hydrosol particles. With similar decreases in $\nu(CO)_{ads}$ at basic pH and large increases in $d\nu/d\psi_0$ at high pH (see Table I), it appears that such competition for CO adsorption sites may also operate in the PVA-protected Rh sol/CO system.

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Registry No. CO, 630-08-0; Rh, 7440-16-6; poly(vinyl alcohol), 9002-89-5.

Selective Leaching of Copper and Barium from the $YBa_2Cu_3O_{7-x}$ Superconductor by Chelating Diamines

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Rapid selective leaching of Cu and Ba from the superconductor $YBa_2Cu_3O_{7-x}$ (1–2–3) is effected by exposure of the solid to aqueous and mixed H_2O/MeOH solutions of ethylenediamine (en). Inductively coupled plasma emission spectroscopy revealed that virtually all of the Cu and most of the Ba are in the solution phase; almost all of the Y is in the solid residue resulting from the reaction. X-ray diffraction analysis and IR spectroscopy are consistent with the solid product being primarily amorphous $Y(OH)_3$. The solid also contains small quantities of $BaCO_3$ and Y_2BaCuO_5(2–1–1); the $BaCO_3$ is formed by reaction of Ba^{2+} ions in the leaching solution with CO_2, while the 2–1–1 was initially present as an impurity in the 1–2–3 samples employed and is comparatively unreactive toward the leachant. The leaching process was monitored spectrophotometrically through the formation of the purple *trans*-diaquobis(ethylenediamine)copper(II) complex. Kinetic studies reveal that the initial reaction rate is directly proportional to the 1–2–3 macroscopic apparent surface area. In mixed H_2O/MeOH solutions the leaching rate follows a first-order rate law with the concentrations of water (2.5–30 M range in 2.0 M en) and ethylenediamine (0.12–2.5 M range in 30 M water). Concentrated en solutions gave corrosion rates of up to $\sim$0.2 μm/min at room temperature, with rates increasing to $\sim$1 μm/min at 65 °C. The temperature dependence of the reaction rate yields an apparent activation energy of 55 ± 5 kJ/mol between 25 and 65 °C. Substitution of D_2O for H_2O in the leachant solution roughly halves the reaction rate at room temperature. Chelation appears to supply a significant driving force for the reaction: 1,2-diaminopropane, 1,3-diaminopropane, *sym*-dimethylenediamine, triethylenediamine, and 2,2′-bipyridine also serve as leachants. The leaching rate is negligible at room temperature with a variety of monoamines and nonchelating diamines.

Introduction

Despite the enormous interest in the superconductor $YBa_2Cu_3O_{7-x}$ (1–2–3), there have been few systematic studies of the reactivity of this compound under ambient conditions. The electrochemical behavior of 1–2–3 in various aqueous media has been investigated.[1,2] Also, aqueous solutions of EDTA have been used to decompose 1–2–3, presumably by chelating the constituent cations, and can etch micropatterns into the solid.[3] Among the reactions that have been characterized are those with water and CO_2, which lead to nonsuperconducting products.[4-9] Yan et al. have proposed that the reaction with water proceeds by

$$2YBa_2Cu_3O_7 + 3H_2O \rightarrow Y_2BaCuO_5 + 3Ba(OH)_2 + 5CuO + \tfrac{1}{2}O_2 \quad (1)$$

with the $Ba(OH)_2$ undergoing further reaction with CO_2 to yield $BaCO_3$:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O \quad (2)$$

In this paper we provide evidence that chelation by aqueous and mixed H_2O/MeOH ethylenediamine (en) solutions can rapidly and selectively solubilize Cu and Ba cations from the 1–2–3 lattice at room temperature, resulting in a Y-rich, insulating solid residue. The reaction, which can be monitored spectrophotometrically, has been measured to proceed at a rate of up to $\sim$0.2 μm/min at room temperature. We demonstrate herein that the reactivity depends strongly on solvent, temperature, and amine, permitting the rate to be tuned over several orders of magnitude. The ability to control etching rate in this manner may be useful in device fabrication schemes employing 1–2–3.

Experimental Section

Materials. Unless otherwise specified, all experiments involving 1–2–3 were conducted with powder or sintered pellets obtained from HiT_c Superconco, Inc., Lambertville, NJ, that contained nearly exclusively single-phase 1–2–3 as shown by X-ray powder diffraction. Additional sample details were provided by

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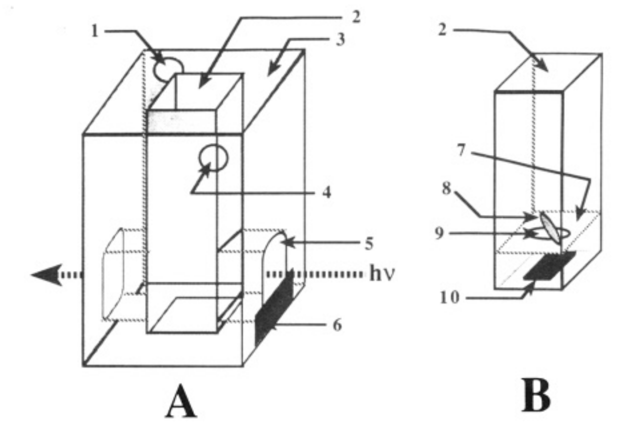

