

COMPOSITION OF THE INTERMEDIATE OF THE FAST INTERACTION BETWEEN COPPER(II) AND THIOSULFATE IONS IN AQUEOUS SOLUTION

Mihaela Ligia UNGUREȘAN* and Gavril NIAC

Department of Chemistry, Technical University of Cluj-Napoca, The Faculty of Materials Science and Engineering
B-dul Muncii 103-105, 400641 Cluj-Napoca, Roumania

Received December 28, 2006

The fast reduction of copper(II) by the thiosulfate ion in aqueous solution is preceded by the extremely rapid formation of a CuS_2O_3 -complex. The tetrathionate ion and a (thiosulfato) copper(I) complex are formed in the redox reaction. Job's method was used^{1,2} to identify the intermediate compound formed by the reaction of the two components. Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ react in a 1:1 ratio, consistent with the formation of CuS_2O_3 .

INTRODUCTION

Oscillatory kinetics has been reported for the oxidations of the thiosulfate ion by hydrogen peroxide³ and by the peroxodisulfate ion⁴ in a continuous-flow stirred tank reactor (CSTR). A catalytic amount of copper(II) was found to be

essential for the oscillation that occurs in this system.⁵ It has long been known that copper(II) can greatly accelerate the oxidation of thiosulfate by a variety of oxidizing agents in aqueous solution.⁶⁻⁸

The presence of copper ions also accelerates the acidic decomposition of thiosulfate. The catalytic action of Cu^{2+} could be explained by the sequence:



The knowledge of the Cu^{2+} -thiosulfate reaction kinetics is of interest since Cu^{2+} is being used as catalyst in the reaction between Fe^{3+} and thiosulfate allowing the determination of traces of copper (Hahn and Leimbach⁹, Siniakova¹⁰ and Yatzimirski^{11, 12}), but also because the copper ions play important roles in biological processes as components of enzymes and as antioxidants like Cu-ceruloplasmin.¹³ The kinetics of Cu^{2+} reduction with $\text{S}_2\text{O}_3^{2-}$ in aqueous acidic solutions is not yet

known, there is just one paper dealing with the reaction of $\text{Cu}[\text{NH}_3]_4^{2+}$ with $\text{S}_2\text{O}_3^{2-}$, the observed half time of this reaction being about 15s.¹⁴

A new redox indicator between Cu^{2+} , Mn^{2+} and $\text{S}_2\text{O}_3^{2-}$ in presence of 2,2'-bicinechonic acid is investigated through a kinetic method.¹⁵

The catalytic activity of copper (II) is usually explained by assuming that the copper(II) ion undergoes a facile, rapid reduction by the thiosulfate ion to copper (I):



This paper deals with the first part of our investigation of reaction (4). The main objective in this study is to explore the interaction between copper(II) and thiosulfate in aqueous solution.

When solutions of copper(II) perchlorate and sodium thiosulfate are rapidly mixed, a blue intermediate forms and then it quickly fades away.

This experiment suggests that the reaction mechanism involves the incorporation of one thiosulfato ligand into the inner coordination sphere of the copper(II) ion prior to an electron-transfer step. The very fast complex-forming process can be investigated by the stopped-flow technique.

* Corresponding author: mihaela@chimie.utcluj.ro

EXPERIMENTAL PART

Chemicals

Analytical grade reagents were used without further purification. $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ was prepared from copper(II) oxide. Solutions used in kinetic runs were prepared from basic $5 \cdot 10^{-2} \text{ M}$ CuClO_4 and $5 \cdot 10^{-2} \text{ M}$ $\text{Na}_2\text{S}_2\text{O}_3$ solutions.

A solution of NaClO_4 $5 \cdot 10^{-2} \text{ M}$ was used in order to adjust the ionic strength. HClO_4 was used for the dilution of the

CuClO_4 solution. Concentrations of the solutions are given in Table 1. Perchloric acid is not added to the solution of $\text{Na}_2\text{S}_2\text{O}_3$, in order to avoid the decomposition of sodium thiosulfate. The solutions have been prepared so that $\text{Na}_2\text{S}_2\text{O}_3$ has been brought to a quota of distilled water that contains NaClO_4 , and CuClO_4 to a quota with perchloric acid, in order to get the same pH of the mixture, $[\text{HClO}_4]_{\text{total}} = 10^{-1} \text{ M}$. The initial solution of copper perchlorate had a concentration of HClO_4 of $2 \cdot 10^{-2} \text{ M}$.

