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Kinetics and Mechanism of Oxidation of 5-Sulfosalicylic Acid by Ditelluratocuprate(III) in Alkaline Medium

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The kinetics of oxidation of 5-sulfosalicylic acid by ditelluratocuprate(III) (DTC) has been studied spectrophotometrically between 283.2 and 303.2 K in alkaline liquids. The reaction rate showed first order dependence in ditelluratocuprate(III) and fractional order in 5-sulfosalicylic acid. It was shown that the pseudo-first order rate constant k_{obs} increased with an increase in concentration of OH^- and a decrease in concentration of TeO_4^{2-}. There is a negative salt effect. A plausible mechanism of reaction involving a pre-equilibrium of adduct formation between the complex and 5-sulfosalicylic acid was proposed. The rate equations derived from mechanism can explain all experimental phenomena. The activation parameters of the rate-determining step have also been computed.

Key Words: Ditelluratocuprate(III) (DTC), 5-Sulfosalicylic acid, Kinetics and mechanism, Oxidation.

INTRODUCTION

Transition metals in higher oxidation state can generally be intrigued by many researchers in recent years. A fairly large amount of work has been done on the metal chelates such as ditelluratocuprate(III)[1,2], diperiodatocuprate(III)[3,4], diperiodatoargentate(III)[5,6] and diperiodatonickelate(IV)[7] which are good oxidants in a medium with an appropriate pH value. The use of Cu(III) as an oxidation agent is well known in analytical chemistry in the estimation of glucose, sugars and organic acids. Many biological systems involve electron-transfer processes in which Cu(III) plays an important role[8]. Based on the studies of oxidation of some organic compounds by Cu(III) complex, Indian researchers proposed that in the alkaline medium the formula of ditelluratocuprate(III) may be represented by $[Cu(H_4TeO_6)_2]^-$ and the mechanism involving a pre-equilibrium of a adduct formation between the complex and reductant was also proposed[9]. Because Cu(III) is in a higher oxidation state and the reaction is complicated in this kind of reaction system, it is of importance to have a further study on it. Investigation on them will certainly provide us with more kinetics parameters and will provide theoretical foundation for the design of reaction route in the organic synthesis and quantitative analysis in analytical chemistry.

5-Sulfosalicylic acid is methylene oxytetracycline hydrochloride intermediate and it can also be used as dye, surfactant and oxycycline medicine intermediates. Furthermore, 5-sulfosalicylic acid is served as albumin reagent and iron colorimetric reagents. The kinetics and mechanisms of oxidation of 5-sulfosalicylic acid can provide some valuable information for chemical industry.

EXPERIMENTAL

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solutions of ditelluratocuprate(III) and reductions were always freshly prepared before using. The stock solution of ditelluratocuprate(III) was prepared and standardized by the method given by Jaiswal and Yadava[10,11]. Its electronic spectrum was found to be consistent with that reported by Jaiswal and Yadava[11].

Kinetics measurements and apparatus: All kinetics measurements were carried out under pseudo-first order conditions. Solution (2 mL) containing definite concentration of Cu(III), OH^-, TeO_4^{2-} and ionic strength and reductant solution (2 mL) of appropriate concentration were transferred separately to the upper and lower branch tubes of a γ type two-cell reactor. The concentration of ditelluratocuprate(III) was derived from its absorption at 405 nm. The ionic strength μ was maintained by adding KNO_3 solution and the pH of the reaction mixture was adjusted with a KOH solution. The kinetic measurements were performed on a UV-VIS spectrophotometer (TU-1900, Beijing Puxi Inc., China), which had a cell holder kept at constant temperature (± 0.1 ℃) by circulating water from a thermostat (DC-2010, Baoding, China). All other species did not absorb significantly at this wavelength.

Product analysis: A solution with known concentrations of Cu(III), OH^-, TeO_4^{2-} was mixed with an excess of reductants. With the complete fading of ditelluratocuprate(III) colour marked the completion of the reaction. The product of oxidation was identified as CO_2 by its $Ba(OH)_2$ water test[12].

RESULTS AND DISCUSSION

Under the conditions of $[reductant]_0 \gg [Cu(III)]_0$, the plots of $\ln(A_t - A_\infty)$ *versus* time were straight lines, indicating the reaction is first order with respect to Cu(III), where A_t and A_∞ are the absorbance at time t and at infinite time, respectively. The pseudo-first-order rate constants k_{obs} were calculated by the method of least-squares. Generally, more than 8 A_t values within three times the half-lives were used to calculate k_{obs}. The k_{obs} values were the average value of at least three independent experiments and reproducibility is within ± 5 %.

