lowed by quick freezing to −190° yielded only the spectrum of ClO_2 in a rigid lattice,[16,17] Figure 4.

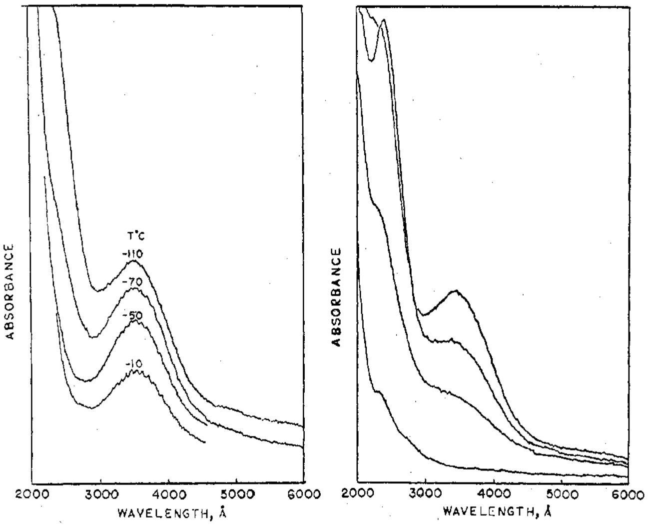

Figure 5.—Electronic spectra of ClO_2 in solution: right, increasing absorbance as electrolysis proceeds; left, decreasing absorbance with resolution of vibrational fine structure as the solution is warmed.

Ultraviolet spectra of a solution contained in the anode compartment of the cell are shown in Figure 5 (right). As electrolysis proceeds, the spectrum of chlorine dioxide increases in intensity as a function of time (30 min total at 30 μA). The absorbance maximum is at 355 nm and the spectrum is identical with that of chemically prepared ClO_2 dissolved in tetrahydrofuran. The absorbance decreases upon warming, Figure 5 (left), with increased resolution of vibrational fine structure being observed. The decrease in absorbance is due to reaction with the solvent, where in some cases the tetrahydrofuran polymerized in the cell at room temperature. The increased resolution of vibrational fine structure with increasing temperature is the reverse of what is observed for benzene in tetrahydrofuran. The uv spectrum of benzene in solution becomes extremely sharp and well defined as the temperature is lowered to −110°.

The electrolytic oxidation of perchlorate solutions yields, in addition to ClO_2, small bubbles of a colorless gas, oxygen. The oxidation of perchlorate ion proceeds according to the reaction

$$ClO_4^- \xrightarrow{-e} ClO_2 + O_2$$

with no evidence supporting the formation of the perchlorate radical from either esr or uv spectral measurements. The esr spectrum previously assigned[4,5] to the perchlorate radical was that of chlorine dioxide.

Acknowledgment.—The authors wish to express their appreciation to Dr. James Chickos and Joseph Wheeler for their assistance on this project.

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Kinetics of the Reaction of Some First-Row Transition Metals with Protoporphyrin IX Dimethyl Ester

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Glacial acetic acid has been used as the solvent to study the kinetics of protoporphyrin dimethyl ester with some of the first-row transition metals, a continuation of earlier work in this medium.[1,2]

Experimental Section

Materials.—Metals were used as the divalent acetates. Manganese and zinc acetate were obtained from British Drug Houses Ltd., and cupric acetate was from Anachemia Chemicals Ltd. Glacial acetic acid was obtained from Allied Chemicals Ltd. and was found to contain less than 0.04% water as analyzed using the Karl Fischer reagent.

Protoporphyrin dimethyl ester was purchased from Sigma Chemicals Co., St. Louis, Mo. Its spectra in pyridine and chloroform were in good agreement with those published.[1,3]

Kinetic Measurements.—A Beckman DB-G recording spectrophotometer, with a thermostated cell compartment maintained to within ±0.1°, was used to follow the reaction.

Treatment of the Data.—An excess of metal was used. A graph was drawn of $-\log (A_\infty - A_t)$ against time, where A_∞ is the absorbance of the solution after all the porphyrin has been complexed, and A_t is the absorbance of the solution at any time t. If the reaction is first order in metal as well as in porphyrin, the rate constant is $k_1 = 2.303m/[M]$, where m is the slope of the graph and $[M]$ is the average metal concentration for the points used in the graph. If the reaction is half order in metal, the rate constant is $k_{1/2} = 2.303m/[M]$. In most cases the excess of metal was >10, so that $[M] \simeq [M]_0$, the initial concentration of metal. However, for some runs, particularly those of zinc, the reaction was so fast that smaller excesses of metal had to be used. Even on these runs, although $[M]$ might be as little as 3 times the initial porphyrin concentration $[P]_0$, more than half the porphyrin had complexed before the first readings were taken so that the graph was usually close to a straight line.

