

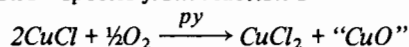
Homogeneous Oxidative Coupling Catalysts. Solid Products from the Oxidative Coupling Initiator Obtained from the Reaction of Copper(I) Chloride with Oxygen in Pyridine

I. BODEK and G. DAVIES

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

Received August 8, 1977

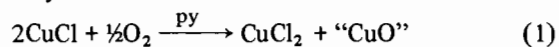
Solid products have been obtained from the "CuO" species from reaction 1



by treatment with sodium tetraphenylborate, sodium carbonate and lithium perchlorate in aqueous pyridine. All solids lacked the catalytic activity of the homogeneous product mixture from (1) in the absence of these added solutes. The solid obtained in the presence of sodium tetraphenylborate or sodium carbonate was shown by analysis to be inactive CuO, whereas analytical and spectral data indicate that lithium perchlorate causes the "CuO" initiator fraction of reaction 1 to disproportionate to an insoluble mixture of CuO and $\text{Cu}_2\text{Py}_4(\text{ClO}_4)_2$. These results are compared with previous investigations with CHCl_3 as the precipitating agent. The implications for synthetic strategies in the isolation of stable, solid copper–oxygen initiator complexes for oxidative coupling are discussed.

Introduction

Although much effort has been expended on trying to understand the origin of various products obtained in the oxidative coupling reactions of acetyles [1], aromatic amines [2] and phenols [3] which are catalyzed by the products of stoichiometric reaction 1, progress towards an identification of the actual catalytic constituents of this mixture is comparatively recent.



I

Previous work in our laboratory [4] has allowed a tentative identification of species I in pyridine, py. These species initiate [5] the oxidative coupling of 2,6-dimethylphenol to poly(2,6-dimethyl-1,4-phenylene ether) and 3,3',5,5'-tetramethyl-4,4'-diphenoquinone, with the former product apparently favored

by basic conditions (either from the presence of a large excess of pyridine over copper [6] or in the presence of high proportions of KOH in the corresponding CuCl_2/KOH catalytic system [7]). The identification of species I as a growing $(-\text{Cu}-\text{O}-\text{Cu}-\text{O}-)_n$ polymer, which is stabilized against decomposition to insoluble, inactive CuO by coordinated pyridine, is based on its time- and temperature-dependent properties as an initiator for phenolic coupling and by its decreasing rate of reaction with acids such as pyHCl [4]. Stoichiometric and kinetic studies of the latter reaction indicate that the oxygen atoms of the polymeric initiator are significantly more basic than is pyridine and suggest that smaller polymeric units are more active initiators for phenolic oxidative coupling than are larger ones [4].

An absolute identification of these initiator species requires the isolation of solid, active derivatives. This is not a trivial problem, since dissolved initiator species I in pyridine seem to rely for their existence on a large excess of the solvent and attempts to prepare solid derivatives by ligand exchange with such ligands as 2-methylpyridine and hexamethylphosphoramide show that such processes are slow in pyridine and are, as far as we are aware, always accompanied by oxidation of the substituting ligand, as evidenced by the consumption of additional molecular oxygen.

In a recent paper [8], Praliaud and co-workers reported the isolation of green solids from the reaction of copper(I) chloride with oxygen in chloroform containing pyridine at $\text{py}/\text{Cu} = 0.1\text{--}50$. Some of these solids were found to redissolve in this solvent mixture to give green solutions which were active catalysts in the oxidative coupling of 2,6-dimethylphenol. Solubility studies in pyridine/chloroform mixtures suggested the empirical formula $(\text{CuCl})_2\text{py}_2\text{O}$ (calc. 194; obsd. 183 ± 3 gm/mol), which approximates the copper/oxygen stoichiometry of eq. 1. However, electronic [8], ESR [8] and IR [9] spectral results were interpreted as indicating that these active solids did not consist of an equimolar mixture of CuCl_2py_2 and CuO. This conclusion

is supported by the following observations: 1) the solids redissolve to give green or green-brown solutions (depending on the pyridine mole fraction in the solvent mixture), whereas solutions of CuCl_2 in pyridine are blue and CuO is virtually insoluble in pyridine and 2) the solids were found to react slowly with water to give blue CuCl_2py_2 , as does the product solution from reaction 1 [4].

