Reactions of Monomeric Cobalt–Oxygen Complexes. I. Thermodynamics of Reaction of Molecular Oxygen with Five- and Six-Coordinate Amine Complexes of a Cobalt Porphyrin[1a,b]

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Abstract: The equilibrium constants, free energies, enthalpies, and entropies of coordination of molecular oxygen to five- and six-coordinate $\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphinatocobalt(II) as a function of amine as the fifth (and sixth) ligand(s) are reported. The equilibrium constants were determined in toluene as a function of temperature by an epr technique. The results show that, for addition of molecular O_2 to the five-coordinate complexes, typical values of ΔH are -8.5 to -9.5 kcal/mol and $\Delta S \sim -30$ eu. No apparent relationship between the pK_a of the conjugate acid of the amine and ΔH or ΔG is found. The relationship of these results to other systems, including coboglobin and coenzyme B_{12} reactions, is discussed. For the replacement reaction, $CoP\cdot B_2 + O_2 \rightleftarrows CoP\cdot B\cdot O_2 + B$, $\Delta H = -7.5$ kcal/mol (3,4-lutidine) and -6.7 kcal/mol (piperidine). These values represent the difference in bond energy between the Co–O_2 and Co–N bond; derived values of ΔH and ΔS for the reaction $CoP\cdot B + B \rightleftarrows CoP\cdot B_2$ are -1.8 kcal/mol and -10 eu for 3,4-lutidine.

From conclusions reached in an epr investigation of the reactions of cobalt(II) porphyrins with amines and molecular oxygen,[2] and the preceding paper,[3] it has been shown that some of these reactions are summarized by the following equations

$$CoP + B \xrightleftharpoons{K_1} CoP\cdot B \qquad \text{“five-coordinate amine adduct”} \qquad (1)$$

$$CoP\cdot B + B \xrightleftharpoons{K_2} CoP\cdot B_2 \qquad \text{“six-coordinate amine adduct”} \qquad (2)$$

$$CoP\cdot B + O_2 \xrightleftharpoons{K_3} CoP\cdot B\cdot O_2 \qquad \text{“}O_2\text{ adduct”} \qquad (3)$$

$$CoP\cdot B_2 + O_2 \xrightleftharpoons{K_4} CoP\cdot B\cdot O_2 + B \qquad \text{“}O_2\text{ adduct”} \qquad (4)$$

$$CoP\cdot B + CoP\cdot B\cdot O_2 \xrightleftharpoons{K_5} B\cdot CoP\cdot O_2\cdot CoP\cdot B \qquad \text{“binuclear complex”} \qquad (5)$$

where P represents a series of para-substituted *meso*-tetraphenylporphyrins ((p-X)TPP) and B represents some Lewis base. Each of the above cobalt-containing species was found to exhibit a characteristically different epr spectrum,[2] except for the product of reaction 5, which leads to a decrease in the epr signal intensity of the reactants.[2] Reaction 5 is extremely slow at room temperature and does not interfere with the investigation of reactions 1–4 (see below and ref 2).

The product of reactions 3 and 4, $CoP\cdot B\cdot O_2$, as as well as vitamin B_{12r}[4a] and similar Schiff's base complexes such as $Co(acac_2en)\cdot B\cdot O_2$,[4b] have been described, on the basis of epr parameters,[2,4] to have the electronic configuration $Co(III)–O_2^-$, where O_2^- is the superoxide ion. The structure of one such oxygen adduct, $Co(bzacen)(pyridine)O_2$, where bzacen = N,N'-ethylenebis(benzoylacetoniminide), has been reported.[5] It shows that the O_2 moiety is unsymmetrically bound to the cobalt atom, with a Co–O–O bond angle of 126°. This is in agreement with the superoxide formulation for O_2 bound to square-pyramidal cobalt(II).

Reactions 1–4 have an important relationship both to the hemoglobin–O_2[6] reactions (and those of the cobalt containing "coboglobin"[7]) and to the postulated radical reactions of coenzyme B_{12}.[8] It is, therefore, of interest to investigate systematically the equilibria described by reactions 1–4. Reaction 1 was the subject of the preceding paper.[3] Reactions 2, 3, and 4 are the subject of this report. Of these, only two are independent, since by Hess' law, eq 4 = (3) − (2), and $K_4 = K_3/K_2$. For convenience we have measured the equilibrium constants for reactions 3 and 4 and calculated those for (2).

A preliminary report of this work has been presented.[1a] Since that time, some thermodynamic data for reaction 3 on a similar system, cobalt protoporphyrin IX dimethyl ester, Co(protoDME), have appeared.[9,10] However, this report presents a more extensive investigation of reaction 3; it differs in some details from that of Stynes and Ibers,[9,10] and includes information not previously presented on reactions 2 and 4.

