Reactions of Cobalt(II) Protoporphyrin IX Dimethyl Ester,† $[Co^{II}P]$, and $[Co^{III}P(Cl)]$ in Co-ordinating Aliphatic Alcohols

Dušanka Pavlović,* Smiljko Ašperger,* Zdravko Dokuzović, Blaženka Jurišić, Xhavit Ahmeti, Mira Sertić, and Ivo Murati
Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

---

Chlorocobalt(III) protoporphyrin IX dimethyl ester, $[Co^{III}P(Cl)]$, releases its chloride immediately on dissolution in methanol, and equilibrates as shown below. Species (**2**) predominates if no acid

$$\underset{(\mathbf{1})}{[Co^{III}P(CH_3OH)_2]^+} \underset{H^+}{\rightleftharpoons} \underset{(\mathbf{2})}{[Co^{III}P(CH_3O)(CH_3OH)]} \overset{CH_3O^-}{\rightleftharpoons} \underset{(\mathbf{3})}{[Co^{III}P(CH_3O)_2]^-}$$

or alkali is added. $[Co^{II}P]$ dissolved in methanol, in the presence of air, undergoes oxidation yielding (**2**). The identities of the products obtained in both ways were established by comparison of absorption spectra and rates of replacements of their axial ligands. Kinetics of the reactions of (**2**) and various ligands L in methanol (L = pyridine, substituted pyridine, or nicotinamide) show that methanol is replaced first, and methoxide second, both in a dissociative manner. The replacements of methanol by L attain a limiting rate which does not depend on L [$k_{obs.}$(25 °C) = 57.8 s^{-1}]. The existence of a limiting rate here reveals that a *D* mechanism [S_N1(lim.)] operates, whereas an I_d mechanism is excluded. This case appears to be a unique example of a fully established *D* mechanism in a polar, co-ordinating solvent. Values of $k_{obs.}$ for the slower replacement of methoxide by L show a linear dependence on [L], with small differences in slopes for different entering ligands. This excludes a bimolecular mechanism, and suggests that the replacements of methoxide by L take place *via* the complex conjugate acid in a dissociative manner; the kinetic results do not allow a distinction between *D* and I_d mechanisms.

Recently we have shown that the oxidation of cobalt in cobalt(II) protoporphyrin IX dimethyl ester,† $[Co^{II}P]$, in the presence of molecular oxygen and amine ligands L [pyridine (py), 3-cyanopyridine (3CN-py), 4-cyanopyridine (4CN-py), 4-methylpyridine (4Me-py), piperidine (pip), and imidazole (Him)] proceeds readily in alcoholic media.[1] The equilibria (1)—(4) were proposed.

$$[Co^{II}P] + ROH \rightleftharpoons [Co^{II}P(ROH)] \quad (1)$$

$$[Co^{II}P(ROH)] + L \rightleftharpoons [Co^{II}P(L)] + ROH \quad (2)$$

$$[Co^{II}P(L)] + O_2 \rightleftharpoons [Co^{II}P(L)(O_2)] \quad (3)$$

$$[Co^{II}P(L)(O_2)] + HL^+ \longrightarrow [Co^{III}P(L)_2]^+ + HO_2^{\cdot} \quad (4)$$

We now report that, in the absence of amine ligand, $[Co^{II}P]$ in methanol also undergoes oxidation, yielding $[Co^{III}P(CH_3O)(CH_3OH)]$. The mechanism is essentially analogous to that found in the presence of amine ligands, equations (1)—(4), with methanol acting as a directing ligand. The overall reaction rate is *ca.* 10^{-2} times that in the presence of L ([L] $\sim 10^{-2}$ mol dm^{-3}). In the absence of oxygen (argon atmosphere) the above Co^{III} complexes are not formed. Also, in aprotic, non-co-ordinating solvents, in the presence of O_2 and L, $[Co^{III}P(L)_2]^+$ is not formed, which reveals the importance of protons in the elimination of O_2^-. The formation of $[Co^{II}P(L)(O_2)]$ intermediates has been widely recognised.[2–9] These species are stabilized by the polar and protic properties of the alcoholic media.[1]

The complex $[Co^{III}P(Cl)]$ was found to release its chloride immediately on dissolution in methanol, and equilibrate as in equation (5). If no acid or alkali is added to methanol, species (**2**)

$$\underset{(\mathbf{1})}{[Co^{III}P(CH_3OH)_2]^+} \underset{H^+}{\rightleftharpoons} \underset{(\mathbf{2})}{[Co^{III}P(CH_3O)(CH_3OH)]} \overset{CH_3O^-}{\rightleftharpoons} \underset{(\mathbf{3})}{[Co^{III}P(CH_3O)_2]^-} \quad (5)$$

widely predominates. The spectrum of species (**2**) is practically identical with the spectrum of the reaction product obtained from $[Co^{II}P]$ in methanol in the presence of O_2. The kinetics of the reactions of (**2**) and various L in methanol (L = py, 4Me-py, and 4CN-py) show that methanol is replaced first, and methoxide second, both in a dissociative manner. The replacement of methanol with any ligand L attains a limiting rate. This indicates that a *D* mechanism is operative. The value of $k_{obs.}$ for the slower replacement of methoxide by L shows a linear dependence on [L], which suggests that the replacement takes place *via* the complex conjugate acid. We believe that the replacement of CH_3OH in $[Co^{III}P(CH_3O)(CH_3OH)]$, in solvent methanol, is a unique example of a reaction for which a *D* mechanism is fully established in a polar, co-ordinating solvent. Identical kinetic data were obtained with (**2**) and with the reaction product of $[Co^{II}P]$ and methanol in air, which provides additional proof that this product is $[Co^{III}P(CH_3O)(CH_3OH)]$.

