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# Homogeneous Oxidative Coupling Catalysts. Properties of the Oxidative Coupling Initiator Obtained from the Reaction of Copper(I) Chloride with Oxygen in Pyridine

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The stoichiometric reaction $2CuCl + {}^1/_2O_2 \rightarrow CuCl_2 +$ "CuO" in pyridine (where "CuO" represents a pyridine-coordinated structural unit) gives a dark brown solution which is an active catalyst in the oxidative coupling of acetylenes, aromatic amines, and phenols. The reaction products can be completely separated by gel permeation chromatography (pyridine eluent) and the "CuO" component shown to be the initiator for phenolic oxidative coupling. Evaporation of the stabilizing pyridine solvent from initiator solutions gives insoluble, catalytically inactive CuO. Cryoscopic measurements on freshly prepared initiator solutions in pyridine indicate that the initiator is polymeric, and the time-dependent properties of these solutions suggest that polymerization continues, although there is little change in the UV–visible spectrum. Extensive polymerization of the initiator causes the development of long induction periods in the oxidative coupling of 2,6-dimethylphenol and also results in a decreasing rate of decomposition in the presence of water, $HClO_4$, and HCl in pyridine. A stopped-flow kinetic study of the latter reaction of high molecular weight initiator species suggests a mechanism involving protonation of the "CuO" units followed by rate-determining decomposition of the protonated initiator. Rate measurements in the presence of 2-methylpyridine and dipropylamine support this mechanism. The "CuO" units in the initiator are evidently more basic than is 2-methylpyridine. The implications of these results for the initiation of the oxidative coupling of phenols are discussed.

## Introduction

Studies of the stoichiometric[1,2] reaction of copper(I) chloride with oxygen in pyridine, py, eq 1,[3] are of interest from several viewpoints.

$$2CuCl + {}^1/_2O_2 \xrightarrow{py} CuCl_2 + \text{"CuO"} \qquad (1)$$

First, investigations of this reaction form part of a current effort to better understand the nature of the $Cu^I \rightarrow Cu^{II}$ transformation in general and its role in biochemical cycles in particular.[4] Second, reaction (1) in several polar, aprotic solvents (e.g., pyridine, dimethylacetamide, dimethyl sulfoxide, and hexamethylphosphoramide) provides a useful series of catalysts for the oxidative coupling of acetylenes, aromatic amines, and phenols by molecular oxygen[5] and has recently been applied in interesting, biomimetic alkaloid syntheses.[6] Third, the product distribution and selective reactivity of the catalyst mixture in eq 1 bear a striking formal resemblance[7] to those of copper metalloenzymes such as laccase,[8] which are the subject of considerable current interest.[9] Fourth, the intense, brown color of the product solutions represents an unusual spectral phenomenon in copper coordination chemistry.[1]

Aniline, $PhNH_2$, can be oxidized to azobenzene in high yield in the presence of this catalyst system, eq 2.[10] Our characterization work (ref 1 and this paper) was prompted by frustrated attempts to produce high molecular weight polyazobenzenes through the corresponding oxidative coupling of *p*-phenylenediamine[11] and its derivatives. An important breakthrough in our work was the discovery that the two products in eq 1 can be completely separated without decomposition by gel permeation chromatography on cross-linked polystyrene/poly(divinylbenzene) resins with pyridine as the eluent.[1,12] Of the solvent systems we have employed in eq 1, pyridine appears to provide the easiest separation of products without appreciable catalyst decomposition. This separation of products enabled us to show that the oxidative coupling of 2,6-dimethylphenol (a representative substrate)[13] was *initiated* in pyridine by the brown component "CuO".[1]

$$2PhNH_2 + O_2 \xrightarrow{py} PhNNPh + 2H_2O \qquad (2)$$

Characterization of the initiator species in this catalyst system is complicated by the following chemical factors: (1) evaporation of the pyridine solvent from separated "CuO" solution fractions gives insoluble, catalytically inactive copper(II) oxide and (2) attempted preparation of stable, solid, catalytically active complexes through ligand exchange with such representative complexing agents as 2,9-dimethyl-1,10-phenanthroline in pyridine is slow and results in extensive oxidation of the substituting ligand.[1] It is evident from our attempts to prepare solid catalyst derivatives[1,7] that rather stringent requirements must obtain with regard to the properties of the ligands coordinated to the initiator metal centers. For example, whereas separated "CuO" solution fractions from eq 1 are apparently oxidatively stable in the absence of protic substances (vide infra), addition of 2-methylpyridine results in further oxidation, as evidenced by the consumption of additional molecular oxygen by the system.

In this paper we report the results of cryoscopic measurements on initiator solutions in pyridine, which indicate that the initiator is a pyridine-stabilized polymer. Extensive polymerization of the initiator results in long induction periods in the oxidative coupling of 2,6-dimethylphenol and lower rates of decomposition by HCl, added as pyridinium chloride, pyHCl, in pyridine. The stoichiometry of the latter reaction has been determined by standard methods and the kinetics have been investigated by computer-assisted stopped-flow spectrophotometry.

