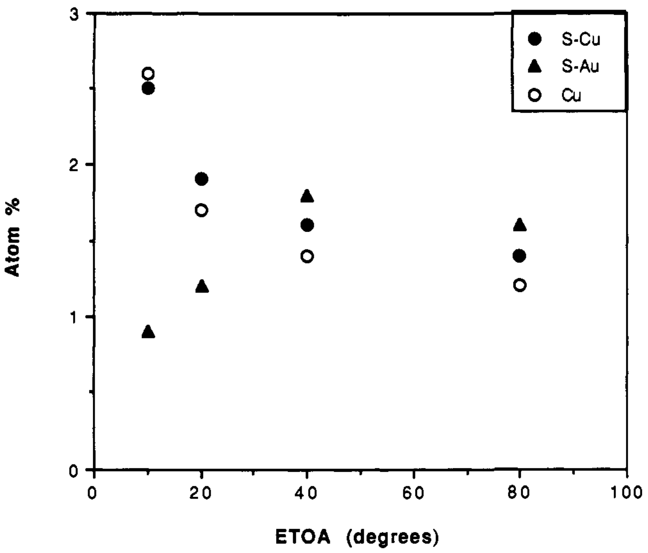

Figure 3. Angle resolved XPS data for a bilayer of ω-mercaptohexadecanoic acid. Note that S–Cu and Cu track each other in 1:1 ratio at all angles, suggesting their close proximity in the bilayer.

Usually, a thiolate is the preferred ligand, even when a carboxylate group is present.[13a,14] Furthermore, weakly bound short chain carboxylic acid species have been used in self-assembly to "protect" gold surfaces from unwanted adventitious contaminants. The acid is removed easily during the subsequent thiol adsorption. From angle-resolved XPS studies to determine whether there is any competitive adsorption between the carboxylate and the thiol functionalities on gold surfaces, we have found that there is, within the detectable limits, no carboxylate–substrate binding and that the thiolate–substrate reaction is dominant.[15] Finally, it has been found that the binding energies of alkanethiols to copper and to gold surfaces are similar.[16]

The structure emerging from the data presented so far is that multilayer formation occurs via the formation of copper(II) thiolate adsorbed on an acid surface. Figure 2 shows an XPS spectrum indicating the two types of sulfur species in the system, one bonded to gold (161.8 eV) and one to the Cu(II) (163.5 eV). We note that the interlayer bonding is not clear, however, given the surface stoichiometry, it is unlikely that we have a simple $-CO_2-Cu-S-$ connection. From the wetting data it is concluded that the ω-mercaptoalkanoic acid is attached to the copper carboxylate surface through the thiol end (the advancing contact angle on an SH surface is 71 ± 3°).[17] As a control reaction, we exposed the Cu^{2+} surface to a 1 mM solution of arachidic acid in an ethanol–dodecane mixture. No adsorption of the arachidic acid could be detected. Figure 3 presents the XPS as a function of electron takeoff angle (ETOA) for the two sulfur species and copper, clearly indicating that the second monolayer is adsorbed through the Cu–S bonding mode.[18] However, there are two disturbing points in Figure 3. The first is the S–Cu and Cu that track each other in 1:1 to 1.1:1 ratio at all angles, thus suggesting their close proximity in the bilayer, but in disagreement with an expected 2:1 ratio. Note that if the ratio of 1:1 is correct, the number of molecules in the second layer should be half of that in the first one, and so on. This sharp decrease in monolayer density is in complete disagreement with both the ellipsometric and the IR data. The second is that the angle-dependent XPS data are inconsistent with a structure in which the copper and the sulfur bound to it are buried beneath ~16 Å of hydrocarbon and may suggest a chemisorption of the carboxylic group on the Cu^{2+} surface. This, however, is in disagreement with the fact that arachidic acid does not adsorb on these Cu^{2+} surfaces. Thus, while all evidence suggests the formation of complete monolayers, the XPS data suggest otherwise. We believe that complete monolayers are formed with thiol adsorption and with a 2:1 S/Cu ratio and that XPS is not a quantitative analytical tool in this case. A careful examination of many XPS spectra shows that even in the "best" cases, the Cu^{2+} peak is skewed, suggesting some reduction of the copper, even upon very short exposure to X-rays. Such reduction, for example to Cu^{1+}, results immediately in the formation of disulfides that would desorb in the ultrahigh vacuum, leaving a partial monolayer. If this is correct—we could not find any evidence in the XPS data to dispute it—both the S/Cu ratio and the takeoff angle results can be understood. Still, we cannot explain why we could not produce complete monolayers from simple alkanethiols (e.g., octadecanethiol $CH_3(CH_2)_{17}SH$) on the copper carboxylate surface. The only speculation we can provide is that since there is only one Cu^{2+} ion for two alkyl chains, the carboxylic groups play an important role in the adsorption, probably through H-bond stabilization of molecular dimers.

