Contribution from the Department of Chemistry,
Northeastern University, Boston, Massachusetts 02115

Homogeneous Oxidative Coupling Catalysts. Stoichiometry and Kinetics of the Reactions of Two Structurally Distinct (μ-Carbonato)-dicopper(II) Oxidative Coupling Initiators with 2,4,6-Trichlorophenol in Methylene Chloride

GEOFFREY DAVIES,* MOHAMED F. EL-SHAZLY, and MARTIN W. RUPICH

The reaction of (*sym*-μ-carbonato)-dichlorobis(*N,N,N',N'*-tetramethyl-1,3-propanediamine)dicopper(II), (tmpd)CuCl-(CO₃)ClCu(tmpd) (**3**), with 2,4,6-trichlorophenol, TCPH, gives quantitative yields of (tmpd)CuCl(TCP) at molar ratios $[TCPH]_0/[3]_0 = 0.1$–10. Stopped-flow spectrophotometric measurements with excess **3** reveal two easily resolvable kinetic processes. The first step at high $[3]_0$ is postulated to be the formation of the asymmetrical intermediate (tmpd)CuCl-(HCO₃)ClCu(TCP) (**7**), which decomposes spontaneously or decomposes by reaction with **3** in subsequent rate-determining steps. Deviations from simple second-order kinetics are observed at low $[3]_0$. There is no kinetic evidence for reactant preassociation in any of these processes. The corresponding reaction of (*asym*-μ-carbonato)-dichlorobis(*N,N,N',N'*-tetraethylethylenediamine)dicopper(II), (teed)CuCl(CO₃)ClCu(teed) (**4**), with TCPH gives (teed)CuCl(HCO₃,TCP)-ClCu(teed) (**6**) at $[TCHP]_0/[4]_0 = 1.0$ and an equimolar mixture of (teed)CuCl₂ and (teed)Cu(TCP)₂ at $[TCPH]_0/[4]_0 \geq 2$. Stopped-flow kinetic measurements with excess **4** show that **6** is preceded by an intermediate complex that is postulated to be the 1:1 ion pair **9** (formed by protonation of **4** by TCPH) on the basis of the magnitude of its formation constant ($K_4 = 1500 \pm 200$ M⁻¹ between 0 and –23 °C). The product **6** appears to be a symmetrical μ,μ'-(bicarbonate, phenolate)-bridged dimer, which reacts with excess TCPH via a second intermediate ion pair ($K_5 = 500 \pm 100$ M at 0 °C) to give (teed)CuCl₂ and (teed)Cu(TCP)₂. The trans- and cis-chloro ligand configurations of **3** and **4**, respectively, and the different basicities of **3** and **4** are apparently responsible for the different stoichiometries and kinetic patterns observed. The possible effects of these differences on the mechanisms of phenolic oxidative coupling reactions initiated by (μ-carbonato)-dicopper(II) complexes are discussed briefly.

Introduction

The discovery[1] of high molecular weight polymeric products **1** from the copper-catalyzed aprotic oxidative coupling of
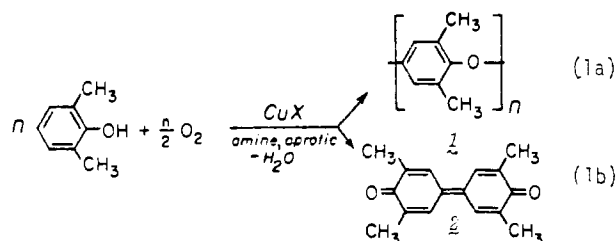
2,6-dimethylphenol by dioxygen in pyridine, reaction 1a, has led to the development of several commercial engineering thermoplastics with outstanding chemical, mechanical, and thermal properties.[2] Polymers prepared from various substituted phenols may be modified through metallation[3] and other processing to yield block and copolymeric[4] materials with many useful applications.[2] Detailed studies have established the mechanism of polymer growth[5] and general reaction conditions (solvent, temperature, monomer, etc.) that affect the relative proportions of the alternative products in reactions analogous to (1).[6]

Substituted phenols are stoichiometrically oxidized by Ag₂O[7] and alkaline ferricyanide[8] to free radicals, which react with dioxygen to give peroxides. By contrast, reactions 1a and 1b are *catalyzed* by copper complexes, the majority of systems[6] employing the products of oxidation of copper(I) salts and complexes by dioxygen as initiators in the presence of pyridine and alkylamines.[9,10] The actual initiator in pyridine is the polymeric, basic μ-oxo complex ((py)ₘCuO)ₙ.[11] In the presence of methanol and pyridine, the reaction of copper(I) chloride with dioxygen produces the initiator (py)₂Cu₂-(OMe)₂Cl₂,[12,13] whose structure is known.[14] This latter complex reacts with 2,6-dimethylphenol to produce monophenolate complexes that decompose to the products of reaction 1 in the absence of dioxygen, clearly establishing the role of dioxygen as an oxidizing agent for copper(I) in completing the catalytic cycle.[2] Studies with other substituted phenols support this view by showing that the rates of oxidation of phenols decrease with increasing oxidation potential.[15] Careful work under strictly anaerobic conditions confirms that oxocopper(II) species will also directly oxidize catechols and benzoquinones.[13]

The primary products of oxidation of excess copper(I) by dioxygen in the aprotic solvents used for oxidative coupling processes are μ-oxo copper(II) species.[11] The rates of oxidation, structures, and properties of the products depend on the

