Inorganica Chimica Acta, *91* (1984) 251–255

Oxygen and Nitric Oxide Affinities of Iron(II) 'Capped' Porphyrins

MAKOTO SHIMIZU, FRED BASOLO*
Department of Chemistry, Northwestern University, Evanston, Ill. 60201, U.S.A.
MARIA N. VALLEJO and JACK E. BALDWIN
The University, Oxford OX1 3QY, U.K.

Received August 25, 1983

Oxygen and NO binding constants are reported for Fe(Por)(B) [1] complexes. The results show a good correlation between O_2 and NO affinities, and this is attributed to the similar bent structures of the Fe–O–O and Fe–N–O moieties. Evidence is presented to show that iron(II) C_3-capped porphyrins have a low affinity for O_2 because of ligand coordination on the cavity side of the cap.

Introduction

Extensive studies [2] have been done on the binding of O_2 and of CO to iron(II) porphyrins, Fe(Por)(B). To our knowledge, only one such study of NO binding has been reported. This is the elegant work of Romberg and Kassner [3] on the binding of NO to horse myoglobin and to 1-methylimidazole protoheme. Their study showed that O_2 and NO, both with stable bent structures of Fe–O–O and Fe–NO, bind similarly to the protein and to the model; whereas CO, with a stable linear Fe–C–O structure, binds more weakly to the protein than to the model compound.

We have explained our studies [4] on O_2 and on CO binding in Fe(Cap)(B) on the basis of distal steric effects. If valid, this interpretation requires that NO binding mirror O_2 and not CO binding. This is what was found, as is reported here.

Experimental

Reagent

Toluene was reagent grade and distilled under N_2 from sodium metal prior to use. 1-MeIm and 1,2-Me_2Im were dried over KOH, distilled under vacuum and stored under N_2 at 0 °C. The N_2 gas was Matheson prepurified grade and was passed through Redox column to remove residual O_2. Gaseous dioxygen was Air Product Ultra-Pure Carrier Gas (containing less than 1.0 ppm H_2O) or Matheson Primary Standard 0.999% O_2 in N_2 for the measurement of O_2 binding constants. Gaseous carbon monoxide was Matheson Ultra High Purity and gaseous nitric oxide was Matheson Certified Standard 5 ppm NO in N_2 for the measurement of NO and CO equilibrium constants.

Synthesis

1,5-DCIm was synthesized by the method of Traylor and coworkers [5]. The synthetic methods of Fe(C_2-Cap)Cl, Fe(C_3-Cap)Cl, Fe(TPP)Cl and F(T(P–OMe)PP)Cl were described in our previous paper [4]. Fe(C_4-Cap)Cl was obtained from Baldwin and coworkers.

Procedure

Oxygen Affinity Measurements

The procedure used was described in a previous paper [4]. The O_2 binding to five-coordinate iron(II) porphyrin complexes is illustrated by eqn. 1.

$$\mathrm{Fe(Por)(B)} + O_2 \overset{K_B^{O_2}}{\rightleftharpoons} \mathrm{Fe(Por)(B)(O_2)} \quad (1)$$

$$\text{where } P_{1/2}^{O_2} = \frac{1}{K_B^{O_2}}$$

The Fe(Por)(B) solutions were prepared as described in a previous paper [4]. The base concentration was chosen to give greater than 99% of five-coordinate complex in the capped porphyrin systems and 98% of that in the open-flat porphyrin systems such as Fe(TPP)(1,2-Me_2Im) and Fe(T(*p*-OMe)PP)(1,2-Me_2Im). The concentration of base required was determined from the reported equilibrium constants K_B and K_B^B [6].

Nitric Oxide Affinity Measurements

Since NO affinity is too large for us to obtain directly $P_{1/2}^{NO}$ values by the titration with NO of toluene solutions of five-coordinate iron(II) porphyrins, (eqn. 2), we used the

$$\mathrm{Fe(Por)(B)} + \mathrm{NO} \overset{K_B^{NO}}{\rightleftharpoons} \mathrm{Fe(Por)(B)(NO)} \quad (2)$$

$$\text{where } P_{1/2}^{NO} = (K_B^{NO})^{-1}$$

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*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

method of Romberg and Kassner [3] which requires titration with NO of toluene solutions of six-coordinate carbonyl complexes Fe(Por)(B)(CO), (eqn. 3).