Figure 1. Schematic of the cell used for kinetic studies under thermostatic conditions. A: Diagram of the cuvette in a water jacket, illustrating that the beam path passes only through the cuvette. B: Diagram of the cuvette showing the arrangement of the sample used for the kinetics experiments. The cell components are as follows: (1) thermostated water outlet; (2) 1.0-cm path length, 4.5-mL quartz cuvette; (3) polycarbonate water jacket; (4) thermostated water inlet; (5) window through water jacket to cuvette; (6) black tape used to partially block beam; (7) polycarbonate shield, separating the sample from the stir bar; (8) SmCo alloy, epoxy-coated magnetic stir bar; (9) circulation hole to sample; (10) 1–2–3 sample with exposed face pointed up.

the manufacturer: The density of the bulk 1–2–3 samples was roughly 82% of the theoretical value; the powder samples were received finely ground with 90% of the particles having diameters of less than 5 μm. An additional 1–2–3 sample was prepared in our laboratory by repeated grinding and calcining.

A sample of Y_2BaCuO_5 (2–1–1) was obtained through the courtesy of Mr. Mike Field and Prof. D. C. Larbalestier. Synthesis of 2–1–1 was accomplished with the stoichiometric amounts of Y_2O_3, $BaCO_3$, and CuO needed for a 10.0-g batch of product. The powders were ground together, calcined at 880 °C for 24 h in an air flow of 3.0 sccf/h, furnace cooled, reground, and heated a second time under the same conditions. X-ray analysis showed nearly pure 2–1–1 phase with traces of $BaCO_3$ and possible traces of the other starting materials. An authentic sample of $Y(OH)_3$ was prepared by literature procedure.[10]

Reagent grade compounds were used without further purification. Ethylenediamine (en), 1,2-diaminopropane, 1,3-diaminopropane, *sym*-dimethylenediamine, triethylenetetramine, 2,2′-bipyridine, 1,2-phenylenediamine, *n*-propylamine, *n*-butylamine, dimethyl sulfoxide, acetonitrile, $BaCO_3$, Y_2O_3, and deuterium oxide (99%) were obtained from Aldrich Chemical Co. Dimethylformamide was obtained from J. T. Baker Inc. 1,6–Diaminohexane was obtained from Eastman Kodak Co. Concentrated HNO_3 was obtained from EM Science. $Cu(NO_3)_2 \cdot 3H_2O$ was obtained from Fischer Scientific Co. Absolute methanol was obtained from Mallinckrodt Specialty Chemicals. 1,4-Diaminobutane was obtained from Pfaltz and Bauer, Inc. CuO was obtained from ProChem, Inc. 2,9-Dimethyl-1,10-phenanthroline was obtained from G. Frederick Smith Chemical Co.

Initially, en was distilled over KOH before use; however, no difference in reactivity was observed in the products and kinetics of the reaction without distillation, and the procedure was abandoned. Millipore water was used for all experiments, which were performed at room temperature in air unless otherwise noted.

Equipment. All X-ray data were obtained with a Nicolet I2/V polycrystalline X-ray diffraction system using Cu K_α radiation. Infrared spectra were taken on a Mattson Polaris NU-10000 FT-IR spectrometer. All kinetic data were acquired using a Cary 17-D UV–vis–near IR spectrophotometer and fitted with the cell shown in Figure 1, which provided thermostatic control. The temperature of the cell was controlled to ±0.5 °C by a Precision Scientific Group R20 constant-temperature bath and was monitored with a mercury thermometer to ±1.0 °C. Electronic spectra were also obtained using a Hewlett-Packard 8452 A diode array UV–vis spectrophotometer. Inductively coupled plasma (ICP) microanalysis data were acquired with a Leeman Labs Inc. ICP 2.5-kW Plasma-Spect, equipped with a Minuteman 0.5-m monochromator and a 1P28A photomultiplier tube.

Solvent and Leachant Studies. The reactivity of various amines in water toward 1–2–3 was determined qualitatively by visually watching for evidence of copper leaching via the formation of a colored Cu(II) complex. For all systems, 0.25 g of 1–2–3 powder was placed in 50-mL portions of the leaching solutions. The solutions were stirred continuously and monitored for 96 h. Stirring was periodically stopped to determine whether Cu was being leached. All amines miscible with water were used at concentrations of ~2.5 M. Solid and immiscible amines were used as saturated solutions. For all systems where no reaction was noted, X-ray analysis was done on the 1–2–3 solid to verify that no structural changes had occurred. For the most reactive amines—en, 1,2-diaminopropane, and 1,3-diaminopropane—the leaching reaction was run to completion as described in the characterization studies (see below) and X-ray analysis was performed on the residue.

For en, reactivity was also investigated in nonaqueous solvents using the aforementioned procedure.

