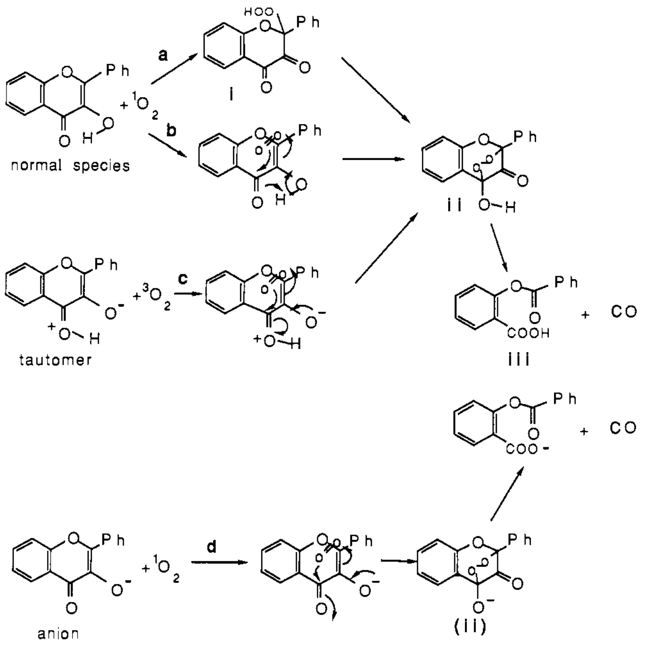
Scheme I



CD$_3$OD. This result implies that the rate-determining step for the 3HF + $^1\Delta_g$ O$_2$ reaction may be due to the thermally activated proton transfer during the peroxidation reaction. The extremely high reactivity of the 3HF anion species toward $^1\Delta_g$ O$_2$ is due to the strong nucleophilic C=C—O$^-$ enolate ion which reacts with the electrophilic $^1\Delta_g$ O$_2$ (mechanism d).[12]

(ii) In the Tautomer State. The photooxygenation was also performed upon direct excitation (320–360 nm) of 3HF in O$_2$-saturated nonpolar solvents. The reaction product is qualitatively the same as that of the sensitization experiment. According to the above results, the mechanism of the photoreaction cannot be ascribed to the 3HF (normal form) + $^1\Delta_g$ O$_2$ reaction. Since the proton-transfer reaction of 3HF occurs rapidly in the excited state,[1] the tautomer is concluded to be the reactive species. On the basis of the mechanism deduced from the 3HF (normal form) + $^1\Delta_g$ O$_2$ reaction, the mechanism of the tautomer + $^3\Sigma_g$ O$_2$ reaction can be rationalized by the strong electrophilic C=OH$^+$ functional group and the highly nucleophilic C=C—O$^-$ functional group of the tautomer species (mechanism c).

The possible role of the tautomer S$_1$ state in the photooxygenation reaction is ruled out since the quenching of the steady-state tautomer emission by molecular oxygen ($^3\Sigma_g$ O$_2$ state) is negligible. Applying transient absorption and two-step laser excitation (TSLE) techniques, the existence of a long-lived tautomer ground state (lifetime of ~13 μs in nonpolar solvent) has been reported by Itoh et al.[11–o] We recently confirmed Itoh's results, but the assignment of the long-lived tautomer species to either the ground state or the triplet state is uncertain. By monitoring the dynamics of the transient tautomer emission from a TSLE experiment,[14] our results show that $^3\Sigma_g$ O$_2$ quenches the long-lived tautomer species with a bimolecular rate constant of 3×10^9 M^{-1} s^{-1}. However, the yield of the photoreaction monitored by the decrease of absorbance at 360 nm is <0.01, indicating that the rate of quenching by $^3\Sigma_g$ O$_2$ is dominated by physical deactivation. The observed quenching rate constant by $^3\Sigma_g$ O$_2$ is close to $^1/_9$ of the diffusional controlled rate, which is the expected value for a T–T energy transfer based on theoretical calculations.[14] Furthermore, the tautomer triplet state + $^3\Sigma_g$ O$_2$ reaction is spin allowed, while the tautomer (S$_0$) + $^3\Sigma_g$ O$_2$ reaction to form the five-membered cyclic peroxide (ii, Scheme I) is strictly a spin forbidden process. Thus, the long-lived transient species is likely ascribed to the tautomer triplet state rather than the singlet ground state.[11–o] If this is the case, the observed 437 nm transient absorption band[11,14] can be interpreted as the tautomer T$_1$ → T$_n$ transition. In order to explain the observed tautomer emission from the TSLE experiment, we further propose that the excitation of the tautomer triplet state to a highly excited triplet state by the probe pulse (437 nm) is followed by rapid intersystem crossing to a tautomer excited singlet state (S$_n$), which subsequently leads to the observed tautomer fluorescence. It is noted, however, that the high efficiency of the T–S intersystem crossing is quite anomalous for nonhalogenated aromatic compounds.[22,23] Further research focusing on the intriguing photophysics of the triplet state is currently in progress.

