Kinetics and Mechanism of Oxidation of Some Hydroxy Butyric Acid Salts by Ditelluratocuprate(III) in Alkaline Medium

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The kinetics of oxidation of 2-hydroxy butyric acid salt (2-HBAS) and 3-hydroxy butyric acid salt (3-HBAS) by ditelluratocuprate(III) (DTC) were studied spectrophotometrically between 298.2 K and 313.2 K in alkaline medium. The reaction rate showed first order dependence in DTC and a fractional order in HBAS. It was found that the pseudo-first order rate constant k_{obs} increased with an increase in the concentration of OH^- and a decrease in the concentration of TeO_4^{2-}. The reaction rate changed with the position of the hydroxyl group. There was a negative salt effect. A plausible mechanism involving a pre-equilibrium of adduct formation between the complex and HBAS was proposed. The rate equations derived from the mechanism can explain all experimental observations. The activation parameters along with the rate constants of the rate-determining step were calculated.

Key Words: Ditelluratocuprate(III), 2-hydroxy butyric acid salt, 3-hydroxy butyric acid salt, Redox reaction, Kinetics and mechanism

Introduction

Recently, studies on the highest oxidation state of transition metals have intrigued many researchers. Transition metals in a higher oxidation state can generally be stabilized by chelation with suitable polydentate ligands. Metal chelates such as ditelluratocuprate(III)[1], diperiodatocuprate(III)[2], diperiodatoargentate(III)[3] and ditelluratoargentate(III)[4], diperiodatonickelate(IV)[5] 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[6], sugars and organic acids[7,8]. The use of Cu(III) as an oxidation agent is also known in organic mixture qualitative analysis[9]. Cu(III) is also shown to be an intermediate in the Cu(II)-catalysed oxidation of amino acids by peroxodisulphate[10]. Many biological systems involve electron-transfer processes wherein Cu(III) plays an important role[11]. Based on the studies of oxidation of some organic compounds by Cu(III) complex, Indian researchers have proposed that in the alkaline medium the formula of DTC may be represented by $[Cu(OH)_2(H_4TeO_6)_2]^{3-}$ and the mechanism involving a pre-equilibrium of adduct formation

between the complex and reductant was also proposed[12,13]. Because Cu(III) is in the highest oxidation state and the reaction is complicated in this kind of reaction system, it is of significance to carry out further research on this kind of reaction system. This will certainly provide us with more dynamic parameters, and will provide a theoretical foundation for the design of a reaction route in organic synthesis and quantitative analysis in analytical chemistry. In the present paper, the mechanism of oxidation of 2-hydroxy butyric acid salt and 3-hydroxy butyric acid salt by ditelluratocuprate(III) is reported.

Chemicals and apparatus

All the reagents used were of A.R. grade. All solutions were prepared with doubly distilled water. Solutions of $[Cu(OH)_2(H_4TeO_6)_2]^{3-}$ (DTC) and $H_3CCH(OH)CH_2COO^-$ and $H_3CCH_2CH(OH)COO^-$ were always freshly prepared before use. The stock solution of DTC was prepared and standardized by the method given by Jaiswal and Yadava[7]. Its electronic spectrum was found to be consistent with that reported by Jaiswal and Yadava.

All kinetics measurements were carried out under pseudo-first order conditions. A solution (2 mL) containing definite concentrations of Cu(III), OH^- and TeO_4^{2-} and of ionic strength, and HBAS solution (2 mL) of appropriate concentration were transferred separately to the upper and lower branch tubes of a λ type two-cell reactor. After it was thermally equilibrated at the desired temperature in a 501 thermo-bath (Shanghai), the two solutions were mixed well and immediately transferred to a 1 cm thick glass cell in a constant temperature cell-holder (± 0.1 K). The progress of the reaction was monitored automatically by recording the disappearance of Cu(III) with time (t) at 405 nm with a UV-8500 spectrophotometer (Shanghai). All other species did not absorb significantly at this wavelength.

A solution with known concentrations of Cu(III), OH^-, TeO_4^{2-} was mixed with an excess of HBAS. The complete fading of DTC colour (reddish brown) marked the completion of the reaction. The product of oxidation was identified as butanone acid salt by its characteristic spot test[14]. It was found that one mole of HBAS consumed two moles of Cu(III) by weight.

