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Oxidation of L-cystine by 12-tungstocobaltate(III) in aqueous perchlorate medium: A kinetic approach

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The oxidation reaction of L-cystine with 12-tungstocobaltate(III) ($Co^{III}W_{12}O_{40}^{5-}$ or $Co^{III}W^{5-}$) has been studied spectrophotometrically over the range $1.15 \leq 10^3[H_4L^{2+}]_T. \leq 3.5$; $2.0 \leq pH \leq 5.0$; $25°C \leq t \leq 40°C$ and $I = 0.3$ mol dm^{-3} ($NaClO_4$). Both the conjugate bases of L-cystine participate in the electron transfer reaction. The rate of the reaction has been found to increase with the increase in *p*H and [L-cystine]$_T$. The reaction shows first order dependence both on [$Co^{III}W^{5-}$] and [L-cystine]$_T$. The $\Delta H^{\neq}$ (kJ mol^{-1}) and $\Delta S^{\neq}$ (J K^{-1} mol^{-1}) for k_1 and k_2 paths are 16.9±2.0, 16.1±0.5 and –205±6, –204±1.5, respectively. Negative activation entropy is indicative of ordered transition state for the reaction. The product of the reaction has been found to be the cystinesulphoxide.

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Transition metal substituted heteropolymetalates exhibit different chemical and electrochemical properties, which make them good catalysts[1]. The complexes of transition metal ions with polyoxo anions such as polytungstates are well known outersphere electron transfer reagents[2]. The redox reactions of $Co^{III}W^{5-}$ have been recently reviewed[3,4]. The electron transfer mechanism involved in the present study may throw some more light in this area.

12-Tungstocobaltate(III) ($Co^{III}W^{5-}$) has the well-known twelve tungsten atoms Keggin structure[5] and has a reduction potential ($E_{Co^{III}W/Co^{II}W}$ = 1.0 V)[6]. The kinetics of the oxidation of a number of inorganic compounds such as thiourea[7], thiocyanate[8], thallium(I)[9], antimony(III)[10], platinum(II)[11], arsenous acid[12] and a number of organic compounds such as thiols[13,14], citric acid[15], ascorbic acid[16], catechol[16], DL-methionine[17] by 12-tungstocobaltate(III) in acidic medium have also been reported.

There is increasing interest in the study of electron transfer processes that are important in biological systems. Oxidation reactions of sulphur containing aminoacids are studied mostly for their biochemical importance[18,19]. The kinetic investigation of the oxidation of biologically important aminoacids by a number of oxidants has been carried out under different conditions[20]. Much work on the electron transfer reaction of L-cystine has not been carried out[21]. However, oxidation of L-cystine by potassium ferrate[22], alkaline permanganate[23] and electrolytic oxidation of L-cystine at a carbon paste electrode modified with Ruthenium (IV) oxide[24] has been reported.

In order to examine the redox behaviour of 12-tungstocobaltate(III) towards amino acids, we report herein the detailed kinetics and mechanism of the oxidation of L-cystine by 12-tungstocobaltate(III).

Materials and Methods

The reactant complex 12-tungstocobaltate(III) ($Co^{III}W^{5-}$) was prepared as reported already[16] and characterized spectrophotometrically[25] (at 388 nm, ε_{388} = 1150 ± 2 dm^3 mol^{-1}cm^{-1}). All other chemicals used were of Analar grade. Doubly distilled water was used to prepare all the solutions. The *p*H of the solution was adjusted by adding NaOH/$HClO_4$ and the measurements were carried out with the help of a pre-standardised Elico (India) digital *p*H meter equipped with glass electrode with an accuracy of ±0.01 *p*H unit. During kinetic investigation, a constant ionic strength (0.3 mol dm^{-3} $NaClO_4$) was maintained.

On mixing L-cystine with $Co^{III}W^{5-}$ solution, a decrease of absorbance at 390 nm with a simultaneous increase in absorbance at 624 nm at the same *p*H was observed. An increase in absorbance at 624 nm (low ε_{624} = 180 ± 2 dm^{3}mol^{-1}cm^{-1}) indicates the formation of $Co^{II}W^{6-}$. The decrease in absorbance of the mixture at different time intervals is observed.

