KINEFICS AND MECHANISH OF RU(III) CATALYZED OXIDATION OF Se(IV) BY Ce(IV)

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Recently we nave reported the kinetics and mechanism of oxidation of De(IV) by Ge(IV) in percanoric acid medium (1). Since this reaction has been observed, to be considerably catalyzed by Ru(III), we have undertaken a detailed kinetic study of the catalyzed reaction with a view of elucidating the mechanism.

# EXPERIMENTAL

Solutions of Se(IV), Se(VI), Ce(III), Ce(IV) and  $NaCLO_4$  were prepared and standardized as descriped earlier (1).

0.01M solution of Ru(III) in perchabric acid was prepared from Ru(III) culoride (Johnson Matney Chemicals Ltd.) in 2M perculoric acid and its strength cnecked (2). Aqueous solution of ruthenium tetroxide was prepared from Hu(111) solution as described by Lee and Engh (3) and standardized spectrophotometrically (4) just before use.

Snimadzu double beam spectrophotometer (Japan) with 1 cm cells was used for absorbance measurements. Saw Lap constant temperature liquid circulatory bath, 5-36 was used as the thermostat.

kinetics Procedure: All kinetic rons were carried out at a constant temperature of 30+0.1°C unless otherwise mentioned. Requisite amounts of all reactants except Ge(IV) were taken in a jena glass reaction pottle and placed in the thermostat. Ge(IV) was taken in another bottle and brought to the same temperature in the thermostat. After the solutions attained the temperature of the batn, the reaction was initiated by transferring the calculated amounts of Ce(IV) into the reaction bottle. The rate measurements were made keeping atleast a 10-fold excess of [se(IV)] and  $[H^+]$  over [Ge(IV)] and following the absorbance of Ce(IV) at 350 nm. (Under these conditions the rate of the uncatalyzed reaction was found to be negligible). The plots of absorpance versus time were found to be straight lines upto 90% completion of the reaction and the zero order rate constants were represented by 'Ko'. The reaction could not be studied over a wide range of reactant concentrations owing to the formation of a precipitate at nigher concentrations as reported earlier (1).

## RESULTS AND DISCUSSION

Stoicniometry: The stoicniometry was found to be correspond to the equation:  $Se(IV) + 2 Ce(IV) \longrightarrow Se(VI) + 2 Ce(III)$ 

Effect of ionic strength: The effect of ionic strength on the rate of the reaction was studied using NaC+O\_A in 3.5M perchioric acid medium and the increase in ionic strength was found to cause a slight decrease in zero order rate constants as may be seen from Table 1.

#### TABLE 1

Effect of Ionic Strength on the Zero Order Rate Jonstant, K<sub>o</sub> [Se(IV)]=5.0x10<sup>-3</sup>M; [Ce(IV)]=5.0x10<sup>-4</sup>M; [Ru(III)]=1.0x10<sup>-7</sup>M; [H<sup>+</sup>]=3.5M; t=30<sup>o</sup>C

I [Naclo <sub>4</sub> ],M	3.5	4.0	4.5	5.0	5.5
$LU^{5}k_{n}$ (mol lit <sup>-1</sup> sec <sup>-1</sup> )	20.0	19.2	18.3	17.5	16.7

Order with respect to cerium(IV): The plots of absorbance versus time were found to be good straight lines upto 90% completion of the reaction indicating zero order dependence on  $[Ce(IV)_2]$ . Also, the zero order rate constants obtained at various initial concentrations of Ce(IV) were found to remain constant(Table 2)

# ТАВЫЕ 2

mfrect of [Ce(I	V)] on t	he Zero (	Uraer Ha	te Constan	t, K <sub>o</sub>	
$[be(1V)] = 5.0x \pm 0^{-3}M;$	[Ru(III)	]=1.0x10	-7 <sub>14</sub> ; [	n <sup>+</sup> j=4.0M;	t=30°0	
lu <sup>4</sup> [de(IV)],M	3.0	4.0	5.0	6.0	7.0	
10 <sup>5</sup> K <sub>0</sub> (moi lit <sup>-1</sup> sec <sup>-1</sup> )	13.3	12.5	13.3	13.3	13.8	

Order with respect to selenium(IV): The effect of [Se(IV)] on the rate of the reaction was studied keeping the concentrations of all other reactants constant and the data thus obtained are shown in Table 3. The plot of log k<sub>o</sub> versus log [Se(IV)] gave a straight line with a stope of 0.73 thus showing the order with respect to Se(IV) to be fractional.