Results and Discussion

Evaluation of pseudo-first order rate constants

Under the conditions $[HBAS]_0 >> [Cu(III)]_0$, the plots of $\ln(A_t-A_\infty)$ versus time t for more than three half lives of the reaction were good straight lines (r $\geq$ 0.9999) (Figure 1), showing the order in DTC to be unity. The pseudo-first order rate constants, k_{obs}, were calculated by using the least-squares method. The rate constants reported here are averages of three independent runs. Deviations in duplicate determinations are generally less than $\pm 5\%$.

Rate dependence on concentration of HBAS

At fixed concentrations of Cu(III), OH^- and TeO_4^{2-}, and fixed ionic strength and temperature, k_{obs} values increase with the increasing concentration of HBAS and the order in HBAS was found to be fractional (Table 1). The plots of $1/k_{obs}$ versus $1/[HBAS]$ were straight lines with a positive intercept (r $\geq$ 0.997) (Figure 2).
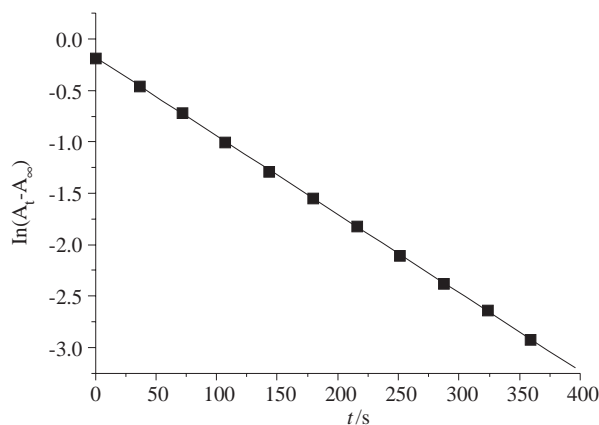
Figure 1. Plot of $\ln(A_t\text{-}A_\infty)$ vs. t at T = 298.2K

$[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{TeO}_4^{2-}] = 3.500 \times 10^{-3}$ mol·L^{-1}

$[\text{OH}^-] = 3.007 \times 10^{-3}$ mol·L^{-1}, $\mu = 38.50 \times 10^{-3}$ mol·L^{-1}

$[\text{2-HBAS}] = 1.000 \times 10^{-2}$ mol·L^{-1}.

Table 1. $10^3 k_{obs}/\text{s}^{-1}$ varying with the different [3-HBAS] at different temperatures.

C/mol·L^{-1}	0.040	0.050	0.065	0.100	0.140	b	r
T/K							
298.2	1.3073	1.5345	2.0318	2.8590	3.4270	0.793	0.995
303.2	2.0764	2.5811	3.1227	4.3167	5.8982	0.812	0.999
308.2	3.6127	4.4753	5.3645	8.0290	9.8590	0.810	0.998
313.2	6.5359	8.2645	10.152	14.490	16.873	0.762	0.993

b and r respectively stand for the slope and the relative coefficient of the plot of $\ln k_{obs}$ vs. $\ln C$

$[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{TeO}_4^{2-}] = 8.000 \times 10^{-4}$ mol·L^{-1}, $[\text{OH}^-] = 0.020$ mol·L^{-1},

$\mu = 0.162$ mol·L^{-1}
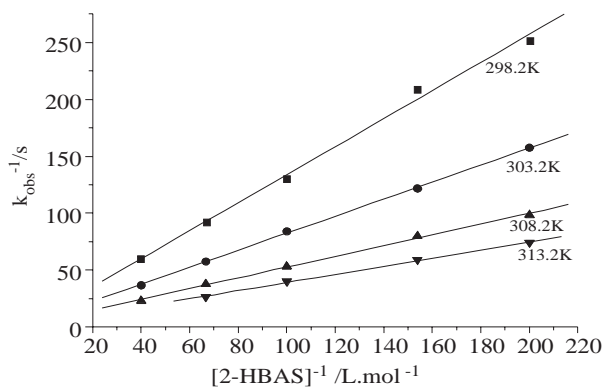
Figure 2. Plots of k_{obs}^{-1} vs $[\text{2-HBAS}]^{-1}$ at different temperatures.

$[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{TeO}_4^{2-}] = 3.500 \times 10^{-3}$ mol·L^{-1}

$[\text{OH}^-] = 3.007 \times 10^{-3}$ mol·L^{-1}, $\mu = 38.50 \times 10^{-3}$ mol·L^{-1}

Rate dependence on concentration of OH^-

At fixed concentrations of Cu(III), HBAS and TeO_4^{2-}, μ and fixed temperature, k_{obs} values increase with the increasing concentration of OH^- and the order with respect to OH^- was found to be fractional (Table 2). The plot of $1/k_{obs}$ versus $1/[OH^-]$ was linear (r $\geq$ 0.998) (Figure 3).

