The Dioxygen Ligand in Mononuclear Group VIII Transition Metal Complexes

JOAN S. VALENTINE

Department of Chemistry, Douglass College, Rutgers University, New Brunswick, New Jersey 08903

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Contents

I. Introduction

Molecular oxygen functions both as a ligand and as a reagent in transition metal organometallic chemistry. Recent interest in the chemistry of molecular oxygen has involved biochemists interested in biological oxygen transport and oxidase function as well as industrial chemists interested in developing homogeneous analogs to heterogeneous metal-catalyzed oxidation reactions. The isolation and characterization of stable dioxygen complexes and the variety of reactions that they themselves undergo are beginning to yield general information about bonding, structure, and reactivity of coordinated molecular oxygen.

Biochemical interest in the interaction of molecular oxygen with group VIII transition metal complexes is based upon the search for model systems[1-3] which mimic hemoglobin and related iron-containing molecular oxygen carriers in reversibly combining with molecular oxygen[4] and also models for oxidases, nonheme iron proteins which catalyze the insertion of oxygen atoms derived from molecular oxygen into biological substrates.[5,6]

Systems studied as models for industrial processes are usually soluble metal complexes that in homogeneous solution undergo stoichiometric reactions similar to those observed in heterogeneous metal catalysis. The contact process for manufacture of sulfuric acid involves conversion of SO_2 and O_2 to SO_3 over a platinum catalyst.[7] Possible models for this process are reactions 1 and 2.[8] Several related reactions are also known.[9,10]

$$\mathrm{Pt(PPh_3)_2(O_2) + SO_2} \rightarrow \mathrm{Pt(PPh_3)_2(SO_4)} \quad (1)$$

$$\mathrm{Pt(PPh_3)_2(SO_2) + O_2} \rightarrow \mathrm{Pt(PPh_3)_2(SO_4)} \quad (2)$$

Another industrial reaction, the Ostwald process, which is used in the synthesis of nitric acid, involves the combination of ammonia with molecular oxygen over a platinum or platinum-rhodium catalyst producing nitric oxide according to reaction 3, whereas burning of ammonia in air gives molecular nitrogen according to reaction 4.[11]

$$4NH_3 + 5O_2 \overset{Pt}{\rightleftarrows} 4NO + 6H_2O \qquad K_{25^\circ} = 10^{168} \quad (3)$$

$$4NH_3 + 3O_2 \rightleftarrows 2N_2 + 6H_2O \qquad K_{25^\circ} = 10^{228} \quad (4)$$

Because of the importance of molecular oxygen as a reagent in biological and industrial processes and because dioxygen is an interesting ligand in its own right, current research in this area has been directed toward understanding the bonding of dioxygen to transition metal complexes and the effect of this bonding upon its reactivity toward other substrates.

This review is primarily concerned with the reactions of d^8 or d^{10} metal complexes with molecular oxygen. This subject has not been reviewed previously. This review covers the literature through February 1972. Although the reactions of cobalt(II) complexes with oxygen are discussed, a complete review of these complexes must cover the biochemical literature, and this has not been attempted. Moreover, a recent review of cobalt(II) dioxygen complexes is available.[12,12a]

II. The Oxygen Molecule

A. Bonding

The bonding in molecular oxygen is best described by molecular orbital theory.[13] According to this theory, the valence orbitals of the two oxygen atoms ($2s^22p^4$) combine to give molecular orbitals whose relative energies are shown in Figure 1. The ground state of molecular oxygen is predicted and observed to be a triplet state ($^3\Sigma$) with two unpaired electrons occupying a pair of degenerate π^* antibonding orbitals. The two lowest excited states are formed by redistributing the two electrons

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(1) L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963).

(2) J. H. Wang, *Accounts Chem. Res.*, **3**, 90 (1970).

(3) E. Bayer and P. Schretzmann, *Struct. Bonding (Berlin)*, **2**, 181 (1967).

(4) G. Buse, *Angew. Chem., Int. Ed. Engl.*, **10**, 663 (1971).

(5) O. Hayaishi, "Oxygenases," Academic Press, New York, N. Y., 1962.

(6) K. B. Sharpless and T. C. Flood, *J. Amer. Chem. Soc.*, **93**, 2316 (1971).

(7) L. C. Schroeter, "Sulfur Dioxide," Pergamon Press, Oxford, 1966, p 34.

(8) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **89**, 3066 (1967).

(9) J. Valentine, D. Valentine Jr., and J. P. Collman, *Inorg. Chem.*, **10**, 219 (1971).

(10) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 762 (1971).

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 333.

(12) R. G. Wilkins, *Advan. Chem. Ser.*, **No. 100**, 111 (1971).

(12a) Note Added in Proof. A related review has recently appeared: V. J. Choy and C. J. O'Connor, *Coord. Chem. Rev.*, **9**, 145 (1972/73).

(13) H. Taube, *J. Gen. Physiol.*, **49** (2), 29 (1965).

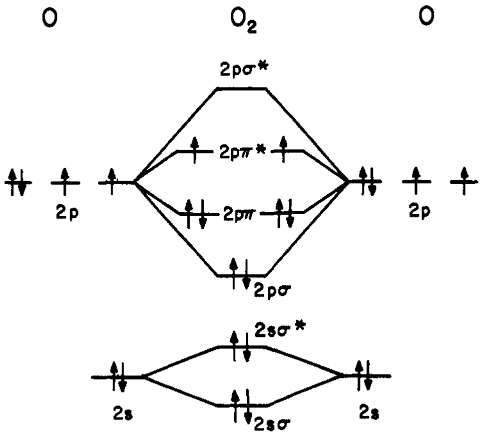


Figure 1. Molecular orbital diagram for O_2.

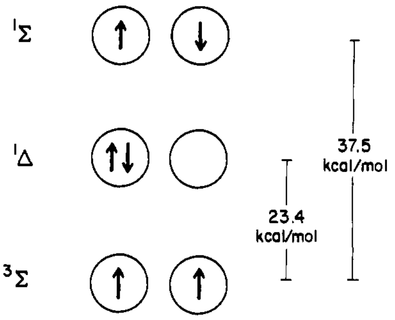


Figure 2. π* orbital occupancy and energies of the first two electronically excited states of O_2.

TABLE I. Inorganic Compounds of Dioxygen

	Example compd	O-O, Å[a]	Bond energy,[b] kcal/mol
O_2^+	O_2PtF_6	1.12	
O_2		1.21	118
O_2^- (superoxide)	KO_2	1.28	
O_2^{2-} (peroxide)	H_2O_2	1.49	35

[a] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 333. [b] Reference 13.

in these 2pπ* antibonding orbitals. The configurations and energies for the ground state and first two excited states are shown in Figure 2.

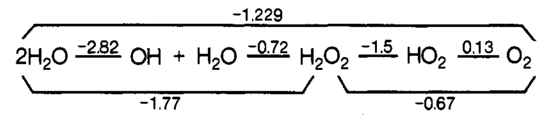
Molecular orbital theory also predicts bond orders of 2.5, 2, 1.5, and 1 for the dioxygenyl cation O_2^+, molecular oxygen O_2, superoxide O_2^-, and peroxide O_2^{2-}, respectively. The bond lengths and bond energies of these species reflect this order (see Table I).

B. Reactivity

The redox potential for the reduction of molecular oxygen to water in acidic solution (reaction 5) is that of a

$$2H_2O = O_2 + 4H^+ + 4e^- \quad -1.23\ V \qquad (5)$$

powerful oxidizing agent. Varying degrees of reactivity are observed in different systems.[14] This is probably due to the stepwise nature of the reduction and the fact that formation of HO_2 (one-electron reduction of O_2) is energetically unfavorable. Redox potentials for O_2 in acidic solution at 25° in volts are summarized below.[15]



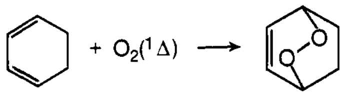
Ground-state molecular oxygen reacts with organic substrates by stepwise free-radical mechanisms as might be expected since it is paramagnetic. A typical reaction sequence is outlined in reactions 6-8 where X· is a radical initiator.

$$X\cdot + RH \longrightarrow R\cdot + XH \qquad (6)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (7)$$

$$RO_2\cdot + RH \longrightarrow ROOH + R\cdot \longrightarrow \text{etc.} \qquad (8)$$

Molecular mechanisms are usually observed for reactions of excited singlet molecular oxygen (probably mostly $O_2(^1\Delta)$) with organic substrates (for example, reaction 9). Although a concerted mechanism is not disallowed by spin conservation, there is no compelling evidence that these reactions are concerted. In fact, some recent studies of addition of $^1\Delta(O_2)$ to olefins suggests that the addition may be stepwise.[16]



(9)