## Experimental Section

**Reagents and Analytical Procedures.** All materials used were of reagent grade unless otherwise specified. Pyridine (Fisher) and 2-methylpyridine, Me(py) (Eastman), were refluxed overnight with barium oxide and distilled onto molecular sieves.[15] Standard solutions of Me(py) in pyridine were made by volumetric dilution. Pyridinium chloride (Eastman) was recrystallized twice from 40% v/v carbon tetrachloride in ethyl acetate and vacuum dried for 24 h (mp 143–144 °C).[16] Solutions in pyridine were standardized gravimetrically as silver chloride after addition of excess base and evaporation of the solvent. 2,6-Dimethylphenol (Aldrich) (mp 46–47 °C) was distilled under vacuum and 5A molecular sieves (Grace) were dried at 150 °C under vacuum for 24 h. Sulfur dioxide (Matheson) was dried by passage through phosphorus pentoxide. Sulfate formed by its rapid reaction with the separated initiator was determined gravimetrically as $BaSO_4$. Lithium chloride was dried at 120 °C under vacuum for 5 h. Solutions of the dry solid in pyridine were standardized gravimetrically as silver chloride after evaporation of the solvent. Copper(I) chloride was prepared and purified as described in the literature.[17] Copper(II) chloride was dried at 110 °C under vacuum for 24 h. Solutions of the solid in pyridine were standardized spectrophotometrically ($\epsilon_{750}$ 141 $M^{-1}$ $cm^{-1}$).[18]

**Preparation and Isolation of the "CuO" Initiator in Pyridine.** Solutions of the initiator species in pyridine were obtained from the

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reaction of copper(I) chloride with oxygen, eq 1.[1,14] In a typical experiment, copper(I) chloride (2.00 g, $2 \times 10^{-2}$ mol) was weighed into a 100-mL, three-neck round-bottom flask fitted with a gas inlet connection to a Warburg apparatus filled with oxygen, a pressure equalizing dropping funnel, and a magnetic stirrer. Pyridine (64 mL, 0.8 mol) was added dropwise with stirring and oxygen consumption was monitored as a function of time. After 140 min the reaction of eq 1 had consumed 125 mL of $O_2$ at 1 atm and 26 °C (theoretical 123 mL) to give a dark green-brown solution. It was found that the rate of pyridine addition did not alter the stoichiometry of eq 1. However, addition of the pyridine in one portion resulted in reaction times of up to 24 h.[1,14]

The product solution was rapidly filtered through a medium-porosity glass sinter funnel and then passed in 10-mL portions through a 90 × 4 cm column of Biobeads SX-12 copolymer resin (Bio-Rad Laboratories) with pyridine as the eluent. Two fractions were collected. A brown component which appeared to coat the column[19] was eluted first, followed by a second green band which had chromatographic properties idential with those of copper(II) chloride.[1] Traces of chloride were removed from brown solution fractions by repassage of 1-mL samples through a 90 × 1 cm column of the same resin with pyridine as the eluent. Brown, chloride-free solutions obtained in this manner initiated the oxidative coupling of 2,6-dimethylphenol (see below) and exhibited no detectable ESR signal.[1] The concentration of copper in solutions of the separated initiator was determined by spectrophotometry ($\epsilon_{433}$ 634 $cm^{-1}$ L (g-atom of Cu)$^{-1}$)[1] or by analyzing for copper(I) as the 2,9-dimethyl-1,10-phenanthroline complex.[20] Elemental analyses of solid samples were performed by Galbraith Laboratories, Knoxville, Tenn. Samples of initiator-containing solutions (separated or unseparated) which were to be heated for long periods of time were sealed in glass vials (2–12 mL) under vacuum. These vials were immersed in an oil bath which maintained the desired temperature to within ±5 °C.

**Catalytic Activity.** The oxidative coupling of 2,6-dimethylphenol,[13] as evidenced by the consumption of a stoichiometric amount of oxygen in the Warburg apparatus, was used as a test of catalytic activity. Experiments were performed by adding a catalytic amount of sample ($2–5 \times 10^{-4}$ g-atom of Cu) to $5 \times 10^{-3}$ mol of 2,6-dimethylphenol in pyridine (25 mL) and monitoring the oxygen uptake as a function of time at ambient temperature.

**Apparatus.** All glassware was flame dried or heated in an oven at 100 °C for 1 h to eliminate moisture. UV–visible spectra were determined with a Beckman DK-1A recording spectrophotometer using 1-mm and 1-cm matched quartz cells. Infrared spectra were recorded on a Perkin-Elmer 21 spectrophotometer and were calibrated using the polystyrene band at 1601.0 $cm^{-1}$. Raman sepctra were determined with a Ramalog 4 spectrophotometer at the United States Army Materials Laboratory, Natick, Mass., which utilizes an argon ion laser with excitation at 5145 Å. ESR spectra were recorded on a Stand Labs Model 602X spectrometer at Brandeis University using $CuCl_2 \cdot 2H_2O$ as a standard.

**Polarographic Experiments.** Differential pulse polarography was performed with a Princeton Applied Research (Model 174) polarographic analyzer.[21] The current/potential curves were recorded on a Hewlett-Packard X-Y recorder (Model 3030 AM). Unless otherwise indicated, all polarographic experiments were run in a 0.1 M tetraethylammonium perchlorate (Eastman) medium in pyridine. A dropping mercury electrode with a drop time of 0.5 s was used as the working electrode and aqueous calomel and a 2-mm platinum wire served as reference and counter electrodes, respectively. All solutions were deoxygenated with a stream of purified nitrogen for 1 h before electrolysis. Duplicate scans were performed from 0 to −1.65 V, with deoxygenation between scans.

**Cryoscopic Measurements.** The freezing point of pyridine (−41.9 ± 0.1 °C) and its freezing point depression constant ($K_f = 3.4 \pm 0.1$ °C/*m* from seven determinations with benzene and *o*-dichlorobenzene standards) were measured in a standard[22] apparatus with a NBS certified thermometer (Haake, Berlin, Model NB 1150) which could be read to ±0.1 °C. The refrigerant was chloroform/$CO_2$ (−61 °C). A freshly prepared, centrifuged product solution (vide supra) was cooled to −42 °C (acetonitrile/$N_2$) and any precipitated residual $(py)_2CuCl_2$ was removed by centrifugation. The solution was then cooled to −61 °C and allowed to thaw slowly at 2300 rpm in a refrigerated centrifuge.[23] The supernatant was finally diluted by ca. 10% with pyridine and its freezing point determined. Analysis for copper in the initiator solution used in the determination was as described above. The concentration of $(py)_2CuCl_2$ in this solution was too low to measurably decrease the freezing point of pyridine.