Kinetic measurements were carried out with a CECIL-7200 UV-vis spectrophotometer equipped with a thermobath for temperature control (accuracy = ±0.1°C). Progress of the reaction was monitored by following the decrease in absorbance at 390 nm. The conventional mixing technique was followed and pseudo-first order conditions were maintained throughout the course of the reaction. The rate constants (k_{obs}) were obtained from the slopes of ln (A_t-A_∞) versus t plots.

$$\ln (A_t - A_\infty) = k_{obs}\, t + C \quad \ldots (1)$$

where A_t and A_∞ are the absorbances of the reaction mixture at time t and at equilibrium, respectively. Rate data, an average of duplicate runs were reproducible within ±3%. The correlation coefficient of plots used to determine k_{obs} were found to be 0.99 in most of the cases.

Results and Discussion

Stoichiometry

The stoichiometry of the reaction was studied by keeping $[Co^{III}W^{5-}]_T$ constant at 2.3×10^{-4} mol dm^{-3} and varying the concentration of L-cystine from 1.15×10^{-3} to 3.5×10^{-3} mol dm^{-3} at pH = 5.0 and I = 0.3 mol dm^{-3}. After 24 h, $[Co^{II}W^{6-}]$ was analysed spectrophotometrically at 624 nm. The stoichiometry was found to be 2 moles of $Co^{III}W^{5-}$ per mole of L-cystine.

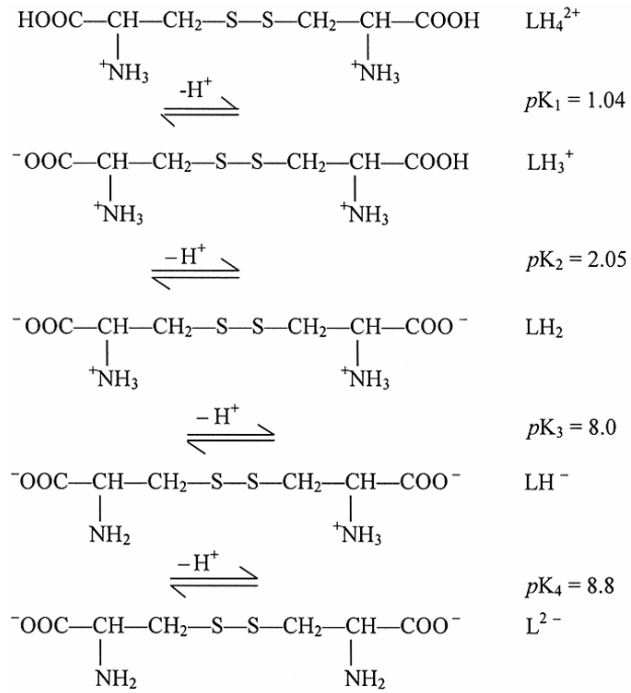
Effect of $[Co^{III}W^{5-}]$ on the rate

In the first set of kinetic experiments, $[Co^{III}W^{5-}]_T$ (T= Total) was varied at fixed excess concentration of L-cystine (3.5×10^{-3} mol dm^{-3}), pH = 5.0, 25°C and ionic strength I = 0.3 mol dm^{-3} ($NaClO_4$). The pseudo first order plots were linear (R^2 = 0.99) in each case giving $10^4\, k_{obs}$ (s^{-1}) = 7.18 ± 0.1. The independence of k_{obs} at 25°C under the conditions [L-cystine]$_T$ = 3.5×10^{-3} mol dm^{-3}, pH = 5.0, I = 0.3 mol dm^{-3} ($NaClO_4$) over the $[Co^{III}W^{5-}]_T$ range from 2.3×10^{-4} to 6.9×10^{-4} mol dm^{-3} is in agreement with first order dependence in $[Co^{III}W^{5-}]_T$. Furthermore, the second order rate constant (25°C) (mol^{-1} dm^3 s^{-1}) = k_{obs} / [L-cystine]$_T$ is 0.2004 ± 0.003. Constancy of second order rate constant indicates the fact that the overall order of the reaction is two. As the order of the reaction is one with respect to [substrate]$_T$, the order would be one with respect to $[Co^{III}W^{5-}]_T$. The rate law therefore is given by:

$$\text{Rate} = k_{obs}\, [Co^{III}W^{5-}]_T \quad \ldots (2)$$

Effect of pH on the rate

L-cystine, which is an oxidation product of L-cysteine has two carboxylic groups. The molecule dissociates in the following manner:



