Visible Spectrum Of The Copper(II)-Thiosuphate Complex

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ABSTRACT

Spectrum between 700nm and 360nm of the short-lived, colored, CuS_2O_3 intermediate complex was determined using a stopped-flow method with 0.005mol/l concentrations of Cu^{2+} and thiosulfate at 28.3^0C. The concentration of the complex was considered equal to that of Cu^{2+} in a special run at Cu^{2+} and thiosulfate concentrations of 0.00173mol/l and 0.18mol/l respectively. The start of the redox reaction $2\ CuS_2O_3 \rightarrow 2\ Cu^+ + S_4O_6^{2-}$ was moved into the time scale of the oscilloscope, reoxidizing Cu^+ by addition of 0.02mol/l Fe^{3+} until complete reduction of Fe^{3+} to Fe^{2+} (a Landolt type process).   © 2007 Trade Science Inc. - INDIA

INTRODUCTION

The oxidation of thiosulfate and organic thiocompounds by transitional metal ions occurs by formation of short-lived, intensively colored, intermediate complexes. Absorption spectra in the visible and/or the UV range were published in the last decades, for $(FeS_2O_4_3)^+$[1-4], $(CrO_3S_2O^{-2}_3)$[5–6], (CrO_3SCN^-)[7], $(CrO_3SC_2H_5^-)$ (CrO_3Et^-)[8] and $(CrO_3SC_3H_6O_2N^-)$ (CrO_3Cy^-)[9], some of them being reproduced in figure 1(thin lines).

Copper(II) reacts also with thiosulfate but much faster then the above mentioned species, therefore flow methods are needed to study the kinetics of the redox reaction[10]. The redox reaction is preceded as in previous cases by rapid formation of an uncharged intermediate complex, CuS_2O_3, identified earlier by means of a job curve having a 1:1 ratio of the reactants[11].

The CuS_2O_3 complex's absorption coefficient, ε, was computed within two steps relying on experimental data and taking in account it's very short lifetime.
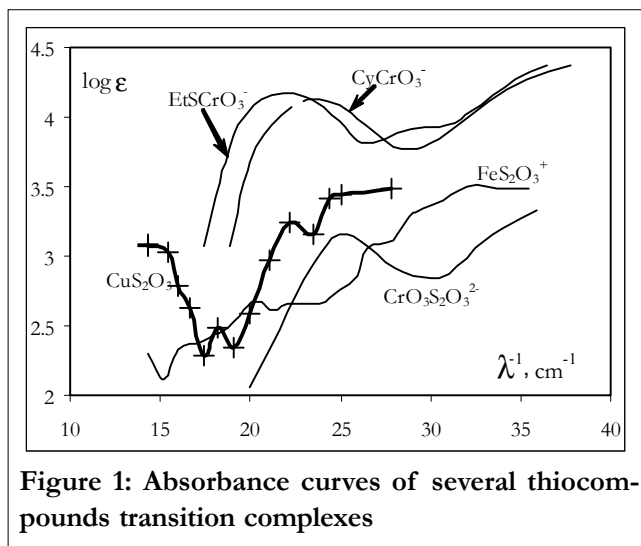
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Figure 1: Absorbance curves of several thiocompounds transition complexes

TABLE 1: Absorbance and molar absorption coefficients of CuS_2O_3 at several wavelengths $[Na_2S_2O_3]$ $=[Cu(ClO_4)]=0.005M$, $[HClO_4]=0.02$, $T=28.3^0C$

| Sample	λ, nm	$\lambda^{-1}cm^{-1}$	Absorbance	Absorbance	log ε
21b	700	14.29	0.06148	1207	3.08
22a	650	15.385	0.055312	1086	3.04
23a	625	16	0.031388	616	2.79
23b	600	16.667	0.021837	429	2.63
24a	575	17.391	0.010103	198	2.30
24b	550	18.182	0.015835	311	2.49
25a	525	19.050	0.011398	224	2.35
25b	500	20	0.019737	388	2.59
26a	475	21.053	0.048319	949	2.98
26b	450	22.222	0.089095	1750	3.24
75a,b	450	22.222	0.605*	1750	3.24
27a	425	23.529	0.074015	1454	3.16
79a	410	24.34	0.700*	2023	3.31
70a	400	25	0.964*	2786	3.44
77a	360	27.78	1.056*	3052	3.48