Rate dependence on the [reductant]: At fixed concentration of Cu(III), OH^-, TeO_4^{2-} and ionic strength µ, the values of k_{obs} were determined at different temperatures. The plots of $\ln k_{obs}$ *versus* ln [reductant] were linear (r = 0.998) and from the slope of such plots, the order with respect to reductant was found to be fractional. In addition, the k_{obs} was found to be increased with the increase of reactant concentration. The plots of $1/k_{obs}$ *versus* 1/[reductant] at different temperatures were straight lines (Fig. 1), the rate constants (k) of the rate-determining step were calculated from intercepts.
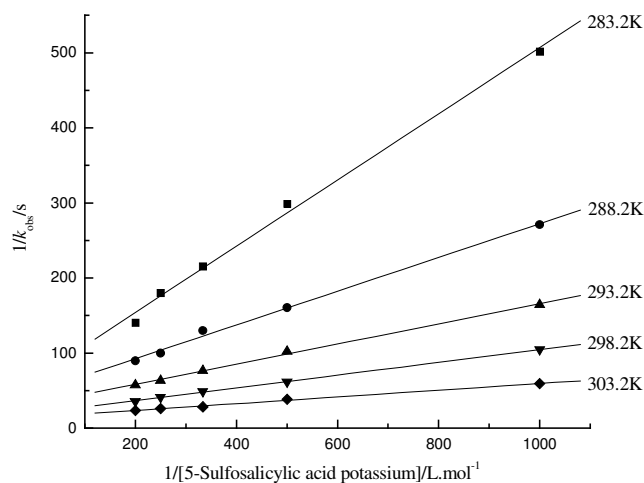

Fig. 1. Plots of $1/k_{obs}$ *versus* 1/[5-sulfosalicylic acid] (r = 0.998) [Cu(III)] = 4.63×10^{-5} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, $[TeO_4^{2-}]$ = 1.00×10^{-3} mol L^{-1}, µ = 3.80×10^{-2} mol L^{-1}

Rate dependence on the $[OH^-]$: At constant [Cu(III)], [reductant], $[TeO_4^{2-}]$, µ and temperature, k_{obs} values increased with the increase in $[OH^-]$. The order with respect to $[OH^-]$ was fractional and the plot of $1/k_{obs}$ *versus* $1/[OH^-]$ was linear with a positive intercept (Fig. 2).

Rate dependence on the $[TeO_4^{2-}]$: At constant [Cu(III)], [reductant], $[OH^-]$, µ and temperature, the experimental results indicate that k_{obs} decreases while increasing the $[TeO_4^{2-}]$. The order with respect to TeO_4^{2-} was derived to be an inverse fraction, which reveals that TeO_4^{2-} is produced in equilibrium before the rate-determining step. A plot of $1/k_{obs}$ *versus* $[TeO_4^{2}]$ was straight line with a positive intercept (Fig. 3).
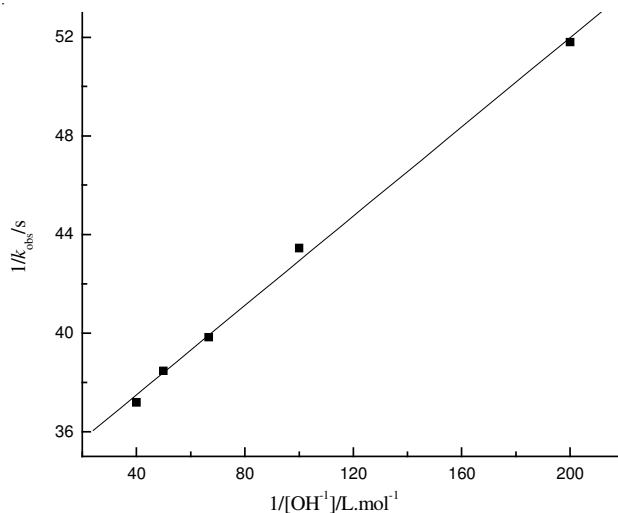