To check the validity of this procedure second-order plots were drawn for some of these runs with less than a tenfold excess of metal. It can be shown that

$$\log \frac{A_\infty - A_t + \dfrac{A_\infty - A_0}{[P]_0}([M]_0 - [P]_0)}{A_\infty - A_t} = \frac{([M]_0 - [P]_0)}{2.303}k_1 t + \log \frac{[M]_0}{[P]_0}$$

In every case the value of k_1 obtained by using this equation graphically agreed very well with that obtained from the pseudo-first-order plot using an estimated value of $[M]$.

Results

Table I gives data for the spectra of the metal complexes of protoporphyrin dimethyl ester in glacial acetic acid.

Isosbestic points were found for all the complexation reactions except that between cobalt and protoporphyrin dimethyl ester, where conversion of the Co^{2+} complex to the Co^{3+} complex produced a third absorbing species.

Figure 1 shows successive spectra of a solution of

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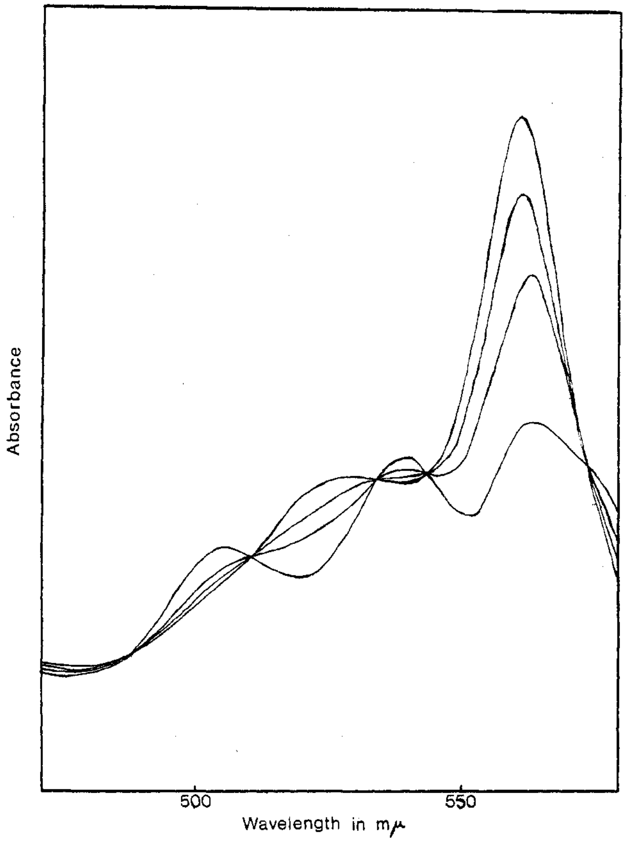

Figure 1.

TABLE I

CHARACTERISTICS OF THE SPECTRA OF COMPLEXES OF METALS WITH PROTOPORPHYRIN DIMETHYL ESTER IN GLACIAL ACETIC ACID

Metal	Parameter	Band α	Band β	Band Other	α/β
Mn	λ, mμ	585	556	469	0.60
	$\epsilon \times 10^{-3}$	6.5	10.6	41.7	
Co^{2+}	λ, mμ	560			
	$\epsilon \times 10^{-3}$	20.0			
Co^{3+}	λ, mμ	567	535		1.27
	$\epsilon \times 10^{-3}$	18.3	14.4		
Ni	λ, mμ	560	524		2.37
	$\epsilon \times 10^{-3}$	26.5	11.2		
Cu	λ, mμ	569	531		2.09
	$\epsilon \times 10^{-3}$	26.3	12.6		
Zn	λ, mμ	580	543		1.27
	$\epsilon \times 10^{-3}$	20.0	15.7		

nickel and protoporphyrin dimethyl ester in glacial acetic acid showing isosbestic points.

The occurrence of isosbestic points is good evidence that only two absorbing species (porphyrin and metalloporphyrin) are present.

Job plots for all the metals with protoporphyrin dimethyl ester indicated a 1:1 complex. The evidence was not as clear for cobalt and nickel as for the other metals, however. Job plots of manganese, copper, and zinc with hematoporphyrin dimethyl ester also indicated a 1:1 complex.