Experimental Section

The cobalt porphyrin used for the work described below was $\alpha,\beta,\gamma,\delta$-tetra($p$-methoxyphenyl)porphinatocobalt(II), Co(p-OCH_3)-

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[1] (a) Preliminary report presented at the 161st National Meeting of the American Chemical Society, Los Angeles, California, April 1, 1971, No. INOR 146. (b) Presented at the XIV International Conference on Coordination Chemistry, Toronto, Canada, June 27, 1972.

[2] F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

[3] F. A. Walker, *ibid.*, **95**, 1150 (1973).

[4] (a) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *ibid.*, **91**, 2775 (1969); (b) B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, **92**, 61 (1970).

[5] G. A. Rodley and W. T. Robinson, *Nature (London)*, **235**, 438 (1972).

[6] M. F. Perutz, *ibid.*, **228**, 726, 734 (1970).

[7] B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U. S.*, **67**, 637 (1970); B. M. Hoffman, C. A. Spilburg, and D. H. Petering, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 343 (1971).

[8] B. Babior and D. C. Gould, *Biochem. Biophys. Res. Commun.*, **34**, 441 (1969); B. M. Babior, *J. Biol. Chem.*, **245**, 6125 (1970).

[9] H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 1559 (1972).

[10] H. C. Stynes and J. A. Ibers, presented at the 1972 ACS–CIC Summer Symposium on "Coordination and Activation of Small Molecules by Transition Metals," Buffalo, N. Y., June 20, 1972.

TPP, which was prepared according to the procedure described in ref 2. It was found necessary to chromatograph the cobalt porphyrin within a few days of use, in order to avoid a catalytic decomposition to a Co(III) complex[11] (also, see below).

Amines and toluene were purified as described previously,[3] carbon disulfide was purified by standard methods,[12] and prepurified oxygen was obtained from Matheson Gas Products.

Reactions 3 and, where possible, 4 were investigated by epr techniques at low temperatures in toluene solution. The method used relies upon the fact that the five- (or six-) coordinate amine complex, CoP·B (or CoP·B_2), and the oxygen adduct, CoP·B·O_2, have very different solution epr spectra, as shown in Figure 1. The method is described for reaction 3, but the same techniques were employed for reaction 4. The derivative epr spectrum, Figure 1a, was integrated to give the absorption spectrum, Figure 1b; the ratio [O_2 adduct]/[5-coord] is then [(area of II) × $\langle g\rangle_{5\ \text{coord}}$]/[(area of I) × $\langle g\rangle_{O_2\ \text{add}}$], where "area of II" is the area of the CoP·B·O_2 peak, "area of I" is the area of the CoP·B peak, and $\langle g\rangle$ represents the average or isotropic g value ($\langle g\rangle = (g_{\|} + 2g_{\perp})/3$, $g_{\|}$ and $g_{\perp}$ taken from ref 2). Areas were determined by use of a planimeter (Gelman Instrument Co., West Germany). The g-value correction is necessary to account for magnetic susceptibility differences in the two systems.[13]

It was found that once the spectrum of one sample at any given temperature had been integrated and the areas of I and II determined, the ratio of concentrations of O_2 adduct and five-coordinate amine complex could be determined for other samples (i) by comparison of the peak-to-peak derivative amplitudes of the two species for each sample to that for the sample on which the graphical integration had been performed (st)

$$\left(\frac{[O_2\ \text{adduct}]}{[5\text{-coord}]}\right)_{\text{i}} = \left(\frac{[O_2\ \text{adduct}]}{[5\text{-coord}]}\right)_{\text{st}}\left(\frac{5\text{-coord ht}}{O_2\ \text{add ht}}\right)_{\text{st}}\left(\frac{O_2\ \text{add ht}}{5\text{-coord ht}}\right)_{\text{i}} \qquad (6)$$

where the same power, modulation, and amplifier gain settings were used in each case. Power settings below those required to begin saturation of the O_2 adduct signal were used. In general, the graphical integration was found to be more reproducible for a sample in which the ratio [O_2 adduct]/[5-coord] was small.

Samples containing various pressures of oxygen were prepared by first degassing solutions of Co(p-X)TPP (8–10 × 10^{-4} M) and the desired amine in toluene or CS_2 (~1 × 10^{-2}–1 × 10^{-3} M amine for reaction 3, 1–2 M for reaction 4) on a vacuum line by the freeze-pump-thaw method and then introducing a known pressure of O_2 ranging from 50 to 250 Torr at the ambient temperature. The partial pressure of O_2 in the sample tubes was then corrected for the partial pressure of toluene at the ambient temperature. The sample tubes consisted of 3-mm i.d. quartz tubes about 6 in. in length connected, through a graded quartz-to-Pyrex seal, to vacuum stopcocks each of which had a female standard-taper joint on the other side of the stopcock for connection to the vacuum line. When the known pressure of O_2 had been introduced into the sample tube, which contained the CoP·B solution to a depth of about 1.5 in., the stopcock was closed and the tube was tipped several times to allow equilibration of oxygen with the solution.