Fig. 2. Plots of $1/k_{obs}$ *versus* $1/[OH^-]$ at 298.2 K (r = 0.999) [Cu(III)] = 4.63×10^{-5} mol L^{-1}, [5-sulfosalicylic acid] = 3.00×10^{-3} mol L^{-1}, $[TeO_4^{2-}]$ = 1.00×10^{-3} mol L^{-1}, µ = 3.80×10^{-2} mol L^{-1}
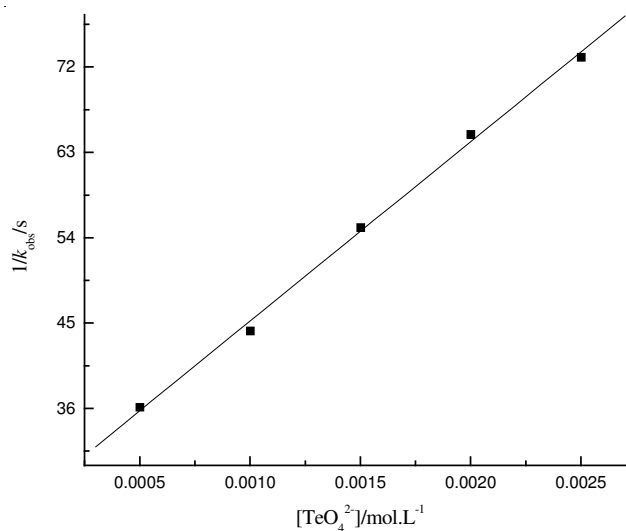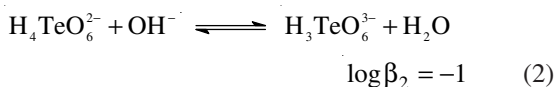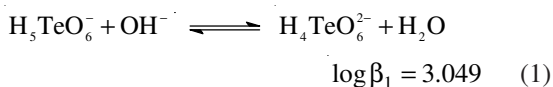

Fig. 3. Plots of $1/k_{obs}$ *versus* $[TeO_4^{2-}]$ at 298.2 K (r = 0.999) [Cu(III)] = 4.63×10^{-5} mol L^{-1}, [5-sulfosalicylic acid] = 3.00×10^{-3} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, µ = 3.80×10^{-2} mol L^{-1}

Rate dependence on the ionic strength: With other conditions fixed, the reaction rate was decreased by the addition of KNO_3 solution (Table-1), which indicate that there is negative salt effect which consistent with the common regulation of the kinetics[13].

TABLE-1
RATE DEPENDENCE ON IONIC STRENGTH µ AT 298.2 K

10^2 (µ/mol L^{-1})	1.50	3.00	4.50	6.00	7.50
$10^2 k_{obs}$ (s^{-1})	2.83	2.34	2.31	2.23	2.17

[Cu(III)] = 4.63×10^{-5} mol L^{-1}, [5-sulfosalicylic acid] = 3.00×10^{-3} mol L^{-1}, $[OH^-]$ = 1.00×10^{-2} mol L^{-1}, $[TeO_4^{2-}]$ = 1.00×10^{-3} mol L^{-1}.

Reaction mechanism: Acrylamide was added under the protection of nitrogen atmosphere during the course of reaction. The appearance of white polyacrylamide was consistent with free radical intermediates in the oxidation by Cu(III) complexes. Blank experiments in reaction system gave no polymeric suspensions.
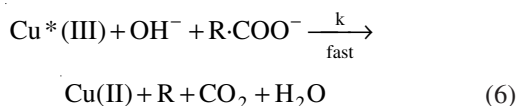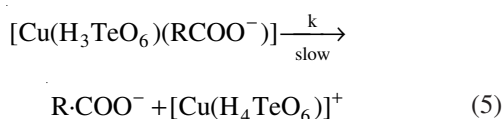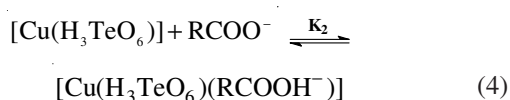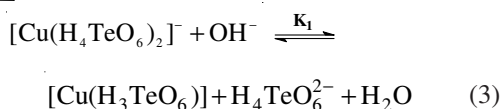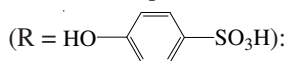
In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier (here $pK_w = 14$).

$$H_5TeO_6^- + OH^- \rightleftharpoons H_4TeO_6^{2-} + H_2O$$

$$\log \beta_1 = 3.049 \quad (1)$$

$$H_4TeO_6^{2-} + OH^- \rightleftharpoons H_3TeO_6^{3-} + H_2O$$

$$\log \beta_2 = -1 \quad (2)$$

The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibriums (1)-(2). In alkaline medium such as $[OH^-] = 0.01$ mol L^{-1}, $[H_4TeO_6^{2-}]$: $[H_5TeO_6^-]$:$[H_3TeO_6^{3-}] = 1000:89:1$, so in the concentration of OH$^-$ range used in this work, $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ can be neglected, the main tellurate species was $H_4TeO_6^{2-}$.

The fractional order in OH$^-$ indicated that OH$^-$ takes part in a pre-equilibrium with Cu(III) before the rate-determing step. The plot of $1/k_{obs}$ *versus* $[TeO_4^{2-}]$ is straight line with a positive intercept which indicates a dissociation equilibrium in which the Cu(III) loses a tellurate ligand $H_4TeO_6^{2-}$ from its coordination sphere and forms a reactive monotelluratocuprate(III) complex (MTC). The fractional order in reductant indicated complex formation between reductant and monotelluratocuprate(III) and the plots of $1/k_{obs}$ *versus* $1/$[reductant] was straight line with a positive intercept providing kinetic evidence for the formation of 2:1 complex. Hence, the following inner-sphere electron transfer mechanism involving a pre-equilibrium of a adduct formation between the complex and reductant is proposed for the reaction.

