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# Kinetics and Mechanism of Reaction of Cobalt(II) Protoporphyrin IX Dimethyl Ester with Pyridine and Related Compounds in Predominantly Alcoholic Media in the Presence and Absence of Air[1,2]

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Pyridine (py), 3CN-py, 4CN-py, 4CH$_3$-py, piperidine (pip), and imidazole (im) (ligands (L), $10^{-4}$–$10^{-1}$ mol dm$^{-3}$) added to a freshly prepared alcoholic (methanol, ethanol, 2-propanol plus 2–10% v/v chloroform) solution of cobalt(II) protoporphyrin IX dimethyl ester (Co$^{II}$P, $5 \times 10^{-6}$ mol dm$^{-3}$) at 25 °C, in the presence of air, moved the Soret peak of the complex 20 nm bathochromically. This shift is attributed to LCo$^{II}$P $\rightarrow$ [L$_2$Co$^{III}$P]$^+$, via L$^{\delta+}$Co$^{II}$P(O$_2^{\delta-}$). The rate of formation of [L$_2$Co$^{III}$P]$^+$ increases with increasing concentration of L and of hydrogen ions and decreases when the O$_2$ content is lowered. When O$_2$ is completely removed, no [L$_2$Co$^{III}$P]$^+$ is formed. The reaction rate also increases with increased ligand-electron-donating ability and solvent acidity and polarity. The rate constants of the overall reaction of Co$^{II}$P with a 2000-fold molar excess of 4CH$_3$-py, py, 4CN-py, and 3CN-py in methanol are $10^{-2}$, $10^{-3}$, $4 \times 10^{-4}$, and $3 \times 10^{-4}$ s$^{-1}$, respectively, at 25 °C. The rates in methanol are about 10–20 times faster than in 2-propanol. In aprotic nonpolar solvents, in the presence of oxygen, [L$_2$Co$^{III}$P]$^+$ is not formed. Polar and protic properties of the solvent are important in stabilizing the intermediate L$^{\delta+}$Co$^{II}$P(O$_2^{\delta-}$). In methanolic solution, in the presence of oxygen, Co$^{II}$P yields $^\delta$Co$^{II}$P(CH$_3$OH)(O$_2^{\delta-}$). The kinetics of the reaction of this complex ($5 \times 10^{-6}$ mol dm$^{-3}$) with py, im, and pip, in methanol, indicates that oxygen is replaced first and methanol second. Limiting rates of oxygen replacement (25 °C) were about $2 \times 10^{-2}$ s$^{-1}$. The corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for im reagent were $61.5 \pm 2$ kJ mol$^{-1}$ and $-70 \pm 5$ J K$^{-1}$ mol$^{-1}$, respectively. The replacement of methanol takes place at a ligand/complex concentration ratio of about 400, and $k_{obsd}$ appears to depend linearly on $C_L$. The second-order rate constants for methanol replacement by py, im, and pip were 250, 100, and 2 s$^{-1}$ mol$^{-1}$ dm$^3$, respectively. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for im were $75 \pm 3$ kJ mol$^{-1}$ and $30 \pm 4$ J K$^{-1}$ mol$^{-1}$, respectively. A mechanism is discussed.

Several ligands can be easily coordinated in axial positions of Co(III) porphyrins in a variety of aprotic and mixed protic–aprotic solvents.[3,4] On the other hand, binding of amine ligands in the sixth position of Co(II) porphyrins is very unfavorable.[5,6] For example, in toluene, this binding takes place at high ligand concentrations only (with piperidine (pip) a $10^5$-fold excess over complex concentration is required[5]). With ligands coordinating less strongly than pip, there is practically no binding to the sixth position at room temperature.[5] We have studied the kinetics of the reaction of cobalt(II) protoporphyrin IX dimethyl ester (Co$^{II}$P, $5 \times 10^{-6}$ mol dm$^{-3}$) with amines as ligands (L: pyridine (py), 3CN-py, 4CN-py, 4CH$_3$-py, and imidazole (im), in concentrations $5 \times 10^{-5}$ to $5 \times 10^{-1}$ mol dm$^{-3}$) at 25 °C. The reactions were carried out in the presence of air, with use of alcoholic solvents that contained 2–10% v/v chloroform. Spectrophotometric measurements show that the final reaction product is a hexacoordinated [L$_2$Co$^{III}$P]$^+$ complex. The rate of formation of [L$_2$Co$^{III}$P]$^+$ increases with increasing entering-ligand concentration and decreases when the O$_2$ content is lowered. When O$_2$ is completely removed, no [L$_2$Co$^{III}$P]$^+$ is formed. The reaction is very strongly proton catalyzed. Furthermore the rates are dependent on basicity and $\pi$-bonding characteristics of L. This dependence is well established for promotion of oxidation of LCo$^{II}$P via L$^{\delta+}$Co$^{II}$P(O$_2^{\delta-}$) in toluene.[5,7] The reaction rates also increase with solvent acidity and polarity. The purpose of this work is to show that, in the presence

of O$_2$, the formation of [L$_2$Co$^{III}$P]$^+$ proceeds via L$^{\delta+}$Co$^{II}$P-(O$_2^{\delta-}$) species that are stabilized by the polar and protic properties of the alcoholic solvents. This enables elimination of O$_2^-$ as HO$_2$· followed by the binding of the amine. If the reaction media do not contain the source of protons, the oxidation, practically, does not take place, and [L$_2$Co$^{III}$P]$^+$ is not formed.

