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Kinetics of the Reaction of Some Divalent Transition Metal Ions with α,β,γ,δ-Tetra-(4-pyridyl)-porphine[1]

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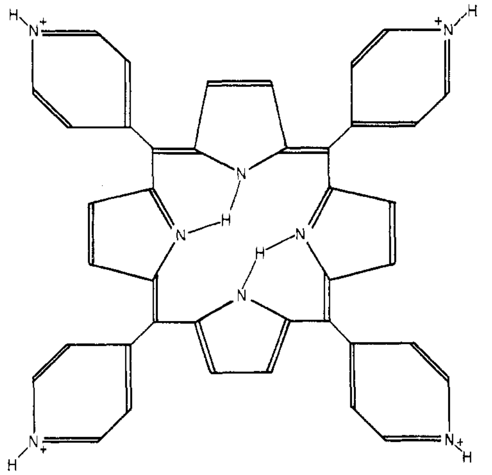
Received August 3, 1962

The reaction of divalent transition metal ions with α,β,γ,δ-tetra-(4-pyridyl)-porphine was investigated. The rate of the reaction was determined for Cu(II), Co(II), Mn(II), Ni(II), and Zn(II). From a study of the temperature variation of the reaction rates activation energies were determined for the reaction. The effect of solvent composition on the reaction rate was studied in an acetic acid–water solvent system.

We are interested in the rate of formation of metal–ligand bonds. Our general purpose is to define which parameters influence the rates of formation of metal–ligand bonds and what the dependence of the rate is with respect to each parameter. The specific case treated in this report is the rates of reaction of some divalent transition metal ions with a porphyrin chelating agent.

The ligand, α,β,γ,δ-tetra-(4-pyridyl)-porphine,[2] hereafter denoted as TPyP, is very susceptible to investigation because of its favorable properties. It is soluble in a variety of solvents, both aqueous and non-aqueous, reacts with transition metal ions at measurable rates, and has a spectrum which allows the reaction to be easily followed with a spectrophotometer. Another important feature of the reaction is the well known stability of the products of the reaction, the metalloporphyrins.



The reaction we have studied involves the porphyrin free base reacting with a transition metal ion to form a metalloporphyrin complex and two protons

$$\text{TPyP} + \text{M}^{2+}(\text{solvent})_n \xrightarrow{k_1} \text{TPyP-M}(\text{solvent})_{n-m} + 2\text{H}^+ + m(\text{solvent}) \quad (1)$$

where TPyP is the α,β,γ,δ-tetra-(4-pyridyl)-porphine free base, TPyP-M is the metalloporphyrin of TPyP, and k_1 is the rate constant for reaction 1. The value of the rate constant for reaction 1 was determined as a function of transition metal ion, solvent, temperature, and metal ion geometry.

Experimental

The α,β,γ,δ-tetra-(4-pyridyl)-porphine has previously been described.[2] All the metal ion solutions were prepared with reagent grade chemicals. The glacial acetic acid was refluxed over anhydrous boric acid to remove water. The amount of water in the glacial acetic acid was less than 0.05%. The metal acetates and perchlorates used were usually the hydrates. This introduced some water into the solvent; but tests showed that an introduction of 1% water into the solvent acetic acid caused less than a 10% change in the rate constants. Since our water content is much lower than 1%, we have confidence that the trace amounts of water introduced by the hydrated salts did not appreciably affect our results.

The reactions were followed spectrophotometrically with a Beckman DU spectrophotometer with a thermostated cell compartment maintained within ±0.1° or better. An energy recording adapter was employed for continuous recording of the reaction progress. All the reactions were carried out in 1.00-cm. cells by mixing the reactants that had been pre-equilibrated at the reaction temperature. The reaction was followed either at 512 or at 589 mμ if the transition metal ion color interfered with the 512 mμ peak. An excess of metal ion always was used and pseudo-first-order rate constants were obtained from the data. The rate constants were obtained by a plot of $\log (D_t - D_\infty)$ against time, which yielded a straight line of slope $-k'/2.303$, or by the Guggenheim method,[3] which does not require a D_∞ point. The pseudo-first-order rate constants were transformed into second-order rate constants by dividing by the metal ion concentration.