Experimental

Materials.—Two batches of $[Co^{II}P]$ were prepared. (*a*) The first was from cobalt acetate (Merck, AR grade) and protoporphyrin IX dimethyl ester (H_2P) (Fluka, purum) according to the literature.[10] The complex was recrystallized from chloroform–methanol and then from benzene. (*b*)

---

† 13,17-Di[2-(methoxycarbonyl)ethyl]-2,7,12,18-tetramethyl-3,8-divinylporphyrinatocobalt(II).

Non-S.I. unit employed: Torr ≈ 133 Pa.

Protohemin was prepared from horse blood by the glacial acetic acid method.[11] Protoporphyrin IX dimethyl ester was prepared from protohemin by the method of Grinstein;[12] [$Co^{II}P$] was then prepared as described above.

Chlorocobalt(III) protoporphyrin IX dimethyl ester, [$Co^{III}P(Cl)$], was prepared from H_2P according to the procedure described by McConnel *et al.*[13] However, the product obtained by us had an unsatisfactory α/β peak ratio and gave a blurred Soret peak. We therefore modified the procedure as follows. A solution of cobalt(II) acetate (100 mg) in acetic acid (25 cm^3) was added to H_2P (100 mg) in acetic acid (100 cm^3). After a few minutes 100 cm^3 of chloroform was added, the solution washed with water and dilute hydrochloric acid (3.5%), and the chloroform layer dried over anhydrous sodium sulphate and filtered. A dry mixture of air and HCl was then bubbled through the filtrate for *ca.* 1 min. After evaporation to dryness a very pure product was obtained, as judged from an α/β peak ratio of 1.2.

All solvents were Merck AR grade. Chloroform was washed several times with 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 first introducing dry hydrogen chloride into absolute ethanol, at *ca.* -15 °C, followed by addition of cold pyridine; the precipitated pyridinium chloride was filtered off and recrystallized several times from ethanol. 4-Methylpyridine (Fluka, purum) was distilled before use; 4CN-py (Fluka, purum) and 3CN-py (Pliva, purum) were recrystallized several times from ethanol. Imidazole (Fluka, purissimum pro analysi) was recrystallized from ethanol.

Spectrophotometry.—Absorption spectra were recorded on a Cary 16 K spectrophotometer. The sample absorption cell was adapted for work under an oxygen-free atmosphere. E.s.r. spectra were recorded on a Varian E-109 e.s.r. spectrometer.

Kinetics.—The Cary 16K and Durrum D-110 stopped-flow spectrophotometers were used for kinetic 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 methanol, or methanolic solutions of the amine ligands. Final complex concentration was 5×10^{-6} mol dm^{-3} (the alcoholic solutions contained 2—10% of chloroform; variation of chloroform concentration in this range did not affect absorption spectra or kinetics). The thermostatted absorption cell (25 ± 0.05 °C) was used as the reaction vessel. In the presence of air the concentration of oxygen in the reaction mixture was considered constant, since oxygen was in 50—60-fold excess[14] over the complex concentration (5×10^{-6} mol dm^{-3}). For kinetic measurements, in the absence of oxygen, very pure argon (99.999%) was further purified by passing through a cylindrical glass column, inside diameter 7 cm, height 90 cm, filled with chromium(II) salts dispersed on silica.* An Oxi 9 apparatus with an E 090 WTW O_2-membrane electrode (provided by Labor Center, Nürnberg) could not detect any O_2 in a water sample saturated with argon purified as described; on the basis of instrument sensitivity it was inferred that the O_2 concentration was < 10 μg dm^{-3}. The apparatus used for kinetic measurements in the absence of oxygen is shown in Figure 1. Methanol (*ca.* 60 cm^3) was placed in the flask (A), and [$Co^{II}P$] in chloroform (2.5 cm^3 of 1×10^{-4} mol dm^{-3} solution) into the tube (B). The quartz absorption cell (C) was sealed at the tap (D). A vacuum line was connected at (F). The vessels (A) and (B) were immersed into an ultrasonic bath (50 kHz, 200 W). With the stop-cock (D) opened and (E) closed the solutions in (A) and (B) were sonicated for *ca.* 3 min. Stop-cock (E) was then opened for *ca.* 2 min and the inside pressure thereby reduced to *ca.* 0.13 Pa (10^{-3} Torr). After another few minutes the vacuum was switched to the argon container and stop-cock (E) reopened. After filling the system with argon to normal pressure the cycle starting with sonication was repeated three times more. Finally, the whole system was evacuated again and stop-cock (D) closed. Subsequent filling of the system with argon left the absorption cell under reduced pressure. [This is absolutely necessary for quick transfer of the reaction solution from (A) into (C).] Reaction vessel (A) was then thermostatted at 20 ± 0.01 °C, and after thermal equilibrium was secured, the solution from (B) was transferred to (A). The reaction mixture was then admitted to the spectrophotometric cell (C), *via* stop-cock (D). The cell arm was then disconnected at (G), and transferred into the thermostatted compartment of the spectrophotometer. If the procedure is carried out under the strictly defined conditions described, the loss of the solvent (methanol) is practically constant (12—13 cm^3).

