Kinetics and mechanism of oxidation of $S_2O_3^{2-}$ by potassium *bis*(tellurato) cuprate(III)

G P PANIGRAHI* and A C PATHY

Department of Chemistry, Berhampur University, Berhampur 760007, India

Abstract. The kinetics of oxidation of sodium thiosulphate by potassium *bis*(tellurato) cuprate(III) in an alkaline medium has been reported. The reaction is first order in $[S_2O_3^{2-}]$ but zero order in copper(III). Hydroxide ions are found to retard the oxidation rate. A rate expression rationalising the kinetic data has been derived. Sodium tetrathionate has been found to be the product of oxidation.

Keywords. Potassium *bis*(tellurato) cuprate(III); oxidation, thiosulphate; kinetics.

1. Introduction

Several complexes of copper(III) have been demonstrated to be efficient oxidants with analytical utility (Malprade 1937; Malatesta 1941; Beck 1950, 1951, 1952, 1953). Recently we reported the kinetics of oxidation of methyl ethyl ketone and cyclohexanone (Panigrahi and Pathy 1984) by potassium *bis*(tellurato) cuprate(III) where a hydroxo tellurato cuprate(III) species was shown to be the active species. The oxidation of nitrophenols (Panigrahi and Pathy 1985a) on the other hand followed a combined first and second order kinetics with more complicated inverse dependence on $[OH^-]$. Strangely, retardation by OH^- was also observed in the oxidation (Panigrahi and Pathy 1985b) of CNS^- by Cu(III). In order to throw further light on the behaviour of Cu(III), we report the results of our studies on the kinetics of oxidation of thiosulphate ion by potassium *bis*(tellurato) cuprate(III).

2. Experimental

All the chemicals used were of either AR or *Pro Analysi* grade. A stock solution of potassium *bis*(tellurato) cuprate(III) was prepared and standardised by the procedure of Chandra and Yadav (1968). The solution was stable when preserved in a refrigerator. An appropriate amount of this stock solution was used to prepare the oxidant for kinetic study. Sodium thiosulphate was prepared afresh each time and standardised against standard iodine solution. A suitable quantity of this solution mixed with an appropriate amount of KOH, potassium tellurate and other salts if necessary, were added and made up in a volumetric flask. Potassium nitrate was used to maintain the ionic strength. Both the solutions were thermostated at 30°C ($\pm$0·2°C) for one hour before the reaction was commenced. The reaction was followed at 415 nm using a uv-visible spectrophotometer (Zeiss vsu 2P) fitted with a thermostatic cell holder which

---

* To whom all correspondence should be addressed.

was maintained at the desired temperature by circulation of water from a thermostat. Quartz cells of 10 mm thickness were used to hold the solutions. The hydroxide ion concentration in the reaction mixtures was determined by acidimetry. Hydroxide ion concentration remained constant during the period of the reaction. The self-decomposition of Cu(III) was routinely checked and was found to be negligible. The rate constants reported here are the average of at least three independent runs.

