

## Kinetics of Ce(IV) Oxidation of Monothioglycerol in Carbonate Medium

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Received 23 June 1975; accepted 23 December 1975

The oxidation of monothioglycerol by Ce(IV) carbonate complex shows a first order dependence in Ce(IV) but the order with respect to monothioglycerol is less than one. The rate limiting step involves the disproportionation of Ce(IV)-thioglycerol complex or complexes. The rate is retarded by increasing pH,  $[\text{CO}_3^{2-}]$  and  $[\text{Ce(III)}]$ . The reaction rate shows an inverse dependence on  $[\text{CO}_3^{2-}]$  but no mathematical correlation can be established between the rate and  $[\text{Ce(III)}]$ . There is a linear correlation between  $\log k'$  and pH of the medium where  $k'$  is the observed first order rate coefficient with respect to Ce(IV). The isokinetic temperature ( $\beta$ ) of the reaction is found to be  $27^\circ$  which helps to explain the reasonably invariant free energy ( $\Delta G^\ddagger = 23 \pm 0.5 \text{ kcal mole}^{-1}$ ) of the reaction. The reaction takes place through an inner sphere mechanism in which the substrate (thioglycerol) displaces the ligand (carbonate ion) from the coordination sphere of the metal ion in an equilibrium or a number of equilibria prior to the rate limiting disproportionation of the complex.

THE oxidation of some  $\alpha$ -mercaptocarboxylic acids<sup>1</sup>, thiourea and its N-substituted derivatives<sup>2</sup> by Ce(IV) in sulphate medium has been studied by McAuley and coworkers. These reactions were fast owing to the high redox potential of Ce(IV)-Ce(III) couple in  $\text{H}_2\text{SO}_4$  and could be followed only by the stopped flow technique. The formal redox potential of Ce(IV)-Ce(III) couple measured in potassium carbonate medium was found to be  $-0.14 \text{ V}$  (vs. SCE). Thus the oxidation of organic substrates by Ce(IV) in carbonate medium is expected to be slow and amenable to spectrophotometric investigation. The present paper deals with the kinetics of oxidation of monothioglycerol in carbonate medium.

### Materials and Methods

Cerium(IV) carbonate was prepared as described by Kapoor and Aggarwal<sup>3</sup>. Cerium(IV) sulphate ( $0.02M$  in  $1M \text{ H}_2\text{SO}_4$ ) or Ce(IV) ammonium nitrate ( $0.02M$  in  $2M \text{ HNO}_3$ ) was added to a known excess of  $\text{K}_2\text{CO}_3$  solution making an allowance for the alkali neutralized by the free acid present in Ce(IV) solution. Similar values of the first order rate constant  $k'$ , with respect to Ce(IV), were obtained in both the cases.

Solutions of monothioglycerol (Evans Chemetics grade, 98% pure) were freshly prepared in conductivity water, kept under nitrogen, and standardized against standard iodine. The iodine oxidation of thioglycerol yielded the disulphide.

Potassium carbonate used was of AR May-Baker grade and its solution was also prepared in conductivity water. All other chemicals used were of either analar BDH or S. Merck grades.

**Rate measurement**—The kinetics were studied in potassium carbonate solutions  $>0.75M$  because Ce(IV) is precipitated out<sup>3</sup> in solutions  $<0.75M$

$\text{K}_2\text{CO}_3$ . The reaction was carried out under nitrogen atmosphere because Ce(III) carbonate complex, formed in the reaction mixture, is susceptible to atmospheric oxidation. It was initiated by mixing the reactant solutions after thermal equilibrium at the desired temperature.

The reaction was followed by measuring the absorbance of Ce(IV) carbonate at various intervals at 300-305 nm on a Beckman DU-2 spectrophotometer and a cell of 1 cm path. The  $\lambda_{\text{max}}$  was not affected by the anion of Ce(IV) salt used for the preparation of the carbonate complex of Ce(IV). The  $\lambda_{\text{max}}$  for monothioglycerol and its oxidation product, the corresponding disulphide, were found to be 218 and 220 nm respectively. The validity of Beer's law was checked for the entire range of [oxidant] used.

