

## Kinetics of Oxidation of Tl(I) by Ce(IV) Catalysed by Thiocyanate Ion in Aqueous Perchloric Acid Medium

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Kinetics of oxidation of Tl(I) by Ce(IV) in aqueous perchloric acid medium have been investigated by following the depletion in concentration of Ce(IV) with time. At a series of equivalent concentration of the two reactants, the total order of the reaction is two; being unity in each reactant. The order with respect to thiocyanate ion is also unity. The rate is directly proportional to the square root of  $[H^+]$ . The reaction shows a primary positive salt effect. While the addition of one of the reaction products, viz. Ce(III) retards the rate, the addition of Tl(III) produces no effect. Arrhenius parameters have been determined and a reaction scheme which explains the salient features of the reaction has been proposed.

A SERIES of cations were found to effectively catalyse, otherwise immeasurably slow<sup>1</sup>, non-complementary reaction between Tl(I) and Ce(IV) and the oxidation kinetics in presence of such cations were investigated by Sinha *et al.*<sup>2-6</sup> and also by other workers<sup>7-10</sup>. Of the various explanations put forth to account for the slow nature of this reaction, one relates to the coulombic force of repulsion which would be existent between two positively charged cations particularly when one of these happens to be highly positively charged. Obviously, the introduction of an anion should be able to reduce this force either through complexation with any of the cations or by acting as a bridge and in consequence catalyse the reaction. It is in this connection that the authors have found that thiocyanate ion, a well known ligand<sup>11</sup>, acts as a catalyst and the present paper describes the oxidation kinetics of this reaction in the presence of this anion. The catalysis of this anion in the above reaction has not been investigated so far.

### Materials and Methods

Ceric perchlorate solution was prepared and standardized as described earlier<sup>5</sup> from ceric ammonium nitrate (E. Merck). Thallous perchlorate solution was prepared<sup>5</sup> from thallous carbonate (E. Merck) and thallous content in the solution determined as thallous chromate<sup>12</sup>. The solution of ammonium thiocyanate (GR) was prepared by dissolving a known quantity of the sample in the requisite volume of doubly distilled water. Other reagents used were of AR grade and all solutions were invariably prepared in doubly distilled water. The kinetic procedure was the same as described earlier<sup>2(a)</sup>.

### Results

A number of runs at equivalent concentrations of thallous perchlorate and ceric perchlorate in the range  $4.444 \times 10^{-4}N$ - $5.715 \times 10^{-4}N$  were made in

perchloric acid medium at constant [catalyst] and ionic strength. It was found that the reaction follows an overall second order kinetics as revealed by the linear plots of  $1/(a-x)$  versus time. The total order of the reaction was further confirmed by van't Hoff's differential method. In order to ascertain the order in ceric ion, a number of runs with different initial [ceric perchlorate] were followed while keeping all other variables unchanged. The order in ceric ion was determined by plotting concentration versus time curves and determining the slope at that point at which 10% of the reductant was oxidized. Table 1 gives the initial rate for four runs with different initial [Ce(IV)].

Substitution of the values of initial rate in van't Hoff's differential formula<sup>13</sup>

$$n = \frac{\log (-dc/dt)_1 - \log (-dc/dt)_2}{\log C_1 - \log C_2} \quad \dots(1)$$

(where  $n$  gives the order in ceric ion) confirmed the first order kinetics in Ce(IV).

It would be seen that the rate constants (Table 1) decrease with increase in the initial [Ce(IV)], although the reaction adhered to second order kinetics. It is interesting to note that a reasonable constancy is observed for the product of  $k_2 \times [Ce(ClO_4)_4]$  for concentrations of Ce(IV) close to the initial [thallous ion] ( $\sim 5.262 \times 10^{-4}N$ ), but at higher [Ce(IV)] the value of the product decreased markedly. The effect of increasing initial [Ce(IV)] which leads to decrease in the value of rate constants may be attributed to the formation of unreactive dimers of Ce(IV) at higher [Ce(IV)].