$$\mathrm{Fe(Por)(B)(CO)} + \mathrm{NO} \underset{}{\overset{K_B^{CO,NO}}{\rightleftharpoons}} \mathrm{Fe(Por)(B)(NO)} + \mathrm{CO} \qquad (3)$$

where $N = K_B^{CO,NO}$

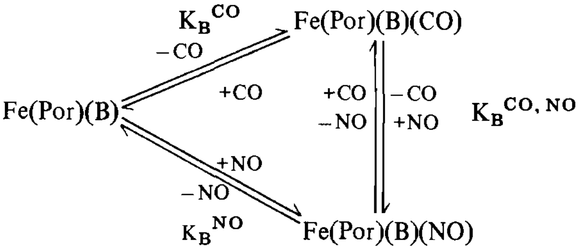
The partition coefficient between NO and CO, N, is defined by the equation

$$N = \frac{[\mathrm{Fe(Por)(B)(NO)}]\cdot P^{CO}}{[\mathrm{Fe(Por)(B)(CO)}]\cdot P^{NO}} \qquad (4)$$

where P^{CO} and P^{NO} correspond to the partial pressures of CO and NO. At 50% nitrosyl complex the ratio of the partial pressure of the gases is equal to $P_{1/2}{}^{CO}/P_{1/2}{}^{NO}$, where $P_{1/2}$ is the partial pressure of a gas when a compound is half complexed. Thus

$$N = \frac{P_{1/2}{}^{CO}}{P_{1/2}{}^{NO}} \qquad (5)$$

The following binding scheme may be used for the titration with NO



The equilibrium constants are related by the relationship;

$$K_B^{NO} = K_B^{CO}\cdot K_B^{CO,NO} \qquad (6)$$

This equation can be expressed in terms of $P_{1/2}$ and N;

$$P_{1/2}{}^{NO} = \frac{P_{1/2}{}^{CO}}{N} \qquad (7)$$

The $P_{1/2}{}^{NO}$ for five-coordinate iron(II) porphyrin was calculated from the reported [6] $P_{1/2}{}^{CO}$ value and the experimentally determined value for N (Table I).

The partition coefficients, N, corresponding to the ratio $P_{1/2}{}^{CO}/P_{1/2}{}^{NO}$, were determined spectrophotometrically using 4.0 cm path length visible cell. In general the spectra were recorded in the 550 ~ 350 nm ranges. The differences between the ferrous carbonyl and nitrosyl compounds were much greater in the Soret region than in the visible region, so the Soret regions were chosen to follow absorption changes in the titration of carbonyl compounds with NO.

The Fe(Por)(B) solutions were prepared as described in a previous paper [4]. The base concentration was chosen to give greater than 99% of the five-coordinate complex in the capped porphyrin complexes and 98% of that in the flat-open porphyrin complex Fe(TPP)(1,2-Me_2Im). The concentration of the base solution was determined from the reported equilibrium constants K_B and $K_B{}^B$ [6]. More than 20 mL of the base solution prepared as described above was added to the Fe(Por) residue and mixed for a few minutes. Pure CO gas (Matheson, Ultra High Purity) was then bubbled through the porphyrin solution for ~2 h to produce the Fe(Por)(B)(CO) complexes. The spectrum was then taken. Pure CO gas was passed through the solution for an additional 1 h to obtain pure carbonyl complex, as indicated by constant measurement of absorbance. This Fe(Por)(B)(CO) solution was then transferred to the visible cell, which contained a small magnetic stir bar.

Once the solution was in the visible cell, it was brought to the chosen temperature (25 °C), and then the cell was attached to the solution NO apparatus. This apparatus was equipped with gas inlet and outlet tubes, by which the mixture gas containing varying partial pressures of CO and NO was bubbled through the porphyrin solution. The partial pressure of CO and NO in the gas was adjusted by mixing pure CO

TABLE I. Oxygen Affinities and Nitric Oxide Affinities [Partition Coefficient] of Some 'Capped' Iron(II) Porphyrins in Toluene.

Affinity	$P_{1/2}{}^{O_2}$ (torr)[a]		$P_{1/2}{}^{NO}$(torr)[a]	[N][b]
	1.0 *M* 1,2-Me_2Im −45 °C	0.1 *M* 1,5-DClm 0 °C	1.0 *M* 1,2-Me_2Im 25 °C	
TPP	5.3[c]		1.1×10^{-7}	$[1.3 \times 10^{6}]$[d]
C_2-Cap	27[e]	19.4	2.0×10^{-6}	$[1.0 \times 10^{5}]$
C_3-Cap	6,000[e,f]	54.2[e]	3.3×10^{-6}	$[4.2 \times 10^{4}]$
C_4-Cap	–[g]	–[h]	4.1×10^{-5}	$[1.0 \times 10^{5}]$