Table II. Kinetic Data for the Reaction of Separated Initiator with Pyridinium Chloride[a,b]

| Temp, °C | $10^5 \times$ ["CuO"]$_0$ | $10^2 \times$ $[HCl]_T$ | $10k_{obsd}$[c] | $10k_{calcd}$[c,d] |
|---|---|---|---|---|
| 15.0 | 4.0 | 1.0 | 0.35 | 0.33 |
| | | 2.0 | 0.47 | 0.53 |
| | | 3.0 | 0.52 | 0.68 |
| | | 4.0 | 0.58 | 0.79 |
| | | 5.0 | 0.66 | 0.87 |
| 25.0 | 10.0 | 0.26 | 0.45 | 0.35 |
| | | 0.40 | 0.62 | 0.50 |
| | | 0.44 | 0.63 | 0.54 |
| | | 0.62 | 0.81 | 0.70 |
| | 4.0 | 0.71 | 0.85 | 0.77 |
| | | 0.80 | 0.91 | 0.83 |
| | | 0.88 | 1.0 | 0.88 |
| | | 1.32 | 1.1 | 1.1 |
| | 16 | 2.3 | 1.4 ± 0.2[e] | 1.5 |
| | | 2.5 | 1.6 | 1.6 |
| | | 4.6 | 1.9 | 1.8 |
| | | 5.0 | 1.8 ± 0.3[f] | 1.9 |
| | | 5.0 | 1.8 ± 0.2[g] | 1.9 |
| 35.0 | 4.0 | 0.25 | 0.95 | 0.90 |
| | | 0.33 | 1.2 | 1.2 |
| | | 0.44 | 1.4 | 1.5 |
| | | 0.61 | 1.8 | 1.8 |
| | | 0.88 | 2.1 | 2.1 |
| | | 1.3 | 2.4 | 2.5 |
| | | 1.8 | 2.8 | 2.8 |
| | | 2.7 | 3.0 | 3.1 |
| | | 3.3 | 3.1 ± 0.1[h] | 3.2 |
| | | 5.0 | 3.6 ± 0.2[i] | 3.4 |
| | | 5.0 | 3.4[j] | 3.4 |

[a] Initiator reactant separated and aged for 1 week at room temperature. [b] All concentrations are M. Reaction media: 0.1 M pyHCl/LiCl mixtures in pyridine. [c] Units are $s^{-1}$. [d] Calculated from a nonlinear least-squares fit of data to eq 4. [e] Average of eight runs at 375, 400, 433, and 450 nm. [f] Average of eight runs with oxygenated and deoxygenated solutions. [g] Average of four runs with and without added copper(II) chloride ($4 \times 10^{-4}$ M). [h] Run repeated over a span of 2 weeks. [i] Duplicate experiments performed with and without heating the initiator solution at 35 °C for 0.5 h prior to kinetic measurements. [j] Added $H_2O$ (0.027 M).

**Stoichiometry Measurements.** The stoichiometry of the reaction of HCl with "CuO" was determined by adding a known amount of pyHCl to a measured excess of the separated initiator species in 0.1 M LiCl in pyridine at 25 °C. The remaining complex was estimated spectrophotometrically at 433 and 450 nm ($\epsilon_{450}$ 537 $cm^{-1}$ L (g-atom of Cu)$^{-1}$). The absorptivity of the $CuCl_2$ coproduct is negligible in this region.[1,18] The stoichiometry was also checked in the presence of excess pyHCl by spectrophotometric determination of the copper(II) chloride product at 750 nm (vide supra). Concentrations used were ["CuO"]$_0$ = $(10.6–24.4) \times 10^{-4}$ M and $[HCl]_{T,0} = (2.1–4.4) \times 10^{-3}$ M at 25 °C.

**Kinetic Measurements.** Most of the experimental data were obtained in 0.1 M pyridinium chloride/lithium chloride mixtures in pyridine. The kinetics of all the reactions were monitored spectrophotometrically in a stopped-flow apparatus.[24] Experimental conditions were ["CuO"]$_0$ = $(4.0–16.0) \times 10^{-5}$ M and $[HCl]_T = (0.25–5.0) \times 10^{-2}$ M at a total chloride concentration of 0.1 M in the temperature range 15.0–35.0 °C. In all cases the disappearance of the complex was monitored in the wavelength region 375–450 nm in the presence of at least a tenfold excess of pyHCl. The first-order rate constants quoted in Table II are averages of five independent measurements and replicate determinations were reproducible to ±5%.

