Equilibrium and Kinetic Study of the Reaction between Phthalocyaninatoiron(II) and Carbon Monoxide in Dimethyl Sulphoxide

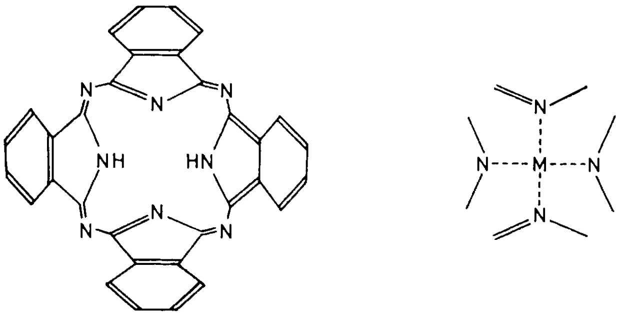
By **Claudio Ercolani,* Fabrizio Monacelli, Giovanna Pennesi,** and **Gentilina Rossi,** Istituto di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del C.N.R., Via Salaria Km 29.500, Casella Postale 10, 00016 Monterotondo Stazione and Istituto di Chimica Generale e Inorganica, Università di Roma, P. le A. Moro 6, 00185 Roma, Italy

Eraldo Antonini, Paolo Ascenzi, and **Maurizio Brunori,** Istituti di Chimica e Chimica Biologica e Centro di Biologia Molecolare del C.N.R., Università di Roma, P. le A. Moro 6, 00185 Roma, Italy

The reaction between carbon monoxide and phthalocyaninatoiron(II) in dimethyl sulphoxide (dmso) has been studied kinetically and from the equilibrium point of view. In the presence of a large excess of CO, the iron complex adds carbon monoxide in a 1 : 1 mole ratio *via* pseudo-first-order kinetics. The observed rate constant has the form $k_{obs.} = k_f[\mathrm{CO}] + k_r$ with $k_f = 1.28 \pm 0.05 \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_r = 0.12 \pm 0.02$ s^{-1} at 20 °C. The equilibrium constant K is close to 1×10^4 dm^3 mol^{-1} and is virtually independent of temperature. The effect of temperature on the rate constants has been investigated and the activation parameters determined; their mechanistic implications are discussed.

EXTENSIVE work is being carried out on phthalocyanine [Figure 1(*a*)] and its metal derivatives [Figure 1(*b*)] although these systems have been widely studied since their syntheses in the 1930's by Linstead and co-workers.[1]

One of the main reasons for such interest lies in the porphyrin-like structure of these compounds which makes them useful models for investigating biological processes involving haemoproteins. In particular, phthalocyaninatoiron(II) [Fe(pc)] may be considered analogous to the haeme group of haemoglobin and myoglobin, and the study of the reaction of [Fe(pc)] with small molecules, such as O_2, CO, and NO, may help in understanding the role of different factors on the reactivity of the iron atom.



(*a*) (*b*)

FIGURE 1 Phthalocyanine molecule (*a*) and its bivalent metal ion derivative (*b*)

Brief accounts of the reversible interaction between [Fe(pc)] and O_2, CO, and NO in 96% H_2SO_4 and dimethyl sulphoxide (dmso) were previously reported.[2,3] More recently, an investigation of the kinetics and mechanism of the reaction of [Fe(pc)] with dioxygen in 96% H_2SO_4 has been carried out.[4] This system has also been studied in dmso,[5] and a solid oxygen-containing [Fe(pc)] derivative was isolated and characterized.[6] This paper presents the results of a study on the kinetics and equilibria of the reaction between [Fe(pc)] and carbon monoxide in dimethyl sulphoxide.

EXPERIMENTAL

Materials.—Phthalocyaninatoiron(II) was purchased from Eastman and purified by vacuum sublimation (10^{-2}—10^{-3} Torr †) at 380—400 °C. The purity was checked by elemental analysis and magnetic susceptibility measurements ($\mu_{eff.} = 3.87\ \mu_B$). Dimethyl sulphoxide (Merck) was refluxed and distilled over CaH_2 before use and stored in a desiccator.

Solubility of Carbon Monoxide in dmso.—No literature data were available for the solubility of CO in dmso. Thus, the concentration of CO in this solvent at a pressure of 760 Torr was determined at different temperatures by titration with haemoglobin (HbA), which is known[7] to readily bind CO in a 1 : 1 stoicheiometry. An aqueous solution of oxygenated HbA was prepared by diluting human haemoglobin with 2% borate buffer at pH = 9.2.