Results

Acetic Acid.—The reaction of the transition metal ions Cu(II), Co(II), Mn(II), and Ni(II) with TPyP was studied in glacial acetic acid. The TPyP is completely in the free base form in glacial acetic acid. The reaction is first order with respect to both the TPyP and the metal ion. A plot of $\log (D_\infty - D_0/D_t - D_\infty)$ *vs.* time results in a straight line plot for all the kinetic data. Table I shows that the reaction is first order with respect to the copper ion. The second-order rate constants for the reaction of TPyP and Cu(II) are constant over the range of Cu(II) concentrations studied. Table I also indicates the reproducibility of our data.

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(1) This research was supported by a Public Health Service Grant.

(2) E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962).

(3) A. Frost and R. Pearson, "Kinetics and Mechanism," Second Ed., John Wiley and Sons, New York, N. Y., 1961, p. 49.

TABLE I

RATES OF REACTION OF TPyP WITH Cu(II) IN GLACIAL ACETIC ACID, T = 25.00°

Cu(II), M[a]	TPyP × 10^{+5}, M	Rate constant, l. min.$^{-1}$ mole^{-1}
0.00529	6.15	22.6
.00593	5.56	22.3
.00358	6.62	23.4
.00509	6.23	23.9
.00359	6.23	22.8
.00416	6.05	23.7
.00430	5.89	24.4
		Average 23.3 ± 0.6.

[a] Cu(II) from copper acetate.

The reaction (1) was carried out in glacial acetic acid with various ions at various temperatures. The results are summarized in Table II.

TABLE II

REACTION OF TPyP IN GLACIAL ACETIC ACID WITH TRANSITION METAL IONS

Ion[a,b,c]	Temp., °C.	Rate constant, l. min.$^{-1}$ mole^{-1}
Cu(II)	20.00	16.9
Cu(II)	25.00	23.3
Cu(II)	30.00	34.0
Cu(II)	32.50	41.6
Cu(II)	35.00	56.1
Co(II)	25.00	5.18
Co(II)	30.00	8.39
Co(II)	35.00	13.41
Co(II)[d]	25.00	3.81
Mn(II)	25.00	0.35
Mn(II)	30.00	.53
Mn(II)	35.00	.97
Ni(II)	25.00	1.44

[a] From the acetates. [b] Metal concentration range: 0.003–0.006 M. [c] TPyP concentration range: 5–6 × 10^{-5} M. [d] 0.5 M in sodium acetate.

Aqueous Solutions.—The reaction (1) was studied in aqueous solution at a pH of 1.92. The porphyrin was in the free base form at this pH. The reaction was complicated in aqueous solutions by a precipitation that sometimes occurred during the course of the reaction. It was found that a small amount of acetic acid present in the solutions prevented any precipitation from occurring during the course of the reaction. The reaction was carried out in 8.3% acetic acid. The solutions were prepared with 0.01 N $HClO_4$ and the metal perchlorates were employed. The acetic acid present kept any precipitate from forming during the reaction. Table III gives the results of this experiment.

Variation of Rate with Solvent Composition.—The rate of reaction 1 was determined in an acetic acid–water solvent system. The rate of formation of CuTPyP was examined in solvents containing 16 to 100% acetic acid content. Figure 1 shows the results of this study. Similar results were obtained for copper perchlorate solutions except that the range of acetic acid content examined was limited to 30–80% acetic acid because at higher acetic acid content a precipitation of a green solid occurred when the reactants were mixed.

