Equilibrium and Redox Kinetics of Copper(II)−Thiourea Complexes

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Stopped-flow spectrophotometric measurements identify and determine equilibrium data for thiourea (tu) complexes of copper(II) formed in aqueous solution. In excess Cu(II), the complex ion $[Cu(tu)]^{2+}$ has a stability constant $\beta_1 = 2.3 \pm 0.1$ M^{-1} and molar absorptivity at 340 nm of $\epsilon_1 = (4.0 \pm 0.2) \times 10^3$ M^{-1} cm^{-1} at 25.0 °C, 2.48 mM $HClO_4$, and $\mu = 464$ mM $(NaClO_4)$. The fast reduction of Cu(II) by excess tu obeys the rate law $-d[Cu(II)]/dt = k'[Cu(II)]^2[tu]^7$ with a value for the ninth-order rate constant $k' = (1.60 \pm 0.18) \times 10^{14}$ M^{-8} s^{-1}, which derives from a rate-determining step involving the bimolecular decomposition of two complexed Cu(II) species. Copper-(II) catalyzes the reduction of hexachloroiridate(IV) by tu according to the rate law $-d[IrCl_6^{2-}]/dt = (k_{2,unc}[tu]^2 + k_{1,cat}[tu]^5[Cu(II)])[IrCl_6^{2-}]$. Least-squares analysis yields values of $k_{2,unc}$ and $k_{1,cat}$ equaling 385 ± 4 M^{-2} s^{-1} and $(3.7 \pm 0.1) \times 10^{13}$ M^{-6} s^{-1}, respectively, at $\mu = 115$ mM $(NaClO_4)$. The corresponding mechanism has a rate-determining step that involves the oxidation of $[Cu^{II}(tu)_5]^{2+}$ by $[IrCl_6]^{2-}$ rather than the bimolecular reaction of two cupric−tu complexes.

Introduction

Several factors suggest that metal ion contaminants might have influenced the oscillatory behaviors displayed by the chlorite−thiourea $(ClO_2^−$−tu) reaction under continuous-flow conditions,[2−4] much as iron(III) impurities have affected the Belousov−Zhabotinskii reaction.[5,6] First, we demonstrated[2] that trace levels of Cu(II), a putative catalyst of oxidations of tu,[2,7,8] catalyze the kinetics of the $ClO_2^−$−tu reaction under batch conditions and influence oscillations displayed by this reaction under continuous-flow conditions. Second, some oscillatory behaviors displayed by the $ClO_2^−$−tu oscillator have been reproduced under different experimental conditions.[3,4] Third, independently determined values of rate constants for elementary steps in this reaction have shown large discrepancies.[9,10] And, fourth, the reaction in unstirred media is both initiated by the walls of the supporting vessel and sensitive to the material from which the reactor is constructed.[11,12] Since kinetics studies[10,13] of the $ClO_2^−$ oxidation of tu have led to a plausible chemical mechanism that so far is unable to model the chaos and various periodic states exhibited by this complex reaction in continuous-flow systems, it is possible that including the kinetics of the reactions of copper(II) with either $ClO_2^−$ or tu could play factors in modeling this system's oscillatory behaviors.[14] The decom-

position of $ClO_2^−$ to ClO_2 is catalyzed by copper(II), and stability data for the coordination of $ClO_2^−$ by Cu(II) have been determined.[15] Presently, we focus our investigation on the equilibrium characteristics and kinetics behavior associated with the interactions of the transition metal copper and the reductant tu in order to augment our understanding of the roles of Cu(II) in catalyzing oxidations of tu[2,7] and possibly in influencing the exotic oscillatory dynamics,[2−4] spatial patterns,[12] and traveling waves[11] exhibited by the $ClO_2^−$−tu reaction.

Copper(I) is a soft acid with increased polarizability and often a lower number of coordination sites compared to Cu(II) and, with its closed shell $((Ar)3d^{10})$, usually forms diamagnetic, colorless complexes.[16] Copper(I) commonly binds soft sulfur-containing ligands, forming strong complexes with the unidentate ligand tu and its substituted derivatives N,N'-ethylenethiourea, N,N'-dimethylthiourea, and N,N,N',N'-tetramethylthiourea by coordination through the S atom of the ligand molecules.[17] Polarographic methods have been used to evaluate the overall binding constants for di, tri, and tetra tu complexes of Cu(I) that form when Cu^+ is combined with various excesses of tu.[18] More recently, the complete set of all four binding constants was determined for the complexes $[Cu^I(tu)_n]^+$ as a function of $n = 1−4$ by use of a potentiometric method.[19−21] At higher Cu(I) concentrations, there is some evidence for the formation of the dinuclear complex $[Cu_2(tu)_2]^{2+}$.[22] In contrast to the cuprous state, Cu(II) is a borderline hard acid showing characteristics of both classes of metals, usually has either five or six coordination sites, tends to form colorful, paramagnetic complexes, and is a weak oxidant that binds tu,[21,23] $CN^−$, $SO_3^{2−}$, and dithizone,[24] and π-acids.[25] Binding ligands such as these

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generates thermodynamic conditions that promote the rapid reduction of copper(II) to copper(I). The fast redox reaction between Cu(II) and tu prevented the use of slow polarographic methods to detect and measure formation constants for cupric−tu complexes,[23] although the binding constant was readily measured in these studies for the resultant $[Cu^I(tu)_4]^+$ complex. In the more recent series of reports mentioned above,[19−21] the stoichiometry of the Cu^{2+}−tu reaction was identified as

$$Cu^{2+} + (n+1)tu \rightarrow [Cu^I(tu)_n]^+ + \tfrac{1}{2}(tu)_2^{2+} \quad (n = 1{-}4)$$

$$(1)$$
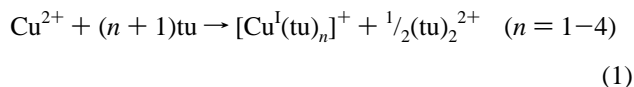
and the equilibrium constants for this redox reaction were determined.

