[D]-Ru(bpy) were reproducible even on repeated use. We feel that [D]-Ru(bpy) should be at least as stable as [Ru(bpy)$_3$]$^{2+}$ in PVC.

Conclusions

[D]-Ru(bpy) and [D]-Ru(phen) are shown to be relatively inexpensive, easily prepared sensitizers for $^1O_2$ generation. The yields for $^1O_2$ production from the Dowex-bound sensitizers are comparable to homogeneous rose bengal and somewhat better than any other heterogeneous sensitizers. [D]-Ru(bpy)'s ability to efficiently generate $^1O_2$ in protic solvents, including water, should make it useful for the studies of $^1O_2$ effects on biological systems and with $^1O_2$ acceptors that are insoluble in organic solvents.

We have successfully utilized the luminescence properties of the bound [Ru(bpy)$_3$]$^{2+}$ and deuterium isotope effects to probe the microscopic heterogeneity of these porous photosensitizers. Utilizing these data we were able to develop a successful two-solvent phase model for explaining the general behavior of the hydrophilic photosensitizers in MeOH or in water-containing MeOH. The important role of solvent phase separation with concomitant separation of reactants is demonstrated.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work, and to the Air Force Office of Scientific Research (Chemistry) (Grant AFOSR 78-3590) and the National Science Foundation (Grant CHE 82-06279) for additional support. We also acknowledge the use of the University of Virginia laser facility, which was purchased in part from NSF Grant CHE 77-09296. We are grateful to Dr. F. S. Richardson for the use of his laser, to Drs. R. B. Martin and C. M. Grisham for the use of their spectrophotometers, and to Dr. J. Gainer for helpful discussions about the diffusion model. We also thank T. D. L. Pearson for his assistance in the relative luminescence quantum yield determination. We thank the reviewers and Dr. B. A. DeGraff for helpful comments.

Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; Ru(phen)$_3^{2+}$, 22873-66-1; O_2, 7782-44-7; H_2O, 7732-18-5; D_2O, 7789-20-0; MeOH, 67-56-1; Dowex 50W-X1, 39453-27-5.

Kinetic Study of the Reduction of Molecular Oxygen by Cuprous Chloride and Cuprous Acetate in Pyridine

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The solution-phase kinetics of the reaction of cuprous chloride with molecular oxygen in pyridine were studied by monitoring product formation. The reaction was found to be third order in cuprous chloride and first order in oxygen by initial rate studies and pseudo-first-order rate constant determinations. A single rate law was found for solutions in which initial cuprous chloride concentrations were varied by more than a factor of 350 and initial oxygen concentrations were varied by more than a factor of 40. The integrated form of the resulting rate expression was found to precisely predict product vs. time curves. A more limited kinetic study of the reaction of cuprous acetate with oxygen in pyridine demonstrated that this reaction is first order in oxygen and second order in cuprous acetate.

Introduction

The "activation" of molecular oxygen by transition-metal systems has been the subject of intense investigation over the past few years. The reasons for high interest in this area include its possible relevance to certain biological oxidations[1] and its potential application to the development of more efficient oxygen electrodes for fuel cells[2] and improved commercial oxidation processes.[3]

In earlier accounts we have discussed the oxidative bond cleavage of *o*-benzoquinone, catechols, and phenols to muconic acid derivatives induced by certain copper(II) reagents in both the presence and absence of molecular oxygen.[4] Reports by others further demonstrate the potency of oxygen–copper(I) systems for oxidative and coupling reactions.[5]

The reaction of cuprous chloride with molecular oxygen in pyridine has been shown to exhibit 4CuCl/O_2 stoi-

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chiometry[4b,e,f,6a] and results in irreversible oxidation of the copper(I) substrate. In spite of the great deal of attention that this system has received, the reaction products have not been fully characterized.[4-6] When the concentrations of the reactants are such that the solubility limit of the product(s) is exceeded, bispyridine cupric chloride has been isolated as one of the reaction products.[4c,6d]

The literature contains more than 20 pertinent kinetic studies of the reaction of copper(I) species with molecular oxygen in a variety of solvents including dimethyl sulfoxide,[6a] nitromethane,[6b] acetic acid,[6c] many mixed organic/aqueous mixtures,[6d] and water.[6e] In mixed aqueous/nonaqueous media, the copper(I) species was frequently complexed by 2,2′-bipyridine or 2,2′,2″-terpyridine ligands. The reaction was found to be first order with respect to oxygen and first or second order with respect to the copper(I) substrate.

Several groups have studied the kinetics of this transformation in pyridine by monitoring oxygen uptake and concluded that the reaction is first order in both oxygen and cuprous chloride.[7,8] Qualitative observations made in our laboratory contradicted these conclusions. Moderately concentrated solutions of cuprous chloride (10^{-2} M) reacted very rapidly with oxygen while many days were needed to significantly convert dilute (10^{-4} M) solutions to products. These observations led us to the hypothesis that the reaction must be higher order in the copper(I) substrate and prompted us to undertake this kinetic study.