Since the total order of the reaction is two and the order in Ce(IV) is unity, it may be naturally expected that the order in Tl(I) is also unity. However, for verification, the concentration of thallous ion was varied over a wide range ( $\sim 5.262 \times 10^{-4}N$ - $10.00 \times 10^{-4}N$ ), keeping all other factors, including the ionic strength unchanged. It was observed that the reaction follows second order

TABLE 1 — INITIAL RATE AND THE VALUES OF RATE CONSTANTS AT DIFFERENT INITIAL [CERIC PERCHLORATE]

$$\{[\text{Ce}(\text{ClO}_4)_4] = 5.262 \times 10^{-4}N; [\text{NH}_4\text{SCN}] = 1.000 \times 10^{-5}N; [\text{HClO}_4] = 5.000 \times 10^{-1}N \text{ temp.} = 30^\circ; \mu = 1.00M\}$$

Initial concentration of $[\text{Ce}(\text{ClO}_4)_4] \times 10^4N$	$(-dc/dt) \times 10^6$ (g. equiv. litre <sup>-1</sup> min <sup>-1</sup> )	$k_2$ (litre g equiv. <sup>-1</sup> min <sup>-1</sup> )
6.00	7.461	21.42
5.500	6.836	28.49
5.262	6.570	32.77
5.000	6.233	34.22

TABLE 4 — VALUES OF SECOND ORDER RATE CONSTANTS FOR DIFFERENT CONCENTRATIONS OF HYDROGEN IONS

$$\{[\text{Ce}(\text{ClO}_4)_4] = 5.262 \times 10^{-4}N; [\text{TlClO}_4] = 5.262 \times 10^{-4}N; [\text{NH}_4\text{SCN}] = 1.000 \times 10^{-5}N; \text{temp.} = 30^\circ\text{C}; \mu = 1.00M\}$$

$[\text{HClO}_4] \times 10N$	$k_2$ (litre g equiv. <sup>-1</sup> min. <sup>-1</sup> )	$k_2/[\text{HClO}_4]^\ddagger$
2.0	21.70	48.53
3.0	25.45	46.36
4.0	29.69	46.95
5.0	33.19	46.93
6.0	35.54	45.88
7.0	37.80	45.17
8.0	40.80	45.62
9.0	43.99	46.37

TABLE 2 — SECOND ORDER RATE CONSTANTS FOR VARIOUS INITIAL [THALLOUS PERCHLORATE]

$$\{[\text{Ce}(\text{ClO}_4)_4] = 5.262 \times 10^{-4}N; [\text{NH}_4\text{SCN}] = 1.000 \times 10^{-5}N; [\text{HClO}_4] = 5.000 \times 10^{-1}N; \text{temp.} = 30^\circ\text{C}; \mu = 1.00M\}$$

$[\text{TlClO}_4] \times 10^4N$	$k_2$ (litre g. equiv. <sup>-1</sup> min <sup>-1</sup> )	$[\text{TlClO}_4] \times 10^4N$	$k_2$ (litre g equiv. <sup>-1</sup> min <sup>-1</sup> )
5.262	32.77	7.500	19.91
6.000	26.85	10.000	14.04

TABLE 3 — VALUES OF SECOND ORDER RATE CONSTANTS AT DIFFERENT [CATALYST]

$$\{[\text{Ce}(\text{ClO}_4)_4] = 5.262 \times 10^{-4}N; [\text{TlClO}_4] = 5.262 \times 10^{-4}N; [\text{HClO}_4] = 5.000 \times 10^{-1}N; \text{temp.} = 30^\circ\text{C}; \mu = 1.00M\}$$

$[\text{NH}_4\text{SCN}] \times 10^6N$	$k_2$ (litre g. equiv. <sup>-1</sup> min <sup>-1</sup> )	$k_2 \times 10^6/[\text{SCN}^-]$
7.0	21.99	3.141
8.0	25.89	3.236
9.0	29.42	3.269
10.0	33.19	3.319
11.0	36.78	3.344
12.0	40.34	3.382
13.0	43.73	3.364