(1) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6335 (1959).
(2) A. S. Hay, P. Shenian, A. C. Gowan, P. F. Erhardt, W. R. Haaf, and J. E. Theberge, *Encycl. Polym. Sci. Technol.*, **10**, 92 (1969); H. L. Finkbeiner, A. S. Hay, and D. M. White, "Polymerizations by Oxidative Coupling" in "Polymerization Processes", C. E. Schildknecht and I. Skeist, Eds., Wiley-Interscience, New York, 1977, p 537.
(3) A. J. Chalk and A. S. Hay, *J. Polym. Sci., Polym. Chem. Ed.*, **7**, 691 (1969).
(4) G. D. Cooper, J. G. Bennett, Jr., and A. Katchman, *Adv. Chem. Ser.*, No. 99, 431 (1971); G. D. Cooper, J. G. Bennett, Jr., and A. Factor, *ibid.*, No. 128, 230 (1973).
(5) D. M. White, *J. Org. Chem.*, **34**, 297 (1969).
(6) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963); G. F. Endres and J. Kwiatek, *J. Polym. Sci.*, **58**, 593 (1962); D. A. Bolon, *J. Am. Chem. Soc.*, **88**, 3148 (1966); A. S. Hay, *J. Org. Chem.*, **34**, 1160 (1969); *Macromolecules*, **2**, 107 (1969); D. M. White and H. J. Klopfer, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 1565 (1972); S. Tsuruya, K. Nakamae, and T. Yonezawa, *J. Catal.* **44**, 40 (1976); S. Tsuruya, T. Shirai, T. Kawamura, and T. Yonezawa, *Makromol. Chem.*, **132**, 57 (1970); H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).
(7) H. S. Blanchard, *J. Org. Chem.*, **25**, 264 (1960).
(8) D. A. Bolon, *J. Am. Chem. Soc.*, **88**, 3148 (1966).
(9) A. S. Hay, *Adv. Polym. Sci.*, **4**, 496 (1967); A. S. Hay and D. M. White, *Polym. Prepn., Am. Chem. Soc., Div. Polym. Sci.*, **10**, 92 (1969); A. S. Hay, *Macromolecules*, **2**, 107 (1969); J. G. Bennett, Jr., and G. D. Cooper, *ibid.*, **3**, 101 (1970).
(10) D. M. White and H. J. Klopfer, *J. Polym. Sci., Polym. Chem. Ed.*, **8**, 1427 (1970); **10**, 1565 (1972); A. J. Chalk and A. S. Hay, *ibid.*, **7**, 691 (1969); G. D. Cooper and D. E. Floryan, German Offen. 2 754 887 (1978).
(11) I. Bodek and G. Davies, *Inorg. Chem.*, **17**, 1814 (1978); *Inorg. Chim. Acta*, **27**, 213 (1978).
(12) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.*, **50**, 469 (1962); H. S. Blanchard, H. L. Finkbeiner, and G. F. Endres, *SPE Trans.*, **2**, 110 (1962).
(13) M. M. Rogić and T. R. Demmin, *J. Am. Chem. Soc.*, **100**, 5472 (1978).
(14) R. D. Willett, unpublished structure quoted in ref 13.
(15) H. S. Blanchard, H. L. Finkbeiner, and G. A. Russell, *J. Polym. Sci.*, **50**, 469 (1962).

structure of the copper(I) starting material and the ligand environment.[16] Examples of characterized initiator products are the series $L_3Cu_4X_4O_2$ (L = dimethylacetamide, dimethyl sulfoxide or N-methyl-2-pyrrolidinone (nmp))[16,17] and the crystalline derivative $(nmp)_3Cu_4Cl_6O(OH_2)\cdot nmp$,[18] prepared by the relatively slow oxidation of slurries of copper(I) halides by dioxygen in the respective neat ligands. Much faster oxidations of soluble LCuX,XCuL complexes (L = alkyldiamine) by dioxygen in methylene chloride or nitrobenzene produce polymeric μ-oxo copper(II) species, which react with carbon dioxide to provide a large series of (μ-carbonato)-dicopper(II) initiator complexes, $LCuX(CO_3)XCuL$.[19,20] In the absence of added ligands, the latter complexes are highly specific initiators for reaction 1b.[20]

The inner-sphere, aprotic oxidation of copper(I) by dioxygen gives oxo copper(II) centers that deprotonate, coordinate, and oxidize phenols.[2,13,21] The resulting copper(I) species can be expected to release oxidation products and coordinated water or hydroxide[21,22] to complete the catalytic cycle. If the copper(I)–dioxygen reaction is not rate determining, then the efficiency and specificity of initiation depend on the mechanism of interaction between the oxo copper(II) center and the phenol.[23]

Kinetic studies with structurally characterized reactants will provide a better understanding of the origin of efficiency and specificity in aprotic, copper-catalyzed oxidative coupling processes. Of particular interest is the origin of the different product distributions observed in reaction 1.[6] This paper reports the stoichiometry and kinetics of the reactions of 2,4,6-trichlorophenol, TCPH, with two structurally distinct (μ-carbonato)-dicopper(II) oxidative coupling initiators. The phenol reactant was chosen to allow mechanisms of complex formation to be investigated in the absence of electron transfer.[24] The structures of the copper(II) reactants differ significantly: $(tmpd)CuCl(CO_3)ClCu(tmpd)$ (**3**) (tmpd = N,N,N',N'-tetramethyl-1,3-propanediamine) contains a symmetrical μ-carbonato bridge and trans-chloro ligands,[19] while $(teed)CuCl(CO_3)ClCu(teed)$ (**4**) (teed = N,N,N',N'-tetraethylethylenediamine) contains a cis-chloro arrangement disposed about an asymmetrical μ-carbonato bridge.[20] These structural differences are reflected in distinct stoichiometries and kinetic patterns for reactions with TCPH.

Experimental Section

Materials. The (μ-carbonato)-dicopper(II) reactants **3** and **4** were synthesized as previously described.[19,20] TCPH (Aldrich) was distilled under vacuum. The O-deuterated phenol TCPD was prepared by reaction of TCPH with excess D_2O in anhydrous acetonitrile. Complete deuteration was verified by the absence of ^{1}H NMR resonance in the 2–6 τ region.[25] Methylene chloride (Aldrich or Burdick and Jackson) was washed with concentrated H_2SO_4, dried with $CaCl_2$, refluxed over and then fractionally distilled from phosphorus(V) oxide, and stored in the dark over anhydrous sodium carbonate. The
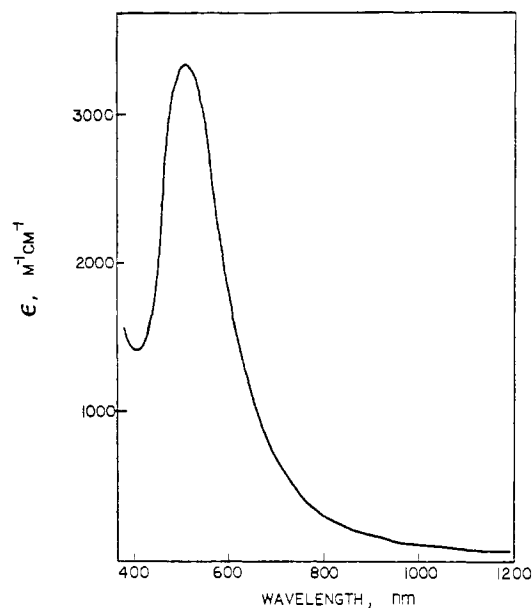
(16) G. Davies, M. F. El-Shazly, D. R. Kozlowski, C. E. Kramer, M. W. Rupich, and R. W. Slaven, *Adv. Chem. Ser.*, No. **173**, 178 (1979).
(17) M. W. Rupich, Doctoral Dissertation, Northeastern University, 1980.
(18) G. Davies, M. F. El-Shazly, M. W. Rupich, M. R. Churchill, and F. J. Rotella, *J. Chem. Soc., Chem. Commun.*, 1045 (1978); M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, **18**, 853 (1979).
(19) M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, M. W. Rupich, and K. O. Watkins, *Inorg. Chem.*, **18**, 2296 (1979).
(20) M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, and M. W. Rupich, *Inorg. Chem.*, **19**, 201 (1980).
(21) E. Tsuchida, M. Kaneko, and H. Nishide, *Makromol. Chem.*, **15**, 235 (1972).
(22) G. Davies, R. Higgins, and D. J. Loose, *Inorg. Chem.*, **15**, 700 (1976).
(23) D. M. White and H. J. Klopfer, *J. Polym. Sci., Polym. Chem. Ed.*, **10**, 1565 (1972).
(24) J. F. Harrod, *Can. J. Chem.*, **47**, 637 (1969).
(25) J. R. Deyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, Chapter 4.