Results and Discussion

Oxygen-Uptake Experiments. Our initial experiments were to monitor simultaneously oxygen disappearance and copper(II) appearance as a function of time. This was accomplished by injecting concentrated cuprous chloride solutions under nitrogen into oxygen-saturated pyridine. Oxygen uptake was measured with a gas buret and aliquots were withdrawn at various intervals, quenched, and analyzed by visible spectroscopy for copper(II) appearance. Enough dissolved oxygen was present in solution to react with all the cuprous chloride. Most of the cuprous chloride was found to be converted from copper(II) before significant oxygen uptake was measured on the gas buret. After long lag times, the buret-measured oxygen uptake approached a ratio of $4CuCl/O_2$. The rate-limiting step in this two-phase system was concluded to be the mass transport of oxygen from the gas phase to solution.

In order to study the reaction of cuprous chloride with dissolved oxygen, all subsequent determinations were made in closed systems not in contact with a gas phase.

TABLE I: Initial Rates of Copper(II) Formation for the Reaction of Cuprous Chloride with Oxygen in Pyridine

no.	$(d[Cu(II)]/dt)_0$,[a] mol L^{-1} s^{-1}	$10^3 \cdot [CuCl]_0$, mol L^{-1}	$10^3 \cdot [O_2]_0$, mol L^{-1}	$10^{-3} \cdot k$,[b] L^3 mol^{-3} s^{-1}
1	$(4.3 \pm 0.8) \times 10^{-6}$	5.1	4.0	8.1
2	$(3.8 \pm 0.7) \times 10^{-6}$	5.1	3.4	8.4
3	$(3.7 \pm 0.5) \times 10^{-6}$	5.1	2.9	9.4
4	$(2.7 \pm 0.3) \times 10^{-6}$	5.1	2.3	8.8
5	$(2.0 \pm 0.2) \times 10^{-6}$	5.1	1.7	8.9
6	$(1.2 \pm 0.2) \times 10^{-6}$	5.1	1.1	8.2
7	$(0.7 \pm 0.1) \times 10^{-6}$	5.1	0.57	9.3
8	$(1.2 \pm 0.5) \times 10^{-6}$	25.2	1.1	6.8
9	$(7.1 \pm 0.9) \times 10^{-6}$	10.2	1.1	6.1
10	$(5.1 \pm 0.8) \times 10^{-6}$	8.7	1.1	7.0
11	$(3.8 \pm 0.9) \times 10^{-6}$	7.4	1.1	8.5
12	$(1.8 \pm 0.3) \times 10^{-6}$	5.8	1.1	8.4
13	$(9.6 \pm 1.0) \times 10^{-7}$	4.5	1.1	9.1
14	$(8.2 \pm 0.8) \times 10^{-7}$	4.3	1.1	9.4
15	$(5.6 \pm 1.0) \times 10^{-8}$	1.4	1.1	18.5
16	$(1.2 \pm 0.5) \times 10^{-2}$	161.7	1.7	1.7
17	$(4.4 \pm 1.5) \times 10^{-3}$	82.0	1.7	4.7
18	$(2.1 \pm 0.8) \times 10^{-3}$	67.0	1.7	4.1
19	$(2.7 \pm 0.9) \times 10^{-4}$	33.6	1.7	4.2
20	$(5.8 \pm 2.0) \times 10^{-6}$	23.1	0.11	4.3
21	$(1.1 \pm 0.4) \times 10^{-5}$	20.2	0.26	5.1
22	$(8.6 \pm 1.0) \times 10^{-6}$	14.4	0.50	5.8
23	$(2.7 \pm 1.0) \times 10^{-7}$	2.2	2.9	8.7
24	$(2.3 \pm 1.0) \times 10^{-7}$	2.2	2.9	8.7
25	$(5.5 \pm 1.0) \times 10^{-9}$	0.46	4.8	11.8

[a] Determined by visible spectroscopy. [b] $k = (d[Cu(II)]/dt)_0/[CuCl]_0^3[O_2]$.

Reaction Order with Respect to Oxygen. The reaction order with respect to oxygen was determined by measuring initial rates of product formation for a series of solutions in which the initial concentration of oxygen, $[O_2]_0$, was varied and the initial concentration of cuprous chloride, $[CuCl]_0$, was held constant. In these experiments air- or oxygen-saturated pyridine was syringed into septum-covered tubes containing cuprous chloride–pyridine solutions under nitrogen. The final volume was such that there was virtually no gas phase above the solution. The tubes were then inserted into the visible spectrophotometer and the product–time curves were recorded. The initial rates of product formation, $(d[Cu(II)]/dt)_0$, were evaluated graphically form the product–time curves. These results are shown in Table I (experiments 1–7). The reaction order was determined from the data as follows. Equation 1 is a generalized rate expression in which X is the reaction

$$(d[Cu(II)]/dt)_0 = k[CuCl]_0^X[O_2]_0^Y \tag{1}$$

order with respect to cuprous chloride and Y is the reaction order with respect to oxygen. Taking the logarithm of this expression results in the following equation:

$$\log (d[Cu(II)]/dt)_0 = \log k + X \log [CuCl]_0 + Y \log [O_2]_0 \tag{2}$$

A graph of log $(d[Cu(II)]/dt)_0$ vs. log $[O_2]_0$ resulted in a line whose slope, the reaction order with respect to oxygen, was found to be 0.96 ± 0.15.