During the course of attempts to measure the stoichiometry and kinetics of the latter reaction in pyridine, we noticed different results on addition of aqueous solutions of various alkali metal salts to separated [4, 5] heated initiator solutions. Although no solids were precipitated on addition of aqueous lithium chloride, sodium, tungstate, potassium hexafluoroarsenate, sodium sulfate or sodium tetrafluoroborate, (the solutions simply changed from brown to blue due to reaction with water), addition of sodium tetraphenylborate and sodium carbonate gave brown, suspended particles. Moreover, addition of water to pyridine solutions from reaction 1 which contained excess lithium perchlorate also gave brown solid products. This paper reports an investigation of the properties of these solid derivatives.

Experimental

Reagents and Analytical Procedures

All materials were of reagent grade unless otherwise specified. Deionized, distilled water was fractionally redistilled from alkaline permanganate.

The procedures for synthesis, separation and analysis of the products of reaction 1 were as previously described [4, 5]. Separated and unseparated product solutions from reaction 1 which had been heated for various lengths of time [4] were used in derivative preparation. 2,6-Dimethylphenol was recrystallized twice from 40% v/v carbon tetrachloride-ethyl acetate (m.p. 46–47 °C).

Elemental analyses of solid samples were performed by Galbraith Laboratories, Knoxville, Tennessee.

Isolation of Solid Products

Sodium tetraphenylborate and sodium carbonate

Addition of 0.1 *M* aqueous solutions of sodium tetraphenylborate or sodium carbonate to heated and filtered [4] product mixtures from eq. 1 resulted in the formation of brown particles which were isolated by centrifugation. The blue supernatant solutions were discarded. The resulting solids were washed with water and dried overnight under vacuum.

Precipitation in the presence of lithium perchlorate

A brown perchlorate derivative was isolated from heated unseparated product mixtures (eq. 1) as follows. A slurry of 2.5 gm copper(I) chloride in 200

ml pyridine was oxidized with oxygen overnight [4]. A 20-ml portion of the resulting green-brown solution was heated in a sealed vial for 10 days at 60 °C and then filtered successively through glass sinters of coarse, medium and fine porosities. An equal volume of lithium perchlorate solution in pyridine (2 *M*) was added to the filtrate to give a deep brown solution. Water (30 ml) was then added dropwise to precipitate a brown solid. The supernatant solution was blue. The solid was washed with water until no chloride could be detected in the washings and dried under vacuum for 24 hours. Typical yield 0.41 g (sample 1). Repetition of the above procedure with all quantities halved gave 0.21 g of material (sample 2) with very similar analytical and solubility properties and infrared spectra (see Results).

An attempted preparation using a variation of the above method where a sample of the catalyst mixture in pyridine was added to an aqueous solution of lithium perchlorate gave a solid (sample 3) which was considerably darker and contained a higher percentage of copper and oxygen than the previous preparations (see Results).

Apparatus

All glassware to be used in reaction 1 was flame dried or heated in an oven at 100 °C for 1 hour to eliminate moisture. UV-visible spectra were determined with a Beckman DK-1A ratio recording spectrophotometer using 1 mm and 1 cm matched quartz cells. Infra-red spectra were recorded on a Perkin-Elmer 21 spectrophotometer and were calibrated using the polystyrene band at 1601.0 cm^{-1} . Raman spectra 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. Magnetic susceptibility measurements were made at Northeastern University on a Faraday balance constructed from a Cahn RG electrobalance and a Varian Model 4000 electromagnet. Inspection of the homogeneity of solid samples were made using a NMR Model 1000 Scanning Electron Microscope at a magnification factor of 3750.

Stoichiometry of Reaction of the Perchlorate Derivative with HCl

The stoichiometry of the reaction of the solid perchlorate derivative with HCl was determined by addition of a known amount of solid to a known excess of HCl and determination of the remaining acid by titration with standard sodium hydroxide using phenolphthalein as indicator. Potassium citrate (0.02 *M*) was added as a masking agent to prevent the precipitation of copper(II) at high pH. A correction for copper(II) was employed since the citrate complex of copper(II) was found to behave as a monoprotic acid under these conditions.