Additional information can be gleaned from a study in which the UV spectrum of an unidentified intermediate formed in the Cu^{2+}−tu reaction was reported.[26] A subsequent investigation showed that similar species are formed in the reactions of Cu-(II) with substituted thioureas.[27] In the case of the reaction with tu, the composition of the intermediate was assigned as $[Cu^I$-$(tu)]^+$; it was reported to form on the time scale of 10 min and to decay over several hours, with both phases obeying first-order kinetics. Similar intermediates were detected in the reactions of substituted thioureas with Cu(II) in acetonitrile, but they were assigned as Cu(II) complexes of the thioureas.[28] Studies of the kinetics of oxidation of tu by Cu^{2+} are seriously lacking in detail, although there are two detailed reports describing reactions of the complexes $[Cu(dmp)_2]^{2+}$, $Cu^{II}(edta)$, and $Cu^{II}(hedta)$ with tu.[29,30] The first kinetic study with Cu^{2+} as the oxidant apparently was conducted with only one set of initial concentrations: 0.025 M Cu^{2+} and tu.[31] Reasons to be skeptical of this report include the lack of any experiments to determine the kinetic orders with respect to the individual components, the unusual overall order of 1.5, and the observation of a precipitate during the reaction. A more recent report presented qualitative evidence that Cu(II) is reduced to Cu(I) only when tu is in at least 4-fold excess.[32] Polarographic studies on the reaction have not been particularly informative because of complications relating to the reduction of Cu(I) to Cu(0), the reduction of $(tu)_2^{2+}$, and the adsorption of copper complexes onto the electrode surfaces.[33,34] In summary, it seems clear that Cu^{2+} is reduced by tu according to the overall reaction (1), but there are disagreement and few firm data regarding the nature of the intermediates formed and the reaction kinetics.

In recent years, it has become evident that Cu(II) commonly forms intensely absorbing complexes with oxidizable ligands and that monitoring their decay can establish the overall kinetics of the redox reactions. This approach has been used to detect and characterize the transients bis(thiosulfato)cuprate(II) ($[Cu(S_2O_3)_2]^{2-}$),[35] chloritocopper(II) ($[CuClO_2]^+$),[15] and various

sulfitocopper(II) complexes ($[Cu_n(SO_3)_m]^{2(n-m)+}$),[36,37] the last of which are important in atmospheric chemistry involving the reactions of acid rain precursors. Presently, we use rapid-scanning monochromator (RSM) stopped-flow spectrophotometry to detect a series of intensely absorbing cupric−tu complexes ($[Cu(tu)_x]^{2+}$) that form as forerunners to reduction of the metal center. We determine the equilibrium constant (β) and molar absorptivity (ϵ) characterizing the complex $[Cu(tu)]^{2+}$ formed under conditions of excess copper(II).[38−40] We use absorbance measurements also to evaluate the redox kinetics of the direct reaction of Cu^{2+} with tu under conditions of excess tu. From these results we proffer a rate law and a chemical mechanism satisfying the kinetics of this reaction. Furthermore, we present the rate law for the copper-catalyzed oxidation of tu by the outer-sphere oxidant hexachloroiridate(IV), whose uncatalyzed reaction was studied previously.[7] These two complementary studies form the basis for an understanding of copper catalysis of oxidations of tu in general and more specifically for its potential effects in systems displaying nonlinear behavior.

Experimental Section

$Cu(ClO_4)_2\cdot6H_2O$ (Alfa) and tu (Eastman Kodak) were each recrystallized twice from water, then stored in vessels wrapped in aluminum foil, and dried with anhydrous P_2O_5 in a vacuum desiccator. Copper-(II) solutions were standardized iodometrically.[41] $Na_2IrCl_6\cdot6H_2O$ (Alfa) and 1,10-phenanthroline (phen, Aldrich) were used as purchased. All measurements of the Cu(II)−tu reaction were carried out at 25 °C using an Olis RSM-1000 optical/data-acquisition/analysis system interfaced to an Olis USA-SF stopped-flow unit with a 1.7 cm path length. A Hi-Tech SF-51 stopped flow instrument (1.0 cm path length) operating at 410 nm and interfaced to an Olis 4300 data acquisition and analysis system was used to measure the $[IrCl_6]^{2-}$−tu reaction at 25 °C with and without added copper(II). Absorbance spectra of the Cu(II)−tu reaction products qualitatively confirm the formation[42] of $(tu)_2^{2+}$, which parallels the disulfides produced by many copper(II) oxidations of thiols.[43] The water used throughout this entire work was purified by distilling doubly-deionized water with a Barnstead/Fi-streem glass still.

Results

Cu(II)−tu Reaction. We previously examined the Cu(II)−tu reaction over the wavelength range 300−820 nm and found that this reaction produces an absorbance band with a maximum at 340 nm (Figure 1) virtually instantaneously on the stopped-flow time scale.[2] The qualitative appearance of this absorption band is in agreement with that reported by other workers,[26] although we are unable to reproduce the slow kinetics of its appearance that they observed.[27] The rapidity of this reaction in which tu replaces a water molecule coordinated to $[Cu(H_2O)_6]^{2+}$ is characteristic of ligand substitution reactions involving aquated copper(II), whose fast water exchange rate

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(38) A value for the Cu^{2+}−tu binding constant has been reported previously.[39] The result, however, must be rejected because it depends on the erroneous assumption that tu is easily protonated with a value of 5.5 for the pK_a of Htu^+.[40] In fact, Htu^+ is a moderately strong acid with $pK_a < 0$.[42]