Table I. Solvent Quenching Rate Constants (k_{sol}) of $^1O_2$ and Bimolecular Quenching Rate Constants for the 3HF + $^1O_2$ Reaction (k_q)

	k_{sol}^{-1} (μs)		
solvent	this work	literature	k_q (M^{-1} s^{-1})
CCl$_4$	769	900 (16), 700 (17)	1.72×10^4
C$_6$H$_6$	30	32 (16)	1.87×10^4
C$_6$D$_6$ (95%-*d*)	250	700 (18)	1.6×10^4
CH$_3$CN	83	87 (19), 68 (20)	1.05×10^5
CD$_3$CN	1219	599 (19), 621 (21)	1.14×10^5
CH$_3$OH	10.25	10.4 (21)	2.3×10^5
CD$_3$OD	245	227 (21)	9.0×10^4
C$_5$H$_5$N	5.7		7.5×10^7
D$_2$O (pD = 3)	70	63 (19)	2.5×10^5
D$_2$O (1.0 N NaOD)	64		1.9×10^8
H$_2$O (1.0 N NaOH)	4.1	4.1 (19), 4.2 (21)	2.3×10^8

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Metal Oxide Bound Rhodium Dioxygen and Ozone Complexes

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The search for species capable of catalyzing oxidation of organic substrates by oxygen or by simple oxidizing reagents has been assisted by the development of catalyst species which are themselves nondegradable under oxidizing reaction conditions. In this regard, metal oxides have long been known as oxidation catalysts[1] of tremendous value. Soluble analogues[2] of many of these oxides have been created to help understand the reactivity of bulk materials; species with properties different from those exhibited by bulk materials may be obtained through controlled synthesis. Our approach[3] involves preparing, in a controlled fashion, surface-bound organometallic species, and we now report the oxidation of two such rhodium species which can be converted under mild

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(1) For example, see: Wachs, I. E.; Saleh, R. Y.; Chan, S. S.; Chersich, C. *Chemtech* **1985**, 756; *Appl. Catal.* **1985**, *15*, 339. Wachs, I. E.; Chan, S. S. *Appl. Surf. Sci.* **1984**, *20*, 181.

(2) For example, see: Renneke, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **1986**, *108*, 3528 and references cited therein.

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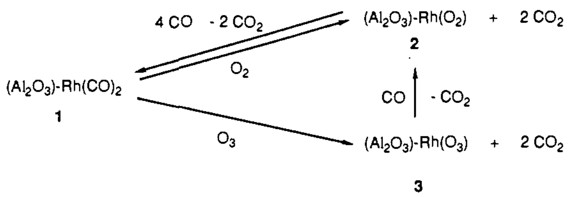
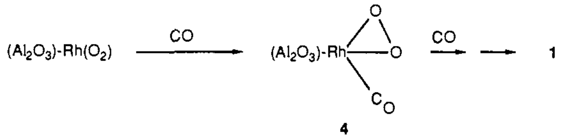
Scheme I



Scheme II



conditions to dioxygen or ozone adducts using O_2 or O_3, respectively. We believe the latter compound to be the first example of an ozone complex prepared and stable under ambient conditions.[4]

Reaction between an octane solution of (allyl)$Rh(CO)_2$ and alumina or between a toluene solution of $(allyl)_3Rh$ and alumina followed by carbonylation gives bound, mononuclear rhodium dicarbonyl compound **1**.[5] When this material was treated in a stream of dry O_2 (1 atm, 140 °C, 500 h), the characteristic metal dicarbonyl infrared absorption at 2060 and 2090 cm^{-1} was lost resulting in a spectrum for **2** which is featureless in the region 3000–1000 cm^{-1}, and which was masked by oxide absorption below that energy. Similar infrared results were obtained when **1** was treated with dry ozone (1% in O_2, 25 °C, 5 h) to give **3**. X-ray photoelectron spectroscopy was performed on **2** and **3** to assign them as oxidized rhodium compounds.[6] In this way, binding energies for Rh $3d_{5/2}$ = 309.0 and 310.0 eV (vs C 1s = 284.3 eV) were obtained for **2** and **3**, respectively. (For comparison, Rh_2O_3 $3d_{5/2}$ = 309.1 eV;[7] for **1**, 308.9 eV; for Rh(metal)/Al_2O_3, 307.5 eV.[8]) Treating either **2** or **3** with CO regenerated **1**, and quantitative analysis of the oxidation of **1**, or recarbonylation of **2** or **3** confirms the stoichiometries of these materials as O_2 and O_3 adducts, respectively. For example, **2** reacted with CO in a closed system by sequential CO addition at 20–30 mm at 120 °C for a total reaction time of 466 h to give 2 equiv of CO_2. An additional 2 equiv of CO were absorbed to regenerate **1**. A similar procedure with **3** gave 3 equiv of CO_2 and **1** (a net uptake of 5 equiv of CO).[9] In this latter study it was found that 1 equiv of CO_2 was produced rapidly, but the next 2 equiv of CO_2 were produced slowly (Scheme I).