Reaction Order with Respect to Cuprous Chloride. Vapor pressure osmometry determinations have shown that cuprous chloride is "almost quantitatively" mononuclear in pyridine with a molecular formula of $CuClPy_3$.[8b] Initial rates of product formation were measured for a series of solutions, in which the initial oxygen concentration, $[O_2]_0$, was held constant and the initial cuprous chloride concentrations, $[CuCl]_0$, were varied. These results are shown in Table I (experiments 6, 8–15). The reaction order with respect to cuprous chloride was determined graphically from eq 2. A plot of log $(d[Cu(II)]/dt)_0$ vs. log $[CuCl]_0$ resulted in a line whose slope, the reaction order with respect to cuprous chloride, was found to be 2.8 ± 0.4.

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TABLE II: Psuedo-First-Order Rate Constant Determinations for the Reaction of Cuprous Chloride with Oxygen in Pyridine Solutions

$10^2 \cdot [CuCl]_0$, mol L^{-1}	$10^3 \cdot [O_2]_0$, mol L^{-1}	$[CuCl]_0/[O_2]_0$	k',[a] s^{-1}	$10^{-3}k'/[CuCl]_0^3$, L^3 mol^{-3} s^{-1}
16.2	1.71	95	8.8 ± 0.8	2.1
16.2	0.34	476	8.7 ± 0.4	2.0
8.2	1.71	48	2.3 ± 0.2	4.0
8.2	0.34	227	2.3 ± 0.2	4.2
6.7	0.34	186	1.2 ± 0.1	4.0
3.4	0.34	93	$(2.2 \pm 0.1) \times 10^{-1}$	4.8
2.3	0.11	200	$(7.8 \pm 0.3) \times 10^{-2}$ [b]	6.5
2.0	0.26	77	$(4.0 \pm 0.4) \times 10^{-3}$ [b]	6.0

[a] Determined by visible spectroscopy using a Durrum stopped-flow apparatus except as noted. [b] Determined by visible spectroscopy in a conventional visible spectrophotometer.

Pseudo-First-Order Rate Constant Determinations. Additional confirmation of the reaction order of both reactants was obtained from a series of reaction mixtures in which the initial cuprous chloride concentration was in large excess of the initial oxygen concentration. The reaction of relatively concentrated (>5 × 10^{-2} M) solutions of cuprous chloride was too rapid to be conveniently studied by conventional visible spectrophotometry. A stopped-flow experiment, however, readily afforded kinetic data in this concentration range.

According to eq 1, the observed pseudo-first-order rate constant, k', should be a function of the cuprous chloride concentration.

$$k' = k[\mathrm{CuCl}]^X \qquad (3)$$

Assuming that the concentration of intermediates is small, the following expressions result from the stoichiometry of the reaction:

$$[\mathrm{O_2}]_0 = \tfrac{1}{4}[\mathrm{Cu(II)}]_\infty \qquad (4)$$

$$[\mathrm{O_2}] = \tfrac{1}{4}([\mathrm{Cu(II)}]_\infty - [\mathrm{Cu(II)}]) \qquad (5)$$

Substituting eq 5 and 3 into eq 1 and rearranging yields eq 6. Equation 7 results from integrating eq 6. Plots of

$$4\left(\frac{\mathrm{d}[\mathrm{Cu(II)}]}{[\mathrm{Cu(II)}]_\infty - [\mathrm{Cu(II)}]}\right) = k'\,\mathrm{d}t \qquad (6)$$

$$4 \ln \frac{[\mathrm{Cu(II)}]_\infty - [\mathrm{Cu(II)}]_{t_1}}{[\mathrm{Cu(II)}]_\infty - [\mathrm{Cu(II)}]_{t_2}} = k'(t_2 - t_1) \qquad (7)$$

ln ($[\mathrm{Cu(II)}]_\infty - [\mathrm{Cu(II)}]_t$) vs. time exhibited linearity for at least three half-reactions. This provided additional confirmation that the reaction is first order in oxygen. These results are shown in Table II. The value of X was estimated by plotting log k' against log [CuCl].

$$\log k' = X \log [\mathrm{CuCl}] + \log k \qquad (8)$$

The slope is 2.8 ± 0.2 when the data point of the most concentrated solution is discarded.