[a] Values reproducible within 10%. [b] $N = P_{1/2}{}^{CO}/P_{1/2}{}^{NO}$. [c] For Fe(T(*p*-OMe)PP) from Ref. 4. [d] Solution is 3.1×10^{-3} 1,2-Me_2Im. [e] Reference 4. [f] Value estimated from $P_{1/2}{}^{O_2}$ = 880 torr at −63 °C. [g] Large $P_{1/2}{}^{O_2}$ could not be determined at one atmosphere of O_2. [h] Not determined because of formation of Fe(4-Cap)(1,5-DClm)$_2$.

with commercially prepared NO in N_2 (5 ppm), using two Matheson 600 rotometers and two precision needle valves. The rotometers were individually calibrated throughout their ranges with both pure CO and 5 ppm NO in N_2.

In order to prevent concentration changes during bubbling, the gas mixture was saturated with toluene at the same temperature as the porphyrin solution, also a large amount of Fe(Por)(B)(CO) solution (>20 mL) was used. Each gas mixture was passed through the solution until equilibrium was attained, as indicated by constant measurement of absorbance. This method is essentially the same as that used by Collman and coworkers [7] for the measurement of O_2 affinity.

Reversibility was checked after the last NO addition by purging with pure CO gas for ~12 h to obtain the identical initial spectrum.

Data from the spectrophotometric titrations were treated with eqn. 8

$$\frac{P^{NO}}{P^{CO}} = [M(Por)]_T \cdot b \cdot \Delta\epsilon' \left(\frac{P^{NO}/P^{CO}}{\Delta A'}\right) - \frac{P_{1/2}{}^{NO}}{P_{1/2}{}^{CO}} \qquad (8)$$

derived from Collman's [7] eqn. 9

$$P_{O_2} = [M(Por)]_T \cdot b \cdot \Delta\epsilon \left(\frac{P^{O_2}}{\Delta A}\right) - P_{1/2}{}^{O_2} \qquad (9)$$

for calculating oxygen affinity. In these equations $\Delta\epsilon'$ is the difference in molar absorptivity of the carbonyl and nitrosyl complexes, and $\Delta A'$ is the difference between the absorbance at a particular P^{NO}/P^{CO} and the absorbance of the carbonyl complex at the same wavelength. Also $[M(Por)]_T$ is the total metal porphyrin concentration, b is the cell path length, $\Delta\epsilon$ is the difference in molar absorptivity of the oxy and deoxy complexes, and ΔA is the difference between the absorbance at a particular P_{O_2} and the absorbance of the deoxy complex at the same wavelength. Since $[M(Por)]_T \cdot b \cdot \Delta\epsilon'$ is a constant, a plot of P^{NO}/P^{CO} *vs.* $(P^{NO}/P^{CO})/\Delta A'$ will give a straight line with y intercept equal to $P_{1/2}{}^{NO}/P_{1/2}{}^{CO}$. All data were fitted using a nonweighted linear least-squares method.

Results

Table I contains data on O_2 and NO affinities of some Fe(Por)(B) complexes. Spectrophotometric O_2 titrations of toluene solutions of Fe(Cap)(1,5-DCIm), where cap = C_2- and C_3-cap, gave spectral changes with good isosbestic points (Fig. 1). Unfortunately the O_2 affinity of Fe(C_4-Cap)(B) for B = 1,2-Me_2Im and 1,5-DCIm could not be measured.

Spectrophotometric NO titrations of toluene solutions of Fe(Por)(1,2-Me_2Im)(CO) gave spectral changes with good isosbestic points (Fig. 2). Data obtained from such optical spectra were used to determine values of $P_{1/2}{}^{NO}$ (Table I).