Product Characterization Studies. To determine the decomposition products of the leaching reaction, ~1.5 g of 1–2–3 powder was added to 50 mL of a solution that was prepared from 167 mL of en, 540 mL of water, and 293 mL of MeOH, corresponding to concentrations of ~2.5 M en/30 M H_2O/7.2 M MeOH, assuming a total solution volume of 1000 mL. This will hereafter be referred to as the standard leaching solution. These mixtures were allowed to react with continuous stirring using a glass stir bar (a Teflon stir bar was physically abraded by the gritty 1–2–3 powder) for 24 h at room temperature. The solution was then centrifuged, and the leachate decanted for ICP analysis. The remaining solid was then added to 50 mL of fresh leaching solution, and the above leaching procedure was repeated until negligible quantities of leached metals were found in the leachate by ICP; typically this required 96 h or four fresh solutions. At this point, the solid residue was washed twice with Millipore water and dried under vacuum (10^{-3} Torr). A portion of the powder was dissolved in nitric acid, and its ICP analysis obtained. The residue was also analyzed by X-ray powder diffraction as well as by IR spectroscopy of a KBr pellet containing the solid. Identical X-ray analyses were obtained when the standard leaching solution was used with two different batches of 1–2–3 powder from the supplier as well as with the sample we had synthesized. The ICP analyses employed standards containing Ba, Cu, and Y in the leaching medium that were made by dissolving $BaCO_3$, $Cu(NO_3)_2 \cdot 3H_2O$, and Y_2O_3 in solutions that had been acidified by addition of HNO_3. The leaching solution was acidified before analysis to prevent precipitation of $BaCO_3$, which would cause the Ba value to be low. Exhaustive leaching of 1–2–3 was also carried out with leaching solutions containing 1,2-diaminopropane, or 1,3-diaminopropane in place of en. Qualitatively, similar reactivity was observed, but only X-ray analysis of the residue was performed.

Reaction Kinetics. Leaching rates were determined, using the apparatus shown in Figure 1, as a function of apparent sample surface area; water and en concentration in the leaching solution; temperature; and with D_2O used in place of H_2O.

In the D_2O experiment, the water in the leaching solution (~2.0 M en/30 M H_2O/8.1 M MeOH) was replaced with 99% D_2O. This results in replacement of roughly 80% of the exchangeable hydrogen atoms with deuterium. The sample was etched, and then leaching was first done with the H_2O-based solution. While still in the reaction cell, the sample was both rinsed thoroughly and then leached with the D_2O-based solution; finally, it was again rinsed thoroughly and leached, this time with the H_2O-based solution. The sample was removed and re-etched. The entire leaching cycle then was repeated and shown to yield reproducible results within experimental error.

Rates were estimated based on the assumption of exclusive formation of the purple *trans*-diaquobis(ethylenediamine)copper(II) complex. A calibration curve was constructed from standards made by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ in the leaching solutions and employing the method of successive dilutions; the

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standards covered the concentration regime 0.10–0.000 040 M. Absorption spectra (380–820 nm) were taken of standards for copper in ~0.50 M en/30 M H_2O/10.6 M MeOH, ~2.0 M en/30 M H_2O/8.1 M MeOH, and ~4.0 M en/30 M H_2O/4.8 M MeOH (the MeOH concentration is adjusted to provide the desired en and H_2O concentration) leaching solutions at 25, 35, 45, 55, 65, and 75 °C using the diode array spectrophotometer. The absorbance peak was very broad and generally occurred between 560 and 575 nm; typical absorptivities were in the range 64–83 M^{-1} cm^{-1} for the solutions used. Absorption changes were generally monitored at 570 nm; the standards gave excellent fits to Beer's law at this wavelength, with correlation coefficients exceeding 0.9999.

Several trials of each experiment were run using samples cut from the sintered pellets, that had typical dimensions of ~7 × 4 × 1 mm^3; dimensions were determined with a micrometer to ±0.05 mm. The samples were coated on all but one rectangular face with clear epoxy (Dexter Corp.), which was cured for 12 h at 100 °C. The epoxy overlying the exposed face was sanded down to the sample surface, which was then polished with 1-μm lapping paper. At the start of each series of trials, the 1–2–3 sample was etched for 2 min in a 10% Br_2/isopropyl alcohol solution, rinsed with MeOH, and then dried under flowing nitrogen.[11-13] To minimize splattering, the bromine was added slowly with complete mixing, and a fresh solution was made for each etch.[14] Generally, a scattering of results was found for the first few trials after an etch, with later trials yielding reproducible results that were used for the kinetic analysis.

In using the cell shown in Figure 1, the 1–2–3 sample was placed in the bottom of the cuvette with the exposed face up, and a polycarbonate protector was placed over it to guard against mechanical abrasion by the stir bar. The cell was then mounted in the spectrometer, 3.0 mL of the desired leaching solution was pipetted into the cell, and the solution was stirred for 1 min before spectroscopic monitoring was begun. The absorbance at 570 nm was then monitored vs time for 10 min. When experiments were conducted above room temperature, the leaching solution was brought to the cell temperature before adding it to the cell by immersing the solution in the constant-temperature bath's reservoir for 30 min. Vigorous stirring was used throughout all the trials at a rate that ensured the reaction rate was not limited by mass transport. After the trials with a particular sample of 1–2–3 were complete, the sample was removed. The cell was rinsed three times with the appropriate leaching solution, and then the absorbances for the applicable series of standards were measured.