A fourth-order rate constant, k, can be derived by dividing k' by $[\mathrm{CuCl}]^3$ as shown in Table II. A trend of lower values at higher cuprous chloride concentrations, a deviation of the reaction order with respect to cuprous chloride, can be seen in these data. This is to be expected and simply reflects the fact that the data are analyzed as a function of total copper(I) and not monomeric cuprous chloride. Any significant reversible aggregation of cuprous chloride such as dimer formation will give this apparent lowering of the reaction order. The deviation in these data from third order in cuprous chloride allows the calculation of a dimerization equilibrium constant and results in $K = [\mathrm{CuCl}]^2/[\mathrm{Cu_2Cl_2}] \cong 1$.

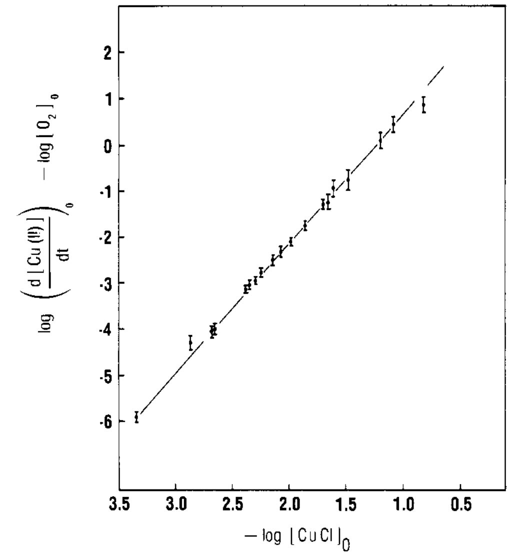

Figure 1. Plot of log ($\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t_0$ − log $[\mathrm{O_2}]_0$) vs. log $[\mathrm{CuCl}]_0$ for the reaction of cuprous chloride with oxygen in pyridine.

Initial rates of reaction were also measured for these more concentrated cuprous chloride solutions. It is instructive to compare these data (Table I, experiments 16–21) and other data from more dilute cuprous chloride solutions (experiments 22–25) with experiments 1–15. Here the initial rates vary by 7 orders of magnitude with the initial cuprous chloride concentrations varying by a factor of 350. The initial oxygen concentrations are not all the same but may be factored out by subtracting log $[\mathrm{O_2}]_0$ from log $(\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t)_0$. A plot of log $(\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t)_0$ − log $[\mathrm{O_2}]_0$ vs. log $[\mathrm{CuCl}]_0$ results in a single straight line over the entire concentration range as shown in Figure 1. The slope of this line, the reaction order with respect to cuprous chloride, is 2.8 ± 0.4. The fourth-order rate constant, k, can be derived by extrapolation of the line to $[\mathrm{CuCl}]_0 = 1$ or may be numerically evaluated for each run by dividing $(\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t)_0$ by $[\mathrm{CuCl}]_0^3[\mathrm{O_2}]_0$ as shown in Table I. Both procedures give the same answer: $k = (7 \pm 4) \times 10^3$ L^3 mol^{-3} s^{-1}.

Comparison of Calculated and Observed Product–Time Curves. Equations 9 and 10 follow from the stoichiometry of the reaction.

$$[\mathrm{CuCl}] = [\mathrm{CuCl}]_0 - [\mathrm{Cu(II)}] \qquad (9)$$

$$[\mathrm{O_2}] = [\mathrm{O_2}]_0 - \tfrac{1}{4}[\mathrm{Cu(II)}] \qquad (10)$$

Using these relationships with $X = 3$ and $Y = 1$, eq 1 can be integrated giving eq 11 in which $A = 1/4[\mathrm{CuCl}]_0 - [\mathrm{O_2}]_0$.

$$kt = -\frac{1}{2A}\left[\frac{1}{([\mathrm{CuCl}]_0 - [\mathrm{Cu(II)}])^2} - \frac{1}{[\mathrm{CuCl}]_0^2}\right] - \frac{1}{4A^2}\left[\frac{1}{[\mathrm{CuCl}]_0 - [\mathrm{Cu(II)}]} - \frac{1}{[\mathrm{CuCl}]}\right] + \frac{1}{16A^3} \ln \frac{[\mathrm{O_2}]_0([\mathrm{CuCl}] - [\mathrm{Cu(II)}])}{[\mathrm{CuCl}]_0([\mathrm{O_2}]_0 - \tfrac{1}{4}[\mathrm{Cu(II)}])} \qquad (11)$$

Equation 11 was tested by determining its ability to predict [Cu(II)]–time curves. In most cases excellent agreement was observed between calculated and observed curves. Such a comparison is shown in Figure 2. Less satisfactory agreement was found in one case where the