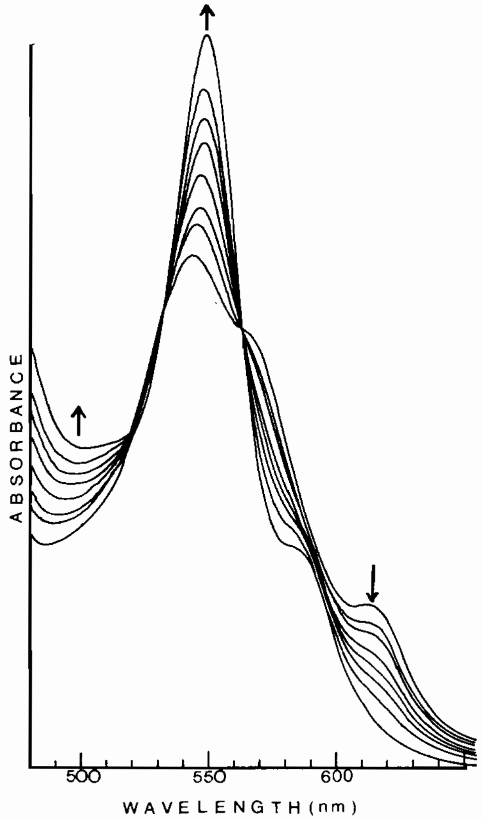
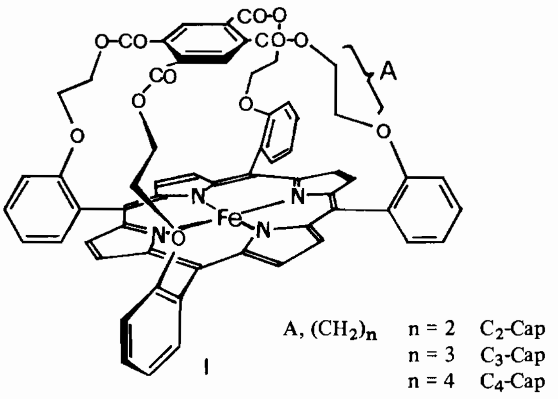


Fig. 1. Spectral changes occurring upon titration of a toluene solution of ~10^{-5} *M* in Fe(C_2-Cap)(1,5-DCIm), 0.1 *M* in 1,5-DCIm, with the following pressures of dioxygen at 0 °C; 0, 3.0, 5.5, 11.4, 19.8, 31.4, 60.1, and 878.0 torr.

Discussion

Our earlier studies [4] dealt with the binding of O_2 and of CO to some iron(II) C_2- and C_3-capped porphyrins, (I).



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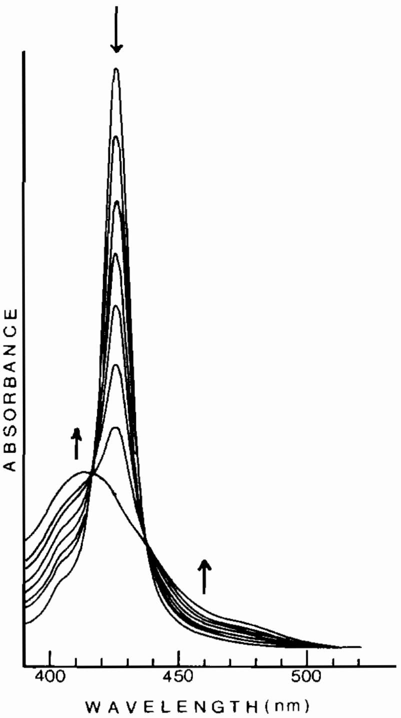


Fig. 2. Spectral changes occurring upon titration of a toluene solution of $\sim 10^{-6}$ *M* in Fe(C_4-Cap)(1,2-Me_2Im)(CO), 1.0 *M* in 1,2-Me_2Im, with the following pressure ratios of carbon monoxide and nitric oxide, P^{CO}/P^{NO}, at 25 °C; Fe(C_4-Cap)(1,2-Me_2Im)(CO), 4.95×10^5, 2.48×10^5, 1.42×10^5, 8.85×10^4, 4.81×10^4, 2.39×10^4 and 0[$P^{CO} = 0$ torr, $P^{NO} = 3.66 \times 10^{-3}$ torr].

The results of those studies showed that O_2 binding of capped systems is less than that of analogous flat-open complexes such as Fe(TPP)(B). This was attributed to an interference with the stable bent structure of Fe–O–O in the capped complexes by peripheral steric effects. In contrast to this, it was found [4, 6] that the capped and the flat-open porphyrin iron(II) complexes have similar affinities for CO. This was said to be due to there being little central steric effect in the capped systems, providing no detectable interference with the stable Fe–C–O linear structure.

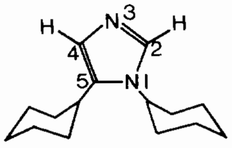
If the explanation is correct that O_2 binding in Fe(Cap)(B) complexes suffers from peripheral steric effects due to the stable bent structure of Fe–O–O, then it follows that similarly bent Fe–N–O should experience similar steric effects. Data in Table I support this, showing that both O_2 and NO affinities decrease in the order Fe(flat-openPor)(B) > Fe(Cap)(B). Qualitatively, NO affinities do correlate O_2 affinities in these systems, in accord with prediction.

