Kinetics of Oxidation of Azide Ion by Bis(dihydrogentellurato)-cuprate(III) and -argentate(III) in Alkaline Media†

Kalyan Kali Sen Gupta,[*,a] **Ankan Sanyal**[a] **and Sakti Prosad Ghosh**[b]
[a] *Department of Chemistry, Jadavpur University, Calcutta 700 032, India*
[b] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India*

The kinetics of the oxidation of azide ion by bis(dihydrogentellurato)-cuprate(III) and -argentate(III) has been studied in alkaline media. The rate of the reaction increases with increasing azide ion but decreases with the increasing of alkali concentration. The reactions proceed through initial 1:1 complex formation between the reactants followed by decomposition of the complex to give nitrogen. Copper(III) is reduced by the substrate in a one-electron process, whereas one-step two-electron reduction has been shown to occur with silver(III). Thermodynamic parameters associated with the complex-formation step and the activation parameters for the decomposition step have been evaluated. The mechanism of the reactions is discussed.

Kinetic studies of the reaction of HN_3 with Cr^{II} and HNO_2 have been reported [1-3] and in both the reactions N_2 was formed. The oxidations of HN_3 by aqua ions of Mn^{III},[4,5] Co^{III}[6-8] and Ce^{IV}[9] in acidic media have also been studied. These reactions exhibit diverse mechanistic behaviour. There are no literature data involving the oxidation of N_3^- by copper(III) or silver(III) under comparable experimental conditions. Copper(III) has been prepared [10] in aqueous solution using oxidising agents such as hypochlorite ion,[11] chlorine gas [12] and disulfate [13] anion under alkaline conditions. However as $[Cu(H_2O)_6]^{3+}$ is still unknown and the hypothetical $[Cu(OH)_4]^-$ is very unstable, the use of rather unusual oxyanions such as $[TeO_6]^{6-}$ and $[IO_6]^{5-}$ results in the preparation of relatively stable copper(III) complexes even from aqueous solution. The ion $[Ag(OH)_4]^-$ [14] on the other hand has been conveniently prepared by anodic oxidation of silver metal in aqueous sodium hydroxide, and Borish and Kirschenbaum [15] have studied its oxidation of azide in alkaline media. There are no literature data on the oxidation of azide ion by hydroxocopper(III) species.

Both copper(III) and silver(III) are known to be stabilised in alkaline media by $[TeO_6]^{6-}$. It was therefore interesting to see whether the presence of tellurate ligand in the co-ordination sphere of these ions changes the rate and mechanism of the reactions with azide ion. The present paper reports the kinetics and mechanism of the oxidation of azide ion by (dihydrogentellurato)-cuprate(III) and -argentate(III) in alkaline media.

Experimental

Reagents and Instruments.—Sodium azide (Loba) was the source of azide ion. All other inorganic materials were of the highest purities available. The solutions were made from doubly distilled water. Absorbances were measured on a Cary 17D UV/VIS spectrophotometer, EPR spectra with a Varian (Model E 112) spectrometer. Magnetic susceptibility was measured at room temperature by a Princeton Applied Research vibrating-sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. Cyclic voltammograms were recorded by a Bio Analytical System (BAS) CV-27 instrument in a dry argon atmosphere using a three-electrode configuration. A planar Beckman platinum electrode was used as working electrode and a saturated calomel electrode (SCE) as the reference. Raman spectra were recorded in a Ramalog double-grating monochromator fitted with an argon ion laser and a cooled photomultiplier detector. The excitation wavelength was 488 nm.

Bis(dihydrogentellurato)-cuprate(III) and -argentate(III) were prepared by a modification of the literature method.[16] Copper sulfate (1.56 g) was added to a mixture of potassium tellurite (3.17 g), potassium disulfate (4.22 g) and potassium hydroxide (8.0 g) in water (80 cm^3). The mixture was heated until it was intense red and then boiled for 15 min to ensure complete removal of disulfate. The mixture was cooled and filtered (sintered glass crucible, porosity 4). The filtrate was diluted with water to 100 cm^3. In order to isolate the complex, 50% $NaNO_3$ (40 cm^3) was added and the mixture left to crystallise. The crystallisation was complete after 24 h, when the supernatant liquid became colourless. The crystals were filtered off and washed with water. The IR spectrum of the solid complex was found to be identical to that reported earlier.[17] Bis(dihydrogentellurato)cuprate(III) solution shows bands at 406 ± 3 and 274 ± 2 nm. The copper(III) complex was estimated as follows. An aliquot (5 cm^3) was taken from the stock solution and added to arsenite solution (2×10^{-2} mol dm^{-3}, 10 cm^3). The mixture was allowed to stand for 3–4 min and then acidified with 0.5 mol dm^{-3} H_2SO_4 until the green suspension disappeared. A solution of $NaHCO_3$ (0.5 mol dm^{-3}, 5 cm^3) was added and the unused arsenite was back titrated against standard iodine solution using starch indicator to a blue end-point.