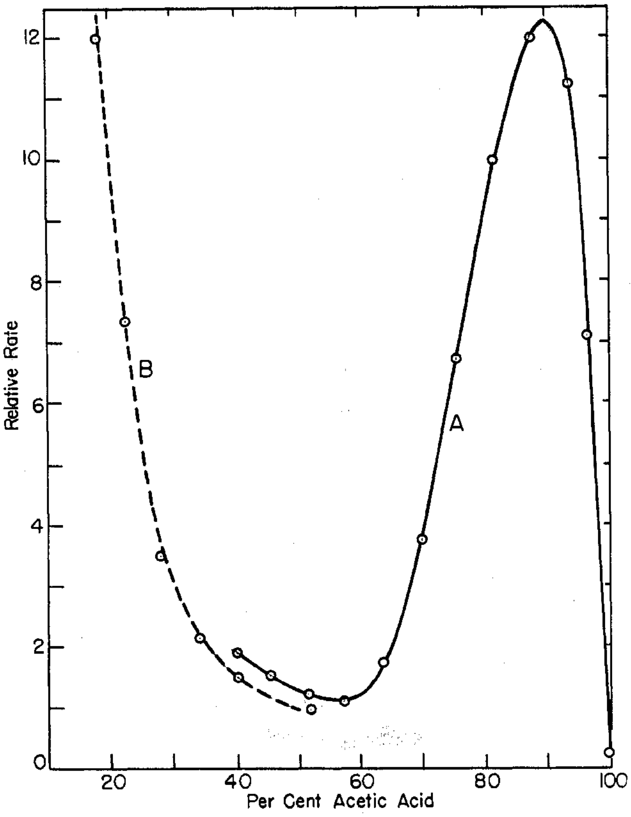

Fig. 1.—The relative rates of the reaction of copper acetate with TPyP as a function of acetic acid content. Initial concentrations: Cu(II) = 1.67 × 10^{-2} M; curve A, TPyP = 6.67 × 10^{-5} M; curve B, TPyP = 6.60 × 10^{-5} M; temperature, 25.00°.

Variation of Rate as a Function of pH.—The rate of reaction of Cu(II) with TPyP was studied as a function of hydrogen ion activity. The reactions were carried out in 4.5% acetic acid solutions. The pH was adjusted with $HClO_4$. Table IV summarizes the results.

A plot of the rate constant for the reaction against $1/a_{H^+}$ gives a straight line (Fig. 2). This shows that the reaction is inversely proportional to the hydrogen ion activity in the range of pH values of the experiments.

A similar plot results if the data of Fig. 1 are plotted as rate *vs.* $1/a_{H^+}$ from 17 to 35% acetic acid. Thus the

TABLE III

REACTION RATES OF TPyP WITH METAL IONS IN 0.01 N $HClO_4$ WITH 8.3% ACETIC ACID

Ion	Concn., M	Temp., °C.	Rate constant, l. min.$^{-1}$ mole^{-1}
Cu(II)	0.0266	25.00	10.4
Cu(II)	.00793	25.00	10.5
Cu(II)	.0177	30.00	14.1
Cu(II)	.0177	35.00	18.3
Zn(II)	.0194	25.00	0.37
Zn(II)	.0194	30.00	.61
Zn(II)	.0194	35.00	.88
Zn(II)	.0194	49.6	1.99

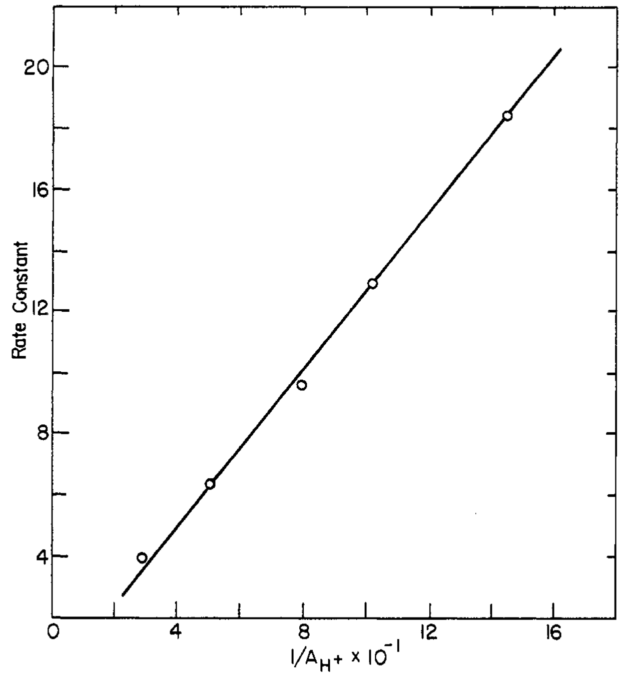

Fig. 2.—Rate of the reaction of Cu(II) with TPyP as a function of H^+ activity.

Table IV

Reaction of TPyP with Cu(II) in Solutions of Varying $HClO_4$ Concentration

Initial concentrations: TPyP = 6.25×10^{-5} M; Cu(II) = 6.5×10^{-3} M

pH	Rate constant, l. min.$^{-1}$ mole^{-1}	$1/a_{H^+} \times 10^{-1}$ [a]
1.44	3.97	2.8
1.70	6.39	5.0
1.90	9.63	8.0
2.01	12.91	10.2
2.16	18.38	14.5

[a] a_{H^+} is the hydrogen ion activity calculated from the measured pH.

reaction rate k_1 is inversely proportional to the H^+ activity for both copper acetate and copper perchlorate solutions.

