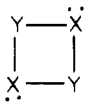

4

tronegativity of X is greater than that of Y to the extent that each X formally contributes two π electrons and each Y no π electrons, to the conjugated network. In particular, the highest occupied (lowest unoccupied) π MO is completely localized on the X(Y) π atomic orbitals and has energy equivalent to an X(Y) nonbonding orbital in such systems. When X = Y (as in cyclobutadiene), an exact degeneracy occurs between these two MO's, resulting in an "alternating" geometry for the lowest singlet state and in a small energy gap between the lowest singlet and triplet state.[6]

To establish the optimum geometry for **2**, STO-2G calculations were performed first for a square ring; the optimum B-N distance found of 1.47 Å is 0.07 Å longer than predicted for BH_2NH_2 itself and 0.04 Å longer than for an N-B-N chain.[7] Subsequent calculations for the rectangular form of **2** and using an *average* B-N separation of 1.47 Å indicate that the D_{2h} form is stable relative to such displacements, in agreement with the arguments advanced above. Finally, calculations (again with a B-N distance of 1.47 Å) indicate that the optimum NBN angle for the D_{2h} form of **2** is 93°. These structural predictions agree reasonably well with X-ray diffraction results[8] for the hexakis(trimethylsilyl)2,4-diamino derivative of **2**, in which the four almost-equal ring B-N distances are 1.45 ± 0.02 Å, and the ring NBN angle is 98°.

Although the $(BHNH)_2$ ring is expected to be destabilized by both strain and antiaromaticity effects, the optimum energy calculated[9] for **2** is some 74.3 kcal/mol more bonding than for two iminoborane monomers, in good agreement with the value of 63.3 kcal/mol calculated by Armstrong and Clark.[4b] In contrast, *ab initio* calculations predict that $(BH_2NH_2)_2$ is only $\sim$3 kcal/mol more stable than two aminoborane monomers.[10] It is evident from these results that both B-N coordinate covalent and π bonds are weak relative to the "normal" σ bonds formed between trivalent boron and nitrogen atoms.

To test the Huckel method prediction that the antiaromaticity of type **4** four-membered rings decreases as the electronegativity difference between X and Y increases,[11] SCF wavefunctions and energies were redetermined for **2** and for BH_2NH_2 using a basis set which does *not* include a $2p_\pi$ orbital on boron (and thus localizes the π electrons on the nitrogen atoms). In contrast to cyclobutadiene, for which the delocalization energy is predicted by semiempirical calculations to be zero or even negative,[11,12] the π-bonding energy calculated for **2** is predicted to be 11 kcal/mol more stabilizing than for two isolated boron-nitrogen π bonds. Thus, the residual antiaromaticity for **2** must be slight.

A crude estimate of 53 kcal/mol for the σ-bond strain energy in **2** was deduced by comparison of the total bonding energy in the $(BHNH)_2$ ring (calculated with the π electrons localized on N) with the effective energies for four B-N, two B-H, and two N-H σ bonds; the latter were obtained from total energies for BH_2NH_2, $NH_2B(H)NH_2$, and $BH_2N(H)BH_2$ (again calculated with localized π electrons) by assuming that each type of σ-bond energy remains the same in the different molecules.[13] While the rather high strain energy calculated for **2** gains some support from the value of 55.4 kcal/mol (deduced from semiempirical calculations and the experimental heat of formation) for the cyclobutadiene derivative biphenylene,[14] previous experience with the STO-3G method indicates that strain energies are usually overestimated.[15]

As expected from the orbital energy arguments above, the highest occupied MO for **2** is localized on the nitrogen $2p_\pi$ orbitals and has a rather low stabilization (predicted ionization potential 8.1 eV, compared to 11.1 eV for BH_2NH_2).[16] The vertical excitation energy to the lowest triplet state T_1 is also relatively low at 119 kcal/mol (compare to 157 for BH_2NH_2) since the transition involved is from a nonbinding N to a nonbonding B π orbital. The predicted S_0-T_1 split for *square* cyclobutadiene is only $\sim$15 kcal/mol.[6]

Registry No. $(BHNH)_2$, 18464-81-8.