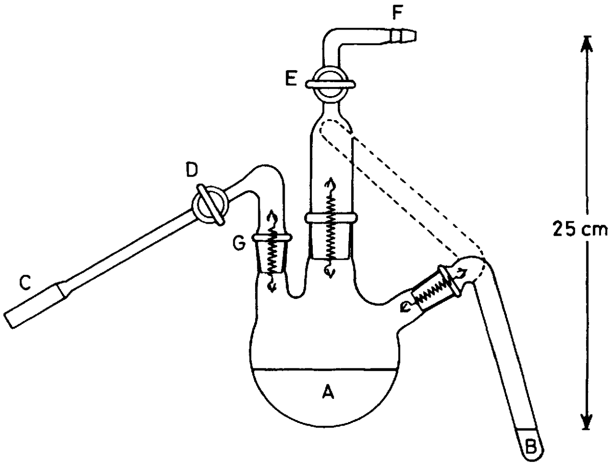

Figure 1. Apparatus for reactions in oxygen-free atmosphere

Results

The solutions of [$Co^{II}P$] in aprotic, non-co-ordinating solvents (*e.g.* chloroform, methylene chloride, benzene) in the presence of air are stable and can be used as stock solutions.[1] The alcoholic solutions of [$Co^{II}P$] are stable only in the absence of oxygen. In the presence of air the Soret, β, and α bands shift with time from 402, 528, and 557 to 416, 531, and 565 nm, respectively, in methanol; 401, 528, and 558 to 419, 533, and 567 nm in ethanol; 401, 528, and 559 to 419, 533, and 568 nm in propan-2-ol. From the above shifts it can be seen that the position of the Soret band is most sensitive to chemical changes. We found that the absorption spectrum of the methanolic solution of [$Co^{II}P$], in the absence of oxygen (oxygen-free argon), is identical to the spectrum of [$Co^{II}P$] in the same solvent but in the presence of air, as recorded at the initial stage of the reaction which causes the above mentioned spectral changes. Since the reaction product is [$Co^{III}P(CH_3O)(CH_3OH)$], see Figure 2, the reaction scheme (6)—(8) can be proposed.

It is assumed that (8) is the rate-determining step because we found that the addition of an acid (perchloric or *p*-toluenesulphonic) accelerates the overall reaction rate, until the limiting value is reached {$k_{\text{lim.}}(25\ ^\circ C) = 4.7 \times 10^{-2}\ s^{-1}$; [$HClO_4$] ~ 6×10^{-5}, [$p\text{-}CH_3C_6H_4SO_3H$] ~ 8×10^{-5} mol dm^{-3}}. The fact that the absorption spectra of [$Co^{II}P$] in methanol are the same

---

* This highly efficient column was a gift from Professor H. L. Krauss, Department of Inorganic Chemistry, University of Bayreuth, West Germany.

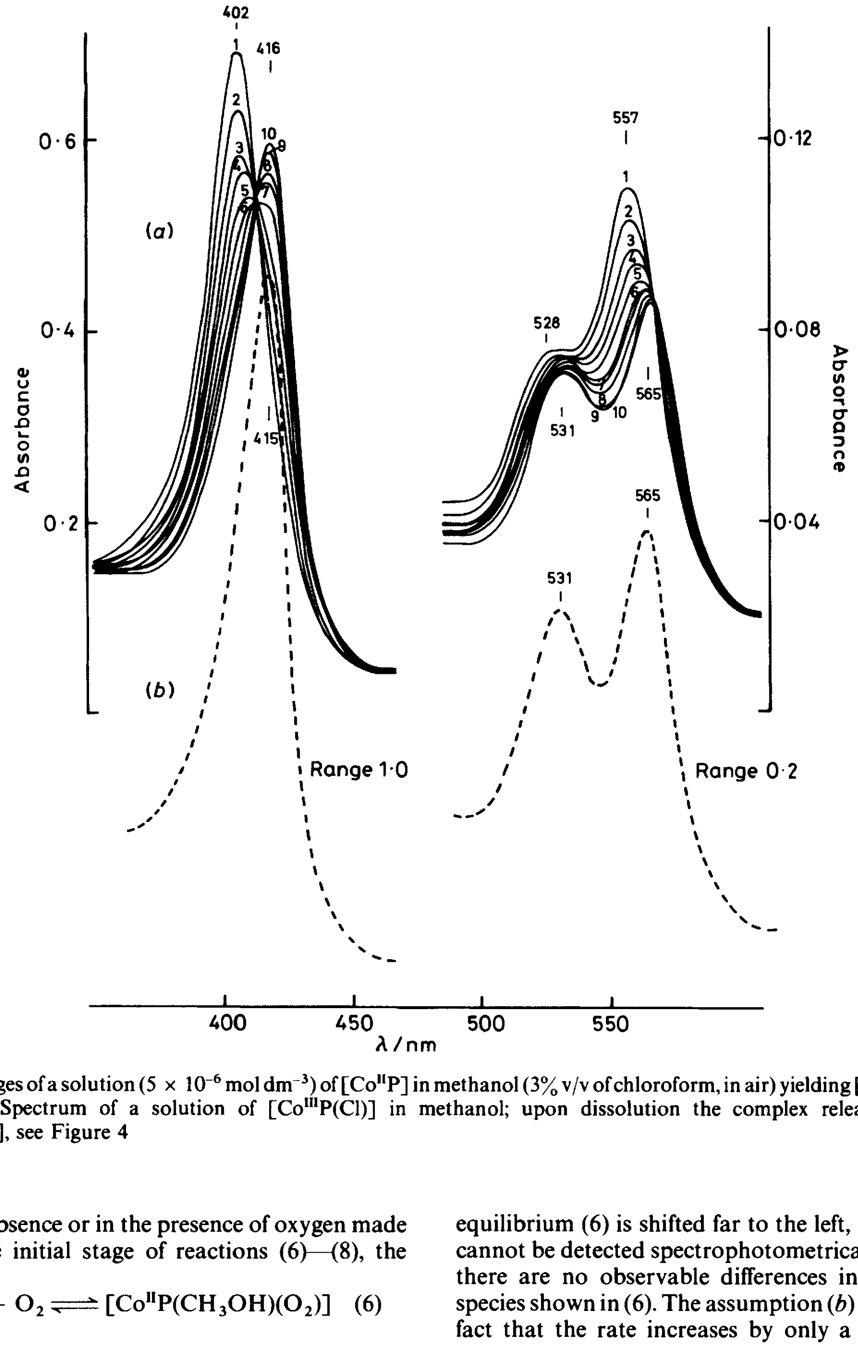

Figure 2. (*a*) Spectral changes of a solution (5×10^{-6} mol dm^{-3}) of [Co^{II}P] in methanol (3% v/v of chloroform, in air) yielding [Co^{III}P(CH$_3$O)(CH$_3$OH)] (thickened line 10). (*b*) Spectrum of a solution of [Co^{III}P(Cl)] in methanol; upon dissolution the complex releases its chloride yielding [Co^{III}P(CH$_3$O)(CH$_3$OH)], see Figure 4