Table 1

The individual and average values of the mixtures absorbances

$[\text{Cu}^{2+}]$ mol/l	$[(\text{S}_2\text{O}_3)_t]$ mol/l	γ	Exp.1	Exp.2	Exp.3	Exp. 4	Exp.5	Exp. 6	Exp. 7	A_{average}
0.008	0.002	0.8	0.0291	0.0322	0.0295	0.0334	0.0323	0.0329	0.0323	0.031671
0.006	0.004	0.6	0.0661	0.0661	0.0659	0.0661	0.0659	0.0659	0.0660	0.066010
0.005	0.005	0.5	0.0753	0.0748	0.0731	0.0715	0.0705	0.0728	0.0745	0.073219
0.004	0.006	0.4	0.0689	0.0698	0.0688	0.0699	0.0689	0.0695	0.0668	0.068953
0.002	0.008	0.2	0.0371	0.0369	0.0373	0.0371	0.0371	0.0370	0.0371	0.037082

Method

The combination ratio between the two ions in the colored complex has been spectrophotometrically verified using a stopped-flow apparatus, described in Fig. 1.

The essential parts are: two syringes (1) needed to rapidly inject the reactants into the mixing chamber (6). After leaving the mixing chamber the mixture flows into a third syringe whose piston (11) is suddenly stopped after a predetermined volume of solutions has been injected. A photodiode OPT 301¹⁶ has been used as detector. A source of monochromatic light at a wavelength 430nm has been used. It assures a high stability of the light emission with time.

The signal obtained at the exit of the photodiode's amplifier is applied to a digital oscilloscope Le Croy LT 262 DSO, 350 MB, 1GS/s.¹⁷ The oscilloscope works in the 0 - 350 MHz band and it is provided with its own memory and floppy disk for the acquisition of the experimental data.

Unless noted otherwise, all stopped-flow measurements were conducted at $21.0 \pm 0.2^\circ\text{C}$. The prethermostated reactant solutions are mixed in a ratio of 1:1 by volume.

From the curves obtained in the coordinates transmitted light intensity – time, calculated the maximum absorbance for each experiment was computed. The plots of the absorbance versus the concentration ratio of a reactant results in an exact, direct information about the molar combination ratio of the two reactants in the intermediate compound.

RESULTS AND DISCUSSION

A convenient graphical method for determining the number of (and changes in the number of)

distinct absorbing species in a series of solution absorption spectra is presented.

For $[\text{Cu}(\text{ClO}_4)_2] + [\text{Na}_2\text{S}_2\text{O}_3] = 10^{-2} \text{ M}$, $T = 21^\circ\text{C}$ and $\lambda = 430 \text{ nm}$ we have obtained 5 sets of experimental data, for each set having at least 15 determinations, so that their reproducibility could be observed. For $[\text{Cu}(\text{ClO}_4)_2] = 5 \cdot 10^{-3} \text{ M}$ and $[\text{Na}_2\text{S}_2\text{O}_3] = 5 \cdot 10^{-3} \text{ M}$ we have obtained $I(\text{mV}) = f(t(\text{ms}))$ (Fig. 2).

We have then measured the maximum absorbances of the continuous mixtures for drawing the Job curve, of total concentration: $[\text{Cu}^{2+}] + [(\text{S}_2\text{O}_3)_{\text{total}}] = 10^{-2} \text{ M}$.

Table 1 presents the individual values of the absorbances of the continuous mixtures indicated for 7 experiments for each concentration that has been studied, as well as the averages of these values.

The first column gives the concentration $[\text{Cu}^{2+}]$, the second, the concentration $[(\text{S}_2\text{O}_3)_{\text{total}}] = [\text{S}_2\text{O}_3^{2-}] + [\text{HS}_2\text{O}_3^-]$, the concentration of $\text{H}_2\text{S}_2\text{O}_3$ being considered negligible.¹⁸

The third column of Table 1 represents the ratio $\gamma = [\text{Cu}^{2+}] / \{[\text{Cu}^{2+}] + [(\text{S}_2\text{O}_3)_{\text{total}}]\}$, while the last column contains the average value of the maximum absorbance, A_{average} , for 7 samples of the same mixture.