Experimental procedures for obtaining rate constants from the stopped-flow apparatus and determining empirical kinetic coefficients and their activation parameters were as previously described.[24]

## Results

Polarographic measurements[25] were consistent with the discrete formation of $(py)_2CuCl_2$ in eq 1 and confirmed the previous spectral and ESR measurements.[1,27] Separated

**Table IV.** Empirical Kinetic Parameters for the Reaction of Separated Initiator with Pyridinium Chloride[a]

| Temp, °C | $A$[b] | $B$[c] | $A/B$[d] | $\Delta H_A$[e] | $\Delta S_A$[f] | $\Delta H_B$[e] | $\Delta S_B$[f] |
|---|---|---|---|---|---|---|---|
| 15.0 | 5.0 ± 0.8 | 58 ± 10 | 0.084 ± 0.008 | | | | |
| 25.0 | 20 ± 1 | 84 ± 7 | 0.24 ± 0.01 | 22 ± 2 | 21 ± 6 | 14 ± 3 | 57 ± 10 |
| 35.0 | 50 ± 4 | 130 ± 10 | 0.38 ± 0.01 | | | | |

[a] Reaction medium 0.1 M pyHCl/LiCl in pyridine. Parameters $A$ and $B$ obtained from a unit-weighted, nonlinear least-squares fit of the data to eq 4 at the temperature shown. The thermodynamic parameters for $A$ and $B$ were obtained by fitting all of the data to eq 4 in its temperature-dependent form ($A = (kT/h)\exp(\Delta S_A/R)\exp(-\Delta H_A/RT)$, $B = \exp(\Delta S_B/R)\exp(-\Delta H_B/RT)$). [b] Units are $M^{-1}\ s^{-1}$. [c] Units are $M^{-1}$. [d] Units are $s^{-1}$. [e] Units are kcal $mol^{-1}$. [f] Units are cal $deg^{-1}\ mol^{-1}$.

initiator solutions were found to be electrochemically inactive in the 0 to −1.65 V vs. SCE potential range.

**Cryoscopic Measurements.** The freezing point (five determinations) of a freshly prepared, nearly saturated solution of the initiator (0.17 g-atom/kg in "CuO")[28] was indistinguishable (to ±0.1 °C) from that of pure pyridine, consistent with at least five "CuO" units per solute species.[29] The initiator is thus polymeric, even when freshly prepared, at this concentration level.[30] On standing in a closed vessel at room temperature, the solution used in the cryoscopic measurements precipitated brown material which gave insoluble CuO on evaporation of the solvent (see Introduction).

**Time-Dependent Properties of Initiator Solutions.** Continuous polymerization of much more dilute initiator solutions ($4.2 \times 10^{-4}$ g-atom $L^{-1}$ "CuO" in pyridine) was accompanied by only minor spectral changes, with a relative increase in absorbance at higher energies about an isosbestic point at 435 nm.[31] These spectral changes were accelerated by heating at 100 °C (Figure 1)[32] or by increasing the initiator concentration. Long induction periods and lower overall rates of oxygen consumption developed in the oxidative coupling of 2,6-dimethylphenol, particularly if the initiator solutions were heated[33] (see Figure 2[32]).

The rate of reaction of "CuO" solutions with excess water in the presence of dissolved salts ($LiClO_4$, $Et_4NClO_4$ at 0.1 M) gave half-lives varying from <5 s for fresh, dilute solutions to more than an hour for solutions stored for 2 months at room temperature or for heated (50–100 °C) solutions. The spectral changes on reaction with water were irreproducible and were often accompanied by the precipitation of solid material, precluding detailed kinetic study.

By contrast, the spectral changes on reaction with excess pyHCl in LiCl media were always reproducible at every stage of initiator transformation. Initial rates corresponding to an observed first-order rate constant, $k_{\mathrm{obsd}}$, of ca. 2–5 $s^{-1}$ at 25 °C were obtained for reaction of freshly prepared dilute initiator solutions in the presence of 0.025 M pyHCl and 0.075 M LiCl. However, computer analysis of the absorbance changes showed that the reaction was not first order and that at least two different processes were occurring.[34] These observations suggest that these solutions contain polymerized initiator species of different molecular weights.

Standing of initiator solutions at room temperature for periods up to ca. 1 week or heating them at 60 °C for shorter periods (Table I[32]) had two effects. First, the overall rate of reaction with a fixed excess concentration of pyHCl decreased, although kinetic complexity remained; upon prolong standing (ca. 2 weeks) or heating (10 h at 60 °C), the first-order plots for the absorbance change on reaction became linear for at least 80% reaction. Second, the rates approached limiting and reproducible values (Tables I[32] and II).[35] We interpret these effects as indicating that polymerization of the initiator is accelerated by heat (see above) and that highly polymerized species, whose kinetic and spectral properties are experimentally indistinguishable, are eventually formed. It is the latter solutions which have been subjected to the detailed kinetic investigation described below. The rate of polymerization on standing or heating does not appear to be affected by the presence of copper(II) chloride.

A rapid reaction with $SO_2$ was observed with freshly prepared or heated initiator solutions which had been chromatographically separated. Sulfate was confirmed as a product in all cases.[36]

**Reaction with Pyridinium Chloride. Stoichiometry Measurements.** The results of the stoichiometric measurements for the reaction of separated "CuO" with HCl, with either reagent in excess, are presented in Table III.[32] The spectra of final product solutions in the presence of excess HCl were identical with that of copper(II) chloride in pyridine and were unaffected by the presence of 0.1 M LiCl or 0.1 M pyHCl. These results indicate, within an experimental uncertainty of ±3%, that reaction 3 occurs over the experimental concentration ranges and throughout the time-dependent changes noted above.

$$2\mathrm{HCl} + \text{“CuO”} \xrightarrow{\mathrm{py}} \mathrm{CuCl_2} + \mathrm{H_2O} \qquad (3)$$

**Kinetics.** The kinetic results for reaction of highly polymerized initiator solutions with HCl (added as excess pyHCl) collected in Table II allow the following conclusions to be drawn. For high molecular weight initiator species, $k_{\mathrm{obsd}}$ is independent of the total analytical concentration of chloride (0.01–0.3 M), the presence of $CuCl_2$, oxygen, or $H_2O$ (up to 0.027 M), or variation of the monitoring wavelength in the range 375–450 nm. At fixed ["CuO"] and temperature, $k_{\mathrm{obsd}}$ increases to a limiting value with increasing $[\mathrm{HCl}]_T$,[40] consistent with an empirical rate law of the form of eq 4.

$$-\frac{\mathrm{d}\ln[\text{“CuO”}]}{\mathrm{d}t} = k_{\mathrm{obsd}} = \frac{A[\mathrm{HCl}]_T}{1 + B[\mathrm{HCl}]_T} \qquad (4)$$

A computerized, nonlinear least-squares fit of the data to eq 4 gave empirical parameters $A$ and $B$ which are collected together with their corresponding activation parameters in Table IV. Calculated values of the first-order rate constants from this fit of the data are included in Table II for comparison with $k_{\mathrm{obsd}}$. The fit of the data is considered acceptable in view of the time-dependent properties of the initiator.