TABLE 5 — VALUES OF SECOND ORDER RATE CONSTANTS IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF Tl(III) AND Ce(III)

$$\{[\text{Ce}(\text{ClO}_4)_4] = 5.262 \times 10^{-4}N; [\text{TlClO}_4] = 5.262 \times 10^{-4}N; [\text{NH}_4\text{SCN}] = 1.000 \times 10^{-5}N; [\text{HClO}_4] = 5.000 \times 10^{-1}N; \text{temp.} = 30^\circ\text{C}; \mu = 1.00M\}$$

Amount added $\times 10^4M$	$k_2$ (litre g equiv. <sup>-1</sup> min <sup>-1</sup> )	Amount added $\times 10^4M$	$k_2$ (litre g equiv. <sup>-1</sup> min <sup>-1</sup> )
$\text{Ce}(\text{ClO}_4)_3$		$\text{Tl}(\text{ClO}_4)_3$	
2.50	30.01	2.50	33.30
5.00	27.33	5.00	33.06
7.50	24.22	7.50	33.01
10.00	20.49	10.00	33.19

kinetics. Again 'c-t' curves were drawn and employing van't Hoff's differential formula the order in thallos ion was found to be unity. A perusal of Table 2 shows that the rate decreases with increase in the initial  $[\text{Tl(I)}]$ , analogous to that obtained by varying initial  $[\text{Ce(IV)}]$ . This may again be attributed to the formation of unreactive complex species of Tl(I) with Ce(IV) or to the different less reactive thiocyanate complex of Tl(I).

As stated earlier, thiocyanate ion effectively catalyses the reaction. A linear proportionality between the rate and concentration of thiocyanate was observed as is evident from the data in Table 3.

In all previous studies it has been generally reported that the rate of oxidation of Tl(I) by Ce(IV) depends significantly on  $[\text{H}^+]$ . An analogous observation was found in the present case as well (Table 4). The reaction rate was found to depend directly on  $[\text{H}^+]^{1/2}$ .

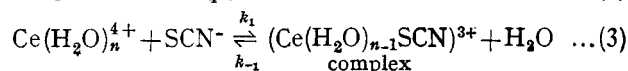
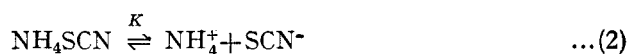
The reaction was found to show primary positive salt effect in the presence of a number of neutral electrolytes. However, no quantitative conclusion could be drawn as the ionic strength region investigated was beyond the limit permitted by Debye-Hückel limiting law. The effect of added Ce(III)

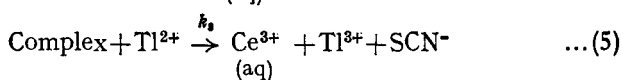
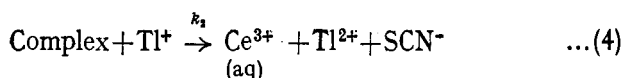
and Tl(III) was also investigated and it was found that while Tl(III) has no influence on the rate, Ce(III) causes retardation.

For determining the activation parameters, the reaction was studied at different temperatures and it was found that the data adhere to Arrhenius equation. The temperature coefficient is 1.78. The heat of activation was evaluated from the slope of Arrhenius plots and was found  $\Delta H^* = 10.48$  kcal mole<sup>-1</sup>. The entropy of activation,  $\Delta S^*$  was evaluated from Eyring's equation and the free energy of activation,  $\Delta F^*$  was calculated from the thermodynamic relationship ( $\Delta F^* = \Delta H^* - T\Delta S^*$ ). These values are  $\Delta S^* = -25.22$  e.u. and  $\Delta F^* = 18.12$  kcal mole<sup>-1</sup>.