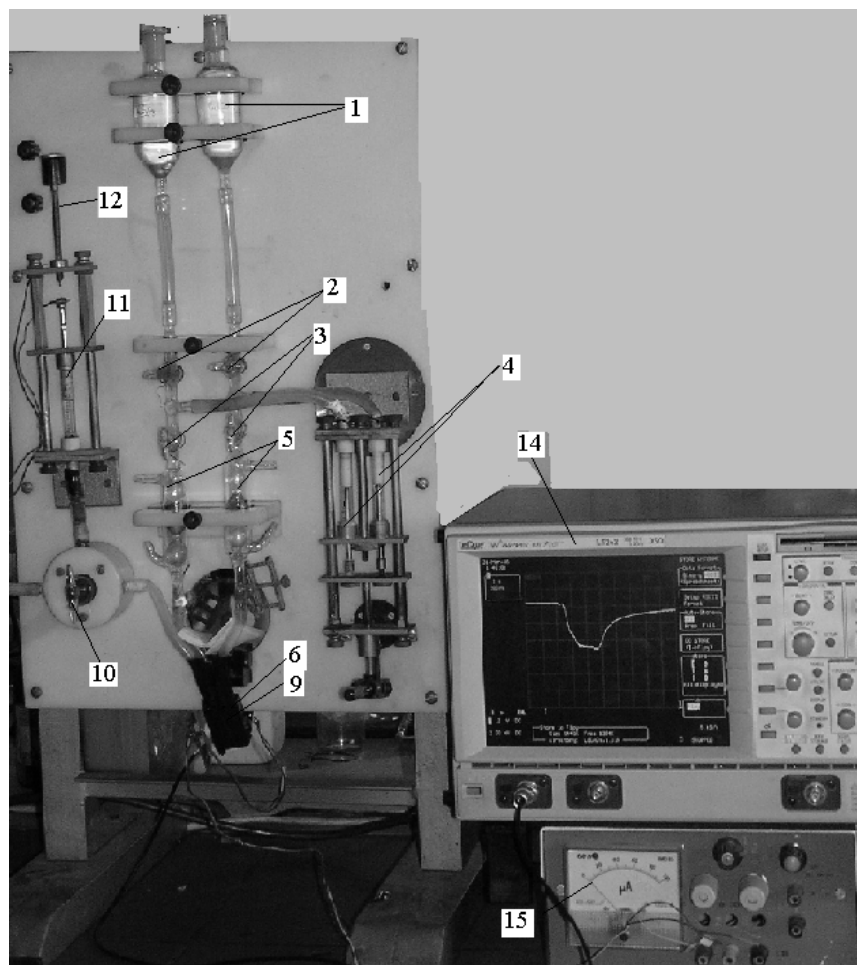


Fig. 1 – The laboratory experimental installation for kinetic runs.

