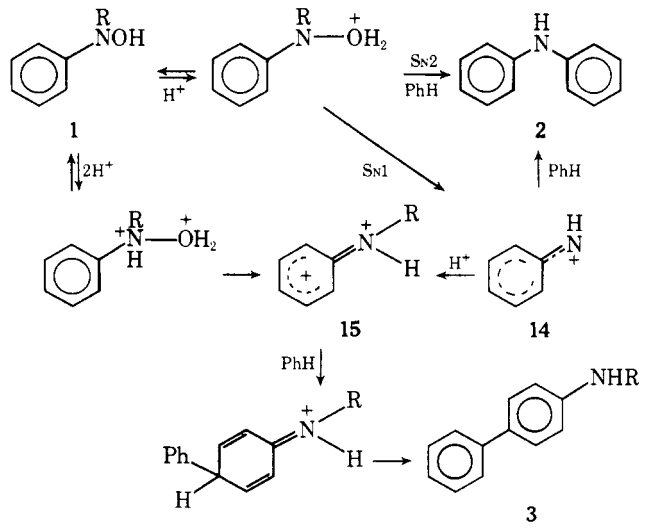
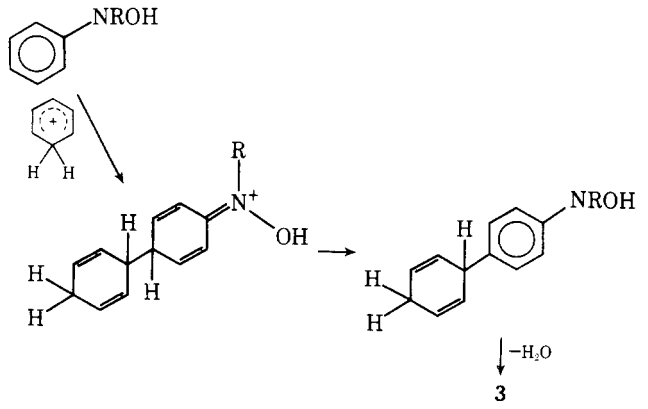
Scheme II



Scheme III



ble species generated by anodic oxidation in a strongly acidic medium,[10] supports the participation of the intermediate ion in this reaction.

Another mechanism which may lead to aminobiphenyls should be considered (Scheme III). This involves an electrophilic attack of benzenium ion on phenylhydroxylamine, followed by aromatization and dehydration. However, this mechanism hardly explains the formation of **8** and **11** from 4-methylphenylhydroxylamine (**7**).

References and Notes

(1) K. Shudo and T. Okamoto, *Tetrahedron Lett.*, 1839 (1973).
(2) The products identified were **2** (12%), **3a** (6%), **4a** (2%), **3b** (5%), **4b** (1%), and azoxybenzene (5%). *N-tert*-Butyldiphenylamine could not be identified.
(3) Both **2** and **3** are stable under these reaction conditions.
(4) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6295 (1953), L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).
(5) It is possible to explain the formation of **8** by nucleophilic attack of benzene on **13**.
(6) G. A. Olah and J. Welch, *J. Am. Chem. Soc.*, **97**, 208 (1975).
(7) Products from these reactions are 4-aminobiphenyl, 4-amino-*p*-terphenyl, 4′-amino-*m*-terphenyl, and probably 4′-amino-*o*-terphenyl. Identification of the last compound has not been done yet.
(8) A simple discussion that SN2 reaction leads to **2** and SN1 reaction leads to **3** does not explain the role of the acids used, though the slow reaction of **1b** in the presence of TFA may suggest the importance of bimolecular mechanism in the TFA-catalyzed reaction which gives **2**. An alternative pathway, which cannot be eliminated, involves phenylhydroxylamine *O*-ester formed in the presence of TFSA. The ester solvolyzes to anilenium ion **14**, which reacts with benzene. Even in this case, protonation of **14** is very probable. The formation of azoxybenzene (run 4), which is suppressed by the presence of ascorbic acid, is explained by the homolytic cleavage of the N–O bond, probably the Loeffler–Freytag type homolysis of $PhNH_2^+$–OH. This and the reactions of para-substituted phenylhydroxylamines eliminate the homolytic process in the present reactions.
(9) P. G. Gassman, *Acc. Chem. Res.*, **3**, 26 (1970); P. G. Gassman, G. A. Campbell, and F. C. Fredrick, *J. Am. Chem. Soc.*, **94**, 3884 (1972).
(10) U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 1234 (1974); D. Serve, *ibid.*, **97**, 434 (1975).