when recorded in the absence or in the presence of oxygen made us believe that, at the initial stage of reactions (6)—(8), the

$$[\mathrm{Co^{II}P(CH_3OH)}] + \mathrm{O_2} \rightleftharpoons [\mathrm{Co^{II}P(CH_3OH)(O_2)}] \quad (6)$$

$$[\mathrm{Co^{II}P(CH_3OH)(O_2)}] + \mathrm{CH_3OH} \rightleftharpoons [\mathrm{Co^{II}P(CH_3OH)(O_2H)}]^+ + \mathrm{CH_3O^-} \quad (7)$$

$$[\mathrm{Co^{II}P(CH_3OH)(O_2H)}]^+ + \mathrm{CH_3OH} \longrightarrow [\mathrm{Co^{III}P(CH_3OH)_2}]^+ + \mathrm{HO_2^{\bullet}}$$
$$\downarrow\uparrow$$
$$[\mathrm{Co^{III}P(CH_3O)(CH_3OH)}] + \mathrm{H^+} \quad (8)$$

appearance of the absorption maximum at 416 nm is associated with the formation of a 1:1 oxygen complex.[1] This proved not to be correct, since we found later that the appearance of the absorption at 416 nm is connected with a complete loss of the e.s.r. signal. The freshly prepared methanolic solution of [Co^{II}P] (1×10^{-5} mol dm^{-3}, in the presence of air, 77 K) gave an e.s.r. signal (Figure 3). The fact that the absorption spectra of the solutions of [Co^{II}P] in methanol in the presence and absence of oxygen are identical can be explained, by (*a*) supposing that the equilibrium (6) is shifted far to the left, so that the O$_2$ complex cannot be detected spectrophotometrically, and (*b*) the fact that there are no observable differences in absorption spectra of species shown in (6). The assumption (*b*) appears more likely: the fact that the rate increases by only a factor of 1.8 when O$_2$ concentration increases by a factor of 5 (see below) suggests that, under our reaction conditions, equilibrium (6) does not lie very far to the left.

Figure 2 shows the spectrum of the solution of [Co^{II}P] in methanol and the spectral changes due to the formation of the reaction product. It can be seen that the spectrum of the reaction product is identical with the spectrum of the solution of [Co^{III}P(Cl)] in methanol. As already said, [Co^{III}P(Cl)] releases its chloride upon dissolution in methanol, and yields [Co^{III}P(CH$_3$O)(CH$_3$OH)] (see also Figure 4).

Dependence of the Rate of Reaction of [Co^{II}P] *in Methanol on the Partial Pressure of Oxygen.*—As already said, in the absence of oxygen (argon atmosphere) the methanolic solutions of [Co^{II}P] are stable. In air, at 25 °C ($P_{\mathrm{O_2}} \sim 150$ Torr), $k_{\mathrm{obs.}}$ was $\sim 2 \times 10^{-4}$ s^{-1}. In pure oxygen, at the same temperature ($P_{\mathrm{O_2}} \sim 760$ Torr), $k_{\mathrm{obs.}}$ was $\sim 3.5 \times 10^{-4}$ s^{-1}. Thus the increase of O$_2$ pressure

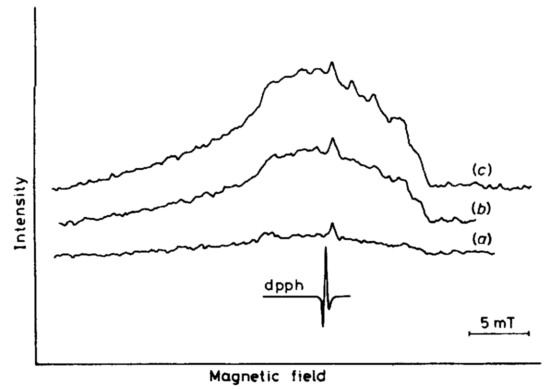

Figure 3. Second-harmonic e.s.r. spectra of freshly prepared [Co^{II}P] in methanol, in the presence of air: (*a*) 1 × 10^{-5}, (*b*) 5 × 10^{-5}, (*c*) 1 × 10^{-4} mol dm^{-3}; T = 77 K; dpph = diphenylpicrylhydrazyl

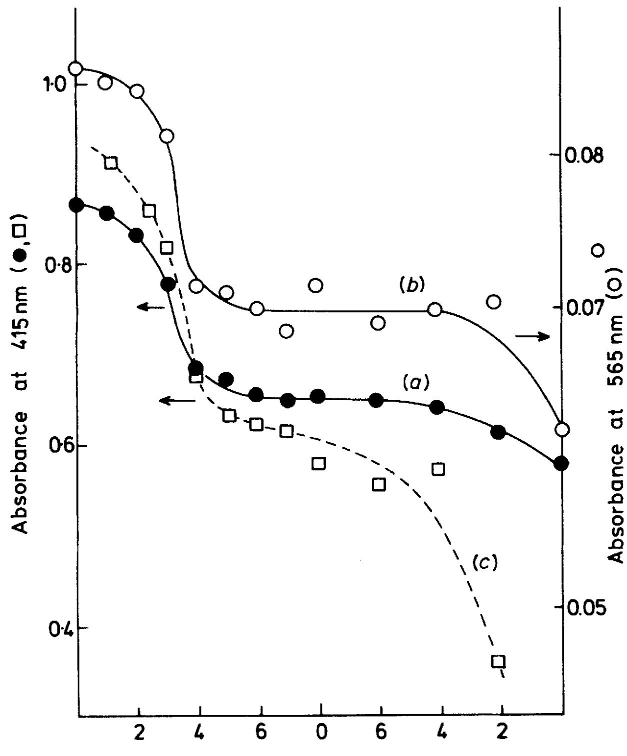

Figure 4. Spectrophotometric titration of [Co^{III}P(CH$_3$O)(CH$_3$OH)] in methanol with methanolic solutions of HCl {product [Co^{III}P(CH$_3$OH)$_2$]$^+$}, and of NaOCH$_3$ {product [Co^{III}P(CH$_3$O)$_2$]$^-$}. Total concentration of [Co^{III}P] was kept constant during titration (1 × 10^{-5} mol dm^{-3}). (*a*) λ = 415 nm; (*b*) λ = 565 nm; measurements were made immediately after each addition of acid or alkali. (*c*) λ = 415 nm, measurements were made 48 h after corresponding additions of acid or alkali. Temperature 25 ± 0.02 °C