## Experimental Section

**Materials.** Cobalt(II) protoporphyrin IX dimethyl ester was prepared from cobalt acetate (Merck, AR grade) and protoporphyrin IX dimethyl ester (Fluka, purum) according to the literature.[8] The complex was recrystallized from chloroform–methanol and then from benzene. All solvents were Merck AR grade. Absolute methanol was prepared by Lund and Bjerrum's method.[9] Chloroform was washed several times by redistilled water to remove phosgene and other impurities, dried over CaCl$_2$, filtered, and distilled. Pyridine was kept over KOH and freshly distilled before use. Pyridinium chloride was prepared by introducing dry hydrogen chloride into absolute ethanol, at about −15 °C. Cold pyridine was then added, and precipitated pyridinium chloride was filtered off and recrystallized several times from ethanol. Imidazole (Fluka, puriss, p.a.), 4CN-py (Fluka, purum), and 3CN-py (Pliva, purum) were recrystallized several times from ethanol. 4CH$_3$-py (Fluka, purum) was distilled before use. The removal of oxygen from the reaction solution was achieved in the following way: the solution was subjected to sonication at $10^5$ Hz under reduced pressure followed by introduction of oxygen-free argon, reevacuation, and several repetitions of the entire treatment.

**Spectrophotometry.** Absorption spectra were recorded on Cary 16 K and Zeiss DMR 10 spectrophotometers. The sample absorption cell was adapted for work under an oxygen-free atmosphere.

**Kinetics.** The Cary 16 K and Durrum D-110 stopped-flow spectrophotometers were used for kinetics measurements. The stock solution of Co$^{II}$P was $10^{-4}$ mol dm$^{-3}$ in chloroform. The reaction solutions were prepared by mixing the stock solution with one of the following alcohols containing the amount of ligand to give $5 \times 10^{-6}$ mol dm$^{-3}$ of complex (and 10% v/v of chloroform): methanol, ethanol, or 2-propanol. In some experiments the reaction solution contained 2% chloroform. Variation of chloroform concentration between 2%

(1) Taken from the thesis submitted by Z. Dokuzović in partial fulfillment of the requirements for the M.Sc. degree at the University of Zagreb, 1979, and from a M.Sc. thesis in preparation by Xh. Ahmeti.
(2) Presented in part at the 20th International Conference on Coordination Chemistry, Dec 1979, Calcutta, India; see Abstracts, II-29, p 293.
(3) Kiyoko Yamamoto, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)*, **71**, 111 (1977).
(4) N. Datta-Gupta, *J. Inorg. Nucl. Chem.*, **33**, 4219 (1972).
(5) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 1796 (1973).
(6) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 1320 (1972).
(7) F. Ann Walker, *J. Am. Chem. Soc.*, **95**, 1150, 1154 (1973), and references therein.

(8) J. E. Falk, "Porphyrins and Metalloporphyrins", Vol. 2, Elsevier, Amsterdam, 1964, p 139.
(9) H. Lund and J. Bjerrum, *Ber. Dtsch. Chem. Ges.*, **64**, 210 (1931).

and 10% did not affect absorption spectra and kinetics. The thermostated absorption cell (25 ± 0.05 °C) was used as the reaction vessel. The kinetics were followed under pseudo-first-order conditions with $10-10^5$-fold molar excess of the amine ligand over the complex. In the presence of air the concentration of oxygen in the reaction mixture was considered as constant, and oxygen was always in large excess $(50-60\text{-fold}^{10})$ over the $5 \times 10^{-6}$ mol dm$^{-3}$ complex. The kinetics were monitored at the wavelength of the Soret peak of $[L_2Co^{III}P]^+$ and in some cases additionally at the wavelength of the Soret peak of $Co^{II}P$.

The reaction of $^{\delta+}Co^{II}P(CH_3OH)(O_2{}^{\delta-})$ with amine bases was followed by the stopped-flow technique. The solution of the complex $(10^{-5}$ mol dm$^{-3}$ in methanol containing 5% v/v chloroform) was thermostated at 25 ± 0.05 °C and mixed with a thermostated methanolic solution of amine bases in excess $(2 \times 10^3$ to $10^5$ molar). At this excess the replacement of $O_2$ is too fast to be followed, but the replacement of $CH_3OH$ in $[Co^{III}P(CH_3OH)(L)]^+$ formed in the fast step could be easily monitored.

## Results

**Absorption Spectra of the Co$^{II}$P Solutions.** The absorption spectra of Co(II) protoporphyrin IX dimethyl ester in organic solvents are well characterized.[11] For example, the absorption maxima in the Soret region and of $\beta$ and $\alpha$ bands are 404, 530, and 563 nm in benzene and 403, 528.5, and 561.5 nm in carbon tetrachloride. We found the following absorption maxima (nm): 401, 528, 562 in chloroform; 402, 528, 558 in methanol; 401, 528, 558 in ethanol; 401, 528, 562 in 2-propanol. The solvents have apparently only a small influence on peak positions.

On the other hand marked differences exist between the molar absorptivities ($\epsilon$) of solutions in alcoholic and nonalcoholic solvents at Soret and $\alpha$-band wavelengths. The values of $\epsilon$, at the Soret wavelength, of alcoholic solutions are about 30% below those of nonalcoholic solutions. Likewise the $\epsilon$ values of $\alpha$- and $\beta$-band wavelengths of methanolic solutions are 15% and 4%, respectively, smaller than those of nonalcoholic solutions. Corresponding figures for ethanolic solutions are 25% and 22%. The stated differences of molar absorptivities suggest that, in alcoholic solution, a penta-coordinated solvent complex is instantaneously formed, whereas no marked solvent coordinations seem to take place in the nonalcoholic media. This is in agreement with literature data. In fact the addition of a ligand $(10^{-3}$ mol dm$^{-3}$) to a toluene solution of Co$^{II}$P, in the absence of air, decreased the intensity of both the Soret peak (404 nm) and the $\alpha$ peak (563 nm), with a concomitant small blue shift (8–10 nm) of the latter.[5] No shift of the Soret peak was observed.[5]