The silver(III) complex was prepared as follows. Silver nitrate (1.36 g), potassium tellurite (3.8 g) and potassium disulfate (6.5 g) were added to water (150 cm^3). Potassium hydroxide (9 g in 50 cm^3) was added very slowly with constant stirring. The mixture was then heated to boiling on a hot-plate, with constant agitation (≈1 h) until the last trace of excess of disulfate was decomposed. The light red solution was filtered as before. The silver(III) complex was isolated by the same procedure as for copper(III) complex. The filtrate containing bis(dihydrogentellurato)argentate(III) shows maxima at 355 ± 2 and 264 ± 2 nm. The silver(III) complex was standardised by treating 5 cm^3 of the solution with 2×10^{-2} mol dm^{-3} sodium arsenite solution (10

---

† *Non-SI units employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Stoichiometric results for the oxidation of N_3^- by copper(III) and silver(III) complexes

M^{III}	10^3 [M^{III}] mol dm^{-3}	10^2 [N_3^-]	[OH^-]	10^3 [M^{III}]$_{left}$	10^2 [N_3^-]$_{left}$	Δ[N_3^-]/ Δ[M^{III}]
Cu^{III}	4.0	1.6	0.1	0.00	1.21	0.97
	4.0	3.2	0.1	0.00	2.78	1.05
	4.0	4.8	0.1	0.00	4.39	1.02
	8.0	0.4	0.1	4.10	0.00	1.02
	16.0	0.4	0.1	11.80	0.00	0.95
	16.0	0.4	0.2	12.10	0.00	1.02
Ag^{III}	3.0	1.2	0.1	0.00	0.57	2.10
	3.0	2.4	0.1	0.00	1.79	1.96
	3.0	4.8	0.1	0.00	4.20	2.00
	6.0	0.4	0.1	4.05	0.00	2.05
	10.0	0.4	0.1	7.95	0.00	1.95
	16.0	0.4	0.2	13.98	0.00	1.98

cm^3), allowing to stand for 1 min and then acidifying with dilute 0.5 mol dm^{-3} H_2SO_4 until the solution became colourless. Then 0.5 mol dm^{-3} $NaHCO_3$ solution (5 cm^3) and 10% KI solution (1 cm^3) were added followed by back titration of the unconsumed arsenite with standard iodine solution.

Kinetic Studies.—The disappearance of bis(dihydrogentellurato)cuprate(III) and -argentate(III) was followed titrimetrically under conditions at which [N_3^-] $\gg$ [$M^{III}(H_2TeO_6)_2$]$^{5-}$. The reactants were equilibrated for at least 1 h in a thermostatted water-bath at the desired temperature (± 0.1 K) before the kinetics was monitored. Each reaction was started by adding the oxidants to the other reactants. An aliquot from the reaction mixture was withdrawn and added to a known excess of sodium arsenite solution. The unconsumed arsenite after acidification by dilute H_2SO_4 was titrated against standard iodine with starch as an indicator. Generally 8–10 experimental points were taken in each run and the pseudo-first-order rate constant (k_{obs}) were reproducible to within ± 5%.

Stoichiometry and Product Analysis.—The stoichiometry of the reactions was studied both at excess of N_3^- and excess of oxidant. The reaction mixture containing an excess of N_3^- was allowed to stand for 24 h. Blank experiments using the oxidants when kept for 24 h indicated that the compounds are stable towards reduction. The bluish green and the black precipitates formed in the reactions with the respective oxidants were filtered off and a known excess of cerium(IV) solution was added to the filtrate. The excess of Ce^{IV} was then titrated against ammonium iron(II) sulfate solution using ferroin as indicator. The average ratios for three different experiments were [N_3^-]:[Cu^{III}] = 1.00:1.01 and [N_3^-]:[Ag^{III}] = 2:1.02. Again when the reaction was studied in an excess of oxidant the mixture was allowed to stand for 24 h followed by the addition of a known excess of standard sodium arsenite solution. The unconsumed arsenite after acidification by dilute H_2SO_4 was titrated against standard iodine using starch as indicator. The average ratios from three different experiments were [N_3^-]:[Cu^{III}] = 1:1 and [N_3^-]:[Ag^{III}] = 2:1. The results are recorded in Table 1. On standing of the reaction mixture from the copper(III) oxidation for several hours a green precipitate was formed which was filtered off, washed, dried and analysed (Found: Cu, 44.1. Calc. based[18] on Na_2CuO_2: Cu, 44.7%). There is literature evidence to indicate[18] that Na_2CuO_2 is formed in the alkaline medium. The room-temperature magnetic moment of the solid compound was calculated to be 1.27 μ_B which is much less than the 1.73 μ_B expected for a d^9 system. However for a number of copper(II) complexes, magnetic moments lower than the theoretical value has also been obtained.[18]