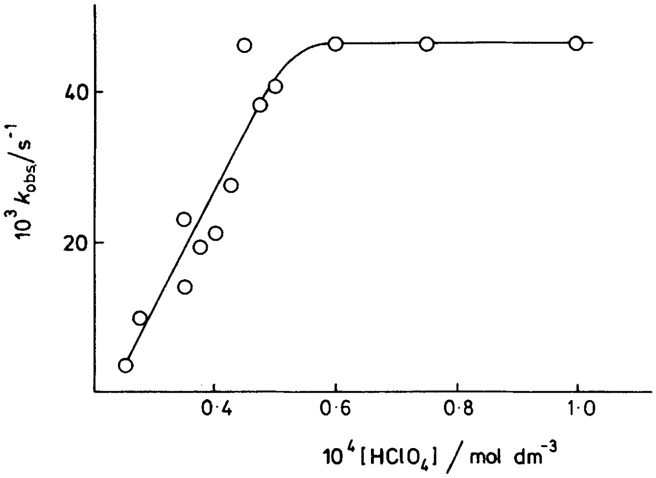

Figure 5. Dependence of the overall rate of reactions (6)—(8) ([Co^{II}P], 5 × 10^{-6} mol dm^{-3} in methanol) on concentration of added HClO$_4$. The rate was followed by measuring the increase of absorbance of the Soret peak at 416 nm; temperature 25 ± 0.02 °C

by a factor of 5 increases the rate merely by a factor of 1.8. This, we suppose, is due to the composite equilibria (6)—(8). The rate was followed spectrophotometrically by measuring the decrease of the Soret peak of [Co^{II}P(CH$_3$OH)] at 402 nm, as well as the increase of the Soret peak of [Co^{III}P(CH$_3$O)(CH$_3$OH)] at 416 nm. It is important to note that the rate of the reaction of [Co^{II}P] in methanol, in the absence of amine ligand, is very sensitive to basic and acidic impurities, always present in an A.R. grade methanol. Therefore the rates measured in 'pure' solvents of different makes can vary appreciably.

Dependence of the Rate of Reaction of [Co^{II}P] *in Methanol on Solution Acidity*.—The acidity of methanolic solutions of [Co^{II}P] was varied by addition of perchloric and *p*-toluenesulphonic acids. Figure 5 shows the results of the addition of perchloric acid; analogous results were obtained with *p*-toluenesulphonic acid. It can be seen that limiting rates are obtained. This supports the suggestion that reaction (8) is rate determining and that the elimination of the superoxide takes place from the ion pair. If this is true, the limiting rates correspond to the saturation of the ion pair. According to this mechanism, when the rate becomes independent of H$^+$ concentration, all of the Co^{II} is converted to [Co^{II}P(CH$_3$OH)(O$_2$H)]$^+$, and the rate should become independent of the partial pressure of O$_2$. Indeed, at [*p*-CH$_3$C$_6$H$_4$SO$_3$H] = 2.0 × 10^{-4} mol dm^{-3}, the ratios of $10^2 k_{obs.}/s^{-1}$ for the reactions in pure oxygen and in air were found to be 3.04/3.12 = 0.98 and 3.55/3.30 = 1.08, respectively (average 1.03).

Replacements in Co^{III}P *Complexes*.—*Solvolytic reactions of* [Co^{III}P(Cl)]. Upon dissolving in methanol, [Co^{III}P(Cl)] (dark violet-red crystals) releases its chloride practically instantaneously and Co^{III}P reacts with the solvent. The composition of the equilibrium mixture depends on the acidity of the solution. The species were characterised by their absorption spectra. Spectrophotometric titrations of the substrate with acid and base suggested the existence of the equilibria (5). Since the solvent is unbuffered the relative amount of (**2**) will depend on the total concentration of the complex, (**2**) being favoured by dilution.

Spectrophotometric titration of the solution obtained upon dissolving [Co^{III}P(Cl)] *in methanol*. The titrations were carried out with solutions of gaseous HCl and sodium methoxide in methanol. Changes in absorbance were followed at 415 nm (Soret peak) and at 565 nm (α peak), see Figure 4. Curves (*a*) and (*b*) correspond to measurements made immediately after each addition of acid or base. Curve (*c*) shows the results of measurements made 48 h after each addition of acid or alkali. It is reasonable to assume that the absorbances corresponding to the plateaus of the titration curves (*a*) and (*b*) correspond to [Co^{III}P(CH$_3$O)(CH$_3$OH)] and the higher absorbances in strongly acidic solutions correspond to [Co^{III}P(CH$_3$OH)$_2$]$^+$.