Autoxidation of transition metal ions (reaction 10) seems to occur by different pathways depending upon the nature of the metal ion. In general, formation of HO_2 appears to be the unfavorable but necessary pathway unless a two-electron reduction can occur or the reaction can proceed through a binuclear intermediate.[14]

$$4M^{n+} + O_2 + 4H^+ \longrightarrow 4M^{n+1} + 2H_2O \qquad (10)$$

In the context of this review, it is interesting to note that although some oxidations of transition metal complexes by molecular oxygen appear to go by an outer-sphere mechanism, others are thought to involve the reversible formation of an unstable metal-dioxygen complex as a first step. This metal-dioxygen complex then undergoes electron transfer to form coordinated O_2^- or coordination of another metal ion followed by electron transfer to form coordinated O_2^{2-}. For example, reactions 11-14 have been postulated as first steps in autoxidation mechanisms.[14]

$$Fe^{2+} + O_2 \rightleftharpoons FeO_2^{2+} \qquad (11)$$

$$Cr^{2+} + O_2 \rightleftharpoons CrO_2^{2+} \qquad (12)$$

$$Cu(NH_3)_3^+ + O_2 \rightleftharpoons Cu(NH_3)_3O_2^+ \qquad (13)$$

$$Co(CN)_5^{3-} + O_2 \rightleftharpoons Co(CN)_5O_2^{3-} \qquad (14)$$

III. Organometallic Dioxygen Complexes of Group VIII Transition Metals

A. Structure and Bonding

Two different classes of 1:1 bonding of the dioxygen ligand to transition metal complexes (I and II) have been demonstrated. Class I compounds whose structures are known from X-ray crystallography are summarized in Table II. These compounds are diamagnetic 1:1 adducts of dioxygen with organometallic group VIII transition metal complexes in which the O-O bond remains intact but is longer than in free O_2 and the two M-O distances

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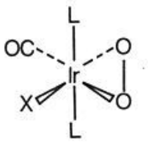
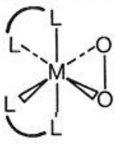
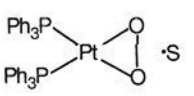
(14) S. Fallab, *Angew. Chem., Int. Ed. Engl.*, **6**, 496 (1967).

(15) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," 2nd ed, Prentice-Hall, New York, N. Y., 1952, p 50.

(16) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, **No.** 77, 102 (1968).

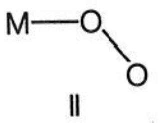
TABLE II. Known Structures of Class I Mononuclear Dioxygen Complexes

Structure	L	X	O–O, Å	Ref
	PPh_3	Cl	1.30 ± 0.03	*a*
	PPh_3	Br	1.36 ± 0.04	*b*
	PPh_3	I	1.509 ± 0.026	*c*
	PPh_2Et	Cl	1.461 ± 0.014	*d*
	M	L—L	O–O, Å	Ref
	Rh	$Ph_2PCH_2CH_2PPh_2$	1.418 ± 0.011	*e*
	Ir	$Ph_2PCH_2CH_2PPh_2$	1.625 ± 0.023	*f*
	Co	$Ph_2PCH{=}CHPPh_2$	*1.420 ± 0.010*	*g*
	S	O–O, Å	Ref	
	$C_6H_5CH_3$	1.26 ± 0.05	*h*	
	$1.5C_6H_6$	*1.45 ± 0.04*	*i*	
	$2CHCl_3$	1.505 ± 0.016	*j*	

[a] J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965). [b] *W. A. Spofford III and E. L. Amma, unpublished results quoted in footnote g.* [c] References 53 and 56. [d] Reference 54. [e] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969). [f] J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968). [g] N. W. Terry III. E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, **94**, 653 (1972). [h] C. D. Cook, P. -T. Cheng, and S. C. Nyburg, *ibid.*, **91**, 2123 (1969), but see also ref *28.* [i] T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Commun.*, 743 (1969). [j] Ref 28, P. -T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Can. J. Chem.*, **49**, 3772 (1971).

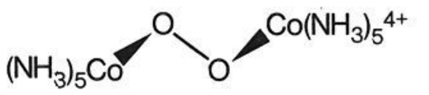
are equal. This configuration has also been observed in an iridium S_2 complex, $[Ir(diphos)_2(S_2)]^+$, in which the S–S distance is 2.10 ± 0.02 Å *vs.* 1.92 Å in free S_2.[17]

I



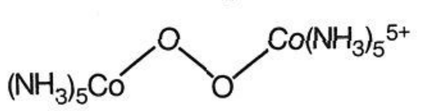
II

Class II compounds whose structures are inferred from electron spin resonance studies are paramagnetic cobalt(II) complexes with dioxygen in which the two M–O distances are believed to be unequal.[18,19] This is also apparently the configuration of the 1:1 vitamin B_{12r} dioxygen adduct.[20] A configuration resembling II is commonly found in binuclear μ-peroxo- and μ-superoxo-dicobalt ammines.[21]



μ-peroxo-bis(pentaamminecobalt)(4+)

O–O 1.47 Å,
dihedral angle 146°



μ-superoxo-bis(pentaamminecobalt)(5+)

O–O 1.31 Å, planar

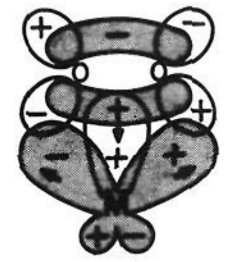


Figure 3. Bonding orbitals for class I dioxygen complexes.

Table V *summarizes known mononuclear dioxygen* complexes. In this table, complexes whose structures are unknown have generally been assigned to either class I or II on the basis of chemical and spectroscopic properties analogous to those of complexes of known structure. There are, however, some complexes for which this assignment cannot be made, for example, dioxygen complexes with properties similar to class I complexes but which have unusual coordination numbers or which are *paramagnetic. These have been labeled class* III complexes in Table V.

One very important type of metal–dioxygen complex which cannot be conclusively assigned to class I or II includes oxyhemoglobin and oxymyoglobin. These iron–heme containing proteins are diamagnetic iron dioxygen adducts whose protein structure and configuration are known but whose metal–dioxygen configuration is not. The controversy has been between those who favor configuration I, with equal M–O distances, and those who favor configuration II, with unequal M–O distances. Suggested oxidation states for iron have been 2, 3, and 4.[22-25]

The bonding of metals to O_2 in configuration I can be described by analogy to the description of acetylene–metal complexes given by Greaves, Lock, and Maitlis.[26] Both π and π^* orbitals of molecular oxygen have proper symmetry to interact with the bonding set of s, p, and d orbitals on the metal. The bonding orbitals are shown in Figure 3.[27] Conceptually a σ bond is formed by transfer of electron density from a filled dioxygen π bonding orbital to s, p, and d orbitals of appropriate symmetry on the metal, and two π bonds are formed by transfer from filled metal d orbitals into empty π^* orbitals of dioxygen.

The relative bonding depends upon the relative energies of the metal valence s, p, and d orbitals and the dioxygen π and π^* orbitals.

Three different situations can be imagined in the bonding of dioxygen to the metal. When the metal orbitals lie as high or higher than the π^* orbitals of dioxygen (case A, Figure 4), the bonding orbitals formed from metal orbitals and dioxygen π orbitals will be mostly dioxygen in character. Therefore, there will be little dioxygen-to-metal σ bonding. The π-*bonding orbitals formed conceptually* from electron transfer from the metal orbitals to dioxygen π^* orbitals, however, should have both metal and dioxygen character and hence form strong bonds. If enough electron density is transferred to the dioxygen π^* orbitals, the O–O bond will become in effect a single bond and hence longer (Figure 5, case A). By similar arguments, case C in Figure 5 should produce largely σ bonding from dioxygen to metal with little lengthening of the O–O bond and case B *should be intermediate.*

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(17) A. P. Ginsberg and W. E. Lindsell, *Chem. Commun.*, 232 (1971); W. D. Bonds and J. A. Ibers, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D.C., 1971, No. INORG 156.

(18) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, *61 (1970).*

(19) D. Diemente, B. M. Hoffman, and F. Basolo, *Chem. Commun.*, 467 (1970).

(20) G. N. Schrauzer and L. P. Lee, *J. Amer. Chem. Soc.*, **92**, 1551 (1970).

(21) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968); W. P. Schaefer and R. E. Marsh, *J. Amer. Chem. Soc.*, **88**, 178 (1966); W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966).

(22) L. Pauling and C. D. Coryell, *Proc. Nat. Acad. Sci. U. S.*, **22**, 210 (1936).

(23) J. S. Griffith, *Proc. Roy. Soc., Ser. A*, **235**, 23 (1956).

(24) J. L. Hoard in A. Rich and N. Davidson, "Structural Chemistry and Molecular Biology," W. H. Freeman, San Francisco, Calif., 1968, p 573.