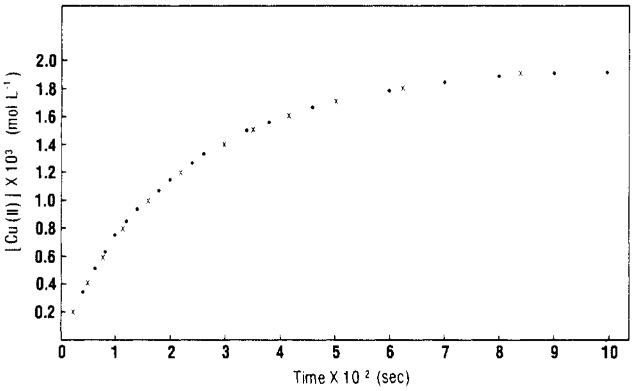

Figure 2. Comparison of experimental and calculated product-time curves. The initial oxygen concentration was 5.0×10^{-4} M. The initial cuprous chloride concentration was 1.44×10^{-2} M. The calculated values (X) were obtained from eq 11 by using a rate constant $k = 6.5 \times 10^3$ L^3 mol^{-3} s^{-1}. The experimental points (●) were measured by visible spectroscopy.

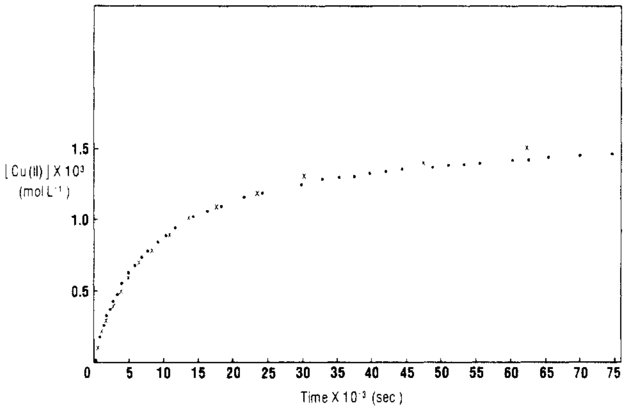

Figure 3. Comparison of experimental and calculated product-time curves. The initial oxygen concentration was 2.10×10^{-3} M. The initial cuprous chloride concentration was 2.86×10^{-3} M. The calculated values (X) were obtained from eq 11 by using a rate constant $k = 8 \times 10^3$ L^3 mol^{-3} s^{-1}. The experimental points (●) were measured by visible spectroscopy.

cuprous chloride and oxygen concentrations were both about 2×10^{-3} M. This comparison is shown in Figure 3. Good agreement is seen up to the first half-reaction, but the observed reaction becomes slower than predicted by the model. However, this experiment took many tens of hours to complete two half-reactions. The pressure of oxygen inside the tube was higher than that of atmospheric oxygen so that some equilibration with the atmosphere may have occurred by diffusion of gas through the rubber septum.

Kinetics of the Reaction of Cuprous Acetate with Oxygen in Pyridine. The reaction of cuprous acetate was found to exhibit $4CuOAc/O_2$ stoichiometry as determined by oxygen-uptake experiments (see Experimental Section). Cuprous acetate, however, reacted much more rapidly with oxygen in pyridine than cuprous chloride under comparable conditions. This precluded convenient study of the kinetics over a wide range of cuprous acetate concentrations. We examined several oxygen/cuprous acetate mixtures in pyridine by visible spectroscopy in the stopped-flow experiment as before. These results are shown in Table III. The mixtures with high $[CuOAc]_0/[O_2]_0$ ratios allowed the determination of pseudo-first-order rate constants. Plots of ln $([Cu(II)]_\infty - [Cu(II)]_t)$ vs. time exhibited linearity for at least three half-lives, indicating that the reaction is first order in oxygen. A plot of the logarithm of initial rates of product formation, $(d[Cu(II)]/dt)_0$, vs. the logarithm of initial concentrations of cuprous acetate, $[CuOAc]_0$, resulted in a line whose slope, the reaction order with respect to cuprous acetate, is 2.0 ± 0.2. Division of the observed pseudo-first-order rate constants, k', by $[CuOAc]^2$ allows the calculation of an overall third-order rate constant and results in $k \cong 8 \times 10^5$ L^2 mol^{-2} s^{-1}.

TABLE III: Kinetic Data for the Reaction of Cuprous Acetate with Oxygen in Pyridine[a]

$10^3 \cdot [CuOAc]_0$,[b] mol L^{-1}	$(d[Cu(II)]/dt)_0$,[c] mol L^{-1} s^{-1}	k',[d] s^{-1}	$10^{-5}k'/[CuOAc]^2$, L^2 mol^{-2} s^{-1}
20.0	$(2.1 \pm 0.4) \times 10^{-1}$	310 ± 20	7.7
7.0	$(3.3 \pm 0.2) \times 10^{-2}$	48 ± 4	8.4
6.8	$(2.4 \pm 0.2) \times 10^{-2}$	35 ± 4	7.6
2.8	$(4.3 \pm 0.2) \times 10^{-3}$	*e*	*e*

[a] The initial oxygen concentration was 1.7×10^{-4} mol L^{-1}. [b] Initial concentration of cuprous acetate. [c] Initial rates of copper(II) formation as measured by visible spectroscopy. [d] Observed pseudo-first-order rate constants. [e] The $[CuOAc]_0/[O_2]_0$ ratio was too small to accurately determine a pseudo-first-order rate constant.