**Spectral Changes during the Reaction Co$^{II}$P + L.** The amine ligand, L (about 2000 times the concentration of Co$^{II}$P), was added to the alcoholic solution of Co$^{II}$P containing 2% or 10% v/v chloroform, in the presence of air. When py was the entering ligand, the decrease of the Soret peak was accompanied by a simultaneous appearance of five new absorption maxima at 238, 244, 251, 257, and 263 nm. The decrease of Soret absorbance (at 401–404 nm, depending on the alcohol used) and the simultaneous appearance of a new Soret band (at about 420–423 nm, depending on the alcohol) are accompanied by a decrease of the $\alpha$ peak and its bathochromic shift (8–9 nm). In addition, the $\beta/\alpha$ peak ratio increased due predominantly to the decrease of the $\alpha$ peak. In our opinion the appearance of a new Soret band 20 nm bathochromically to the first is due to the formation of a six-coordinated Co(III) complex from a five-coordinated Co(II) complex. This appears to be in agreement with observations of other authors.[5,12,13]
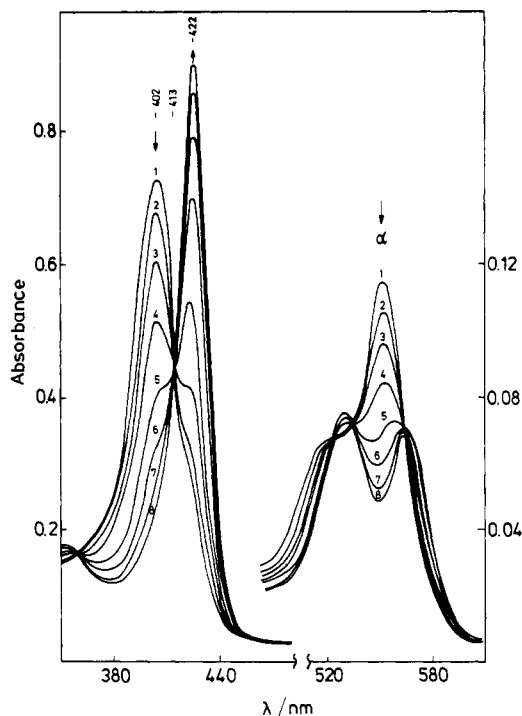


**Figure 1.** Spectral changes of a $5 \times 10^{-6}$ mol dm$^{-3}$ solution of Co$^{II}$P in methanol (10% v/v chloroform). The entering ligand is imidazole in a 100-fold molar excess over the complex; the temperature is 25 °C. Repetitive scans are numbered consecutively at 3-min intervals.
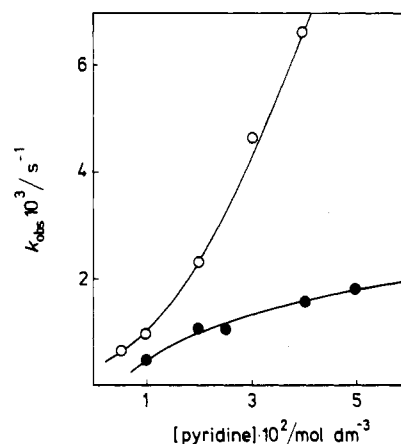


**Figure 2.** Dependence of the rate of formation of $[L_2Co^{III}P]^+$ from Co$^{II}$P $(5 \times 10^{-6}$ mol dm$^{-3})$ in the presence of air on pyridine concentration (25 °C) in methanol (O) and ethanol (●), each containing 10% v/v chloroform.

These authors attribute a smaller shift of 16 nm, observed under certain circumstances, to the formation of a six-coordinated Co(II) complex from a five-coordinated cobalt(II) complex. Therefore we conclude that under our reaction conditions (alcoholic media, amine ligands, presence of oxygen) the final reaction product is $[L_2Co^{III}P]^+$. The $[L_2Co^{III}P]^+$ complex, with L = py, was previously prepared and its spectrum recorded (in the visible region only[14]). The spectrum shows two maxima, one between 534 and 538 nm and the other between 567 and 570 nm. The small shifts were caused by changes in solvent composition. Our reaction product with py reagent showed the absorption maxima at 534–535 and 568–570 nm, depending on the alcohol used. Almost the same maxima were also found with all other amine ligands. Figure 1 shows the change of absorption spectra of the solution of

(10) The concentration of $O_2$ in air-saturated aqueous solution is $2.7 \times 10^{-4}$ mol dm$^{-3}$ at 25 °C. The solubility of $O_2$ in methanolic solutions is approximately 10% smaller; "Chemical Handbook of Japan", Chemical Society of Japan, Maruzen, Tokyo, Japan, 1973, p 571.
(11) Reference 6, p 243.
(12) N. Datta-Gupta, *J. Inorg. Nucl. Chem.*, **33**, 419 (1972).
(13) N. Datta-Gupta and T. J. Bardos, *J. Pharm. Sci.*, **57**, 300 (1968).

(14) R. J. McConnel, B. G. Overell, V. Petrov, and B. Sturgeon, *J. Pharm. Pharmacol.*, **5**, 179 (1953).

