Kinetics and Mechanism of Oxidation of Selenium(IV) by Ditelluratoargentate(III)

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The title oxidation is first order each in oxidant, selenium(IV) and alakli and inverse first order in tellurium(VI). The rate of the reaction increases with increase in ionic strength. E_a and $\Delta S^{\neq}$ values at 40° are found to be 23.3 ± 1.5 kJ mol^{-1} and 12.6 ± 4.8 JK^{-1} mol^{-1} respectively. A suitable mechanism is proposed.

Recently we reported the oxidation of selenium(IV) by a two equivalent oxidant, periodate, wherein we proposed the oxidation to be taking place through an oxygen atom transfer from periodate to selenite[1]. We now report the oxidation of selenium(IV) by a two equivalent metal ion complex, ditelluratoargentate(III).
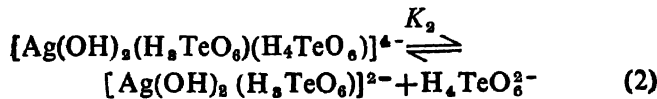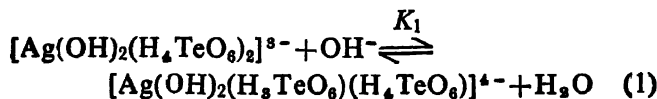
Results and Discussion

When [Se^{IV}] ≫ [DTA], the plots of log (absorbance) versus time were found to be linear upto two half-lives indicating the order with respect to DTA to be unity (after 75% completion of the reaction, points started slightly deviating upwards due to retardation by Te^{VI} accumalated). Further, the pseudo-first order rate constants (k_0) obtained from the slopes of these plots at different initial concentrations of DTA were found to be constant, confirming the unit order dependence of rate on [DTA]. k_0 value was found to increase with increase in the concentration of selenium(IV) (Table 1), the plot of k_0 vs [Se^{IV}] being a straight line passing through the origin, indicating the order in [Se^{IV}] to be unity. At constant [DTA], [Se^{IV}] and [OH$^-$], the reaction was found to exhibit an inverse first order dependence of rate on [Te^{VI}] (Fig. 1). On the other hand, k_0 values were found to increase with increase in [OH$^-$] at constant [DTA], [Se^{IV}] and [Te^{VI}] (Table 1), the increase being indicative of an order of unity in [OH$^-$]. The k_0 values also increased with increase in ionic strength (maintained with NaClO$_4$) indicating participation of ions of similar charge in the transition state. The effect of selenium(VI) and silver(I) on the rate of the reaction (studied upto 20 times and 5 times [DTA] respectively) was negligible. The reaction was found to obey Arrhenius temperature dependence, the k_0 values obtained at 30, 35, 40 and 45° being 3.23×10^{-4}, 3.69×10^{-4}, 4.34×10^{-4} and 4.94×10^{-4} s^{-1} respectively. The activation parameters E_a and $\Delta S^{\neq}$ at 40° computed by the method of linear least-squares were 23.3±1 5 kJ mol^{-1} and 12.6±4.8 JK^{-1} mol^{-1} respectively.

In 0.05—0.5 mol dm^{-3} aqueous alkaline solutions employed in the present investigation,· selenium(IV) exists exclusively as SeO$_3^{2-}$ (Ref. 2) In analogy with the structure of ditelluratocuprate(III), Raviprasad et al.[3] assumed ditelluratoargentate(III) to be a dihydroxyditellurato complex, [Ag(OH)$_2$ (H$_4$TeO$_6$)$_2$]$^{3-}$. They also showed that in basic medium ditelluratoargentate(III) exists in equilibrium with the deprotonated species which dissociates into a monotelluratoargentate(III). The observed first order with respect to alkali and the inverse first order with respect to tellurium(VI) indicate that monotelluratoargentate(III) is the reactive silver(III) species in the present investigation. This species has been proposed to be the reactive one in the oxidation of other compounds[3,4].