Mechanistic Implications of the Cuprous Chloride–Oxygen Rate Law. The kinetic stoichiometry implies that the transition state of the rate-determining reaction has the composition $Cu_3Cl_3O_2$ but, of course, gives no information about the mechanism whereby the elements are assembled. A family of degenerate mechanisms which are chemically plausible can be formulated in which rapid equilibration among species such as $CuClO_2$, $Cu_2Cl_2O_2$, and Cu_2Cl_2 is assumed. It is tempting to postulate that the rate-limiting step involves reaction of CuCl with a μ-peroxo species containing two copper atoms.

$$2CuCl + O_2 \rightleftarrows ClCuO_2CuCl \qquad (12)$$

$$ClCuO_2CuCl + CuCl \rightarrow \text{products} \qquad (13)$$

The immediate products of reaction 13 might be species such as ClCuO and Cl_2Cu_2O although we have no way of knowing with certainty. Oxidation of another CuCl and equilibration of ligands among Cu(II) species would follow rapidly. Equation 12 could, of course, be formulated in terms of pairwise equilibrium reactions involving reversible binding of oxygen.

Conclusions

The kinetics of the reaction of cuprous chloride with oxygen in pyridine were studied for reaction mixtures in which the initial oxygen concentrations were varied by a factor of more than 40 and the initial cuprous chloride concentrations were varied by more than 350. A single rate law was found to hold over this entire concentration range. Initial rate studies demonstrated that the reaction is first order in oxygen and third order in cuprous chloride. These reaction orders were confirmed by pseudo-first-order rate constant determinations for reaction mixtures in which the concentration of cuprous chloride was in large excess of the initial oxygen concentrations. The integrated form of the resulting rate expression was found to precisely predict product vs. time curves. These results are in conflict with earlier reports that this reaction is first order in both oxygen and cuprous chloride. These earlier studies, however, were conducted in a two-phase system in which the uptake of oxygen from the gas phase to the pyridine solution was used to monitor the reaction kinetics. Our results show that the mass transport of oxygen from the gas phase to the solution phase is rate limiting in this system. Comparison should also be made with numerous other reports of the reduction of oxygen by copper(I) substrates in similar systems in which a maximum copper(I) reaction order of 2 was observed.

A limited kinetic study of the reaction of cuprous acetate with oxygen in pyridine demonstrated that this reaction is first order in oxygen and second order in cuprous acetate.

Experimental Section

Solvents, Reagents, and Instrumentation Used. Reagent-grade pyridine was freshly distilled from calcium oxide under a dry nitrogen atmosphere before use and was stored over activated 4A molecular sieves. All other solvents were distilled prior to use.

Commercially available cuprous chloride was reduced with dilute sulfurous acid,[9] dried, and stored under nitrogen at 5 °C. Cuprous acetate was prepared by reaction of dry copper metal and anhydrous cupric acetate, followed by vacuum sublimation of the cuprous acetate.[10]

All air- or moisture-sensitive compounds and solutions were kept under a positive pressure of high-purity, dry-grade nitrogen. All transfers of air-sensitive solutions were made under nitrogen via glass or Teflon tubing or nitrogen-purged, precision-fit glass syringes equipped with stainless steel needles.

Reaction flasks (where access for sample withdrawal, etc., was necessary) were sealed with fresh neoprene rubber septa. All glassware and other equipment were oven dried for a minimum of 24 h at 130 °C before use. Such equipment was kept under a positive nitrogen atmosphere immediately after removal from the oven.

Ultraviolet–visible spectrophotometric measurements were recorded on a Cary-219 instrument. A Durrum Model D-100 series stopped-flow instrument connected to a Hewlett-Packard 1223-A oscilloscope was used for rapid kinetic studies.

Pyridine solutions of cuprous chloride were prepared in either of two ways: (1) A sample of cuprous chloride was weighed into an empty flask kept under nitrogen, and then rigorously nitrogen-deaerated pyridine was admitted under nitrogen. (2) A weighed sample of cuprous chloride was added to a rigorously deaerated volumetric flask of pyridine kept under a stream of nitrogen. All pyridine samples were deaerated with a nitrogen stream for a minimum of 60 min before reagents were added. All cuprous acetate manipulations and preparation of pyridine solutions of cuprous acetate by either of the above procedures were done in a drybox under a nitrogen atmosphere.

