

This reaction is extremely sensitive to temperature. At room temperature,  $\text{Fe}(\text{py})_2\text{TPP}$  in methylene chloride irreversibly oxidizes with no detectable spectral evidence of adduct formation. At  $-45^\circ$ , after 9 min of exposure to oxygen, the spectrum shows that the primary species present is the oxygen adduct. Upon purging with nitrogen, the final spectrum indicates that only about 70% of the initial ferrous complex can be regenerated. However, at  $-78^\circ$ , after 17 hr of exposure to oxygen, 85% of the dioxygen complex could still be reversed to the iron(II) state.

In the case of cobalt oxygen carriers, as the dielectric constant of the solvent increases (provided that the solvent is noncoordinating), the equilibrium constant for the formation of the oxygen adduct likewise increases.<sup>13,14</sup> A similar relationship has been found for  $\text{Fe}(\text{py})_2\text{TPP}$  in various solvents at  $-78^\circ$ . Under 1 atm of oxygen, complete adduct formation occurs in methylene chloride; only a small amount of adduct is formed in toluene, whereas the degree of adduct formation in ethyl ether lies in between these extremes. This is consistent with the dielectric constants of these solvents; at  $20^\circ$  the values for methylene chloride, ethyl ether, and toluene are<sup>15</sup> respectively 9.08, 4.34, and 2.39. At  $-78^\circ$ , these constants are larger, but the same relative order applies. It should be emphasized that in all three solvents, despite varying degrees of adduct formation, the reaction with molecular oxygen is completely reversible at  $-78^\circ$ .

**Acknowledgments.** We would like to thank Professors J. E. Baldwin<sup>16</sup> and J. P. Collman and Dr. R. R. Gagne for helpful discussions. This research was supported by a grant from the National Institutes of Health.

(13) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, **94**, 5125 (1972).

(14) M. J. Carter, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1973.

(15) "Handbook of Chemistry and Physics," 43rd ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, pp 2552-2557.

(16) Subsequent to our observations, Professor Baldwin has found similar reversible oxygen behavior with mesoporphyrin IX bis(1-methylimidazole)iron(II) in methylene chloride at  $-52^\circ$ . See J. Almog, J. E. Baldwin, R. L. Dyer, J. Huff, and C. J. Wilkerson, *J. Amer. Chem. Soc.*, **96**, 5600 (1974).

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Received May 1, 1974

## Reversible Binding of Dioxygen to Mesoporphyrin IX Derivatives at Low Temperatures

Sir:

The reversible formation of dioxygen complexes with iron(II) derivatives, initially at low temperatures<sup>1-3</sup> and subsequently at  $25^\circ$ ,<sup>4,5</sup> has recently been reported. The factors influencing the stability of such complexes

(1) J. E. Baldwin and J. Huff, *J. Amer. Chem. Soc.*, **95**, 5757 (1973).

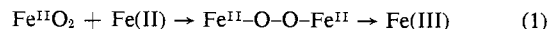
(2) (a) C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, **95**, 5810 (1973); (b) *ibid.*, **95**, 8475 (1973); (c) *ibid.*, **95**, 8477 (1973).

(3) Professor F. Basolo has kindly informed us of the observed reversible behavior of *meso*-tetraphenylporphyriniron(II) derivatives at  $-78^\circ$ . The apical ligands used in these experiments were pyridine, 1-methylimidazole, and piperidine.

(4) (a) J. P. Collman, R. R. Gagné, T. R. Halbert, J.-C. Mardion, and C. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973); (b) J. P. Collman, R. R. Gagné, and C. A. Reed, *ibid.*, **96**, 2629 (1974).

(5) J. Almog, J. E. Baldwin and J. Huff, in preparation.

toward irreversible oxidation to iron(III) species are becoming clear. Thus in the original octaazamacrocyclic iron complex it was shown that steric hindrance protected the bound oxygen molecule,<sup>1</sup> and subsequently<sup>4,5</sup> the same influence was found to stabilize porphyrin derived iron(II) dioxygen complexes at room temperature. The current explanation of this phenomenon is found in a reduction, by steric hindrance, of the rate of the bimolecular redox process, eq 1. Re-