Results and Discussion

In sections below we describe the relative reactivity of 1–2–3 toward various amines, the reaction products obtained with aqueous and H_2O/MeOH solutions of ethylenediamine (en), and the dependence of the reaction rate on experimental parameters.

Relative Reactivity. The leaching of Cu from 1–2–3 to yield colored copper(II) complexes provides a means for qualitatively assessing relative leaching rates of amines. Our data provide evidence that chelation provides a substantial driving force for the decomposition of 1–2–3 in aqueous solution. We found that en provides the most rapid reaction, with 1,2-diaminopropane, 1,3-diaminopropane, *sym*-dimethylenediamine, and triethylenetetramine, which can also chelate to Cu(II),[15] exhibiting comparable reactivity. The slower rates found with the other potential chelating agents, 2,2′-bipyridine, 2,9-dimethyl-1,10-phenanthroline, and 1,2-phenylenediamine, could reflect their increased steric demands and decreased basicity relative to en.[16] None of the monoamines (*n*-propylamine, *n*-butylamine, *n*-pentylamine) or diamines that are less likely to chelate (1,4-diaminobutane and 1,6-diaminohexane) showed evidence of appreciable reactivity at room temperature, reinforcing the notion that chelation serves to drive the leaching reaction.

Table I. Reaction Stoichiometry[a]

(A) Distribution of Elements into the Leachant and Residue[b]

element	initial moles in 1-2-3	moles in leachant[c]	moles in residue[c]
Y	0.002 32	0.000 046 (2.0%)	0.002 2 (95%)
Ba	0.004 64	0.004 4 (94%)	0.000 46 (10%)
Cu	0.006 97	0.007 2 (104%)	0.000 14 (2.0%)

(B) Composition of the Residue[d]

component of residue	moles in residue	calculated mass,[h] g
Y_2BaCuO_5 (2-1-1)	0.00014[e]	0.064
$BaCO_3$	0.00032[f]	0.063
$Y(OH)_3$	0.0019[g]	0.27[i]

[a] Decomposition of a 1.547 ± 0.002 g sample of 1-2-3 starting material by the standard leaching solution of ~2.5 M en/30 M H_2O/7.2 M MeOH. The mass of the residue was 0.388 ± 0.002 g. [b] Moles were determined by ICP analysis; the error is estimated to be about ±5%. [c] Moles of the indicated element appearing in the leachant and residue. The percent values shown parenthetically indicate the fraction of the initial moles available that each result represents. [d] Components of the residue determined by X-ray diffraction are Y_2BaCuO_5 (2-1-1) and $BaCO_3$; $Y(OH)_3$ was inferred as described in the text. [e] The moles Cu in the residue (part A of the table) are treated as being present exclusively as 2-1-1. [f] Moles of $BaCO_3$ is calculated as: [total moles of Ba in residue (from part A of table)] − [moles of Ba in 2-1-1]. [g] Moles of $Y(OH)_3$ is calculated as: [total moles of Y in residue (from part A of table)] − [moles of Y in 2-1-1]. [h] Masses were calculated by multiplying the molar amounts determined in the previous column by the gram formula weights for the compounds. [i] Subtracting the masses of the two known components in the residue, viz., 2-1-1 and $BaCO_3$, from the total mass of the residue (0.388 g) leaves 0.261 g unaccounted for. This is close to the value of 0.27 g entered for the "calculated mass" of $Y(OH)_3$ in the table, which was calculated by assuming that the remaining component of the residue is exclusively $Y(OH)_3$. The agreement in the two values supports the identification of the remaining residue as a single component consisting of amorphous $Y(OH)_3$.

Having established the rapid reactivity of en in water, we investigated the role of the solvent in promoting reactivity. A variety of polar solvents that were miscible with en were investigated, viz., methanol, dimethyl sulfoxide, acetonitrile, and dimethylformamide, yet in each case no evidence of reaction could be seen even after several days. Water thus appears to be critical to the ability of en to enhance decomposition of 1–2–3, presumably by promoting solubilization of the reaction products.

Reaction Products. To independently vary en and H_2O concentrations for later kinetics experiments, all subsequent experiments were conducted in H_2O/MeOH solutions. A standard leaching solution of ~2.5 M en/30 M H_2O/7.2 M MeOH was used to determine the products of the leaching reaction.