The deoxygenated derivative was obtained by adding sodium dithionite, and the solution was transferred anaerobically into a spectrophotometric cuvette. The concentration of deoxy-HbA was determined spectrophotometrically using the Soret band with a maximum at 420 nm ($\varepsilon = 1.33 \times 10^5$ dm^3 mol^{-1} cm^{-1}).[7] The absorption spectrum of a known volume of the haemoglobin solution was recorded after successive additions (by a syringe) of known volumes of dmso (kept in a closed vessel under CO at 1 atm) in a constant temperature bath. The increase in absorbance at 420 nm as a function of the volume of CO solution added is reported (Figure 2). Reproducibility of the results was better than ±3%. The solubilities of CO in dmso at different temperatures were 1.1×10^{-3} mol dm^{-3} (20 ± 1 °C), 8.1×10^{-4} mol dm^{-3} (35 ± 1 °C), and 6.2×10^{-4} mol dm^{-3} (50 ± 1 °C), yielding a solution enthalpy $\Delta H_s = 3.5 \pm 0.5$ kcal mol^{-1}. Both solubilities and ΔH_s are of the expected order of magnitude when compared with data obtained with other solvents.[8]

Equilibrium Measurements.—A solution of [Fe(pc)] (*ca.* 8×10^{-5} mol dm^{-3}), prepared by dissolving the complex in

---

† Throughout this paper: 1 Torr = (101 325/760) Pa; 1 atm = 101 325 Pa; 1 cal = 4.184 J.

dmso under an inert atmosphere (N_2),* was introduced into a 1-cm spectrophotometric cell sealed to a *ca.* 250-cm^3 glass vessel fitted with a stopcock for connection to a vacuum line, and with a serum cap for gas injection.

After complete degassing under vacuum at room temperature, various CO pressures were obtained by introducing with a precision syringe known volumes of CO, at 1 atm and 20 ± 2 °C. The system was then equilibrated at the desired temperature (20, 30, or 40 °C). No more than 5 min were needed to reach equilibrium. The spectrum of the solution was then recorded and the procedure repeated again.

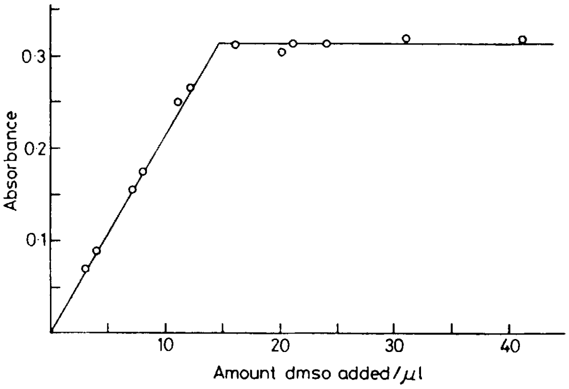


FIGURE 2 Titration of deoxygenated haemoglobin A (from man) with carbon monoxide in dmso. The increase in absorbance at 420 nm of a solution of HbA (in borate buffer at pH 9.2) is plotted against the volume of dmso added to a fixed volume of the Hb solution. dmso was previously equilibrated with pure CO at 1 atm and 40 °C. From the break point (= equivalence point) and the known stoicheiometry for the binding of CO to HbA (*i.e.* 1 : 1), the concentration of the gas in dmso can be easily calculated

Figure 3 shows the spectral changes in a typical experiment. The reaction is completely reversible, as the spectrum reverts to the initial one by merely pumping off the carbon monoxide or bubbling nitrogen through the solution. No ageing effects were observed.

Kinetic Measurements.—Flash photolysis. Measurements of CO recombination after photolysis were carried out using a cross-illumination apparatus equipped with a steady light source and a flash lamp, essentially as described by Antonini *et al.*[10]

The photolysing light was the total output of a 300-J flash lamp, which provided enough intensity to induce complete photodissociation. Variations of the intensity of both monitoring and photolysing light were achieved by interposing calibrated neutral-density filters (transmission from 20 to 50%).

The cell compartment was thermostatted with an accuracy of *ca.* ±1 °C at the highest temperature, and ±0.5 °C near room temperature.

Measurements were carried out using either [Fe(pc)] solutions (10^{-5}—10^{-4} mol dm^{-3}) equilibrated at a known CO pressure, or solutions obtained by mixing known volumes of CO-free [Fe(pc)] solutions and CO-saturated dmso.