* Absorbance in very large excess of thiosulfate, when all copper is in form of CuS_2O_3 ($[Cu^{2+}]=0.00173mol/l$, $[Na_2S_2O_3]_{initial}=0.2mol/l$, $[Fe^{3+}]=0.02mol/l$, and 19.8^0C).

1. By means of a sutin[12], stopped flow apparatus[13] the absorbance at several wavelengths was established under identical conditions of temperature, pH, ionic strength and flow rate, with equal concentrations of Cu^{2+} and thiosulfate.

2. (a) The formation equilibrium of the complex was shifted to the right by an excess of thiosulfate.

   (b) The formation rate of the complex being much faster than its decomposition rate and the light beam located some distance downstream the mixing chamber, assuming a very fast formation of Fe intermediate complex, at the light spot zone the redox reaction is already underway. Therefore sufficient Fe^{3+} ions were added to the reaction mixture in order to delay the start of the decomposition, and to move it into the recorded time scale(A Landolt type process). The start of the delayed decomposition may be observed as a visible slope change of the light intensity curve at a given wavelength(450 nm). The absorbance at the start of the complex decomposition is given by its concentration(equal to the initial concentration of Cu^{2+}); therefore the molar absorption coefficient ε_{450} can be computed.

The determination of the absorbance curve of CuS_2O_3

The absorbance of CuS_2O_3 at different wavelengths but for the same conditions(concentrations, temperature and solution admission speeds) was recorded using a Slater type stopped-flow device. The continuous flow absorbance A_o are given in the 4th column of TABLE 1[14].

The determination of the molar absorption coefficient at 450 nm

Experimental conditions were: 450nm, 19.8^0C, $[S_2O_3^{2-}]=0.2mol/l$, $[Cu^{2+}]=0.00173mol/l$, $[Fe^{3+}]=0.02mol/l$, $[HClO_4]=0.008mol/l$.

Thiosulfate reduces Cu(II) in a very fast reaction to Cu(I). In the presence of Fe(III), Cu(I) is oxidized again in a very fast reaction back to Cu(II):

$$Cu^{+2} + S_2O_3^{2-} \rightarrow Cu^{+1} + \tfrac{1}{2} S_4O_6^{2-} \qquad (1)$$
$$Cu^{2+} + Fe^{3+} \rightarrow Cu^{+2} + Fe^{+2} \qquad (2)$$
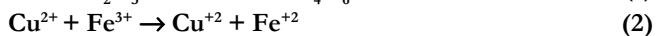
This Landolt-sequence goes on, and consequently Cu^{2+} concentration rests constant, until Fe^{3+} is completely consumed.

Thiosulfate and Fe(III) reacts also in 1:1 ratio resulting tetrathionate and Fe(II), but this reaction is much slower than the reactions above. At the same time both reactions of thiosulfate with Cu^{2+} and Fe^{3+} proceed by formation of colored intermediate complexes, CuS_2O_3 and $FeS_2O_3^+$ respectively, in very fast reactions. Mixing the solution of thiosulfate with the mixture of Cu(II) and Fe(III) solutions, a strong color appears, due to formation of both colored complexes.

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This color fades away as $FeS_2O_3^+$-concentration diminishes.