---

(6) *Ab initio* calculations for various geometries and states of cyclobutadiene have been reported: R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(7) N. C. Baird, to be submitted for publication. Calculations for BH_2NH_2 indicate that bond lengths calculated at the STO-2G level are $\sim$0.01 Å longer than those predicted by STO-3G expansions. See also N. C. Baird, *Chem. Phys. Lett.*, **6**, 61 (1970).

(8) V. H. Hess, *Acta Crystallogr., Sect. B*, **25**, 2342 (1969).

(9) All energy values quoted henceforth are based upon STO-3G calculations using the optimum calculated geometry for the ring (R_{BN} = 1.47 Å, NBN angle = 98°). The total energy for **2** is −158.6912 au.

(10) (a) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 2748 (1970). (b) Although the errors in the total bonding energies for both **1** and **2** are expected to be rather large due to correlation effects, the calculated dimerization energy should be of the correct order of magnitude since both **1** and **2** are closed-shell species and since the total number of bonds does not change in the dimerization process.

(11) See for example the calculations in (a) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967); (b) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(12) According to the Huckel method including overlap integrals *S*, the total π-bonding energy for two ethylenes is $4\beta/(1 + S)$ whereas that for D_{4h} cyclobutadiene is only $4\beta/(1 + 2S)$.

(13) This assumption is supported by the calculated overlap populations[7] which do not vary significantly from one chain to another.

(14) See C. de Llano, Ph.D. Thesis, University of Texas, Austin, Texas, 1968, p 134. The strain energy quoted by de Llano has been corrected in the present study on the basis of the revised heat of vaporization reported by E. Morawetz, *J. Chem. Thermodynamics*, 4, 455 (1972).

(15) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(16) Armstrong and Clark[4b] predicted an ionization potential of 10.9 eV for **2**.

Contribution from the Department of Chemistry,
Howard University, Washington, D. C. 20001

Kinetics of Copper Incorporation into Porphyrins in Acetic Acid

Jeffrey James and Peter Hambright*

Received May 26, 1972

Acetic acid has been used as a solvent to study the kinetics of incorporation of Cu, Fe, Co, Ni, and Mn species into porphyrin molecules.[1-3] In two separate studies, the rate laws for copper acetate insertion were found to be first order in porphyrin (either hematoporphyrin[1] or tetrapyridylpor-

---

(1) D. J. Kingham and D. A. Brisbin, *Inorg. Chem.*, **9**, 2034 (1970).

(2) D. A. Brisbin and R. J. Balahura, *Can. J. Chem.*, **46**, 3431 (1968).

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

phine[3]) and first order in copper acetate. A formation constant for copper hematoporphyrin from the diacid porphyrin and copper has been measured in acetic acid.[4] Since it is known that copper acetate exists in acetic acid primarily as a dimer,[5-7] the implication is that the dimer is reactive for metal incorporation. This is in disagreement with the notion that predissociation of a metal ion occurs before metal ion incorporation.[8]

It has been shown that in acetic acid, depending on the metal ion, the free base, monocation, and dication porphyrins are all capable of metal ion incorporation.[1-4] In aqueous solution, however, only the free base form is known to be reactive.[9] We report the kinetics of copper porphyrin formation in acetic acid using copper acetate and porphyrins existing as mixtures of protonated species. The results indicate that only the copper monomer is reactive and that the diacid porphyrin is very unreactive.

Experimental Section

The kinetics of copper ion incorporation were run at 25° in glacial acetic acid containing 1% water. Copper acetate monohydrate was used as the source of copper, and anhydrous lithium acetate was prepared by literature methods.[5] The kinetics were followed at constant wavelength under pseudo-first-order conditions on a Beckman Acta III recording spectrophotometer. Plots of log $(D_\infty - D_t)$ *vs.* time were linear over 3 half-lives, and the observed pseudo-first-order rate constant, k_0, was calculated in the usual manner.[9]

The reactions were followed in the visible region using at least a 20-fold excess of copper to total porphyrin. As an example of the general procedure consider hematoporphyrin dimethyl ester, which had major bands at 605, 557, 535, and 505 nm. Upon addition of copper, isosbestic points occurred at 700, 577, 552, 539, 510, and 475 nm, and the resulting copper porphyrin had peaks at 563 and 527 nm. The kinetics were monitored at 563 nm, and the reaction was found to be first order in porphyrin. The first-order rate constant was independent of total porphyrin concentration over a fourfold range ($(1.8\text{–}7.2) \times 10^{-6}$ *M*).