The dried green precipitate was dissolved in dilute $HClO_4$ followed by the addition of ammonia solution. The formation of a blue colour suggests that the co-ordination sphere of copper(III) is altered. The EPR spectrum of the dried green product as well as that of the blue solution (Fig. 1) indicates that copper(III) is reduced to copper(II). The black residue obtained from the other reaction was then analysed and found to contain 87% silver, *cf.* 88.8% calculated for AgO which is a diamagnetic mixture of Ag^I and Ag^{III}, and not Ag^{II}. The magnetic moment of the black residue indicated it to be diamagnetic and rules out the possibility of formation of d^9 silver(II). The black product was dissolved in dilute nitric acid and the solution gave a yellow precipitate of AgI with KI.

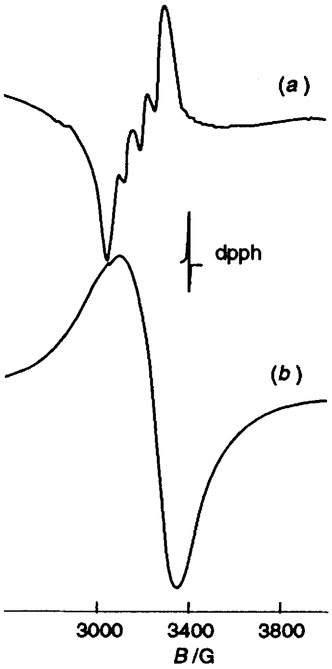


Fig. 1 The EPR spectra of (*a*) the blue solution and (*b*) the green product of the copper(III) oxidation; dpph = diphenylpicrylhydrazyl

That the azide is oxidised to nitrogen gas by both oxidants was established in the following manner. A closed reaction cell containing the reactants and kept at constant temperature (298 K) was continuously purged with pure and dry argon and the outgoing gas passed for 1 h through a solution of [$Ru(NH_3)_5(H_2O)$]$^{2+}$ prepared by a standard procedure.[19a] A red complex [$(NH_3)_5Ru(N_2)Ru(NH_3)_5$]$^{4+}$ was isolated from this solution.[19b] The Raman spectrum of this complex exhibited a strong band around 3100 cm^{-1} which is known to originate from the $\nu(N\equiv N)$[20] of the co-ordinated N_2 which must have been generated by oxidation of azide ion by Cu^{III} or Ag^{III}. The reaction takes place according to the equations (1) and (2).

$$2N_3^- + 2[Cu^{III}(H_2TeO_6)_2]^{5-} \longrightarrow 3N_2 + 2[Cu^{II}(H_2TeO_6)_2]^{6-} \quad (1)$$

$$2N_3^- + [Ag^{III}(H_2TeO_6)_2]^{5-} \longrightarrow 3N_2 + [Ag^{I}(H_2TeO_6)_2]^{7-} \quad (2)$$

Test for Free Radicals.—Acrylonitrile [50% (v/v)] was added during the course of the reactions. An immediate haziness appeared during the oxidation of N_3^- ion by copper(III). When an excess of methanol was added to the reaction mixture a thick precipitate of polyacrylonitrile was formed, demonstrating that free-radical intermediates participate in the oxidation. Blank experiments from which either copper(III) or azide were excluded gave no detectable polymers. On the other hand, no precipitation of white polyacrylonitrile in the absence or presence of methanol appeared during the oxidation of N_3^- by silver(III). This result is consistent with a one-step two-electron transfer mechanism with no free-radical intermediate, and in accord with observations made earlier[15] on the oxidation of N_3^- by $[Ag(OH)_4]^-$.

Results and Discussion

The pseudo-first-order rate constants were determined at different concentrations of $[M^{III}(H_2TeO_6)_2]^{5-}$ in the range (0.5–5.0) × 10^{-3} mol dm^{-3} but at constant $[N_3^-]$, $[OH^-]$ and temperature (1.0 × 10^{-1}, 2 × 10^{-1} mol dm^{-3} and 303 K respectively). The values were (1.49 ± 0.06) × 10^{-4} and (0.423 ± 0.02) × 10^{-4} s^{-1} for the oxidation by Cu^{III} and Ag^{III} respectively, independent of the initial concentration of $[M^{III}(H_2TeO_6)_2]^{5-}$. That copper(III) reacts more rapidly than silver(III) is not unexpected since the third ionisation potential of silver is less than that for copper.[21] Moreover, where Ag^{III}–Ag^{II} couples[22] can be compared with Cu^{III}–Cu^{II} couples,[23] the results indicate that the redox potential for silver is less than that for copper.

