



Formation Constant Of CuS_2O_3 In Aqueous Solution



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ABSTRACT

The formation constant of the short-lived CuS_2O_3 was determined in 0.005mol/l aqueous solution of both Cu^{2+} and thiosulfate, extrapolating the absorbance at the start of kinetic runs to zero reciprocal flow rates. Molar absorption coefficient at 450nm, $\epsilon = 1750 \text{ mol}^{-1}\text{cm}^{-1}$, as found in a previous study, was used. At 19.5°C the value of K is 21.2 lmol^{-1} .

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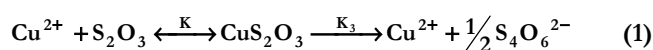
KEYWORDS

Fast redox reaction;
 Copper ions;
 Thiocompounds;
 Stopped-flow technique;
 Molar absorption
 coefficient;
 Formation constant
 of CuS_2O_3 .

INTRODUCTION

In a previous paper absorbance coefficients of CuS_2O_3 at several wavelengths, in the visible range, were found. In the present paper the determination of the formation constant, K, of this short-lived intermediate complex is attempted.

The approach postulated preequilibrium kinetics:



Since the fast formation of the complex is followed by a slower, but still very fast redox reaction, stopped flow methods are needed to fulfill the task.

The problem is how to find the concentration of the complex right at the beginning of the redox reaction. For this purpose runs at several pumping speeds have been done, and the absorbance were extrapolated to zero reciprocal speed, i.e. to zero time, corresponding to the start of the redox reaction, where the complex concentration is not yet altered by decomposition. The known absorbance coefficient, ϵ , and solution layer width, d, lead to the unknown concentration of the complex at the very moment of formation. The initial concentrations of the reacting ions being known, the stability constant of CuS_2O_3 can be calculated.

Full Paper

EXPERIMENTAL

A Sutin type stopped flow device^[1] was used with Cu^{2+} and thiosulfate solutions, both 0.005M in the mixture, with 0.02mol/l HClO_4 added, at $T=19.5^\circ\text{C}$.

Four runs at 450nm wavelength were done at piston speeds 25, 35, 40 and 41.5 in arbitrary units. One of the oscilloscope screen photographs is reproduced in figure 1^[2]. The absorbance vs. reciprocal speed graph shows figure 2.

RESULTS AND DISCUSSION

The equation of the regression line absorbance(A) vs. reciprocal piston speed of syringes($1/v$) is:

$$A = -0.7628(1/v) + 0.1069 \quad (2)$$

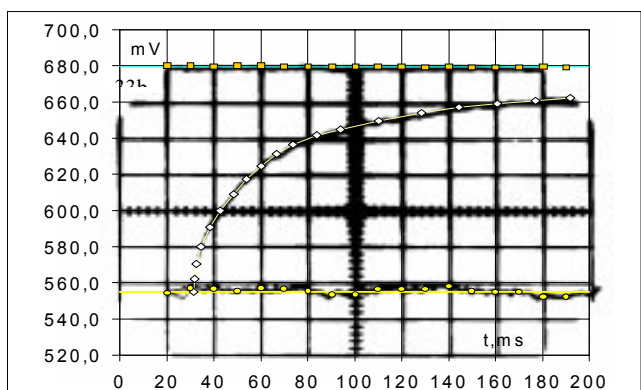


Figure 1: Kinetic run at $\lambda=450\text{nm}$, $T=19.5^\circ\text{C}$ and 40 arbitrary units of pistons speed; $[\text{Cu}^{2+}]=0.005\text{mol/l}$; $[\text{S}_2\text{O}_3^{2-}]=0.005\text{mol/l}$; $[\text{HClO}_4]=0.02\text{mol/l}$

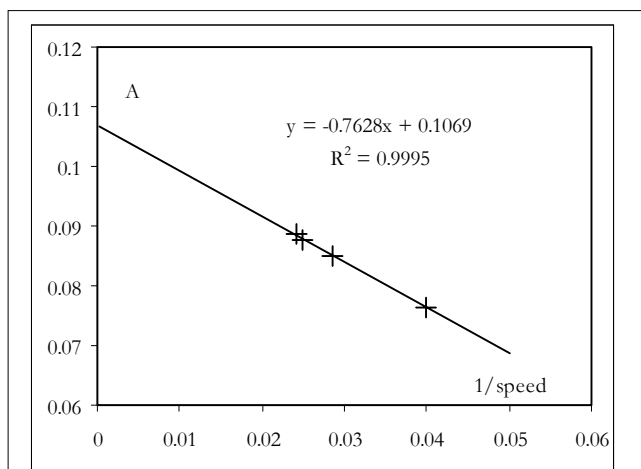


Figure 2: Absorbance vs. reciprocal speed of syringes, at $\lambda=450\text{nm}$, $T=19.5^\circ\text{C}$; $[\text{Cu}^{2+}]=0.005\text{mol/l}$; $[\text{S}_2\text{O}_3^{2-}]=0.005\text{mol/l}$; $[\text{HClO}_4]=0.02\text{mol/l}$

with a very good correlation coefficient $R=-0.9997$ ^[3].

The molar absorption coefficient was determined in an earlier paper^[4] at 450nm and 19.5°C , as $\epsilon=1750\text{mol}^{-1}\text{lcm}^{-1}$.

From equation(2) absorbance at zero time (reciprocal speed), $A_0=0.1069$. According to Lambert-Beer's law, $A_0=\epsilon lc$; $l=0.2\text{cm}$; $c=[\text{CuS}_2\text{O}_3]_0$ and $\epsilon=1750\text{mol}^{-1}\text{lcm}^{-1}$, the concentration of the CuS_2O_3 complex, $[\text{CuS}_2\text{O}_3]_0=0.000305\text{mol/l}$, results.

The value of formation constant K is:

$$K = \frac{[\text{CuS}_2\text{O}_3]}{[\text{Cu}^{2+}][\text{S}_2\text{O}_3^{2-}]} = \frac{0.305 \cdot 10^{-3}}{(5 \cdot 10^{-3} - 0.305 \cdot 10^{-3})^2} = 13.83\text{mol}^{-1} \cdot \text{l} \quad (3)$$

CONCLUSIONS

The formation constant of the short-lived CuS_2O_3 was determined for $[\text{Cu}^{2+}]=0.005\text{mol/l}$; $[\text{S}_2\text{O}_3^{2-}]=0.005\text{mol/l}$; $[\text{HClO}_4]=0.02\text{mol/l}$ in aqueous solution. Taking into account the incomplete dissociation of the HS_2O_3^- ion, with the acidity constant $K_a=0.337\text{l mol}^{-1}$, the corrected value of K is 21.2l mol^{-1} .

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