(25) H. B. Gray, *Advan. Chem. Ser.*, **No. 100**, 382 (1971), and references therein.

(26) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

(27) Adapted from J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

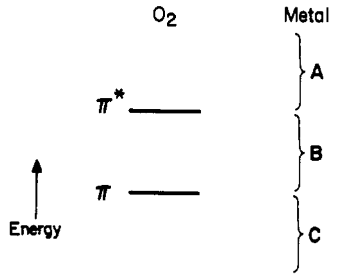


Figure 4. Relative energies of O_2 and metal bonding orbitals.

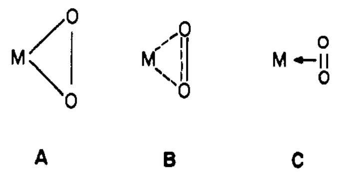


Figure 5. Schematic representations of different modes of metal-dioxygen bonding.

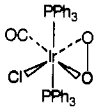
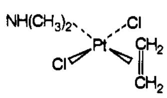
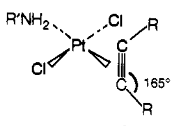
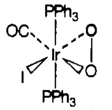
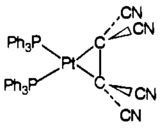
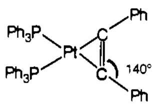
A similar situation is encountered in olefin and acetylene complexes. In these complexes, both the C-C bond distance and the bending of substituents on the olefin or acetylene away from the metal reflect the degree of reduction of the ligand (see Table III for examples).

The energies of the π and π* orbitals in olefins and acetylenes are dependent upon substituents, while those of molecular oxygen are fixed; therefore, the differences in bonding of various dioxygen complexes and especially the O-O bond length derive from differences in metal valence orbital energies. In the compounds $Ir(PPh_3)_2(CO)X(O_2)$, X = Cl or I, for example, the O-O bond lengthens from 1.30 Å for X = Cl to 1.51 Å for X = I (see Table II). The less electronegative, more polarizable iodide ligand appears to have raised the metal valence orbitals to the level in case A of Figure 4, while the chloride complex seems to be an example of B or C. Likewise, for the complex with X = Cl, when triphenylphosphine is substituted by ethyldiphenylphosphine, a more weakly back-bonding ligand, the O-O bond length increases from 1.30 to 1.46 Å reflecting a change in the metal valence orbital energies again from case B or C to case A (see Table II). There are, moreover, results from an ESCA (electron spectroscopy for chemical analysis) study that indicate that from 1.4 to 1.8 electrons are transferred from the metal to the dioxygen ligand in $Pt(PPh_3)_2(O_2)$, placing this compound in class A.[28] This is in accord with the O-O bond lengths reported for $Pt(PPh_3)_2(O_2)\cdot 1.5C_6H_6$, 1.45 Å, and $Pt(PPh_3)_2(O_2)\cdot 2CHCl_3$, 1.50 Å, but not with that reported for $Pt(PPh_3)_2(O_2)\cdot C_6H_5CH_3$, 1.26 Å[28] (see Table II).

It should also be noted that formally peroxide occupies two coordination positions as do tetracyanoethylene and diphenylacetylene in the examples in Table III. Neutral dioxygen, ethylene, and di-*tert*-butylacetylene in Table III, on the other hand, formally occupy only one. The number of coordination positions and the oxidation state of the metal and the dioxygen ligand in intermediate cases cannot be formally assigned.

The bonding of dioxygen in various 1:1 cobalt(II) molecular oxygen adducts is different from that discussed above. The one crystal structure that is known is of Co(bzacen)(pyridine)(O_2) (see Table V) which has configuration II with the Co-O-O angle 126° and the O-O distance 1.26 Å.[29] The adducts are paramagnetic and give eight-line electron spin resonance spectra (^{59}Co, $I = 7/2$) with g values and hyperfine parameters consistent with the presence of the $Co(III)-O_2^-$ group and not with that of $Co(II)-O_2^0$.[12] The esr spectra are consistent with configuration II.[18,19] One especially interesting complex in this class is coboglobin in which the four iron(II) ions in hemoglobin have been substituted by cobalt(II) ions and which reversibly combines with molecular oxygen.[30]

TABLE III. Examples of Metal Complexes with π-Bonded Ligands

O=O	$R_2C=CR_2$	RC≡CR
 O-O 1.30 Å[a]	 C-C 1.47 Å[b]	 C-C 1.24 Å[c] R = $C(CH_3)_3$
 O-O 1.51 Å[d]	 *e*	 C-C 1.32 Å[f]

[a] J. A. Ibers and S. J. La Placa, *Science*, **145**, 920 (1964); S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965). [b] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960). [c] G. R. Davies, W. Hewerston, R. H. B. Mais, P. G. Owston, and C. G. Patel, *J. Chem. Soc. A*, 1873 (1970). [d] Reference 53. [e] W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966). [f] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, **7**, P9 (1967).

The different geometries of binding of dioxygen to group VIII transition metal complexes appear to arise from the different geometries expected for complexed superoxide *vs.* complexed neutral dioxygen or peroxide.[31,32] Supporting evidence for this hypothesis is the fact that adducts of complexes that typically undergo two-electron oxidative addition reactions are found to have configuration I. Cobalt(II), however, is a one-electron reductant and thus typically forms superoxo complexes with configuration II. The difference may also be caused by different relative energy levels of metal valence orbitals and dioxygen π,π* and nonbonding orbitals.

B. Preparation and Properties

The majority of organometallic metal-dioxygen complexes are formed by reaction of gaseous molecular oxygen with d^7, d^8, or d^{10} complexes in solution. The combination of molecular oxygen with these classes of compounds can give the following results.

(1) No reaction

$$Rh(PPh_3)_2(CO)Cl \xrightarrow[\text{ref 33}]{O_2} \text{no reaction} \tag{15}$$

(2) Formation of a mononuclear dioxygen adduct with or without displacement of ligands

$$Ir(PPh_3)_2(CO)Cl \xrightarrow[\text{ref 34}]{O_2} Ir(PPh_3)_2(CO)Cl(O_2) \tag{16}$$

$$Co(DMG)_2 \xrightarrow[\text{ref 20}]{O_2,\ \text{pyridine}} Co(DMG)_2(\text{pyridine})(O_2) \tag{17}$$

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(3) Formation of a dimer or a binuclear dioxygen adduct

$$2Rh(PPh_3)_3Cl \xrightarrow[\text{ref 35}]{2O_2} [Rh(PPh_3)_2(O_2)Cl]_2 \tag{18}$$

$$2Co(histidine)_2 \xrightarrow[\text{ref 37}]{O_2} Co_2(histidine)_4(O_2) \tag{19}$$

(4) Oxidation of ligands with the oxidized ligand remaining coordinated

$$Ru(PPh_3)_2(CO)_2(SO_2) \xrightarrow[\text{ref 9}]{O_2} Ru(PPh_3)_2(CO)_2(SO_4) \tag{20}$$

(5) Displacement of free oxidized ligand

$$Pt(PPh_3)_4 \xrightarrow[\text{ref 38–40}]{2O_2} Pt(PPh_3)_2(O_2) + 2Ph_3PO \tag{21}$$

The reactivity of the d^7 cobalt(II) complexes toward molecular oxygen is a function of their ligand environments which greatly influence the redox potentials.[41] The more difficult question of why some mononuclear dioxygen complexes of cobalt(II) can be isolated before they form binuclear complexes while others cannot is probably a function of kinetics and finding the correct isolation techniques.