Exhaustive leaching of 1–2–3 was carried out with the standard leachant and with solutions in which en was replaced by 1,2-diaminopropane or 1,3-diaminopropane. All three of these leaching reactions resulted in a purple coloration of the leaching solution and in greenish solid residues having similar X-ray diffraction patterns. This

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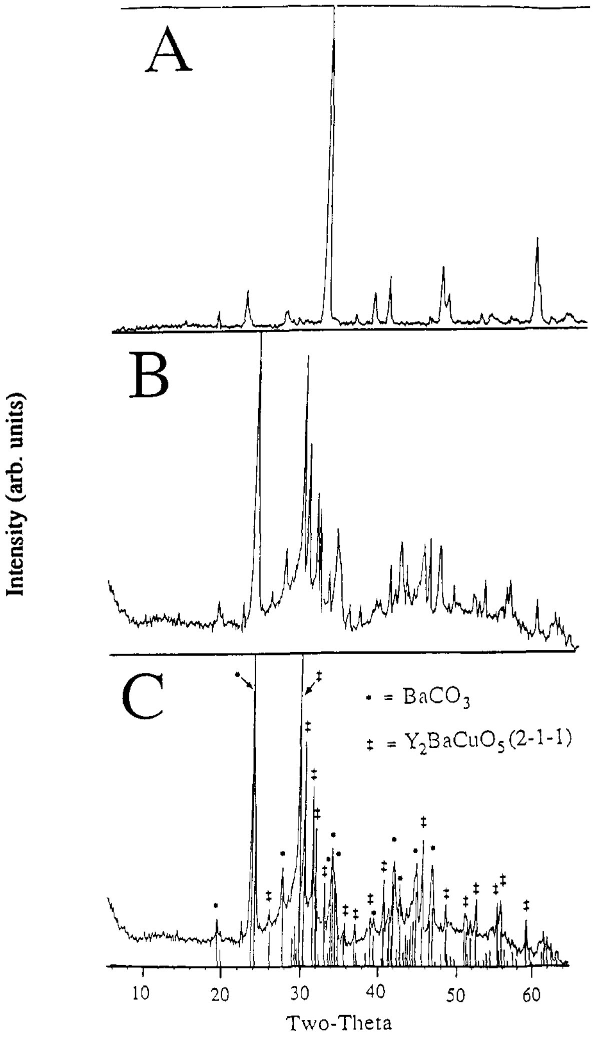

Figure 2. X-ray powder diffraction patterns of a typical sample during a leaching trial. (A) Pattern of the nearly pure 1–2–3 sample before leaching. (B) Pattern of the solid residue after exhaustive leaching by the standard en leaching solution (96 h). (C) Pattern of the solid residue with peaks matched to standard JCPDS phases.[19]

suggests that essentially the same reaction occurs in all three solutions.

For quantitative product analysis, only the standard leaching solution containing en was employed. In these experiments, both the combined purple leaching solutions and the final greenish solid residue were analyzed. A slight fizzing was often noted at the start of the reaction and has previously been attributed to oxygen release.[8,17,18]

The leaching solutions were analyzed by ICP, which revealed that virtually all of the Cu, about 90% of the Ba, and no Y were contained therein, as shown in Table I. This result is qualitatively similar to that seen by others in the electrochemical dissolution of a 1–2–3 electrode in strongly alkaline aqueous media.[2]

Powder X-ray diffraction of the residue (Figure 2) established the identity of two products, viz., $BaCO_3$ and Y_2BaCuO_5 (2–1–1).[19] The $BaCO_3$ results from reaction of Ba^{2+} in solution, presumably as $Ba(OH)_2$, with CO_2 (eq. 2): a white precipitate appears over time, and repetition of the leaching experiment under a N_2 atmosphere results in markedly retarded reactivity. Formation of the carbonate may thus provide some of the driving force for the reaction and represents a source of variable stoichiometry in the reaction products.

We have no evidence that the 2–1–1 phase is a reaction product; rather, we believe that it is simply present from the start of the reaction as a minor impurity in the 1–2–3 samples, with its diffraction peaks dwarfed by those of 1–2–3.[20] Moreover, when authentic powdered samples of 2–1–1 are placed in the leaching solution, they show no evidence of reactivity over a period of several days. The 2–1–1 lattice is thus considerably less reactive than 1–2–3, perhaps reflecting the greater lattice energy of this phase.

Although $BaCO_3$ and 2–1–1 account for all of the X-ray diffraction peaks observed (Figure 2), quantitative ICP analysis, obtained by dissolving the residue in HNO_3, indicated that they account for only about 30% of the residue's total mass (Table I). Since a negligible amount of Y was found in the leaching solution and only a small fraction of the total Y available occurred in the 2–1–1 phase identified by X-ray diffraction, it must be present as an amorphous solid making up the bulk of the residue's mass.

Possible Y-containing products are the oxide, hydroxide, and carbonate. Of these, the most likely solid is $Y(OH)_3$, which XPS results had suggested was a product in the reaction of 1–2–3 with water and which is known to occur in an amorphous form.[7,9,10,21,22] Analysis of the residue by IR spectroscopy is consistent with this assignment, Figure 3, but not definitive: Unfortunately, the strong sharp peak at 3617 cm^{-1} in $Y(OH)_3$ does not appear in the spectrum of the residue. If present, it is masked, presumably by absorption due to 2–1–1 and/or water. The sharp peak at 1385 cm^{-1} in the residue is, however, seen in the spectrum of an authentic sample of $Y(OH)_3$. The relatively broad absorbance around 1455 cm^{-1} and the sharp peaks at 2452, 1750, 1060, 856, and 693 cm^{-1} correspond to peaks seen in the spectrum of $BaCO_3$.