## Discussion

Ce(IV) is known to exist in perchloric acid medium in a variety of forms such as  $\text{Ce}^{4+}$ ,  $\text{CeOH}^{3+}$  and  $\text{Ce}(\text{OH})_2^{2+}$  etc., alongside the formation of small amounts of dimers or even trimers. Various equilibria have also been suggested<sup>14-21</sup> and corresponding equilibrium constants have been evaluated<sup>17-19</sup>. Since highly charged Ce(IV) has a strong affinity for water<sup>22</sup>, it would be more logical if it is written as  $\text{Ce}(\text{H}_2\text{O})_n^{4+}$ . The ion steps (2-5) are suggested to account for the observed kinetic data.





On the basis of above steps the rate is given as:

$$-\frac{d[\text{Ce}(\text{H}_2\text{O})_n^{4+}]}{dt} = k_2[\text{complex}][\text{Tl}^+] + k_3[\text{complex}][\text{Tl}^{2+}] \quad \dots(6)$$

Assuming steady state for  $\text{Tl}^{2+}$  and the complex

$$[\text{Tl}^{2+}] = \frac{k_2[\text{Tl}^+]}{k_3} \quad \dots(7)$$

$$[\text{Complex}] = \frac{k_1[\text{Ce}(\text{H}_2\text{O})_n^{4+}][\text{SCN}^-]}{k'_{-1} + 2k_2[\text{Tl}^+]} \quad \dots(8)$$

where  $k'_{-1} = k_{-1}[\text{H}_2\text{O}]$ .

Substitution of these concentration terms in Eq. (6) leads to the rate equation:

$$-\frac{d[\text{Ce}(\text{H}_2\text{O})_n^{4+}]}{dt} = \frac{2k_1k_2[\text{Ce}(\text{H}_2\text{O})_n^{4+}][\text{Tl}^+][\text{SCN}^-]}{k'_{-1} + 2k_2[\text{Tl}^+]} \quad \dots(9)$$

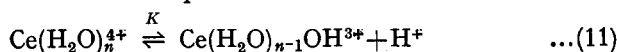
when  $k'_{-1} \gg 2k_2[\text{Tl}^+]$ , and at constant  $[\text{SCN}^-]$  the rate is given as

$$-\frac{d[\text{Ce}(\text{H}_2\text{O})_n^{4+}]}{dt} = k_0[\text{Ce}(\text{H}_2\text{O})_n^{4+}][\text{Tl}^+] \quad \dots(10)$$

where  $k_0 = \frac{2k_1k_2[\text{SCN}^-]}{k'_{-1}}$  and is the observed second order rate constant.

The rate expression is found to explain the principal kinetic features. However, it fails as such to account for the decrease in rate with increase in initial concentrations of either Ce(IV), Tl(I) or Ce(III). In this connection it would be relevant to add that at higher  $[\text{Ce(IV)}]$  the formation of dimers or even trimers of Ce(IV) has been reported<sup>18,19</sup>. Also the formation of mixed dimers of  $[\text{Ce(IV)} + \text{Ce(III)}]$  are now known<sup>9</sup>. The formation of such species, in all probability, is expected to retard the rate because of the less reactivity. The decrease in rate with increasing initial  $[\text{Tl(I)}]$  may be attributed to two reasons. (i) It is quite likely that on increasing  $[\text{Tl(I)}]$ , the formation of some complex salt may take place similar to that at least found in sulphuric acid medium<sup>24</sup>. Such an explanation has earlier been put forth by Dorfman and Gryder<sup>10</sup> and also by Sinha and coworkers<sup>3a,5</sup>. While complexation in perchloric acid medium are not generally favoured the recent studies by Hala<sup>25</sup> do not preclude such a possibility altogether. (ii) Thallous ion may enter into complexation with thiocyanate ion which may also affect the rate.