TABLE I. Experimental Data for the Reaction of the Perchlorate Derivative with HCl.^a

Exp.	HCl _I	Cu ^{II}	HCl _F ^b	Base ^c	Base/Cu ^{II} ^d
1	0.930	0.416 ^e	1.358	—	—
2	0.935	0.962 ^e	1.892	—	—
3	0.930	0.642 ^f	1.580	—	—
4	0.930	0.550 ^{f,g}	1.490	—	—
5	0.930	0.456 ^{e,h}	1.390	—	—
6	0.930	0.161 ⁱ	0.930	0.156	0.97
7	1.390	0.304 ^j	1.380	0.303	1.00
8	0.930	0.130 ^k	0.930	0.135	1.04
9	1.028	0.432 ^l	0.630	0.830	1.92
10	0.930	0.255 ^m	0.770	0.415	1.63

^aAll amounts are mmol. Subscripts are I = initial, F = final. ^bDetermined by titration with standard NaOH at [citrate] = 0.02M. For experiments 1–5 inclusive, the quantity in this column must be equal to the sum of those in the first two columns for the analytical procedure to be valid. ^cBase = HCl_I + Cu^{II} – HCl_F. This represents the amount of acid reacted with basic species present in the solid. ^dThis ratio represents the number of monoprotic basic species per copper atom in the solid derivative. The results for experiments 6–8 inclusive conform to the stoichiometry shown in eq. 2 or 3, while the ratio for expt 9 is consistent with the stoichiometry of eq. 4 (see text). ^eAdded as CuCl₂·2H₂O. ^fAdded as Cu(NO₃)₂·3H₂O. ^g[py] = 0.25 M. ^h[py] = 0.02 M. ⁱ52.6 mg of sample 2. ^j99.1 mg of sample 2. ^k43.9 mg of sample 1. ^l35.2 mg of solid (78.0% Cu) obtained by precipitation with Na₂CO₃ (see text). ^m50.3 mg of sample 3.

Results

Solids from Treatment with Aqueous Sodium Tetraphenylborate and Sodium Carbonate

IR spectra of the black solids isolated as described in the Experimental Section exhibited bands at 455 and 535 cm⁻¹ with no evidence for the presence of pyridine. Elemental analysis gave 78.0% Cu, consistent with the formulation CuO (calc. 79.9% Cu).

Solids from Treatment with Lithium Perchlorate

The brown solids isolated as described in the Experimental Section contained no detectable chloride, were visibly unaffected by prolonged vacuum drying and were found to be insoluble in H₂O, py, dimethylsulfoxide, dimethylformamide, acetone and acetonitrile. However, addition of dilute, aqueous HCl or HClO₄ in water or pyridine caused rapid decomposition to copper(II) both in the presence and absence of oxygen. Inspection of the solids under high magnification showed them to be homogeneous. All the samples were inactive as catalysts for the oxidative coupling of 2,6-dimethylphenol over a period of 5 hours under standard [4] conditions.

Elemental analysis of sample 1 gave 19.5% Cu, 10.9% Cl, 8.5% N (calc. for Cu₂(py)₄(ClO₄)₂O: 19.3% Cu, 10.6% Cl, 8.5% N), whereas sample 2 analyzed more satisfactorily as Cu₂py₄(ClO₄)₂O·H₂O (obsd. 18.8% Cu, 10.5% Cl, 8.2% N, 35.5% C, 3.3% H, ≤0.01% Li; calc. 18.8% Cu, 10.4% Cl, 8.3% N, 35.5% C, 3.3% H). Sample 3 contained a higher proportion of copper (32.0% Cu, 32.5% C, 3.15% H, 7.0% N, 11.5% Cl) but its spectral and other properties were identical to those of samples 1 and 2. Gravi-

metric analysis indicated that all three samples resulted from the quantitative precipitation of species I (eq. 1) in the presence of lithium perchlorate.