While full structural characterization of these films awaits detailed study, ellipsometry, XPS, and preliminary IR spectra indicate that water-stable multilayers of uniform thickness can be self-assembled via sequential adsorption of ω-mercaptoalkanoic acid and Cu^{2+} ions.

Supplementary Material Available: FTIR reflection absorption spectrum vs number of layers for multilayers of I and an XPS Cu $2p_{3/2}$ spectrum (2 pages). Ordering information is given on any current masthead page.

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Kinetic, Thermodynamic, and Spectral Characterization of the Primary Cu–O_2 Adduct in a Reversibly Formed and Structurally Characterized Peroxo–Dicopper(II) Complex

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Received April 12, 1991

As a part of our continuing investigations of biomimetic Cu^{I}_{n}/O_2 reactivity,[2,3] we recently described the reversible reaction of the mononuclear cuprous complex $[LCu(RCN)]^+$ (**1**, L = tris[2-pyridyl)methyl]amine, R = CH_3 or C_2H_5) with O_2 to give the trans-μ-1,2-peroxo-bridged dicopper(II) complex, $[\{LCu\}_2(O_2)]^{2+}$ (**3**) (Cu···Cu = 4.36 Å).[2a] Copper–dioxygen interactions are of fundamental importance in Cu(I) autoxidation and chemical/biological oxidation processes.[4-6] One-to-one Cu–O_2 adducts are implicated in these processes, while recent studies reveal the presence of such entities as important intermediates in the action of copper phenylalanine hydroxylase[7] and amine oxidases.[8]

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Scheme I

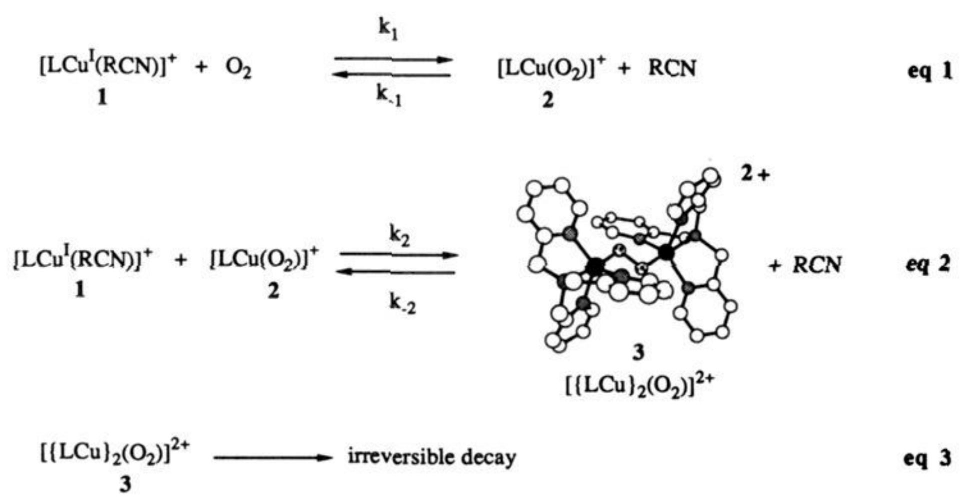

Table I. Summary of Calculated and Derived Kinetic and Thermodynamic Parameters for $[Cu(TMPA)RCN]^{+a}$