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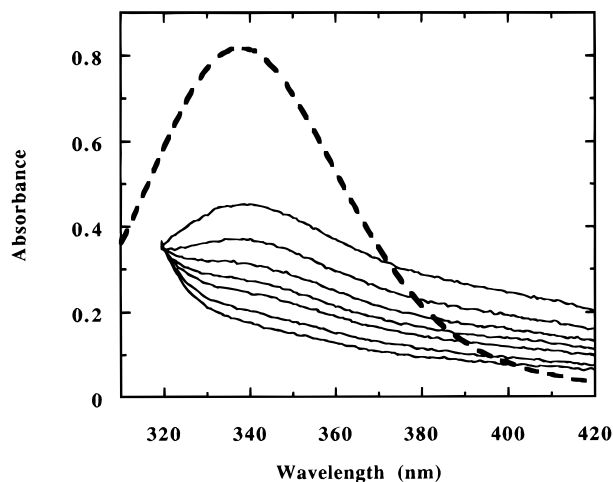
Figure 1. Absorbance spectra of Cu(II)−tu complexes produced in excess copper(II) (dashed line) with 13.7 mM Cu(II), 3.6 mM tu, 100 mM HClO$_4$, and 162 mM NaClO$_4$ and undergoing redox reaction in excess tu (solid lines spaced at 60 ms intervals) with 0.5 mM Cu(II), 40.7 mM tu, 1.2 mM HClO$_4$, and 162 mM NaClO$_4$.
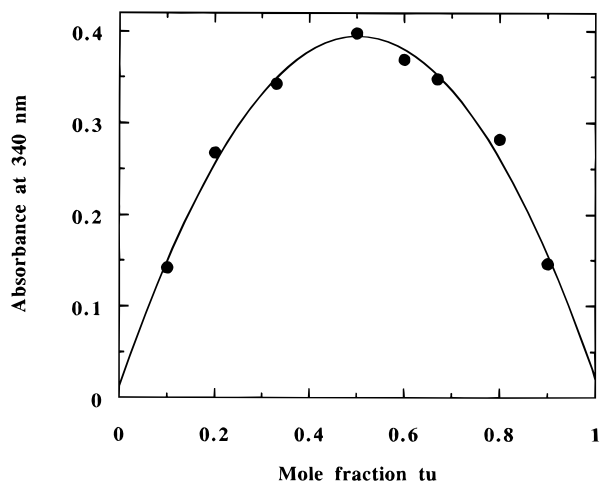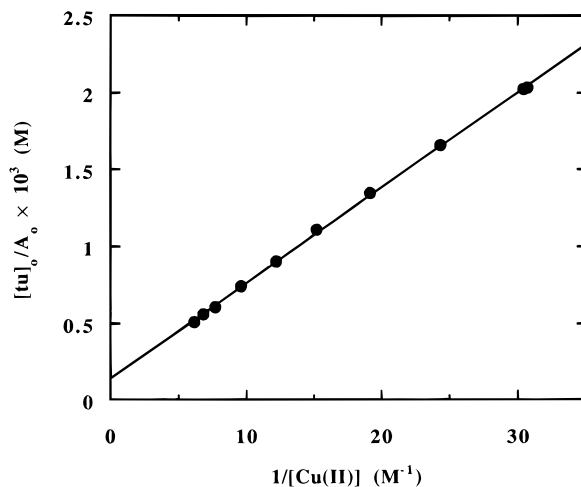

Figure 2. Job's plot of the Cu(II)−tu intermediate at 340 nm with a constant combined concentration of [Cu(ClO$_4$)$_2$·6H$_2$O] + [tu] = 10.0 mM, 200 mM NaClO$_4$, and 1.2 mM HClO$_4$. The solid line is an arbitrary curve to guide the eye.

and extreme lability are attributed to rapid Jahn−Teller inversion.[44] Applying the method of continuous variation[45] to the initial absorbance (A_0) at 340 nm yields a Job plot with a maximum at the mole fraction of tu equal to 0.5 (Figure 2). Our Job plot is in qualitative agreement with that of Javet et al., although those workers attributed the absorption to a Cu(I) complex.[27] In addition, we find that the maximum is independent of wavelength from 320 to 420 nm. Its broad curvature indicates that the predominantly absorbing species is weakly bound. Copper(II) therefore rapidly coordinates one tu molecule to form the mononuclear binary complex [Cu(tu)]$^{2+}$ with a corresponding equilibrium constant β_1 according to

$$Cu^{2+} + tu \rightleftharpoons [Cu(tu)]^{2+} \tag{2a}$$
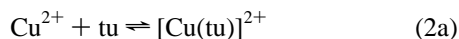
$$\beta_1 = \frac{[Cu(tu)^{2+}]}{[Cu^{2+}][tu]} \tag{2b}$$

Equilibrium data for [Cu(tu)]$^{2+}$ are determined by measuring changes in A_0 at 340 nm as a function of the total copper(II)

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Figure 3. Plot of [tu]$_0$/A_0 versus 1/[Cu(II)] over the [Cu(II)] range 0.033−0.163 M with 0.95 mM tu, 464 mM NaClO$_4$, and 2.48 mM HClO$_4$ yielding stability data for [Cu(tu)]$^{2+}$. The solid line is the linear least-squares fit.

concentration ([Cu(II)]), with [Cu(II)] >> [tu]. The complex ion persists moderately long under these conditions, although its gradual degradation does not follow simple kinetics behavior at this wavelength. The absorbance spectrum of [Cu(tu)]$^{2+}$ from 320 to 390 nm is bell-shaped (Figure 1) and is independent of variations in [HClO$_4$]. Making the two assumptions that [Cu(tu)]$^{2+}$ is the only absorbing species and that [Cu^{2+}] ≈ [Cu(II)], and correcting A_0 ($A_{0,corr}$) for the slight absorbance by the d−d transition of uncomplexed cupric ions, yields the relation

$$\frac{[tu]_0}{A_{0,corr}} = \frac{1}{\epsilon b \beta_1 [Cu(II)]_0} + \frac{1}{\epsilon b} \tag{3}$$

in which ϵ denotes the molar absorptivity of [Cu(tu)]$^{2+}$ at 340 nm and b is the optical path length of the RSM. A plot of [tu]$_0$/$A_{0,corr}$ versus 1/[Cu(II)] is linear (Figure 3) with a slope of $(6.35 \pm 0.04) \times 10^{-5}$ M^2 and an intercept of $(1.48 \pm 0.07) \times 10^{-4}$ M and with corresponding values of $\epsilon = (4.0 \pm 0.2) \times 10^3$ M^{-1} cm^{-1} and $\beta_1 = 2.3 \pm 0.1$ M^{-1}. Although the statistical uncertainties in these values are rather small, systematic errors could lead to a value as large as 4 M^{-1} for β_1. This complex is therefore weakly bound and accompanied by an intense ligand-to-metal charge-transfer electronic transition, as is expected for this bonding situation.[46]