**Table I.** Rates of Reaction of 5 × 10⁻⁶ mol dm⁻³ Co^II P with Ligands (L) in the Presence of Air^a

| solvent | 10²[py]/mol dm⁻³ | | | | | 10²[pip]/mol dm⁻³ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 0.5 | 1 | 3.0 | 5 | 15 |
| methanol^b | 1.0 | 2.3 | 4.5 | 9.5 | 13.0 | 1.7 | 3.7 | 12.0 | | |
| | 0.2 | 0.5 | 0.9 | 2.0 | 2.0 | 0.3 | 0.7 | 2.0 | | |
| | 5 | 5 | 6 | 5 | 4 | 4 | 4 | 4 | | |
| ethanol^b | 0.47 | 1.05 | 1.20 | 1.25 | 1.30 | 0.30 | 0.70 | 2.2 | 3.6 | 10.7 |
| | 0.06 | 0.10 | 0.13 | 0.11 | 0.15 | 0.04 | 0.08 | 0.3 | 0.4 | 1.1 |
| | 4 | 4 | 4 | 4 | 4 | 3 | 3 | 3 | 3 | 3 |
| 2-propanol^b | 0.12 | 0.30 | 0.40 | 0.45 | 0.52 | | 0.100 | 0.40 | 0.600 | 1.9 |
| | 0.01 | 0.04 | 0.03 | 0.04 | 0.05 | | 0.007 | 0.02 | 0.003 | 0.1 |
| | 4 | 4 | 3 | 4 | 3 | | 4 | 4 | 4 | 3 |

^a L = pyridine, piperidine; temperature 25 ± 0.05 °C; product [Co^III PL₂]⁺. Uncertainties are standard errors of the mean. They were determined from variances of observed rate constants at the respective entering ligands' concentrations (L. Saunders and R. Flemming, "Mathematics and Statistics", The Pharmaceutical Press, London, 1957, p 227).   ^b First row: mean rate of reaction ($10^3 k_{obsd}/s^{-1}$). Second row: standard errors of the mean. Third row: number of kinetic runs.

## Co^II P in methanol (containing 10% v/v chloroform) and the im reagent in about 100-fold excess over the complex concentration.

Co^II P in methanol (containing 10% v/v chloroform) and the im reagent in about 100-fold excess over the complex concentration. It can be seen that the two Soret peaks lie 20 nm from each other.

### Kinetics of Formation of [Co^III PL₂]⁺ from Co^II P

**Dependence of the Reaction Rate on Concentration of L.** The rate of formation of [L₂Co^III P]⁺ is influenced by the nature of the solvent and ligand. The different shapes of the curves that present these dependences reveal the complexity of the reaction systems. For example, Figure 2 shows that the observed rate constant depends differently on py concentration in methanolic and ethanolic solutions. A similar type of dependence was obtained with pip in the same solvents. The dependence of rate on concentration with some further ligands and solvents (4CH₃-py and pip in 2-propanol) is represented by upward bent curves, but the combination of 4CH₃-py and methanol gave a downward bent curve. The reaction rates increase with increasing solvent acidity and polarity. For example, reactions of Co^II P with py and pip are faster in methanol than in ethanol, whereas in 2-propanol the rates are the lowest; see Table I.

**Dependence of the Reaction Rate on Basicity of L.** The following qualitative order of reactivities was observed with various entering ligands: im > pip > 4CH₃-py > py > 4CN-py > 3CN-py. The corresponding $pK_a$ values at 25 °C are[7,15] 6.9, 11.1, 6.0, 5.2, 2.2, and 2.0.[16] The rate with im is about 15-fold that with 4CN-py. It appears that the ligand basicity (σ-donor ability) is of primary importance. The exception is imidazole, which reacts faster than expected from its basicity. Since ligands coordinated trans to the oxygen will compete for π-electron density on the cobalt, the binding of O₂ to LCo^II P will be sensitive to the π-donating or -accepting ability of the axial ligand L. As pointed out,[5] good π acceptors will decrease π-electron density on the metal (weaker Co–O₂ bond), while good π donors will promote bonding of oxygen. Since imidazole is a much better π donor than, e.g., pyridine,[5] the high rate with imidazole can be understood.

The additional explanation could be that pip reacts somewhat slower than expected from its σ-donor ability.

The slower reaction of pip is probably due to van der Waals repulsions between the π system of the porphyrin and piperidine hydrogen atoms at the ring positions nearest to the nitrogen.[7] It should be noted that this dependence of the reaction rate on ligand basicity is analogous to that established in oxidation of LCo^II P in toluene, via ^δ+ LCo^II P(O₂^δ−), probably to μ-peroxo-bridged Co(III) dimer.[5]

(15) R. C. Weast, Ed., "Handbook of Chemistry and Physics", 53rd ed., The Chemical Rubber Co., Cleveland, OH, 1972-1973, p D-117.
(16) Value determined in our laboratory by pH measurements at equal concentrations of 3CN-py and 3CN-pyH⁺ in aqueous solution at 25 °C in argon atmosphere.

**Table II.** Rates of Reaction of 5 × 10⁻⁶ mol dm⁻³ Co^II P with Pyridinium Ion, in the Presence of Air^a

| solvent | 10⁴[py·HCl]/mol dm⁻³ | | | | |
|---|---|---|---|---|---|
| | 1 | 3 | 4.5 | 7 | 10.0 |
| methanol^b | 4.5 | 8.0 | 10.5 | 14.7 | 19.8 |
| | 0.2 | 0.5 | 0.5 | 0.8 | 1.0 |
| | 3 | 3 | 3 | 4 | 3 |
| ethanol^b | 1.50 | 4.0 | 5.7 | 8.8 | 12.3 |
| | 0.07 | 0.2 | 0.3 | 0.5 | 0.7 |
| | 3 | 4 | 3 | 3 | 3 |
| 2-propanol^b | 1.9 | 4.7 | 7.0 | 10.6 | 14.7 |
| | 0.1 | 0.3 | 0.4 | 0.6 | 0.8 |
| | 3 | 4 | 4 | 3 | 3 |

^a Temperature 25 ± 0.05 °C, product [Co^III P(py)₂]⁺.  ^b First row: mean rate of reaction ($10^3 k_{obsd}/s^{-1}$). Second row: standard errors of the mean. Third row: number of kinetic runs.