Results

With a constant porphyrin concentration, variation of the total copper gave k_0 values which varied as the *one-half* order of the total copper concentration

$$k_0 = k[\text{copper}]^{1/2}{}_{\text{total}} \qquad (1)$$

as shown in Figure 1. The reactions of tetrapyridylporphine, diacetyldeuteroporphyrin, and hematoporphyrin dimethyl ester all followed a similar half-order dependence. For hemato $k = (13.0 \pm 0.6) \times 10^{-2}$, for diacetyl $k = (7.4 \pm 0.6) \times 10^{-2}$, and for TPyP, $k = (3.2 \pm 0.2) \times 10^{-2}$ $F^{-1/2}$ sec^{-1}.

The addition of lithium acetate to solutions of copper acetate dimers produces monomeric copper species.[7] With 1.0 *M* added LiOAc, the rate law for the diacetyldeuteroporphyrin compound was first order in total copper and first order in porphyrin. The results are shown in Figure 2, and the second-order rate constant was $(12.0 \pm 0.3) \times 10^{-1}$ F^{-1} sec^{-1}.

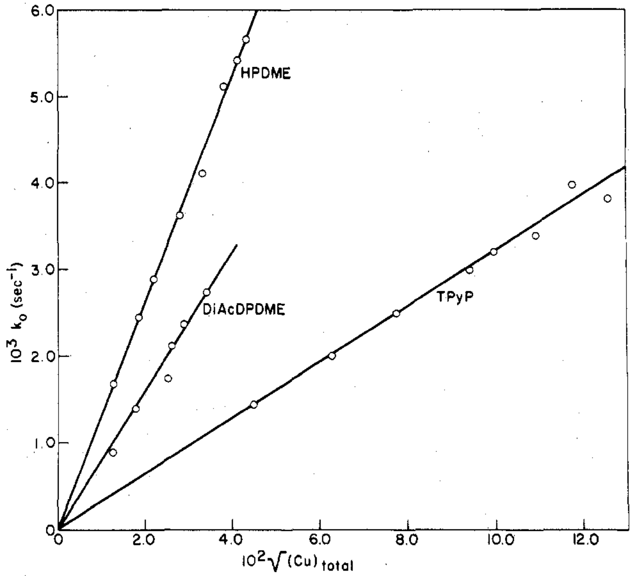

Figure 1. The half-order dependence on total copper acetate concentration of the rate of copper porphyrin formation in acetic acid with three porphyrins.

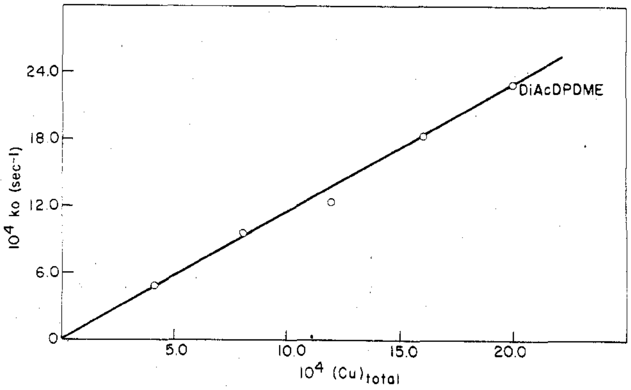

Figure 2. The first-order dependence on total copper acetate concentration of the rate of copper porphyrin formation in acetic acid in the presence of 1.0 *M* lithium acetate.