3.   Results and discussion

A preliminary screening of a mixture of *bis*(tellurato) cuprate(III) ion with sodium thiosulphate in aqueous solution at room temperature indicated slow disappearance of the reddish brown colour due to Cu(III). The reaction mixture after complete consumption of Cu(III) did not contain any turbidity or precipitate. Experiments carried out to determine the stoichiometry using an excess of thiosulphate over Cu(III) indicated the consumption of one mole of oxidant for each mole of thiosulphate
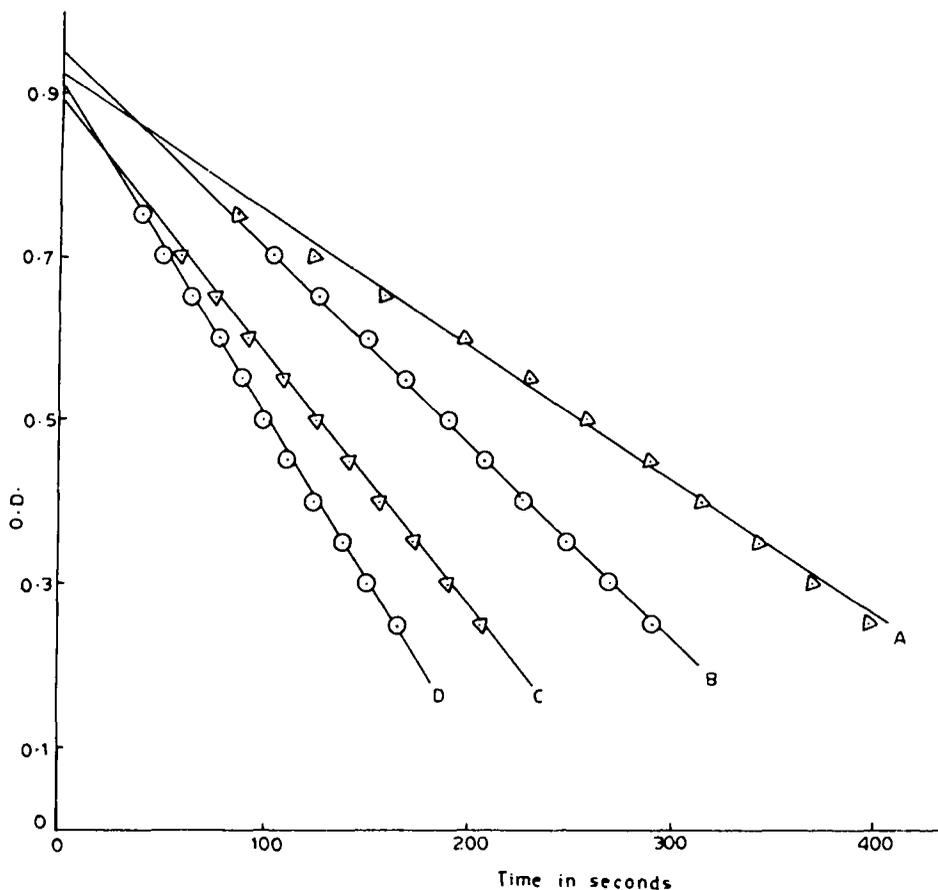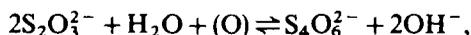

Figure 1.   Plot of optical density versus time ($[Cu^{3+}] = 1.22 \times 10^{-4}M$ $[OH^-] = 1.18 \times 10^{-1}M$, $[NO_3^-] = 1.00 \times 10^{-1}M$, $[TeO_4^-] = 1.0 \times 10^{-1}M$, temperature 30°C). (A) [Sub] $= 0.78 \times 10^{-3}M$, (B) [Sub] $= 1.55 \times 10^{-3}M$, (C) [Sub] $= 1.94 \times 10^{-3}M$, (D) [Sub] $= 2.90 \times 10^{-3}M$. (Sub = substrate

oxidised,

$$2S_2O_3^{2-} + H_2O + (O) \rightleftharpoons S_4O_6^{2-} + 2OH^-,$$

Evidently the product of oxidation is tetrathionate when excess of $S_2O_3^{2-}$ is used. However, formation of diverse oxidation products like S (Howlett and Wedzicha 1976; Panda *et al* 1981), SO_4^{2-} (Deshmukh and Bapat 1957), and S^{2-} (Pryor 1960; Pryor and Tonellato 1967), in addition to $S_4O_6^{2-}$, have been reported with other oxidants.

The kinetics of oxidation of $S_2O_3^{2-}$ by potassium *bis*(tellurato) cuprate(III) in alkaline medium was followed under the conditions of $[S_2O_3^{2-}] \gg [Cu(III)]$ at 415 nm at 30°C. The disappearance of Cu(III) was moderately rapid and the plot of absorbance versus time was perfectly linear (figure 1). Such a linearity is consistent with zero order disappearance of Cu(III). It is therefore to be concluded that oxidation of $S_2O_3^{2-}$ by Cu(III) is kinetically zero order with respect to Cu(III); k_0 was evaluated from the slope of the absorbance versus time plot. To confirm zero order dependence with respect to Cu(III), the runs were carried out with varying initial concentrations of Cu(III). It was observed that the zero order rate constants are constant within the limits of experimental error. This observation confirms zero order dependence in Cu(III).