cently an unhindered pentacoordinate porphyrin iron(II) complex (**1**) was reported<sup>2a</sup> to reversibly bind oxygen at  $-45^\circ$  and the successful binding was attributed to "the neighboring group effect of the covalently attached imidazole" as well as to the temperature effect on process 1. Since the iron(II) species was produced *in situ* by sodium dithionite reduction of the iron(III) species, we felt initially that reversibility could be attributed to residual traces of reductant.<sup>6</sup> Consequently we synthesized the mixture (1:1) of the mesoporphyrin IX derivative **2a** and **2b**<sup>7,8</sup> and converted this through the iron(III) bromo derivative to the iron(II) species by reduction with chromous bis(acetylacetonate) in benzene.<sup>4a</sup> On dissolution of the iron(II) species from **2** in precooled ( $-50^\circ$ ) dichloromethane<sup>10</sup> at low concentrations (*ca.*  $10^{-4}$  M), reversible oxygenation was observed spectrally, confirming *in toto* the previous report<sup>2a</sup> and excluding thereby any possibility of residual reductant. The dioxygen adduct is stable at  $-50^\circ$ , showing no deterioration after 45 min. Addition of excess cold pyridine to this adduct solution results in the typical hemochrome spectrum, Figure 1, thus confirming unambiguously the presence of the iron(II) porphyrin.

To investigate the possibility that the neighboring group effect is not important in stabilizing the oxygen adduct of **2**, we synthesized mesoporphyrin IX bis(1-methylimidazole)iron(II) (**3a**) from the mesoporphyrin dimethyl ester by the method described above. A dilute solution of compound **3a** in dichloromethane, ( $10^{-4}$  M,  $-50^\circ$ ) reacts reversibly with oxygen as shown by regeneration of the hemochrome spectrum on addition of pyridine, Figure 1. The spectral changes observed were identical with those we have recorded for compound **2**.<sup>11</sup> Furthermore we have measured the stoichiometry of oxygen binding of **3a** by our earlier described volumetric procedure<sup>1</sup> and found a value of  $\text{O}_2:\text{Fe}$  of  $1.00 \pm 0.04$  at  $-50^\circ$  and  $10^{-3}$  M. These experiments prove that contrary to the earlier report,<sup>2a,b</sup>

(6) The spectral solutions are dilute [ $10^{-4}$  M], consequently the amount of residual reductant required would be very low. A previous example of this phenomenon in experiments alleged to describe reversible oxygenation has been recorded; *cf.* M. J. Cowan, J. M. F. Drake, and R. J. P. Williams, *Discuss. Faraday Soc.*, **27**, 217 (1959); Thesis of R. C. Davies, Wadham College, Oxford, 1963.

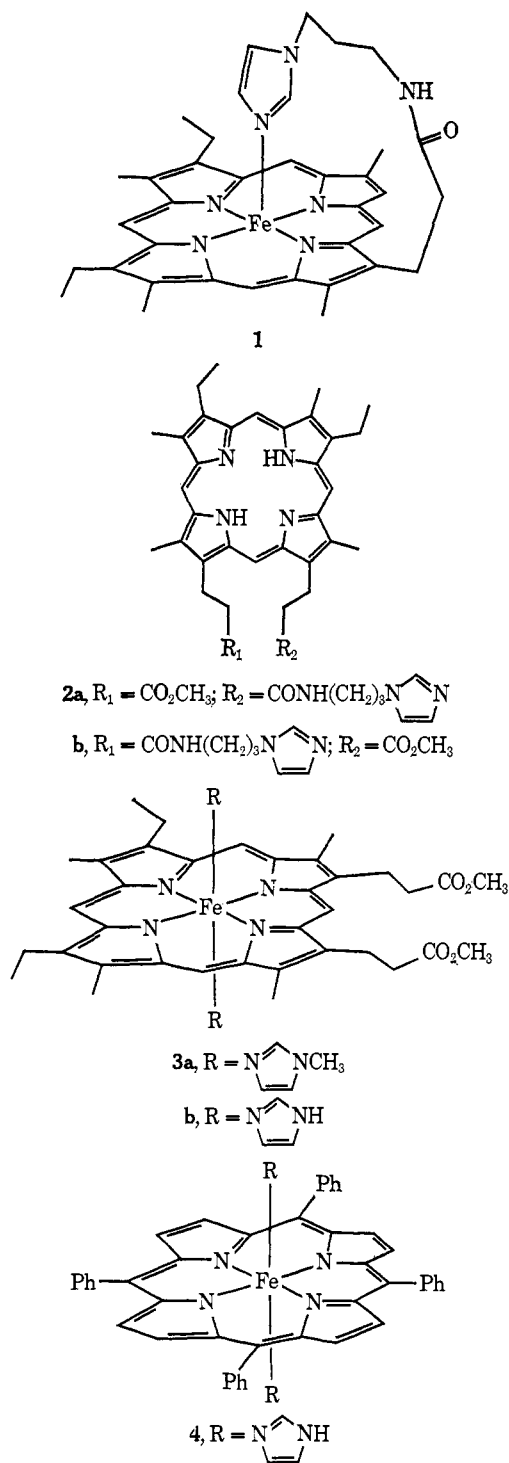
(7) A mixture (1:1) of the two monoesters of mesoporphyrin IX was obtained by partial esterification with diazomethane. This mixture was coupled with 1-(3-aminopropyl)imidazole,<sup>9</sup> through the mixed pivaloyl anhydride to yield the amide **2a, b**.