As a further test for the presence of $Y(OH)_3$, the residue was heated in a dry oxygen atmosphere at 650 °C for 72 h to attempt to form the oxide and to decompose any organics. The temperature was, however, low enough that Y_2O_3, $BaCO_3$, and 2–1–1, if present, would not react.[23] After heating, X-ray analysis showed the bulk of the material was indeed now Y_2O_3 with small amounts of $BaCO_3$ and 2–1–1 remaining.

Additional evidence for $Y(OH)_3$ comes from the ICP analysis of Table I: The formula weight of the part of the residue's mass that is unaccounted for by $BaCO_3$ and 2–1–1 is consistent with being that of $Y(OH)_3$ if it is assumed that (1) all the Cu in the residue is present as 2–1–1, (2) all Ba in the residue is present only as 2–1–1 and $BaCO_3$, and (3) the balance of the residue consists of a single component containing all of the Y not present in the 2–1–1 component.

Collectively, if we treat the 2–1–1 phase as an unreactive impurity, $Ba(OH)_2$ as the initial Ba-containing product, and assume all the Cu is present as the *trans*-$[Cu(en)_2(H_2O)_2]^{2+}$ complex, our data are consistent with the fol-

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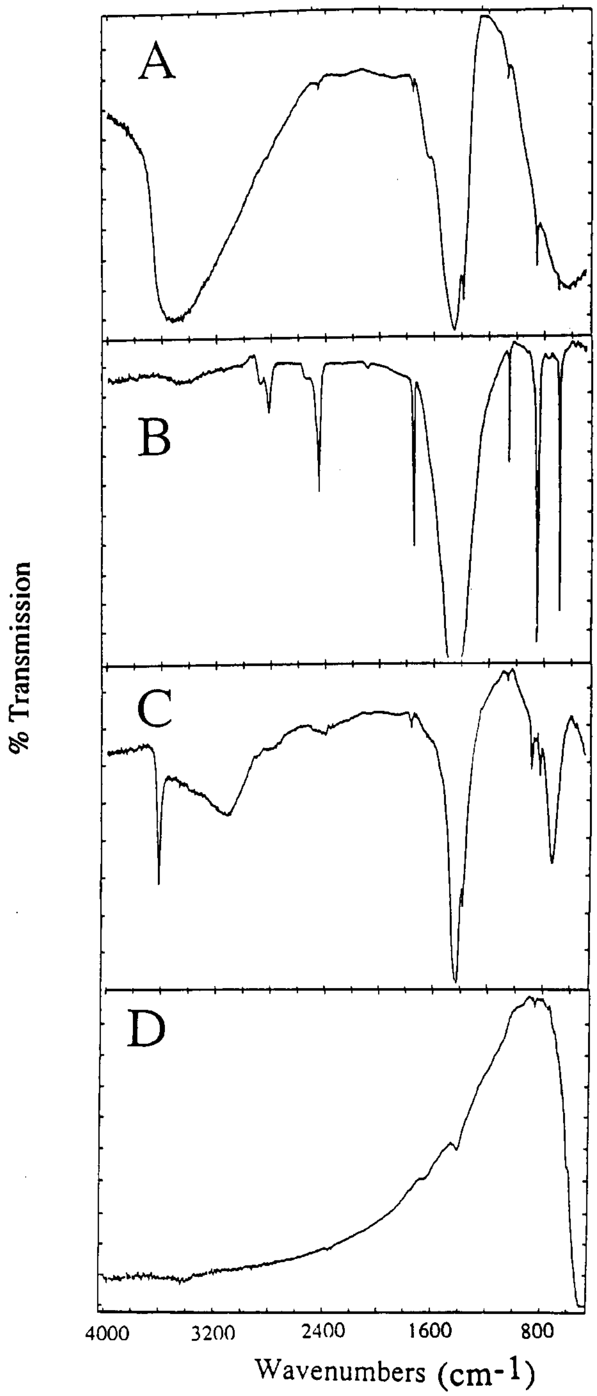

Figure 3. Infrared spectra of a typical residue and several standards. (A) Spectrum of the solid residue after exhaustive leaching by the standard en leaching solution (96 h). (B) Spectrum of an authentic $BaCO_3$ sample. (C) Spectrum of $Y(OH)_3$, prepared as described in the Experimental Section. (D) Spectrum of the 2-1-1 phase, prepared as described in the Experimental Section.

lowing reaction stoichiometry, where water, oxygen, and hydroxide ion have been added to balance the equation:

$$YBa_2Cu_3O_7(s) + 12.5H_2O + 6en \rightarrow 2Ba(OH)_2 + 3[Cu(en)_2(H_2O)_2]^{2+} + Y(OH)_3(s) + 0.25O_2 + 6OH^- \quad (3)$$

Kinetic Results. Formation of the purple *trans*-diaquobis(ethylenediamine)copper(II) complex, which should be the dominant Cu-containing complex present in the leaching solution,[24-26] provides a spectroscopic handle on