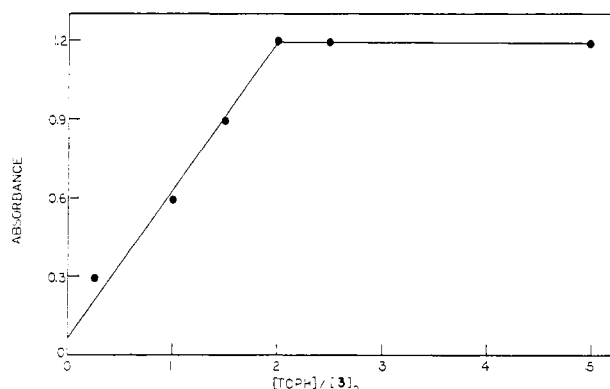**Figure 1.** Electronic spectrum of $(teed)Cu(TCP)_2$ at 25 °C in methylene chloride.

Figure 2. Spectrophotometric titration at 525 nm of $(tmpd)CuCl(CO_3)ClCu(tmpd)$ (0.5 mM) with TCPH at 25 °C in methylene chloride.
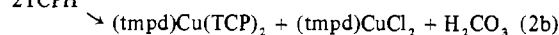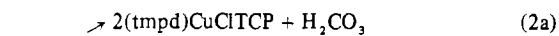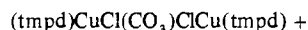
phenoxocopper(II) complexes $LCu(TCP)_2$ (L = tmpd or teed) were prepared by literature methods.[24] The room-temperature electronic spectrum of $(teed)Cu(TCP)_2$ in methylene chloride is shown in Figure 1.

Spectral and Kinetic Measurements. All electronic solution spectral and stoichiometric determinations were obtained with Cary Model 14 or Beckman DK-1A spectrophotometers and matched quartz cells. Kinetic measurements were made with a Nortech SF-3A stopped-flow apparatus (1-mm path length). Temperature was controlled from −23.0 to 24 °C (±0.2 °C) with Neslab refrigeration units and the Nortech control system. Kinetic data were acquired and processed by our local on-line PDP 11/20 computer interface.[11] All kinetic runs were performed with one reactant in sufficient excess to ensure pseudo-first-order conditions. First-order rate constants, k_{obsd}, were derived from linear least-squares plots of $\ln{(A_\infty - A_t)}$ vs. time, where A_∞ and A_t are absorbances at "infinite" time and time t, respectively, measured between 480 and 550 nm.
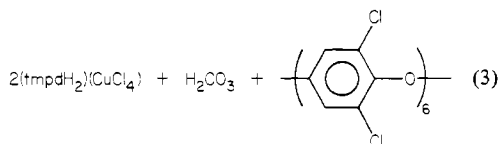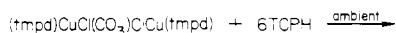
Results and Discussion

Stoichiometry. Reaction with 3. The result of a typical spectrophotometric titration of **3** with TCPH is shown in Figure 2. These data indicate a reaction stoichiometry of $\Delta[TCPH]/\Delta[3] = 2.0$. Chemical and IR spectral[20] examinations of the solids obtained by evaporating methylene chloride solutions containing stoichiometric amounts of **3** and TCPH to dryness under vacuum gave no evidence for the presence of carbonate. Reaction 2a or 2b could account for these observations. Mixtures of $(tmpd)Cu(TCP)_2$ and
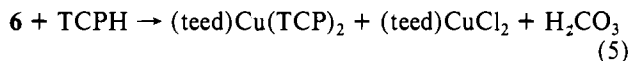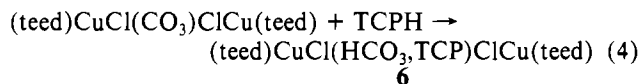
(tmpd)CuCl(CO$_3$)ClCu(tmpd) +

$$\underset{2TCPH}{\overset{\nearrow\;\; 2(tmpd)CuClTCP + H_2CO_3 \qquad\qquad (2a)}{\underset{\searrow\;\; (tmpd)Cu(TCP)_2 + (tmpd)CuCl_2 + H_2CO_3 \;\; (2b)}{}}}$$

(tmpd)CuCl$_2$ can easily be separated by gel permeation chromatography[11] on BioBeads SX-12 resin with methylene chloride as eluant. Chromatography of product solutions obtained by mixing stoichiometric amounts of **3** and TCPH in methylene chloride gave no evidence for the formation of (tmpd)Cu(TCP)$_2$ or (tmpd)CuCl$_2$; only one purple band eluted from the column, and its spectrum (Figure 3) was distinctly different from that of (tmpd)Cu(TCP)$_2$ (λ_{max} = 500 nm, ϵ = 2700 M^{-1} cm^{-1}).[24] A Job plot of spectrophotometric data at 525 nm confirmed the formation of a single (phenolato)copper(II) product under all conditions. We conclude that eq 2a accounts for the reaction of **3** with TCPH. The complex **3** reacts with excess TCPH in methylene chloride (2–3 h) or acetonitrile (5–10 min) at room temperature to precipitate yellow (tmpdH$_2$)(CuCl$_4$). Anal. Calcd: Cu, 18.82; Cl, 42.00; C, 24.90; N, 8.30; H, 6.05. Found: Cu, 18.69; Cl, 41.88; C, 24.98; N, 8.06; H, 6.15. The complete stoichiometry for reaction with excess TCPH is given in eq 3. Similar reactions have been reported for other copper(II) halophenolate complexes.[24]

(tmpd)CuCl(CO$_3$)ClCu(tmpd) + 6TCPH $\xrightarrow{\;ambient\;}$

2(tmpdH$_2$)(CuCl$_4$) + H$_2$CO$_3$ + $\left[\!\!\begin{array}{c}\text{Cl}\\ \text{\Large(}\bigcirc\text{\Large)}\!-\!O\\ \text{Cl}\end{array}\!\!\right]_6$ (3)

Reaction with 4. The reaction of **4** with TCPH in methylene chloride at a 1:1 molar reactant ratio produces a violet solution whose spectrum is shown in Figure 4. Gel permeation chromatography indicated the formation of a single reaction product, which on isolation gave a positive test for carbonate. This hygroscopic product, **6**, of stoichiometric formula (teed)$_2$Cu$_2$Cl$_2$(TCP)(HCO$_3$), is stable in methylene chloride for at least 1 week, but all attempts to obtain single crystals have been unsuccessful. With [TCPH]/[4] $\geq$ 2 in methylene chloride, a different product spectrum was obtained (Figure 4). The spectrum corresponds to the formation of equimolar proportions of violet (teed)Cu(TCP)$_2$ (Figure 1)[24] and green (teed)CuCl$_2$, (λ_{max} = 700 nm),[26] which are easily separable by gel permeation chromatography.[11] The reaction stoichiometries are summarized in eq 4 and 5. The formulation of the product of reaction 4 is discussed below.