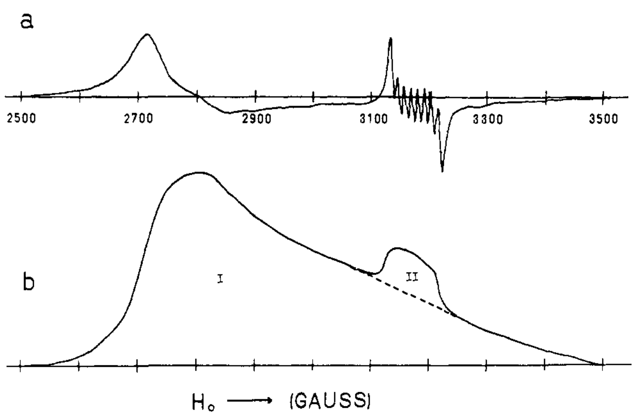

Figure 1. (a) Derivative spectrum of a mixture of Co(p-OCH_3)-TPP·(Py) and Co(p-OCH_3)TPP·(Py)·O_2 at −50° in toluene solution. (b) Integrated spectrum of (a). Species I is the Co(p-OCH_3)TPP·(Py); species II is Co(p-OCH_3)TPP·(Py)·O_2. Field in gauss; microwave frequency ~ 9.42 GHz.

Epr spectra were recorded on either an Alpha Scientific Co. or a Varian E-12 epr spectrometer which were each equipped with a variable temperature controller. The temperature was adjusted to known values in the range −20 to −80° as was appropriate for the system under investigation. Equilibium constants (K_3 or K_4) were determined at a minimum of three temperatures over increments of 20°.

Discussion

Concentration of O_2 in Solution. The standard state used in the calculation of K_3 and K_4 in this investigation was 1 M Co(p-OCH_3)TPP·B, 1 M Co(p-OCH_3)TPP·B·O_2, and 1 M O_2. Thus it was necessary to know the concentration of O_2 in toluene as a function of temperature. From gas solubility data[15] the concentration of O_2 in toluene at 25° is approximately 7 × 10^{-3} M atm^{-1}; to our knowledge, no data on the temperature dependence of this solubility are available. Temperature dependence of the solubility of O_2 in benzene shows that this solubility is essentially constant, at 9.0 × 10^{-3} M, over the temperature range of 10–60°.[16] We have thus assumed that the concentration of O_2 in our sample tubes is independent of temperature; the following additional reasons help to substantiate this assumption.

(1) The diameter of the sample is 3 mm, while the depth of sample is about 1.5 in. Thus there is only a very small surface area across which the O_2 might diffuse for a relatively large sample volume. Thus, even if solubility and partial pressure effects do not balance, the rate of change of the concentration of O_2 in the sample should be slow and observable. Since the epr signal intensities do not change as a function of time, no change in the concentration of O_2 as a function of

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(11) F. A. Walker and R. F. Trecartin, unpublished results.

(12) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966, p 175.

(13) The intensities of the epr signals are directly proportional to the magnetic susceptibilities of the respective species. The number of unpaired electrons in a species calibrated using a standard has been shown to be[14]

$$N = X_0[3kT/g^2\beta^2S(S+1)] = Kg(D/D^*)(G^*/G)(H_m^*/H_m)S_F{}^2[3kT/g^2\beta^2S(S+1)]$$

where X_0 is the magnetic susceptibility of the sample (which is proportional to the first power of g), K is a calibration contant for the system, D is the signal height, G is the relative amplifier gain, H_m is the modulation amplitude, S_F is the line width, and the starred quantities refer to the standard.[14] Cancellation of g factors gives inverse first-order dependence of N on g. This relationship is valid only if the power settings are below those necessary to bring about saturation. For the ratio of concentrations of two species present in the same sample tube, each of which have $S = {}^1/_2$ and are recorded at the same modulation and amplifier gain settings

$$\frac{[\text{II}]}{[\text{I}]} = \frac{D_{\text{II}} \times S_{\text{FII}}{}^2 \times g_{\text{I}}}{D_{\text{I}} \times S_{\text{FI}}{}^2 \times g_{\text{II}}}$$

Since $D_{\text{I}} \times S_{\text{FI}}{}^2$ is an approximation made by Singer and Kommandeur[14] of the area under the absorption peak (which need not be made here, since areas are measured directly by use of a planimeter), for our system

$$\frac{[\text{II}]}{[\text{I}]} = \frac{(\text{area of II})\langle g\rangle_{\text{I}}}{(\text{area of I})\langle g\rangle_{\text{II}}}$$

No calibrating standard was used, since only the ratio of the two concentrations need be determined.