In contrast to the equilibrium experiments described above, the absorbance band generated with excess tu is relatively much larger and more significant at longer wavelengths (Figure 1), which provides the first evidence for the formation of polycoordinated cupric complexes. These spectral features are also independent of variations in [HClO$_4$]. The profile of A_0 at 340 nm as a function of varied excess concentrations of tu and constant [Cu(II)] depicts a nonlinear relationship (Figure 4), which provides the second evidence for the formation of higher order cupric−tu complexes. We have not attempted to resolve the spectra and formation constants for these higher complexes because of complications arising from rapid redox decomposition under these conditions and the likelihood that several of these complexes have nearly identical spectra. Nevertheless, we can gain insight into the composition of these higher order complexes by measuring the rapid decay of absorbance (A) in these circumstances, which portrays the formal reduction kinetics of copper(II) and fits excellently homogeneous pseudo-second-

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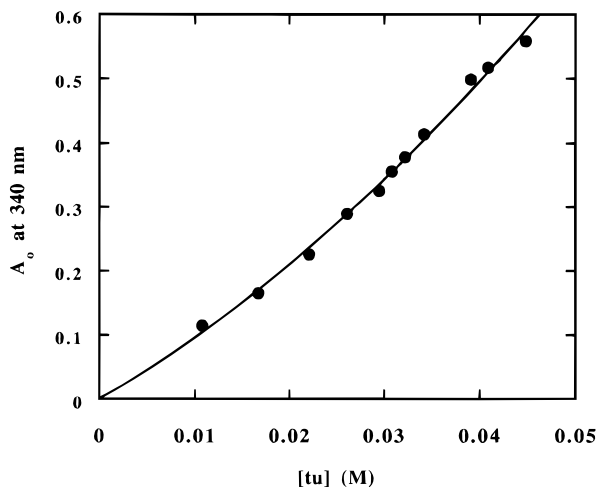
Figure 4. A_0 as a function of varied excesses of [tu] with 0.52 mM $[Cu(II)]_0$, 464 mM $NaClO_4$, and 2.48 mM $HClO_4$. The solid line is a second-order polynomial fit, the nonlinearity of which indicates the formation of higher tu complexes.

order kinetics according to

$$-\frac{dA}{dt} = k_{obs}A^2 \tag{4}$$

Experiments in which O_2 was rigorously excluded from solution showed that dissolved O_2 has no effect on the kinetics. Equation 4 is translatable into an expression for the disappearance of Cu-(II) by converting the observed second-order rate constants k_{obs} ((absorbance units)$^{-1}$ s^{-1}) into apparent rate constants k_{app} (M^{-1} s^{-1}) through the implementation of the relation $k_{app} = k_{obs}(b\epsilon^*)$, in which b is the optical path length and ϵ^* is the composite of the respective molar absorptivities for each of the absorbing copper(II)−tu complexes. Evaluating ϵ^* is done in the following way with the presupposition that ϵ for uncomplexed, "free" cupric ions ($[Cu^{2+}]_f$) is effectively zero:

$$[Cu(II)] = [Cu^{2+}]_f(1 + \sum_{i=1}^{N}\beta_i[tu]^i) \tag{5}$$

$$A = b[Cu^{2+}]_f(\sum_{i=1}^{N}\beta_i[tu]^i\epsilon_i) \tag{6}$$

and so

$$A = b[Cu(II)](\sum_{i=1}^{N}\beta_i[tu]^i\epsilon_i)/(1 + \sum_{i=1}^{N}\beta_i[tu]^i) = b\epsilon^*[Cu(II)] \tag{7}$$

The value of ϵ^* is calculable from A_0, the point at which [Cu-(II)] is known precisely. Rearranging eq 7 and combining it with the definition of k_{app} yield

$$b\epsilon^* = A_0/[Cu(II)]_0 \qquad k_{app} = k_{obs}A_0/[Cu(II)]_0 \tag{8}$$

The disappearance of copper(II) is therefore expressible as

$$-\frac{d[Cu(II)]}{dt} = k_{app}[Cu(II)]^2 \tag{9}$$

The dependence of k_{app} on [tu], as determined from the slopes of log−log plots, is seventh order. Least-squares analysis of the plot of k_{app} versus [tu]^7 (Figure 5) computes a slope
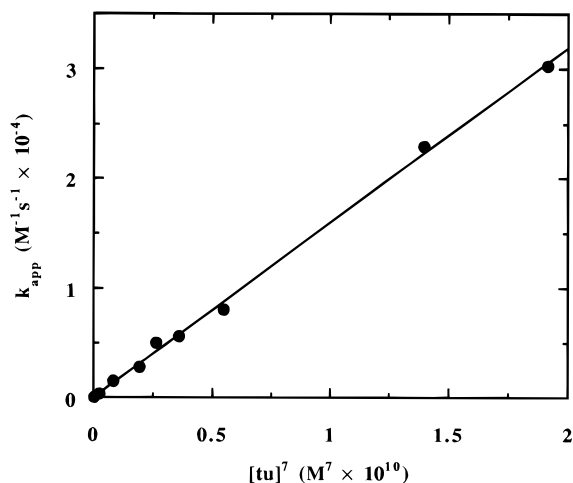
Figure 5. Seventh-order dependence of k_{app} on [tu] for the Cu(II)−tu reaction with 0.52 mM Cu(II), 464 mM $NaClO_4$, and 2.48 mM $HClO_4$. The concentration of tu ranges from 0.0167 to 0.0448 M. The solid line is a linear least-squares fit.

corresponding to the rate constant k'.

$$k_{app} = k'[tu]^7; \quad k' = (1.60 \pm 0.18) \times 10^{14}\,\text{M}^{-8}\,\text{s}^{-1} \tag{10}$$

A trend of slightly increasing k_{app} with increasing $[HClO_4]$ (13%) over the concentration range 2−10 mM most likely reflects differing specific ion effects between Na$^+$ and H$^+$ rather than a strict dependence of k_{app} on [H$^+$].