The rate of the recombination reaction after photolysis was measured at different wavelengths in the range 600—700 nm.

Photolysis by monitoring light was observed and appropriate corrections introduced by extrapolation to zero monitoring light intensity.

The time course of CO recombination after flash photolysis followed pseudo-first-order kinetics. The values of the pseudo-first-order rate constants obtained at various CO concentrations are reported in Table 1. Reproducibility was in general better than ±15% although in some cases (especially at high temperature) it was *ca.* ±30%.

The kinetic difference spectrum agreed with that obtained in static measurements, thus indicating the absence of significant amounts of spectroscopic intermediates.

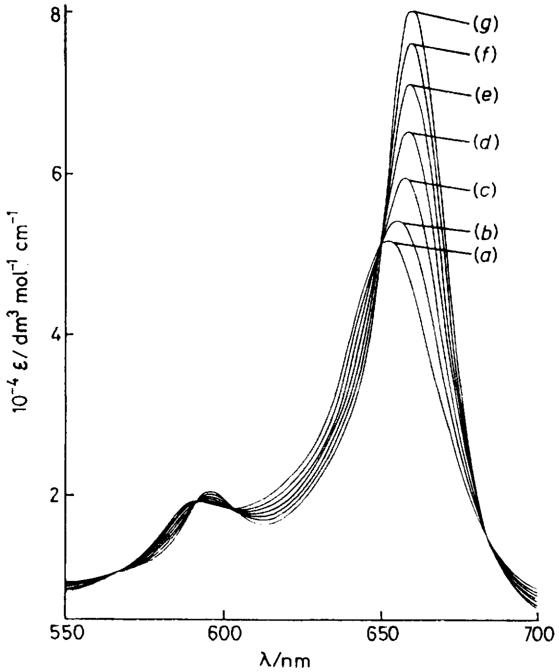


FIGURE 3 Spectral changes due to binding of CO to [Fe(pc)] in dmso. [CO] = 0 (*a*), 1.9 × 10^{-5} (*b*), 5.6 × 10^{-5} (*c*), 1.3 × 10^{-4} (*d*), 2.6 × 10^{-4} (*e*), 5.5 × 10^{-4} (*f*), 2 × 10^{-3} mol dm^{-3} (*g*)

Stopped flow. The kinetics of the reaction between [Fe(pc)] and CO in dmso was also studied using a Durrum stopped-flow apparatus. The reagent reservoirs were filled with a dmso [Fe(pc)] solution of appropriate concentration (1 × 10^{-5} mol dm^{-3} or less) and with a solution of CO in dmso. The concentration of CO varied from 5.5 × 10^{-4} to *ca.* 3 × 10^{-5} mol dm^{-3} and was always at least ten times larger than the concentration of [Fe(pc)]. The experiments were performed at 20 °C.

Again, in all cases pseudo-first-order kinetics were observed and, as expected, only partial reaction with CO was achieved even at the highest CO concentrations.

The data obtained are collected in Table 1.

Reproducibility of the observed rate constants was in general ±10% or better. Rate-constant values obtained by

---

* Dimethyl sulphoxide solutions of [Fe(pc)] of any concentration were stable for days when kept under pure nitrogen. Their spectra were always identical to that of the monomeric species [Fe(pc)], reported in the literature ($\lambda_{max.}$ = 653 nm).[2,9] No evidence for dimeric species was observed; a slow decrease of the maximum at λ = 653 nm and the growth of a lower maximum at 626 nm, previously reported as due to the dimerization of [Fe(pc)],[9] were indeed observed, but only in the presence of oxygen. A complete report on this phenomenon, which has to be related to an oxygenation reaction rather than a dimerization process, is in preparation.[5]

TABLE 1

Pseudo-first-order rate constants and experimental conditions for the carbonylation reaction of [Fe(pc)] in dmso[a]

Temperature (θ_c/°C)	10^3CO/ mol dm^{-3}	$k_{obs.}$/s^{-1}
20	1.1	1.6
	0.55	0.75
	0.55	0.76[b]
	0.53	0.82
	0.275	0.48
	0.264	0.43[c]
	0.11	0.18[c]
	0.11	0.33[b]
	0.066	0.21[c]
	0.033	0.27[b]
28.5	0.55	1.82[c]
	0.15	0.77
40.5	0.55	5.54[c]
	0.15	2.50
	0.05	1.73
53.5	0.55	11.6[c]
	0.15	5.9
	0.05	3.3

[a] Unless otherwise indicated, the data refer to the recombination reaction after flash photolysis. The rate constants are usually the average of at least two measurements. [b] Stopped-flow measurement. [c] Single run.

either stopped-flow or flash-photolysis methods were in good agreement with each other.