In alkaline solution studied, $(H_2TeO_6)^{4-}$ protonated easily and it coordinate with central ion formed $[Cu(H_4TeO_6)_2]^-$. In view of the experiments, the mechanism was poposed as follows ($R = HO$—⟨benzene ring⟩—SO_3H):

$$[Cu(H_4TeO_6)_2]^- + OH^- \xrightarrow{K_1}$$

$$[Cu(H_3TeO_6)] + H_4TeO_6^{2-} + H_2O \quad (3)$$

$$[Cu(H_3TeO_6)] + RCOO^- \xrightarrow{K_2}$$

$$[Cu(H_3TeO_6)(RCOOH^-)] \quad (4)$$

$$[Cu(H_3TeO_6)(RCOO^-)] \xrightarrow[slow]{k}$$

$$R \cdot COO^- + [Cu(H_4TeO_6)]^+ \quad (5)$$

$$Cu*(III) + OH^- + R \cdot COO^- \xrightarrow[fast]{k}$$

$$Cu(II) + R + CO_2 + H_2O \quad (6)$$

where Cu*(III) stands for any kind of species in which Cu^{3+} existed in equilibrium and stands for reductant. subscripts T and e stand for total and equilibrium concentration, respectively.

$$[Cu(III)]_T = [Cu(H_3TeO_6)]_e + [Cu(H_3TeO_6)(RCOO^-)] + [Cu(H_4TeO_6)_2]_e^-$$

Reaction (5) was the rate-determining step.

$$[Cu(H_3TeO_6)(R')] =$$

$$\frac{K_1K_2[Cu(III)]_T[OH^-][R']}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][R']} \quad (7)$$

As the rate of the disappearance of Cu(III) was monitored, the rate law of the reaction can be derived as:

$$-\frac{d[Cu(III)]_T}{dt} = 2k[Cu(H_3TeO_6)(R')] \quad (8)$$

$$-\frac{d[Cu(III)]_T}{dt} = \frac{2kK_1K_2[Cu(III)]_T[OH^-][R']}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][R']} \quad (9)$$

$$k_{obs} = \frac{2kK_1K_2[OH^-][R']}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][R']} \quad (10)$$

Re-arranging eqn. 10 leads to eqns. 11-13:

$$\frac{1}{k_{obs}} = \frac{1}{2k} + \frac{[H_4TeO_6^{2-}] + K_1[OH^-]}{2kK_1K_2[OH^-]} \frac{1}{[R']} \quad (11)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[R']}{2kK_2[R']} + \frac{[H_4TeO_6^{2-}]}{2kK_1K_2[R']} \frac{1}{[OH^-]} \quad (12)$$

$$\frac{1}{k_{obs}} = \frac{1+K_2[R']}{2kK_2[R']} + \frac{[H_4TeO_6^{2-}]}{2kK_1K_2[OH^-][R']} \quad (13)$$

From the eqn. 11, the plots $1/k_{obs}$ *versus* $1/[R']$ are straight lines and the rate constants of the rate-determining step at different temperature were obtained from the intercept of the straight line. Eqns. 12 and 13 suggest that the plots of $1/k_{obs}$ *versus* $1/[OH^-]$ and $1/k_{obs}$ *versus* $[H_4TeO_6^{2-}]$ are straight lines. Activation energy and the thermodynamic parameters were evaluated by the method given earlier (Table-2).

TABLE-2
RATE CONSTANTS (k) AND ACTIVATION PARAMETERS OF THE RATE-DETERMINING STEP (T = 298.2 K)

T (K)	10^2 (k/s^{-1})	Thermodynamic activation parameters (298.2 K)
283.2	0.76	
288.2	1.05	$E_a = 55.46$ kJ mol^{-1}
293.2	1.58	$\Delta H^{\neq} = 52.98$ kJ mol^{-1}
298.2	2.54	$\Delta S^{\neq} = -98.34$ J K^{-1} mol^{-1}
303.2	3.39	

The plot of ln k *versus* 1/T have following intercept (a) slope (b) and relative coefficient (r), a = 18.63; b = -6670.40; r = 0.997.

Conclusion

Based on the above discussion and results, monotelluratocuprate is considered as the active species for the title reaction among various species of Cu*(III) in alkaline liquids. The rate constant of the rate-determining step and activation parameters with respect to the rate-determining step of the reaction were computed. There is slightly negative salt effect which consistent with the common regulation of the kinetics. All the mechanistic sequence described here is consistent with mechanistic and kinetic studies.

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