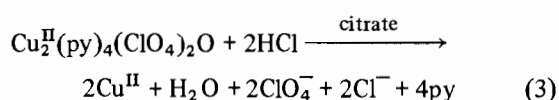
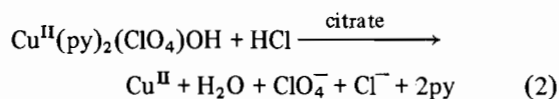
The following bands were observed in the infra-red spectrum (KBr) [10]: 3000–3100 (w), 1600 (s), 1485 (m), 1440 (s), 1240 (w), 1220 (s), 1050–1120 (s), 930–950 (w), 760 (s), 695 (s), 620 (s), 490–530 (w) and 435 (m) cm⁻¹. The following bands were observed in the Raman spectrum of the solid: 947 (s), 962 (w), 1269 (w), 1377 (w), 2068 (s), 2916 (s). The uv–visible spectrum of the solid in halocarbon grease between silica plates showed no maxima in the region 2400–400 nm. Magnetic susceptibility measurements yielded an effective magnetic moment at room temperature of 2.1 ± 0.1 B.M. per mole of Cu (sample 2, based on 18.8% Cu).

Stoichiometry of the Reaction of Isolated Solids with HCl

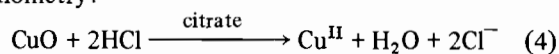
The results of the stoichiometric measurements for the reaction of weighed amounts of the perchlorate derivative with excess HCl are presented in Table I. Since the copper(II) produced in this reaction would be precipitated as the hydroxide during the titration with base, a masking agent was added to prevent this precipitation. Potassium citrate was chosen for this purpose because the citrate ion forms strong complexes with copper(II) [11] and the acid dissociation constants (pK₁ = 3.08, pK₂ = 4.74, pK₃ = 5.40 at 18 °C) [12] of citric acid are all well below the pK of phenolphthalein (pK_a ~ 9) [12]. Addition of weighed amounts of CuCl₂·2H₂O and Cu(NO₃)₂·3H₂O to excess HCl in the presence of citrate ion (0.02 M) followed by titration with base indicated

that one proton per copper(II) complex is titrateable under these conditions (Exp. 1–3, Table I) [13]. Since copper(II) is produced in the reaction of the perchlorate derivative with acid, the total amount (mmol) of titrateable acid is equal to the sum of the copper(II) produced and the added HCl. Added pyridine ($pK_a = 5.2$) [12] has no effect on this result (Exp. 4–5, Table I).

The reaction of samples 1 and 2 with HCl resulted in the consumption of acid after correction for the copper(II) produced (see above) (Exp. 6–8, Table I), consistent with either of the following stoichiometric reactions.



A similar measurement (Exp. 9, Table I) with the black solid produced on treatment of the heated reaction mixture (eq. 1) with sodium carbonate (see above) gave results (after correction for the copper(II) produced) consistent with the following stoichiometry:



Sample 3, which was prepared from a predominantly aqueous medium and gave very different elemental analyses (see above), reacted with HCl according to a stoichiometry which is between those for reactions 2 (or 3) and 4 (Exp. 10, Table I), confirming that it contains a higher proportion of CuO than do samples 1 and 2.

Discussion

A definite assignment of structure for the initiator species in pyridine depends on the isolation and characterization of solid, active derivatives. Unfortunately, evaporation of the solvent from solutions of separated [5] initiator species or addition of non-coordinating solvents such as benzene leads to insoluble, catalytically inactive CuO [4, 5]. The present work shows that the addition of precipitating agents (other than LiClO_4) to initiator solutions in aqueous pyridine results in either formation of blue solutions on standing or in conversion to CuO. The formation of blue solutions (copper(II)) is due to the slow reaction with water [4].

The precipitation of a solid from heated initiator solutions in the presence of LiClO_4 at low water/pyridine ratios is different in that the isolated precipitate

contains both pyridine and perchlorate. Although direct elemental analyses of the solid suggest that it is a copper(I) complex (oxygen was not determined directly, but by difference), the magnetic properties indicate that it is not.

Treatment of CuO precipitates with HCl, followed by titration with base in the presence of citrate, is a reliable analytical method for determination of the oxygen content of these products. The stoichiometry of reaction of the solids with acid (eq. 2–3) indicates the presence of either O^{2-} or OH^- in the empirical formula $\text{Cu}_2(\text{py})_4(\text{ClO}_4)_2\text{O} \cdot n\text{H}_2\text{O}$ ($n = 0$, sample 1 or $n = 1$, sample 2).