RESULTS AND DISCUSSION

Equilibrium Data.—Carbonylation of phthalocyaninatoiron(II)[11] and porphyrinatoiron(II)[12-15] complexes has been studied by several workers in the presence of axial *N*-donor heterocyclic ligands. A 1 : 1 Fe : CO stoicheiometry was found in every case. Only tetraphenylporphyrinatoiron(II) in toluene and in the absence of ligands other than CO requires two CO molecules per metal atom.[16,17] No quantitative information is reported for dmso solutions of [Fe(pc)]; however, a 1 : 1 [Fe(pc)]–CO complex containing a dmso unit has been isolated upon treating [Fe(pc)] solutions in dmso with CO.[18]

Reaction (1) may then be postulated (axial and free

$$[\mathrm{Fe(pc)}] + \mathrm{CO} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [\mathrm{Fe(pc)(CO)}],\ K = k_f/k_r \quad (1)$$

solvent molecules are omitted for simplicity). The spectral changes observed when an [Fe(pc)] solution was titrated with CO (see Figure 3) were analysed in order to obtain the equilibrium constant, K, of reaction (1). Figure 4 shows the plot of log [$\alpha/(1-\alpha)$] against the log of the concentration of carbon monoxide at three temperatures {α is the fraction of carbonylated [Fe(pc)]}. The plot is linear at each temperature. Statistical analysis of the data yields the following values for the slope and the logarithm of the equilibrium constant: 1.03 ± 0.02 and 4.14 ± 0.10 (20 °C); 1.04 ± 0.01 and 4.19 ± 0.03 (30 °C); 0.97 ± 0.01 and 3.83 ± 0.05 (40 °C) respectively. The slope is always close to unity and, thus, consistent with the stoicheiometry of equation (1); the small changes in log K with temperature indicate that the enthalpy of reaction is nearly zero.

The equilibrium constant for the carbonylation of some phthalocyaninatoiron(II) systems having different axial ligands has been measured in toluene at 23 °C.[11] Values ranging from 3×10^{-2} to 7.8 are reported for reaction (2) where L = imidazole, piperidine, pyridine, or

$$[\mathrm{Fe(pc)L_2}] + \mathrm{CO} \rightleftharpoons [\mathrm{Fe(pc)L(CO)}] + \mathrm{L} \quad (2)$$

2-methylimidazole. Since L in the present case is dmso, the equilibrium constants calculated above must be multiplied by 14.1 (*i.e.* the molar concentration of dmso) in order to be compared with the above constants. This yields a value (*ca.* 2×10^5) from 10^7 to 10^4 times higher than those measured for reaction (2).[11] This remarkable difference is likely to be due to the weaker binding of dmso, compared to the nitrogenous bases, rather than to solvation effects. The presence of a mutual *trans* labilizing effect by the two axial dmso molecules[18,19] may be responsible, at least in part, for such a weak binding.

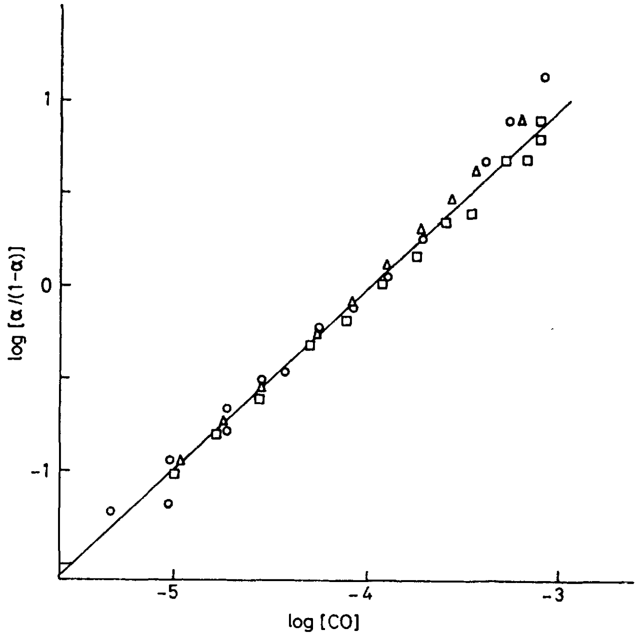


FIGURE 4 Plot of log [$\alpha/(1-\alpha)$] against log of carbon monoxide concentration. θ_c 20 (○), 30 (△), 40 °C (□)