The oxidation of CO by **2** was studied through sequential addition of fractional equivalent amounts of CO.[10] An intermediate carbonyl compound (**4**) was obtained (ν_{CO} = 2100 cm^{-1}). Under these conditions (118 °C, ~0.4 mm p_{CO}, 1 h), uptake of up to 1 equiv of CO occurs with no measurable CO_2 production. When quantities exceeding 1 equiv of CO were used, CO_2 production was observed. We believe that oxidation of CO occurs as shown in Scheme II.

Consistent with the interconversions shown in Scheme I, it was found that **2** would catalyze oxidation of CO to CO_2 by O_2. Under a variety of conditions tested, rates for oxidation of CO catalyzed by these materials which are prepared by specified organometallic deposition routes, compare favorably with results obtained for likely similar (carbonyl) compounds formed by inorganic impregnation, reduction, and carbonylation procedures.[11] (Indeed compounds observed in situ for CO oxidation by these latter species[11] may be **2** and **4**.) Analogues of **2** and **3** were prepared on titania or silica (XPS: for TiO_2–**3**, 311.0 eV; for SiO_2–**2**, 310.0 eV[12]). Oxidation of CO catalyzed by these materials occurs at different relative rates depending on the CO:O_2 ratio. Thus when CO:O_2 = 5 (the "resting species" is likely **1**[13]) relative rates for CO_2 production are 1.84:1.1:1 for titania-, silica-, and alumina-supported materials, respectively, while for CO:O_2 = 0.54 (the "resting species" likely also contains **4**[14]), rates are 9.2:2.1:1. These small but real differences in reactivity may be due to different geometrical requirements for oxide ligand coordination afforded by the various oxides to the rhodium complexes in their reduced (**1**) or oxidized (**2**) forms. Detailed structural investigations of **2** and **3** are now underway, as are examinations of reactivity of these materials with organic substrates.

Acknowledgment. We acknowledge support for this research provided by the Gas Research Institute and the National Science Foundation. We also thank Dr. Dennis Anderson, Englehardt Industries, for XPS data.

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[9] Stoichiometries of these complexes were determined by subjecting a weighed amount of each to a series of aliquots of CO in a closed system at 120 °C. Species **2** was given 14 aliquots of CO (20–30 mmHg, ~8 equiv per Rh) for 12–80 h. At the end of each period the system was assayed for CO_2 content by GC. The reaction was judged to be complete when 80 hours had elapsed with no further detectable conversion. A similar procedure was used with **3**.

[10] Complex **2** was treated with fractional equivalents of CO (0.1–0.3 equiv of CO/Rh, ~0.4 mm p_{CO}) at 118 °C for short periods (~1 h).

[11] For example, see: Kiss, J. T.; Gonzalez, R. D. *J. Phys. Chem.* **1984**, *88*, 898.

[12] Cannon, K. C.; Jo, S. K.; White, J. M. private communication.

[13] Under these conditions (95 °C, p_{CO} = 30 mm, p_{O_2} = 6 mm), determined in situ, ν_{CO} = 2100, 2030 cm^{-1} for the Al_2O_3-bound material. Rates for CO oxidation are as follows: (TiO_2) 1.15 × 10^{-5} equiv/s; (SiO_2) 6.8 × 10^{-6} equiv/s; (Al_2O_3) 6.3 × 10^{-6} equiv/s.

[14] Under these conditions (95 °C, p_{CO} = 10 mm, p_{O_2} = 18.5 mm), determined in situ, ν_{CO} = 2138 (sh), 2100, 2030 cm^{-1} for the Al_2O_3-bound material. Rates for CO oxidation are as follows: (TiO_2) 4.73 × 10^{-5} equiv/s; (SiO_2) 1.06 × 10^{-5} equiv/s; (Al_2O_3) 5.2 × 10^{-6} equiv/s.

Ferromagnetic Coupling via Imidazolate in an Iron(III)-Porphyrin-Dicopper(II) System

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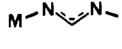
The demonstrated,[1] postulated,[2] or possible[3] existence of histidine-derived imidazolate bridging ligands in multimetal proteins



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