**Mechanism.** The following mechanism is consistent with the kinetic dependences.

$$\text{“CuO”} + \mathrm{HCl} \overset{\text{rapid}}{\rightleftharpoons} \text{“CuOHCl”} \qquad K_1 \qquad (5)$$

$$\text{“CuOHCl”} \xrightarrow{k_2} \text{products} \qquad (6)$$

Here, "CuOHCl" represents a protonated unit of a highly polymerized, pyridine coordinated structure,[3] and step 6 is postulated to be rate determining. This mechanism predicts the observed rate law (eq 4) if $A = k_2K_1$ and $B = K_1$, with $k_2 = A/B$. Calculated values of $k_2$ are included in Table IV. The enthalpy and entropy of activation for step 6 are 8 ± 3 kcal $mol^{-1}$ and −36 ± 10 cal $deg^{-1}\ mol^{-1}$, respectively (see footnotes in Table IV).

**Effect of 2-Methylpyridine on the Rate of Reaction of the Separated Initiator with Pyridinium Chloride.** Further support for rapid protonation (eq 5) followed by rate-determining decomposition of the protonated species (eq 6) was obtained by monitoring the reaction in the presence of various con-

**Table V.** Kinetic Data for Reaction of Separated Initiator with Pyridinium Chloride in the Presence of 2-Methylpyridine[a]

| $10^2[\mathrm{HCl}]_T$ | [Me(py)] | $10^2k_{\mathrm{obsd}}$[b] |
|---|---|---|
| 5.0 | 0.2 | 17 |
| | 0.3 | 16 |
| | 0.5 | 16 |
| | 1.0 | 12 |
| | 5.0 | 5 |
| 2.7 | 0.2 | 11 |
| | 0.5 | 10 |
| | 1.0 | 9 |
| | 2.0 | 7 |
| 1.1 | 0.2 | 5.9 |
| | 0.5 | 5.4 |
| | 1.0 | 4.1 |
| | 3.0 | 2.2 |

[a] Data at 450 nm for 0.1 M pyHCl/LiCl in pyridine at 25 °C with 1 week old separated product. All concentrations are M. $[\text{“CuO”}]_0 = (4\text{–}10) \times 10^{-5}$ M. [b] Units are $s^{-1}$.

centrations of 2-methylpyridine and dipropylamine, which are stronger proton bases than pyridine[41] and thus would be expected to affect the rate by shifting the equilibrium position of reaction 5.

The kinetic data obtained for the reaction of the separated product (aged for at least 1 week at room temperature) with pyridinium chloride in the presence of various concentrations of Me(py) are presented in Table V. All the data were obtained under a nitrogen atmosphere since previous observations[7] indicated Me(py) oxidation in the presence of oxygen.

The data indicate a marked decrease in the rate of the reaction in the presence of added Me(py) under conditions where the rate of reaction with pyHCl at [Me(py)] = 0 is constant (Table II). Furthermore, the rate is dependent on the concentration of Me(py). Since the base strengths of Me(py) and py differ by a factor of more than 100 in water ($pK_a$'s for $\mathrm{Me(py)H^+}$ and $\mathrm{pyH^+}$ are 7.5 and 5.2, respectively, in water),[41] Me(py) would decrease the effective concentration of HCl via reaction 7. The observed rate constant, $k_{\mathrm{obsd}}$, predicted for the mechanism consisting of reactions 5–7 is

$$\mathrm{HCl} + \mathrm{Me(py)} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{Me(py)HCl} \qquad K_b \tag{7}$$

given by eq 8.

$$k_{\mathrm{obsd}} = \frac{k_2K_1[\mathrm{HCl}]_T}{1 + K_b[\mathrm{Me(py)}] + K_1[\mathrm{HCl}]_T} \tag{8}$$

The data in Table V were fitted graphically to the inverted form of eq 8, resulting in values of $k_2 = 0.34 \pm 0.06\ s^{-1}$, $K_1 = 25 \pm 10\ M^{-1}$, and $K_b = 1.0 \pm 0.2\ M^{-1}$, respectively, at 25 °C. Considering the time-dependent properties of the initiator solutions and the likelihood of some variation of kinetic properties between different samples, the agreement between these estimates of $k_2$ and $K_1$ and those in Table IV is reasonable and supports the postulated mechanism.

In the presence of 1–10% v/v dipropylamine ($pK_a$ 10.9 at 25 °C in $H_2O$[41]) the rate of reaction of the separated initiator species with pyHCl was severely decreased, with complete reaction occurring only after a period of many hours. These results are consistent with the much larger proton basicity of dipropylamine relative to that of pyridine, which evidently leads to very effective inhibition of the reaction through an equilibrium analogous to eq 7.