The kinetics results were surprising. Table II gives the values of rate "constants" for different concentrations of metal: $k_{1/2}$, calculated on the assumption that the reaction is half order in metal, and k_1, calculated on the assumption that it is first order in metal.

TABLE II

RATE "CONSTANTS" FOR VARIOUS CONCENTRATIONS OF METAL

Metal	Temp, °C	Estd av concn of metal, M	Rate "constant" if order of reaction in metal is $^1/_2$: $k_{1/2}$, $M^{-1/2}$ sec^{-1}	Rate "constant" if order of reaction in metal is 1: k_1, M^{-1} sec^{-1}
Mn	33	66.7×10^{-4}	6.27×10^{-3}	7.67×10^{-2}
		6.6×10^{-4}	2.53×10^{-3}	9.83×10^{-2}
	40	66.7×10^{-4}	13.0×10^{-3}	15.9×10^{-2}
		8.0×10^{-4}	4.77×10^{-3}	17.0×10^{-2}
		6.0×10^{-4}	4.90×10^{-3}	20.0×10^{-2}
		4.0×10^{-4}	4.22×10^{-3}	21.0×10^{-2}
	47	6.67×10^{-3}		0.306
	55	6.67×10^{-3}		0.567
Co	25	7.93×10^{-4}	5.14×10^{-2}	1.83
		5.9×10^{-4}	5.50×10^{-2}	2.27
		3.90×10^{-4}	4.68×10^{-2}	2.37
		3.86×10^{-4}	6.25×10^{-2}	3.18
		1.9×10^{-4}	5.17×10^{-2}	3.75
	33	6.53×10^{-4}	9.43×10^{-2}	3.73
		3.33×10^{-4}	9.52×10^{-2}	5.22
	40	2.6×10^{-4}	0.156	
	47	1.9×10^{-4}	0.283	
Ni	33	6.67×10^{-3}	5.05×10^{-3}	
	40	8.0×10^{-3}	9.10×10^{-3}	0.100
		6.67×10^{-3}	8.95×10^{-3}	0.120
		4.0×10^{-3}	8.92×10^{-3}	0.138
		0.6×10^{-3}	6.72×10^{-3}	0.268
	47	6.67×10^{-3}	15.6×10^{-3}	
	55	6.67×10^{-3}	27.8×10^{-3}	
Cu	17	3.96×10^{-4}	0.150	7.53
		1.86×10^{-4}	0.263	19.2
		1.17×10^{-4}	0.223	20.7
		0.58×10^{-4}	0.177	23.3
	22.9	1.94×10^{-4}	0.358	25.7
		1.85×10^{-4}	0.357	27.8
	33	25×10^{-5}	1.11	69.8
		7.2×10^{-5}	0.623	73.3
		7.1×10^{-5}	1.06	126
		6.7×10^{-5}	0.670	81.8
Zn	17	15.4×10^{-5}	1.68	137
		8.0×10^{-5}	1.15	143
		4.46×10^{-5}	1.05	157
		2.81×10^{-5}	0.970	178
	22.9	4.4×10^{-5}	1.15	173
		4.3×10^{-5}	1.40	213
	28.0	4.46×10^{-5}	1.62	173
	33.0	4.4×10^{-5}	2.01	303

The reaction appears to be half order in cobalt and nickel and close to half order in copper and shows orders between one-half and one in the other two metals. In manganese the reaction is close to first order, and in zinc it is closer to first than to half order.

From average values of the rate "constants," the activation energies were calculated to be 17.6, 14.3, and 15.4 kcal for manganese, copper, and nickel, respectively. The corresponding values of log A, where A is the frequency factor, were 11.4, 9.2, and 8.7.

The failure of the reaction between protoporphyrin dimethyl ester and zinc, and to some extent manganese, to obey a simple kinetic law may at first seem surprising. Choi and Fleischer[4] found the reaction between $\alpha,\beta,\gamma,\delta$-tetra(4-pyridyl)porphine and manganese, cobalt, nickel, and copper in glacial acetic acid to be first order in metal in every case. Brisbin and Balahura[1] and Kingham[2] found the reaction between hematoporphyrin and manganese, iron, cobalt, copper, and zinc to be first order in metal and that between hematoporphyrin and nickel to be half order in metal.

However, a closer examination of the previously published results reveals that Choi and Fleischer conducted all their experiments over a very narrow range of concentration: (3–6) × 10^{-3} M, the dif-

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[4] E. I. Choi and E. B. Fleischer, *Inorg. Chem.*, **2**, 94 (1963).