**Dependence of the Reaction Rate on Acidity of the Solution.** The addition of acid (hydrochloric, perchloric, acetic, and p-toluenesulfonic acids were used) accelerated the reaction markedly. For example, addition of 4 × 10⁻⁴ mol dm⁻³ p-toluenesulfonic acid to the reaction mixture containing 5 × 10⁻⁶ mol dm⁻³ Co^II P and 3 × 10⁻³ mol dm⁻³ py in methanol increased $k_{obsd}$ from 7 × 10⁻⁴ to 0.1 s⁻¹. The addition of acid reduces the concentration of pyridine, forming pyridinium ion. Under the above concentration conditions pyridine was still in more than 100-fold molar excess over complex concentration.

The reaction of Co^II P with pyH⁺ in the presence of oxygen, yielding [Co^III P(py)₂]⁺, was also carried out. It was found that rates with pyH⁺ are about 100 times as high as those with py. For example, when concentrations of both pyH⁺ and py are 0.001 mol dm⁻³, the observed rate constants in methanol, at 25 °C, are (1.98 ± 0.1) × 10⁻² and (2.2 ± 0.2) × 10⁻⁴ s⁻¹, respectively. Data in Tables I and II reveal that $k_{obsd}$ for pyH⁺ and py are of the same order of magnitude, although concentrations of pyH⁺ used were 100 times lower than those of py. It should also be noted that with pyH⁺ reagent the influence of solvent media is much less pronounced than with py reagent (compare Tables I and II). This observation allows the conclusion that acidity of the media is more important in determining the reaction rate than solvent polarity.

**Dependence of the Reaction Rate on Oxygen Concentration.** The rate of formation of [L₂Co^III P]⁺ decreases with decrease of oxygen concentration. When oxygen is completely removed, there is no formation of [L₂Co^III P]⁺. For example, the absorption spectrum of the reaction mixture containing 5 × 10⁻⁶ mol dm⁻³ Co^II P and 3 × 10⁻³ mol dm⁻³ py in methanol in an oxygen-free atmosphere remained unchanged for several weeks at room temperature. When the reaction vessel was opened to air, the spectrum changed immediately, indicating the formation of [L₂Co^III P]⁺. Hydrogen and nitrogen were used

**Table III.** Rate Constant of Formation of $[Co^{III}PL_2]^+$ at Various Temperatures[a]

| L | [L]/ mol dm$^{-3}$ | $10^4\ k_{obsd}/s^{-1}$ | | | |
|---|---|---|---|---|---|
| | | 17 °C[b] | 25 °C[b] | 35 °C[b] | 40 °C[b] |
| py | 0.001 | 2.1 | 2.2 | 1.8 | 1.3 |
| | 0.1 | 10.1 | 10.0 | 10.8 | |
| im | 0.001 | 8.3 | 8.1 | 5.0 | |

[a] $Co^{II}P$, $5 \times 10^{-6}$ mol dm$^{-3}$; L = pyridine (py), imidazole (im). Solvent: methanol containing 10% v/v chloroform. Measurements made in presence of air. [b] $\theta_c$.



**Figure 4.** Dependence of the rate constant, $k_{obsd}^{(6)-(7)}$, for the replacement of oxygen by pip in $5 \times 10^{-6}$ mol dm$^{-3}$ $^{\delta+}Co^{II}P$-$(CH_3OH)(O_2^{\delta-})$ (O) and of the rate constant $k_{obsd}^{(10)}$ for the replacement of $CH_3OH$ by pip in $[Co^{III}P(CH_3OH)L]^+$ (●) on piperidine concentration (solvent MeOH (5% v/v CHCl$_3$), presence of air, 25 °C).



**Figure 3.** Spectral changes of a $5 \times 10^{-6}$ mol dm$^{-3}$ solution of $Co^{II}P$ in ethanol (containing 10% v/v chloroform) in the presence of air ($k_{obsd} \simeq 2 \times 10^{-4}$ s$^{-1}$ at 25 °C).

for lowering the oxygen content, and oxygen-free argon was used for complete removal of oxygen (see Experimental Section).

**Effect of Temperature on Reaction Rates.** Data are given in Table III for entering ligands py and im. It can be seen that the reaction rate is very little influenced by temperature. This is obviously due to complexity of the reaction which involves exothermic preequilibria, as is binding of L and $O_2$ to $Co^{II}P$ (see Discussion).

**Reaction of $Co^{II}P$ with Molecular Oxygen in Methanol and Ethanol**

The alcoholic solutions of $Co^{II}P$, in the absence of oxygen, are stable for weeks. No spectral evidence to indicate the formation of hexacoordinated species was found in an oxygen-free atmosphere. On the other hand, if alcoholic solutions are exposed to air, slow spectral changes are observed. In methanol the Soret peak shifts from 402 to 418 nm and in ethanol from 401 to 418 nm, with simultaneous increase of the $\beta/\alpha$ peak ratio (Figure 3). After 24 h there are practically no more spectral changes. The starting Soret peaks at 402 and 401 nm disappeared, suggesting that $Co^{II}P$ is practically no more present in the solution. Upon bubbling of oxygen-free argon through the solution, the initial absorption spectrum was restored. We attribute the observed spectral changes to equilibrium 1. The 16–17-nm bathochromic shift of the Soret
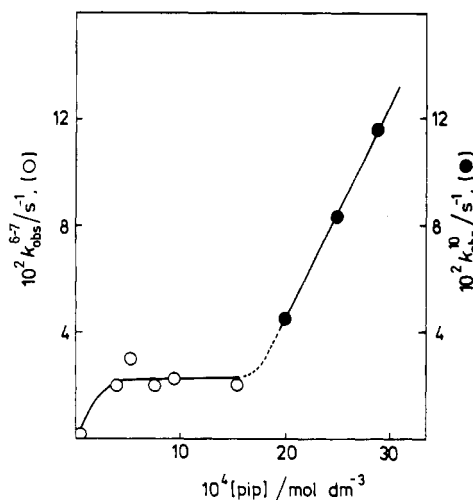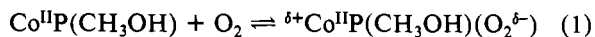
$$Co^{II}P(CH_3OH) + O_2 \rightleftharpoons {}^{\delta+}Co^{II}P(CH_3OH)(O_2^{\delta-}) \quad (1)$$