A few experiments were performed to study the reaction of $HClO_4$ (added as $pyHClO_4$) in pyridine with the unseparated product mixture (eq 1) in tetraethylammonium perchlorate media. The reaction showed similar behavior to that of HCl (see above) except that the rates of reaction were always much lower. The reaction of $HClO_4$ with freshly prepared product (initial conditions $[HClO_4]_T = 0.05$ M, $[Et_4NClO_4] = 0.05$ M, $[\text{“CuO”}]_0 = 7.8 \times 10^{-4}$ g-atom $L^{-1}$ and 25 °C) occurred via a fast process which was complete in ~7 s and a slower one which was complete in ~200 s. First-order plots of the faster process were nonlinear.[34] The slower process exhibited first-order kinetics and gave a value of $k_{\mathrm{obsd}}$ of 0.018 $s^{-1}$ under the above conditions. An experiment performed with unseparted product which had been heated for 5 h at 60 °C under identical reaction conditions exhibited only the slower process with a smaller rate constant (0.011 $s^{-1}$). The reactions are thus about 4–7 times slower when $HClO_4$ replaces HCl as reactant. A complete kinetic investigation of this reaction was precluded by the low solubility of $pyHClO_4$ and $Et_4NClO_4$ in pyridine, which severely limited the available concentration ranges under pseudo-first-order conditions.

## Discussion

The cryoscopic data indicate that the unusual, brown, oxidative coupling initiator species obtained in reaction 1 are polymeric. Further polymerization occurs on standing or concentration and is accelerated by heat. That the polymers contain “CuO” structural units with unit stoichiometry[33] is indicated by the discrete formation of $(py)_2CuCl_2$ in reaction 1, by quantitative titration of the coordinated O atoms,[42] and by the ultimate formation of copper(II) oxide, CuO, on evaporation of pyridine from the solutions. The necessity for stabilization of these polymers by excess pyridine[1,43] is further indicated by the production of insoluble CuO on passing pyridine-saturated oxygen over solid copper(I) chloride.[39] The NMR data[1] are consistent with coordination of pyridine at the initiator copper centers, but the coordination geometry is unknown.

We feel that a pyridine coordinated, polymeric structure $[\mathrm{Cu(py)}_m\mathrm{O}]_n$, rather than a peroxidic (Cu–O–O–Cu) or $\mu$,-$\mu'$-dioxocopper(II) initiator core, is indicated by our results; there is no evidence for the presence of peroxide,[36] and the very few dioxocopper(II) complexes which have been reported[45] exhibit absorption bands in the 600–800-nm region which are absent in the spectra of separated initiator solutions.

The featureless, UV–visible spectrum of initiator species can be attributed to charge-transfer interactions between copper and oxygen, perhaps mediated by pyridine (copper(II) oxide is black, but pyridinecopper(II) complexes with common anions are blue). This characteristic spectrum is observed from the earliest stages of formation of “CuO” at 10–80 °C and suggests either that the primary initiator products of eq 1 are polymeric or that polymerization of mononuclear species $(py)_m$CuO simply is too rapid to be observed (this feature is also observed with ligands other than pyridine).[46] Coordination of oxygen to the surface of solid copper(I) chloride in eq 1 is strongly indicated by the very much lower rates of oxygen uptake when *dissolved* copper(I), rather than a slurry, is employed in pyridine (see Experimental Section and ref 1 and 14).

Highly reproducible kinetic data are not expected for a continuously changing system of this type. We should therefore not attempt a detailed interpretation of the kinetic parameters but should instead point out the characteristic features of this initiator system which our kinetic studies reveal. A continuing process, interpreted as initiator polymerization, results in a decreasing reactivity toward protic substances. Protonated, highly polymerized initiator species are cleaved by HCl in pyridine at a characteristic rate.[47] Perhaps our most important result is that the structural units of high molecular weight initiators are more basic than is Me(py) (compare $K_1$ with $K_b$) and are thus more basic than is the pyridine solvent.[41] We feel that this relatively high basicity of the initiator is important in determining efficiency in the oxidative coupling of phenols, since it would effectively increase the concentration of phenoxide ions, which are expected to have greater affinity for the initiator metal centers than do neutral phenol molecules.[48]

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**Registry No.** Pyridine, 110-86-1; 2-methylpyridine, 109-06-8; copper(I) chloride, 7758-89-6; oxygen, 7782-44-7.