(14) L. S. Singer and J. Kommandeur, *J. Chem. Phys.*, **34**, 133 (1961).

(15) W. F. Linke and A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. II, 4th ed, Van Nostrand, Princeton, N. J., 1958, p 1235.

(16) Reference 15, p 1234.

Table I. Experimental Data and Calculated K_3 for the Reaction of Co(*p*-OCH$_3$)TPP·5-Cl-N-MeIm with O$_2$ at −80° [a]

Sample	P_{O_2} at 27°,[b] Torr	$[O_2]_0$, *M*	[O$_2$ add]/[5-coord][c]	$[O_2]_{eq}$, *M*	K_3, M^{-1}
1	61	5.62×10^{-4}	0.229	4.00×10^{-4}	572
2	84	7.74×10^{-4}	0.348	5.50×10^{-4}	632
3	174	16.0×10^{-4}	0.667	12.6×10^{-4}	531
4	248	22.8×10^{-4}	1.111	18.2×10^{-4}	610
5	268	24.7×10^{-4}	1.102	20.1×10^{-4}	549
					Av 579 ± 34

[a] [5-Cl-N-MeIm]$_0$ = 1×10^{-1} *M*, [Co]$_0$ = $8.67 + 10^{-4}$ *M* = [5-coord]$_0$. [b] Corrected for P_{toluene} = 30 Torr at 27°. [c] Determined by integration of epr signals for sample 1 and use of eq 5.

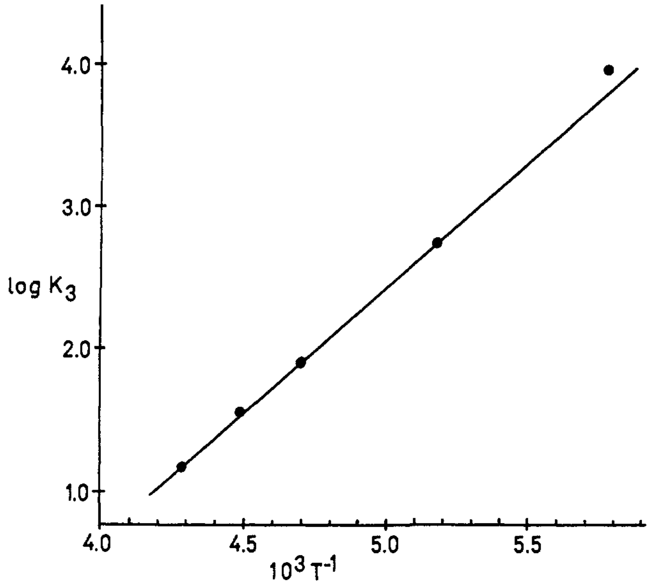

Figure 2. van't Hoff plot of equilibrium constants for reaction 3 where B = 5-chloro-*N*-methylimidazole.

temperature is suggested. When a sample containing a partial pressure of 60 Torr of O$_2$ was opened to the air at −60°, no change in epr signal intensities was observed for 5 min, even though the partial pressure of O$_2$ increased from 60 to 206 Torr upon opening the stopcock. Furthermore, the epr signal intensities are the same when a sample is cooled from room temperature to the desired temperature as when the same sample is cooled considerably *below* the desired temperature for 15 min and then warmed *to* the desired temperature.

(2) Since the epr method is most accurate when [O$_2$ adduct]/[5-coord] is small, fairly low partial pressures of O$_2$ (50–250 Torr) were used in these investigations. Thus if [O$_2$] = 7×10^{-3} *M* atm^{-1}, the samples contained 4.6×10^{-4}–2.3×10^{-3} *M* O$_2$. Since [Co(*p*-OCH$_3$)TPP·B]$_0$ ~ 8–10 × 10^{-4} *M* in these investigations, large corrections for $[O_2]_{eq}$ were necessary, particularly at the lower temperatures. Thus, if $[O_2]_0$ were not correct, trends in the observed values of K_3 or K_4 would be observed within one set of data as $[O_2]_0$ was increased. Although individual values of K_3 and K_4 varied by ±10% from the average, no trends were observed, as shown in a typical set of data, Table I.

(3) Since correction of $[O_2]_{eq}$ for the amount used in complex formation is most important at the lowest temperatures, further evidence for a possible temperature-dependent concentration of O$_2$ in toluene (or any absolute error in $[O_2]_0$) should be found in the van't Hoff plot (Figure 2), where the lowest temperature points should fall significantly off the line if the wrong correction for $[O_2]_{eq}$ has been made. Figure 2 shows such a van't Hoff plot for reaction 3 in which B = 5-chloro-*N*-methylimidazole for the temperature range −20 to −100°. As is clearly demonstrated, good linearity is observed; the deviation of the lowest temperature point from the line represents a possible error in $[O_2]_{eq}$ of less than 20%, or an error in $[O_2]_0$ of less than 10%. It should be pointed out, however, that the precision of the measurement at −100° was poor, due to the large size of the equilibrium constant, with error limits of ±30%, so a possible error in $[O_2]_0$ of 10% is probably an unreasonably large estimate.