After disappearance of Fe(III) starts the reduction of copper(II) ions. The absorbance of the mixture exhibits a different fading kinetics then the copper (II)-thiosulfate reaction alone. As a result the light intensity vs. time curve shows a slope change at the moment of complete iron(III)-consumption, since starting with this point the intensity change is due to the disappearance of the copper-thiosulfate complex alone. Because the large excess of thiosulfate (more then 100✕) and its high concentration at this moment (0,18mol/l), it is reasonable to assume that practically all the copper is in complex form.

In figure 2a grill with photomultiplier response and time units(mV and ms, respectively) is superimposed over the kinetic record. The amplifier response to maximum light intensity(uncolored solution) was 1400mV, while the redox reaction starts at 347 mV, at the point where the curve exhibits a visible slope change. The two curve segments were linearized by 1/A vs. t plots, as shown in figure 3, in order to calculate I at the intersection point of the two straight lines, with the coordinates 42, 4ms and 347mV.

Another kinetic run, under the same conditions, but at a lower time resolution is shown in figure 4, and the respective curve segment linearization may be seen in figure 5.

The reciprocal absorbance vs. time plots are very good straight lines, with correlation coefficients, R, better than 0.999 for the lines in figure 3, and figure 5.
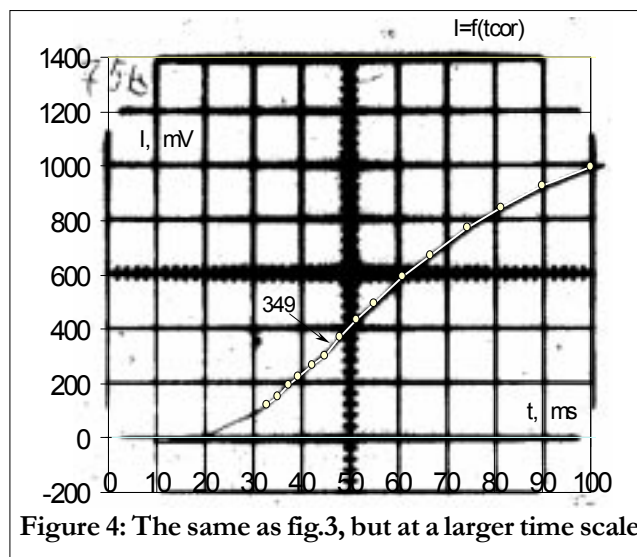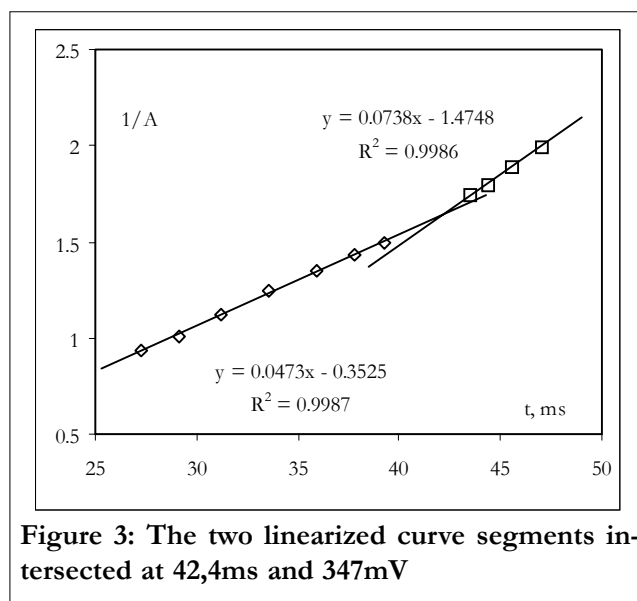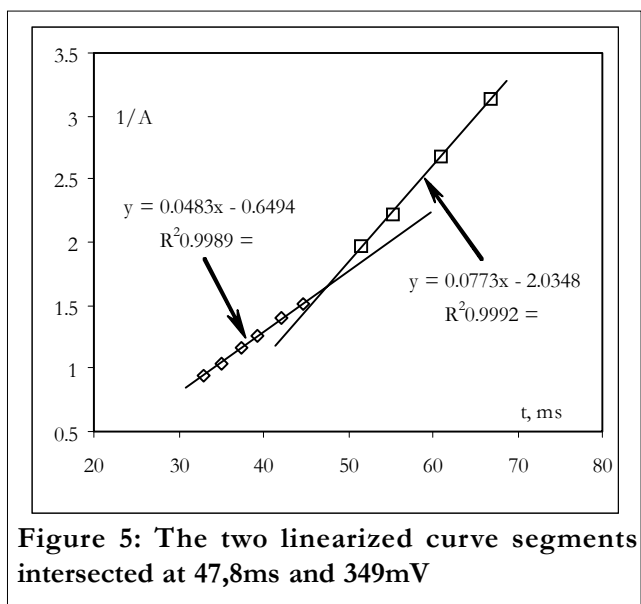
The intersection point in figure 4 is at 349mV.
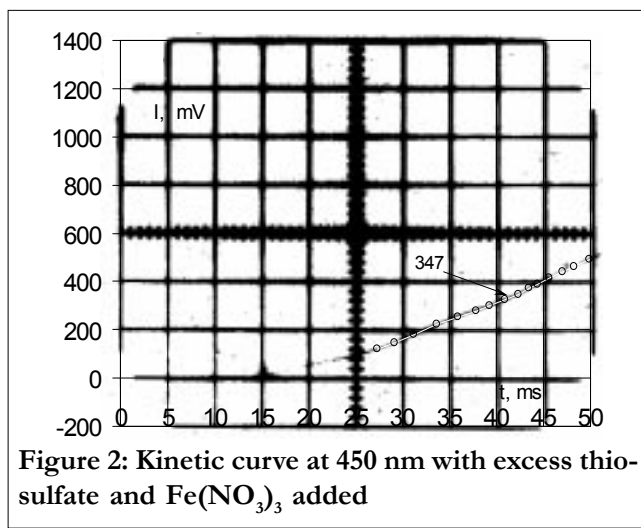
The average of the two values of light intensities is 348mV and consequently the absorbance at the start of the redox reaction is A=log(1400/348)=0.605. Assuming a complete conversion of copper into CuS_2O_3 for the copper concentration of 0.00173mol/l and the width of the reaction capillary of 0,2 cm, an absorption coefficient ε =0.605/(0.2✕0.00173) =1750l/(mol·cm) results at the wavelength of 450nm.