$[IrCl_6]^{2-}$−tu−Cu(II) Reaction. Prior to investigating the $[IrCl_6]^{2-}$−tu−Cu(II) reaction, we reproduced[7] the kinetics of the uncatalyzed $[IrCl_6]^{2-}$−tu reaction

$$2[IrCl_6]^{2-} + 2tu \rightarrow 2[IrCl_6]^{3-} + (tu)_2^{2+} \tag{11}$$

The dependence of the observed, uncatalyzed pseudo-first-order rate constant ($k_{obs,unc}$) on [tu] is second order for the consumption of 87.5 μM $[IrCl_6]^{2-}$ by 4−41 mM tu in 2.0 mM $HClO_4$, 0.3 M $NaClO_4$, and 0.4 mM phen added to sequester residual adventitious metal ions.

$$-\frac{d[IrCl_6^{2-}]}{dt} = k_{obs,unc}[IrCl_6^{2-}] = k_{2,unc}[tu]^2[IrCl_6^{2-}] \tag{12}$$

Although least-squares analysis of the plot of $k_{obs,unc}/[tu]$ versus [tu] calculates a value for the third-order, uncatalyzed rate constant ($k_{2,unc} = 385 \pm 4$ M^{-2} s^{-1}) in agreement with earlier studies,[7] this analysis also reveals a small intercept that might be indicative of a minor contribution to the kinetics from an overall second-order process ($k_{obs,unc} = k_{1,unc}[tu] + k_{2,unc}[tu]^2$ with $k_{1,unc} = 0.53 \pm 0.09$ M^{-1} s^{-1}). The intercept is negligible in the plot of $k_{obs,unc}$ versus [tu]^2, for which $k_{2,unc} = 398 \pm 1$ M^{-2} s^{-1} and the intercept is $(3.7 \pm 0.8) \times 10^{-3}$.

The orders with respect to the individual components in the catalyzed $[IrCl_6]^{2-}$−tu−Cu(II) reaction are determined in the ensuing manner from the observed, total pseudo-first-order rate constants ($k_{obs,tot}$). With constant initial concentrations of $[IrCl_6]^{2-}$ and excess tu, the initial concentration of Cu(II) is varied from 0 to 41 μM (Table 1a). Plotting the logarithm of the differences of the pseudo-first-order rate constant, $k_{obs,tot}$, and its uncatalyzed pseudo-first-order counterpart, $k_{obs,unc}$, as $\log(k_{obs,tot} - k_{obs,unc})$ versus $\log([Cu(II)]_0)$ reveals a first-order (1.00 ± 0.03) dependence on $[Cu(II)]_0$.[47] Similarly, varying

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(47) The first entry in Table 1a was used for the value of the uncatalyzed rate constant in these plots.

Table 1. Kinetics Data for the $[IrCl_6]^{2-}-tu-Cu(II)$ Reaction

k_{obs}, s^{-1}	$[Cu(II)]_0$, μM	[tu], M	k_{obs}, s^{-1}	$[Cu(II)]_0$, μM	[tu], M
		Part a[a]			
0.10	0.00	0.0147	0.44	11.0	0.0147
0.21	3.25	0.0147	1.08	29.3	0.0147
0.32	7.32	0.0147	1.37	40.7	0.0147
0.37	9.35	0.0147			
		Part b[a]			
0.51	7.32	0.0161	1.88	7.32	0.0220
0.58	7.32	0.0169	3.55	7.32	0.0259
1.10	7.32	0.0194	7.20	7.32	0.0301
		Part c[b]			
0.13	0.00	0.0150	0.64	4.07	0.0184
0.42	4.07	0.0167	1.12	4.07	0.0209
0.55	4.07	0.0175			

[a] 92 μM $[IrCl_6]^{2-}$, 1.5 mM $HClO_4$, and 113 mM $NaClO_4$. [b] 82 μM $[IrCl_6]^{2-}$, 4.7 mM $HClO_4$, and 150 mM $NaClO_4$.
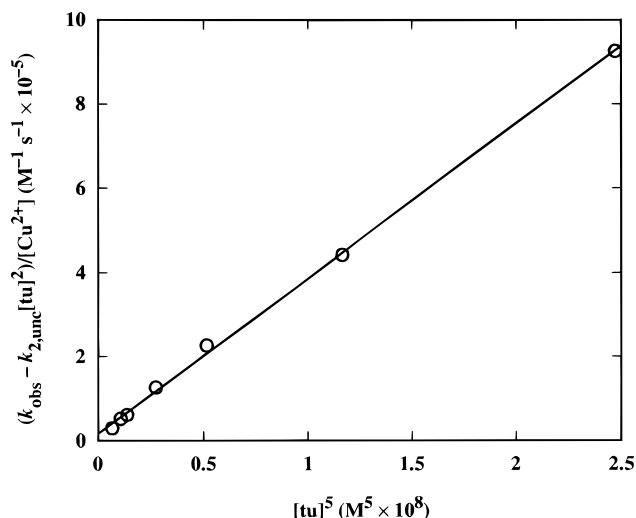
Figure 6. Linear plot of $(k_{obs} - k_{2,unc}[tu]^2)/[Cu(II)]$ versus $[tu]^5$ (experimental conditions enumerated in Table 1b). The solid line is a linear least-squares fit.

the [tu] at constant $[IrCl_6^{2-}]_0$ and $[Cu(II)]_0$ demonstrates (Table 1b,c) an average fifth-order (4.94 ± 0.19) dependence on [tu] in the corresponding graphical determinations of $\log((k_{obs,tot} - k_{2,unc}[tu]^2)/[Cu(II)]_0)$ vs $\log([tu])$. The overall rate expression for the $[IrCl_6]^{2-}$ oxidation of tu in the presence of copper(II) is