The reactions were also studied at different $[N_3^-]$ and constant $[M^{III}(H_2TeO_6)_2]^{5-}$, $[OH^-]$ and temperature. The results indicate that the rate increases with increasing $[N_3^-]$. Plots of $1/k_{obs}$ *versus* $1/[N_3^-]$ gave straight lines with positive intercepts on the *y* axis at four different temperatures (Figs. 2 and 3). The hydroxide concentration was varied in the range (1.0–20) × 10^{-2} mol dm^{-3} at constant ionic strength of 0.95 mol dm^{-3}. The rate constant decreased with increasing in alkali concentration for both Cu^{III} and Ag^{III}. Plots of $1/k_{obs}$ *versus* $[OH^-]$ at different temperatures are shown in Figs. 4 and 5.

The empirical rate law is shown in equation (3) where K_e and

$$-\frac{d[M^{III}_t]}{dt} = \frac{kK_e[N_3^-][M^{III}]_t}{[OH^-] + K_e[N_3^-]} \quad (3)$$

k denote the equilibrium constant for the formation of the 1 : 1 complex between the reactants and the disproportionation constant of this complex respectively. The values of K_e associated with step (6) and *k* associated with step (7) or (12) were then calculated from Figs. 2 and 3 as well as from Figs. 4 and 5 for the respective metal-ion oxidants. The results are in Table 2.

The rate of oxidation of N_3^- was studied at different salt ($NaClO_4$) concentrations, but at constant concentrations of other reactants and temperature. The results indicate that the pseudo-first-order rate constant increases with increase in $[NaClO_4]$ (Table 3).

Plots of log K_e *versus* $1/T$ are linear ($r = -0.99$) and the enthalpy change ($\Delta H^{\ominus}$) associated with the equilibrium step was calculated followed by the estimation of $\Delta S^{\ominus}$ from relation (4). Plots of log (k/T) *versus* $1/T$ are also linear

$$\log K_e = 1/2.303R\,[\Delta S^{\ominus} - (\Delta H^{\ominus}/T)] \quad (4)$$

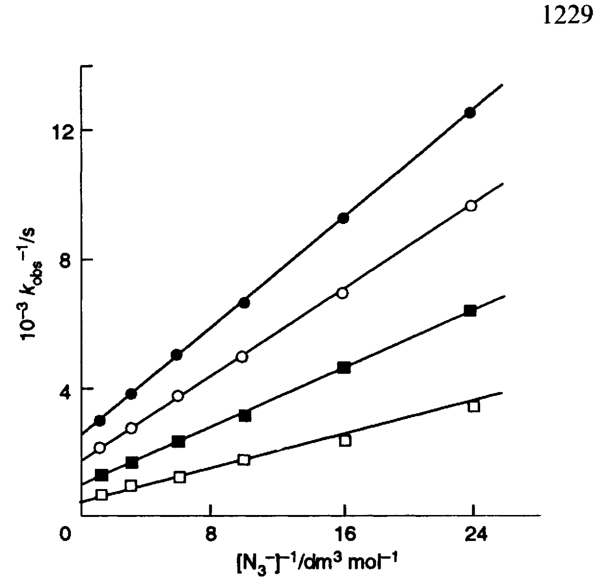


Fig. 2 Variation of the pseudo-first-order rate constant with $[N_3^-]$ in the oxidation by Cu^{III} at 303 (●), 308 (○), 313 (■) and 318 K (□). $[Cu^{III}]$ = 4.01 × 10^{-3}, $[OH^-]$ = 2.0 × 10^{-1} mol dm^{-3}

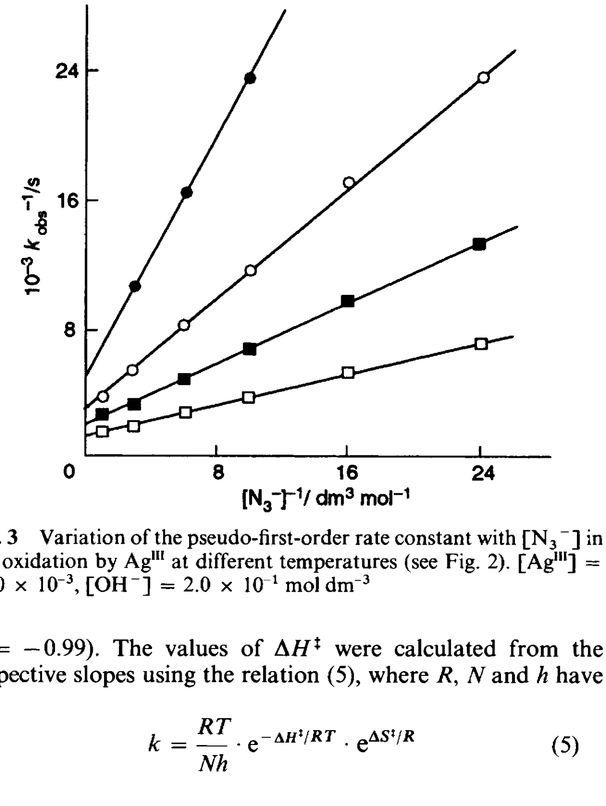


Fig. 3 Variation of the pseudo-first-order rate constant with $[N_3^-]$ in the oxidation by Ag^{III} at different temperatures (see Fig. 2). $[Ag^{III}]$ = 3.10 × 10^{-3}, $[OH^-]$ = 2.0 × 10^{-1} mol dm^{-3}

