbate. With the metal reductants, coordination of this species to the

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(37) See, for example: Toppen, D. L.; Linck, R. G. *Inorg. Chem.* **1971**, *10*, 3635.

(38) (a) Baker, B. R.; Orhanovic, M.; Sutin, N. *J. Am. Chem. Soc.* **1967**, *89*, 722. (b) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3767. (c) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539.

(39) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(40) (a) For a discussion of the difficulties associated with application of the Marcus model to reductions by $Ti(OH)^{2+}$, see: Brunschwig, B. S., Sutin, N. *Inorg. Chem.* **1979**, *18*, 1731. (b) The self-exchange rate for Fe(II,III) used here (1.1 M^{-1} s^{-1}) is the experimental value currently employed by most workers for Marcus-type calculations (see, for example: Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948). Use of a lower value, $10^{-3\pm1}$ M^{-1} s^{-1}, favored in older treatments (see, for example: Macartney, D. H.; McAuley, A.; Olubuyide, O. A. *Inorg. Chem.* **1985**, *24*, 307) increases the gap between the superoxo self-exchange rate calculated for Fe(II) and that calculated for the faster reductants.

(41) See, for example: Sheldon, R. A.; Kochi, J. K., *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 2.

(42) Heterolytic decomposition of di-*t*-butyl peroxalate, one of the more facile O–O initiators, yields 2*t*-BuO• + $2CO_2$ and exhibits a rate constant 1.7×10^{-5} s^{-1} in benzene at 25 °C,[43] i.e. about 10^{-2} as rapid as the Rh(III) peroxo complex **II** in water.

(43) (a) Bartlett, P. A.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762. (b) Johnson, N. A.; Gould, E. S. *ibid.* **1973**, *95*, 5198.

oxidized state (Fe^{III} or Ti^{IV}) or partial additional oxidation ($V^{III} \rightarrow V^{IV}$) may lower its effective concentration and/or its reactivity. Our experiments yield no mechanistic information concerning reaction(s) 10, the formation of the binuclear μ-$(OH)_2$-bridged product which is ultimately observed.[44]

The course of the reaction of the superoxo complex **I** with the 2e⁻ reductants Sn^{II}, U^{IV}, and $(Mo^V)_2$ remains unclear. No detectable quantity of the μ-peroxo complex **II** is formed with these reagents, and the close approach to 1:1 stoichiometry in each case is consistent with conversion to a superoxo complex of $(Rh^{II})_2$. However, neither a 3-peak ESR signal nor strong absorbance in the visible region, both considered to be characteristic of the $(Rh^{II})_2$-superoxo function,[45] was observed with these reaction mixtures. Work on these systems is continuing.

Acknowledgment. We thank Ms. Arla McPherson for technical assistance.

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(44) For evidence that making and breaking of the μ-OH bridges between Rh(III) centers are more facile than the usual ligand exchange reactions about ordinarily substitution-inert Rh(III), see: Christensson, F.; Springborg, J. *Inorg. Chem.* **1985**, *24*, 2129.

(45) See, for example: Bear, J. L.; Yao, C.-L.; Capdevielle, F. J.; Kadish, K. M. *Inorg. Chem.* **1988**, *27*, 3782.