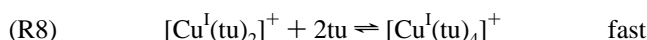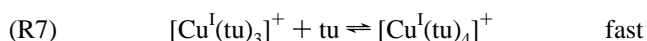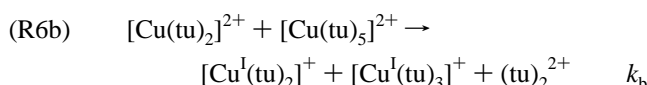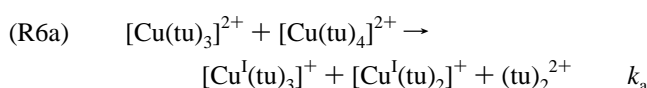$$-\frac{d[IrCl_6^{2-}]}{dt} = k_{obs,tot}[IrCl_6^{2-}] \qquad (13)$$

$$k_{obs,tot} = k_{2,unc}[tu]^2 + k_{1,cat}[tu]^5[Cu(II)]_0 \qquad (14)$$

Least-squares analysis of the data in Table 1b as $(k_{obs,tot} - k_{2,unc}[tu]^2)/[Cu(II)]_0$ versus $[tu]^5$ (Figure 6) calculates a value of $k_{1,cat} = (3.69 ± 0.05) \times 10^{13}$ M^{-6} s^{-1}. Carrying out the same protocol with 81.8 μM $[IrCl_6^{2-}]_0$, 4.68 mM $[HClO_4]$, 150 mM $[NaClO_4]$, and 4.07 μM $[Cu(II)]_0$ also generates pseudo-first-order rate constants (Table 1c), and regression analysis computes the value $k_{1,cat} = (5.46 ± 0.24) \times 10^{13}$ M^{-6} s^{-1}, in close agreement with the first set of experiments, despite the 3-fold increase in $[HClO_4]$.

Discussion

The mechanism of irreversible electron transfer in the Cu(II)−tu reaction is elucidated from the measured second-order decay of absorbance, which reflects the bimolecular decomposition of two complexed cupric species. On the basis of the present

results, we presume the formation of the mono, di, tri, tetra, and penta tu complexes of Cu(II) occurring in rapid pre-equilbrium steps prior to electron transfer and the contribution by all of these complexes to the observed absorbance spectrum. Note that since the various $Cu^{II}(tu)_x$ species are in rapid equilibrium, the form of the rate law leads to a kinetic ambiguity. The following reaction scheme proposes two kinetically equivalent rate-determining steps (RDSs) consisting of two cupric ions combined with a total of seven tu ligands. Steps R6a−R6b might be acting independently or concurrently to produce the observed kinetics. Following these two rate-limiting steps are a pair of reactions that yield $[Cu^I(tu)_4]^+$, the predominant form of Cu(I) under our conditions.[19-21,48]

$$\text{(R1)} \qquad Cu^{2+} + tu \rightleftharpoons [Cu(tu)]^{2+} \qquad \beta_1$$

$$\text{(R2)} \qquad Cu^{2+} + 2tu \rightleftharpoons [Cu(tu)_2]^{2+} \qquad \beta_2$$

$$\text{(R3)} \qquad Cu^{2+} + 3tu \rightleftharpoons [Cu(tu)_3]^{2+} \qquad \beta_3$$

$$\text{(R4)} \qquad Cu^{2+} + 4tu \rightleftharpoons [Cu(tu)_4]^{2+} \qquad \beta_4$$

$$\text{(R5)} \qquad Cu^{2+} + 5tu \rightleftharpoons [Cu(tu)_5]^{2+} \qquad \beta_5$$

$$\text{(R6a)} \qquad [Cu(tu)_3]^{2+} + [Cu(tu)_4]^{2+} \rightarrow$$
$$[Cu^I(tu)_3]^+ + [Cu^I(tu)_2]^+ + (tu)_2^{2+} \qquad k_a$$

$$\text{(R6b)} \qquad [Cu(tu)_2]^{2+} + [Cu(tu)_5]^{2+} \rightarrow$$
$$[Cu^I(tu)_2]^+ + [Cu^I(tu)_3]^+ + (tu)_2^{2+} \qquad k_b$$

$$\text{(R7)} \qquad [Cu^I(tu)_3]^+ + tu \rightleftharpoons [Cu^I(tu)_4]^+ \qquad \text{fast}$$

$$\text{(R8)} \qquad [Cu^I(tu)_2]^+ + 2tu \rightleftharpoons [Cu^I(tu)_4]^+ \qquad \text{fast}$$
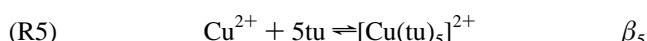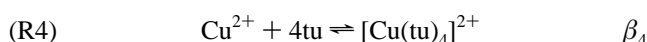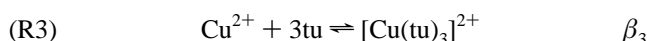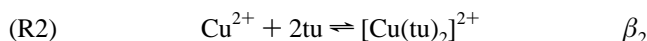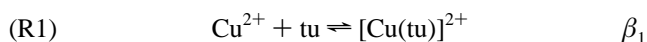
Equations R1−R7 combine to generate the overall rate expressions

$$-\frac{d[Cu(II)]}{dt} = 2k_a[Cu(tu)_3^{2+}][Cu(tu)_4^{2+}]$$
$$\text{and/or} \quad 2k_b[Cu(tu)_2^{2+}][Cu(tu)_5^{2+}] \qquad (15)$$

Inserting the overall stability constants for each of the respective complex ions ($\beta_i = [Cu(tu)_i^{2+}]/[Cu^{2+}][tu]^i$) and expressing copper in terms of the total concentration of Cu(II) (equation 5) lead to

$$-\frac{d[Cu(II)]}{dt} = \frac{2k_a\beta_3\beta_4[Cu(II)]^2[tu]^7}{(1 + \sum\beta_i[tu]^i)^2}$$

$$\text{and/or} \quad \frac{2k_b\beta_2\beta_5[Cu(II)]^2[tu]^7}{(1 + \sum\beta_i[tu]^i)^2} \qquad (16)$$

Approximating that 1 is greater than $\sum\beta_i[tu]^i$ reduces these equations to

$$-\frac{d[Cu(II)]}{dt} = 2k_a\beta_3\beta_4[Cu(II)]^2[tu]^7$$

$$\text{and/or} \quad 2k_b\beta_2\beta_5[Cu(II)]^2[tu]^7 \qquad (17)$$

(48) Krzewska, S.; Glinski, J.; Podsiadly, H. *Polish J. Chem.* **1986**, *60*, 929.