Presumably those organometallic complexes of group VIII transition metals with d^8 and d^{10} electronic configurations which are unreactive toward molecular oxygen have metal valence orbitals which are too low in energy; *i.e.*, they are poor reducing agents, or coordination of dioxygen is unfavorable for steric reasons. Group VIII d^{10} complexes (Ni(0), Pd(0), Pt(0)) generally react with molecular oxygen giving 1:1 adducts with ligand displacement and/or oxidized ligand. Group VIII d^8 complexes may or may not react with molecular oxygen; the reactivity correlates with reactivity in other types of oxidative addition. In general, reactivity toward molecular oxygen is increased in going from second row to third row, *i.e.*, Os(0) > Ru(0), Ir(I) > Rh(I).[42,43] Analogous compounds in the first row have not been available until recently and were assumed to be the least reactive of the triad. In fact, it appears that they may be more reactive than either second row or third row complexes. For example, in the series $[M(Ph_2PCH{=}CHPPh_2)_2]^+$, M = Co, Rh, Ir, for the reaction with H_2 and O_2, the reactivity order is Co > Ir > Rh. A correlation has been suggested between reactivity and ligand field stabilization energy.[44]

For complexes of the same metal, reactivity is increased by strong σ-donor ligands such as phosphines and by polarizable ligands (compare reactions 15 and 23). Partial or total deactivation is caused by strong π-acceptor ligands such as CO (compare reactions 16 and 22), electronegative ligands, or a positive charge on the complex (compare reactions 16 and 24).

$$Ir(PPh_3)_3Cl + O_2 \xrightarrow[\text{ref 9}]{\text{very fast}} Ir(PPh_3)_3Cl(O_2) \tag{22}$$

$$Rh(PPh_3)_2(CO)I + O_2 \xrightarrow[\text{ref 44a}]{} OPPh_3 + [Rh] \tag{23}$$

$$[Ir(PPh_3)_2(NO)Cl]^+ + O_2 \xrightarrow[\text{ref 45}]{} \text{no reaction} \tag{24}$$

The ability of d^8 iridium complexes to react with molecular oxygen also appears to be strongly influenced by steric effects.[46] For example, $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ forms a dioxygen complex (see Table II) while tetrahedrally distorted $[Ir(PPh_2CH_3)_4]^+$ does not.[47] Similarly, $IrL_2(CO)Cl$, where L = triarylphosphine, usually reacts relatively rapidly with molecular oxygen but not when L = $P(o\text{-}CH_3C_6H_4)_3$, presumably because of a steric effect.[48]

The reactivity of five-coordinate d^8 complexes toward molecular oxygen does not follow a predictable sequence. Few stable dioxygen adducts have been obtained although some of the complexes react to give oxidized ligand quite readily. The reactivity of these complexes is expected to be more influenced by steric hindrance since they are coordinatively saturated and do not have a coordination position open for attack. It is interesting in this regard to compare reactions 25 and 26. Sulfur dioxide apparently can attack a coordinatively saturated complex more readily than can molecular oxygen.[49]

$$Ir(PPh_3)_2(CO)Cl \begin{cases} \xrightarrow[\text{ref 34}]{O_2} Ir(PPh_3)_2(CO)Cl(O_2) \\ \xrightarrow[\text{ref 9}]{SO_2} Ir(PPh_3)_2(CO)Cl(SO_2) \end{cases} \tag{25}$$

$$Ru(PPh_3)_2(CO)_3 \begin{cases} \xrightarrow[\text{ref 9}]{O_2} OPPh_3(\text{very slow}) \\ \xrightarrow[\text{ref 9}]{SO_2} Ru(PPh_3)_2(CO)_2(SO_2) \end{cases} \tag{26}$$

It is not yet possible to predict which complexes will form stable dioxygen adducts and which will react further to form oxidized ligands. Possible factors are the configuration of intermediates and the relative energies of formation of metal–oxygen bonds and of oxidation of the ligands. Complexes which have labile, easily oxidizable ligands tend to give oxidized ligand presumably through an unstable intermediate dioxygen adduct. Examples are $Rh(PPh_3)_3(NO)$ and $Ir(PPh_3)_3NO$ which form triphenylphosphine oxide[9] and $M(RNC)_4$, M = Ni or Pd, which form RNCO.[50,51] The stoichiometries of these reactions are not known, however, and it is possible that the oxidation requires more than one molecule of oxygen. For example, $Ir(PPh_3)_3Cl$ forms a stable dioxygen adduct, $Ir(PPh_3)_3Cl(O_2)$, which is stable under vacuum but decomposes in the presence of excess molecular oxygen to give triphenylphosphine oxide.[9]

Complexes of ligands whose oxidized forms are themselves good ligands often react with molecular oxygen to give complexes of the oxidized ligands (*e.g.*, $M(SO_2) \rightarrow M(SO_4)$, $M(CO) \rightarrow M(CO_3)$, $M(PR_3)_2 \rightarrow M(OPR_3)_2$, $M(NO) \rightarrow M(NO_3)$; see discussion below).

Preparation of dioxygen adducts is usually accomplished by allowing a complex in solution to react with molecular oxygen or air. Reaction with air may give

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TABLE IV. Kinetic and Thermodynamic Parameters for the Formation of Dioxygen Complexes

1.[a] $Pt(PPh_3)_3 + O_2 \xrightarrow{k_2} Pt(PPh_3)_2(O_2) + PPh_3$

$k_2 = 2.6 \pm 0.1\ M^{-1}\ sec^{-1}$

(rate unaffected by up to 3×10^{-3} *M* excess PPh_3)

2.[b] $[M(Ph_2PCH{=}CHPPh_2)_2]^+ + O_2 \xrightarrow[\text{chlorobenzene}]{k_2} [M(Ph_2PCH{=}CHPPh_2)_2(O_2)]^+$

M	ΔH^*, kcal/mol	ΔS^*, eu	ΔG^*, kcal/mol	$k_2(25°)$, $M^{-1}\ sec^{-1}$
Co	3.4	−28	10.3	1.7×10^4
Rh	11.6	−24	18.8	0.12
Ir	6.5	−38	17.8	0.47

3.[c] $[M(Ph_2PCH_2CH_2PPh_2)_2]^+ + O_2 \xrightarrow[\text{chlorobenzene}]{k_2} [M(Ph_2PCH_2CH_2PPh_2)_2(O_2)]^+$

M	ΔH^*, kcal/mol	ΔS^*, eu	$k_2(30°)$, $M^{-1}\ sec^{-1}$
Rh	7.9	−35	1.1
Ir	3.6	−44	3.3

4.[d] $Ir(PPh_2)_2(CO)X + O_2 \xrightarrow[\text{benzene}]{k_2} Ir(PPh_3)_2(CO)X(O_2)$

X	ΔH^*, kcal/mol	ΔS^*, eu	$k_2(25°)$, $M^{-1}\ sec^{-1}$
Cl	13.1	−21	3.36×10^{-2}
Br	11.8	−24	0.74×10^{-1}
I	10.9	−24	0.30

5. $IrL_2(CO)X + O_2 \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} IrL_2(CO)X(O_2)$ chlorobenzene, 40°

X	L	10^2k_2, M^{-1} sec^{-1}	10^6k_{-1}, sec^{-1}	$10^{-3}K_{eq}$, M^{-1}	ΔH_2^*, kcal/mol	ΔH_{-1}^*, kcal/mol	ΔS_2^*, eu	ΔS_{-1}^*, eu	Ref
F	PPh_3	1.48	50.9	0.291	13.6	23.7	−24	−0.5	*e*
NCO	PPh_3	2.99	90.2	0.331	11.1	21.0	−30	−10	*e*
$OClO_3$	PPh_3	6.96			4.01		−50		*e*
N_3	PPh_3	7.33	13.1	5.60	9.57	26.2	−33	3	*e*
Cl	PPh_3	10.1	13.8	7.32	9.50	26.5	−33	4	*e*
Br	PPh_3	20.6	3.32	62.0	8.42	28.8	−35	8	*e*
ONO_2	PPh_3	36.3			5.50		−43		*e*
I	PPh_3	72.3	0.84	857	5.76	29.0	−41	6	*e*
NO_2	PPh_3	172			3.48		−46		*e*
Cl	$P(C_6H_{11})_3$	0.127	5.85	0.217	9.5		−42		*f*
Cl	$P(p\text{-}C_6H_4Cl)_3$	3.10	8.67	3.58	10.8		−31		*f*
Cl	$AsPh_3$	14.2	8.25	17.2	8.1		−37		*f*
Cl	$PPh_2C_2H_5$	14.2	6.75	21.0	8.4		−36		*f*
Cl	$P(p\text{-}C_6H_4CH_3)_3$	21.6	12.2	17.7	9.3		−32		*f*
Cl	$P(n\text{-}C_4H_9)_3$	26.1	3.90	66.9	9.0		−33		*f*
Cl	$P(C_2H_5)_3$	33.8	1.57	215	8.5		−34		*f*
Cl	$P(p\text{-}C_6H_4OCH_3)$	48.4	12.5	38.7	8.5		−33		*f*

6.[g] $Ir(PPh_3)_2(CO)Cl + O_2 \underset{k_{-1},\ 30°}{\overset{k_2}{\rightleftarrows}} Ir(PPh_3)_2(CO)Cl(O_2)$ chlorobenzene

$k_2 = 0.060\ M^{-1}\ sec^{-1}$
$k_{-1} = 3.5 \times 10^{-6}\ sec^{-1}$
$K_{eq} = 17{,}100\ M^{-1}$

$\Delta H_2^* = 9.3$ kcal/mol
$\Delta S_2^* = -33$ eu

$\Delta H_2° = -17.1$ kcal/mol
$\Delta S° = -37$ eu
$\Delta F_2° = -5.9$ kcal/mol

7.[h] $Ir(PPh_3)_2(CO)Cl(O_2)$

Enthalpy of removal of O_2 by differential scanning calorimetry is 130 kJ to break each Ir-O bond in crystalline complex at 298°K

[a] References 74 and 75. [b] Reference 44. [c] Reference 33. [d] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966). [e] Reference 44. [f] Reference 48. [g] L. Vaska, *Accounts Chem. Res.*, 1, 335 (1968). [h] S. J. Ashcroft and C. T. Mortimer, *J. Organometal. Chem.*, **24**, 783 (1970).

contaminated products because of further reaction of the dioxygen adduct with CO_2 in air to form a peroxycarbonate.[52] Reaction with molecular oxygen is often rapid and the dioxygen adduct may itself be sensitive to molecular oxygen.[9] Preparation of dioxygen complexes may, therefore, require rapid isolation and storage under an inert atmosphere or under vacuum.