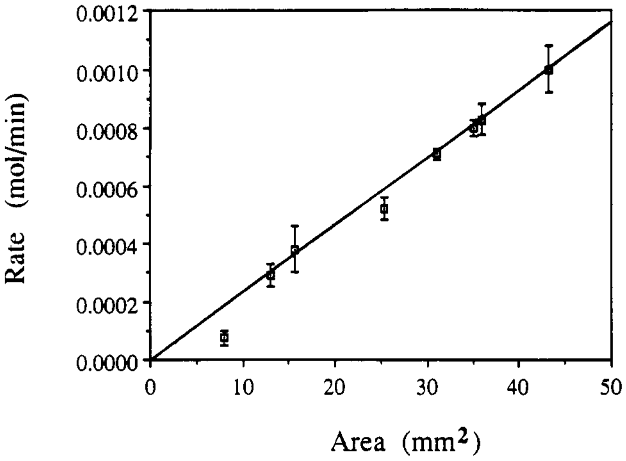

Figure 4. Dependence of 1-2-3 leaching rate (mol of Cu/min) on apparent sample surface area. The leaching solution was ~2.0 M en/30 M H_2O/8.1 M MeOH, and the reaction was conducted at room temperature. The surface area was determined from the macroscopic dimensions. The values shown are not corrected for surface roughness and are the averages of several, typically 3–6, trials. The error bars are taken as standard deviations of the results within a group of trials.

the progress of the leaching reaction. In interpreting kinetic measurements, we note that we are using highly porous samples, having a density of ~82% of the theoretical value, and that the samples are polycrystalline, meaning that we are obtaining an average for the crystallographic faces that are present.

Our initial studies, conducted with the apparatus of Figure 1 and sintered pellets of 1–2–3, employed large stoichiometric excesses of water and en in MeOH, making the reaction pseudo-zeroth-order in water and en as the reaction progresses. As noted above, MeOH is a cosolvent that permits the concentrations of water and en to be independently varied.

For short reaction times, the absorbance of the Cu complex increased linearly with time, permitting extraction of leaching rates. If we assume that the 1–2–3 sample has a density of 5.2 g/cm^3 (82% of the theoretical value of 6.4 g/cm^3), that the reaction occurs uniformly across the single exposed rectangular surface of the sample, and we use the macroscopic surface area, uncorrected for roughness, we calculate a typical corrosion rate of 0.1 μm/min at room temperature.

Figure 4 presents measured initial rates for the appearance of Cu in solution as a function of sample surface area. The initial rate at which Cu is leached from 1–2–3 is roughly proportional to the sample surface area, uncorrected for surface roughness.

Figure 5 presents the observed dependence of the corrosion rate on water and en concentration. The initial rate of the reaction is nearly proportional to water concentration (at 2.0 M en) over the range 2.5–30 M. At lower water concentrations, not shown in Figure 5A, the first-order dependence on water concentration breaks down, with scattered, larger-than-expected rates. The unusually high rates may reflect absorption of water from the air by en, in amounts significant relative to the controlled amounts added.

Figure 5B illustrates the nearly linear dependence of the corrosion rate on en concentration (at 30 M H_2O) over the range 0.12–2.5 M. Trials at higher concentrations, 4.0 and 6.0 M en, which are not shown on Figure 5B, gave mark-

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[24] Jonassen, H. B.; Dexter, T. H. *J. Am. Chem. Soc.* **1949**, *71*, 1553.

[25] Pflaum, R. T.; Brandt, W. W. *J. Am. Chem. Soc.* **1955**, *76*, 6215.

[26] Jonassen, H. B.; Reeves, R. E.; Segal, L. *J. Am. Chem. Soc.* **1955**, *77*, 2667.

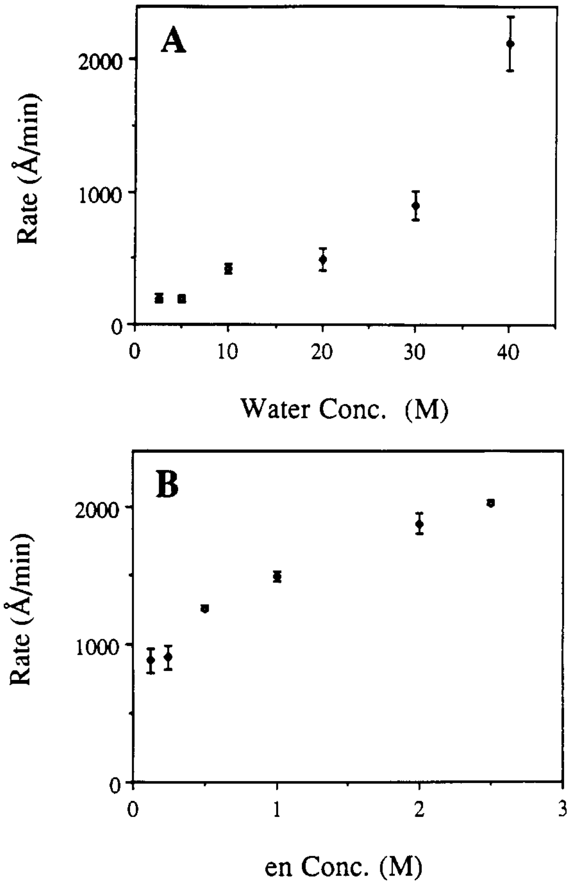

Figure 5. A: Dependence of the rate on water concentration. The leaching solution contained 2.0 M en with varying ratios of water and MeOH. B: Dependence of corrosion rate on ethylenediamine (en) concentration. The leaching solution contained 30 M H_2O with varying ratios of en and MeOH. For both A and B the other experimental conditions and the treatment of data are as described in Figure 4.