Compounding the second-order rate constant k_a or k_b ($M^{-1} s^{-1}$) and the associated stability product constants, either β_3 (M^{-3}) and β_4 (M^{-4}) or β_2 (M^{-2}) and β_5 (M^{-5}), respectively, defines the extraordinary ninth-order rate constant k' according to

$$\frac{k_{app}}{[tu]^7} = k' = 2k_a\beta_3\beta_4 \quad \text{and/or} \quad 2k_b\beta_2\beta_5 \qquad (18)$$

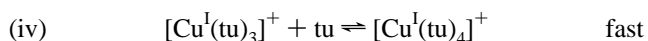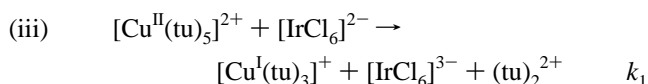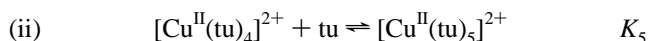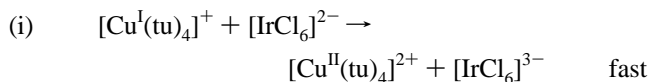in which $k' = (1.60 \pm 0.18) \times 10^{14}$ $M^{-8} s^{-1}$ (eq 10).

The above mechanism places significant constraints on the associated values of β_i. Thus, if a diffusion-controlled maximum (1×10^{10} $M^{-1} s^{-1}$) is accepted for k_a or k_b, then the product $\beta_3\beta_4$ or $\beta_2\beta_5$ (or their sum if the two pathways contribute equally) has a lower limit of 8×10^3 M^{-6}. This lower limit can be achieved if a value of 3.3 M^{-1} or greater is assigned to all of the stepwise formation constants and if the two pathways contribute equally in the reaction; likewise, a lower limit of 3.6 M^{-1} applies if only one of the pathways is significant. In either case, the values are in agreement with the measured value of β_1. The plausibility of this scenario depends on the likelihood that the redox steps could be as fast as required and on whether the successive stability constants could be this large. The first requirement is supported by the experimental observation of comparably large rate constants for electron-transfer reactions of other dipositive metal complexes.[49] The second requirement might seem unlikely in view of the rule that successive stability constants generally decrease. However, this rule is derived largely from reactions of anionic ligands in which electrostatic effects alone will lead to the rule. When attention is focused on monodentate uncharged ligands, the amount of pertinent data is rather sparse. In the case of NH_3 as a ligand, the tables of Smith and Martell show that the successive stability constants usually decrease.[50−52] An exception can be found in the binding of NH_3 by Zn^{2+}, for which the four successive stability constants are essentially identical.[50] Binding of tu also usually shows decreases in the successive stability constants, but in the case of Pb^{2+} the values of the first four constants are essentially identical.[51] In summary, although our proposed mechanism places somewhat unusual demands on the individual steps, there is adequate precedent for each of them.[53]

Currently it is indecipherable whether the reduction of Cu(II) by tu proceeds through an inner-sphere or an outer-sphere mechanism. An outer-sphere mechanism would seem to imply the formation of an undetected Cu(III) or ligand-radical intermediate prior to an internal redox decomposition. Alternatively, an inner-sphere process entailing adjacent rather than remote attack is feasible, given the tendency of metals to coordinate tu through the S atom[17] and the capacity of that moiety to bond two metal ions simultaneously.[54] Establishing two such bridges would create a binuclear activated complex with an unequal distribution of five ligand molecules flanking two cupric centers partitioned by coordination to two distinct sulfur bridges. This species would have the composition

(49) Creutz, C.; Sutin, N. *Inorg. Chem.* **1976**, *15*, 496.
(50) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4, p 41.
(51) Martell, A. E.; Smith, R. M. *Critical Stability Constants;* Plenum Press: New York, 1982; Vol. 5, p 385.
(52) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum Press: New York, 1989; Vol. 6, p 423.
(53) Note that the tabulated values for binding of tu by Cu^{2+} given in vol. 6 of *Critical Stability Constants* by Smith and Martell appear to be in error. The values given were inadvertently calculated as $\log(\log(\beta))$ (R. Motekaitis, personal communication, 1996). However, from the original reference it is evident that they actually refer to the redox reactions given in eq 1 rather than to substitution reactions at Cu(II).
(54) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry;* 4th ed.; John Wiley & Sons: New York, 1980; p 188.

$Cu_2(tu)_7^{4+}$ and would be formed as an intermediate during the process designated as (R6a) (or (R6b)). An analogous bicupric intermediate was proposed for the Cu(II)−CN^- reaction,[55] whose second-order dependence on the absorbing species ($[Cu^{II}(CN)_4^{2-}]$) translated into a second-order dependence on [Cu(II)] and a sixth-order dependence on the excess ligand concentration. Similar kinetics traits were also found in the Cu(II)−$S_2O_3^{2-}$ reaction (in excess $S_2O_3^{2-}$, $v = k[Cu(II)]^2$-$[S_2O_3^{2-}]^4$).[35] If the formation of doubly bridged binuclear activated complexes can be generalized to electron transfers of Cu(II) with reducing ligands, then these comparisons provide some justification of the inner-sphere mechanism currently being postulated for the Cu(II)−tu reaction. The most significant distinction between the Cu(II)−tu reaction and the Cu(II)−CN^- and Cu(II)−$S_2O_3^{2-}$ systems is the nonisolability of a polyco-ordinated cupric−tu complex (or complexes), in contrast to the identifiable reactants $[Cu(CN)_4]^{2-}$ and $[Cu(S_2O_3)_2]^{2-}$. One factor leading to the high order in the tu reaction relative to these other reactions arises from the weaker electrostatic repulsions associated with the neutral tu ligand. Another factor is the strong stabilization conferred upon Cu(I) by several tu ligands, which adds to the driving force of the rate-limiting redox step.[21] Although the mechanistic details of product formation have not been established in any of these systems, an interesting similarity in these three reactions is the production of dimeric species as the end-products (($tu)_2^{2+}$, CN_2, and $S_4O_6^{2-}$).