Attempts have been made to correlate the O-O bond length of dioxygen complexes and M-O bond strength with the degree of reversibility of their formation reactions. The longer O-O bond length was thought to correlate with irreversibility.[53] The discovery that $Ir(PEtPh_2)_2(CO)Cl(O_2)$, which is formed reversibly, has a "long" O-O bond distance of 1.46 Å[54] demonstrates that there is no simple correlation between reversibility and O-O

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TABLE V. Mononuclear Dioxygen Complexes of Group VIII Transition Metals[a]

	ν_{OO}, cm^{-1}	Ref
Class I		
Ruthenium		
1. $Ru(PPh_3)_2(NO)X(O_2)$		
$X = Cl$	875	68
OH, Br, I, NCO, NCS, N_3, CN		87
NO_3		84
2. $Ru(PPh_3)_2(CNR)(CO)(O_2)$	838	81
3. $Ru(PPh_3)_2(CO)_2(O_2)$	849	*b*
Osmium		
1. $Os(PPh_3)_2(CO)_2(O_2)$	820	*b*
Cobalt		
1. $[Co(Ph_2PCH{=}CHPPh_2)_2(O_2)]^+$	909	44, *c*
Rhodium		
1. $[Rh(Ph_2PCH_2CH_2PPh_2)_2(O_2)]^+$		*d*
2. $Rh(PhP(CH_2CH_2CH_2PPh_2)_2)Cl(O_2)$	862	64
3. $RhL_2(CNR)X(O_2)$		
$R = CH_3$; $L = PPh_3$; $X = Cl$	890	*e*
$R = C(CH_3)_3$; $L = PPh_3$, $AsPh_3$; $X = Cl$, Br, I		55
4. $Rh(PPh_3)_2(CO)(OCOCF_3)(O_2)$	833	*f*
5. $\{RhL_4(O_2)]^+$		*g*, *h*
$L = PPh(CH_3)_2$	841, 870	
$AsPh(CH_3)_2$	862, 867	
Iridium		
1. $Ir(PPh_3)_2(CO)X(O_2)$		
$X = Cl$	858	34
Br	862	*i*
I	862	*i*, 53, 56
N_3	855	53, 56
NO_3	862	63
$C{\equiv}CR$	832	61, 62
SO_2-*p*-$C_6H_4CH_3$	835	60
SC_6F_5	860	59
2. $Ir(AsPh_3)_2(CO)X(O_2)$		
$X = Cl$	860	10
Br		43, *j*
I	850	10
3. $Ir(PPhR_2)_2(CO)X(O_2)$		*k*
$X = Cl$, $R = CH_3$	835, 845	
$X = Br$, $R = C_2H_5$	837	
4. $Ir(PPh_2CH_2CH_3)_2(CO)Cl(O_2)$		54
5. $Ir(PPh_3)_2(C_2H_4)Cl(O_2)$	880	*l*
6. $Ir(PPh_3)_2(pyridine)Cl(O_2)$	843	*l*
7. $IrL_3Cl(O_2)$		
$L = PPh_3$	853	9
$AsPh_3$	~840	*m*
$SbPh_3$	~840	*m*
8. $[Ir(Ph_2PCH_2CH_2PPh_2)_2(O_2)]^+$	845	*d*, 91
9. $[Ir(PPh_2R)_3(CO)(O_2)]^+$		47
$R = CH_3$	840	
C_2H_5	845	
10. $[IrL_4(O_2)]^+$		*g*
$L = PPh(CH_3)_2$		
$AsPh(CH_3)_2$	838	
Nickel		
1. $NiL_2(O_2)$		
$L = PPh_3$		39
$P(C_6H_{11})_3$		39
$CNC(CH_3)_3$	898	50, 51, 57
CNC_6H_{11}	904	50, 51
Palladium		
1. $PdL_2(O_2)$		
$L = PPh_3$	875	38, 39, *n*
$CNC(CH_3)_3$	893	50, 51, 57
Platinum		
1. $Pt(PPh_3)_2(O_2)$	830	38–40, *n*, o
Class II		
Cobalt		
1. $CoL(base)(O_2)$		*p*, *q*
L = salen, base = pyridine		*r*, 19
L = 3-methoxysalen, base = pyridine	1140?	*s*
L = acacen	1120–40	18, 19, *t*
L = tetrasulfophthalocyanine		*u*
L = bzacen	1128	29, *v*
2. $CoL_2(base)(O_2)$		
L = dimethylglyoximato		20
3. $(Co(CN)_5(O_2))_3^-$		*w*
4. (Vitamin B_{12r})(O_2)		*x*, 20
5. Oxycoboglobin		30
Class III		
Iron		
1. Oxyhemoglobin		
2. Oxymyoglobin		*y*
Ruthenium		
1. $Ru(AsPh_3)_3Cl_2(O_2)$ (paramagnetic: $\mu_{eff} = 2.90$ BM, coordination number?)	880	66
Rhodium		
1. $Rh(PPh_3)_3(O_2)$		*z*
(diamagnetic, explosive)	815	
2. $Rh(PPh_3)(AsPh_3)_2(O_2)$	810	*z*
3. $(Rh(PPh_3)Cl(O_2))_n$		*aa*

[a] Abbreviations: Ph = C_6H_5, R = alkyl or aryl group, salen = *N,N'*-ethylenebis(salicylideneiminato), acacen = $(CH_3\check{C}(O^-){=}CHC(CH_3){=}NCH_2{}^-)_2$, bzacen = $(C_6H_5C(O^-){=}CHC(CH_3){=}NCH_2{-})_2$. [b] B. E. Cavit, K. R. Grundy, and W. R. Roper, *Chem. Commun.*, 60 (1972). [c] N. W. Terry III, E. L. Amma, and L. Vaska, *J. Amer. Chem. Soc.*, **94**, 653 (1972). [d] J. A. McGinnety, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 6301 (1969). [e] A. L. Balch and J. Miller, *J. Organometal. Chem.*, **32**, 263 (1971). [f] R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3224 (1971). [g] L. M. Haines and E. Singleton, *J. Organometal. Chem.*, **30**, C81 (1971). [h] L. M. Haines, *Inorg. Chem.*, **10**, 1685 (1971). [i] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966). [j] F. Canziani, U. Sartorelli, and F. Zingales, *Chem. Ind. (Milan)*, **49**, 499 (1967). [k] A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969). [l] H. van Gaal, H. G. A. M. Cuppers, and A. van der Ent, *Chem. Commun.*, 1694 (1970). [m] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969). [n] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 561 (1968). [o] C. D. Cook, P.-T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, **91**, 2123 (1969); T. Kashiwagi, N. Yasuoka, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Commun.*, 743 (1969). [p] E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nucl. Chem. Lett.*, 7, 901 (1971). [q] C. Busetto, C. Neri, N. Palladino, and E. Perrotti, *Inorg. Chim. Acta*, **5**, 129 (1971). [r] E. Koubek and C. W. Merwine, *J. Inorg. Nucl. Chem.*, **33**, 3574 (1971). [s] C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969). [t] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970). [u] E. W. Abel, J. M. Pratt, and R. Whelan, *Chem. Commun.*, 449 (1971). [v] J. D. Landels and G. A. Rodley, *Syn. Inorg. Metal.-Org. Chem.*, **2**, 65 (1972). [w] J. H. Bayston, F. D. Looney, and M. E. Winfield, *Aust. J. Chem.*, **16**, 557 (1963). [x] J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969). [y] H. C. Watson and C. L. Nobbs, *Biochem. Sauerst., Colloq. Ges. Biol. Chem., 19th*, 37 (1968). [z] M. Takesada, H. Yamazki, and N. Hahihara, *Bull. Chem. Soc. Jap.*, **41**, 270 (1968). [aa] J. Blum, H. Rosenmann, and E. D. Bergmann, *Tetrahedron Lett.*, 3665 (1967).

bond length. Furthermore, analysis of infrared spectra of ^{18}O-substituted dioxygen complexes indicates no correlation between M–O force constants and reversibility.[55]

Some kinetic and thermodynamic parameters for dioxygen complex formation have been measured. In all cases, the forward reaction was found to obey a bimolecular rate law, *i.e.*, $-d[ML_n]/dt = k_2[ML_n][O_2]$. The parameters are summarized in Table IV.

