Volume 32
Number 24
November 24, 1993

Inorganic Chemistry

Communications

Reactions of Singlet Oxygen with Organometallic Complexes. 2. Formation of a Metastable Rhodium–Dioxygen Complex

Matthias Selke, Christopher S. Foote,* and William L. Karney

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569

Received September 9, 1993

Many coordinatively unsaturated organometallic complexes react with triplet dioxygen to form metal–dioxygen complexes.[1,2] The oxidative addition of triplet oxygen to *trans*-$Ir(CO)Cl(PPh_3)_2$ (Vaska's Complex) was one of the first of these reactions to be discovered.[3,4] However, the rhodium analogue, *trans*-$Rh(CO)Cl(PPh_3)_2$, **1**, does not react with triplet oxygen under normal conditions,[1,5,6] and the corresponding rhodium–dioxygen complex is unknown. We recently reported that *trans*-$Ir(CO)Cl(PPh_3)_2$ react approximately 10^9 times faster with singlet oxygen than with triplet oxygen.[7] We now report that singlet oxygen reacts rapidly with **1** to give a dioxygen adduct that is stable only below 0 °C.

On reaction of **1** with singlet oxygen at low temperature (Methylene Blue or C_{60} sensitizer in $CHCl_3$, Cermax 300-W xenon lamp, cut-off at 554 nm), the previously unknown rhodium-peroxo complex *trans*-$Rh(CO)Cl(PPh_3)_2O_2$ (**2**) is obtained, easily identified by the appearance of a new carbonyl peak at 2044 cm^{-1} (ν_{CO} for **1** = 1980 cm^{-1}) as well as a weak peroxo stretch at 901 cm^{-1} (Table I). Upon warming of the peroxo complex **2** to room temperature, both the stretch at 2044 cm^{-1} (Figure 1) and that at 901 cm^{-1} (not shown) disappear at the same rate. Similar IR bands occur in the analogous iridium–peroxo complexes[1–4] (Table I). The change in carbonyl frequency between **1** and **2** is 64 cm^{-1}, while that between *trans*-$Ir(CO)Cl(PPh_3)_2$ and the corresponding adduct is 50 cm^{-1}. The large shift between ν_{CO} of **1** and **2** suggests that the peroxo complex is very electron poor. For derivatives of Vaska's complex, the difference between ν_{CO} of the starting complex and the peroxo complex and the peroxo complex decreases with increasing basicity of the metal.[8]

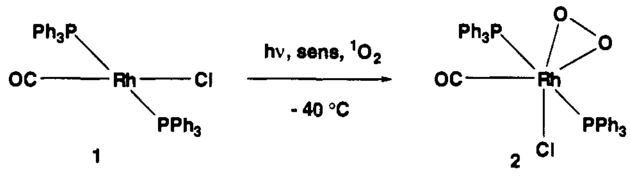

Table I. Spectral Data for **2** and $Ir(CO)Cl(PPh_3)O_2$

compd	ν_{CO}, cm^{-1}	ν_{OO}, cm^{-1}	$\delta(^{31}P)$, ppm
$Ir(CO)Cl(PPh_3)_2O_2$	2000[a]	860[a]	+5.2[b]
$Rh(CO)Cl(PPh_3)_2O_2$	2043[c]	901[c]	+39.6 (d, *J*(PRh) = 84 Hz)[d]

[a] Reference 4. [b] 304 K.[9] [c] In $CHCl_3$, −42 °C. [d] $CDCl_3$, 233 K, external $P(OMe)_3$ reference.

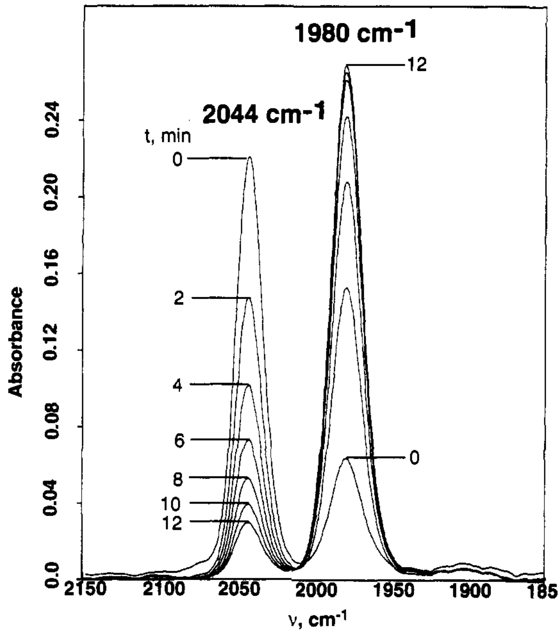

Figure 1. Disappearance of **2** (2044 cm^{-1}) and appearance of **1** at 1980 cm^{-1} at +6 °C in $CHCl_3$.