To account for rather complex dependence of rate on  $[\text{H}^+]$ , an explanation similar to that given by Duke and Borchers<sup>26</sup> appears applicable. If we consider the equilibrium



$$\text{then } K = \frac{[(\text{Ce})_{\text{T}} - \text{Ce}_{(\text{aq})}^{4+}][\text{H}^+]}{[\text{Ce}_{(\text{aq})}^{4+}]} \quad \dots(12)$$

or

$$[\text{Ce}_{(\text{aq})}^{4+}] = \frac{[(\text{Ce})_{\text{T}}][\text{H}^+]}{[\text{H}^+] + K} \quad \dots(13)$$

Substituting Eq. (13) in the rate Eq. (9), we get

$$-\frac{d[(\text{Ce})_{\text{T}}]}{dt} = \frac{k''[(\text{Ce})_{\text{T}}][\text{Tl}^+][\text{H}^+]}{(k'_{-1} + 2k_2[\text{Tl}^+])([\text{H}^+] + K)} \quad \dots(14)$$

where  $k'' = 2k_1k_2[\text{SCN}^-]$ .

Under such circumstances, the fractional linear dependence of rate on  $[\text{H}^+]$  can at least be qualitatively explained.

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### References

- (a) SCHAFFER, P. A., *J. Am. chem. Soc.*, **55** (1933), 2169.  
(b) SCHAFFER, P. A., *J. phys. Chem.*, **40** (1936), 1021.
- (a) KRISHNA, B. & SINHA, B. P., *Z. phys. Chem.*, **212** (1959), 149; (b) **212** (1959), 155; (c) **213** (1960), 177.
- (a) SINHA, B. P., *Z. phys. Chem.*, **233** (1966), 161; (b) **233** (1966), 412.
- SINHA, B. P. & MATHUR, H. P., *Z. phys. Chem.*, **246** (1971), 342.
- SINHA, B. P. & MATHUR, H. P., *J. inorg. nucl. Chem.*, **33** (1971), 1673.
- MATHUR, H. P., Ph.D. thesis, University of Jodhpur, Jodhpur.
- HIGGINSON, W. C. E., *Disc. Faraday Soc.*, **29** (1960), 135.
- HIGGINSON, W. C. E., ROSSEINSKY, D. R., STEAD, J. B. & SYKES, A. G., *Disc. Faraday Soc.*, **29** (1960), 54.
- ZELTMAN, E. W., *Chem. Abstr.*, **68** (1968), 72,723q.
- DORFMAN, M. C. & GRYDER, J. W., *J. inorg. Chem.*, **1** (1962), 799.
- TREINDL, L., *Chem. Abstr.*, **68** (1968), 90205x.
- VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, London), 1961, 549.
- FROST, A. A. & PEARSON, R. G., *Kinetics and mechanism* (John Wiley, New York), 1961, 17.
- SHERRILL, M. S., KING, C. B. & SPOONER, R. C., *J. Am. chem. Soc.*, **65** (1943), 170.
- EVANS, M. G. & URI, N., *Nature, Lond.*, **166** (1950), 602.
- DUKE, F. R. & PARACHEN, R. F., *J. Am. chem. Soc.*, **78** (1956), 150.
- BAKER, F. B., NEWTON, T. W. & KHAN, M., *J. phys. Chem.*, **64** (1960), 109.
- HEIDT, L. & SMITH, M., *J. Am. chem. Soc.*, **70** (1948), 2476.
- HARDWICK, T. J. & ROBERTSON, E., *Can. J. Chem.*, **29** (1951), 818.
- KING, E. L. & PANDOW, M. L., *J. Am. chem. Soc.*, **74** (1952), 1966.
- ARDON, M., *J. chem. Soc.*, (1957), 1811.
- COTTON, F. A. & WILKINSON, G., *Advanced inorganic chemistry* (Interscience, New York), 1967, 1068.
- BLAUSTEIN, B. D. & GRYDER, J. W., *J. Am. chem. Soc.*, **79** (1957), 540.
- MELLOR, J. W., *A comprehensive treatise in inorganic chemistry*, Vol. V (Longmans, London), 1960, 662.
- HALA, J., *J. inorg. nucl. Chem.*, **29** (1967), 187.
- DUKE, F. R. & BORCHERS, C. E., *J. Am. chem. Soc.*, **75** (1953), 5186.