TABLE 1—EFFECT OF [OH$^-$], [Te^{VI}], [Se^{IV}] AND IONIC STRENGTH (μ) ON k_0

Temp. = 40±0.1°

[DTA]×10^4 mol dm^{-3}	[OH$^-$]×10 mol dm^{-3}	[Te^{VI}]×10^3 mol dm^{-3}	[Se^{IV}]×10 mol dm^{-3}	μ mol dm^{-3}	k_0×10^4 s^{-1}
0.5	5.0	1.0	1.0	1.0	4.21
1.0	5.0	1.0	1.0	1.0	4.38
2.0	5.0	1.0	1.0	1.0	4.34
3.0	5.0	1.0	1.0	1.0	4.41
4.0	5.0	1.0	1.0	1.0	4.36
5.0	5.0	1.0	1.0	1.0	4.32
1.0	0.5	1.0	1.0	1.0	0.56
1.0	1.0	1.0	1.0	1.0	0.80
1.0	2.0	1.0	1.0	1.0	1.75
1.0	3.0	1.0	1.0	1.0	2.63
1.0	4.0	1.0	1.0	1.0	3.63
1.0	5 0	1.0	1.0	1.0	4.34
1.0	5.0	0.5	1.0	1.0	8.90
1.0	5.0	1.5	1.0	1.0	3.70
1.0	5.0	2.0	1.0	1.0	2.02
1.0	5.0	2.5	1.0	1.0	1.78
1.0	5.0	3 0	1.0	1.0	1.46
1.0	5.0	4.0	1.0	1.0	1.15
1.0	5.0	1.0	0.3	1.0	1.60
1.0	5.0	1.0	0.5	1.0	2.35
1.0	5 0	1.0	1.2	1.0	5.10
1.0	5.0	1.0	1.5	1.0	6.55
1.0	2.0	1.0	1.0	0 5	0.38
1.0	2.0	1.0	1.0	0.6	0.54
1.0	2.0	1.0	1.0	0.7	0.75
1.0	2.0	1.0	1.0	0.8	1.01
1.0	2.0	1.0	1.0	0.9	1.33

On the basis of the experimental observations made in the present investigation, the following mechanism has been proposed for the oxidation of selenium(IV) by DTA.

$$[Ag(OH)_2(H_4TeO_6)_2]^{3-}+OH^- \overset{K_1}{\rightleftharpoons}$$
$$[Ag(OH)_2(H_3TeO_6)(H_4TeO_6)]^{4-}+H_2O \quad (1)$$

$$[Ag(OH)_2(H_3TeO_6)(H_4TeO_6)]^{4-} \overset{K_2}{\rightleftharpoons}$$
$$[Ag(OH)_2(H_3TeO_6)]^{2-}+H_4TeO_6^{2-} \quad (2)$$

$$[Ag(OH)_2(H_3TeO_6)]^{2-}+SeO_3^{2-} \overset{k_1}{\longrightarrow} products \quad (3)$$

Since selenium(IV) exists exclusively as SeO_3^{2-} (Ref. 2) under the present experimental conditions, this mechanism leads to the rate equation,

$$Rate = -\frac{d[DTA]}{dt}$$
$$= \frac{k_1 K_1 K_2[Ag(OH)_2(H_4TeO_6)_2^{3-}][Se^{IV}][OH^-]}{[H_4TeO_6^{2-}]+K_1K_2[OH^-]} \quad (4)$$

where [DTA] is the total concentration of silver(III).

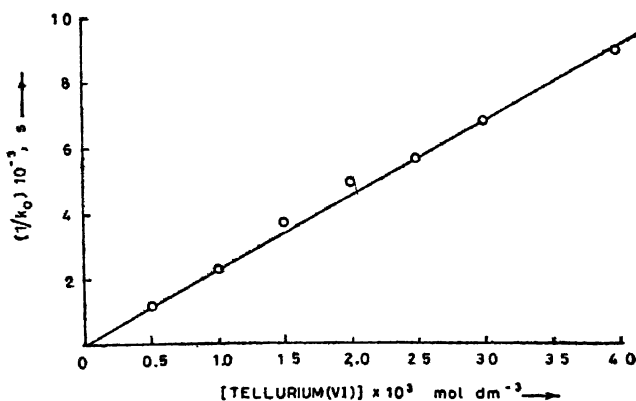Fig. 1. Plot of $1/k_0$ vs $[Te^{VI}]$.