Rate dependence on concentration of TeO_4^{2-}

At fixed concentrations of Cu(III), OH^- and HBAS, μ and fixed temperature, k_{obs} values decrease with the increasing concentration of TeO_4^{2-} and the order in TeO_4^{2-} was found to be negative fractional (Table 2). The plot of $1/k_{obs}$ versus $[TeO_4^{2-}]$ was linear (r $\geq$ 0.998) (Figure 4).

Table 2. $10^3 k_{obs}/s^{-1}$ varying with the different $[TeO_4^{2-}]$, $[OH^-]$.

[3-HBAS]/mol·L^{-1}	$10^4[TeO_4^{2-}]$/mol·L^{-1}	$10^3[OH^-]$/mol·L^{-1}	μ/mol·L^{-1}	$10^3 k_{obs}/s^{-1}$
0.108	6.000	20.00	0.134	10.931
0.108	9.500	20.00	0.134	7.9530
0.108	13.00	20.00	0.134	6.0606
0.108	16.50	20.00	0.134	5.2414
0.108	20.00	20.00	0.134	4.3441
0.098	6.000	6.533	0.119	6.6667
0.098	6.000	7.984	0.119	7.0922
0.098	6.000	10.02	0.119	7.4072
0.098	6.000	13.34	0.119	7.9365
0.098	6.000	20.01	0.119	8.5123

$[Cu(III)] = 9.128 \times 10^{-5}$ mol·L^{-1} T = 308.2 K
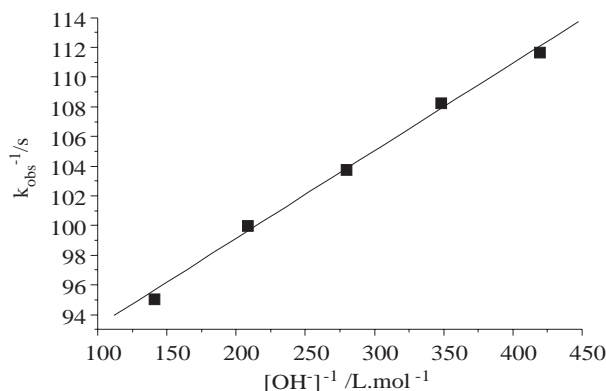
Figure 3. Plot of k_{obs}^{-1} vs $[OH^-]^{-1}$ at T = 303.2 K.
$[Cu(III)] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[TeO_4^{2-}] = 3.500 \times 10^{-3}$ mol·L^{-1}
$[2\text{-HBAS}] = 7.000 \times 10^{-3}$ mol·L^{-1}, $\mu = 24.66 \times 10^{-3}$ mol·L^{-1}
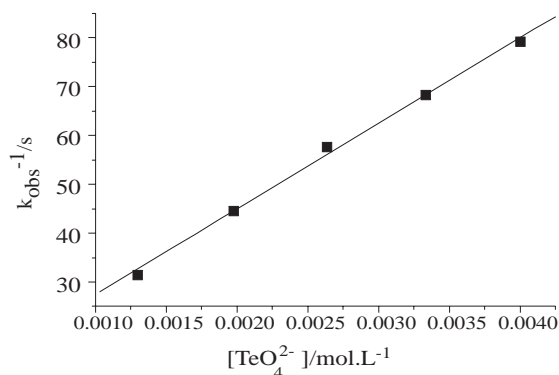
Figure 4. Plot of k_{obs}^{-1} vs. $[\text{TeO}_4^{2-}]$ at T = 303.2 K

$[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{OH}^-] = 3.007 \times 10^{-3}$ mol·L^{-1}

$[\text{2-HBAS}] = 11.67 \times 10^{-3}$ mol·L^{-1}, $\mu = 26.67 \times 10^{-3}$ mol·L^{-1}

Rate dependence on ionic strength μ

The rate was decreased by adding KNO$_3$ solution (Table 3), which indicates there was a negative salt effect consistent with the common regulation of the kinetics[15].

Table 3. Influence of variation ionic strength μ.