Etioporphyrin III in acetic acid is predominantly in the form of monocation and diacid species.[10] Copper acetate was found to form a copper porphyrin at a qualitatively similar rate as the other porphyrins studied. In the presence of 0.1 *N* HCl in acetic acid, etioporphyrin shows only a diacid spectrum. Under these conditions, there was no evidence of copper incorporation even after 4 days of observation. Similar results were found for hematoporphyrin.

Discussion

The half-order dependence on copper acetate in the rate law for copper incorporation into porphyrins can be explained as due to the predissociation of the copper dimer, followed by a monomer reacting with the porphyrin

$$\mathrm{Cu_2(OAc)_4} = 2\mathrm{Cu(OAc)_2} \quad K \qquad (2)$$

$$\mathrm{Cu(OAc)_2} + \text{porphyrin} \rightarrow \text{products} \quad k \qquad (3)$$

An equilibrium constant for reaction 2 of 7.4×10^{-5} M^{-1} at 25° estimated from the data of Kochi and Subramanian[5] is too high to fit the observed data. From the results of physical studies on copper acetate solutions, however, others[6,7] have shown that the dimerization equilibrium constant of copper acetate is several orders of magnitude lower than previously thought. This is consistent with our kinetic results. It is possible that in the previous studies[1,3]

---

(4) D. A. Brisbin and R. J. Balahura, *Can. J. Chem.*, **44**, 2157 (1966).

(5) J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, 4, 1527 (1965).

(6) A. T. A. Cheng and R. A. Howard, *Inorg. Chem.*, 7, 2100 (1968).

(7) K. Sawada, H. Ohtakiano, and M. Tanaka, *J. Inorg. Nucl. Chem.*, 34, 625 (1972).

(8) R. Khosropour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

(9) J. Weaver and P. Hambright, *Inorg. Chem.*, 8, 167 (1969).

(10) W. S. Caughey, W. Y. Fujimoto, and B. P. Johnson, *Biochemistry*, 5, 3830 (1966).

Table I. Rates of Zinc Porphyrin Formation as a Function of Porphyrin Type

Compound	$10^3 k_0$,[a,b] $\sec^{-1}$
Mesoporphyrin IX DME[c]	3.46
Deuteroporphyrin DME	2.66
Hematoporphyrin DME	2.20
Protoporphyrin DME	3.01
Dibromodeuteroporphyrin DME	3.85
Porphine	1.92
Etioporphyrin III	3.01
Uroporphyrin I OME[d]	2.77
Tetraphenylporphine	6.65
p-OCH_3, TPP[e]	10.2
p-CH_3, TPP	5.54
p-Cl, TPP	9.49

[a] Concentration of $ZnCl_2$ is 7.44×10^{-2} *F*. [b] Solvent is 11% water in pyridine, 55.4°. [c] DME is dimethyl ester. [d] OME is octamethyl ester. [e] *p*-Methoxy derivative of tetraphenylporphine.

of copper acetate incorporation, data were not taken over a wide enough range, and this could have led to a mistake in reaction order.

The kinetics of nickel acetate reacting with hematoporphyrin in acetic acid is half order in total nickel.[1] The explanation was that $Ni(OAc)^+$ (from $Ni(OAc)_2$) was the reactant. The observation that monomeric copper acetate produced by the addition of LiOAc to copper dimers shows first-order rate behavior might argue against, for example, $Cu_2(OAc)_3^+$ being a reactant in our system. In related work, the incorporation of copper into TPyP in 8.3% acetic acid, pH 1.92, showed a first-order dependence on total copper. Under these conditions, the copper monomer would be predominant.

The acidity of acetic acid has been used to rank the inherent basicity of porphyrins toward proton acceptance.[10] In this study, the order would be tetrapyridylporphine and diacetyldeuteroporphyrin (primarily PH_2), hematoporphyrin (primarily PH_2 and PH_3^+), and etioporphyrin (PH_2, PH_3^+ and PH_4^{2+}). The observation that all of the porphyrins incorporate copper, except when the porphyrin is almost exclusively in the diacid form with HCl, suggests that the diacid is extremely unreactive compared to the free base and monocation porphyrins. Since the hydrogen ion concentration is by necessity constant in this study, the reactions of monomeric copper with either the monocation or the free base porphyrin, or both, give the same empirical rate law. In aqueous solution, however, only the free base has shown appreciable reactivity.[3,9]