## ТАВЫЫ 3

Effect of	[Se(IV	7)] on 1	the Zero	Order	Rate Co	onstant,	, k <sub>o</sub>	
$[0e(1V)]=5.0x10^{-4}M;$	[Ru(]	III)]=1	.0x10 <sup>-7</sup> M	·; [	H <sup>+</sup> ]=4.04	1; t=	=30 <sup>°</sup> C	
10 <sup>3</sup> [Se(1V)],M	3.0	3.5	4.0	4.5	5.0	5.5	6.0	
$10^5 k_o \pmod{\text{lit}^{-1} \text{sec}^{-1}}$	9.2	11.0	11.3	12.3	13.3	14.0	15.0	

Order with respect to Ru(III): kinetic runs were carried out varying the [Ru(III)] from 2.0x10<sup>-8</sup> to 24.0x10<sup>-8</sup> M in 4.0M perchioric acid medium keeping the concentrations of all other reactants constant. The zero order rate constants thus obtained (Facle 4) when plotted against [Ru(III)], gave a straight line passing through origin showing the order with respect to the catalyst to be one.

#### TABLE 4

Effect of [Ru(III)]	on the Z	ero Orde	r Rate Co	onstant,	ko	
$[Ce(IV)]=5.0x10^{-4}M;$	[5e(IV)]	=5.0x10	· <sup>3</sup> м; [н <sup>+</sup> ]=	=4.0M; t=	30 <sup>0</sup> 0	
10 <sup>8</sup> [Ra(III)],M	2.0	6.0	10.0	14.0	20.0	24.0
$10^5$ k (mol lit <sup>-1</sup> sec <sup>-1</sup> )	2.91	7.91	13.3	19.2	27.5	32.5

Effect of  $[H^+]$ : The effect of  $[n^+]$  on the rate of the reaction was studied at a constant ionic strength of 5.5M and it may be seen from the data (Table 5) that there is considerable decrease in the rate with the increase of  $[n^+]$ .

#### TABLE 5

Hilect of  $[n^+]$  on the Zero Order Rate Constant,  $k_o$ [Se(IV)]=5.0x10<sup>-3</sup>M; [Ce(IV)]=5.0x10<sup>-4</sup>M; [Ru(III)]=1.0x10<sup>-7</sup>M; I=5.5M (NaClO<sub>A</sub>); t=30°C

[н <b>+</b> ],М	3.5	4.0	4.5	5.0	5.5	
$10^5 \kappa_0 (mo \perp lit^{-1} sec^{-1})$	16.7	10.7	6.7	5.4	4.2	

Activation parameters: The effect of temperature on the rate of the reaction was studied at four different temperatures (Table 6) and the activation parameters were computed from the plot of log k versus 1/T. The values of  $E_a, \Delta H \neq$ ,  $\Delta S \neq$  and  $\Delta G \neq$  calculated were found to be 17.3 kJ mol<sup>-1</sup>, 14.7 kJ mol<sup>-1</sup>, -262.6 JA<sup>-1</sup> mol<sup>-1</sup> and 94.3 kJ mol<sup>-1</sup> respectively.