	k_1 (M^{-1} s^{-1})	$k_{-1}{}^b$ (s^{-1}) = k_1/K_1	k_2 (M^{-1} s^{-1})	k_2 (s^{-1})	$k_{on}{}^b$ (M^{-2} s^{-1}) ≈ K_1k_2	K_1 (M^{-1})	$K_2{}^b$ (M^{-1}) ≈ k_2/k_{-2}	$K_{eq}{}^b$ (M^{-2}) = K_1K_2
(−90 °C)	1.8×10^4	13	4.3×10^4	$1.9 \times 10^{-4\,c}$	6.0×10^7	1.4×10^3	$2.3 \times 10^{8\,c}$	$3.2 \times 10^{11\,c}$
(25 °C)	$9.0 \times 10^{7\,c}$	$3.2 \times 10^{8\,c}$	1.5×10^6	1.7×10^3	4.4×10^5	0.285^c	890	2.5×10^2
$\Delta H^\ddagger$ (kJ/mol)	31.7 ± 3.3	65.2 ± 4.0	12.2 ± 0.4	61.3 ± 3.2	−21.3 ± 1.1			
$\Delta S^\ddagger$ (J/mol K)	14 ± 17	137 ± 21	−86 ± 2	23 ± 13	−209 ± 6			
ΔH^0 (kJ/mol)						−33.5 ± 0.7	−49.1 ± 3.6	−82.6 ± 4.3
ΔS^0 (J/mol K)						−123 ± 4	−109 ± 15	−232 ± 19

[a] The results presented here are based on the analysis of 118 kinetics runs (50 spectra each) obtained with initial concentrations of $[LCu(RCN)]^+$ of (1.9–6.8) × 10^{-4} M and $[O_2]$ = (0.92–4.4) × 10^{-3} M between −91 and −12 °C. Activation and thermodynamic parameters were obtained from log versus $1/T$ plots with standard linear regression analyses. [b] Derived values, from equations shown. [c] Relatively uncertain values calculated from activation parameters determined in a different temperature range.

Dioxygen interactions with di- or trinuclear copper centers also occur in proteins such as hemocyanin (O_2 carrier),[9] tyrosinase (monooxygenase),[10] and multicopper oxidases (e.g. laccase,[11] ascorbate oxidase[12]). In this report, we provide the *first* kinetic, thermodynamic, and spectral parameters for a primary adduct $[LCu(O_2)]^+$ (**2**), i.e., the intermediate in the formation of $[\{LCu\}_2(O_2)]^{2+}$ (**3**).[13] With the structural characterization of **3**,[2a] we are thus afforded an excellent opportunity to study the kinetics and thermodynamics of formation of this well-defined Cu_2O_2 species, and these data are also provided.

Upon rapid mixing solutions of O_2 and $[LCu(RCN)]^+$ (**1**) in EtCN,[14a] temperature-dependent UV–vis spectral changes occur.[14c] Between −90 and −75 °C, there is rapid formation of a species (**2**, eq 1, vide infra) with λ_{max} at 410 and 747 nm; this quickly decays and is transformed into the stable complex $[\{LCu\}_2(O_2)]^{2+}$ (**3**, eq 2), having 525 and 595 (sh) nm absorptions.[2a] Above −75 °C the rate of formation of the 410-nm band is beyond the instrumental limit, and the thermodynamic stability of the intermediate decreases with increasing temperature. Above −50 °C, formation of **3** is also incomplete. In addition, irreversible decay to secondary products becomes significant and the 410 nm intermediate is reduced to a steady state concentration at higher temperature.