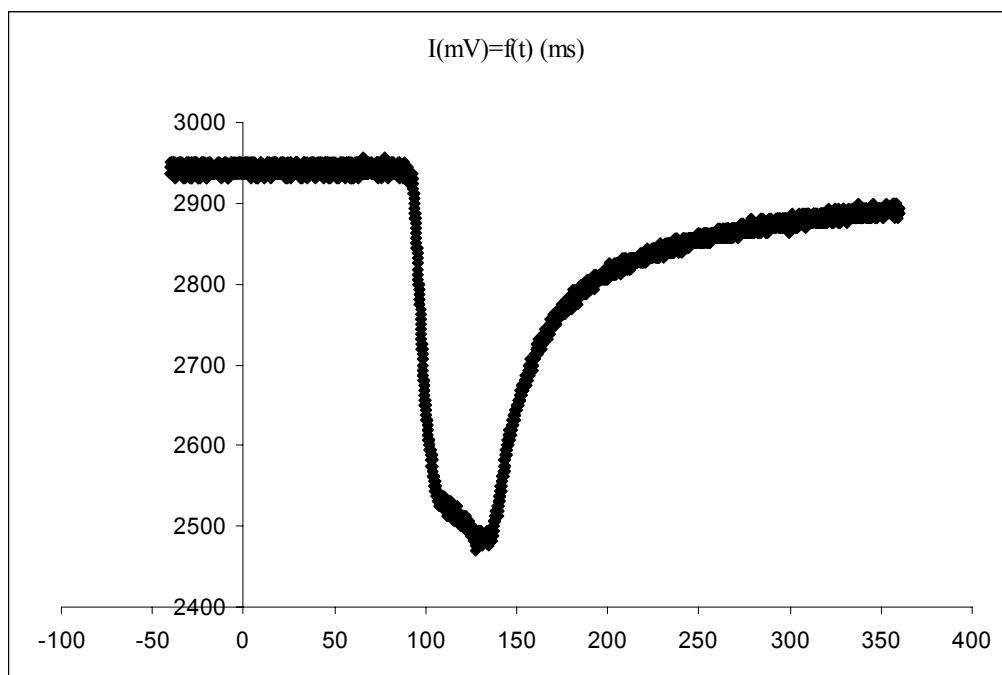


Fig. 2 – The variation of the transmitted light intensity I (mV) with respect to time t (ms) for $[\text{Cu}^{2+}] = 5 \cdot 10^{-3} \text{ M}$, $[\text{S}_2\text{O}_3^{2-}] = 5 \cdot 10^{-3} \text{ M}$; $\lambda = 430 \text{ nm}$, $T = 21^\circ\text{C}$.

The curve $A_{\text{average}} = f(\gamma)$ is marked in Fig. 3 by circles. It can be noticed that the maximum of the curve (not drawn) that passes through the circles is close to $\gamma = 0.5$, but slightly shifted towards smaller values.¹⁹

Due to the fact the deviation from the 1:1 ratio is too small to suggest another combination ratio along the one corresponding to the complex CuS_2O_3 , such as the complex FeS_2O_3^+ ²⁰, it has been checked if this small deviation is not due to the presence of the ion HS_2O_3^- , that doesn't enter the complex.

Considering the acidity constant of the HS_2O_3^- ion $K_a = 0.037$ (an average between the values 0.057²¹, 0.03 and 0.02¹⁸) and using instead of the fraction γ the fraction $\gamma' = [\text{Cu}^{2+}]/([\text{Cu}^{2+}] + [\text{S}_2\text{O}_3^{2-}])$, points slightly shifted towards larger values of the abscise result, the new curve being the continuous one.

We have also marked by the height of the bar the confidence interval given by $A_{\text{average}} \pm t \cdot \mu$, where t is the Student factor for 7 determinations and a probability of 95% and μ is the average square deviation, as it is shown in Table 2.

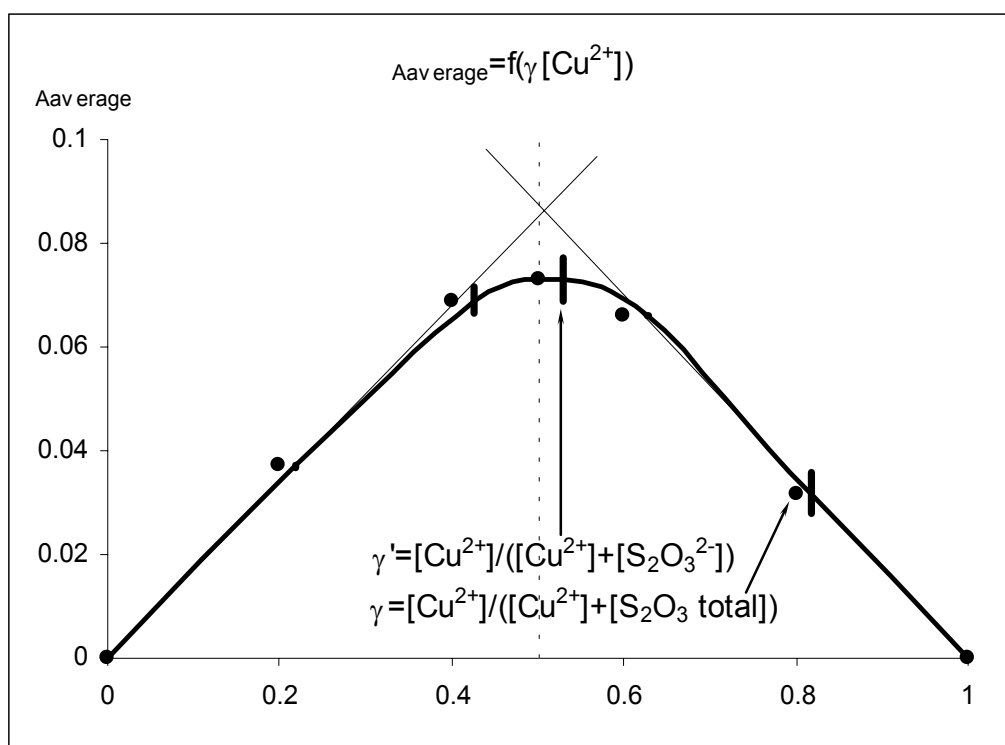


Fig. 3 – Job's Curve: The circles represent $A_{\text{average}} = f(\gamma)$, and the bars and the curve $A_{\text{average}} = f(\gamma')$. The height of the bars corresponds to the average square deviation multiplied by the Student factor for 7 determinations.