Table 1. Average pseudo zero order rate constants for the oxidation of $S_2O_3^{2-}$ by potassium *bis*(tellurato) cuprate(III) in aqueous alkaline medium at 30°C.

$10[OH^-]M$	$10^3[Substrate]M$	$10^3 k_0$
2·2	1·94	2·40
2·2	2·33	3·13
2·2	2·72	3·57
2·2	3·10	4·00
1·18	0·78	1·60
1·18	1·16	1·94
1·18	1·55	2·39
1·18	1·94	3·00
1·18	2·52	3·50
1·18	2·90	4·50
0·7	0·78	4·78
0·7	1·16	5·08
0·7	1·55	5·58
0·7	1·94	6·07
0·7	2·33	6·90
0·7	2·72	7·68
0·695	1·55	5·06
0·94	1·55	3·82
1·20	1·55	3·5
1·45	1·55	2·97
1·70	1·55	2·5
2·18	1·55	2·13
2·7	1·55	1·66
3·2	1·55	1·52

$[Cu(III)] = 1·22 \times 10^{-4}M$, $[TeO_4^-] = 1·00 \times 10^{-1}M$, $[NO_3^-] = 1·00 \times 10^{-1}M$.

To fix the order with respect to the reductant, namely thiosulphate ion, the kinetics was carried out in the presence of varying initial concentrations of the reductant keeping all other reactants constant. The pseudo zero order constant was observed to increase linearly with increase in thiosulphate concentration (table 1) and the linear plot between k_0 versus $[S_2O_3^{2-}]$ yielded an intercept. Linearity of the above plot suggests first order dependence of the oxidation with respect to $S_2O_3^{2-}$. The plot suggests that the substrate is involved in a hydrolytic equilibrium producing the active species. Further, the slopes are proportional to first order rate constants (k_1) pertaining to oxidation of $S_2O_3^{2-}$. The slopes and intercepts at three different alkali concentrations for $S_2O_3^{2-}$ oxidation are given in table 2.

Table 2. Slopes and intercepts in the plot of [sub] versus oxidation rate under different alkali conditions.

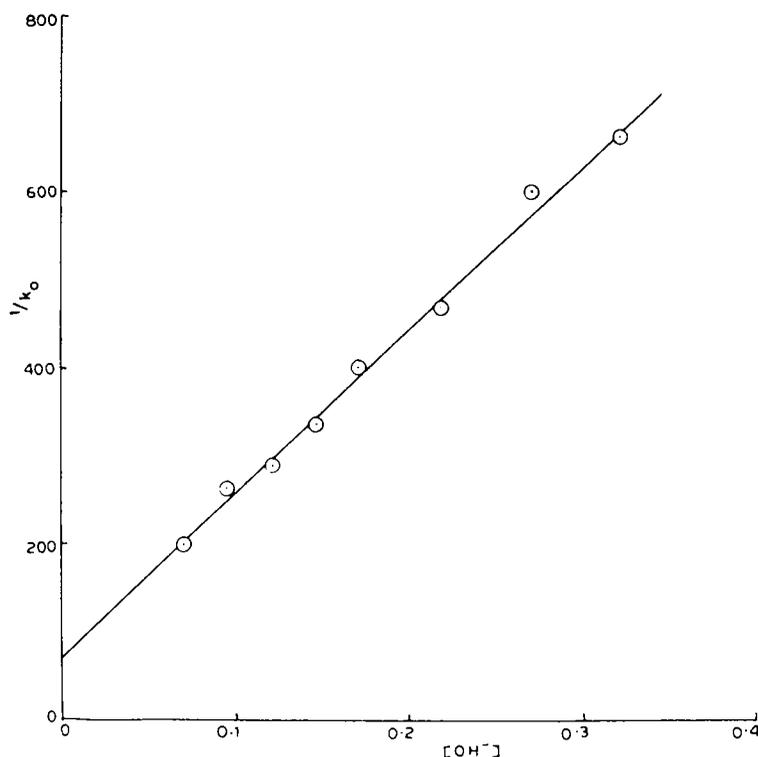| $10 \times [OH^-]$	Slope	Intercept $\times 10^2$
0·7	2	0·24
1·18	1·1	0·065
2·2	1·3	0·00

Sub = substrate.