Table. Rates of replacements of CH_3OH ($k_{obs.}{}^{I}/s^{-1}$) in $[Co^{III}P(CH_3O)(CH_3OH)]$ with py, 4CN-py, and 4Me-py in methanol[a]

$10^4[L]$/ mol dm^{-3}	Entering ligand (L)		
	4CN-py	py	4Me-py
1	3.47[b]	2.89	1.0
	0.15[c]	0.15	0.05
	5[d]	5	5
5	6.93	3.85	3.85
	0.35	0.2	0.2
	4	4	5
10	17.3	8.6	6.93
	0.8	0.4	0.3
	4	3	5
20	34.7	18.2	10.7
	1.6	0.7	0.6
	5	3	4
30		30.0	
		1.5	
		5	
40	53.3	38.5	
	3	2	
	3	5	
50		46.2	27.7
		3	1.8
		4	3
60	**57.8**[e]		
	4		
	4		
80	**57.8**	**57.8**	
	3.0	3.0	
	6	5	
100		**57.8**	49.3
		3.2	3
		4	4
500			**57.8**
			4
			4
1 000			**57.8**
			4
			5

[a] Concentration of $[Co^{III}P(CH_3O)(CH_3OH)] = 5 \times 10^{-6}$ mol dm^{-3}; kinetics were followed by the stopped-flow technique at 430 nm; temperature 25 ± 0.05 °C. Results quoted as follows: [b] mean first-order reaction rate constant; [c] standard error of the mean; [d] number of kinetic runs; [e] bold figures represent limiting rates.

The low absorptions in strongly basic solutions must relate to $[Co^{III}P(CH_3O)_2]^-$. Analogous observations were reported by Ashley *et al.*[15,16] in aqueous solutions of diaqua-[*meso*-tetrakis(*p*-sulphonatophenyl)porphyrinato]cobaltate-(III). Figure 4(*c*) shows that the equilibrium concentrations of species (**1**), (**2**), and (**3**) [equilibrium (5)] change slowly in neutral and basic solutions, in which the absorbances decrease. It is assumed that these changes are due to slow dimerisation processes. All equilibria of type (5) are rapidly established (proton transfer reactions). The relatively slow dimerisation process probably involves (**2**), but the dimerisation of (**3**) cannot be excluded. It is known that dimerisation causes a decrease of absorbance.[17] In acid solutions, eventually practically all of the $Co^{III}P$ complexes are converted to (**1**), which explains the increase of absorbance in strongly acidic solutions [Figure 4(*c*)]. The dimer of (**2**) might be dimethoxo-bridged cobalt(III), by analogy with dihydroxo-bridged iron(III) porphyrins.[18] In acidic media (0.1—1 mol dm^{-3} HCl), where (**1**) strongly dominates, the Beer–Lambert law holds strictly up to 2×10^{-5} mol dm^{-3} of the $[Co^{III}P(CH_3OH)_2]^+$ complex. Its molar absorption coefficient is *ca.* 93 000 dm^3 mol^{-1} cm^{-1} at 25 °C.

Kinetics of reaction of $[Co^{III}P(CH_3O)(CH_3OH)]$ *with pyridine,* 4Me-py, *and* 4CN-py *in methanol.* As already described, $[Co^{III}P(CH_3O)(CH_3OH)]$ is instantaneously formed upon dissolution of $[Co^{III}P(Cl)]$ in methanol. The rates of replacements of initial axial ligands of the complex by the amines were measured by the stopped-flow technique. The dimerisation of the complex did not interfere, since its rate is *ca.* 1 000 times smaller than the rates of replacements. The solutions of the complex were always freshly prepared. The Soret peak of the methanol–methoxo-complex is at 415 nm. Its ε value in methanol is *ca.* 6.5×10^4 dm^3 mol^{-1} cm^{-1} at 25 °C. The kinetics were measured at 430 nm. At this wavelength the kinetics of replacements of the CH_3OH and CH_3O^- ligands can be best followed. The replacements run consecutively: methanol is replaced first and methoxide second. The difference in rates of the two replacements is large enough so as to permit independent determinations of the observed rate constants for each phase. The kinetic results of the replacements of CH_3OH ($k_{obs.}{}^{I}$) in $[Co^{III}P(CH_3O)(CH_3OH)]$ with py, 4CN-py and 4Me-py are summarized in the Table.

Replacement of CH_3OH *by* L *in* $[Co^{III}P(CH_3O)(CH_3OH)]$. The replacement of methanol is obviously dissociative in nature, since the limiting rate was the same with all three entering ligands: $k_{obs.}{}^{I} = 57.8\ s^{-1}$ (Table). Moreover, the limiting rates in replacement of the ligand methanol by L in solvent methanol reveal that the replacement follows a *D* mechanism [S_N1(lim.)]. The replacement of the I_d type, in this case, should not give saturation rates. The observed rate constant ($k_{obs.}{}^{I}$) is equal to $k_1k_2[L]/(k_{-1}[MeOH] + k_2[L])$, where k_1 and k_{-1} are the rate constants of dissociation of ligand methanol and its reverse, respectively, and k_2 is the rate constant of the reaction of the intermediate $[Co^{III}P(CH_3O)]$ with L. The replacement of ligand methanol in solvent methanol usually gives a linear dependence of $k_{obs.}$ on [L]. The fact that limiting rates are obtained reveals that k_2 is much larger than k_{-1}, which is a reasonable expectation. Indeed, by plotting $1/k_{obs.}{}^{I}$ *versus* $1/[L]$ a linear dependence was obtained (slope $k_{-1}[CH_3OH]/k_1k_2$, intercept $1/k_1$). This enabled a graphical determination of competition ratios k_2/k_{-1}. They are 6 800, 3 700, and 2 800 for the entering ligands 4CN-py, py, and 4Me-py, respectively. On increasing the concentration of the entering ligand (4CN-py, py, or 4Me-py, Table) the basicity of the medium increases, which causes partial conversion of $[Co^{III}P(CH_3O)(CH_3OH)]$ to $[Co^{III}P(CH_3O)_2]^-$. However, it appears that the small variations in concentration of the dimethoxo-complex involved are of minor kinetic importance, under our reaction conditions, otherwise the three entering ligands would not give equal limiting rates. Nevertheless, we also carried out the replacement of CH_3OH by py in $[Co^{III}P(CH_3O)(CH_3OH)]$ at constant basicity. This was achieved by addition of crude pyridinium chloride to methanolic solutions of pyridine keeping the ratio $[py]/[Hpy^+] = 1$. The same limiting rate, 57.8 s^{-1}, was obtained with py as entering ligand in unbuffered and in buffered solutions.