**Supplementary Material Available:** Kinetic data illustrating the decreased activity of initiator species toward HCl in py as a result of heating (Table I); stoichiometric data for reaction 3 (Table III); spectral changes on heating initiator solutions (Figure 1); effect of preheating of initiator solutions on $O_2$ uptake in oxidative coupling of 2,6-dimethylphenol (Figure 2) (4 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) A summary of our earlier characterization work on the pyridine system has appeared previously: C. E. Kramer, G. Davies, R. B. Davis, and R. W. Slaven, *J. Chem. Soc., Chem. Commun.*, 606 (1975).
(2) Pyridine ligands are omitted from eq 1 for clarity. The copper(II) product is actually $(py)_2CuCl_2$ (ref 1, 5, and this work).
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(11) Among the anticipated desirable properties of such materials are high-temperature stability, graphite-like semiconductivity, and possible photochromatic behavior through cis–trans isomerization about the N–N double bonds. Low-molecular-weight (poly)azobenzene materials prepared in our laboratory are amorphous (interplanar spacing ca. 4.5 Å) and stable to at least 350 °C and have a remarkable ability to become statically charged.[7]
(12) We include detailed experimental procedures for chromatographic fractionation of the products in the Experimental Section.
(13) The products of the oxidative coupling of 2,6-dimethylphenol in this system are poly(2,6-dimethyl-1,4-phenylene ether) and 3,3′5,5′-tetramethyl-4,4′-diphenoquinone, with the former favored over the latter at high pyridine/copper ratios in an *o*-dichlorobenzene cosolvent.[14] The origin of the variation of product distribution with experimental conditions is unknown (see Discussion).
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(25) Bis(pyridine)copper(II) chloride gave reduction waves at −0.25 and −0.73 V. (vs. SCE), identical in form with those of the unseparated product solution (eq 1). Quantitation was based on area measurement of the latter, more symmetrical derivatized wave.[21] The previously observed[1] wave at −0.93 V (obtained at very high sensitivity and previously assigned to peroxide) was shown to be due to traces of $O_2$,[26] which was rigorously excluded in subsequent work.
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(27) Analyses of typical solid $CuCl_2$ products from eq 1 were consistent with the isolation of $(py)_2CuCl_2$ contaminated with a small amount of CuO. Calcd for $(py)_2CuCl_2$: Cu, 21.73; Cl, 24.27; N, 9.57; H, 3.42; C, 41.0. Obsd: Cu, 22.47; Cl, 23.66; N, 9.17; H, 3.51; C, 39.54. The ESR ($g_x = 2.059$, $g_y = 2.082$, $g_z = 2.082$) and IR spectra were identical with those of an authentic sample of $(py)_2CuCl_2$.
(28) The solubility of freshly prepared initiator species in pyridine is ca. 0.6 g-atom/kg (expressed as "CuO") at ambient temperatures, as compared to ca. $2 \times 10^{-2}$ M for the $(py)_2CuCl_2$ coproduct in eq 1.[18]
(29) A. 0.1 °C depression of the freezing point of pyridine would correspond to an effective solute concentration of 0.03 mol/kg, to be compared with the measured analytical copper concentration (0.17 g-atom of Cu/kg). The cooling curves for standard (benzene, dichlorobenzene) or initiator solutions in pyridine are of similar form, indicating that the latter are true solutions.
(30) Since we have evidence that initiator solutions are continuously polymerizing (see text), it was felt that more precise cryoscopic measurements were not justified since the actual solute molal concentration would be decreasing during the determination of the freezing point of initiator solutions.
(31) Our previous conclusion[1] that the Beer–Lambert law is obeyed by initiator solutions (which are actually undergoing polymerization) was based on measurements near the isosbestic point at 435 nm.
(32) Supplementary data.
(33) Experiments in the Warburg apparatus showed that eq 1 is obeyed to at least 80 °C in pyridine, indicating that the spectral changes and the general decrease in reactivity are not due to oxidation of pyridine and are not accompanied by release of molecular oxygen (see ref 1).
(34) The computer-assisted stopped-flow spectrophotometer in our laboratory is only capable of accurately resolving consecutive first-order systems with rate constants which differ by a factor of ca. 2 or greater. Thus, the possibility remains for the occurrence of more than two processes, with a rate constant spectrum covering less than a factor 2.
(35) We do not recommend heating millimolar (or more concentrated) initiator solutions for more than ca. 120 h at 60 °C. Such millimolar solutions give irreproducible, complex kinetic data and will not pass through a GPC column (even though no solid material is apparent after centrifugation until more than 180 h of heating). See Table I.[32]
(36) See eq 2 of ref 1; this reaction is characteristic of transition-metal peroxides.[37] A peroxide structural unit Cu–O–O–Cu would be expected to exhibit a polarographic reduction wave at ca. −0.9 V,[1] but this is not observed in the strict absence of oxygen in the present system. Other chemical tests for peroxide are not applicable here because they generally require acidic test conditions.[7] The UV–visible spectrum of the initiator contains no bands assignable to a peroxidic structure[38] and the laser-raman band observed[1] at 856 $cm^{-1}$ and assigned[1] to peroxide has been shown in subsequent work[39] to be highly irreproducible and most often not observed. A peroxidic or a $\mu,\mu'$-dioxocopper(II) structure can reasonably be expected to be dimeric and is eliminated by the cryoscopic measurements (see Discussion).
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(47) First-order behavior in the rate of reaction of highly polymerized initiators with HCl and $HClO_4$ is another indication of high molecular weight. Evidently, small polymer units react at significantly higher rates than do larger ones; thus, the reactions would show measurable deviations from first-order behavior toward the end of reaction with acid, which

are not observed (see text and Table II).
(48) Coordination of the phenol substrate has been suggested by other workers[49] as a requirement for oxidative coupling;[50] this view is supported by evidence for pyridine lability in the initiator.[1,43] The manner of coordination may have some bearing on the product distribution.[13] For example, at relatively low pyridine concentrations, coordination of phenol moieties at adjacent metal centers would produce a high, local concentration of phenol radicals, which might favor C–C coupling to give the quinone, rather than coupling to phenol, which would give polymer.[13]
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(50) Formation of phenol radicals could also occur without coordination to the copper center through an outer-sphere electron-transfer process mediated by the oxygen atom of the initiator.[24]

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# Studies on the Base Hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ Complexes

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The product ratios $[Co(NH_3)_5N_3^{2+}]/[Co(NH_3)_5OH_2^{3+}]$ were determined in aqueous solutions of sodium azide at various temperatures and ionic strengths for the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ ($X^{n-} = Cl^-, Br^-, NO_3^-, Me_2SO$) complexes. The results showed that the $S_N1cB$ mechanism involving the five-coordinate $Co(NH_3)_4NH_2^{2+}$ intermediate was inadequate to explain the product ratios obtained. The observed results can be adequately explained by an interchange mechanism of the conjugate base $Co(NH_3)_4NH_2X^{(2-n)+}$ contributing significantly to the observed overall reaction. The temperature dependence of the product ratio indicated that the cobalt(III)–ligand bonds to the leaving and incoming ligands in the activated complexes were essentially completely broken for practical purposes in the interchange mechanism. Alternate mechanisms were considered.