**Figure 5.** Dependence of the rate of replacement of $CH_3OH$ in $5 \times 10^{-6}$ mol dm$^{-3}$ $[Co^{III}P(CH_3OH)L]^+$ by L (pyridine, imidazole, and piperidine) on concentration of L in MeOH (5% v/v CHCl$_3$) at 25 °C.

peak indicates the formation of a $Co^{II}P$ hexacoordinated species.[5] When the alcohol is in the fifth position, electron transfer from cobalt to oxygen is most probably very small. It is claimed to be small even when amine ligands are in the fifth position, as found in nitrile solvents.[21b] The formation of a $\mu$-peroxo complex is unlikely, since this would, most probably, cause a 24-nm shift of the Soret peak toward longer wavelengths.[5] Moreover, the reversibility of reaction 1 speaks against $\mu$-peroxo complex formation.

**Kinetics of Reaction of $^{\delta+}Co^{II}P(CH_3OH)(O_2^{\delta-})$ with Amine Ligands**

The reaction of $^{\delta+}Co^{II}P(CH_3OH)(O_2^{\delta-})$ with amine ligands in alcoholic media, yielding $[Co^{III}PL_2]^+$, proceeds in two steps, as can be inferred from Figure 4. Oxygen appears to be replaced first, with simultaneous oxidation of Co(II) to Co(III), and methanol is replaced second (see Discussion). The concentration of starting complex, $^{\delta+}Co^{II}P(CH_3OH)(O_2^{\delta-})$, was $5 \times 10^{-6}$ mol dm$^{-3}$. Up to a 200-fold molar excess of the entering ligand over the complex concentration, the rate of the second step can be neglected and the first step easily studied. The rates of the second step were measured at $10^3$- to $(5 \times 10^4)$-fold molar excess of the entering ligand, with use of stopped-flow techniques (Figure 5). The kinetics of both steps in methanol were monitored by measuring the absorbance

at 422, 422.5, and 421 nm for py, im, and pip entering ligands, respectively. At these wavelengths were the absorption maxima of both ligando methanolo and diligando reaction products. The measurements were possible because the molar absorptivities of the diligando final reaction product at these wavelengths are larger than those of the monoligando intermediate. Most of the kinetics was in the stopped-flow range. The second-order rate constants for the replacement of $CH_3OH$ by py, im, and pip are 250, 100, and 2 $s^{-1}$ $mol^{-1}$ $dm^3$ at 25 °C. The dependence of $k_{obsd}$ on replacement of oxygen and methanol by pip is shown in Figure 4. Analogous curves are obtained for py and im. The limiting rates for replacement of oxygen, obtained with these ligands, were 2 × $10^{-2}$ $s^{-1}$ at 25 °C. Figure 5 shows that $k_{obsd}$ for the replacement of $CH_3OH$ by L (py, im, pip) depends linearly on the concentration of L up to about 0.2 mol $dm^{-3}$.

**Activation Parameters.** The rate constants for the replacement of oxygen by im (at $C_{im}$ = 9.2 × $10^{-5}$ mol $dm^{-3}$ and $\delta^+Co^{II}P(CH_3OH)(O_2{}^{\delta^-})$ concentration = 5 × $10^{-6}$ mol $dm^{-3}$) were determined at 18, 21, 25, and 30 °C as 4.4, 6.0, 8.9, and 12.5 × $10^{-3}$ $s^{-1}$, respectively. The Arrhenius plot gave a good straight line. From the least-squares method, $\Delta H^*$ and $\Delta S^*$ were found to be 61.5 ± 2 kJ $mol^{-1}$ and −70 ± 5 J $K^{-1}$ $mol^{-1}$, respectively.
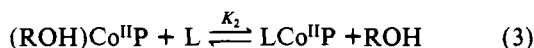
The rate constants for the replacement of $CH_3OH$ by im (8.84 × $10^{-4}$ mol $dm^{-3}$) were determined at 18.5, 21.5, 25.4, 28.0, and 31.0 °C as 2.8, 3.9, 5.5, 8.7, and 9.9 $s^{-1}$, respectively. $\Delta H^*$ and $\Delta S^*$ were 75 ± 3 kJ $mol^{-1}$ and 30 ± 4 J $K^{-1}$ $mol^{-1}$, respectively.