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Class I dioxygen complexes usually exhibit an infrared band between 800 and 900 cm^{-1}. The frequency of this band is not dependent upon the O-O bond length in the structures that are known, implying that the band is not a simple O-O stretch.[50,56-58] Class II dioxygen complexes exhibit an infrared band between 1120 and 1140 cm^{-1} which has been assigned to the O-O stretch (see Table V).

Table V is a summary of mononuclear dioxygen complexes of group VIII transition metal complexes. These complexes are divided into class I and II on the basis of similarities in spectral and magnetic properties, number of d electrons, and coordination number, to complexes whose structures are known. A third class of compounds includes those whose properties do not allow a definitive assignment to class I or II.

C. Reactions of Coordinated Dioxygen

Dioxygen complexes have been observed to react with aqueous acid to give H_2O_2,[34,39] with reducing agents to give coordinatively unsaturated complexes,[40] and with various ligands which displace molecular oxygen.[50] Apart from these reactions, however, there is a class of reactions that appears to involve oxidation of substrates by dioxygen in the coordination sphere of the metal. Under mild conditions with no catalyst, molecular oxygen does not react with sulfur dioxide, carbon dioxide, carbon disulfide, carbon monoxide, nitrogen dioxide, alkyl isocyanides, ketones, aldehydes, or triphenylphosphine (it does react with nitric oxide). Dioxygen complexes of group VIII transition metals, however, do react with all of these substrates to form complexes of the oxidized substrates. For example

$$ML_2(O_2) \xrightarrow[\text{ref 8, 10}]{SO_2} ML_2(SO_4) \qquad (27)$$

$$M = Pt,\ Pd \quad L = PPh_3,\ AsPh_3$$

$$Ir(PPh_3)_2(CO)X(O_2) \xrightarrow[\text{ref 42, 59–63, 10}]{SO_2} Ir(PPh_3)_2(CO)X(SO_4) \qquad (28)$$

$$X = Cl,\ Br,\ I,\ SC_6F_5,\ SO_2\text{-}p\text{-}C_6H_4CH_3,\ C{\equiv}CR,\ NO_3$$

$$Ir(AsPh_3)_2(CO)X(O_2) \xrightarrow[\text{ref 10}]{SO_2} Ir(AsPh_3)_2(CO)X(SO_4) \qquad (29)$$

$$X = Cl,\ Br,\ I$$

$$Ir(PPh_3)_3Cl(O_2) \xrightarrow[\text{ref 9}]{SO_2} \xrightarrow{CO} Ir(PPh_3)_2(CO)(Cl)(SO_4) \qquad (30)$$

$$[Ir(PPh_2CH_3)_3(CO)(O_2)]^+ \xrightarrow[\text{ref 47}]{SO_2} [Ir(PPh_2CH_3)_3(CO)(SO_4)]^+ \qquad (31)$$

$$[Ir(diphos)_2(O_2)]^+ \xrightarrow[\text{ref 10}]{SO_2} [Ir(diphos)_2(SO_4)]^+ \qquad (32)$$

$$RhLCl(O_2) \xrightarrow[\text{ref 64}]{SO_2} RhLCl(SO_4) \qquad (33)$$

$$L = PhP(CH_2CH_2CH_2PPh_2)_2$$

$$Ru(PPh_3)_2(NO)Cl(O_2) \xrightarrow[\text{ref 65}]{SO_2} Ru(PPh_3)_2(NO)Cl(SO_4) \qquad (34)$$

$$Ru(AsPh_3)_3Cl_2(O_2) \xrightarrow[\text{ref 66}]{SO_2} \text{sulfate complex} \qquad (35)$$

$$M(PPh_3)_2(O_2) \xrightarrow[\text{ref 10, 67}]{NO} M(PPh_3)_2(NO_2)_2 \qquad (36)$$

$$M = Pd,\ Pt$$

$$Ru(PPh_3)_2(NO)X(O_2) \xrightarrow[\text{ref 68}]{CO} Ru(PPh_3)_2(CO)_2X(NO_3) \qquad (37)$$

$$X = NO_3,\ Cl$$

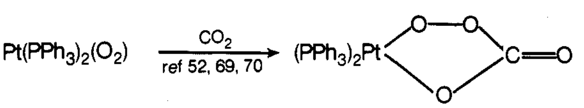
$$M(PPh_3)_2(O_2) \xrightarrow[\text{ref 8, 10}]{NO_2} M(PPh_3)_2(NO_3)_2 \qquad (38)$$

$$M = Pd,\ Pt$$

$$[Ir(PPh_2CH_3)_3(CO)(O_2)]^+ \xrightarrow[\text{ref 47}]{NO_2} [Ir(PPh_2CH_3)_3(CO)(NO_3)_2]^+ \qquad (39)$$

$$IrL_2(CO)X(O_2) \xrightarrow[\text{ref 10}]{NO_2} IrL_2(CO)X(NO_3)_2 \qquad (40)$$

$$L = PPh_3,\ AsPh_3;\ X = Cl,\ Br,\ I$$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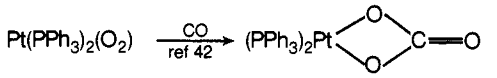
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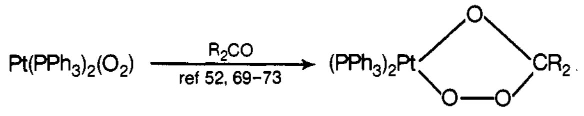
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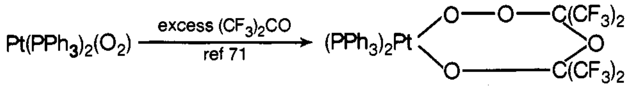
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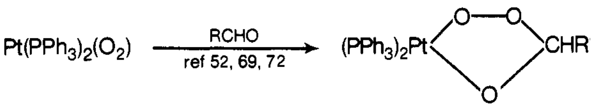
(45)

$$Pt(PPh_3)_4 \xrightarrow[\text{ref 52, 69}]{O_2,\ RCHO} Pt(PPh_3)_2(OCOR)_2 \qquad (46)$$

$$Pt(PPh_3)_2(O_2) \xrightarrow[\text{ref 52, 69}]{CS_2} Pt(PPh_3)_2(S_2CO) \qquad (47)$$

$$Pt(PPh_3)_2(O_2) + 3PPh_3 \xrightarrow[\text{ref 74, 75}]{} Pt(PPh_3)_3 + 2OPPh_3 \qquad (48)$$

$$Ni(RNC)_2(O_2) + 4PPh_3 \xrightarrow[\text{ref 50, 51, 57}]{} Ni(RNC)_2(PPh_3)_2 + 2OPPh_3 \qquad (49)$$

$$Ni(RNC)_2(O_2) + 4RNC \xrightarrow[\text{ref 50, 51, 57}]{} Ni(RNC)_4 + 2RNCO \qquad (50)$$

It is interesting to note some similar reactions of binuclear cobalt/dioxygen complexes.

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$$[(en)_2Co(O_2)(NH_2)Co(en)_2]^{3+ \text{ or } 4+} \xrightarrow[\text{ref 76}]{SO_2,\ H_2O} [(en)_2Co(SO_4)(NH_2)Co(en)_2]^{3+} \quad (51)$$

$(en = H_2NCH_2CH_2NH_2)$

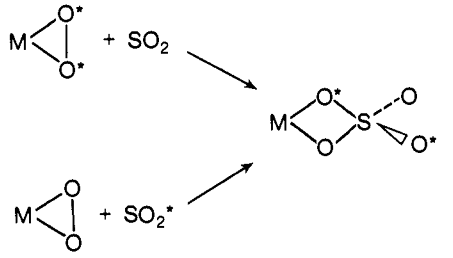
$$[(en)_2Co(O_2)(NH_2)Co(en)_2]^{4+} \xrightarrow[\text{ref 76}]{NO_2,\ H_2O} [(en)_2Co(NO_2)(NH_2)Co(en)_2]^{4+} \quad (52)$$

$$[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+} + 2SO_3^{2-} \xrightarrow[\text{ref 77}]{H_2O} [Co(NH_3)_5(SO_4)]^+ + Co^{2+} + SO_4^{2-} + 5NH_3 \quad (53)$$

There are three possible explanations for the increase in reactivity of molecular oxygen upon coordination. (1) Coordinated dioxygen (configuration I) is in general diamagnetic; therefore, reactions with diamagnetic substrates to form diamagnetic products are not hindered by the requirement for spin conservation. (2) The metal may hold dioxygen and the substrate in cis positions, lowering the activation energy for oxidation of the substrate. (3) Coordinated dioxygen is, in most cases, partially reduced; increased electron density on the O_2 may activate it.