When catalyzed by Cu(II), the $[IrCl_6]^{2-}$ oxidation of excess tu involves a reaction pathway first-order in [Cu(II)] and fifth-order in [tu], which implies the involvement of polycoordinated cupric−tu complexes. It is the second-order dependence on [Cu(II)] in the Cu(II)−tu reaction compared to the first-order dependence on [Cu(II)] in the $[IrCl_6]^{2-}$−tu reaction that is the crucial distinction between these two systems. These results imply that the Cu(II)−tu redox reaction is not the regulator of the catalyzed cycle of the $[IrCl_6]^{2-}$−tu−Cu(II) reaction and that this process involves the $[IrCl_6]^{2-}$ oxidation of the pentakis-(thiourea)copper(II) complex ion. This conclusion is consistent with the values of $k_{1,cat}$ in the $[IrCl_6]^{2-}$−tu reaction and of k' in the Cu(II)−tu reaction, which under these experimental conditions predict a much faster rate of reduction of Cu(II) via oxidation by $[IrCl_6^{2-}]$ than by another cupric−tu complex.

Simpler mechanisms can be deduced for Cu(II) catalysis in the $[IrCl_6]^{2-}$−tu reaction to accommodate the first-order dependence on copper(II). Since Cu^{2+} is added to the syringe containing tu, the oxidation of the most prevalent cuprous product ($[Cu^{I}(tu)_4]^+$) begins the postulated mechanism. This arrangement is equivalent to the regeneration step of the catalytic cycle, should the proposed mechanism begin with the oxidation of the cupric complexes.

(i) $\quad [Cu^{I}(tu)_4]^+ + [IrCl_6]^{2-} \rightarrow$
$$[Cu^{II}(tu)_4]^{2+} + [IrCl_6]^{3-} \qquad \text{fast}$$

(ii) $\quad [Cu^{II}(tu)_4]^{2+} + tu \rightleftharpoons [Cu^{II}(tu)_5]^{2+} \qquad K_5$

(iii) $\quad [Cu^{II}(tu)_5]^{2+} + [IrCl_6]^{2-} \rightarrow$
$$[Cu^{I}(tu)_3]^+ + [IrCl_6]^{3-} + (tu)_2^{2+} \qquad k_1$$

(iv) $\quad [Cu^{I}(tu)_3]^+ + tu \rightleftharpoons [Cu^{I}(tu)_4]^+ \qquad \text{fast}$

Assuming rapid equilibrium in step ii yields the overall rate expression

(55) Katagiri, A.; Yoshimura, S.; Yoshizawa, S. *Inorg. Chem.* **1981**, *20*, 4143.

$$-\frac{d[IrCl_6^{2-}]}{dt} = 2k_1\beta_5[IrCl_6^{2-}][Cu(II)][tu]^5 \qquad (19)$$

such that $2k_1\beta_5 = k_{1,cat}$, whose value was calculated in the least-squares analysis above (eq 14). If it is assumed that $\beta_5 = \beta_1^5$ and a value of 4 M^{-1} is taken for β_1, this mechanism leads to a value of 1.8×10^{10} M^{-1} s^{-1} for k_1, which is not implausibly large for a reaction of this charge type. Note that this assumption regarding the magnitudes of the succesive stability constants is the same as that made above in the discussion of the direct redox reaction of tu with Cu^{2+}. It should also be noted that, despite the conventional appellation of $[IrCl_6]^{2-}$ as an outer-sphere oxidant, inner-sphere exceptions have been observed, and there remains a possibility that alternative explanations (e.g. an inner-sphere Cl^- bridge) can describe the details of step iii. Since the mechanisms for the Cu(II)−tu and the $[IrCl_6]^{2-}$−tu−Cu(II) reactions contain a common species, $Cu(tu)_5^{2+}$, it is possible that both reactions proceed by similar inner-sphere or outer-sphere mechanisms involving this complex, although there is no stringent requirement for $Cu(tu)_5^{2+}$ to fulfill identical functions in these different reactions.

Conclusion

The interactions of tu with metal ions have practical applications in the removal of copper deposits encrusting power plant boilers,[18] the anticorrosion of steel, and the masking of interference by copper in hydride generation/atomic absorption determinations of selenium[56] and potentially in the treatment of metalliferous industrial wastewaters.[57] The present results exhibit physical evidence of and furnish quantitative stability

(56) Bye, R.; Engvik, L.; Lund, W. *Anal. Chem.* **1983**, *55*, 2457.
(57) Mihaylov, B.; Hendrix, J. In *EPD Congr., 1992, Proc. Symp. TMS Annu. Meet.* **1992**, 81−97.

data for some of these interactions. Complexes of both copper-(II) and copper(I) are of paramount importance in the Cu(II)-catalyzed $[IrCl_6]^{2-}$−tu reaction, and these complexes are most likely the copper species that accelerate the reactions of tu with other oxidants, particularly those with ClO_2^-, IO_3^-, BrO_3^-, and ClO_2 in batch and the oscillatory ClO_2^-−tu reaction in open systems,[2] as mentioned earlier. The use in continuous-flow studies of the ClO_2^-−tu reaction of unrecrystallized tu, which can be contaminated by substantial amounts of metal ion impurities,[2] has evoked the question of the extent catalysis by adventitious Cu(II) might have had on the exotic nonlinear phenomena displayed by the ClO_2^-−tu oscillator, perhaps having induced or suppressed oscillatory dynamics or having displaced bifurcation boundaries, the points at which these behaviors are most sensitive to perturbations. However, in all of these cases biphthalate was also used to buffer the pH, and the capacity of this organic compound to sequester metal ions and obscure their catalytic effects on the oscillatory behaviors should be recognized. Studies of the kinetics, traveling waves, and spatial patterns with the ClO_2^-−tu reaction were not carried out in biphthalate media or with recrystallized tu, and adventitious metal ions may have affected the system under these conditions. As the chemical mechanism of this reaction continues to be unraveled, experimental protocols should incorporate the precautions of recrystallizing tu and adding chelating agents to the reaction mixtures.

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