Replacement of CH_3O^- *by* L *in* $[Co^{III}P(CH_3O)(L)]$. (*a*) *Kinetics with the complex obtained from* $[Co^{III}P(Cl)]$. The dependence of $k_{obs.}{}^{II}$ on concentration of L (L, 4CN-py, py, 4Me-py) for the replacement of methoxide by L in methanol is linear for all three ligands. All gave roughly the same slope, which excludes the bimolecular mechanism.[19]

(*b*) *Kinetics with the complex obtained from* $[Co^{II}P]$ *in methanol in the presence of air.* Most careful kinetic measurements showed that there are still differences in the slopes of the

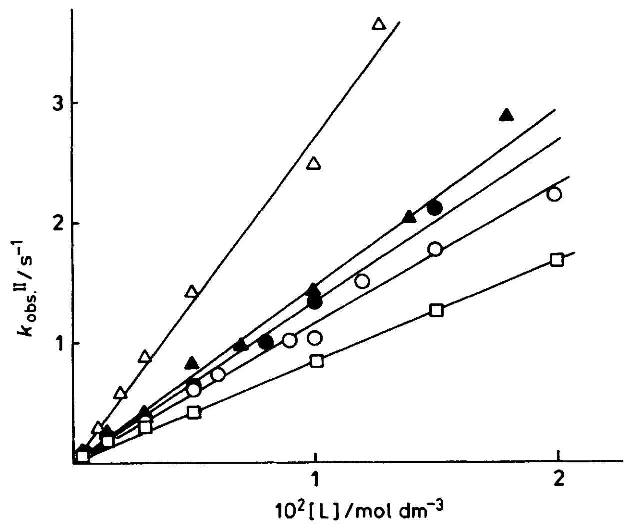

Figure 6. Dependence of $k_{obs.}^{II}$ on [L] for the reaction $[Co^{III}P(CH_3O)(L)] + L \xrightarrow{H^+} [Co^{III}P(L)_2]^+ + CH_3OH$. Complex (prepared from $[Co^{II}P]$) concentration *ca.* 5×10^{-6} mol dm^{-3}; L = 4CN-py (□), py (○), 4Me-py (●), nicotinamide (▲), $4NH_2$-py (△); methanol solvent; λ = 430 nm; temperature 25 ± 0.05 °C; stopped-flow technique

straight lines obtained by plotting $k_{obs.}^{II}$ *versus* concentration of L (L = $4NH_2$-py, 4Me-py, py, 4CN-py, or nicotinamide), Figure 6: the better the electron donating ability of L the larger is the rate.

Discussion

In the replacements of CH_3OH in $[Co^{III}P(CH_3O)(CH_3OH)]$ by 4CN-py, py, or 4Me-py the competition ratios k_2/k_{-1} were 6 800, 3 700, and 2 800, respectively. Large values of competition ratios should be expected, because the amine ligands are more reactive than methanol. On the other hand the order of reactivity of the amine ligands is somewhat puzzling. One might expect that the most basic amine ligand will react at the largest rate, but just the opposite is the case. Figure 7 shows that there is a linear dependence of the logarithm of the competition ratio on the pK_a of the conjugate acids of the entering amine ligands. Since k_{-1} has the same value in replacements with all three amine ligands the plot in Figure 7 represents a linear free energy relationship. It appears that methoxide in the $[Co^{III}P(CH_3O)]$ intermediate strongly increases the electron density at the *trans*-axial position, which favours the entry of the less basic amine ligand. The metal–ligand π bonding is considered to be small in metal(III) complexes. The 'soft' character of the cobalt porphyrin complex may make π back-bonding a more important interaction than might otherwise be the case with a metal(III)–ligand bond.[20] This back-bonding stabilises the transition state. It might be expected that the back-bonding is largest with 4CN-py. The distinction between *D* and I_d mechanisms in polar co-ordinating solvents is difficult. The most thoroughly investigated replacements in this respect are the replacements of H_2O by L in $[Fe(CN)_5(H_2O)]^{3-}$, but the mechanism is still a matter of debate.[21,22] For several years replacements of X by L in $[Co^{III}(CN)_5X]^{n-}$ (*n* = 2 or 3) were considered to follow a *D* mechanism, but recently an I_d mechanism was proposed.[23] It appears that the replacement of CH_3OH by L in $[Co^{III}P(CH_3O)(CH_3OH)]$ is probably a unique, well documented case, involving the *D* mechanism in a polar co-ordinating solvent. The arguments we used in support of our claim that the replacement of CH_3OH in $[Co^{III}P(CH_3O)(CH_3OH)]$ by amine ligands follows a *D* mechanism [S_N1(lim.) mechanism] are essentially the same as those put forward by Haim and Wilmarth[24] for replacement of H_2O of $[Co(CN)_5(OH_2)]^{2-}$ by N_3^-. They claimed that the tendency for saturation rates is observed when plotting $k_{obs.}$ against azide concentration. Recently their results were corrected,[25] and a linear dependence of $k_{obs.}$ *versus* azide concentration was established. Therefore, it could not be decided whether a *D* or I_d mechanism is operating. Regarding the mechanism of replacement of CH_3O^- by L in $[Co^{III}P(CH_3O)(L)]$ we have pointed out that a bimolecular mechanism can be excluded. If the replacements were bimolecular the rates (slopes of the straight lines, Figure 6) should exhibit much stronger dependence upon the nature of the entering ligand. The replacement of methoxide by L in a *D* [S_N1(lim.)] mechanism, as well as in an I_d mechanism, *via* a short-lived solvent-containing intermediate, should exhibit limiting rates. Therefore these two mechanisms cannot operate. The linearity in Figure 6 can be explained: (*a*) by assuming that CH_3O^- is replaced by L in an I_d mechanism with no solvent-containing intermediate; (*b*) by assuming that the replacement of CH_3OH by L takes place in the conjugate acid, $[Co^{III}P(L)(CH_3OH)]^+$, of the methoxo-complex. In this case the conjugate acid is assumed to be formed in a fast proton transfer pre-equilibrium. This replacement can give a linear dependence when either a *D* or an I_d mechanism is operative. We prefer assumption (*b*). Several factors might influence rates of replacements in Figure 6: L in the starting complex is different in all five cases, therefore the rates of dissociation of CH_3OH should be somewhat different; the rates of the reverse reactions should also differ, as well as the rates of reactions of the potential intermediate with L, either $[Co^{III}P(L)]^+$, in case of a *D* mechanism, or $[Co^{III}P(L)(CH_3OH)]^+$ in case of an I_d mechanism. The directing axial ligand, which is a better electron donor, will promote a faster release of the ligand methanol. The nature of the axial L might also influence the equilibrium concentration of the conjugate acid. It is interesting to note that in the replacement of