Oxygen-Uptake Experiments. Reactions of Cuprous Chloride or Cuprous Acetate with Oxygen-Saturated Pyridine. A three-neck, 1-L round-bottom flask was used as the reaction vessel. This flask was filled with freshly distilled pyridine. One neck was closed with a septum for syringe addition and withdrawal of samples. A Teflon-coated stirrer bar was added for vigorous stirring of the solutions. The middle neck of the flask held the outlet (medium-frit gas dispersion tube) from a ceramic pump which pumped gas at a volume of 100 mL min^{-1}. The third outlet of the flask was connected to a 1-L gas reservoir which was connected to a gas buret which utilized di-*n*-butyl phthalate as leveling fluid. The entire system was kept in a thermostated bath at 25 ± 0.2 °C. The system was saturated with a stream of oxygen for a minimum of 2 h prior to reaction.

Concentrated nitrogen-deaerated cuprous compound in pyridine solution was syringed into the setup to initiate oxygen absorption. Aliquots (1 mL) were removed under nitrogen and added to a nitrogen-deaerated 1:2 (v/v) solution of concentrated aqueous ammonia/pyridine. Visible absorption spectra were determined in cuvettes kept under a positive nitrogen atmosphere. Absorption of $Cu(NH_3)_4^{2+}$ at 640 nm was monitored.[11] Since the copper(I) salts have no absorption in this region in this solvent system, copper(II) could be directly measured.

The results of several such measurements indicated that Cu(II) formation in concentrated solutions occurred much more rapidly than was indicated by buret-measured oxygen uptake. The rates of formation of Cu(II) in concentrated solutions were too rapid for accurate spectrophotometric determination. After large lag times the buret-measured uptake of oxygen approached final ratios of $4Cu(I)/O_2$ for both cuprous chloride and cuprous acetate.

Primary determination of oxygen solubility in pyridine was done by potassium iodide/sodium hydroxide oxidation, followed by titration of the liberated iodide with sodium thiosulfate to starch indicator end point.[12]

Direct Spectrophotometric Determination of Initial Rates of Formation of Oxidation Products. The visible spectrophotometer was initially zeroed with 15 × 75 mm glass tubes filled with pyridine. Stock solutions of nitrogen-deaerated cuprous chloride in pyridine were prepared and kept under a positive nitrogen pressure in septum-covered flasks. Likewise, septum-covered stock solutions of oxygen-saturated pyridine were prepared (minimum of 60 min of oxygen bubbling under a positive oxygen pressure). Similar nitrogen-saturated solutions of pyridine were prepared.

The glass tubes used for the kinetic runs were oven dried, closed with a septum, and nitrogen deaerated for at least 20 min before solutions were added. Kinetic runs were made by completely filling the tubes to final volumes with pyridine solutions so that no head space remained. Appropriate volumes of cuprous chloride/pyridine were first syringed into the tubes under nitrogen. If nitrogen-saturated pyridine was used as a diluent, it was added next. The nitrogen bubbler was removed and the appropriate volume of oxygen-saturated pyridine was added to completely fill the tube. The tube was immediately sealed, shaken, and placed in the spectrophotometer at ambient temperature for absorption vs. time monitoring at 736 nm ($\epsilon = 105$ L mol^{-1} cm^{-1}). The molar absorptivity, ϵ, is based on the concentration of reactant CuCl. The sequence of mixing and positioning in the spectrophotometer was completed in less than 8 s. This allowed study of initial rates over a moderate concentration range.

Stoichiometry was also confirmed by this technique since the concentration of either cuprous chloride or oxygen could be made reaction limiting. In all cases the $4CuCl/O_2$ stoichiometry was observed. Likewise the stoichiometry of the reaction of cuprous acetate with oxygen in pyridine was verified in this way. The reaction product was monitored at 632 nm ($\epsilon = 76$ L mol^{-1} cm^{-1}). The molar absorptivity, ϵ, is based on the concentration of reactant CuOAc. For both CuCl and CuOAc, pyridine solutions within the concentration ranges given in the tables exhibited no absorption at the wavelengths monitored.

Stopped-Flow Determination of Pseudo-First-Order Rate Constants. Concentrated solutions of cuprous chloride/pyridine under nitrogen, and oxygen-saturated or air-saturated pyridine, were charged into the syringes of the instrument. The instrument was flushed and

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(9) R. N. Kellar and H. D. Wycoff, *Inorg. Synth.*, **2**, 1 (1946).

(10) S. J. Kirchner, S. A. Schubert, R. D. Mounts, and A. Fernando, *Inorg. Chim. Acta*, **27**, 180 (1978).

(11) S. A. Shrager and G. Norwitz, *J. Appl. Chem.*, **9**, 1, 384 (1951).

(12) "Official Standardized and Recommended Methods of Analysis", compiled and edited by the Analytical Methods Committee of the Society for Analytical Chemistry by S. C. Jolly, W. Heffer and Sons, Ltc., Cambridge, U.K., 1963, pp 175–99.

charged with reactants as soon as possible to minimize extraneous leakage of oxygen into or out of the solutions. Visible absorption changes vs. time were monitored at 736 nm.