**Stoichiometry and product analysis**—The formation of disulphide as the product of oxidation was confirmed on the basis of polarographic studies<sup>4</sup> which indicated a 1:1 stoichiometry for the reaction. The stoichiometry was further confirmed from the analysis of unreacted Ce(IV) in reaction mixture having different initial concentrations of Ce(IV) and thioglycerol. The unreacted Ce(IV) was estimated spectrophotometrically.

### Results and Discussion

Since the reaction is retarded by Ce(III), the plots of  $\log(\text{absorbance})$  against time were not linear for the entire reaction (Fig. 1). The linearity of the plots improved considerably with increasing [monothioglycerol], and these plots did not show any deviation for the first 25% of the reaction (Fig. 1). The plot relating to  $0.02M$  monothioglycerol was almost linear even beyond first half-life. The first order rate constant  $k'$  was calculated from the slope of the linear portions of these plots.

The first order dependence in Ce(IV) was confirmed by the invariance of  $k'$  over a ten-fold variation

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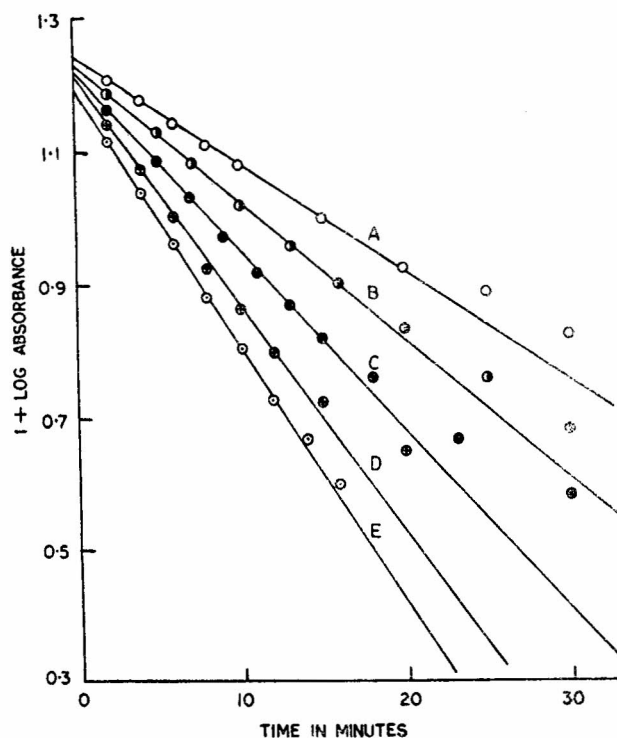


Fig. 1 — First order plots between  $\log$  (absorbance) and time at  $[\text{Ce(IV)}]=0.00024M$ ,  $[\text{K}_2\text{CO}_3]=1M$ ,  $\text{temp.}=35^\circ$ , and  $[\text{monothiolglycerol}]=(A) 0.002M$ ,  $(B) 0.004M$ ,  $(C) 0.008M$ ,  $(D) 0.016M$ , and  $(E) 0.02M$

TABLE 1 — EFFECT OF VARYING  $[\text{Ce(IV)}]$  ON THE OBSERVED FIRST ORDER RATE CONSTANT  $k'$

$\{10^2[\text{Monothiolglycerol}]=1.0M; [\text{K}_2\text{CO}_3]=1.8M; \text{temp.}=35^\circ\}$

$10^4[\text{Ce(IV)}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )	$10^4[\text{Ce(IV)}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )
0.24	5.54	1.60	5.45
0.40	5.47	2.40	5.58
0.80	5.38	—	—

TABLE 2 — DEPENDENCE OF  $k'$  ON THE  $[\text{DISULPHIDE}]$

$\{10^4[\text{Ce(IV)}]=2.4M; [\text{K}_2\text{CO}_3]=1.8M; 10^2[\text{monothiolglycerol}]=1M; \text{temp.}=40^\circ\}$

$10^3[\text{Di-sulphide}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )	$10^3[\text{Di-sulphide}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )
2.0	9.3	8.0	9.3
4.0	9.5	10.0	9.4
6.0	9.5	—	—

in the initial  $[\text{Ce(IV)}]$ . The values of rate constant  $k'$  at different  $[\text{Ce(IV)}]$  are given in Table 1, and these were measured under pseudo first order conditions; the amount of thiol was always in large excess over that of  $\text{Ce(IV)}$ .