From the third dissociation constant of telluric acid (ca 3×10^{-15}) and from the effect of $[OH^-]$ and $[Te^{VI}]$ on the rate of the reaction it may be inferred that K_1 and K_2 are very small. Hence, the term $K_1K_2[OH^-]$ in the denominator of equation (4) may be neglected in comparision with $[H_4TeO_6^{3-}]$. Equation (4) therefore reduces to

$$Rate = -\frac{d[DTA]}{dt}$$
$$= \frac{k_1 K_1 K_2[(Ag(OH)_2(H_4TeO_6)^{3-}][Se^{IV}][OH^-]}{[H_4TeO_6^{3-}]} \quad (5)$$

In the alkaline medium employed in the present investigation, since silver(III) is known to exist predominantly as $[Ag(OH)_2(H_4TeO_6)_2]^{3-}$ and Te^{VI} as $H_4TeO_6^{3-}$, and one could assume $[DTA]=[Ag(OH)_2(H_4TeO_6)_2^{3-}]$ and $[Te^{VI}]=[H_4TeO_6^{3-}]$. Equation (4) therefore reduces to

$$Rate = -\frac{d[DTA]}{dt} = \frac{k_1 K_1 K_2[DTA][Se^{IV}][OH^-]}{[Te^{VI}]}$$

This equation explains all the experimental observations like first order with respect to [DTA], $[Se^{IV}]$ and $[OH^-]$ and inverse first order with respect to $[Te^{VI}]$.

Experimental

An aqueous solution of selenite was prepared from sodium selenite (Aldrich) and its strength verified[5]. Aqueous solution of selenate was prepared from sodium selenate (AnalaR). Ditelluratoargentate(III) (DTA) was prepared and standardised[4]. After decomposing an aliquot of DTA solution by acidifying with 1 N H_2SO_4, the total concentration of tellurium(VI) present in it was determined using sodium arsenite in the presence of traces of osmium(VIII) as a catalyst[7]. The alkali content present in the stock solution of DTA was determined titrimetrically. All other chemicals used were of AnalaR grade. Double-distilled water was used throughout.

The kinetics of the reaction were studied in 0.5 mol dm^{-3} alkali at $40\pm0.1°$ unless otherwise mentioned. The reaction was monitored using a Shimadzu 140.02 spectrophotometer following the absorbance of DTA at 351 nm[8] ($\varepsilon=1.58\times10^3$) where all other ions involved have negligible absorbances. All kinetic runs were carried out under the condition, $[Se^{IV}]\gg[DTA]$. The rate constants are reproducible within an error of $\pm5\%$. The stoichiometry of the reaction was determined by allowing six to eight-fold excess of selenium(IV) to react completely with DTA in 0.5 mol dm^{-3} alkali and determining the concentration of the excess selenium(IV) with permanganate after acidifying the reaction mixture[5]. The stoichiometry thus obtained was found to correspond to the mole ratio of 1 : 1 which was in agreement with the earlier reportr that silver(III) is a two-equivalent oxidant[3,4,9].

Acknowledgement

References

1. N. SRIDEVI, R. RAMBABU, P. VANI and L. S. A. DIKSHITULU, Indian J. Chem., Sect. A, 1990, 29, 63.
2. L. BARCZA and L. C. SILLEN, Acta Chem. Scand., 1971, 25, 1250.
3. T. RAVIPRASAD, B. SETHURAM and T. N. RAO, Indian J. Chem., Sect. A, 1979, 18, 40.
4. T. RAVIPRASAD, B. SETHURAM and T. N. RAO, Indian J. Chem., Sect. A, 1980, 19, 261 ; 1982, 21, 169, 170.
5. S. BARBAS and W. C. COOPER, Anal. Chem., 1956, 28, 129.
6. P. K. JAISWAL and K. L. YADAVA, Talanta, 1970, 17, 236.
7. V. P. TOLSTIKOV and P. A. EPIK, UKR Khim. Zh., 1969, 38, 1219 (Chem. Abstr., 1970, 72, 38579).
8. L. J. KIRSCHENBAUM, J. H. AMBRUS and G. ATKINSON, Inorg. Chem., 1973, 12, 2832.
9. L. J. KIRSCHENBAUM, J. Inorg. Nucl. Chem., 1976, 38, 881.