2-HBAS	$10^2\mu/$ mol·L^{-1}	1.000	1.750	2.500	3.250	4.000
	$10^2k_{obs}/\text{s}^{-1}$	1.3869	1.3629	1.3448	1.3221	1.2918
3-HBAS	$\mu/$ mol·L^{-1}	0.100	0.160	0.220	0.280	0.340
	$10^3k_{obs}/\text{s}^{-1}$	6.7916	6.7080	6.6163	6.5233	6.4814

$[\text{2-HBAS}] = 11.25 \times 10^{-3}$ mol·L^{-1}, $[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{OH}^-] = 3.007 \times 10^{-3}$ mol·L^{-1},

$[\text{TeO}_4^{2-}] = 3.500 \times 10^{-3}$ mol·L^{-1}, T = 303.2 K

$[\text{3-HBAS}] = 7.500 \times 10^{-2}$ mol·L^{-1}, $[\text{Cu(III)}] = 9.128 \times 10^{-5}$ mol·L^{-1}, $[\text{OH}^-] = 2.000 \times 10^{-2}$ mol·L^{-1},

$[\text{TeO}_4^{2-}] = 6.000 \times 10^{-4}$ mol·L^{-1}, T = 308.2 K

Free radical detection

Acrylamide was added under the protection of nitrogen atmosphere during the course of the reaction. The appearance of white polyacrylamide was consistent with free radical intermediates in the oxidation by Cu(III) complexes. Blank experiments in the reaction system gave no polymeric suspensions.
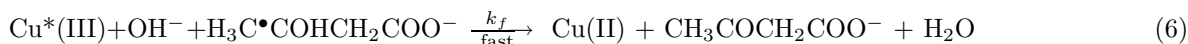
In the alkaline medium, the electric dissociation equilibrium of telluric acid was given earlier[16] (here $pK_w = 14$)

$$\text{H}_5\text{TeO}_6^- + \text{OH}^- \rightleftharpoons \text{H}_4\text{TeO}_6^{2-} + \text{H}_2\text{O} \quad \lg\beta_1 = 3.049 \tag{1}$$

$$\text{H}_4\text{TeO}_6^{2-} + \text{OH}^- \rightleftharpoons \text{H}_3\text{TeO}_6^{3-} + \text{H}_2\text{O} \quad \lg\beta_2 = -1 \tag{2}$$
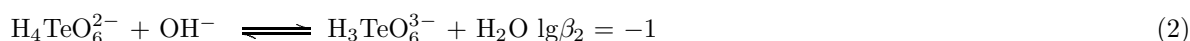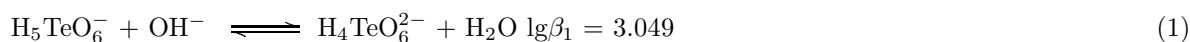
The distribution of all species of tellurate in aqueous alkaline solution can be calculated from equilibriums (1)-(2). In alkaline medium such as $[\text{OH}^-] = 0.01$ mol·L^{-1}, $[\text{H}_4\text{TeO}_6^{2-}]$:$[\text{H}_5\text{TeO}_6^-]$:$[\text{H}_3\text{TeO}_6^{3-}] =$

1000:89:1, so in the concentration of OH^- range used in this work, $H_5TeO_6^-$ and $H_3TeO_6^{3-}$ can be ignored; the main tellurate species was $H_4TeO_6^{2-}$. Based on such distribution and Navaneeth Rao's[12,13] argument, the formula of DTC may be represented by $[Cu(OH)_2(H_4TeO_6)_2]^{3-}$, which is close to the formula of ditelluratoargentate(III) suggested by Dirshitulu[17].

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 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 $(MTC)^{12,13,17}$. The fractional order in HBAS indicated complex formation between HBAS and MTC, and the plot of $1/k_{obs}$ versus $1/[HBAS]$ was a straight line with a positive intercept providing kinetic evidence for the formation of 1:1 complex. Hence the following inner-sphere electron transfer mechanism involving a pre-equilibrium of adduct formation between the complex and HBAS is proposed for the reaction[12,13].

$$[Cu(OH)_2(H_4TeO_6)_2]^{3-} + OH^- \underset{}{\overset{k_1}{\rightleftharpoons}} [Cu(OH)_2(H_3TeO_6)]^{2-} + H_4TeO_6^{2-} + H_2O \tag{3}$$

$$[Cu(OH)_2(H_3TeO_6)]^{2-} + HBAS \underset{}{\overset{K_2}{\rightleftharpoons}} [Cu(OH)_2(H_3TeO_6)(HBAS)]^{3-} \tag{4}$$

$$[Cu(OH)_2(H_3TeO_6)(HBAS)]^{3-} \underset{slow}{\overset{k}{\rightarrow}} H_3C^\bullet COHCH_2COO^- + [Cu(OH)_2(H_3TeO_6)]^{3-} + H^+ \tag{5}$$