($r = -0.99$). The values of $\Delta H^{\ddagger}$ were calculated from the respective slopes using the relation (5), where *R*, *N* and *h* have

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^{\ddagger}/RT} \cdot e^{\Delta S^{\ddagger}/R} \quad (5)$$

their usual significance. The thermodynamic parameters associated with the equilibrium step and the activation parameters associated with the rate-determining step are recorded in Table 4. The results indicate the silver(III) oxidation of N_3^- is characterised by lower activation parameters.

The reactions are first order with respect to $[M^{III}(H_2TeO_6)_2{}^{5-}]$ but the order with respect to $[N_3^-]$ is complex. An increase in hydroxide ion concentration retards the rate whereas increase in ionic strength (varied by the addition of sodium perchlorate) increases the rate.

The dissociation constant[24] of hydrazoic acid to give H^+ and N_3^- is 1.8 × 10^{-5} mol dm^{-3}. Since the present reactions were studied in alkaline media, N_3^- rather than HN_3 is the reactive species. The azide ion is a symmetrical linear molecule containing sixteen electrons.[25] The formulae of the copper(III) and silver(III) tellurato complexes were previously proposed[26]

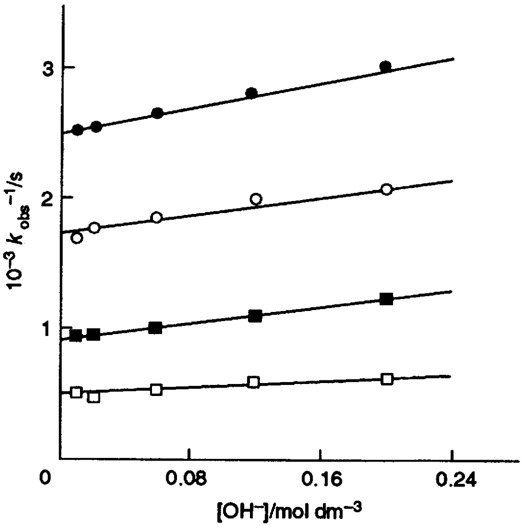


Fig. 4 Variation of the pseudo-first-order rate constant with alkali concentration in the oxidation of N_3^- by Cu^{III} at different temperatures (see Fig. 2). $[Cu^{III}] = 4.01 \times 10^{-3}$, $[N_3^-] = 7.5 \times 10^{-1}$ mol dm^{-3} and $I = 9.5 \times 10^{-1}$ mol dm^{-3}

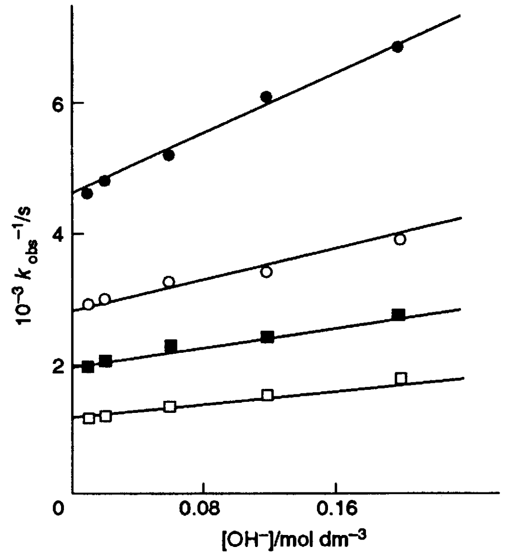


Fig. 5 Variation of the pseudo-first-order rate constant with alkali concentration in the oxidation by silver(III) at different temperatures (see Fig. 2). $[Ag^{III}] = 3.10 \times 10^{-3}$, $[N_3^-] = 7.5 \times 10^{-1}$ and $I = 9.5 \times 10^{-1}$ mol dm^{-3}

Table 2 Equilibrium constants for the fast step and disproportionation constants for the slow step at different temperatures

	Copper(III)		Silver(III)	
T/K	K_e^{a}	$10^3\,k$/dm^3 mol^{-1} s^{-1}	K_e	$10^3\,k$/dm^3 mol^{-1} s^{-1}
303	0.735	0.4	0.486	0.217
	(0.749)	(0.395)	(0.507)	(0.225)
308	0.84	0.588	0.661	0.357
	(0.82)	(0.60)	(0.668)	(0.373)
313	1.05	1.02	0.760	0.526
	(1.03)	(1.07)	(0.730)	(0.541)
318	1.26	2.0	0.928	0.833
	(1.18)	(1.95)	(0.890)	(0.859)

Values were calculated from Figs. 2 and 3 respectively (those in parentheses were calculated from Figs. 4 and 5 respectively). Average errors for Ke and k are ± 4 and ± 5% respectively.