For these reasons we feel that the [O$_2$] in toluene does not vary significantly over the temperature range of these investigations and that the value of 7×10^{-3} *M* atm^{-1} at room temperature is characteristic, under our experimental conditions, of the whole temperature range. For purposes of comparison with other workers, we have, however, reported ΔG_3 and ΔS_3 in the standard state of this investigation (1 *M* O$_2$) and also in that of 1 Torr of O$_2$ (see Table II).

Reaction 3. Since it was found impossible to measure the equilibrium constant for reaction 2 by visible spectral methods at room temperature, K_2 was calculated from the equilibrium constants of reactions 3 and 4, when it was possible to push reaction 2 far enough to the right to allow measurement of K_4. Thermodynamic data for reaction 3 at −65° are given in Table II. This temperature was chosen because it falls close to the average temperature of these investigations, so that inherent errors may be minimized.

Examination of the data of Table II points out several interesting features. First, the data show that within experimental error, for all bases investigated, neither ΔG_3 nor ΔH_3 is correlated with the pK_a of the conjugate acid of the amine; that is, the σ donor strength of the amine does not appear to be important in determining the stability of the Co–O$_2$ complex, nor the strength of the Co–O bond. A plot of ΔH_3 *vs.* ΔS_3 (Table II) gives an isoequilibrium temperature[17] of about 130°K, which is far enough away from the temperature of the data of Table II (−65°C, 208°K) that pK_a (BH$^+$) should be a sensitive function of log K_3, if such a relationship exists. Apparently it does not.

Comparison of the series of amines of Table II in their effectiveness at strengthening the Co–O bond shows that the variation in ΔH_3 is remarkably small. It appears that aromatic amines (pyridines and imidazoles) may provide a slight stabilization of the Co–O bond, when one considers that they are less basic than aliphatic amines. Thus π back-bonding from Co to the amine may be somewhat important in strengthening the Co–O bond. One might expect this to be the case,

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(17) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 324–326.

Table II. Equilibrium Data for Reaction 3 at −65°

Amine	pK_a (BH$^+$)	Log $K_3{}^a$ ±0.03	ΔG_3,^{a} kcal/mol	ΔH_3, kcal/mol	ΔS_3,^{a} cal/(mol deg)	ΔG_3,^{b} kcal/mol, ±0.03	ΔS_3,^{b} cal/(mol deg)
Solvent = Toluene							
Pyridine	5.22	2.84	−2.70	−9.3 ± 1.1	−32 ± 4	+2.34	−55
4-Picoline	5.98	2.95	−2.81	−8.8 ± 0.9	−29 ± 3	+2.09	−52
3,4-Lutidine	6.46	2.81	−2.68	−9.2 ± 0.1	−31 ± 1	+2.23	−54
4-Dimethylaminopyridine	9.70	3.41	−3.25	−8.5 ± 0.8	−25 ± 1	+1.79	−48
γ-Collidine	7.43	2.41	−2.29	−9.5 ± 1.3	−35 ± 4	+2.75	−58
5-Chloro-*N*-methylimidazole	5.45	2.10	−2.00	−8.6 ± 0.1	−31 ± 1	+3.04	−54
N-Methylimidazole	7.06	3.58	−3.41	−8.9 ± 0.5	−26 ± 2	+2.63	−49
Piperidine	11.22	2.87	−2.73	−8.2 ± 0.1	−26 ± 1	+2.17	−49
Solvent = Carbon Disulfide							
Pyridine	5.22	−2.18^b		−8.5 ± 0.5		+2.08	−51
3,4-Lutidine	6.46	−2.10^b		−9.0 ± 0.6		+2.00	−53
Other Systems							
1. Cobalt(II) protoporphyrin IX dimethyl ester							
Solvent = Toluene (Stynes and Ibers)^{c,d}							
Pyridine^{c,d}	5.27			−9.2 ± 1.0		+2.87	−58
Benzimidazole^d	5.48			−9.6		+1.96	−56
tert-Butylpyridine^{c,d}	5.99			−10.0 ± 0.5		+1.86	−57
Imidazole^d	6.95			−11.2		+1.87	−58
N-Methylimidazole^{c,d}	7.06			−11.5 ± 1.0		+0.57	−58
Solvent = Water (Hoffman)^e							
2. Cobalt–myoglobin^e				−12.7 ± 0.5		−2.09	−51

^{a} Standard state of 1 M O_2. ^{b} Standard state of 1 Torr of O_2. ^{c} Reference 9. ^{d} Reference 10. ^{e} Reference 7.