Discussion of Results

The variation of the rates of the reaction of divalent metal ions with TPyP is given in Tables I, II, and III. The order of reactivities in glacial acetic acid is Cu(II) > Co(II) > Ni(II) > Mn(II), while in 8.3% acetic acid Cu(II) > Zn(II). By using the equation

$$k_1 = A \exp(-E_a/RT)$$

the activation energy, E_a, and log A were determined for reaction 1. The results are given in Table V.

The order of the reaction rates of the Cu(II), Co(II), and Ni(II) ions is similar to that found by Connick[4] for water exchange reactions, by Eigen[5] for fast substitution reactions, by Wilkins[6] for the formation and dissociation of dipyridyl complexes, by Garner[7] for ammonia exchange, and by Long[8] for EDTA metal ion exchange.

Table V

Activation Energies for TPyP Reaction

Ion	E_a, kcal./mole	log A
Cu(II)[a]	12.6 ± 0.5	10.6
Co(II)[a]	17.4 ± 0.5	13.5
Mn(II)[a]	18.7 ± 3.0	13.3
Cu(II)[b]	10.2 ± 0.5	8.5
Zn(II)[b]	15.9 ± 1.0	11.1

[a] In glacial acetic acid. [b] In 8.3% glacial acetic acid, pH 1.92.

The Mn(II) reacts relatively slower in reaction 1 than in other reactions.[4-8] The Zn(II) ion also reacts relatively slower than usually is found. The nontransition metal ions Cd(II), Pb(II), and Hg(II) react either very slowly or not at all with TPyP. This indicates that reaction 1 requires or at least prefers a transition metal type ion with a partially empty d shell.

Reaction 1 is further complicated by the fact that under the experimental conditions the reactant metal is in a weak-ligand field, either water or acetate ion, while the product metalloporphyrin is a strong field ligand. The effect of this change in field in addition to a change in electronic spin sometimes occurring during the course of the reaction cannot be determined at this time.[9]

The reaction rate varies inversely with the hydrogen ion activity. This also has been found in the reaction of transition metals with phthalocyanine tetrasulfonic acid.[10]

The variation of the reaction rate with the hydrogen ion is not understood at this time. The mechanism proposed by Schiller,[10] that the reacting species is the singly dissociated form of the porphyrin (the porphyrin minus one proton), is a possible mechanism for the reaction, but we do not believe there is enough evidence to support this mechanism. The lack of evidence for the existence of a dissociated porphyrin in the pH ranges investigated weighs against Schiller's mechanism. The copper ion also could be involved in an equilibrium with the hydroxide ion that would affect the reaction rate.

The variation of the reaction rate with acetic acid content (Fig. 2) shows a maximum at about 90% and a minimum at about 50% acetic acid. This unusual behavior cannot be explained by any physical properties of the acetic acid–water mixtures. Thus it must have a chemical origin. The most likely interpretation is that the most reactive species is one with a mixed coördination sphere. It would have both water and acetic acid complexing to the copper ion. It is hoped to better understand this effect by studying the

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(4) R. Connick, "Advances in the Chemistry of Coördination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 15.

(5) M. Eigen, ref. 4, p. 371.

(6) R. Wilkins, *et al.*, ref. 4, p. 391.

(7) C. Garner, *et al.*, *J. Chem. Phys.*, **27**, 668 (1957).

(8) C. Cook and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).

(9) Studies are being carried out on reaction 1 in which the metal ion reactant is in a strong ligand field.

(10) J. Schiller, *et al.*, *Experientia*, **17**, 540 (1961).

equilibria of copper ions in acetic acid–water mixtures. The functional form of the behavior of the rate with solvent composition is similar to that of the racemization of trisphenanthrolenenickel(II) in ethanol–water mixtures.[11]

The geometry of the metal ion species does not seem to be very critical in determining the reaction rate. This is true at least in the case of Co(II) in glacial acetic acid. When cobalt acetate is dissolved in acetic acid the Co(II) is octahedrally coördinated.[12]

If an excess of sodium acetate is added to the system the Co(II) becomes tetrahedrally coördinated.[12] This change is evident by the color change of the solution from pink to blue. The rates of the reaction of Co(II) with TPyP in the octahedral and tetrahedral forms are 5.18 and 3.81 l. min.$^{-1}$ mole^{-1}, respectively. These rates are very similar and the difference could be due to the change in ionic strength of the solutions. Thus the geometry of the metal ion does not seem to affect the reaction rate greatly.