Table 3 Influence of salt concentration on the pseudo-first-order rate constants at $[N_3^-] = 0.1$ mol dm^{-3}, $[OH^-] = 2.0 \times 10^{-1}$ mol dm^{-3}, and 313 K

$[NaClO_4]$/ mol dm^{-3}	$10^4\,k_{obs}$/s^{-1}	
	a	b
0.0	3.22	1.26
0.2	3.65	1.55
0.4	3.89	1.76
0.6	4.66	2.25
0.8	5.31	2.49
1.0	6.15	2.74

^{a} $[Cu^{III}] = 4.01 \times 10^{-3}$ mol dm^{-3}. ^{b} $[Ag^{III}] = 3.10 \times 10^{-3}$ mol dm^{-3}.

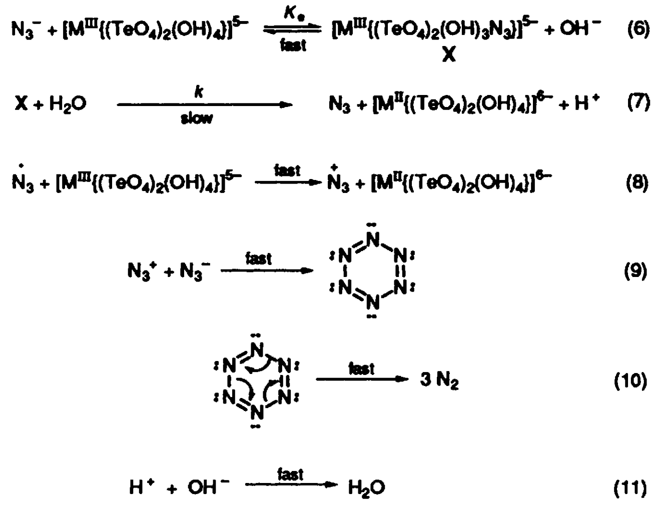
Table 4 Thermodynamic parameters associated with the equilibrium step and activation parameters for the slow step

	M^{III}	
Parameter	Cu^{III}	Ag^{III}
ΔH°/kJ mol^{-1}	27 ± 2	31 ± 2
ΔS°/J K^{-1} mol^{-1}	19 ± 7	24 ± 7
$\Delta H^{\ddagger}$/kJ mol^{-1}	83 ± 1	68 ± 1
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−37 ± 4	−91 ± 4

to be as $[Cu(TeO_6)_2]^{9-}$ and $[Ag(TeO_6)_2]^{9-}$ but later found to be incorrect. The infrared, analytical and conductometric measurements used for the study of the copper(III) and silver(III) complexes suggest the presence of protons in these complexes which are bonded to the tellurate ligand and the charge on the anion was found to be 5.[17]

The formation of a polymeric suspension of acrylonitrile in the oxidation by copper(III) suggests that the latter undergoes a one- rather than a two-electron transfer. One-electron reduction of copper(III) had been postulated earlier by Meyerstein and co-workers.[27,28] A radical intermediate was also proposed in the decomposition of copper(III) tetramine complexes[19,20] which produce copper(II) complexes containing imine donors. In the oxidation of some ketones by copper(III)[29] it has been shown that the metal undergoes one- rather than two-electron transfer. The oxidation of N_3^- by copper(III) occurs through the intermediate formation of free radicals. The azide radical N_3 is known to be involved in flash photolysis and molecular beam studies.[30] On the other hand, we were unable to adduce any experimental evidence for the formation of a polymeric suspension of acrylonitrile in the oxidation by the silver(III) complex. This suggests that the reaction between silver(III) and N_3^- ion may not proceed through the formation of intermediate free radicals, rather that silver(III) undergoes a two-electron transfer process. This is in keeping with the results obtained by Kirschenbaum and co-workers for the oxidation of thiosulfate,[31] azide[15] and $H_2PO_2^-$ [32] by $[Ag(OH)_4]^-$. There is literature evidence[4] to indicate that N_3^+ is generated by the decomposition of $[Mn(N_3)_2]^{2+}$ during the oxidation of HN_3 by manganese(III).