The electron transfer reaction has been carried out in the pH range 2.0 to 5.0. Hence, both LH_3^+ and LH_2 will participate in the electron transfer reactions. Since the oxidant $[Co^{III}W^{5-}]$ does not show any pH dependence in the above pH range, the acid dependence is due to the presence of LH_3^+ and LH_2. With the increase in pH from 2.0 to 5.0, $10^4\, k_{obs}$ (25°C) changed from 2.37 to 3.53 s^{-1}, when $[Co^{III}W^{5-}]_T = 2.3 \times 10^{-4}$, [L-cystine]$_T$ = 1.75×10^{-3} and I = 0.3 mol dm^{-3}. The k_{obs} data relating to pH variation are collected in Table 1.

Effect of variation of [L-cystine] and temperature on the reaction rate

At a fixed $[Co^{III}W^{5-}]$ (2.3×10^{-4} mol dm^{-3}), pH = 5.0 and ionic strength (0.3 mol dm^{-3} $NaClO_4$), the effect of [L-cystine] on the rate was studied in the 1.5×10^{-3} to 3.5×10^{-3} mol dm^{-3} range at 25, 30, 35 and 40°C. The results are collected in Table 2. The rate of the reaction was found to increase with the increase in temperature and increase in [L-cystine]$_T$. The plots of k_{obs} versus [L-cystine]$_T$ were linear passing through origin at the experimental temperatures. This indicates that there is no reverse

reaction and the reaction exhibits first order dependence in $[\text{L-cystine}]_T$.

Product analysis

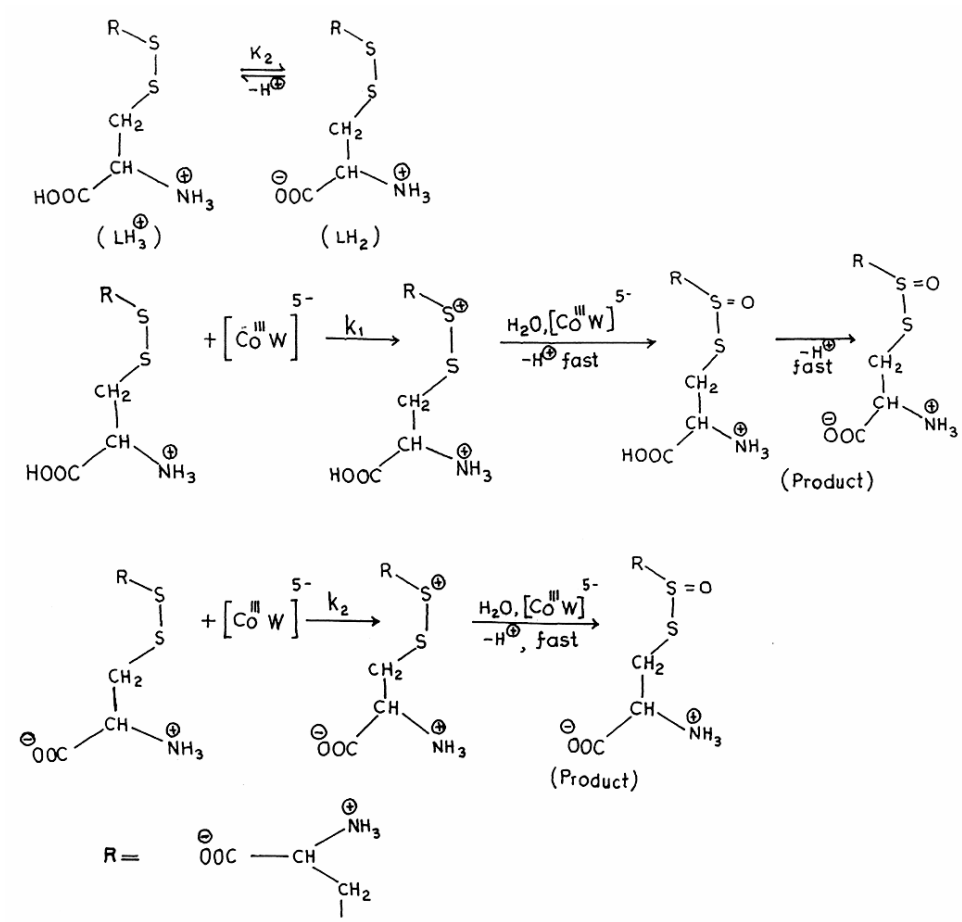
In order to get the reaction product $Co^{III}W^{5-}$ and L-cystine were mixed in 1:10 mole ratio at pH = 5.0. The solution was left for evaporation at room temperature in a vacuum desiccator for few days. Fine light green coloured crystals of the product appeared which were washed with ethanol and dried in a desiccator. IR spectra of the product were recorded in a FTLA-2000-104 FTIR ABB Bomem (Canada) spectrophotometer. A broad strong NH_3^+ Stretching band appeared at around 3400 cm^{-1} in the product compared to that at 3130-3030 cm^{-1} in L-cystine. The