Kinetic Data.—When the observed pseudo-first-order rate constant, $k_{obs.}$, is plotted as a function of carbon monoxide concentration, a linear plot with a definitely non-zero intercept is obtained at each temperature, as shown in Figure 5 for the case θ_c = 20 °C. This is in agreement with the simple reaction scheme of equation (1), hence, equation (3) holds. The data reported in

$$k_{obs.} = k_f[\mathrm{CO}] + k_r \quad (3)$$

Table 1 were analysed according to equation (3) to obtain k_f and k_r at each temperature. These data are shown in Table 2. Note that the value of k_f/k_r is in good agreement with that of K obtained independently from equilibrium experiments. The difference $\Delta H_f^\ddagger - \Delta H_r^\ddagger$ (-3.5 ± 3 kcal mol^{-1}) is very small in agreement with the small temperature effect observed on the values of K. It is generally accepted[11,13,15,19-21] that the substitution reactions at the metal centre of six-coordinated phthalocyaninato- and porphyrinato-iron(II) complexes proceed through a dissociative mechanism of the type (4) where mc is the macrocycle, X the leaving

$$\mathrm{L{-}Fe(mc){-}X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{L{-}Fe(mc)} + \mathrm{X} \tag{4a}$$

$$\mathrm{L{-}Fe(mc)} + \mathrm{Y} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{L{-}Fe(mc){-}Y} \tag{4b}$$

group, Y the entering nucleophile, and L the inert ligand *trans* to X. According to equations (4a) and (4b), if both [Y] and [X] are kept constant, the overall reaction is first order with respect to L–Fe(mc)–X with an observed rate constant equal to that given in (5). When

$$k_{\mathrm{obs.}} = (k_1k_2[\mathrm{Y}] + k_{-1}k_{-2}[\mathrm{X}])/(k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]) \tag{5}$$

$k_2[\mathrm{Y}] << k_{-1}[\mathrm{X}]$, equation (5) predicts an inverse dependence of $k_{\mathrm{obs.}}$ on [X]. On the other hand, when $k_2[\mathrm{Y}] >> k_{-1}[\mathrm{X}]$ and k_{-2} is low, a limiting case is reached where $k_{\mathrm{obs.}}$ is independent of the entering ligand concentration. Both situations have been found in a number of cases[11,13,15,19] for which, thus, the mechanism proposed may be considered well established.

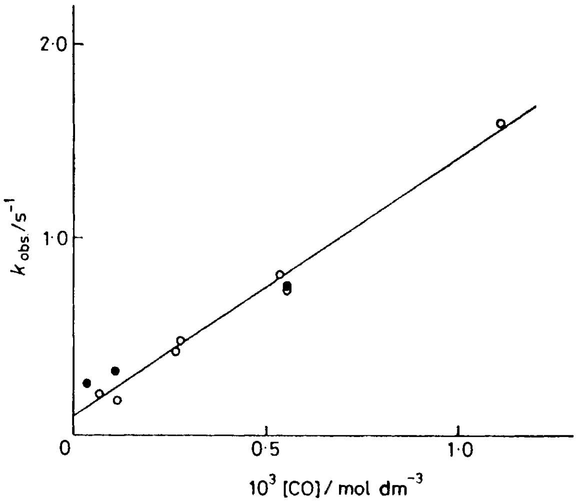


FIGURE 5 Dependence of the observed pseudo-first-order rate constant for carbonylation of [Fe(pc)] in dmso on the concentration of carbon monoxide. θ_c = 20 °C, flash photolysis experiments (○); stopped-flow experiments (●)

TABLE 2

Rate constants, activation parameters, and equilibrium constants for reaction (1)

Temperature (θ_c/°C)	$10^{-3}k_f$/ dm^3 mol^{-1} s^{-1}	k_r/s^{-1}	10^{-4} K^a/ dm^3 mol^{-1}
20	1.28 ± 0.05 [b]	0.12 ± 0.02 [b]	1.03
28.5	2.6	0.37	0.71
40.5	7.6	1.35	0.56
53.5	16	3.0	0.54
	Forward reaction	Reverse reaction	
$\Delta H^{\ddagger c}$/kcal mol^{-1}	14 ± 1	17.5 ± 2	
$\Delta S^{\ddagger c}$/ cal K^{-1} mol^{-1}	3 ± 3	−3 ± 6	

[a] As obtained from k_f/k_r. [b] Uncertainty is the probable error. [c] Uncertainties are estimated errors.