(teed)CuCl(CO$_3$)ClCu(teed) + TCPH $\rightarrow$

(teed)CuCl(HCO$_3$,TCP)ClCu(teed) (4)
6

6 + TCPH $\rightarrow$ (teed)Cu(TCP)$_2$ + (teed)CuCl$_2$ + H$_2$CO$_3$ (5)

Kinetics. Reproducible kinetic data could only be obtained with freshly purified methylene chloride. With this precaution, crystalline and powdered samples of **3** or **4** gave identical kinetic results with TCPH and TCPD. However, distinctly different kinetic dependences were observed for the two copper reactants, as follows.

Reaction of 3 with TCPH. A kinetically unresolvable series of absorbance changes was observed on mixing **3** with excess TCPH in the stopped-flow apparatus. However, with **3** in

(26) I. Bertini and F. Mani, *Inorg. Chem.*, **6**, 2032 (1967).
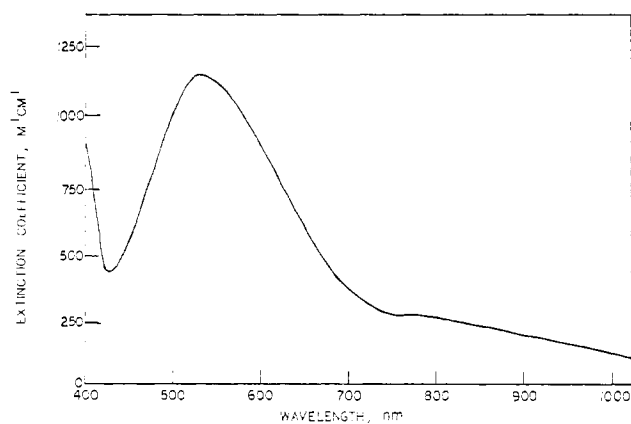
Figure 3. Electronic spectrum of (tmpd)CuCl(TCP) at 25 °C in methylene chloride.
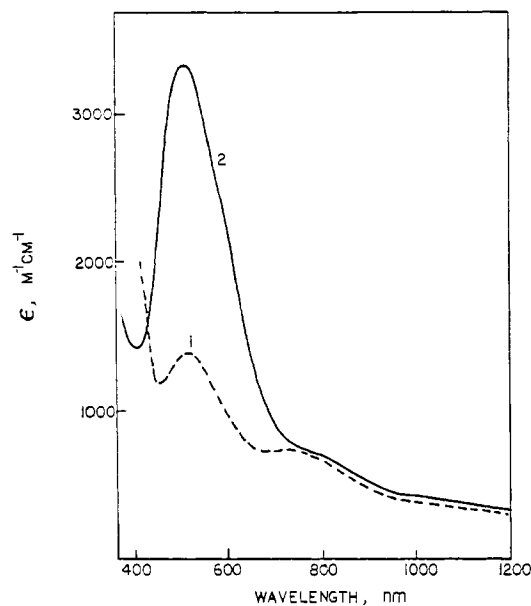
Figure 4. Electronic spectra of products of the reaction between (teed)CuCl(CO$_3$)CuCl(teed) (**4**) and TCPH at 25 °C in methylene chloride: 1, [TCPH]$_0$/[4]$_0$ = 1; 2, [TCPH]$_0$/[4]$_0$ = 2.

Figure 5. Plots of k_{obsd} vs. [**3**] for the rapid reaction of TCPH with excess **3** at the following temperatures: O, −8.0 °C; ●, 0.0 °C; □, 9.5 °C.

Table I. Kinetic Data for the First Reaction of (tmpd)CuCl(CO$_3$)ClCu(tmpd) with TCPH

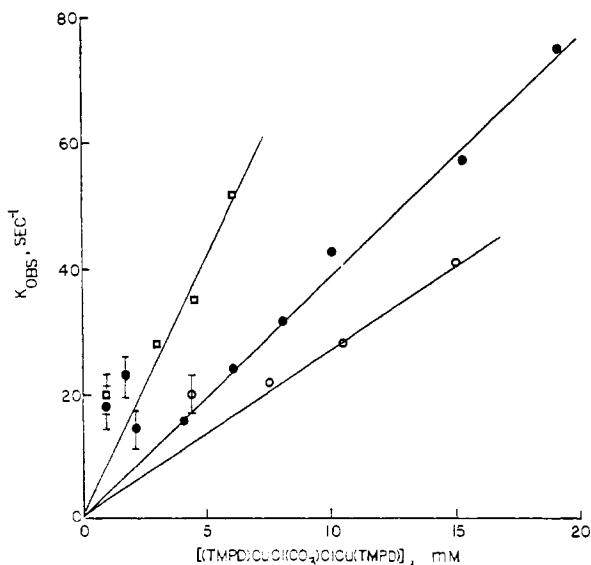| T, °C	[TCPH], mM	[(tmpd)CuCl(CO$_3$)-ClCu(tmpd)], mM	$k_{obsd}{}^{a,b}$	$k_{calcd}{}^{b,c}$
−8.0	0.16	4.5	20^d	12
		7.5	22^d	21
		10.5	28.0 ± 2.0	29
		15.0	41.0 ± 3.0	40
0.0	0.16	1.0	18^d	4.0
		1.7	23^d	6.8
		2.0	14^d	8.0
		4.0	16.2 ± 0.6	17.0
		6.1	24.5 ± 0.7	25.0
		6.1^e	24.1 ± 0.5	25.0
		8.0	31.9 ± 0.4	32.1
		10.0	43.4 ± 0.8	39.7
		10.0^e	42.1 ± 0.6	39.7
		15.3	57.0 ± 2.0	59.5
		19.1	75.0 ± 5.0	73.9
	0.08	1.0	14^d	4
		1.7	22^d	7
		6.1	24.0 ± 1.0	25
	0.12	6.1	22.0 ± 3.0	25
	0.20	6.1	25.0 ± 1.0	25
	0.32	1.0	23^d	4
		1.7	28^d	7
9.5	0.16	1.0	20^d	4
		3.0	28.0 ± 2.0	26
		4.5	35.0 ± 3.0	38
		6.0	52.0 ± 5.0	50

^{a} Average of four or more runs. ^{b} Units are s^{-1}. ^{c} Calculated for eq 6 by using a nonlinear least-squares program. ^{d} Rate constants were reproducible to only ±20%. ^{e} Deuterated trichlorophenol.

pseudo-first-order excess, two easily resolved first-order processes were observed. The kinetic data for the first process are collected in Table I and illustrated in Figure 5. With [3]$_0$ >> [TCPH]$_0$, the first process has all the properties expected for an irreversible, second-order process at each temperature: the total observed absorbance change, ΔA, is independent of [3]$_0$, the pseudo-first-order rate constant, k_{obsd}, is proportional to [3]$_0$, and k_{obsd} extrapolates through the origin of Figure 5 at [3]$_0$ = 0. At lower copper concentrations ΔA decreases abruptly at a particular copper concentration at each temperature, signaling the appearance of a change of mechanism and primary products. Below this limit $\Delta A \lesssim 0.001$ and the anomalously high rate constants are essentially independent of [3]$_0$ and temperature (Figure 5) but increase slightly with [TCPH]$_0$ even under pseudo-first-order conditions (Table I). The rate constants obtained from such small ΔA values are too imprecise (±20%) to allow a detailed kinetic investigation of this "low [3]$_0$" phenomenon with our equipment. Spectral examinations of the separate reactants under identical conditions provide no indications of its origin. We emphasize that, at high [3]$_0$, the first observable process is first-order in [3]$_0$ and [TCPH] and that the deviations observed at low [3]$_0$ do not affect our observations on the slower subsequent reactions (see data in Table II).