It is not possible to distinguish between a pure compound and an equimolar mixture of CuO and $\text{Cu}(\text{py})_4(\text{ClO}_4)_2$ on the basis of the elemental and stoichiometric analyses. However, the infra-red spectra are indistinguishable from those expected for the mixture. The lack of three of the bands in the Raman spectrum expected for an ionic ClO_4^- (T_d symmetry, 460, 636, 930, 1028 cm^{-1}) [14] is also consistent with the presence of $\text{Cu}(\text{py})_4(\text{ClO}_4)_2$, in which the perchlorate anion is reported to be in C_{3v} symmetry [15]. If this sample is indeed a mixture it is not surprising that the ratio of the constituents can be varied (sample 3). It is notable, however, that in two of the isolated samples the ratio is equimolar and that it accounts for 100% of the copper initially present as the initiator fraction from the products of reaction 1.

The homogeneity of the particles obtained from aqueous pyridine/lithium perchlorate media indicates that disproportionation of initiator species takes place under these conditions. A higher proportion of water in the precipitating medium causes solubilization of some $\text{Cu}(\text{ClO}_4)_2$ and results in a higher percentage of CuO in the solid (sample 3). It is apparent that the high stability of $\text{Cu}(\text{py})_4^{2+}$ centers in the presence of solid state perchlorate leads to very effective removal of stabilizing pyridine [5] from the original initiator species. The particles isolated from lithium perchlorate media (even in the presence of a large excess of pyridine) must be coated with a layer of CuO which renders them insoluble in all our test solvents except for mineral acids. This insolubility accounts for a lack of catalytic activity in oxidative coupling reactions.

Irrespective of the chemical identity of the solids obtained from lithium perchlorate media, the ratio of copper to oxygen is now half of that in the original initiator, indicating loss of O^{2-} in the reaction with perchlorate (eq. 5).



Since loss of O^{2-} must occur in order to produce a copper(II) derivative containing perchlorate, this

observation does not lead to a unique identity for the initiator species.

Comparison of the Solids Obtained from LiClO₄/py/-H₂O and CHCl₃/py Media

The significant difference between the present results and those of Praliaud *et al.* [8, 9] for CHCl₃/py media is that some soluble initiator species seem to survive the precipitation procedure in the latter case. The spectral data of Praliaud [8, 9] for precipitates from CHCl₃/py media are not very reproducible, although they do seem to depend on the CHCl₃/py mol fraction in the precipitating medium [9]. However, the differences between the observed spectra for these green, solid products and those expected for equimolar mixtures of CuO and Cu₂-Cl₂ are very small. A definite structure for the initiator species from reaction 1 cannot be assigned with confidence on the basis of these spectral data [8, 9].

Addition of chloroform to unseparated catalyst mixtures from reaction 1 precipitates most of the copper present in the product mixture and thus the observed ratio of copper to oxygen in the solid would be the same as that initially present in the solution (*i.e.* Cu/O = 2). By contrast, only the "CuO" fraction from reaction 1 is precipitated by LiClO₄ in aqueous pyridine. The properties of the solid precipitates are consistent with their formulation as a mixture of CuO and Cu(py)₄(ClO₄)₂, produced by disproportionation of (CuO)_n initiator species.

We feel that the present and previous [8] investigations convincingly demonstrate the paramount importance of non-oxidizable, stabilizing ligands such as pyridine in the maintenance of soluble, active copper-oxygen initiators from reaction 1. In addition, our work indicates, for catalyst mixtures with the stoichiometry of reaction 1, that the CuX₂ coproduct has a high solid state affinity for the stabilizing ligand py in the presence of ClO₄⁻ anions. The possibility that a similar effect will lead to disproportionation should not be overlooked in future attempts to isolate active initiator species from the products of reaction 1.

Acknowledgments

This work was supported by grants from the Research Corporation, the Donors of the Petroleum Research Fund of the American Chemical Society, Biomedical Research Grant No. RRO7143 from the Department of Health, Education and Welfare and the National Science Foundation (Grant CHE-7522453), which are gratefully acknowledged. We thank Drs. Charles E. Kramer, Robert W. Slaven and M. F. El-Shazly for valuable discussions and Raymond Hoover, Deborah Kazlowskas, N. Nakashima and Professors W. M. Reiff and T. R. Tuttle for experimental assistance.

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