Compound **2** has a doublet at 39.6 ppm (d, *J*(PRh) = 84 Hz) in the 360-Mhz ^{31}P NMR spectrum at −40 °C; upon warming of the sample to room temperature, this doublet disappears as the

---

(1) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235–245 and references cited therein.
(2) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175–183.
(3) Vaska, L. *Science* **1963**, *140*, 840–841.
(4) Vaska, L.; Bath, S. S. *J. Am. Chem. Soc.* **1966**, *88*, 1333–1335.
(5) Vaska, L. *Inorg. Chim. Acta* **1971**, *5*, 295–300.
(6) Prolonged reflux of 1 in oxygen-saturated solution leads to loss of a PPh_3 ligand and formation of the tetramer $Rh_4Cl_4(CO)_4(O_2)_2P_2$: Cullen, W. R.; James, B. R.; Strukul, G. *Inorg. Chem.* **1978**, *17*, 484–486.
(7) Selke, M.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 1166–1167.
(8) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511–3514.
(9) Vanderpool, R. A.; Abrahamson, H. B. *Inorg. Chem.* **1985**, *24*, 2985–2989.

0020-1669/93/1332-5425$04.00/0

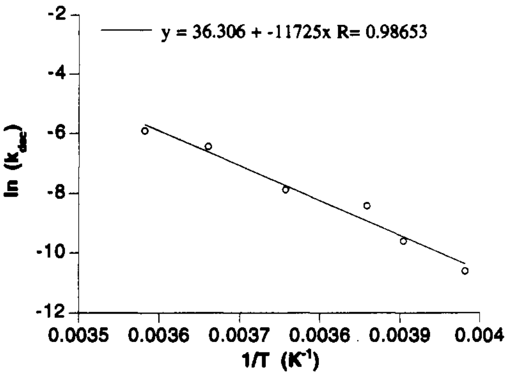

Figure 2. Arrhenius plot for the decomposition of **2**. Measurements of the decay rate were taken from 279 to 251 K in $CHCl_3$.

Table II. Kinetic Parameters ($\times 10^8$ M^{-1} s^{-1}) for *trans*-$Ir(CO)Cl(PPh_3)$ and **1** in $CDCl_3$

	$k_R + k_Q$	k_R	k_Q
trans-$Ir(CO)Cl(PPh_3)_2$[a]	2.6 ± 0.2	0.2 ± 0.08	2.4 ± 0.3
trans-$Rh(CO)Cl(PPh_3)_2$	3.1 ± 0.2	1.2 ± 0.5	1.9 ± 0.7

[a] From ref 7.

adduct loses oxygen and that of the starting material at 34.4 ppm (d, $J(PRh)$ = 124 Hz) reappears. Spectral data for **2** and $Ir(CO)Cl(PPh_3)_2O_2$ are summarized in Table I.

Compound **2** has a half-life of less than 1 min in $CHCl_3$ at room temperature and rapidly re-forms starting material **1**, losing molecular oxygen. The half-life of **2** is approximately 7 min at 0 °C, and it is indefinitely stable below -40 °C in $CHCl_3$. The decomposition of **2** in $CHCl_3$ at various temperatures was monitored by disappearance of the carbonyl peak and the corresponding appearance of that of **1** (Figure 1).[10] In all cases, first-order kinetics were observed.

The natural logs of the rate constants (k_{dec}) measured by changes in the infrared spectra were plotted against the reciprocals of the corresponding temperatures. The resulting Arrhenius plot is shown in Figure 2; $\Delta H^{\ddagger}$ = 23 ± 2 kcal/mol and $\Delta S^{\ddagger}$ = 13 eu for the decomposition of **2** at 0 °C.

As with the $Ir(CO)Cl(PPh_3)_2O_2$ complex, decomposition of **2** released oxygen only in the triplet state. When a sample of diphenylisobenzofuran (DPBF) is added to a 2–5-fold excess of **2** at 231 K, no change (≤1%, at 450 nm) in the DPBF concentration is observed upon warming the mixture to room temperature. If as much as 1% of the oxygen had been in the singlet state, measurable loss of DPBF would have occurred.

The sum of the rates of physical (k_Q) and chemical (k_R) quenching of singlet oxygen by **1** was determined by $^1O_2$ luminescence quenching[11] to be (3.1 ± 0.2) × 10^8 M^{-1} s^{-1} in $CDCl_3$. This value is approximately 20% larger than that for *trans*-$Ir(CO)Cl(PPh_3)_2$ in $CDCl_3$ ((2.6 ± 0.2) × 10^8 M^{-1} s^{-1}).[7]

In order to obtain the rate constant of chemical quenching (k_R), the disappearance of **1** was measured at different concentrations in $CDCl_3$ at room temperature. Since the resulting peroxide **2** rapidly re-forms **1** at room temperature, measurements were done by rapidly firing 6–15 laser shots at the solution within 2 or 3 s and measuring the decrease in observed decay rate of singlet oxygen caused by loss of **1**. The concentration of **1** after irradiation is given by eq 1 (where k_{obs} is the rate constant of singlet oxygen luminescence decay and k_d is the rate constant of singlet oxygen decay in the solvent and the superscripts 0 and f refer to initial and final, respectively).