[11] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, **50**, 1325 (1954).

[12] P. J. Proll, L. H. Sutcliffe, and J. Walkley, *J. Phys. Chem.*, **65**, 455 (1961).

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Electronic Spectra of β-Diketone Complexes. III. α-Substituted β-Diketone Complexes of Copper(II)

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Received July 16, 1962

The electronic spectra of α-substituted β-diketone complexes of copper(II) are presented and the assignments of the various bands discussed. It is concluded that the band at $\sim$250 mμ arises from electron transfer from a ligand orbital to an antibonding orbital associated with the metal. A band observed at $\sim$200 mμ is tentatively assigned to a π–π^* transition primarily localized in the ligand. Hückel molecular orbital calculations for Cu(acac)$_2$ are used in support of these assignments.

Introduction

In an earlier paper in this series,[2] the electronic spectra of an extensive list of acetylacetonate complexes were presented and the general trends in the spectra were discussed. This paper and the following one[3] (part IV) are concerned with the electronic spectra of β-diketone complexes of copper(II).

Belford,[4] *et al.*, attempted to assign the bands observed in the spectrum of copper(II) acetylacetonate, Cu(acac)$_2$, with the help of a simple molecular orbital calculation for the ligand anion. Their assignment (π–π^*) for the 296 mμ band observed in the spectrum of Cu(acac)$_2$ is confirmed[3] by the present study. Belford, *et al.*, also observed but did not discuss the intense band at $\sim$245 mμ but their observations did not extend far enough to detect another strong peak at $\sim$205 mμ. Graddon[5] pointed out the presence of the 245 mμ band but did not discuss its assignment. The band at $\sim$205 mμ has not been reported prior to this study.

Spectra and discussion are presented in this paper establishing the origin of the 245 mμ band in the spectrum of Cu(acac)$_2$ and the changes observed in the ultraviolet and visible spectra, resulting from changes in the α-substituents of the β-diketone, also are discussed. The results obtained from a semi-empirical Hückel molecular orbital calculation are used to support proposed assignments.

Experimental

Preparation of Materials.—The copper(II) complexes of the β-diketones used in this study were prepared by standard methods available in the literature, Table I. Analyses were performed by S. M. Nagy, M.I.T., and Schwarzkopf Microanalytical Laboratory, Woodside, New York. The complexes were found to be stable, when dry, with no decomposition even after two years storage.

Spectra.—Ultraviolet and visible spectra were observed using a Beckman DK-2 spectrophotometer equipped with a microswitch to synchronize the recorder with the wave length scroll. The instrument was calibrated with benzene vapor and a mercury arc.

Spectra were repeated on Cary Model 11 and Model 14 spectrophotometers and were found to be reproducible to better than ± 2 mμ from $\sim$450 to $\sim$1200 mμ and ± 1 mμ from $\sim$230 to $\sim$450 mμ. Over the region from 180–220 mμ, it was observed that spectra recorded on the DK-2 appeared at $\sim$5 mμ longer wave lengths than on the Cary instrument. Repeated runs with other Cary instruments, flushed with dry nitrogen, were reproducible. These results are given here.

Freshly opened Fisher reagent grade chloroform, Baker "analyzed" cyclohexane, Phillips "Spectrograde" cyclohexane, and Fisher reagent grade methanol were used as solvents. Solutions were prepared to $\sim 10^{-2}$ M concentration for visible spectra and $\sim 10^{-4}$–10^{-5} M for ultraviolet studies. Calibrated quartz cells were used. The Beer–Lambert law was found to be

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[1] Communications regarding this paper should be directed to J. P. F., Department of Chemistry, Case Institute of Technology, Cleveland, Ohio.

[2] R. H. Holm and F. A. Cotton (part I), *J. Am. Chem. Soc.*, **80**, 5658 (1958).

[3] J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).

[4] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[5] D. P. Graddon, *ibid.*, **14**, 161 (1960).