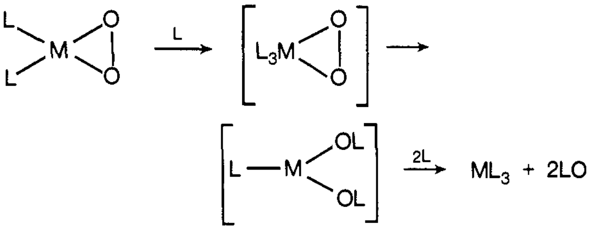
The first undoubtedly contributes to the increased reactivity of coordinated dioxygen in some cases. There is no obvious means of assessing the magnitude of the contribution. Moreover, there is at least one paramagnetic dioxygen complex, $Ru(AsPh_3)_3Cl_2(O_2)$, in which, unlike the paramagnetic cobalt complexes, the ground state is a triplet with the spins presumably residing on the dioxygen ligand, and this complex is reported to react readily with SO_2 to give a sulfate complex (see reaction 35).

The second assumes that the substrate is coordinated before oxidation. There is some evidence for this from an ^{18}O labelling study.[58] In this study, reactions 54 and 55 were carried out with $S(^{18}O_2)$ and $^{18}O_2$. Analysis of the infrared spectra of the products indicated that one of the oxygen atoms from the coordinated oxygen molecule remains coordinated directly and the other does not, *i.e.*, eq 54 and 55. This result implies that one end of the oxygen molecule remains attached to the metal throughout the reaction while the other does not, thus opening up a coordination position cis to the first oxygen atom. The same type of intermediate is implied by the product of reaction of coordinated dioxygen with CO_2 (see reaction 41). While there is strong evidence that some reactions proceed through end-bonded dioxygen intermediates, it is possible that different mechanisms operate in different systems. For example, attack of a reagent on a coordinatively unsaturated four-coordinate d^8 complex to form a five-coordinate intermediate *before* M-O bond cleavage is more likely than attack on a coordinatively saturated six-coordinate d^6 complex without M-O bond cleavage. It has been suggested that the reactions of $ML_2(O_2)$ (M = Ni, Pd, Pt; L = PPh_3, RNC) with RNC or PPh_3 involve five-coordinate intermediates in which increased ligation of the metal facilitates O-O bond cleavage (reaction 56), although the only evidence is that the attacking PPh_3 or RNC is coordinated prior to dissociation of $OPPh_3$ or RNCO.[51,74,75]



(54)

(55)



(56)

The third, activation of coordinated dioxygen by partial reduction, is difficult to assess experimentally. Increased electron density on the metal results in increased reduction of the dioxygen ligand. This should make O-O bond breaking easier but make the M-O bond stronger, inhibiting MO_2 ring opening. It would be interesting to see if a series of dioxygen complexes with ligands of differing donor properties, *i.e.*, $PtL_2(O_2)$, L = PPh_3, PPh_2R, $PPhR_2$, etc., displayed the same order of reactivity toward different types of substrates.

In summary, until more is known about the mechanism of these reactions, the factors involved in activation of the oxygen molecule by coordination to a metal cannot be evaluated. There is no correlation of reactivity with O-O bond lengths (although there may be an inverse correlation of reactivity with M-O bond strengths evaluated from force constants[55]). There does seem to be a general difference in reactivity between four-coordinate d^8 and six-coordinate d^6 complexes. The coordinatively saturated complexes show a general reactivity only toward SO_2 and NO_2, both of which may be able to interact with nonbonding electron pairs on the metal unlike less electrophilic reagents such as CO_2 and PPh_3. In general, the coordinatively unsaturated complexes are substantially more reactive (see reactions 27-50). It is interesting that, with one exception, the reactivity of molecular oxygen toward all the substrates tried is increased upon coordination. Nitric oxide, which reacts spontaneously with free molecular oxygen and with the four-coordinate d^8 dioxygen complexes, does not react with six-coordinate d^6 dioxygen complexes.[10]

IV. Formation of Oxidized Ligands in Reactions of Group VIII Transition Metal Complexes with Molecular Oxygen

Reactions from which dioxygen complexes are not isolated often produce oxidized ligands or complexes of oxidized ligands presumably derived from intermediate dioxygen complexes. The similarity of the products of these reactions to those in which coordinated dioxygen is allowed to react with various substrates suggests that there may be common intermediates in some cases. The following are examples of these types of reactions.

$$M(PPh_3)_3(SO_2) \xrightarrow[\text{ref 8, 78}]{O_2} M(PPh_3)_2(SO_4) \quad (57)$$

M = Pt, Pd

$$Ir(PPh_3)_2(CO)X(SO_2) \xrightarrow[\text{ref 59, 61, 62}]{O_2} Ir(PPh_3)_2(CO)X(SO_4) \quad (58)$$

X = Cl, Br, I, SC_6F_5, C≡CR (see text below)

$$M(TDPME)Cl(SO_2) \xrightarrow[\text{ref 79}]{O_2} M(TDPME)Cl(SO_4) \quad (59)$$

M = Rh, Ir; TDPME = 1,1,1-tris(diphenylphosphinomethyl)ethane

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$$\mathrm{Rh(PPh_3)_2(CO)Cl(SO_2)} \xrightarrow[\text{ref 59}]{\mathrm{O_2}} \mathrm{Rh(PPh_3)_2(CO)Cl(SO_4)} \quad (60)$$

$$\mathrm{M(PPh_3)_3(NO)} \xrightarrow[\text{ref 9}]{\mathrm{SO_2}} \xrightarrow{\mathrm{O_2}} \mathrm{M(PPh_3)_2(NO)(SO_4)} \quad (61)$$

$$\mathrm{M = Rh,\ Ir}$$

$$\mathrm{Ru(PPh_3)_2(CO)_2(SO_2)} \xrightarrow[\text{ref 9}]{\mathrm{O_2}} \mathrm{Ru(PPh_3)_2(CO)_2(SO_4)} \quad (62)$$

$$\mathrm{Ru(PPh_3)_2(NO)Cl(SO_2)} \xrightarrow[\text{ref 59}]{\mathrm{O_2}} \mathrm{Ru(PPh_3)_2(NO)Cl(SO_4)} \quad (63)$$

$$\mathrm{Ru(PPh_3)_2(SO_2)Cl_2{\cdot}acetone} \xrightarrow[\text{ref 80}]{\mathrm{O_2}} \text{sulfato complex} \quad (64)$$

$$\mathrm{Ir(PPh_3)_2(N_2)Cl} \xrightarrow[\text{ref 9}]{\mathrm{SO_2}} \mathrm{Ir(PPh_3)_2Cl(SO_2)_2} \xrightarrow{\mathrm{O_2}}$$
$$\mathrm{[Ir(PPh_3)_2Cl(SO_4)]} \xrightarrow{\mathrm{CO}} \mathrm{Ir(PPh_3)_2(CO)Cl(SO_4)} \quad (65)$$

$$\mathrm{Rh(PPh_3)_3X} \xrightarrow[\text{ref 10}]{\mathrm{SO_2\ +\ O_2,\ H_2O}} \mathrm{Rh(PPh_3)_2X(SO_4)(H_2O)} \quad (66)$$

$$\mathrm{Ir(TDPME)(CO)(Cl)} \xrightarrow[\text{ref 79}]{\mathrm{O_2}} \mathrm{Ir(TDPME)Cl(CO_3)} \quad (67)$$

$$\mathrm{Ru(PPh_3)_2(CNR)(CO)_2} \xrightarrow[\text{ref 81}]{\mathrm{O_2}} \mathrm{Ru(PPh_3)_2(CNR)(CO)(CO_3)} \quad (68)$$

$$\mathrm{Os(PPh_3)_2(CO)(NO)Cl} \xrightarrow[\text{ref 68}]{\mathrm{O_2}} \mathrm{Os(PPh_3)_2(NO)Cl(CO_3)} \quad (69)$$

$$\text{(but } \mathrm{Ru(PPh_3)_2(CO)(NO)Cl} \xrightarrow[\text{ref 68}]{\mathrm{O_2}} \mathrm{Ru(PPh_3)_2(NO)Cl(O_2)}) \quad (70)$$

$$\mathrm{Ru(PPh_3)_2(CO)_3(solid)} \xrightarrow[\text{ref 9}]{\text{air}} \mathrm{Ru(PPh_3)_2(CO)_2(CO_3)} + \text{other products} \quad (71)$$

$$\text{(but } \mathrm{Ru(PPh_3)_2(CO)_3} \xrightarrow[\text{ref 9}]{\mathrm{O_2},\ \text{benzene, } 60^\circ} \mathrm{[Ru]?\ +\ OPPh_3}) \quad (72)$$