(8) All new substances have been characterized by spectroscopic and where possible analytical data.

(9) J. J. Schwan, *J. Heterocycl. Chem.*, **4**, 633 (1967).

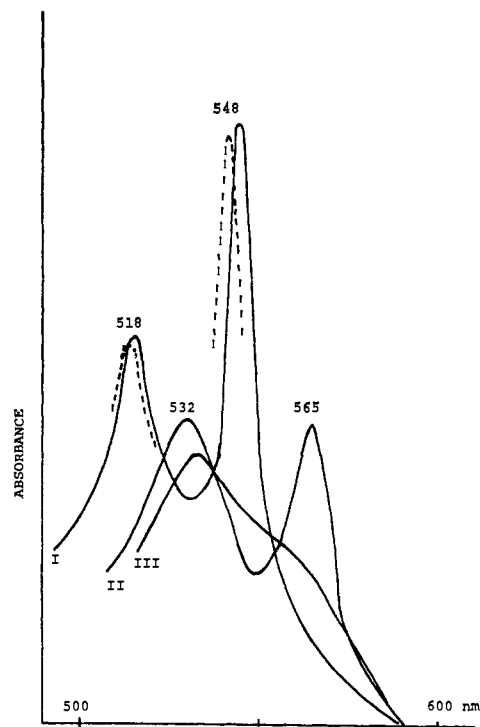
(10) These iron(II) complexes, from **2** and **3**, react at room temperature with dichloromethane to yield the iron(III) species. At  $-50^\circ$  this reaction is very slow.

(11) We have also repeated the earlier report<sup>2a</sup> by reducing the iron(III) bromo derivative of **2a, b** with aqueous sodium dithionite solution and then filtering at  $-45^\circ$  under argon. The reversible spectral changes are identical with those previously recorded<sup>2a</sup> for this solution and are identical with those observed for **3a**.



the neighboring group effect of the covalently attached imidazole of **2**, is not necessary for reversible oxygen binding at these low temperatures and low concentrations.

In related experiments we observed that *meso*-tetraphenylporphyrinbis(imidazole)iron(II) (**4**) reacts instantaneously and *irreversibly* with oxygen even at  $-78^\circ$  in toluene ( $10^{-4} M$ ). Stoichiometric oxygen determination gave a value of  $\text{O}_2:\text{Fe}$  of  $0.21 \pm 0.05$ , which is close to the expected value (0.25) for irreversible autoxidation. The cause of this irreversibility, which is in contrast to other reports,<sup>3</sup> has been traced to the imidazole ligand. Thus unlike the complex **3** with 1-methylimidazole, the related species, mesoporphyrin IX bis(imidazole)iron(II) (**3b**), was irreversibly oxidized in



**Figure 1.** Visible spectra of **2** and **3** in dichloromethane at  $-50^\circ$ : I, **2** and **3** under argon; II, **2** and **3a** exposed to  $\text{O}_2$ ; III, **3b** exposed to  $\text{O}_2$ ; ---, the hemochrome obtained by addition of pyridine to oxygenated solutions of **2** and **3a**.

dichloromethane ( $10^{-4} M$ ) at  $-50^\circ$ . Similarly, addition of excess imidazole to the cool ( $-50^\circ$ ) oxygenated solution of the pentacoordinate complex from ligand **2** gave rise to irreversible oxidation, Figure 1.

In summary, dilute solutions of iron(II) complexes of mesoporphyrin IX dimethyl ester reversibly bind oxygen at  $-50^\circ$ , in the presence of 1-methylimidazole. There is no requirement for a neighboring group effect of a covalently bound ligand to observe this behavior. Also, imidazole causes irreversible oxidation in both the mesoporphyrin IX diester and the *meso*-tetraphenylporphyriniron(II) complexes. The cause of the latter effect is under investigation.

**Acknowledgments.** We thank Professor F. Basolo for helpful discussions and the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly and Company, and the Alfred H. Caspary Fund for financial support.

(12) NSF Predoctoral Fellow, 1971-1974.

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#### Reaction of Trialkylboranes and 2-Bromo-6-lithiopyridine. Stereospecific Alkylative Cleavage of Pyridine Ring to 5-Alkyl-2(Z),4(E)-pentadienenitrile

Sir:

We wish to report the operationally simple, stereospecific procedure affording high yields of 2(Z),4(E)-