Table 2

The absorbances average A' for corrected γ'

γ'	$A'_{\text{average}} \pm t \cdot \mu$
0.8187	0.0317 ± 0.0040
0.6275	0.0660 ± 0.0002
0.5284	0.0732 ± 0.0042
0.4270	0.0689 ± 0.0025
0.2177	0.0371 ± 0.0002

Table 2 presents the average individual values of the absorbances of the continuous mixtures from table 1, with the confidence interval for a

probability of 95% ($t = 2.365$) at the values corrected for the partial dissociation of HS_2O_3^- , $\gamma' = [\text{Cu}^{2+}]/([\text{Cu}^{2+}] + [\text{S}_2\text{O}_3^{2-}])$.

It should be mentioned that the maximum of the curve shifts close to the $[\text{Cu}^{2+}]/[\text{S}_2\text{O}_3^{2-}]$ ratio 1. The straight lines drawn through (0, 0) and the first point in Table 2, respectively through the last point and (1, 0) intersect very close to the vertical $\gamma' = 0.5$.

CONCLUSIONS

The position of the maximum indicates that the intermediate contains 1 mol of Cu^{2+} to 1 mol of $\text{S}_2\text{O}_3^{2-}$. We conclude from these results that a mono(thiosulfato)copper(II) complex is rapidly formed in the mixture of aqueous Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ prior to the reduction of copper(II):



REFERENCES

1. P. Job, *Ann. Chim.*, **1928**, 10, 9, 113-203.
2. Mc. Carthy Patrick, *Analytical Chem.*, **1978**, 50, 14, 2165.
3. M. Orbin and I. R. Epstein, *J. Am. Chem. Soc.*, **1987**, 109, 101.
4. M. Orbin and I. R. Epstein, *J. Am. Chem. Soc.*, **1989**, 111, 2891.
5. M. Orbin, *React. Kinet. Catal. Lett.*, **1990**, 42, 343.
6. E. Abel, *Monatsh. Chem.*, **1913**, 34, 1361.
7. E. Abel, *Ber. Deut. Chem. Ges.*, **1923**, 56, 1076.
8. R. Sarala, S. B. Rabin and D. M. Stanbury, *Inorg. Chem.*, **1991**, 30, 3999.
9. F. L. Hahn and G. Leimbach, *Ber. Deut. Chem. Ges.*, **1922**, 55, 3070.
10. S. I. Siniacova, *J. Prikl. Himii*, **1937**, 10, 2109.
11. K. B. Iațimirschi, *J. Anal. Himii*, **1955**, 10, 335.
12. K. B. Iațimirschi, *J. Anal. Himii*, **1955**, 10, 345.
13. H. K. Biesalski and P. Grimm, "Taschenatlas der Ernährung, Thieme Verlag", Stuttgart, 1999, p. 242-245.
14. J. Byerley, A. F. Safaa and G. L. Rempel, *J. C. S. Dalton*, **1973**, 889-893.
15. I.V. Pulyaieva, N. L. Yegorova, L. P. Experiandova and A. B. Blank, *Talanta*, **1998**, 47, 213 – 221.
16. Burr Brouwn IC, "Data Book – Linear Products", 2002.
17. Le Croy Corporation, "Test & Measurement Products Catalog", 700 Chestnut Ridge Road, NY 0977, 2000.
18. www.swbic.org/education/env-engn/acidconstants.html
19. J. S. Coleman, L. P. Varga and S. H. Mastin, *Am. Chem. Soc.*, **1970**, 9, 1015 – 1017.
20. G. Niac and I. Cădăriu, *Studia Universitatis Babeș-Bolyai, Chemia*, **1959**, 25-33.
21. D. Negoiu, "Tratat de Chimie Anorganică", Ed. Tehnică, București, 1972, p. 462.