since back-bonding would decrease the electron density on the Co(III) product, which would aid in strengthening its bond to the electron-rich O_2^- product species. However, the data of Table II show that any such stabilization of the Co–O bond is minor. Extrapolation of these data to 298°K shows that in the most favorable cases (4-dimethylaminopyridine or *N*-methylimidazole as the axial base) only about 0.8% of the cobalt would be in the form of the oxygen adduct when solutions are exposed to the atmosphere. Therefore, the formation of the oxygen adduct (reaction 3) does not interfere with the measurement of K_1 at room temperature and above.[3]

The entropy of reaction 3 is somewhat more negative than is usually found for reactions of highly solvated molecules. However, it is interesting to note that it is very similar to the entropies of activation for the reaction of alkyl halides with cobaloxime[18]

$$\mathrm{Co(DMGH)_2\cdot B + RX \xrightarrow{k} Co(DMGH)_2\cdot B\cdot X + R\cdot}$$

$$\mathrm{Co(DMGH)_2\cdot B + R\cdot \xrightarrow{fast} Co(DMGH)_2\cdot B\cdot R}$$

$\Delta S^{\ddagger} = -30$ cal/(deg mol) in benzene solution.

It is easier to explain the large negative entropy values in the present work than in the reactions investigated by Halpern,[18] since O_2 is a particularly small molecule, in comparison to solvent molecules such as toluene, benzene, or carbon disulfide and solute molecules such as alkyl halides[18] or amines.[3] The entropy of solution of O_2 in benzene (standard state = 1 atm $O_2 \rightarrow 1\ M\ O_2$) is only −8.2 eu at 25°[19] (and similar for other organic solvents), which represents loss of very little of its gas-phase entropy of translation and rotation upon dissolution in organic solvents. A larger molecule, ClO_2, shows quantized rotational states in toluene solution,[20] which indicates that ClO_2 still retains a considerable amount of gas-phase freedom in the liquid phase. This is undoubtedly due to the fact that ClO_2, and to an even greater extent O_2, are much smaller than organic solvent molecules, and are thus able to translate and rotate relatively freely within the solvent cavities provided by the relatively large organic molecules. Therefore, upon coordination to a cobalt porphyrin, O_2 loses more entropy than, for example, a larger amine molecule which cannot translate or rotate so freely in solution. Thus ΔS_3 is much more negative than ΔS_1 (see ref 3) or ΔS_2 (see below and Table III). A slightly more negative value of ΔS_3 is observed when the base is γ-collidine (2,4,6-trimethylpyridine), probably due to loss of entropy of internal rotation of the amine in this sterically hindered complex. The entropy and enthalpy of coordination of O_2 to cobalt-containing myoglobin,[7] cMb, are fairly similar in magnitude to those of this work and also to those reported by Stynes and Ibers[9,10] (see Table II). However, the balance of enthalpy and entropy effects appears to be much more favorable when the cobalt porphyrin is contained within the protein. Whether the protein is solely responsible for the much more favorable ΔG for coordination of O_2 at room temperature, or whether the effects of smaller solvent cavity size in aqueous solution may produce added stability by decreasing the effect of the unfavorable entropy change has not yet been determined. We are now investigating reaction 3 in aqueous solution to determine what effect the aqueous medium may have on the free energy of the reaction.

The data of Table II differ somewhat from those re-

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(18) J. Halpern and P. F. Phelan, *J. Amer. Chem. Soc.*, **94**, 1881 (1972), and references therein.

(19) Converted to the standard state of 1 M O_2 from the data of Table 4.2; J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962, p 44.

(20) R. E. D. McClung and D. Kivelson, *J. Chem. Phys.*, **49**, 3380 (1963).

Table III. Equilibrium Data for Reactions 2 and 4 at −65°

Amine	K_4	ΔH_4, kcal/mol	ΔS_4, cal/(deg mol)	K_2, M^{-1}	ΔH_2, kcal/mol	ΔS_2, cal/(deg mol)
3,4-Lutidine	730	−7.5 ± 1.0	−23	0.8	−1.8 ± 1.0	−10
Piperidine	210	−6.7 ± 1.0	−21	4.0	−1.7 ± 1.0	−6

ported by Stynes and Ibers[9,10] for the similar cobalt protoporphyrin IX dimethyl ester·B system with pyridine, 4-*tert*-butylpyridine, *N*-methylimidazole, and several others as the axial base (see Table II). Their results showed a direct relationship between the pK_a of the conjugate acid of the amine and the ΔH of formation of the Co–O bond. Such a correlation is not observed in this work. In their investigation, amine concentrations in the range of ~2 × 10^{-5} M were used.[9] Although this may be sufficient for Co(protoDME), for Co(p-OCH$_3$)TPP (Table I of ref 3) this concentration would not be large enough to push equilibrium 1 far to the right. The degree of five-coordination of Co(p-OCH$_3$)TPP would then be expected to be a sensitive function of temperature and K_1 (and thus pK_a, as shown in Figure 2, ref 3). Alkyl substituents on the porphyrin ring, as in Co(protoDME), should enhance the equilibrium constants for reaction 1, thus reducing any temperature dependence of the degree of five-coordination in the investigation of Stynes and Ibers.[9,10] Solvation of the porphyrin ring, which is expected to differ between alkyl- and aryl-substituted porphyrins, may also be partly responsible for the existence or nonexistence of a pK_a dependence of ΔH_3 in these otherwise similar systems. Further experiments are in progress to test this hypothesis.