Figure 2. Plot of k_0^{-1} versus $[OH^-]$ ($[Oxid] = 1·22 \times 10^{-4}M$, $[Sub] = 1·55 \times 10^{-3}M$, $[NO_3^-] = 1·00 \times 10^{-1}M$, $[TeO_4^-] = 1·00 \times 10^{-1}M$, temperature 30°C).

3.1 *Effect of added alkali*

The oxidation of thiosulphate was retarded by increase in alkali concentration and the k_0 values at different NaOH concentrations are included in table 1. Similar observations were also reported by Lee and Lister (1979) in the BrO_2 oxidation of $S_2O_3^{2-}$. A plot of k_0^{-1} versus [NaOH] is linear (figure 2) with an intercept and a positive slope. This observation is consistent with a rate law of the type,

$$k_0^{-1} = a + b[OH^-],$$

where a and b are terms including the rate constants pertaining to alkali independent and dependent paths.

3.2 *Effect of tellurate ion*

Unlike oxidation of CNS^- by Cu(III), the tellurate ion concentration inhibited oxidation till 0·15 M of tellurate ion concentration beyond which the rate was found to be indifferent to further increase of tellurate ion concentration (table 3). Decrease of rate with increase of tellurate ion concentration has been normally attributed to shift in the ionisation equilibria (1) (Movious 1973) to the left since the ditellurato anion is less active than the mono anion species,

$$[Cu(H_2TeO_6)_2]^{5-} \rightleftharpoons [Cu(H_2TeO_6)]^{1-} + H_2TeO_6^{4-}. \qquad (1)$$
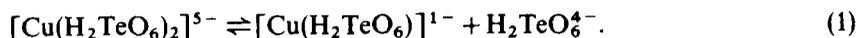
In the present study, since Cu(III) is not involved in the rate limiting step, the above explanation seems to be irrelevant, and to explain the observation one has to presume some sort of interaction between $S_2O_3^{2-}$ and tellurate ions. It appears that the tellurate ion is able to remove $S_2O_3^{2-}$ by complexation forming an inactive species and hence is stable towards Cu(III). For a given concentration of $S_2O_3^{2-}$, after the optimum concentration of tellurate ion is reached, further increase of tellurate ion has practically no effect.

3.3 *Salt effect*

The k_0 values in the $S_2O_3^{2-}$-Cu(III) reaction were unaffected by added salt concentration which is quite contrary to the CNS^--Cu(III) reaction (table 4).

Table 3. Average pseudo zero order rate constants for the oxidation of $S_2O_3^{2-}$ by potassium *bis*(tellurato)cuprate(III) in the presence of varying tellurate in an aqueous alkaline medium at 30°C.

$10 \times [TeO_4^-]$	$k_0 \times 10^{-3}$
0·2	11·87
0·5	4·77
1·0	2·68
1·5	2·13
2·0	2·13
2·5	2·13

[Cu(III)] = 1·22 × 10⁻⁴ M, [Sub]
= 1·55 × 10⁻³ M, [OH⁻] = 1·44
× 10⁻¹ M, [NO₃⁻] = 1·00
× 10⁻¹ M.

Constancy of the zero order rate constants in the presence of varying KNO_3 concentration is self-explanatory since the magnitude of charge does not change as one goes from reactant to activated complex and hence no salt effect or ionic strength effect (Espenson 1981) is observed.

Inspection of the plot (figure 2) of k_0 versus substrate concentration (substrate = sub) at different constant alkali concentrations indicates that the intercept

Table 4. Average pseudo zero order rate constants for the oxidation of $S_2O_3^{2-}$ by potassium bis(tellurato) cuprate(III) in the presence of KNO_3 in an aqueous alkaline medium at 30°C.