## Introduction

The $S_N1cB$ mechanism shown in reactions 1–3 seems to be

$$Co(NH_3)_5X^{(3-n)+} + OH^- \overset{K}{\rightleftharpoons} Co(NH_3)_4NH_2X^{(2-n)+} + H_2O \qquad (1)$$

$$Co(NH_3)_4NH_2X^{(2-n)+} \xrightarrow[\text{slow}]{k} Co(NH_3)_4NH_2^{2+} + X^{n-} \qquad (2)$$

$$Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow[\text{rapid}]{} Co(NH_3)_5OH^{2+} \qquad (3)$$

presently accepted as the mechanism for the base hydrolysis of various pentaammine complexes of cobalt(III) with the five-coordinate, trigonal-bipyramidal $Co(NH_3)_4NH_2^{2+}$ complex as the intermediate.[1] When a nucleophile $Y^{m-}$ which can compete with water is added to the reaction mixture initially, the intermediate can also react with this nucleophile to form a second product (reaction 4) in a competition reaction

$$Co(NH_3)_4NH_2^{2+} + Y^{m-} + H_2O \xrightarrow[\text{rapid}]{} Co(NH_3)_5Y^{(3-m)+} + OH^- \qquad (4)$$

with water for the intermediate. Certainly the general features of these base hydrolyses and competition reactions are explained by this mechanism and by this one intermediate. However, as it has already been pointed out,[2] an important experimental fact is not explained by this mechanism: the fact is that all starting complexes, or substrates $Co(NH_3)_5X^{(3-n)+}$, do not form the products $Co(NH_3)_5Y^{(3-m)+}$ and $Co(NH_3)_5OH_2^{3+}$ in the same ratio for the same concentration of a given $Y^{m-}$ as is required for the common intermediate $Co(NH_3)_4NH_2^{2+}$ of the $S_N1cB$ mechanism. The intermediate $Co(NH_3)_4NH_2^{2+}$ will react with a nucleophile such as $N_3^-$ in competition with $H_2O$ in the same way whether it came from, say, $Co(NH_3)_5NO_3^{2+}$ or $Co(NH_3)_5(Me_2SO)^{3+}$. But if the product ratio is dependent on the nature of the leaving group, then the intermediate in the hydrolysis is not solely the one pictured for the $S_N1cB$ mechanism.

The $S_N2$ and $S_N2cB$ mechanisms for the base hydrolyses of these pentaammine complexes were examined[1d] and rejected. However, an interchange mechanism for the conjugate base was not examined. Thus, the leaving group of the conjugate base may leave the first coordination shell by an interchange reaction with the competing incoming ligands as well as, or instead of, by the dissociation mechanism which produces the $Co(NH_3)_4NH_2^{2+}$ intermediate.

Here we report on the $[Co(NH_3)_5N_3^{2+}]/[Co(NH_3)_5OH_2^{3+}]$ product ratios formed when the substrates $Co(NH_3)_5X^{(3-n)+}$ ($X^{n-} = Cl^-, Br^-, NO_3^-, Me_2SO$) are hydrolyzed in aqueous basic $NaN_3$ media. The results show that the product ratios obtained from the various substrates (except possibly $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$) are not all equal.

## Experimental Section

**Chemicals.** Concentrated reagent grade acids were diluted and standardized by the usual methods. The complexes $[Co(NH_3)_5Cl](ClO_4)_2$ and $[Co(NH_3)_5Br](ClO_4)_2$ were prepared from the chloride and bromide salts, respectively, by dissolving in water, adding concentrated perchloric acid, cooling in ice, and recrystallizing from water with sodium perchlorate until pure.[3,4] The complex $[Co(NH_3)_5OH_2](ClO_4)_3$ was obtained by dissolving the nitrate salt in water, adding concentrated perchloric acid, cooling in ice, and then recrystallizing from water with sodium perchlorate.[5] The complex $[Co(NH_3)_5NO_3](ClO_4)_2$ was prepared by heating $[Co(NH_3)_5OH_2](NO_3)_3$ at 80 °C as described,[6] dissolving in water, adding concentrated perchloric acid, cooling in ice, and recrystallizing from water with sodium perchlorate until pure. The complexes $[Co(NH_3)_5N_3](ClO_4)_2$[7] and $[Co(NH_3)_5Me_2SO](ClO_4)_3$[8] were prepared as described and were recrystallized from water with perchloric acid until pure. The purity of the complexes was checked by comparing the wavelength maxima and corresponding extinction coefficients with literature values. The purity of the chloro, bromo, nitrato, azido, and $Me_2SO$ complexes was also checked by conversion to the aquo complex by both acid and base hydrolyses where possible (nitrous acid oxidation in acid medium for the azido complex) and determination of the amount of the aquo complex formed. All complexes were better than 98% pure.

The wavelengths (molar extinction coefficients), in nm ($M^{-1}$ $cm^{-1}$), respectively, used were the following: $Co(NH_3)_5OH_2^{3+}$ 490 (48.0), 508.5 (45.0); $Co(NH_3)_5Cl^{2+}$ 532 (50.4), 508.5 (45.0); $Co(NH_3)_5Br^{2+}$ 550 (57.7); $Co(NH_3)_5NO_3^{2+}$ 500 (57.4); $Co(NH_3)_5Me_2SO^{3+}$ 515 (62.3); $Co(NH_3)_5N_3^{2+}$ 518 (266).

**Procedure.** Usually 0.100 to 0.150 mmol of the desired complex was dissolved in a few milliliters of water, $NaN_3$ solution was added to give the desired $N_3^-$ concentration for the final volume, and the

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