The linear dependence of k_{obsd} on [3]$_0$ at [3]$_0 \gtrsim 3 \times 10^{-3}$ M is ascribed to reaction 6, in which the intermediate product

$$3 + TCPH \xrightarrow{k_1} (tmpd)CuCl(HCO_3)ClCu(tmpd)(TCP)$$
$$\mathbf{7}$$
$$(6)$$
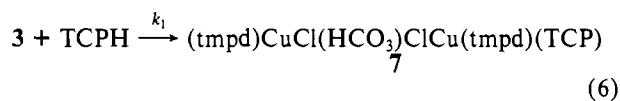
7 has TCP$^-$ coordinated to one of the copper centers (see below).

The observed rate constant for the second, slower reaction of **7** with excess **3** obeys eq 7. Kinetic data are given in Table

$$k_{obsd} = k_2 + k_3[3] \tag{7}$$

Table II. Kinetic Data for the Second Reaction of (tmpd)CuCl(CO$_3$)ClCu(tmpd) with TCPH

T, °C	[TCPH], mM	[(tmpd)CuCl(CO$_3$)-ClCu(tmpd)], mM	$k_{obsd}{}^{a,b}$	$k_{calcd}{}^{b,c}$
15.0	0.16	0.30	0.010 ± 0.001	0.013
		0.75	0.020 ± 0.001	0.020
		0.82	0.023 ± 0.004	0.021
		1.00	0.028 ± 0.003	0.023
		1.50	0.031 ± 0.001	0.030
		1.67	0.033 ± 0.002	0.033
		2.00	0.038 ± 0.004	0.037
		3.00	0.047 ± 0.006	0.051
		4.00	0.062 ± 0.007	0.065
		7.90	0.126 ± 0.003	0.120
		10.50	0.146 ± 0.002	0.156
		14.60	0.220 ± 0.007	0.214
	0.10	2.00	0.037 ± 0.003	0.037
		4.00	0.067 ± 0.005	0.065
19.5	0.16	2.00	0.069 ± 0.002	0.069
		3.20	0.095 ± 0.006	0.096
		8.00	0.204 ± 0.005	0.203
24.0	0.16	2.00	0.19 ± 0.01	0.18
		3.20	0.25 ± 0.01	0.24
		8.00	0.48 ± 0.02	0.48

^{a} Average of four or more runs. ^{b} Units are s^{-1}. ^{c} Calculated from eq 7 by using a nonlinear least-squares program.

Table III. Rate Constants and Activation Parameters for the Reaction of (tmpd)CuCl(CO$_3$)ClCu(tmpd) with TCPH^a

T, °C	$k_1{}^b$	$k_2{}^c$	$k_3{}^b$
−8.0	2550 ± 300		
0.0	3770 ± 200		
9.5	8000 ± 1900		
15.0		0.011 ± 0.002	14.0 ± 0.3
19.5		0.028 ± 0.001	22.4 ± 0.1
24.0		0.095 ± 0.008	49.5 ± 1.5
$\Delta H^{\ddagger\,d}$	9200 ± 1500	39 000 ± 4000	23 000 ± 4000
$\Delta S^{\ddagger\,e}$	−8 ± 5	69 ± 13	27 ± 13

^{a} Calculated by using a nonlinear least-squares program. ^{b} Units are M^{-1} s^{-1}. ^{c} Units are s^{-1}. ^{d} Units are cal mol^{-1}. ^{e} Units are cal deg^{-1} mol^{-1}.
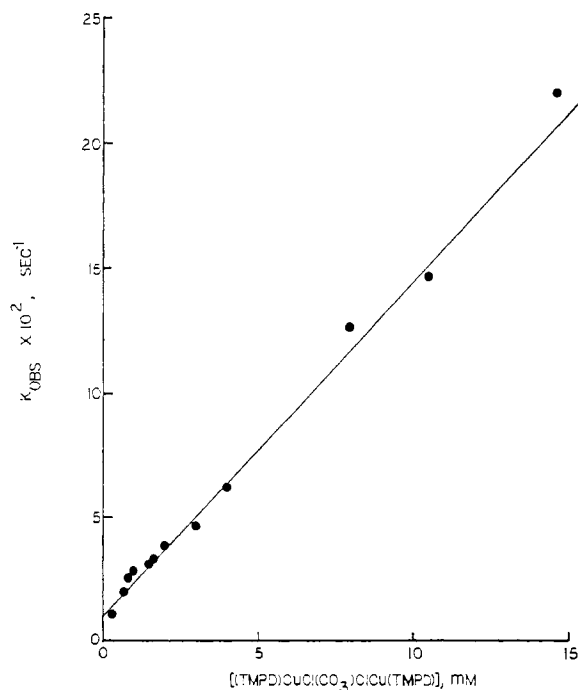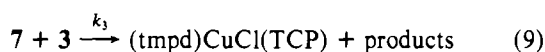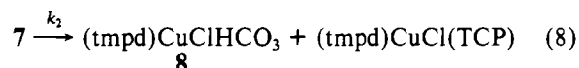

Figure 6. Plot of k_{obsd} vs. [3] for the reaction of (tmpd)CuCl-(HCO$_3$)ClCu(tmpd)(TCP), **7**, with excess **3**.