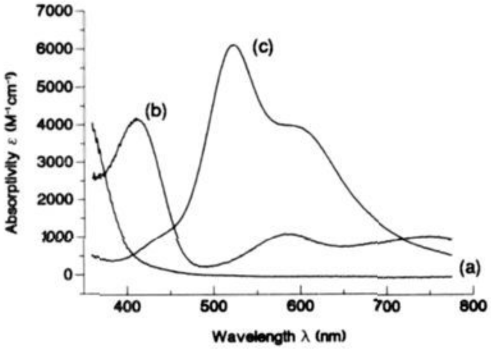

Figure 1. Spectra calculated from the kinetic data analysis for (a) Cu(I) precursor $[LCu(RCN)]^+$ (**1**), (b) 1:1 Cu–O_2 adduct $[LCu(O_2)]^+$ (**2**), and (c) peroxo complex $[\{LCu\}_2(O_2)]^{2+}$ (**3**). Absorptivity units were calculated per mol of copper ion.

Complete analyses[14b] provide kinetic and thermodynamic parameters for the O_2-binding process (eqs 1 and 2). The 410 nm (ϵ = 4000 M^{-1} cm^{-1}) and 747 (ϵ = 1000 M^{-1} cm^{-1}) nm absorptions are attributed to the primary Cu–O_2 adduct $[LCu(O_2)]^+$ (**2**), *generated initially (eq 1) with* $k_1 = 1.8 \times 10^4$ M^{-1} s^{-1} *at* −90 °C (Table I).[15] The equilibrium constant for formation of **2** is $K_1 = k_1/k_{-1} = 1.4 \times 10^3$ M^{-1} at −90 °C. Above −50 °C, in place

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(13) There is only one other rate constant known for formation of an unstable and uncharacterized primary O_2 adduct of cuprous ion: $k = 1 \times 10^6$ M^{-1} s^{-1} (20 °C) for formation of Cu–O_2 from $Cu^I_{(aq)}$. See: Zuberbühler, A. D. *Helv. Chim. Acta* **1970**, *53*, 473–485 and ref 5.

(14) (a) A multiwavelength (360–750 nm) and variable-temperature stopped-flow kinetics technique was used to study the reaction of O_2 with Cu(I) complexes. A Canterbury SF-3A stopped-flow system was coupled with a Zeiss MCS 512 diode-array detector and a Hewlett Packard 300-series computer for data collection. (b) Data reduction by factor analysis and nonlinear least-squares refinement for the rate constants was performed with the program package KINFIT (to be published). The underlying mathematics are closely analogous to those described previously for spectroscopic equilibrium studies (Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbühler, A. D. *Talanta* **1985**, *32*, 95–101), the evolution of species concentrations being calculated by numerical integration based on the predictor–corrector method for stiff differential equations. (Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice Hall: Englewood, NJ, 1971.) (c) A figure showing the UV–vis spectral changes during the oxygenation of **1** is given in the supplementary material.

(15) In accordance with the X-ray structural study of **3** along with coordination chemical considerations, we presently have to assume that RCN is lost upon dioxygen binding to **1**.

of the individual rate constants k_1, k_{-1}, and k_2, a composite rate constant $k_{on} = k_1k_2/k_{-1} = K_1k_2$ can be calculated directly (Table I) to describe the formation of the final 2:1 adduct $[\{LCu\}_2(O_2)]^{2+}$ (**3**). This has a negative temperature dependence (i.e., $\Delta H^{\ddagger} = -21$ kJ mol^{-1}), clearly explained by the fact that k_{-1} has a stronger temperature dependence than k_1 and k_2 combined; thus binding of O_2 to form the 2:1 adduct (**3**) is slower at higher temperatures. The overall data analysis leads to the calculated final spectra shown in Figure 1; the spectrum of **3** agrees very closely with that observed under "synthetic" conditions.[2a]