The same procedure was followed in studying the kinetics of oxidation of cuprous acetate in pyridine, except that visible absorption changes vs. time were monitored at 632 nm.

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Mechanistic Details of the Oxidation of Oxalate by Manganese(III)

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Oxalate complexes of manganese(III) decompose by a net process that can be generalized as $2Mn(III) + C_2O_4^{2-} \rightarrow 2Mn(II) + 2CO_2$. The rate-determining step is a unimolecular reaction of a single Mn(III) complex to form Mn(II) and a radical intermediate assigned the formula $\cdot CO_2^-$. That radical may then react either with $\cdot CO_2^-$ or with Mn(III). Adding acrylic acid as a radical scavenger has little effect on the rate of Mn(III) consumption, and we reach a somewhat qualified conclusion that $2\cdot CO_2^- \rightarrow C_2O_4^{2-}$ is a more important radical consumption reaction than is $\cdot CO_2^- + Mn(III) \rightarrow CO_2 + Mn(II)$ even though $[Mn(III)] \gg [\cdot CO_2^-]$. In the presence of air, the decomposition of manganic oxalate induces the reaction $O_2 + C_2O_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2O_2$. However, as Kolthoff showed almost 60 years ago, this induced reaction does not affect the quantitative stoichiometry of the overall reaction between permanganate and oxalate.

Introduction

Oxalate is oxidized by permanganate. Under certain conditions, the stoichiometry of process T is obeyed so

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \qquad (T)$$

precisely that the reaction serves as an excellent standardization procedure for quantitative volumetric analysis.

Although kinetic study of the reaction was initiated well over a century ago,[1] some aspects of the mechanism are still unclear. If sufficient manganous ion and oxalate are both present initially, the stoichiometry of the fast initial process is well described by process A. Intermediate

$$Mn(VII) + 4Mn(II) \rightarrow 5Mn(III) \qquad (A)$$

oxidation states of manganese are certainly involved, and oxalate can compete with manganese(II) for the reduction of some of them. The dynamics of this complex overall process are not of concern to the present paper.

The manganese(III) produced in process A is present as complexes that can be generalized as $Mn(C_2O_4)_n^{3-2n}$ where n may be 1, 2, or 3. The subsequent behavior obeys the stoichiometry of process B. The overall stoichiometry is then generated by (T) ≡ 2(A) + 5(B).

$$2Mn(C_2O_4)_n^{3-2n} \rightarrow 2Mn^{2+} + (2n - 1)C_2O_4^{2-} + 2CO_2 \qquad (B)$$

Kinetic studies, including those by Taube[2] and by Adler and Noyes,[3] show that process B is cleanly first order in manganese(III); therefore, only one manganese is present in the transition state of the rate-determining step. There is general agreement that this step initiates process B by producing a radical intermediate such as $\cdot CO_2^-$ or $\cdot C_2O_4^-$ derived by a 1-equiv oxidation of oxalate. The rate is slower the larger the value of n and the more compressed the transition state. We interpret this trend to indicate that the C–C bond is broken in the rate-determining step B1. This assignment of the structure of the radical intermediate is not essential to the argument that follows.

$$Mn(C_2O_4)_n^{3-2n} \rightarrow Mn^{2+} + (n - 1)C_2O_4^{2-} + CO_2 + \cdot CO_2^- \qquad (B1)$$

The radical intermediate must react further and could conceivably do so either by step B2α or by step B2β.

$$Mn(III) + \cdot CO_2^- \rightarrow Mn^{2+} + CO_2 \qquad (B2\alpha)$$

$$2\cdot CO_2^- \rightarrow C_2O_4^{2-} \qquad (B2\beta)$$

If the mechanism involves step B2α, (B) ≡ (B1) + (B2α) and the experimentally observable rate of process B is equal to the rate of step B1. If the mechanism involves step B2β, (B) ≡ 2(B1) + (B1β) and the observed rate of process B is equal to half the rate of step B1.

A mechanistic decision between steps B2α and B2β could be made by introducing a scavenger S so that process C competed efficiently with the appropriate step B2. If

$$\cdot CO_2^- + S \rightarrow P \qquad (C)$$

the mechanism in the absence of scavenger involves step B2α, introduction of S will reduce the observed $-d \ln [Mn(III)]/dt$ by a factor of up to 2. If the mechanism involves step B2β, introduction of S will have no effect on $-d \ln [Mn(III)]/dt$.

The scavenger species S must satisfy several requirements. It must not react directly with Mn(III) species, it must be sufficiently reactive with $\cdot CO_2^-$ that process C can compete with step B2α, and any further reactions of species P must not involve reduction of manganese(III). In the experiments reported here, we have attempted to use a polymerizable vinyl monomer for species S.

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