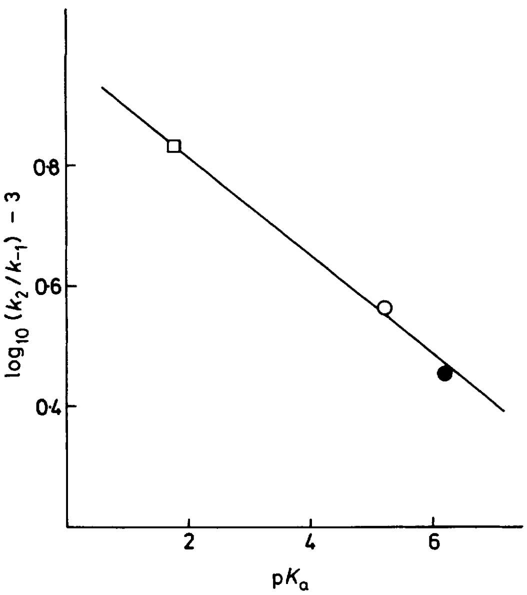

Figure 7. Dependence of log (rate ratio) on entering ligand basicity for reactions of intermediate $[Co^{III}P(CH_3O)]$ with amine ligands (k_2) and methanol (k_{-1}). Reaction $[Co^{III}P(CH_3O)(CH_3OH)] + L \rightleftharpoons [Co^{III}P(CH_3O)(L)] + CH_3OH$; methanol solvent; complex concentration 5×10^{-6} mol dm^{-3}; λ = 330 nm; temperature 25 ± 0.05 °C. L = 4CN-py (□), py (○), 4Me-py (●)

methoxide by L the magnitude of the slopes of the straight lines for $4NH_2$-py, 4Me-py, py, and 4CN-py, respectively, are in order of their electron-donating ability, as normally expected for a dissociative type mechanism.

Acknowledgements

We thank Professors Henry Taube and Martin L. Tobe for helpful discussions and suggestions.

References

1 Z. Dokuzović, Xh. Ahmeti, D. Pavlović, I. Murati, and S. Ašperger, *Inorg. Chem.*, 1982, **21**, 1576.
2 D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Am. Chem. Soc.*, 1973, **95**, 1142, 1796; 1974, **96**, 1358.
3 F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, 1976, **98**, 1484; F. A. Walker, *ibid.*, 1970, **92**, 4234.
4 F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, 1975, **8**, 384.
5 R. S. Drago, T. Beugelsdijk, J. A. Breese, and J. P. Cannady, *J. Am. Chem. Soc.*, 1978, **100**, 5374.
6 B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, 1976, **98**, 5144.
7 R. Dreos, G. Tauzher, G. Costa, and M. Green, *J. Chem. Soc., Dalton Trans.*, 1975, 2329.
8 J. A. Cohen and W. S. Caughey, *Biochemistry*, 1968, **7**, 636.
9 P. Zanello, R. Cini, A. Cinquantini, and P. L. Orioli, *J. Chem. Soc., Dalton Trans.*, 1983, 2159.
10 J. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964, vol. 2, p. 139.
11 H. Fischer, *Org. Synth.*, 1955, **3**, 442.
12 M. Grinstein, *J. Biol. Chem.*, 1947, **167**, 515.
13 R. J. McConnel, B. G. Overell, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol.*, 1953, **5**, 179.
14 'Chemical Handbook of Japan,' Chemical Society of Japan, Maruzen, Tokyo, 1973, p. 571.
15 K. R. Ashley and J. G. Leipold, *Inorg. Chem.*, 1981, **20**, 2326.
16 K. R. Ashley and S. Au-Young, *Inorg. Chem.*, 1976, **15**, 1937.
17 P. Jones, K. Prudhoe, and S. B. Brown, *J. Chem. Soc., Dalton Trans.*, 1974, 911.
18 H. Goff and L. O. Morgan, *Inorg. Chem.*, 1976, **15**, 2062.
19 Z. Dokuzović, D. Pavlović, S. Ašperger, and I. Murati, *J. Chem. Soc., Chem. Commun.*, 1984, 1060.
20 R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, 1975, **14**, 866.
21 S. Ašperger, in 'Advances in Solution Chemistry,' Plenum Press, New York, 1981, p. 105.
22 C. H. Langford, *Inorg. Chem.*, 1979, **18**, 3288; D. Pavlović, D. Šutić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 1976, 2406; I. Murati, D. Pavlović, A. Šustra, and S. Ašperger, *ibid.*, 1978, 500; R. Juretić, D. Pavlović, and S. Ašperger, *ibid.*, 1979, 2029 and refs. therein; A. L. Coelho, H. E. Toma, and J. M. Malin, *Inorg. Chem.*, 1983, **22**, 2703.
23 M. H. M. Abou-El-Wafe and M. G. Burnett, *J. Chem. Soc., Chem. Commun.*, 1983, 833.
24 A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573.
25 A. Haim, *Inorg. Chem.*, 1982, **21**, 2887.

Received 12*th June* 1984; *Paper* 4/984