It is interesting to compare the results here with the limited data available in other copper-containing systems[3] as well as for iron and cobalt.[16-18] The present study provides the first full data for 1:1 Cu(I)-dioxygen adduct development, either in protein or synthetic systems. The formation of $[LCu(O_2)]^+$ (**2**) ($k_1 \sim 10^8$ M^{-1} s^{-1}, calcd at 25 °C, Table I) is faster than the rates seen for most LCo(II) 1:1 oxygenation reactions ($k_1 = 10^3$–10^6 M^{-1} s^{-1}, 25 °C).[16] The molecularity of the reaction of O_2 with **1** precludes meaningful comparisons of k_{on} with other Cu_2O_2 complexes derived from discrete dinuclear precursors.[3] However, $k_{on} = 4.4 \times 10^5$ M^{-2} s^{-1} at 25 °C for **3** (6.0×10^7 at -90 °C) parallels ligand-dependent values seen for peroxo–dicobalt(III) (Co_2O_2) complexes analogously derived from mononuclear LCo(II) species.[18] For heme–proteins or porphyrin–Fe^{II} model complexes, the O_2 on-rates ($k_1 \sim 10^6$–10^9 M^{-1} s^{-1}) are similar to that seen for formation of **2**. However, it appears that off-rates for iron species are much smaller, giving rise to larger K_1 values ($K_1 \sim 10^4$–10^6, 20 °C).[16]

For **1** and other nonprotein Cu(I) complexes,[3] the strong low-temperature O_2 binding for either 1:1 or 2:1 adducts is enthalpic in origin.[3] Large negative $\Delta S°$ values preclude room-temperature stability of the Cu_2O_2 synthetic complexes; this effect is not present in the multisubunit protein hemocyanin.[3,19] Co_2O_2 complexes also exhibit large negative $\Delta S°$ values, but considerable room-temperature stabilities ($\log K_{eq} \sim 6$–15)[16,17,18b] are derived from much larger negative $\Delta H°_{formation}$ values (e.g., -120 to -150 kJ/mol).[16,17]

The 1:1 Cu/O_2 species is of considerable interest as the important primary cuprous ion–dioxygen adduct, since its further reduction leads to O_2 activation in both chemical and biological systems.[4-6,20,21] Chemical investigations of Valentine and coworkers[22] and Thompson[23] lead to the formulation of such species as superoxo–cupric complexes (e.g., Cu^{II}–O_2^-), and Thompson was able to isolate a stable solid compound $[LCu(O_2)]$ (L = hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $\nu_{O-O} = 1015$ cm^{-1} for $^{18}O_2$; $\lambda_{max} = 524$ nm ($\epsilon = 600$ M^{-1} cm^{-1}). The structure of this complex was suggested to contain an unsymmetrical terminally coordinated O_2^- ligand, but a symmetric side-on η^2-superoxo ligation probably merits consideration.[24] Further efforts will be aimed at the characterization and reactivity studies of stable analogues of $[LCu(O_2)]^+$ (**2**).

Acknowledgment. We thank the National Institutes of Health (K.D.K.) and Swiss National Science Foundation (A.D.Z.) for support of this research.

Supplementary Material Available: Spectra illustrating the UV–vis changes occurring during the oxygenation of **1** (1 page). Ordering information is given on any current masthead page.

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Preparation of Functionalized Alkynyl(phenyl)iodonium Salts via a Novel Iodonium-Transfer Process between Alkynylstannanes and PhI^+CN^-OTf

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Received April 1, 1991

Alkynyliodonium species, **1**, have become useful reagents for the preparation of monofunctionalized acetylenes and other valuable synthetic transformations.[1-3] However, to date, with

$$RC{\equiv}CI^+Ph\,X^-$$

1

the exception of the β-Me_3Si-substituted system (**1**: R = Me_3Si), no β-functionalized alkynyliodonium species are known,[4] the full synthetic potential of these novel tricoordinate iodine species[5] thereby being limited.

Hence in this communication, we report the preparation of a variety of hitherto unknown β-functionalized alkynyl(phenyl)iodonium triflates via a new, unique iodonium-transfer process involving the readily available[6] PhI^+CN^-OTf as the transfer agent.[7]

A variety of functionalized alkynyliodonium salts may be prepared in good yields in a single step by the interaction of the appropriate alkynylstannanes[8] **2** with PhI^+CN^-OTf (Scheme I) in CH_2Cl_2 at low temperature. Compounds **4a–f** are isolated by low-temperature filtration under a N_2 atmosphere and are re-

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