## TABLE 6

Effect of Temperature on the Zero Order Rate Constant,  $k_0$ [Se(1V)]=5.0x10<sup>-3</sup>M; [Ce(1V)]=5.0x10<sup>-4</sup>M, [Ru(111)]=1.0x10<sup>-7</sup>M; [H<sup>+</sup>]=4.0M

والمستعلقات والمتصورين والتبديلية والمناه بتعار فكروستك وتقاعا فتنبع ومرود ومواجه والمستا والمتقاة المتعوني والماطن					
Temperature, <sup>C</sup> A	303	308	313	318	
ιυ <sup>5</sup> κ <sub>ο</sub> (moi lit <sup>-1</sup> sec <sup>-1</sup> )	13.3	15.0	16.7	18.3	

<u>Mechanism</u>: Selenious acid has a dissociation constant of  $3.0 \times 10^{-3}$  at  $25^{\circ}$ C (5) and Raman spectrum snows that it is dissociated only to a small extent in aqueous solution (c). Se(IV) is known to dimerise (5) in concentrated solutions but in the concentration range employed in the present investigation the percentage of monomer is more than 94%. In view of these reports Se(IV) may be regarded as existing mainly in the form of  $H_2$ SeO<sub>3</sub> under our present experimental conditions.

Ru(111) solutions when mixed with excess of Ce(IV), are known to get oxidized readily and quantitatively to Ru(VIII) (2,7-10). Surasiti and Sandel1 (11) while studying the kinetics of ruthenium catalyzed oxidation of As(III) by Ce(IV) observed that Ru(III) shows the same catalytic activity as Ru(VIII) added to the reaction mixture initially. In our present investigation also we have observed that the rate of the Ru(III) catalyzed reaction is in good agreement with that of Ru(VIII) catalyzed reaction of the same ruthenium content. The order in Ru(VIII) has also been found to be one. The active oxidizing species involved in the catalyzed reaction may therefore be regarded as Ru(VIII). Further, the plot of  $1/k_0$  versus 1/[Se(IV)] is a straight line with an intercept on the rate axis, which indicates complexation between Se(IV) and Ru(VIII).

In view of these observations the following mechanism has been proposed.

$$Ru(III) + 5 Ce(IV) \xrightarrow{IBSV} Ru(VIII) + 5 Ce(III) \dots (1)$$
  
Se(IV) + Ru(VIII)  $\xrightarrow{K}$  Complex (C)  $\dots (2)$   
C  $\xrightarrow{k}$  Se(VI) + Ru(VI) \dots (3)

$$Ru(VI) + Ce(IV) \xrightarrow{fast} Ru(VII) + Ce(III) \dots (4)$$

$$Ru(VII) + Ce(IV) \xrightarrow{Iasc} Ru(VIII) + Ce(III) \dots (5)$$

This leads to the rate equation

$$Rate = -d[Ce(IV)] = \frac{kK [Se(IV)] [Ru(III)]}{dt} \dots (6)$$

Equation (6) may be rearranged and written as

$$\frac{[Bu(III)]}{rate} = \frac{1}{kK [Se(IV)]} + \frac{1}{k} \qquad \dots \qquad (7)$$

Thus, if [Ru(III)]/k is plotted against l/[Se(IV)] the resultant plot should be a straight line with an intercept on the rate axis (Fig. 1) the





Plot of [Ru(III)]/k<sub>o</sub> versus 1/[Se(IV)]
[Ce(IV)]=5.0x10<sup>-4</sup>H; [Ru(III)]=1.0x10<sup>-7</sup>H; 1=5.5M (HaClo<sub>4</sub>); t=30<sup>o</sup>C

slope corresponding to 1/kK and the intercept corresponding to 1/k. The variation of rate with [Se(IV)] has been studied at 3.5M, 4.5M and 5.5M [HClO<sub>4</sub>] and from the slopes and intercepts of the resultant plots (Fig. 1) the values of K at these acid concentrations have been found to be 97.6 mol<sup>-1</sup> lit, 72.7 mol<sup>-1</sup> lit and 58.1 mol<sup>-1</sup> lit respectively.

From these values it may be concluded that the decrease in rate with increase in  $[H^+]$  is mainly due to the decomposition of Se(IV) - Ru(VIII) complex as the  $[H^+]$  is increased.

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