Toshihiko Okamoto,* Koichi Shudo, Toshiharu Ohta

Faculty of Pharmaceutical Sciences, University of Tokyo Hongo, Bunkyo-ku, Tokyo, 113, Japan

Received July 11, 1975

Oxygen Binding to Iron Porphyrins

Sir:

The current literature abounds with simple synthetic models of myoglobin and hemoglobin,[1-5] all of which are capable of binding oxygen reversibly. In addition to reversible binding, however, a good model must be inert towards oxidation and reproduce the thermodynamic constants of the biological systems. We report here the first such comparison of a synthetic ferrous porphyrin model with myoglobin, the results of which help to delineate the role of the aproprotein in oxymyoglobin.

Using the "picket fence" porphyrin model, Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm),[4,6] we have determined the enthalpy and entropy of oxygen binding in the solid state. The porosity of the crystals of this material allows the full equilibration of the solid with oxygen without the difficulties of most solution studies: the eventual irreversible oxidation of the compound and the complex equilibria with axial base. The solid–gas approach has the further advantage of a known molecular geometry as determined from x-ray diffraction data.[7] A simple manometric adsorption apparatus[8] in conjunction with an electronic manometer[9] was used in all experiments. The temperature of the apparatus was controlled to ±0.1°C, while connected to a vacuum line, which could be evacuated to a pressure of 10^{-6} Torr. Volumes were calibrated by expanding nitrogen from an outside gas bulb of known volume and pressure into the evacuated apparatus.

Isotherms were determined by desorption of a fully saturated[10] sample of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm)·$O_2$ into an evacuated volume. Each isotherm consists of at least six points, each point representing the extrapolation to equilibrium of 4 hr of data.[11] These isotherms followed the Langmuir equation at low pressures (less than 15 Torr), indicating that the iron binding sites are noninteracting in the crystal lattice. A typical plot of $\theta/(1-\theta)$ vs. p_{O_2}, where θ is the fraction of saturation at equilibrium, is shown in Figure 1 for the data collected at 25.0°. The thermodynamic enthalpy and entropy of reaction with oxygen were derived from a weighted least-squares fit to a van't Hoff plot ranging over 50°.[12] The calculated constants are $\Delta H° = -15.6 \pm 0.2$ kcal/mol and $\Delta S° = -38 \pm 1$ cal deg^{-1} mol^{-1} (standard state of 1 atm). The interpolated $K_{eq}^{20°}$ is 2400 atm^{-1} or equivalently, $p_{1/2}^{20°} = 0.31$ Torr. It should be noted that some deviation from the Langmuir isotherm was observed at high pressures at 0°; this is attributable to a strong physical adsorption of oxygen on the porphyrin rather than to the binding at the iron atom: the metal free ligand, $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP, physically adsorbs oxygen with an equilibrium binding constant of roughly 2 atm^{-1} at 0°. It should also be noted that in contrast to solution models, our solid samples are remarkably inert to oxidation. For example, one sample has been cycled between O_2 and vacuum more than 200 times with no observable irreversible oxidation.