$[NO_3^-]$	$k_0 \times 10^{-3}$
0·05	2·5
0·10	2·5
0·15	2·5
0·2	2·5
0·25	2·5

$[Cu(III)] = 1·22 \times 10^{-4}$ M, $[Sub] = 1·55$ $\times 10^{-3}$ M, $[TeO_4^-] = 1·00 \times 10^{-1}$ M.

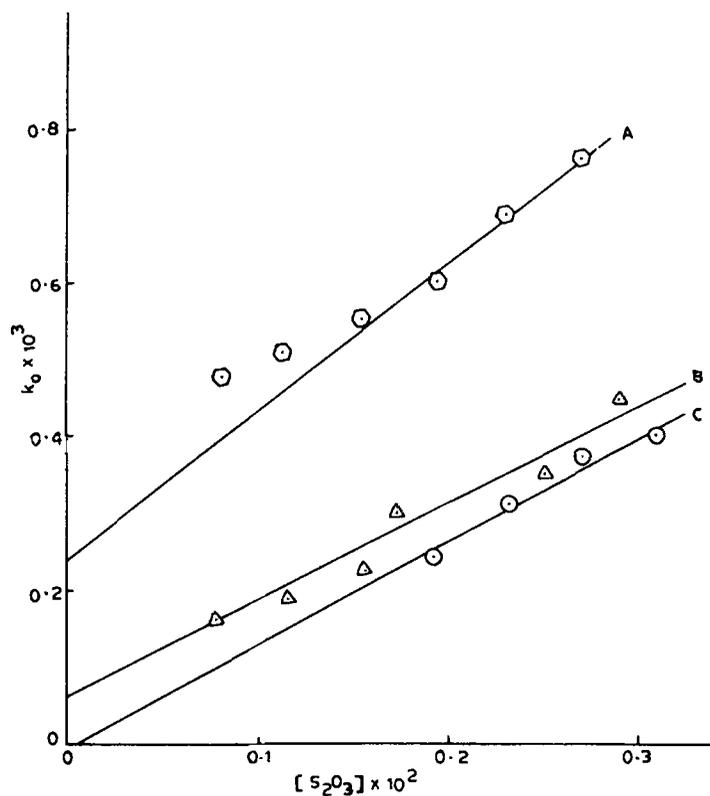**Figure 3.** Plot of k_0 versus $[S_2O_3^{2-}]$ at different [alkali] ($[Cu^{3+}] = 1·22 \times 10^{-4}$ M, $[TeO_4^-] = 1·00 \times 10^{-1}$ M, $[NO_3^-] = 1·00 \times 10^{-1}$ M, temperature 30°C). (A) $[OH^-] = 0·7 \times 10^{-1}$ M, (B) $[OH^-] = 1·18 \times 10^{-1}$ M, (C) $[OH^-] = 2·2 \times 10^{-1}$ M.

values decrease with increase in alkali concentration. Since intercepts in such plots indicate self decomposition of Cu(III), the higher rate of self decomposition at low alkali concentration is consistent with the greater instability of potassium *bis*(tellurato) cuprate(III) in low OH^- concentrations. Similarly the slope of the plot at low alkali concentration is quite high compared to that at high alkali concentration indicating that the rate of oxidation of $S_2O_3^{2-}$ is higher at low $[OH^-]$, which is consistent with the decrease of the rate with increase of $[OH^-]$ (table 2).

In earlier reports of oxidation of $S_2O_3^{2-}$ by several metal ions (Beyerley *et al* 1975; Panda *et al* 1982) it has been invariably found to be a case of precursor complex formation between the metal ion and $S_2O_3^{2-}$ before the rate limiting decomposition of the precursor complex to products. Recently Panda *et al* (1981), however, had reported zero order dependence with respect to $Fe(CN)_6^{3-}$ in the oxidation of $S_2O_3^{2-}$ in an alkaline medium. In the present investigation also, zero order dependence with respect to Cu(III) rules out participation of the oxidant, either in the rate limiting step or in steps preceding this. Further attempts to detect any precursor complex formation between $S_2O_3^{2-}$ and Cu(III) did not succeed.