**Discussion**

We have shown that the reaction $Co^{II}P$ + 2L yielding $[L_2Co^{III}P]^+$, in the presence of oxygen, can be readily carried out in alcoholic media. It was also shown that the reaction is acid catalyzed and that the rate is increased by increase of solvent polarity. The importance of solvent polarity in stabilization of the polar $L^{\delta^+}Co^{II}P(O_2{}^{\delta^-})$ species was previously recognized.[17] On the other hand it is important to note that the reaction mentioned above does not take place in dry toluene[5] but, we found, does in toluene containing about 0.01% water. However, in this case the reaction is a few hundred times slower than in methanol. It is reasonable to assume that 0.01% water in toluene did not significantly change the solvent polarity. Probably the effect of water (which was in about $10^4$-fold molar excess over the 5 × $10^{-6}$ molar $Co^{II}P$ complex) is caused by hydrogen bonding to the $L^{\delta^+}Co^{II}P(O_2{}^{\delta^-})$ species.[18,19] This leads to a stabilization of $L^{\delta^+}Co^{II}P(O_2{}^{\delta^-})$. The reaction probably proceeds by steps 2–5. We assume the existence of equilibrium 2 because of the quite large (30%)

$$Co^{II}P + ROH \underset{}{\overset{K_1}{\rightleftharpoons}} (ROH)Co^{II}P \qquad (2)$$

decrease in the molar extinction coefficient of the Soret peak of $Co^{II}P$ when the solvent is changed from chloroform to alcohol. Addition of amine ligands L leads to formation of new equilibria. Alcohol coordinated in the axial (fifth) position is replaced by L (eq 3). The position of equilibrium 3 depends

$$(ROH)Co^{II}P + L \underset{}{\overset{K_2}{\rightleftharpoons}} LCo^{II}P + ROH \qquad (3)$$

on σ- and π-bonding characteristics of L. If the reaction solution is exposed to air, equilibrium 4 is quickly established.

$$LCo^{II}P + O_2 \underset{}{\overset{K_3}{\rightleftharpoons}} L^{\delta^+}Co^{II}P(O_2{}^{\delta^-}) \qquad (4)$$



**Figure 6.** Dependence of reaction rate of 5 × $10^{-6}$ mol $dm^{-3}$ $Co^{II}P$ with imidazole on imidazole concentration. Solvent: ethanol (25 °C), in presence of air. Absorbance increase at 424 nm (formation of $[Co^{III}P(im)_2]^+$ (●)) and decrease at 401 nm (disappearance of $Co^{II}P$ (○)) were monitored.

As already mentioned the coordination of L in the sixth position of $Co^{II}$ is very unfavorable.[5,6] On the other hand $O_2$ can coordinate,[5,7,20–23] with the tendency of accepting $(z^2/\pi^*)_\sigma$ and $(xz, \pi^*)_{\pi^*}$ electrons, which leads to partial oxidation of cobalt, giving the oxygen superoxide character.[24,25] It was also pointed out[23] that there is a wide variation in the amount of electron transfer to $O_2$, which depends on the nature of ligands coordinated to cobalt. The extent of electron transfer depends also on solvent acidity and solvent polarity. The rate-determining step is, most probably, reaction 5. The fact

$$L^{\delta^+}Co^{II}P(O_2{}^{\delta^-}) + L \xrightarrow{H^+} [L_2Co^{III}P]^+ + HO_2\cdot \qquad (5)$$
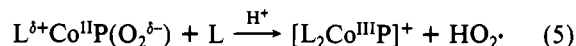
that the overall reaction rate is strongly accelerated by hydrogen ions supports the above claim. The $HO_2\cdot$ radical might initiate subsequent radical reactions involving $HO_2^-$ and $HO\cdot$, ending up[26–28] with $HO^-$. Large standard errors of some of our kinetic results (up to 20%; see Table I) might be partly due to radical-induced oxidations of Co(II).

In the overall reaction, eq 2–5, there seems to be no accumulation of reaction intermediates. This can be inferred (a) from the existence of isosbestic points in Figure 1 and (b) from the fact that rates of disappearance of $Co^{II}P$ and rates of formation of $[Co^{III}PL_2]^+$ in the overall reaction are equal (see Figure 6).

In the overall reaction (2)–(5), unfortunately, we could not separate reaction 5 from its preequilibria (2)–(4) and study the kinetics of $O_2$ replacement in $L^{\delta^+}Co^{II}P(O_2{}^{\delta^-})$. But, as already described, we prepared, in the solution, $\delta^+Co^{II}P$-$(CH_3OH)(O_2{}^{\delta^-})$ and were able to study the kinetics of $O_2$ replacement by L in this complex. The fact that practically

(17) H. C. Stynes and J. A. Ibers, *J. Am. Chem. Soc.*, **94**, 5125 (1972).
(18) The possibility of hydrogen bonding of imidazole to $L^{\delta^+}Co^{II}P(O_2{}^{\delta^-})$ was recognized by D. V. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, **95**, 1142 (1973).
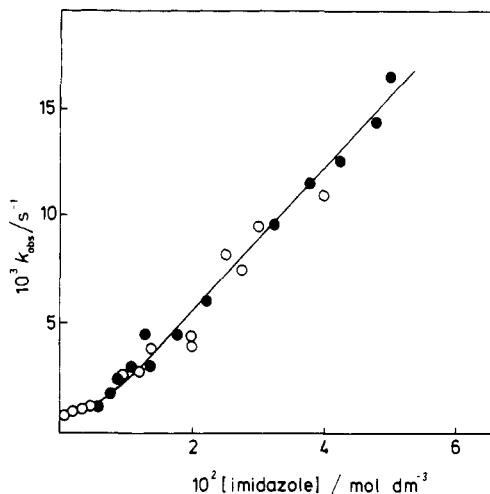(19) R. S. Drago, J. P. Cannady, and K. A. Leslie, *J. Am. Chem. Soc.*, **102**, 6014 (1980).