A cyclic voltammogram of bis(dihydrogentellurato)copper(III) (10^{-3} mol dm^{-3}) in aqueous alkaline solution containing lithium perchlorate (0.1 mol dm^{-3}) exhibited an irreversible reduction at −0.506 V and at 298 K, whereas under the same experimental conditions bis(dihydrogentellurato)silver(III) shows an irreversible reduction at −0.571 V. In the electrochemical experiments the results were referenced to the standard one-electron redox system ferrocene–ferrocenium under comparable conditions. If Cu^{III} were first reduced to Cu^{I} the current height of the corresponding peak in the cyclic voltammogram would have been much higher because of the transfer of two electrons in a single step. On the other hand, it is comparable to the height of the peak of ferrocene under identical conditions. So, reduction of Cu^{III} to Cu^{I} followed by a



Scheme 1

$$N_3^- + [M^{III}\{(TeO_4)_2(OH)_4\}]^{5-} \underset{\text{fast}}{\overset{K_e}{\rightleftharpoons}} \underset{\textbf{X}}{[M^{III}\{(TeO_4)_2(OH)_3N_3\}]^{5-}} + OH^- \quad (6)$$

$$X + H_2O \xrightarrow[\text{slow}]{k} N_3^+ + [M^I\{(TeO_4)_2(OH)_4\}]^{7-} + H^+ \quad (12)$$

followed by steps (9)–(11)

Scheme 2

fast reaction between Cu^{III} and Cu^I producing Cu^{II} can be discounted. The current height of the voltammogram clearly indicated that the copper(III) species experiences a one-electron reduction, while the silver(III) species undergoes a one-step two-electron process under identical experimental conditions. It has been shown that in an oxidation–reduction reaction the formation of a free radical by a one-equivalent oxidant is likely to be more endothermic[33] than the corresponding two-equivalent reaction. The two-equivalent exothermic process is able to lower the activation energy of the reaction below that of the corresponding one-electron process.[34] The enthalpy of activation is higher and entropy of activation is less negative in the oxidation reaction involving copper(III) than silver(III) which corroborate the above contention.

The oxidants $[M^{III}(H_2TeO_6)_2]^{5-}$ may be represented as $[M^{III}\{(TeO_4)_2(OH)_4\}]^{5-}$ in which hydroxyl ions are bonded to tellurium and the structure has been designated as square planar.[26] The present results suggest that the reactions occur through the formation of intermediate complexes $[M\{(TeO_4)_2(OH)_3N_3\}]^{5-}$ between the reactants in which OH^- is replaced by N_3^- which is bonded to Te and the rate decreases with increasing hydroxide-ion concentration which may be due to an acid–base equilibrium. The present values of K_e which have been calculated to be 0.735 and 0.486 at 303 K for Cu^{III} and Ag^{III} are similar to the formation constants of 0.33 and 0.78 at 288 K obtained in the oxidation of N_3^- ion[15] by $[Ag(OH)_4]^-$ and $[Ag(OH)_3(H_2O)]$ respectively. It may be mentioned that the reactivities (or nucleophilicities) of N_3^- and OH^- towards Ag^{III} are similar.[15] The complexes decompose to give products. The pseudohalogen derivative N_3–N_3 corresponding to dichlorine Cl_2 is not known. This is possibly because of the breakdown of the N–N–N group leading to the formation of simpler nitrogen species *e.g.* N_2 during the reactions of hydrogen azide with different metal ions. However during the photoinduced reductive elimination of *cis*-$[Pt(N_3)_2(PPh_3)_2]$, transient formation of hexazine (N_6) was suggested.[35] It is not unlikely that N_3^+ which is formed in step (7) reacts with N_3^- to give the unstable intermediate which then decomposes to give dinitrogen. Although the formation of nitrogen has been shown to occur through a cyclic intermediate, the involvement of an open-chain structure to give an oxidation product cannot be totally ruled out.

Schemes 1 and 2 are proposed for the reactions of N_3^- with copper(III) and silver(III) respectively. The rate of disappearance of M^{III} may be written using either steps (6) and (7) or (6) and (12) as in equation (13). Since $[M^{III}]_t$ =

$$-d[M^{III}]_t/dt = k[X] \quad (13)$$

$[M^{III}]_f + [X]$ and $[X] = K_e[M^{III}]_f[N_3^-]/[OH^-]$, $[M^{III}]_t = [M^{III}]_f + (K_e[M^{III}]_f[N_3^-]/[OH^-])$ and we obtain expression (14). Equation (13) can be transformed into (15).

$$[M^{III}]_f = [M^{III}]_t/\{1 + (K_e[N_3^-]/[OH^-])\} \quad (14)$$

$$-\frac{d}{dt}[M^{III}]_t = \frac{[M^{III}]_t}{\{1 + (K_e[N_3^-]/[OH^-])\}} \frac{kK_e[N_3^-]}{[OH^-]} \quad (15)$$

Since, $-(d[M^{III}]_t)/dt\ [M^{III}]_t^{-1} = k_{obs}$, equation (16) can be

$$k_{obs} = \frac{kK_e[N_3^-]}{[OH^-] + K_e[N_3^-]} \quad (16)$$

obtained which on rearrangement gives (17). The values of k

$$\frac{1}{k_{obs}} = \frac{[OH^-]}{kK_e[N_3^-]} + \frac{1}{k} \quad (17)$$

and K_e which were computed individually at different temperatures from Figs. 2,4 and 3,5 (Table 2) are not widely different, thus supporting the derived rate expression (17).