The similar magnitude of ΔH_1[3] and ΔH_3 is interesting ($\Delta H_1 \sim -8$ to -11 kcal/mol,[3] $\Delta H_3 \sim -8.5$ to -9.5 kcal/mol), since one might have expected that the electron transfer from Co(II) to O$_2$ upon bond formation (reaction 3) would cause the enthalpy of Co–O bond formation to be considerably more negative than in the case of the formation of the coordinate covalent Co(II)–amine bond (reaction 1[3]), where the electron is clearly localized on Co(II).[2] However, these two reactions differ in type in one important respect; reaction 1 is the addition of a ligand to the four-coordinate Co(II) porphyrin, which apparently acts to activate the Co(II) for the reaction with O$_2$ to form a covalent bond (reaction 3). By comparison, the reaction of five-coordinate Co(II) porphyrins with an additional amine to form a coordinate covalent bond (reaction 2) is quite unfavorable (*vida infra*), suggesting that the Co(II) species, activated by addition of one ligand (reaction 1), is much more reactive as a free radical than it is as a Lewis acid. The strength of the Co–O bond (reaction 3) is 9 kcal, on the average, whereas the strength of a Co–N bond (reaction 2) is about 1.8 kcal. By comparison the cobalt–carbon bond of methyl cobalamin is estimated to be greater than 32 kcal in strength, although the actual value is not known.[21]

Reactions 2 and 4. Table III shows the results of investigation of reaction 4 and the calculated data for reaction 2 for two amines, 3,4-lutidine and piperidine. In most other cases equilibrium 2 was not favorable enough to allow measurement of the equilibrium constant of reaction 4. At −65°, K_2 is quite small in these favorable cases and, since ΔH_2 is also very small, there is only weak temperature dependence of this equilibrium constant. At room temperature the extrapolated values for K_2 are ~1 (piperidine) and ~0.132 (3,4-lutidine). A small negative ΔH_2 and a small equilibrium constant for reaction 2 are consistent with the fact that the Co–N bonds of the bispiperidine adduct of Co(II)TPP are extremely long (2.44 Å),[23] which suggests only weak bonding of the amine molecules to Co(II). The entropy change for reaction 2 is similar in magnitude to that reported for reaction 1,[3] as expected. The data of Table III also point out that the Co–O bond is ~7–8 kcal stronger than the Co–N bond it replaces (ΔH_4), which is again an interesting comparison between covalent bond formation and coordinate covalent bond formation (or between free radical reaction and Lewis acid reaction of Co(II)).

Side Reactions. At room temperature and above, the oxygen adduct of Co(p-OCH$_3$)TPP·B is stable to the extent of less than 0.8% of the cobalt present in the five-coordinate amine complex form, in the most favorable cases. Therefore, the oxygen adduct was not an interference in the measurement of K_1 at and above room temperature in air.[3] However, a side reaction sometimes took place when the reagents were not carefully purified before use. This side reaction took place on the time scale of the experimental measurement and produced a species which showed absorption peaks at 437 nm (ϵ 1.53 × 10^5 M^{-1} cm^{-1}), 514 (4.27 × 10^3, shoulder), 553 (1.22 × 10^4), and 591 (7.00 × 10^3). Upon standing this product crystallized out. The electronic spectral properties of the product are those of a cobalt(III) porphyrin species, and it gives no epr spectrum.[11] The mass spectrum of the sample indicates that it is a mixture of the chloride and hydroperoxide complexes of the cobalt(III) porphyrin.[11]

When carefully purified solutions of Co(p-OCH$_3$)TPP·B in the presence of 1 atm of O$_2$ are left for long periods of time, the intensity of the epr signal slowly decreases, presumably due to formation of the binuclear complex (reaction 5 above). After 18 months at room temperature the epr signal intensity of a sample containing pyridine as the axial base and greater than 1 atm of O$_2$ had decreased to 54% of the original integrated signal intensity. Heating the sample to 100° for 15 min restored the epr signal to 87% of its original intensity. This suggests that reaction 6 is, at least to a reasonable degree, reversible and points out a striking contrast between this system and those of Wilkins,[24] in

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[21] In homolytic bond cleavages it is generally expected that the enthalpy of activation, $\Delta H^{\ddagger}$, is similar to the thermodynamic bond strength, as measured by $\Delta H°$. Although the rate of dissociation of methyl cobalamin is not known, the half-life is certainly much longer than 1 day at room temperature.[22] Taking this as the minimum half-life, $\Delta G^{\ddagger} \geq 24$ kcal/mol. Since one expects $\Delta S^{\ddagger}$ to be of the order of −25 to −30 eu, $\Delta H^{\ddagger} \geq 32$ kcal/mol.