Table 1 — Values of $10^4\ k_{obs}(s^{-1})$ at different pH and at different temperatures. $\{[Co^{III}W^{5-}] = 2.3 \times 10^{-4}$ mol dm^{-3}, [L-cystine] = 1.75×10^{-3} mol dm^{-3}, $I = 0.3$ mol dm^{-3} $(NaClO_4)\}$

pH	Temp. (°C)			
	25	30	35	40
2.0	2.37	2.72	3.08	3.40
2.5	2.56	2.92	3.29	3.62
3.0	2.77	3.13	3.47	3.84
3.5	2.94	3.35	3.75	4.12
4.0	3.10	3.55	4.02	4.37
4.5	3.33	3.77	4.21	4.61
5.0	3.53	3.99	4.43	4.87

Table 2 — Values of $10^4\ k_{obs}\ (s^{-1})$ at different [L-cystine] and at different temperatures. $\{[Co^{III}W^{5-}] = 2.3 \times 10^{-4}$ mol dm^{-3}, pH = 5.0, $I = 0.3$ mol dm^{-3} $(NaClO_4)\}$

10^3[L-cystine] (mol dm^{-3})	Temp. (°C)			
	25	30	35	40
1.15	2.32	2.63	2.93	3.23
1.75	3.53	3.99	4.43	4.87
2.30	4.50	5.13	5.83	6.24
2.9	5.80	6.59	7.40	8.02
3.5	7.08	7.93	8.72	9.58



Scheme 1

shift to higher frequency is probably due to association of water molecules with the product. A weak asymmetric NH_3^+ bending band near 1640 cm^{-1} and a strong symmetric NH_3^+ bending band near 1500 cm^{-1} are present in L-cystine. A strong peak at around 1600 cm^{-1} and a weak peak at around 1400 cm^{-1} are present in L-cystine due to absorption by carboxylate ion. Two NH_3^+ bending bands and the strong absorption peak due to carboxylate ion are mixed up and a broad band is obtained at around 1640 cm^{-1} in the product. The weak peak at around 1400 cm^{-1} due to absorption of carboxylate ion is retained in the product. A characteristic strong band appears at around 1100 cm^{-1} in the product which is probably due to $S = O$ stretching vibration. The corresponding peak of sulphoxides is obtained in 1070-1030 cm^{-1} region. From the individual assignment of different peaks and bands, it can be inferred that the product is cystinesulfoxide.