The values available in these cases for $\Delta S_1^{\ddagger}$ are in general large and positive (15—20 cal K^{-1} mol^{-1})[11,12,19] consistent with the proposed mechanism. The enthalpy of activation $\Delta H_1^{\ddagger}$ is found to be of the order of 24—27 kcal mol^{-1}. In this case the values of $\Delta S_f^{\ddagger}$ and $\Delta S_r^{\ddagger}$ might appear too low when compared with the above activation entropies.

However, it may be noted that the above values of $\Delta S_1^{\ddagger}$ refer to *N*-donor leaving groups and/or non-coordinating solvents.[11,12,19]

The dmso exchange reaction of [Fe(pc)(dmso)$_2$] in solvent dmso[21] shows, instead, activation parameters very close to the present ones ($\Delta S_{\mathrm{ex.}}^{\ddagger}$ = 1.8 cal K^{-1} mol^{-1}, $\Delta H_{\mathrm{ex.}}^{\ddagger}$ = 17.3 kcal mol^{-1}). This is not surprising as the activation process of both solvent exchange and carbonylation reactions of [Fe(pc)(dmso)$_2$] must be the same if a dissociative mechanism is operating in both cases.

An interesting implication of this type of investigation resides in the comparison of the equilibrium and kinetic parameters for the reaction with CO of both iron(II) phthalocyanine and iron(II) porphyrin. However in view of the complexities introduced by the number of parameters which affect the reactivity of these molecules (*e.g.* coordinating ligands and solvent effects, side-chain substituents and so on), any meaningful and rigorous comparison seems at present unfruitful, and remains to be explored.

[0/1147 *Received, 21st July,* 1980]

REFERENCES

[1] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719—1736.

[2] C. Ercolani, I. Collamati, and G. Rossi, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 799.

[3] S. Gaspard, R. Viovy, J. M. Bregeault, C. Jarjour, and S. Yolou, *C.R. Acad. Sci., Ser. C*, 1975, **281**, 925.

[4] C. Ercolani, F. Monacelli, and G. Rossi, *Inorg. Chem.*, 1979, **18**, 712.

[5] C. Ercolani, F. Monacelli, and G. Rossi, unpublished work.

[6] C. Ercolani, F. Monacelli, and G. Rossi, *Inorg. Chim. Acta Lett.*, 1980, **44**, L125.

[7] E. Antonini, and M. Brunori, ' Hemoglobin and Myoglobin in their Reactions with Ligands,' eds. A. Neuberger and E. L. Tatum, North Holland Publishers, Amsterdam and London, 1971, p. 170.

[8] A. G. Loomis, in ' International Critical Tables of Numerical Data Physics, Chemistry, and Technology,' ed. E. W. Washburn, McGraw-Hill, New York and London, 1928, vol. 3, p. 261.

[9] J. G. Jones and M. V. Twigg, *Inorg. Nucl. Chem. Lett.*, 1972, **44**, 305.

[10] E. Antonini, E. Chiancione, and M. Brunori, *J. Biol. Chem.*, 1967, **242**, 4360—4366.

[11] D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, 1974, **96**, 2733.

[12] L. Vaska and T. Yamaji, *J. Am. Chem. Soc.*, 1971, **93**, 6673.

[13] C. J. Weschler, D. L. Anderson, and F. Basolo, *J. Am. Chem. Soc.*, 1975, **97**, 6707.

[14] D. V. Stynes and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1973, 325.

[15] B. R. James, K. J. Reimer, and T. C. T. Wong, *J. Am. Chem. Soc.*, 1977, **99**, 4815.

[16] B. B. Wayland, L. F. Mehne, and J. Swartz, *J. Am. Chem. Soc.*, 1978, **100**, 2379.

[17] M. Rougee and D. Brault, *Biochemistry*, 1975, **14**, 4100.

[18] F. Calderazzo, G. Pampaloni, D. Vitali, G. Pelizzi, I. Collamati, S. Frediani, and A. Serra, *J. Organomet. Chem.*, 1980, **191**, 217.

[19] J. G. Jones and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1978, 1709.

[20] H. P. Bennetto, J. G. Jones, and M. V. Twigg, *Inorg. Chim. Acta*, 1969, **4**, 180.

[21] J. G. Jones and M. V. Twigg, *Inorg. Chem.*, 1969, **8**, 2120.