The deviation in the linearity of the plots of  $\log$  (absorbance) versus time (Fig. 1) may be attributed to the accumulation of oxidation products in the system. The results in Table 2 indicate that the initial addition of the disulphide does not affect

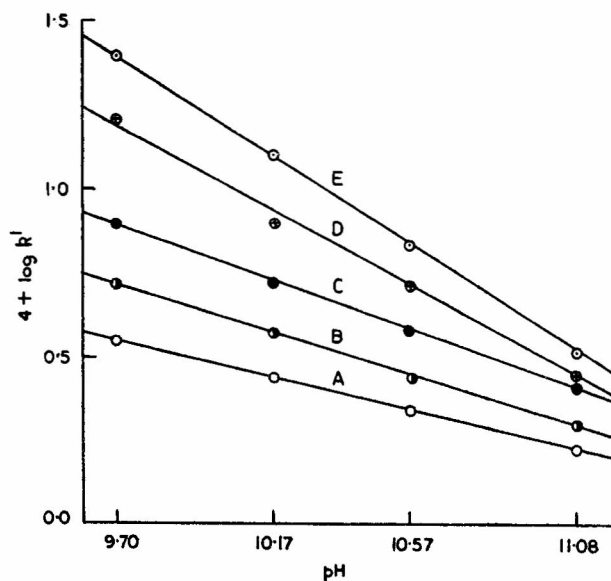


Fig. 2 — Plots between  $\log k'$  and  $pH$  of the reaction medium ( $pH$  was varied using mixtures of carbonate and bicarbonate of potassium) for  $[\text{monothiolglycerol}]=(A) 0.002M$ ,  $(B) 0.004M$ ,  $(C) 0.008M$ ,  $(D) 0.012M$ , and  $(E) 0.016M$

TABLE 3 — DEPENDENCE OF  $k'$  ON INITIAL  $[\text{Ce(III)}]$

$\{10^4[\text{Ce(IV)}]=2.4M; [\text{K}_2\text{CO}_3]=1M; 10^2[\text{monothiolglycerol}]=1M; \text{temp.}=40^\circ\}$

$10^4[\text{Ce(III)}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )	$10^4[\text{Ce(III)}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )
0.0	9.3	1.5	7.5
0.5	8.6	2.0	6.9
1.0	8.3	2.5	4.5

TABLE 4 — DEPENDENCE OF  $k'$  ON INITIAL  $[\text{MONOTHIOLGLYCEROL}]$

$\{10^4[\text{Ce(IV)}]=2.4M; [\text{K}_2\text{CO}_3]=0.75M; \text{temp.}=35^\circ\}$

$10^2[\text{Thiol}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )	$10^2[\text{Thiol}]$ (M)	$10^4k'$ ( $\text{sec}^{-1}$ )
0.2	5.7	1.2	13.5
0.4	8.7	1.6	14.5
0.8	11.9	2.0	16.9
1.0	12.8	—	—

$k'$ . However, an initial addition of  $\text{Ce(III)}$  retarded the rate of the reaction as shown by the results in Table 3.

The results of varying  $[\text{thiol}]$ , given in Table 4, indicate that the order with respect to thioglycerol is fractional. This was further supported by the linearity of the plots between  $1/k'$  and  $[\text{thiol}]^{-1}$  at different  $[\text{CO}_3^{2-}]$ .

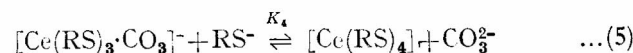
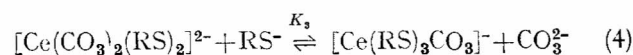
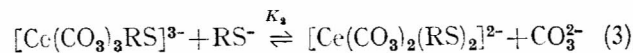
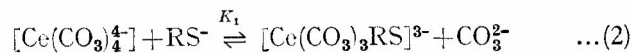
An increase in the initial  $[\text{K}_2\text{CO}_3]$  is found to retard the reaction rate (Table 5). It is further observed that the plot between the inverse  $k'$  and  $[\text{CO}_3^{2-}]$  is linear. The reaction rate is also retarded by the increase in  $pH$  of the medium as is indicated by the negative slope of the linear plots (Fig. 2) between  $\log k'$  and  $pH$ . The values of  $k'$  obtained at different initial  $[\text{thioglycerol}]$  are given in Table 6.