Mechanism

Based on the above facts the possible mechanism may be delineated as in Scheme 1. The rate law for the electron transfer reaction can be derived as:

$$\text{Rate} = k_1[Co^{III}W^{5-}]\,[LH_3^+]_e + k_2\,[Co^{III}W^{5-}]\,[LH_2]_e \quad \ldots (3)$$

$$K_2 = [LH_2]_e\,[H^+] / [LH_3^+]_e$$

Or $[LH_2]_e = K_2\,[LH_3^+]_e / [H^+]$

Substituting the value of $[LH_2]_e$ in Eq. (3)

$$\text{Rate} = k_1[Co^{III}W^{5-}]\,[LH_3^+]_e + k_2\,K_2[Co^{III}W^{5-}][LH_3^+]_e/[H^+]$$

$$= [Co^{III}W^{5-}]\,[LH_3^+]_e\,(k_1[H^+] + k_2\,K_2) / [H^+] \quad \ldots (4)$$

$$[LH_3^+]_T = [LH_3^+]_e + [LH_2]_e$$

$$= [LH_3^+]_e + K_2\,[LH_3^+]_e / [H^+]$$

$$= [LH_3^+]_e\,([H^+] + K_2) / [H^+]$$

$$[LH_3^+]_e = ([LH_3^+]_T\,[H^+]) / ([H^+] + K_2) \quad \ldots (5)$$

Substituting the value of $[LH_3^+]_e$ in Eq. (4)

$$\text{Rate} = [Co^{III}W^{5-}]\,[LH_3^+]_T\,(k_1[H^+] + k_2\,K_2) /([H^+] + K_2) \quad \ldots (6)$$

$$\text{Since Rate} = k_{obs}\,[Co^{III}W^{5-}] \quad \ldots (7)$$

Relation (6) can be written as:

$$k_{obs} = [LH_3^+]_T\,(k_1[H^+] + k_2\,K_2) / ([H^+] + K_2)$$

At the experimental pH = 5.0, $[LH_3^+]_T \approx [LH_4^{2+}]_T$

$$k_{obs} / [LH_4^{2+}]_T = k_2' = (k_1[H^+] + k_2\,K_2) / ([H^+] + K_2) \quad \ldots (8)$$

$$k_2'[H^+] + k_2'\,K_2 = k_1[H^+] + k_2K_2 \quad \ldots (9)$$

Equation (9) may be rearranged to give:

$$[H^+]\,(k_2' — k_1) = k_2K_2 — k_2'\,K_2 \quad \ldots (10)$$

The value of k_1 was gradually changed in such a manner that the plot of $[H^+]\,(k_2' — k_1)$ versus k_2' has maximum correlation coefficient value. With the best fitting, the slope and intercept were calculated. The k_1 (best fitted value) and k_2 (Intercept/slope) are computed at four different temperatures. $\Delta H^{\neq}$ (kJ mol^{-1}) and $\Delta S^{\neq}$ ($JK^{-1}mol^{-1}$) were determined from the temperature variation data of k_1 and k_2 using Eyring equation. The values of k_1 and k_2 at 25°C along with the corresponding activation parameters are provided in Table 3. Activation parameters for the present system have been compared with the corresponding values of analogous systems and the data are collected in Table 3.

Negative $\Delta S^{\neq}$ is in support of an ordered transition state. Earlier workers have also reported the same fact. The values of k_2 were found to be higher than those of k_1 at all temperatures which is indicative of the fact that LH_2 is a stronger nucleophile in comparison to LH_3^+.

Table 3 — Activation parameters for analogous systems for the studied reaction.

System	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	Ref.
Antimony(III)	36.5 ± 3	-104 ± 5	10
Nitrilotriacetate	20.5 ± 4	-45.8 ± 3	26
Hydrazine	17 ± 1	-216± 2	27
TGA	25± 2	-196 ± 3	28
TMA	48±3	-118±9	28
TLA	52±1	-105±3	28
Azide ion	53±6	-61±21	29
Hydroxylamine	9±1	-70±2	30
Arsenous acid	17±2	-107±1	31
L-Cystine	16.9±2	-205±6	This work*