$$Cu^*(III) + OH^- + H_3C^\bullet COHCH_2COO^- \underset{fast}{\overset{k_f}{\rightarrow}} Cu(II) + CH_3COCH_2COO^- + H_2O \tag{6}$$
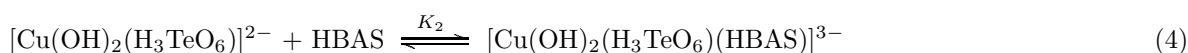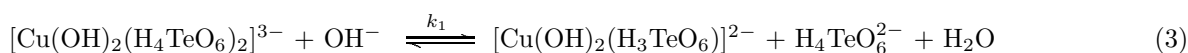
where $Cu^*(III)$ stands for any kind of form which Cu^{3+} existed in equilibrium. Subscripts T and e stand for total and equilibrium concentration respectively. $[Cu(III)]_T = [Cu(OH)_2(H_3TeO_6)]_e^{2-} + [Cu(OH)_2(H_3TeO_6)(HBAS)]_e^{3-} + [Cu(OH)_2(H_4TeO_6)_2]_e^{3-}$. Reaction (5) was the rate-determining step.

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

$$-d[Cu(III)]_T/dt = 2k[Cu(OH)_2(H_3TeO_6)(HBAS)]^{3-} \tag{7}$$

$$\frac{-d[Cu(III)]_T}{dt} = \frac{2kK_1K_2[OH^-][HBAS][Cu(III)]_T}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][HBAS]} = k_{obs}[Cu(III)]_T \tag{8}$$

$$k_{obs} = \frac{2kK_1K_2[OH^-][HBAS]}{[H_4TeO_6^{2-}] + K_1[OH^-] + K_1K_2[OH^-][HBAS]} \tag{9}$$

Re-arranging equation (9) leads to equations (10-12):

$$\frac{1}{k_{obs}} = \frac{1}{2k} + \frac{[H_4TeO_6^{2-}] + K_1[OH^-]}{2kK_1K_2[OH^-]} \frac{1}{[HBAS]} \tag{10}$$

$$\frac{1}{k_{obs}} = \frac{1 + K_2[HBAS]}{2kK_2[HBAS]} + \frac{[H_4TeO_6^{2-}]}{2kK_1K_2[HBAS]} \frac{1}{[OH^-]} \tag{11}$$

$$\frac{1}{k_{obs}} = \frac{1 + K_2[HBAS]}{2kK_2[HBAS]} + \frac{[H_4TeO_6^{2-}]}{2kK_1K_2[HBAS][OH^-]} \tag{12}$$

From equation (10), the plots $1/k_{obs}$ vs. $1/[HBAS]$ are straight lines and the rate constants of the rate-determining step at different temperatures were obtained from the intercept of the straight line. Equations (11) and (12) suggest that the plots of $1/k_{obs}$ vs. $1/[OH^-]$ and $1/k_{obs}$ vs. $[H_4TeO_6^{2-}]$ are straight lines. The activation energy and thermodynamic parameters were evaluated by the method given earlier[18] (Table 4).

Based on the above discussion and results, we know that the reaction rate changed with the position of the hydroxyl group, the observed rate constants and the rate-determining step constants of 2-hydroxy butyric acid salt are larger than those of 3-hydroxy butyric acid salt. Because the hexa-cyclic compound formed by a meta-compound has a larger spatial hindrance than the penta-cyclic compound formed by an ortho-compound, the latter is more stable which is consistent with experimental results.

Table 4. Rate constants (k) and activation parameters of the rate-determining step.

	T/K				Activation parameters (298.2K)		
	298.2	303.2	308.2	313.2	Ea	$\Delta H^{\#}$	$\Delta S^{\#}$
$10^3 k$ /s^{-1}					(kJ·mol^{-1})	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
2-HBAS	46.95	66.14	92.42	137.7	55.54 $\pm$ 2.0	53.06 $\pm$ 2.0	-92.56 $\pm$ 3.8
3-HBAS	5.838	9.186	16.82	26.99	81.05 $\pm$ 3.5	78.57 $\pm$ 3.5	-24.43 $\pm$ 1.2

The plot of ln$k$ vs. 1/T has following intercepts (a) slope (b) and relative coefficient (r)
2-HBAS: a=19.32 b = -6680.27 r = 0.999 3-HBAS: a = 27.52 b = -9749.11 r = 0.998

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