Table IV. Kinetic Data for the Reaction of (teed)CuCl(CO$_3$)ClCu(teed) with TCPH

T, °C	[TCPH], mM	[(teed)CuCl(CO$_3$)-ClCu(teed)], mM	$k_{obsd}^{a,b}$	$k_{calcd}^{b,c}$
-23.0	0.16	0.8	6.0 ± 0.4	5.5
		1.2	7.0 ± 0.3	6.5
		2.4	8.5 ± 0.4	7.9
		4.0	9.3 ± 0.3	8.6
-11.2	0.16	0.9	10.1 ± 0.6	11.5
		1.3	13.6 ± 0.3	13.2
		4.8	17.4 ± 0.4	17.6
		8.0	17.7 ± 0.5	18.4
0.0	0.16	0.75	20.4 ± 0.4	21.1
		1.0	22.5 ± 0.3	24.0
		1.5	29.1 ± 0.5	27.7
		2.0	30.5 ± 0.9	30.0
		3.0	31.9 ± 0.7	32.7
		4.0^d	33.1 ± 0.2	34.2
		4.0	33.2 ± 0.6	34.2
		6.0	35.2 ± 0.5	35.9
		8.0^d	35.1 ± 0.5	36.8
		8.0	35.4 ± 0.6	36.8
		10.0	34.8 ± 1.0	37.4
		12.0	35.8 ± 0.6	37.8
	0.10	3.0	30.8 ± 0.5	32.7
		6.0	34.9 ± 0.8	35.9

^{a} Average of four or more runs. ^{b} Units are s^{-1}. ^{c} Calculated from eq 10 by using a nonlinear least-squares program. ^{d} Deuterated trichlorophenol.

II. Equation 7 is consistent with the mechanism shown by eq 8 and 9. The spontaneous decomposition of **7**, eq 8, is rep-
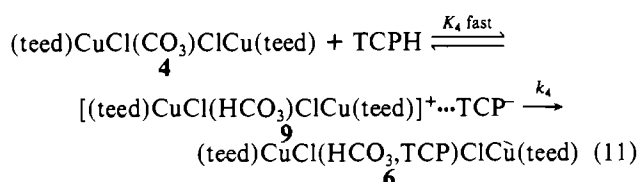
$$7 \xrightarrow{k_2} (\text{tmpd})\text{CuClHCO}_3 + (\text{tmpd})\text{CuCl(TCP)} \quad (8)$$
$$\mathbf{8}$$

$$7 + 3 \xrightarrow{k_3} (\text{tmpd})\text{CuCl(TCP)} + \text{products} \quad (9)$$

resented by the intercept in Figure 6. **7** also reacts with excess **3**, at a rate determined by k_3, also to give (tmpd)CuCl(TCP), which dominates the absorbance change to such an extent that the other products of eq 8 and 9 cannot be identified. Rate constants and activation parameters for reactions 6, 8, and 9 collected in Table III have been used to make comparisons of observed and calculated pseudo-first-order rate constants in Tables I and II. The deviations in reaction 6 at low [3]$_0$ are apparent in Table I.

Reaction of 4 with TCPH. Kinetic measurements with [TCPH]$_0$ >> [4]$_0$ indicated a series of processes that could not be resolved in the 480–550-nm region. However, linear pseudo-first-order plots were obtained with [4] >> [TCPH]$_0$. Kinetic data at temperatures between 0 and –23 °C are collected in Table IV. At fixed temperature and [4]$_0$, derived first-order rate constants, k_{obsd}, were independent of [TCPH]$_0$ and monitoring wavelength. Studies at various excess concentrations [4]$_0$ showed that k_{obsd} is given by

$$k_{obsd} = \frac{A[4]}{1 + B[4]} \quad (10)$$

consistent with the following mechanism for reaction 4:

$$(\text{teed})\text{CuCl(CO}_3)\text{ClCu(teed)} + \text{TCPH} \underset{}{\overset{K_4 \text{ fast}}{\rightleftharpoons}}$$
$$\mathbf{4}$$
$$[(\text{teed})\text{CuCl(HCO}_3)\text{ClCu(teed)}]^+ \cdots \text{TCP}^- \xrightarrow{k_4}$$
$$\mathbf{9}$$
$$(\text{teed})\text{CuCl(HCO}_3,\text{TCP})\text{ClCu(teed)} \quad (11)$$
$$\mathbf{6}$$

This mechanism predicts that $A = k_4 K_4$ and $B = K_4$ in eq 10. Estimates of k_4, K_4, and their thermodynamic parameters, obtained from a nonlinear least-squares fit of the data in Table

**Table V.** Rate Constants and Thermodynamic Parameters for Reactions of (teed)CuCl(CO$_3$)ClCu(teed) and **6** with TCPH^a

T, °C	$K_4{}^b$	$k_4{}^c$	$K_5{}^b$	$k_5{}^c$
-23.0	1450 ± 200	10.1 ± 0.4		
-11.8			740 ± 100	10.0 ± 0.3
-11.2	1500 ± 200	20.0 ± 0.7		
0.0	1500 ± 200	39.9 ± 0.6	500 ± 100	29.9 ± 0.5
ΔH^d	0			
ΔS^e	-45 ± 5			
$\Delta H^{\ddagger\,d}$		6500 ± 2800		
$\Delta S^{\ddagger\,e}$		28 ± 10		

^{a} All estimates were made with nonlinear least-squares computer fits of data to appropriate equations with temperature as an independent variable.[11] ^{b} Units are M^{-1}. ^{c} Units are s^{-1}. ^{d} Units are cal mol^{-1}. ^{e} Units are cal deg^{-1} mol^{-1} at 25.0 °C.

Table VI. Kinetic Data for the Reaction of (teed)CuCl(HCO$_3$,TCP)ClCu(teed) (6) with TCPH

T, °C	[6], mM	[TCPH], mM	$k_{obsd}^{a,b}$	$k_{calcd}^{b,c}$
-11.8	0.20	0.4	2.3 ± 0.1	2.2
		1.2	4.5 ± 0.2	4.6
		2.0	6.0 ± 0.1	5.9
		4.0	7.6 ± 0.3	7.4
0.0	0.20	0.4	4.7 ± 0.1	4.8
		0.8	8.9 ± 0.2	8.2
		2.0	12.1 ± 0.4	14.3
		2.0^d	12.3 ± 0.3	14.3
		4.0	15.4 ± 1.0	19.1
		8.0	25.0 ± 2.0	23.0
	0.10	2.0	13.0 ± 1.0	14.3
		4.0	17.0 ± 2.0	19.1

^{a} Average of four or more runs. ^{b} Units are s^{-1}. ^{c} Calculated from eq 12 by using a nonlinear least-squares program. ^{d} Deuterated trichlorophenol.
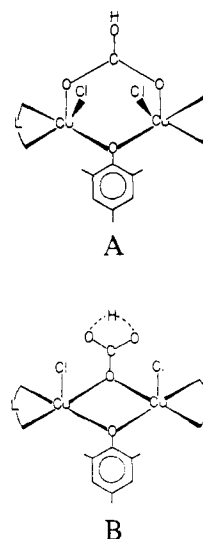
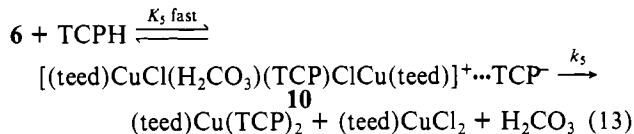**Figure 7.** Possible symmetrical structures for **6**.

IV to eq 10, are given in Table V. Observed and calculated rate constants from the computer fit are compared in Table IV.