The observed kinetic data, namely, zero order dependence with respect to the oxidant, retardation of rate by added alkali and indifference of rate to varying ionic strength can be probably rationalised by the following scheme (2–4):

$$S_2O_3^{2-} + H_2O \overset{K_h}{\rightleftharpoons} HS_2O_3^- + OH^-, \ (K_h' = K_h \, [H_2O]), \tag{2}$$

$$HS_2O_3^- + H_2O \overset{k_2}{\rightarrow} HS_2O_2^+ + 2OH^-, \tag{3}$$

$$HS_2O_2^+ + Cu(III) + S_2O_3^{2-} + H_2O \overset{fast}{\longrightarrow} products. \tag{4}$$
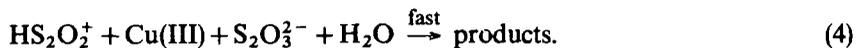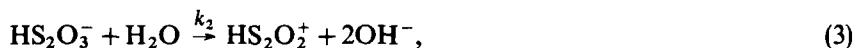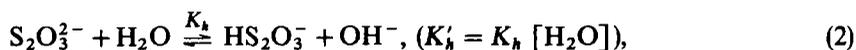
The following rate expression can be derived on the basis of the foregoing steps:

$$-\frac{d[Cu(III)]_T}{dt} = \frac{k_2 K_h' \, [S_2O_3^{2-}]_T}{K_h' + [OH^-]}. \tag{5}$$

As the rate expression predicts, the plot of $-d[Cu(III)]_T/dt$ versus $[S_2O_3^{2-}]$ is linear and, $1/d[Cu(III)]_T/dt$ versus $[OH^-]$ is also linear, confirming the reaction steps (2)–(4). It is interesting to note that added tellurate retards the rate until an optimum concentration of 0·25 M is reached for a given concentration of Cu(III), unlike in ketone or CNS^- oxidation where no such limiting rate is observed with excess of tellurate. This may probably be due to the formation of a less active thiosulphate species by complexation with tellurate. However, with other substrates involvement of tellurate as a complexing agent is probably ruled out.

References

Beck G 1950 *Microchemi* **35** 169
Beck G 1951 *Microchemi* **38** 1, 152
Beck G 1952 *Microchemi* **39** 22, 147
Beck G 1953 *Microchemi* **40** 258
Beyerley J J, Fouda S A and Rampel G L 1975 *J. Chem. Soc. Dalton Trans.* 704
Chandra S and Yadav K L 1968 *Talanta* **15** 349
Deshmukh G S and Bapat M G 1957 *Zeit. Anal. Chem.* **156** 105

Espenson J H 1981 *Chemical kinetics and reaction mechanism* (New York: McGraw Hill) p. 175
Howlett K E and Wedzicha B L 1976 *Inorg. Chim. Acta* **18** 133
Lee C L and Lister M W 1979 *Can. J. Chem.* **57** 1524
Malprade L 1937 *Compte Rendus* **204** 979
Malatesta L 1941 *Gazz. Chim. Ital.* **71** 467, 580
Movious W G 1973 *Inorg. Chem.* **12** 31
Panigrahi G P and Pathy A C 1984 *Inorg. Chem.* **23** 2133
Panigrahi G P and Pathy A C 1985a *Indian J. Chem.* (communicated)
Panigrahi G P and Pathy A C 1985b *Indian J. Chem.* (communicated)
Panda R K, Neogi G and Ramaswamy D 1981 *Bull. Soc. Chim. Belg.* **90**
Panda R K, Neogi G and Ramaswamy D 1982 *Bull. Chem. Soc. Jpn* **55** 587
Pryor W A 1960 *J. Am. Chem. Soc.* **82** 4794
Pryor W A and Tonellato U 1967 *J. Am. Chem. Soc.* **89** 3379, 6391