A comparison of our thermodynamic constants with those of a selection of myoglobins and of the model of Chang and Traylor[3] is made in Table I. It is clear that the "picket fence" is a good model for myoglobin in this respect. The close similarity of the model to the biological sys-

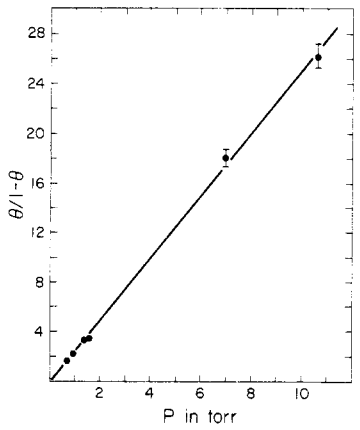


Figure 1. Isotherm of O_2 binding of Fe($\alpha,\alpha,\alpha,\alpha$-TpivPP)(1-MeIm) at 25.0°. Error limits set from accuracy of manometer. The least-squares fit to Langmuir isotherm equation $(\theta/(1-\theta) = (p_{1/2})^{-1}P_{O_2})$ is shown with a slope of 2.53 $Torr^{-1}$ measured over the range of θ = 65% to θ = 96%.

Table I. O_2 Binding by Representative Myoglobins and Myoglobin Models

Source[a]	$p_{1/2}^{20°}$, Torr	$\Delta H°$, kcal/mole	$\Delta S°$, eu[b]
This paper	0.31	−15.6	−38
Chang and Traylor model[d]	0.32	...	...
Human Mb, reconst.[e]	0.72	−13.4	−32[c]
Ox, Mb, adult[f]	0.55	−15	−37[c]
Tuna, Mb[g]	0.90	−13.2	−32[c]
Horse, Mb[h]	0.70	−13.7	−33[c]

[a] It should be noted that some variance exists in the literature concerning these constants due to both the experimental difficulties of the myoglobin systems, as well as to the possible inherent differences between myoglobins of different species. [b] Standard state of O_2 partial pressure = 1 atm. [c] Calculated from reported $p_{1/2}^{20°}$ and $\Delta H°$. [d] C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A.*, 72, 1166 (1975). [e] A. Rossi Fanelli and E. Antonini, *Arch. Biochem. Biophys.*, 77, 478 (1958). [f] A. Rossi Fanelli, E. Antonini, C. DeMarco, and S. Benerecetti, *Biochem. Hum. Genet., Ciba Found. Symp.*, 144 (1958), cited in E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands", American Elsevier, New York, N.Y., 1971, p 221. [g] A. Rossi Fanelli, E. Antonini, and R. Giuffre, *Nature (London)*, 186, 896 (1960). [h] E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands", American Elsevier, New York, N.Y., 1971, p 221.

tem argues that the apoprotein does not contribute significantly to the binding of oxygen,[14] and suggests that the primary role of the protein in myoglobin is to protect the heme from oxidation.

An independent analysis of these thermodynamic constants is possible. One can partition the entropy of an oxygen molecule into its translational, rotational, vibrational, and electronic (i.e., degeneracy) components.[15] Because the frequencies of the FeO_2 vibrations are not known, we cannot accurately calculate their contribution to the entropy of the complex; however, if we assume them to be of low frequency (400–100 cm^{-1}), then they would contribute an additional 3 to 11 eu. If one includes the loss of the fivefold electronic degeneracy of the Fe^{II} (S = 2) and treats the internal rotation of the bent Fe–O–O system as a free rotor (~7 eu), then

$$\Delta S°_{calcd} = -(S_{O_2}^{trans} + S_{O_2}^{rot} + S_{O_2}^{vib} + S_{O_2}^{elec} + S_{Fe}^{elec}) + S_{FeO_2}^{introt} = S_{FeO_2}^{vib}$$
$$= -(36 + 11 + 0 + 2 + 3) + 7 + (7 \pm 4)$$
$$= 38 \pm 4 \text{ eu (standard state of 1 atm)}$$

The agreement between the calculated and experimental values is consistent with the fit to the Langmuir isotherm, which requires independent binding sites, and with the absence of substantial systematic errors in the experimental determination. This demonstration that the "picket fence" porphyrin is a well-behaved system for solid-gas equilibrium studies sets the stage for further studies of parameters such as the nature and closeness of the axial base and the polarity of the oxygen binding site.