The equilibrium constant K_4 is of similar magnitude to those for formation of M$^+$,X$^-$ ion pairs in methylene chloride[27] and supports the formulation of **9** as an ion pair generated by very fast proton transfer from TCPH to **4**. (Proton transfer cannot be rate determining, since deuteration of TCPH has no effect on the kinetic results.)

(27) S. Balt and D. Algra, *Inorg. Chem.*, **20**, 1102 (1981).

Reaction of 6 with TCPH. Data for reaction of **6** with excess TCPH are collected in Table VI. Phenol deuteration had no discernible effect on the results. Rate saturation with increasing excess [TCPH]$_0$ was found to obey eq 12. This

$$k_{obsd} = \frac{C[TCPH]_0}{1 + D[TCPH]_0} \quad (12)$$

empirical relationship is consistent with the mechanism shown in eq 13 with $C = k_5 K_5$ and $D = K_5$ in eq 12. Estimates of

$$6 + TCPH \underset{}{\overset{K_5 \, fast}{\rightleftharpoons}}$$

$$[(teed)CuCl(H_2CO_3)(TCP)ClCu(teed)]^+ \cdots TCP^- \overset{k_5}{\longrightarrow}$$
$$\underset{\textbf{10}}{}$$
$$(teed)Cu(TCP)_2 + (teed)CuCl_2 + H_2CO_3 \quad (13)$$

k_5, K_5, and their thermodynamic parameters from a nonlinear least-squares fit of the data to eq 12 are collected in Table V, and a comparison of observed and calculated rate constants is made in Table VI. The magnitude[27] of K_5 again suggests the formulation of **10** as an ion pair, formed by proton transfer from TCPH to **6**, with which it is in very rapid equilibrium. The first-order conversion of **10** to final products, with rate constant k_5, is postulated to be rate determining. Kinetic measurements for reaction of TCPH with excess **6** gave a series of rapid absorbance changes that could not be resolved, possibly due to reaction of **6** with H_2CO_3 generated in reaction 13.

Likely Origins of the Different Stoichiometric and Kinetic Behavior Observed for 3 and 4. Strong (phenolato)copper(II) complexes are formed in the rapid reactions of **3** and **4** with TCPH in methylene chloride. The essential structural differences between **3** and **4** that appear to be responsible for the

3   **4**
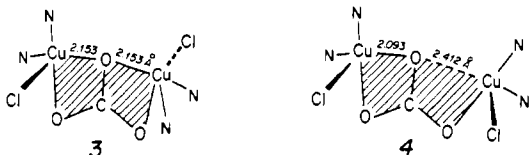
very different stoichiometries and kinetic patterns observed are given schematically below (see ref 19 and 20 for complete structural details). The lack of evidence for a significant rapid preequilibrium in reaction of **3** with TCPH (eq 6) stands in sharp contrast to indications of 1:1 ion pairing[27] in the corresponding reaction of **4** with TCPH (eq 11). We estimate that the equilibrium constant corresponding to the formation of the analogue of **9** (eq 11) in reaction 6 is less than 5 M^{-1} at -8 °C, to be compared with $K_4 \approx 1500$ M^{-1} at the same temperature. Since the equilibrium constant for ion-pair formation would be directly related to differences in basicities of **3**, **4**, and TCP$^-$, we may conclude that **4** is considerably more basic than **3**.[28] Another factor that can affect the strength of ion-pair interactions is the distance between the charge centers.[29] The bulky o-chloro substituents of TCP$^-$ are expected to interact sterically with ligands at the copper centers; **4** contains N-ethyl groups while **3** has N-methyl groups, but much stronger ion pairs are formed with **4**, suggesting that the chloro ligand configuration also may affect the stability of ion pairs.

The fact that distinctly different reaction products are formed argues strongly for 1:1 ion pairs of different strength *and* structure. If the planar[19,20] protonated carbonate systems

of **3** and **4** are regarded as reference planes in the proposed ion pairs, then a stronger interaction of protonated **4** with TCP$^-$ might be expected through the side opposite to that occupied by the cis-chloro ligands of **4**. This ion pair **9** is converted to **6** in the rate-determining step.[30] Two possible symmetrical structures for **6** are given in Figure 7. Both structures A and B involve bridging phenolate, of which there are known examples.[31] Structure A also resembles many known carboxylate-bridged copper(II) systems[32] and is preferred over B on this basis. The formation of either A or B from **9** involves the acid-catalyzed rupture of two different types of Cu–O bonds in **9**.[30] Efforts are continuing to crystallize **6** with the objective of determining its structure.

The stable complex **6** reacts with excess phenol in a process that again involves a likely ion-pair interaction in the reaction intermediate **10**, albeit weaker than in **9** (perhaps because of steric crowding by the phenol moiety in A or B). Evidently, **6** is more basic than **3**. Conversion of **10** to (teed)CuCl$_2$ and (teed)Cu(TCP)$_2$ may require attack of TCP$^-$ on one of the equivalent copper centers in **10**, resulting in rupture of a Cu–OH bond at the same site and loss of Cl$^-$. Evidently, the high thermodynamic stability[24] of (teed)Cu(TCP)$_2$ ensures its appearance as a final product.

Except for the deviations at low [**3**]$_0$ discussed earlier, the reactions of TCPH with **3** are deceptively simple processes. The trans-chloro configuration in **3** evidently prevents stabilization of **7** (eq 6) through phenolate bridging after attack of TCP$^-$ on the opposite side of the plane to a chloro ligand on one of the equivalent coppers (The maintenance of a bridged bicarbonate structure as in A or B presumably prevents rotation of one copper center relative to the other.) The bicarbonate bridge breaks spontaneously (reaction 8) or by proton transfer to **3** (reaction 9). This latter reaction can be rationalized by the higher basicity of **3** relative to **7** (proton transfer is not rate determining). Deprotonated **7** evidently cannot re-form **3** by phenolate loss, and thus the carbonate bridge ruptures, forming 1 mol of (tmpd)CuCl(TCP) and unidentified (carbonato)chlorocopper(II) products.

We have found the reactions of **3** and **4** with excess TCPH to be kinetically intractable in our stopped-flow spectrophotometer. A number of different processes with very similar rates evidently occur under highly protic conditions. The reaction of **3** with TCPH gives only one product, the monophenolate (tmpd)CuCl(TCP), in reaction 2a with either reactant in excess (Figure 2). This primary product slowly reacts with excess TCPH to form polymeric material through Cl$^-$ abstraction (eq 3) at a higher rate in acetonitrile than in methylene chloride. However, the diphenolate complex (teed)Cu(TCP)$_2$, which forms in reaction with **4**, is much more stable under similar conditions.[24]

Each (μ-carbonato)- or μ-oxo-dicopper(II) oxidative coupling initiator has the capacity to deprotonate a total of two phenol molecules. Our work shows that the products of complete carbonate loss depend on the metal coordination environment with TCPH as a reactant. Whether the same pattern emerges with other phenols remains to be seen. If copper(II) oxidation of coordinated 2,6-disubstituted phenolate is rate determining in an oxidative coupling process (e.g., eq 1), then the stoichiometry of (phenolato)copper(II) complex intermediates presumably will determine the actual mechanism

(28) We are in the process of establishing an acidity scale in methylene chloride with the aid of reference indicators.[29]

(29) B. H. Robinson, "Hydrogen-bonding and Proton-Transfer Reactions in Aprotic Solvents" in "Proton-Transfer Reactions", E. F. Caldin and V. Gold, Eds., Halstead Press, New York, 1975, p 121.