(20) D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, **95**, 1142 (1973); J. A. Ibers, D. V. Stynes, H. C. Stynes, and B. R. James, *ibid.*, **96**, 1358 (1974).
(21) (a) F. Ann Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 1484 (1976); (b) F. Ann Walker, *ibid.*, **92**, 4234 (1970).
(22) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).
(23) R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, **100**, 5374 (1978), and references therein.
(24) B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).
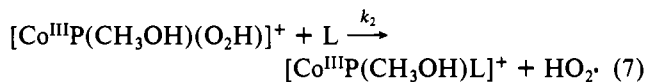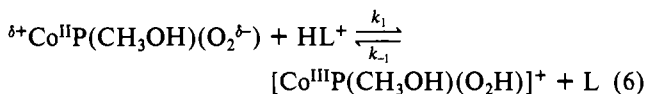(25) R. Dreos, G. Tauzher, G. Costa, and M. Green, *J. Chem. Soc., Dalton Trans.*, 2329 (1975).
(26) J. Weiss, *Naturwissenschaften*, **23**, 64 (1935).
(27) W. G. Barb, J. H. Baxendak, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).
(28) S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc. A*, 2044 (1969).

limiting reaction rates were obtained for the first step (oxygen replacement, Figure 4) is consistent with the following mechanism:

$$^{\delta+}Co^{II}P(CH_3OH)(O_2{}^{\delta-}) + HL^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$[Co^{III}P(CH_3OH)(O_2H)]^+ + L \quad (6)$$

$$[Co^{III}P(CH_3OH)(O_2H)]^+ + L \xrightarrow{k_2}$$
$$[Co^{III}P(CH_3OH)L]^+ + HO_2\cdot \quad (7)$$

A similar mechanism was discussed previously[25] for oxidation of a cobalt(II) dioxatetraazaboracyclotetradecatetraene complex. The application of the steady-state approximation to the short-living intermediate $[Co^{III}P(CH_3OH)(O_2H)]^+$ leads to eq 8 for the $k_{obsd}{}^{(6)-(7)}$. If the only source of protons is

$$k_{obsd}{}^{(6)-(7)} = \frac{k_1 k_2 [HL^+]}{k_{-1} + k_2} \quad (8)$$

methanol, then eq 9 can be used instead of eq 8, where $K =$

$$k_{obsd}{}^{(6)-(7)} = \frac{k_1 k_2 (K[L])^{1/2}}{k_{-1} + k_2} \quad (9)$$

$[HL^+][CH_3O^-]/[L]$. Equation 9 explains well the quasi-limiting reaction rates in replacement of oxygen by L (Figure 4, open circles).

The second step (Figure 4, full circles, and Figure 5) is the replacement of the coordinated solvent molecule, eq 10. If

$$[Co^{III}P(CH_3OH)L]^+ + L \xrightarrow{k_{obsd}{}^{(10)}} [Co^{III}PL_2]^+ + CH_3OH \quad (10)$$
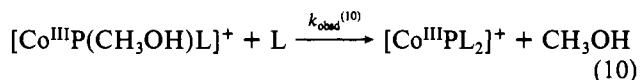
in $^{\delta+}Co^{II}P(CH_3OH)(O_2{}^{\delta-})$ methanol were replaced by L before oxygen, no limiting rates would have been obtained, since this would be a replacement of a methanol molecule by L in methanol as the solvent. Such a replacement must obey the second-order rate law.[29] Indeed, this is true for the second step, eq 10, which exhibits linear dependence of $k_{obsd}{}^{(10)}$ on L concentration (Figure 4, full circles, and Figure 5).

The negative entropy of activation ($\Delta S^{\ddagger} = -70$ J K$^{-1}$ mol$^{-1}$) of the first step, eq 6 and 7, where (6) is considered to be the rate-determining step, is in accordance with the associative nature of this reaction. On the other hand the positive entropy of activation (30 J K$^{-1}$ mol$^{-1}$) of the second step, eq 10, is to be expected for a dissociative-type process.

It is interesting to note that the rate of the overall reaction (2)–(5), as already discussed, increases with increased ligand-electron-donating ability. On the other hand, the order of reactivity in reaction 10 is reversed. In the overall reaction the entering ligand was also a directing ligand for subsequent reactions, which appears to be a dominating feature, whereas in reaction 10 this is not so. The relatively slow reaction with pip is, most probably, due to steric effects.[7]

(29) D. Pavlović, D. Šutić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 2406 (1976).

# Reduction of Copper Tetracyanotetraphenylporphyrin in Nonaqueous Media. Formation of Copper(I)

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The total electrochemical reduction of copper tetracyanotetraphenylporphyrin, (CN)$_4$(TPP)Cu, was investigated in dimethylformamide (DMF) by the techniques of polarography, cyclic voltammetry, thin-layer spectroelectrochemistry, ESR spectroscopy, and extended Hückel calculations. The ESR results establish the existence of a Cu(II) dianion. The electrochemical reactions of (TPP)Cu and (CN)$_4$(TPP)Cu are compared, and the differences in redox behavior can be rationalized by the calculations. Unlike (TPP)Cu, which may be reduced by a total of six electrons in four steps, (CN)$_4$(TPP)Cu is reduced by seven electrons in five steps. This new wave occurs at $E_{1/2} = -1.95$ V in DMF and is attributed to reduction of the Cu(II) dianion to yield a Cu(I) complex. Formation of this species is reversible on the cyclic voltammetry time scale and an electronic spectrum has been obtained. This spectrum consists of a split Soret band at 390.0 and 480.4 nm and a strong band in the visible at 688.2 nm.

## Introduction

During the last 15 years a large number of studies have reported oxidation and reduction potentials for metalloporphyrin complexes.[2,3] In nonaqueous media monomeric metalloporphyrins are reduced (usually reversibly) by at least two single electron transfer steps to yield $\pi$ anions and dianions. This is true for complexes with over 30 different central metals, including copper, and is independent of the charge on the central metal, which may vary from 1+ (in the case of cobalt

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(2) D. Dolphin, Ed., "The Porphyrins", Vol. V, Academic Press, New York, 1978.

(3) K. M. Smith, Ed., "Porphyrins and Metalloporphyrins", Elsevier, London, 1975.