The absorbance in TABLE 1 at 450nm is 0.0891 for the solutions used to draw the absorption curve with equal concentrations of the reactants($[Na_2S_2O_3]=[Cu(ClO_4)]=0,005mol/l$), so the absorption coefficient is 1750/0.0891=19640=f times larger.

The absorption coefficient at other wavelengths can be computed by multiplying the absorbance at

Figure 3: The two linearized curve segments intersected at 42,4ms and 347mV

Figure 2: Kinetic curve at 450 nm with excess thiosulfate and $Fe(NO_3)_3$ added

Figure 4: The same as fig.3, but at a larger time scale

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$y = 0.0483x - 0.6494$
$R^2 0.9989 =$

$y = 0.0773x - 2.0348$
$R^2 0.9992 =$

Figure 5: The two linearized curve segments intersected at 47,8ms and 349mV

the given wavelength with the factor f.

The absorption coefficients and their logarithms are given in columns 5 and 6 of TABLE 1, and the absorption curve of CuS_2O_3 in figure 1(heavy line).

CONCLUSIONS

The CuS_2O_3 complex has a weaker absorbance in the visible range than organic thioesters of chromic acid, but is similar to the $FeS_2O_3^+$ complex, showing the same maximum molar absorption coefficient in the near UV-range, and minima in the visible range. For the copper complex the absorbance rises again at about 650nm while for the iron complex a small rise happens at about 700nm.

ACKNOWLEDGMENT

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