(30) The question of whether the asymmetric bridge in **4** is maintained in ion pair **9** or product **6** cannot be answered in the absence of additional evidence.

(31) A. R. Amundsen, J. Whelan, and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6730 (1977); R. R. Gagne, R. S. Gall, G. C. Lisensky, R. E. Marsh, and L. M. Speltz, *Inorg. Chem.*, **18**, 171 (1979).

(32) K. Nakamoto, "Infra-red Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, 1970, p 222; C. Oldham, *Prog. Inorg. Chem.*, **10**, 223 (1968).

of initiation. We are continuing our work in this area.

Contribution from the Department of Chemistry,
Ithaca College, Ithaca, New York 14850

Copper(II) Incorporation into Tetraphenylporphine in Dimethyl Sulfoxide

ROBERT F. PASTERNACK,* GLENN C. VOGEL, CURTIS A. SKOWRONEK, ROGER K. HARRIS, and JAMES G. MILLER

A kinetic study of copper(II) ion incorporation into tetraphenylporphine (H$_2$TPP) in dimethyl sulfoxide is reported. The kinetic results suggest that the mechanism involves a rapid preequilibrium involving a copper(II) ion and H$_2$TPP prior to metal insertion and proton loss:

$$Cu^{2+} + H_2PPP \underset{}{\overset{K}{\rightleftharpoons}} Cu^{2+};H_2TPP \qquad Cu^{2+};H_2TPP \xrightarrow{k} CuTPP + 2H^+$$

where $K = 5.5$ M^{-1} and $k = 1.7 \times 10^{-3}$ s^{-1} at 25 °C and an ionic strenth of 0.2 M (KNO$_3$ or LiNO$_3$). The thermodynamic parameters for the preequilibrium are $\Delta H° = 6.5 \pm 0.1$ kcal/mol and $\Delta S° = 25.2 \pm 0.5$ eu, while the activation parameters are $\Delta H^* = 11.5 \pm 0.3$ kcal/mol and $\Delta S^* = -32.6 \pm 0.1$ eu. Arguments are presented which suggest that the Cu^{2+};H$_2$TPP species is best interpreted as arising from an outer-sphere ion pair type interaction without appreciable distortion of the porphyrin ring. In the rate-determining step, the ring distorts, protons are freed, and covalent bonds are formed between the porphyrin and copper(II) ion as solvent molecules from the inner coordination sphere of the metal ion are lost.

The rates of the reactions of copper(II) ion with ligands containing four nitrogen donor groups depend markedly on whether the ligand is an open-chain polyamine or macrocyclic.[1] Thus, hematoporphyrin has been shown to be 10^9 times less reactive than the open-chain polyamine *N,N′*-bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet) under similar reaction conditions. In large part, this difference reflects the porphyrin requirement for multiple desolvation of the metal ion for complex formation while 2,3,2-tet can readily react with copper(II) by stepwise replacement of coordinated solvent.[1] Much effort has been expanded to further elucidate the detailed pathway(s) by which metal ions become incorporated into porphyrin ligands in the absence of an "insertase",[2–4] and several papers have appeared in which a general mechanism has been offered.[5–8] Although differences in detail emerge among these suggestions, several features reappear and seem to be generally accepted.

The mechanisms begin with a preequilibrium step involving the metal ion and the free-base porphyrin leading to a deformation of the porphyrin moiety. Some controversy still exists as to whether this complex is of the sitting-atop-type[3] (SAT) or if it is best represented as an outer-sphere ion pair.[8] The SAT complex involves at least partial bonding of the metal ion to two of the pyrrole nitrogens with concomitant loosening of the nitrogen to hydrogen bonds. The porphyrin deformation, while likely to be involved in metal insertion, has been shown to be rapid and would not be rate determining under ordinary conditions.[9] The rate-determining step postulated for porphyrin metalation involves either the multiple desolvation of the inserting metal ion or a dissociative loss of solvent molecule(s) from the metal and a central proton from the porphyrin prior to metal insertion. The weight of experimental evidence suggests that the free-base porphyrin (cf. Figure 1) is the reactive species in that the rate of metal incorporation into *N*-methyltetraphenylporphine (H-N-MeTPP) is more rapid than for tetraphenylporphine (H$_2$TPP) and that both reactions show little dependence on ionic strength and are unaffected by the production of protons during the reaction.[8]

Much of the experimental work upon which these suggestions are based was carried out in aqueous solution. Unfortunately, many porphyrins aggregate in water,[10] limiting the number and type of systems which can be readily investigated. Furthermore, acid/base equilibria further complicate the analysis and interpretation.[11] Studies conducted in DMF have also proven very useful[8,12] although some ambiguity exists as to the reactive form(s) of the metal ion because of the relatively low dielectric constant of the solvent. Furthermore, the rate law in DMF has the simple form:

$$rate = k[M^{II}][porphyrin]$$

which does not provide any direct evidence for a preequilibrium.

In order to avoid both the ion-pairing problem and protolytic equilibria, we have studied the incorporation of copper(II) into tetraphenylporphine in Me$_2$SO. This aprotic solvent has sufficiently high dielectric constant and good electron-donating

(1) D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **92**, 2151 (1970).
(2) P. Hambright in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, New York, 1975, pp 233–278.
(3) F. R. Longo, E. M. Brown, W. G. Rau, and A. D. Adler in "The Porphyrins", Vol. V, D. Dolphin, Ed., Academic Press, New York, 1979, pp 459–481.
(4) W. Schnieder, *Struct. Bonding (Berlin)*, **23**, 123 (1975).
(5) R. Khosropour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).
(6) P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, **96**, 3123 (1974).
(7) J. Turay and P. Hambright, *Inorg. Chem.*, **19**, 562 (1980).
(8) M. J. Bain-Ackerman and D. K. Lavallee, *Inorg. Chem.*, **18**, 3358 (1979).

(9) R. F. Pasternack, N. Sutin, and D. H. Turner, *J. Am. Chem. Soc.*, **98**, 1908 (1976).
(10) R. F. Pasternack, P. R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G. C. Venturo, and L. de C. Hinds, *J. Am. Chem. Soc.*, **94**, 4511 (1972).
(11) H. Baker, P. Hambright, and L. Wagner, *J. Am. Chem. Soc.*, **95**, 5942 (1973).
(12) F. R. Longo, E. M. Brown, D. J. Quimby, A. D. Adler, and M. Meot-Ner, *Ann. N.Y. Acad. Sci.*, **206**, 420 (1973).