$$\mathrm{[Rh(CO)_2Cl_2]^-} \xrightarrow[\text{ref 82}]{\mathrm{O_2,\ HCl,\ H_2O}} \mathrm{Rh(CO)Cl_5{}^{2-} + CO_2} \quad (73)$$

$$\mathrm{Rh_2(CO)_4(PPh_3)_4} \xrightarrow[\text{ref 83}]{\mathrm{O_2}} \mathrm{Rh_2(CO)_2(CO_2)(PPh_3)_3} \quad (74)$$

$$\mathrm{Ru(PPh_3)_2(NO)_2} \xrightarrow[\text{ref 84}]{\mathrm{O_2}} \mathrm{Ru(PPh_3)_2(NO)(NO_3)(O_2)} \quad (75)$$

$$t\text{-}\mathrm{Ru(das)_2Cl(N_3)} \xrightarrow[\text{ref 85}]{\mathrm{O_2},\ h\nu} t\text{-}\mathrm{Ru(das)_2Cl(NO_2)} \quad (76)$$

$$\mathrm{das = o\text{-}C_6H_4\text{-}(As(CH_3)_2)_2}$$

$$\mathrm{[Ru(CH_3NH_2)_6]^{2+}} \xrightarrow[\text{ref 86}]{\mathrm{O_2,\ H_2O}} \mathrm{Ru(CN)_3{\cdot}3H_2O} \quad (77)$$

$$\mathrm{O_2 + 2PPh_3} \xrightarrow{\text{catalyst}} \mathrm{2OPPh_3} \quad (78)$$

catalyst = $\mathrm{Ru(PPh_3)_2(NO)(NCS)(O_2)}$, ref 87
$\mathrm{Ru(PPh_3)_2(CNR)(CO)(O_2)}$, ref 81
$\mathrm{Ru(PPh_3)_3Cl_2}$, ref 80

$$\text{(but } \mathrm{Ru(AsPh_3)_3Cl_2} \xrightarrow[\text{ref 66}]{\mathrm{O_2}} \mathrm{Ru(AsPh_3)_3Cl_2(O_2)}) \quad (79)$$

$$\mathrm{[Fe_2(S_2C_2(CF_3)_2)_4]^{2-}} \xrightarrow[\text{ref 88}]{\mathrm{PPh_3,\ O_2}} \mathrm{[Ph_3POFe(S_2C_2(CF_3)_2)_2]^-} \quad (80)$$

$$\mathrm{[Ir(PPh_3)_3(NO)H]^+} \xrightarrow[\text{ref 84}]{\mathrm{O_2}} \mathrm{[Ir(PPh_3)_2(NO)(OH)]^+ + OPPh_3} \quad (81)$$

$$\mathrm{Rh(PPh_3)_2(CO)Cl} \xrightarrow[\text{ref 89}]{\mathrm{CO,\ O_2}} \mathrm{Rh(CO)_4Cl_2 + Rh(OPPh_3)_2(CO)_2Cl + OPPh_3 + CO_2} \quad (82)$$

$$\mathrm{Co(P(C_2H_5)_3)_2Cl_2} \xrightarrow[\text{ref 90}]{\mathrm{O_2}} \mathrm{Co(OP(C_2H_5)_3)_2Cl_2} \quad (83)$$

$$\mathrm{[Co(diphos)_2]^+} \xrightarrow[\text{ref 91}]{\mathrm{O_2}} \text{(Co diphosphine dioxide derivative)}$$

$$\mathrm{diphos = Ph_2PCH_2CH_2PPh_2} \quad (84)$$

$$\mathrm{[Rh(NH_3)_5H]^{2+}} \xrightarrow[\text{ref 92}]{\mathrm{O_2}} \mathrm{[Rh(NH_3)_4(OH)(OOH)]^+} \quad (85)$$

$$\text{oxime--Co(II)--R} \xrightarrow[\text{ref 93}]{\mathrm{O_2},\ h\nu\ \text{(vis)}} \text{oxime--Co(II)--OOR} \quad (86)$$

$$\mathrm{M(PPh_3)_2(NO)_2} \xrightarrow[\text{ref 84}]{\mathrm{H^+}} \mathrm{[M(PPh_3)_2(NO)_2H]^+} \xrightarrow{\mathrm{O_2}} \mathrm{[M(PPh_3)_2(NO)_2(OH)]^+} \quad (87)$$

$$\mathrm{M = Ru,\ Os}$$

$$\mathrm{O_2 + 2H_2} \xrightarrow{\text{catalyst}} \mathrm{2H_2O} \quad (88)$$

catalyst = $\mathrm{Rh(OCOCH_3)_4}$, ref 94
several Pt, Ir, Rh catalysts, ref 95
$\mathrm{Ru(PPh_3)_3Cl_2}$, ref 80

Some aspects of these reactions deserve specific attention. Sulfur dioxide and nitric oxide as ligands may be able to change oxidation states by changing their mode of bonding. Both ligands are observed in differing geometries, the extremes of which are portrayed in Table VI. Such differing geometries may correspond to changes in the formal charge on the ligand. Changes in geometry may change the oxidation state of the metal and thus change the preferred coordination number of the complex. A formally coordinatively saturated complex may thereby have an easily accessible coordination position for attack by the oxygen molecule.

It is interesting to note that although all dioxygen complexes of configuration I seem to react with SO_2 to give sulfato complexes (at least there has been no report of a failure to react in such cases), not all SO_2 complexes react with molecular oxygen. It may be that while the bidentate dioxygen ligand can always open up to give a coordination position for SO_2, SO_2 complexes cannot always provide a position for attack by molecular oxygen. If this were true, however, we would expect reaction of $\mathrm{Ir(PPh_3)_2(CO)X(O_2)}$ with NO (if the mechanism is analogous) and this does not occur. The facile reaction of $\mathrm{Ru(PPh_3)_2(CO)_2(SO_2)}$ with O_2 to give $\mathrm{Ru(PPh_3)_2(CO)_2(SO_4)}$ (reaction 62) is in sharp contrast to the apparent lack of reactivity of $\mathrm{Ir(PPh_3)_2(CO)Cl(SO_2)}$. This latter complex has been reported to react with molecular oxygen (reaction 58) but the experimenters failed to elimi-

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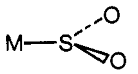
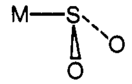
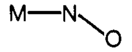
TABLE VI. Modes of Bonding of NO and SO_2 to Transition Metals

	M—N—O
e.g., $[Ru(NH_3)_4Cl(SO_2)]^{+}$[a]	*e.g.*, $Mn(CO)_4(NO)$[b]
	
e.g., $Ir(PPh_3)_2(CO)Cl(SO_2)$[c]	*e.g.*, $[Ir(PPh_3)_2(CO)I(NO)]^{+}$[d]

[a] L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965). [b] B. A. Frenz, J. H. Enemark, and J. A. Ibers, *ibid.*, **8**, 1288 (1969). [c] S. J. La Placa and J. A. Ibers, *ibid.*, **5**, 405 (1966). [d] D. J. Hodgson and J. A. Ibers, *ibid.*, **8**, 1282 (1969).

nate reaction 89. Even if reaction 58 occurs as written, it is much slower than reaction 62 for unexplained reasons.

$$Ir(PPh_3)_2(CO)Cl(SO_2) \xrightarrow{O_2} Ir(PPh_3)_2(CO)Cl(O_2) + SO_2 \longrightarrow Ir(PPh_3)_2(CO)Cl(SO_4) \qquad (89)$$

When the oxidized ligand is itself a good ligand, the reaction with molecular oxygen results in coordinated oxidized ligand; otherwise the reaction produces free oxidized ligand. The most commonly observed reaction of organometallic complexes with molecular oxygen is the formation of free oxidized ligand. This type of reaction is usually responsible for the often undesired air sensitivity of many organometallic complexes. Such a reaction is presumably involved in metal complex catalysis of autooxidation in a variety of organic systems[14,42,67,96-101] (reaction 90). If the oxidized ligand is itself a better ligand than the original ligand, the reaction stops with the complex of oxidized ligand.

$$M + 2L + O_2 \longrightarrow [M(O_2)L_2] \longrightarrow [M(OL)_2] \longrightarrow M + 2OL \qquad (90)$$

The insertion reactions (reaction 91) probably involve free radical intermediates. These reactions are similar to oxidation reactions for transition metal ions by molecular oxygen.

$$M\text{-}R(H) + O_2 \longrightarrow MOOR(H) \text{ or } MOH \qquad (91)$$

Acknowledgments. The author wishes to thank Professor James P. Collman and Dr. Donald Valentine for encouragement and helpful discussions and Miss Jacki Jones for cheerfully typing the manuscript.

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