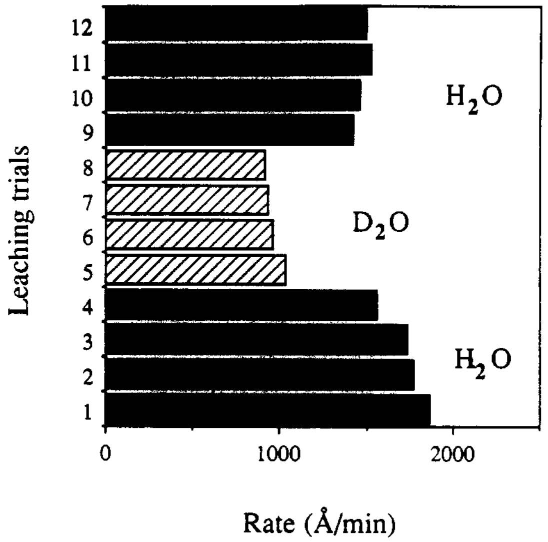

Figure 6. Dependence of the corrosion rate on substitution of D_2O for H_2O in the leaching solution, ~2.0 M en/30 M H_2O/8.1 M MeOH. In this experiment the trials were done sequentially: four with H_2O, four with D_2O, and finally four with H_2O again, as described in the Experimental Section. The reactions were done at room temperature.

edly reduced corrosion rates, perhaps reflecting the increased viscosity of such concentrated solutions.

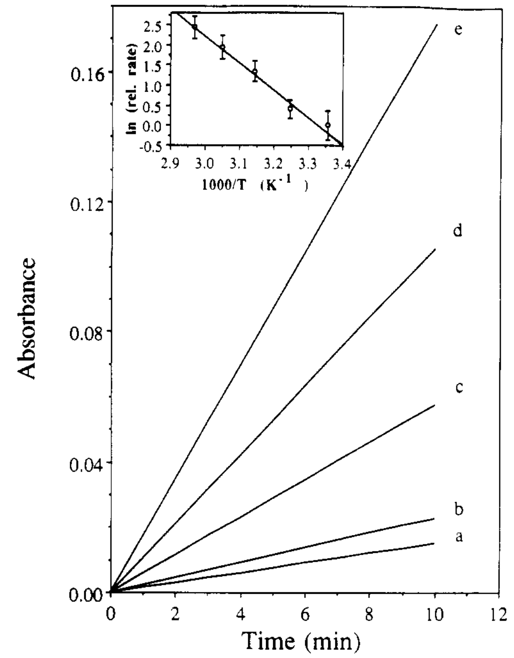

Figure 7. Dependence of the initial leaching rate of 1–2–3 on temperature, as determined by monitoring the absorbance of the *trans*-diaquobis(ethylenediamine)copper(II) complex at 570 nm versus time. Leaching employed a ~2.0 M en/30 M H_2O/8.1 M MeOH solution and a 1–2–3 sample with 31.0 mm^2 apparent surface area, uncorrected for surface roughness. Curves a–e represent data averaged for 3–6 trials done as described in the Experimental Section at the temperatures 25, 35, 45, 55, and 65 °C, respectively (the corrosion rate was 10 100 ± 100 Å/min at 65 °C). The inset shows a semilog plot of the relative initial reaction rates (relative to the rate at 25 °C), taken from the slopes of curves a–e, plotted against reciprocal temperature. The slope of the semilog plot was determined by linear regression and gave an apparent activation energy of 55 ± 5 kJ/mol.

When water in the leaching solution was replaced by D_2O (~2.0 M en/30.0 M D_2O/8.1 M MeOH), the initial reaction rate was roughly halved, as shown by Figure 6, presumably reflecting the more associated nature of the deuterated solvent. This indicates that the breaking of an O–H bond must occur for the reaction to proceed, although the details of this process are unclear at this point.[27]

Data for the temperature dependence of the initial rate of the reaction, obtained using a solution that was ~2.0 M en/30 M H_2O/8.1 M MeOH, are shown in Figure 7. The initial rate increases dramatically in the range from 25 to 65 °C; at 65 °C the corrosion rate has roughly increased by an order of magnitude to ~1 μm/min. The inset in Figure 7 shows a semilog plot of the relative corrosion rates (relative to the value at 25 °C) vs the reciprocal absolute temperature. Over the temperature range studied, the Arrhenius plot is nearly linear and yields an apparent activation energy of 55 ± 5 kJ/mol. The complexity of the reaction precludes a mechanistic assessment of this value.

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Registry No. MeOH, 67-56-1; D_2, 7782-39-0; ethylenediamine, 107-15-3.

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(27) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; Chapter 11.