*k_1 (mol^{-1} dm^3 s^{-1}) 25°C = 0.13; k_2 (mol^{-1} dm^3 s^{-1}) 25°C = 0.20; $\Delta H_1^{\neq}$ (kJ mol^{-1}) = 16.9 ± 2; $\Delta S_1^{\neq}$ (JK^{-1} mol^{-1}) = – 205.0 ± 6; $\Delta H_2^{\neq}$ (kJ mol^{-1}) = 16.1 ± 0.5; $\Delta S_2^{\neq}$ (JK^{-1} mol^{-1}) = –204.0 ± 1.5

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References

1 Sadakane M & Streckhan E, *Chem Rev*, 98 (1998) 219.
2 Nolan A I, Burns R C & Lawrence G A, *J Chem Soc Daltron Trans*, (1998) 3041.
3 Saha S K, Ali M & Banerjee P, *Coord Chem Rev*, 41 (1993) 122.
4 Weinstock I A, *Chem Rev*, 98 (1998) 113.
5 Pope M T, *Heteropoly and Isopolyoxometalates*, (Springer, Berlin) 1983.
6 Eberson L, *J Am Chem Soc*, 105 (1983) 3192.
7 Meherotra M & Meherotra R N, *J Chem Soc Dalton Trans*, 18 (2003) 3606.
8 Ayoko G A & Olatunji M A, *Polyhedron*, 3 (1984) 191.
9 Hasure A M & Gokavi G S, *React Kinet Catal Lett*, 80 (2003) 59.
10 Bhosale B D & Gokavi G S, *Int J Chem Kinet*, 35 (2002) 9.
11 Bhosale B D & Gokavi G S, *Indian J Chem*, 43A (2004) 799.
12 Bhosale BD & Gokavi G S, *Inorg React Mech*, 5 (2004) 79.
13 Ayoko G A & Olatunji M A, *Polyhedron*, 2 (1983) 577.
14 Ayoko G A & Olatunji M A, *Inorg Chim Acta*, 80 (1983) 115.
15 Saha S K, Ghosh Manik C & Banerjee P, *Int J Chem Kinet*, 20 (2004) 699.
16 Amjad Z, Brodovitch J C & Auley A Mc, *Can J Chem*, 55 (1977) 3581.
17 Satpathy P K, Dash G C, Acharya S & Mohanty P, *J Indian Chem Soc*, 83 (2006) 891.
18 Abedinzadeh Z, *Can J Physiol Pharmacol*, 79 (2001) 166.
19 Sconich C, Zhao F, Wilson G S & Borchardt R T, *Biochem Biophys Acta (BBA),* 1158 (1993) 307.
20 Mahadevappa D S, Ananda S, Murthy A S A & Rangappa K S, *Indian J Chem*, 23A (1984) 17; Gowda B T & Vijayalakshmi R, *Oxid Commun*, 11 (1988) 45; Gowda BT & Vijayalakshmi R, *J Indian Chem Soc*, 64 (1987) 403.
21 Annapurna N, Kalyan Kumar A, Vani P & Rao Nageswara G, *J Indian Chem Soc*, 85 (2008) 542
22 Read J F, Bewick S A, Graves C R, Macpherson J M, Salah J C, Theriault A & Wyand A E H, *Inorg Chim Acta,* 303 (2000) 244.
23 Saleem Md, Kembhavi R, Panari G Rafeek & Nadibewoor T Sharanappa, *Inorg React Mech*, 1 (1999) 225.
24 Shaidarova L G, Ziganshina S A & Budnikov G K, *J Analyt Chem*, 58 (2003) 577.
25 Rasmussen P G & Brubaker L H, *Inorg Chem*, 3 (1964) 977.
26 Ayoko G A, Iyun J F & Mamman S, *Indian J Chem,* 32A (1993) 1089.
27 Shah R, Prakash A & Mehrotra R N, *Indian J Chem*, 38A (1999) 680.
28 Dholiya S, Prakash A & Mehrotra R N, *Indian J Chem*, 36A (1997) 959.
29 Goyal B, Mehrotra M, Prakash A & Mehrotra R N, *Inorg React Mech*, 1 (2000) 289.
30 Goyal B, Prakash A & Mehrotra R N, *Indian J Chem*, 38A (1999) 541.
31 Dholiya S, Prakash A & Mehrotra R N, *J Chem Soc Dalton Trans*, 1 (1992) 819.