Along similar lines, Table I is a list of rate constants found for zinc incorporation into 12 porphyrins in a mixed pyridine–water solvent. All of the porphyrins are in the free base form. While explored in detail with mesoporphyrin,[8] the rates are assumed to be half order in total zinc. Figure 3 is a linear plot of $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ for three of these reactions, and this suggests that a common mechanism may be followed. The isokinetic temperature is 160°, over 100° above the temperature at which the measurements were taken. While a detailed mechanism cannot be postulated, it is quite interesting to note that, regardless of the porphyrin type or basicity, the rates of incorporation are quite similar. In general, it appears that it is the charge on the periphery of the porphyrin, and not the porphyrin basicity with respect to the four central nitrogen atoms, which influences the rate of metal ion incorporation.[11] This is in contrast to the results found for three porphyrins in aqueous solution,[12] and further work is needed to clarify this discrepancy.[13]

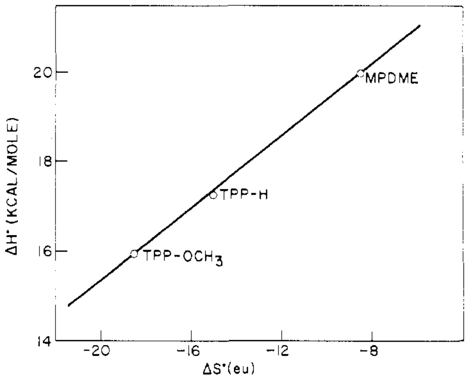

Figure 3. Plot of the activation parameters for three porphyrins for the formation of the zinc porphyrins in a pyridine–water solvent.

Registry No. Mesoporphyrin IX dimethyl ester, 1263-63-4; deuteroporphyrin dimethyl ester, 10589-94-3; hematoporphyrin dimethyl ester, 32562-61-1; protoporphyrin dimethyl ester, 6164-53-0; dibromodeuteroporphyrin dimethyl ester, 14196-91-9; porphine, 101-60-0; etioporphyrin III, 531-16-8; uroporphyrin I octamethyl ester, 10170-03-3; tetraphenylporphine, 917-23-7; tetra-*p*-anisylporphine, 22112-78-3; tetra-*p*-tolylporphine, 14527-51-6; tetrakis(*p*-chlorophenyl)porphine, 22112-77-2; tetrapyridylporphine, 16834-13-2; diacetyldeuteroporphyrin, 7265-15-8; copper, 7440-50-8; zinc, 7440-66-6; acetic acid, 64-19-7.

Acknowledgments. We thank the USAEC, Contract No. AT-(40-1)-4047, and the Gulf Educational Foundation for financial support.

---

[11] P. Hambright, *Coord. Chem. Rev.*, 6, 247 (1971).

[12] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964, p 35.

[13] Note Added in Proof. D. A. Brisbin and G. D. Richards (*Inorg. Chem.*, 11, 2849 (1972)) have recently come to similar conclusions concerning the rate law for copper incorporation in acetic acid. Their observed half-order rate constant for protoporphyrin IX DME is in agreement with our data for similar ligands.

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Kinetics of Tertiary Phosphine Substitution on Di-μ-nitrosyl-decacarbonylruthenium

Jack R. Norton and James P. Collman*

Received June 5, 1972

The kinetics of substitution on mononuclear nitrosylcarbonyl complexes such as $Co(NO)(CO)_3$ and $Fe(NO)_2(CO)_2$ have been the subject of much recent study.[1,2] They display rate laws dominated by terms first order in the entering ligand as well as in the metal complex

$$\text{rate} = [M(NO)_n(CO)_{4-n}][L]$$

In contrast the isoelectronic $Ni(CO)_4$ undergoes substitu-

---

[1] F. Basolo, *Chem. Brit.*, 5, 505 (1969), and references therein.

[2] J. P. Day, D. Diamente, and F. Basolo, *Inorg. Chim. Acta*, 3, 363 (1969).