Now it is necessary to look more closely at the values of $P_{1/2}^{O_2}$, and at the peripheral steric effect hypothesis. We had earlier observed [8] that there is sufficient room inside the C_3-cap, but not the C_2-cap, to permit a second 1-MeIm to coordinate and give Fe(C_3-Cap)(1-MeIm)$_2$. Recent ^1H nmr studies [9] show that dimethylsulfoxide binds inside the cap cavity to give Zn(C_3-Cap)(DMSO)$_2$. Furthermore the nmr results show that dynamic processes are present for C_2-cap and C_3-cap, and that C_3-cap has greater flexibility which gives it a variable cap cavity size.

It now appears that ligand coordination on the cavity side of C_3-cap is responsible for the very low O_2 affinity of iron(II) C_3-capped porphyrins. The importance of ligand coordination on the cavity side of the cap can be illustrated in three different ways, using the data in Table I.

(1) The values of $P_{1/2}^{O_2}$ at –45 °C for Fe(Por)(1,2-Me_2Im)$_n$ vary in the order T(*p*-OMe)PP > C_2-Cap ≫ C_3-Cap, with relative values of 1, 5, and 1000, respectively. If the five-fold effect in going from flat-open to capped porphyrin is due to peripheral steric effects, then what causes the 200-fold effect in going from C_2-cap to C_3-cap? We had attributed this to the greater peripheral effect of the additional methylene group in the C_3-cap, but we now think it is largely due to ligand coordination on the cavity side.

(2) In support of ligand coordination on the cavity side at –45 °C for Fe(C_3-Cap)(1,2-Me_2Im)$_n$ are the results obtained for the bulky ligand 1,5-DCIm, (II).



II

The values of $P_{1/2}^{O_2}$ at 0 °C are 19(C_2-Cap) and 54(C_3-Cap). Assuming the bulky 1,5-DCIm does not coordinate on the cavity side of either cap, at these experimental conditions, it follows that the extra methylene group in C_3-cap causes less than a three-fold decrease in O_2 affinity. Note that even this bulky ligand, at these experimental conditions, gives largely Fe(C_4-Cap)(1,5-DCIm)$_2$, because of the larger more flexible C_4-Cap.

(3) Because of the strong binding of NO to Fe(Por)(1,2-Me_2Im), it is possible to determine $P_{1/2}^{NO}$ at 25 °C (Table I) and to adjust experimental conditions in favor of the five-coordinate iron(II) complexes. The values of $P_{1/2}^{NO}$ are seen to vary in the order TPP > C_2-Cap ~ C_3-Cap > C_4-Cap, with relative values of 1, 10, and 100, respectively. This shows a ten-fold decrease in NO affinity in going from flat-open to capped porphyrins, which may be attributed to peripheral effects. It is of interest that this ten-fold effect is similar to the five-fold effect for O_2 binding, which also was attributed to peripheral steric effects. This is in accord with the

prediction made for the similar bent structures of the moieties Fe–O–O and Fe–N–O. The additional ten-fold effect on NO binding found at C_4-cap may be due to some coordination of 1,2-Me_2Im on the cavity side of the cap, or to the greater squashed [4, 10] or twisted [6] configuration of C_4-cap.

One can further speculate that the dynamic processes [9] involved with the capped porphyrins are more rapid at higher temperature. At such temperatures the flexible cap may sweep back and forth across the top of the porphyrin plane and retard ligand coordination on the cavity side of the cap. At lower temperatures this motion of the cap becomes much more sluggish, permitting a greater tendency of ligand coordination on the cavity side of the cap. For this reason, it is possible to have a solution of five-coordinate Fe(Cap)(B) at room temperature, whereas the same solution at –50 °C may largely contain the six-coordinate complex Fe(Cap)$(B)_2$.

Acknowledgements

We thank the National Institutes of Health for support of this research. We also are grateful to Ube Industries Ltd. for support of M.S., their employee. We thank Professor T. G. Traylor for help with the synthesis of 1,5-DCIm.

References

1 Abbreviations; Por, dianion of porphyrin; C_2-Cap, dianion of the C_2-capped porphyrin; C_3-Cap, dianion of the C_3-capped porphyrin; C_4-Cap, dianion of the C_4-capped porphyrin; TPP, dianion of *meso*-tetraphenylporphyrin; T(*p*-OMe)PP, dianion of tetra-*p*-*m*ethoxy-*meso*-tetraphenylporphyrin; 1,2-Me_2Im, 1,2-dimethylimidazole; 1,5-DCIm; 1,5-dicyclohexylimidazole; B, monodentate ligand; $P_{1/2}^{O_2}$ $(=(K_B^{O_2})^{-1})$, the O_2 pressure at half saturation; $P_{1/2}^{NO}$ $(=(K_B^{NO})^{-1})$, the NO pressure at half saturation.

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