Acknowledgment. We thank Drs. Lowell Wood and Fred Aldridge of Lawrence Livermore Laboratory for the loan of the Barocell, Dr. Susan Hayes for the preparation of iron porphyrin, and the Fannie and John Hertz Foundation for fellowship support (K.S.S.). This work was supported by the National Science Foundation Grant MPS75-17018.

References and Notes

(1) J. Almog, J. E. Baldwin, and J. Huff, *J. Am. Chem. Soc.*, **97**, 227 (1975).
(2) D. L. Anderson, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 5599 (1974).
(3) C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U.S.A.*, **72**, 1166 (1975).
(4) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975). We have recently discovered that the infrared band at 1385 cm^{-1} previously assigned to O_2 is an experimental artifact.
(5) G. C. Wagner and R. J. Kassner, *J. Am. Chem. Soc.*, **96**, 5593 (1974).
(6) Abbreviations used in this work include: $\alpha,\alpha,\alpha,\alpha$-$H_2$TpivPP, *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-o-pivalamidophenyl)porphyrin; Mb, myoglobin; 1-MeIm, 1-methylimidazole.
(7) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Nat. Acad. Sci. U.S.A.*, **71**, 1326 (1974).
(8) S. Ross and J. P. Olivier, "On Physical Adsorption", Interscience, New York, N.Y., 1964, p 29ff.
(9) Barocell Model 523CH-12, from Datametrics, 340 Fordham Rd., Wilmington, Mass. 01887, whose ranges are 0–1, 0–10, 0–100, and 0–1000 Torr with a 3½ digit readout.
(10) Exposure of the sample to 300 Torr of O_2 for 15 hr resulted in better than 99% of stoichiometric binding of O_2.
(11) The half-life of approach to equilibrium was roughly an hour.
(12) Based on ln K_{eq} (°C): 5.34 ± 0.02 (50.0); 6.25 ± 0.05 (37.0); 7.56 ± 0.02 (25.0); 9.76 ± 0.13 (−0.1), with a standard state of 1 atm; error limits of these ln K_{eq} are the standard deviation of the least-squares fit to the Langmuir isotherm at each temperature. Error limits of ΔH and ΔS derived using the extremum method of Benson[13] yield maximum error limits of ±0.5 kcal/mol and ±1.6 eu, respectively. It should be noted that the statistical error limits given are derived from the least-squares fit and may not necessarily reflect the actual experimental error. The reproducibility of the equilibrium constants between separately synthesized samples is less than that of a single sample; K_{eq} varied less than 10% between samples, corresponding to a variation of less than 2% in ln K_{eq}.
(13) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, p 91.
(14) It is not necessary to invoke hydrogen bonding from the distal histidine to O_2 in order to explain the stability of O_2 binding in biological systems, since this model system lacks that feature.
(15) E. A. Moelwyn-Hughes, "Physical Chemistry", Pergamon Press, New York, N.Y., 1961, pp 431–435.

James P. Collman,* John I. Brauman, Kenneth S. Suslick
Department of Chemistry, Stanford University
Stanford, California 94305
Received September 2, 1975

Mechanism of the Cobalt Carbonyl-Catalyzed Homogeneous Hydrogenation of Aromatic Hydrocarbons[1]

Sir:

A variety of polycyclic aromatic hydrocarbons (PAH) are homogeneously hydrogenated in a highly selective manner[2-4] in the presence of $Co_2(CO)_8$ and synthesis gas (CO + H_2) at elevated temperature and pressure ("oxo" conditions). The operation of this catalyst, being one of the few known homogeneous catalysts for aromatic hydrogenation, has special interest. By analogy with the generally accepted mechanism of hydroformylation of olefins with the same catalyst it has been assumed[5] that the key reaction is the