Acknowledgements

Thanks are due to the Council for Scientific and Industrial Research (New Delhi) for a senior research fellowship (to A. S.).

References

1 M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 1962, 2816.
2 G. Stedman, *J. Chem. Soc.*, 1959, 2244; 1960, 1702.
3 C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1959, 3466.
4 G. Davies, L. J. Kirschenbaum and K. Kustin, *Inorg. Chem.*, 1969, **8**, 663.
5 C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1968, 1622.
6 R. K. Murmann, J. C. Sullivan and R. C. Thompson, *Inorg. Chem.*, 1968, 7, 1876.
7 R. C. Thompson and J. C. Sullivan, *Inorg. Chem.*, 1970, **9**, 1590.
8 C. F. Wells and D. Mays, *J. Chem. Soc. A*, 1969, 2175.
9 C. F. Wells and M. Hussain, *J. Chem. Soc. A*, 1969, 2981.
10 D. W. Margerum and G. D. Owens, *Metal ions in Biological Systems*, ed. H. Sigel, Marcel Dekker, New York, 1981, vol. 12, p. 75.
11 E. T. Gray, jun., R. W. Taylor and D. W. Margerum, *Inorg. Chem.*, 1977, **16**, 3047.
12 M. Kruger, *Pogg Ann.*, 1844, **62**, 477; G. Wilkinson, *Comprehensive Co-ordination Chemistry*, Pergamon, Oxford, 1987, vol. 5, p. 745.
13 B. Brauner and B. Kuzma, *Ber. Dtsch. Keram. Ges.*, 1967, **40**, 3362.
14 L. G. Cohen and J. Hutterman, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 524; L. J. Kirschenbaum, J. H. Ambrus and G. Atkinson, *Inorg. Chem.*, 1973, **12**, 2832.
15 E. T. Borish and L. J. Kirschenbaum, *Inorg. Chem.*, 1984, **23**, 2355.
16 S. Chandra and K. L. Yadav, *Talanta*, 1968, **15**, 349.
17 A. Balikungeri, M. Pelletier and D. Monnier, *Inorg. Chim. Acta*, 1977, **23**, 7.
18 A. G. Massey, N. R. Thompson, B. F. G. Johnson and R. Davies, *The Chemistry of Copper, Silver and Gold*, Pergamon, Oxford, 1973, p. 47.
19 (*a*) E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984, p. 251; (*b*) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, 1967, **89**, 5706; D. E. Harrison, H. Taube and E. Weisslerger, *Science*, 1968, **159**, 320.

20 J. Chatt, A. B. Nikolsky, R. L. Richards and J. R. Sanders, *Chem. Commun.*, 1968, 1522.

21 L. J. Kirschenbaum and J. D. Rush, *J. Am. Chem. Soc.*, 1984, **106**, 1003.

22 E. K. Barefield and M. T. Mocella, *J. Am. Chem. Soc.*, 1975, **97**, 4238.

23 D. C. Olsen and J. Vasilevskis, *Inorg. Chem.*, 1971, **10**, 463.

24 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988, p. 319.

25 M. Green, *Developments in Inorganic Nitrogen Chemistry*, ed. C. B. Colborn, Elsevier, Amsterdam, 1966, vol. 1, pp. 1–71.

26 A. G. Massey, N. R. Thompson, B. F. G. Johnson and R. Davis, *The Chemistry of Copper, Silver and Gold*, Pergamon, Oxford, 1973, vol. 17, p. 123.

27 M. A. Frieberg and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1977, 127.

28 W. A. Muale and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 1979, 893.

29 G. P. Panigrahi and A. C. Pathy, *Inorg. Chem.*, 1984, **23**, 2133.

30 P. Gray, *Q. Rev. Chem. Soc.*, 1963, **17**, 441.

31 J. D. Rush and L. J. Kirschenbaum, *Inorg. Chem.*, 1985, **24**, 744.

32 R. N. Mehrotra and L. J. Kirschenbaum, *Inorg. Chem.*, 1989, **28**, 4327.

33 W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 1957, 447.

34 B. B. Pal and K. K. Sen Gupta, *Inorg. Chem.*, 1975, **14**, 2268.

35 A. Volger, R. E. Wright and H. Kunkley, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 717.

Received 12*th September* 1994; *Paper* 4/05548I