$$\frac{[Rh(CO)Cl(PPh_3)_2]^f}{[Rh(CO)Cl(PPh_3)_2]^0} = \frac{k_{obs}{}^f - k_d}{k_{obs}{}^0 - k_d} \tag{1}$$

The relationship between the reciprocal of the rate of disappearance of **1** and $[\mathbf{1}]^{-1}$ is expressed in eq 2, where K is the rate of singlet oxygen formation.[7,12]

$$\Delta[Rh(CO)Cl(PPh_3)_2]^{-1} = (K\Delta t)^{-1}\left(\frac{k_R + k_Q}{k_R} + \frac{k_d}{k_R}[Rh(CO)Cl(PPh_3)_2]^{-1}\right) \tag{2}$$

A plot of $\Delta[Rh(CO)Cl(PPh_3)_2]^{-1}$ vs $[Rh(CO)Cl(PPh_3)_2]^{-1}$ yields a straight line with an intercept of $(K\Delta t)^{-1}(k_R + k_Q)/k_R$ (data not shown).[7,12] The value of $(K\Delta t)^{-1}$ is determined by a similar measurement on tetramethylethylene, which quenches singlet oxygen only by a chemical mechanism. The value of k_R is then obtained by substituting the value of ($k_R + k_Q$); k_R for **1** is (1.2 ± 0.5) × 10^8 M^{-1} s^{-1} in $CDCl_3$. The value for physical quenching alone is the difference, (1.9 ± 0.7) × 10^8 M^{-1} s^{-1}. This value is identical within limits of error to that for the physical quenching by *trans*-$Ir(CO)Cl(PPh_3)_2$ in $CDCl_3$.[7]

Corey and Khan[13,14] and Detty[15] have recently suggested that quenching of singlet oxygen by organometallic complexes can be caused by heavy-atom-promoted spin–orbit coupling which enhances intersystem crossing. Our results are not in agreement with this suggestion. Iridium has a much higher atomic number than rhodium, yet the physical quenching rate of *trans*-$Rh(CO)Cl(PPh_3)_2$ is about the same as that of *trans*-$Ir(CO)Cl(PPh_3)_2$. Kinetic parameters for **1** and for *trans*-$Ir(CO)Cl(PPh_3)_2$ are summarized in Table II.

The enormous increase in the rate constant for reaction of singlet oxygen with both the iridium and rhodium complexes compared to that with triplet oxygen could be due to removal of the spin barrier. However, since both oxygen adducts release oxygen only in the triplet state, spin conservation does not seem to be a problem in these high-Z complexes. It is more likely that the high reactivity comes from the 22.4-kcal increase in energy of singlet oxygen, which is sufficient to decrease or even exceed the activation energy of the reaction with ground-state oxygen. This is the case with Vaska's complex, where $\Delta H^{\ddagger}$ is only 13.1 kcal/mol for reaction with triplet oxygen.[8] Most compounds react with singlet oxygen with very low enthalpies of activation; the reaction rate constant is usually decreased about 2 powers of 10 by an unfavorable entropy of activation. If this is also the case with the rhodium and iridium complexes, the reaction rate constants for these complexes (which are both 2 orders of magnitude below the diffusion rate constant) are limited only by the entropy of activation.

These results suggest that novel energetic and transient metal–oxygen complexes which may have interesting reactivities or may mimic biologically important enzyme intermediates can be readily prepared by reacting singlet oxygen with organometallic compounds at low temperature. Further experiments in this direction are in progress.

Acknowledgment. This work was supported by NSF Grant No. CHO89-14366. We thank Prof. O. L. Chapman for use of the low-temperature IR.

---

(10) A $CHCl_3$ solution of **1** and the sensitizer (Methylene Blue or C_{60}) in a small volumetric flask was cooled to -42 °C (dry ice/CH_3CN). The cooled solution was irradiated in a transparent Dewar flask while a slow stream of oxygen was bubbled through. Excitation of **1** was prevented with a long-pass glass filter with a cut-off at 554 nm. After 20–30 min, an aliquot was drawn into a precooled syringe and transferred to the precooled IR solution cell, an RIIC VLT-2 variable-temperature cell with KBr windows (0.1-mm path length). Temperatures below room temperature were achieved using slush baths of different solvents and either dry ice or liquid N_2. Solutions were kept in the cell for 10–15 min for temperature equilibration. IR spectra were then obtained using a Nicolet 60SX FTIR spectrometer using 16 scans at 2- or 4-cm^{-1} resolution.

(11) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430.

(12) Foote, C. S.; Ching, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 6209–6214.

(13) Corey, E. J.; Mehrotra, M. M.; Kahn, A. U. *Science* **1987**, *236*, 68–69.

(14) Corey, E. J.; Kahn, A. U. *Tetrahedron Lett.* **1990**, *31*, 1389–1392.

(15) Detty, M. R. *Organometallics* **1992**, *11*, 2310–2312.