[22] F. R. Jensen, personal communication.

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which formation of the binculear complex by the reaction

$$2CoL_5 + O_2 \longrightarrow L_5CoOOCoL_5$$

where L is one of a series of nitrogenous bases, was extremely rapid and difficult to reverse. One of the major differences may be the solvent (toluene in our studies, *vs.* water in Wilkins'). For that reason we are extending our investigations to aqueous solution, where we hope to find an answer to the seemingly great differences between the reactions of Co(II) complexes of various ligands in various solvents with molecular oxygen.

One additional reaction of cobalt(II) porphyrins must not be overlooked: the reaction of the four-coordinate cobalt(II) porphyrin directly with molecular oxygen in the absence of amines[2]

$$CoP + O_2 \rightleftharpoons CoP\cdot O_2 \qquad (7)$$

This reaction is not favorable enough to study quantitatively at any accessible temperature in which the solvent is liquid (down to −95° in toluene), and thus it is quite unfavorable in comparison to reactions 3 and 4. A solution of Co(p-OCH$_3$)TPP in toluene containing 1 atm of air at −83.5° showed a detectable amount of its "base-off" O_2 adduct. This suggests that the equilibrium constant for reaction 7 is at least 100 times smaller than the "base on" O_2 adduct at that temperature. Glassy samples of Co(p-OCH$_3$)TPP in toluene which are not degassed show a unique epr spectrum at 77°K, which is present when the samples are not degassed and absent when they are degassed. Wayland[25] has reported the epr parameters of the species CoTPP·O_2 as $g_{\parallel} \sim 2.05$, $g_{\perp} = 1.993$, $|A_{\parallel}|$ not resolved, $|A_{\perp}| = 31$ G (0.0029 cm^{-1}). We observe a similar spectrum for Co(p-OCH$_3$)TPP; it is nonaxial, with $g_1 \sim 2.11$, $g_2 = 1.988$, $g_3 = 1.985$, $|A_1| \sim 0.0014$ cm^{-1} (not resolved), $|A_2| = 0.00251$ cm^{-1}, and $|A_3| = 0.00293$ cm^{-1}. The fact that this spectrum is nonaxial is a strong suggestion that in this "base off" Co–O_2 complex also, the oxygen moiety is unsymmetrically bound to the cobalt.

The fact that this "base off" Co-O_2 complex is significantly less stable than the CoP·B·O_2 species produced by reactions 3 and 4 suggests that the amine plays an important role of activating the cobalt for formation of the Co–O bond. It does appear, however, that the activation of Co(II) porphyrins by axial bases for the reaction with molecular oxygen is much less sensitive to the electronic and steric effects of the axial base than are the amine complexes of Schiff's bases and dimethylglyoxime with alkyl groups.[26]

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The Chemistry of Rhenium(IV) Chloride. II.[1] Structure of One of the Polymorphs (β) and Evidence for a New Polymorph (γ)[2]

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Abstract: The crystal structure of the form of rhenium(IV) chloride which is obtained by reaction of Re_3Cl_9 with $ReCl_5$ or $SbCl_3$ with $ReCl_5$ has been investigated. This substance proves to be identical with that first reported in 1967. The structure is here described in detail. The crystals belong to the monoclinic system, with unit cell parameters $a = 6.362$ (2) Å, $b = 6.273$ (2) Å, $c = 12.165$ (4) Å, $\beta = 93.15$ (5)°, $d_{\mathrm{calcd}} = 4.49$ g cm^{-3} for $Z = 4$, and $d_{\mathrm{measd}} = 4.50$ g cm^{-3}. Successful refinement was carried out in the space group $P2/c$ using 1227 measured intensities, corrected for absorption. In the final cycle of full-matrix, anisotropic refinement the unit-weighted and weighted residuals were both 0.049. The structure consists of confacial bioctahedra, Re_2Cl_9, which are linked by shared terminal chlorine atoms. The Re–Re distance is 2.728 (2) Å which is indicative of metal-to-metal bonding. X-Ray powder diffraction patterns show that the form of $ReCl_4$ obtained by dechlorinating $ReCl_5$ with $CCl_2{=}CCl_2$ has a different structure.

The earliest report[4] of the preparation of rhenium(IV) chloride has not been confirmed.[5,6] In 1966, an authentic sample of $ReCl_4$ was produced by accident in a commercial laboratory. Its identity has been confirmed[7] and some of its chemistry has been investi-

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