TABLE 5 — DEPENDENCE OF  $k'$  ON INITIAL  $[\text{CO}_3^{2-}]$ 
 $\{10^4[\text{Ce(IV)}]=2.4M; 10^2[\text{monothioglycerol}]=1M; \text{temp.}=35^\circ\}$ 

$[\text{K}_2\text{CO}_3]$ (M)	$10^4k'$ (sec <sup>-1</sup> )	$[\text{K}_2\text{CO}_3]$ (M)	$10^4k'$ (sec <sup>-1</sup> )
0.75	12.8	1.8	5.6
1.25	8.0	2.0	5.0
1.50	6.7	3.0	3.4

The linear plot between the inverse  $k'$  and  $[\text{thioglycerol}]^{-1}$  is also consistent with the formation of an intermediate complex or complexes having an appreciable value for the equilibrium constant at least for one complex.

Considering that the coordination number of Ce(IV) is eight<sup>5</sup>, there is a possibility for the formation of mono-, di-, tri- and tetra-substituted thioglycerol complexes of Ce(IV) as shown in Eqs. (2-5).



The formation of successive Ce(IV)-thiol complexes as shown in Eqs. (2-5) is expected to increase with the increase in  $[\text{thioglycerol}]$  at a given  $[\text{CO}_3^{2-}]$ . Formation of such successive intermediates between Ce(IV) and glycol has been suggested earlier in the oxidation of butane-2,3-diol by Ce(IV) both in nitrate<sup>6</sup> and perchlorate<sup>7</sup> media.

Assuming that the complexes formed in Eqs. (2-5) disproportionate with rate constants  $k_1, k_2, k_3$  and  $k_4$  respectively in the rate limiting step, the rate of disappearance of cerium(IV) could be expressed by Eq. (6).

$$\begin{aligned} -\frac{d[\text{Ce(IV)}]}{dt} = & \left( k_1 + \frac{k_2 K_2 [\text{RS}^-]}{[\text{CO}_3^{2-}]} + \frac{k_3 K_3 K_2 [\text{RS}^-]^2}{[\text{CO}_3^{2-}]^2} + \frac{k_4 K_4 K_3 K_2 [\text{RS}^-]^3}{[\text{CO}_3^{2-}]^3} \right) \\ & \times \frac{K_1 [\text{Ce}(\text{CO}_3)_4]_0 [\text{RS}^-]}{[\text{CO}_3^{2-}]} \\ & \frac{1 + \frac{K_1 [\text{RS}^-]}{[\text{CO}_3^{2-}]} + \frac{K_2 K_1 [\text{RS}^-]^2}{[\text{CO}_3^{2-}]^2} + \frac{K_3 K_2 K_1 [\text{RS}^-]^3}{[\text{CO}_3^{2-}]^3}}{+ \frac{K_4 K_3 K_2 K_1 [\text{RS}^-]^4}{[\text{CO}_3^{2-}]^4}} \quad \dots(6) \end{aligned}$$

In the first approximation, Eq. (6) could be reduced to Eq. (7) because of the appreciable  $[\text{CO}_3^{2-}]$  used.

$$\frac{-d[\text{Ce(IV)}]}{dt} = \frac{k_1 K_1 [\text{Ce}(\text{CO}_3)_4]_0 [\text{RS}^-]}{[\text{CO}_3^{2-}] + K_1 [\text{RS}^-]} \quad \dots(7)$$

where  $[\text{Ce}(\text{CO}_3)_4]_0$  is the total  $[\text{Ce(IV)}]$  and  $-d[\text{Ce(IV)}]/dt[\text{Ce(IV)}] = k'$ , the observed first order rate constant.

The equation (7) could also be written as Eq. (8) which indicates a linear plot between inverse  $k'$  and  $[\text{thioglycerol}]^{-1}$ . The observation that  $k'/[\text{thiol}]$  ratio decreases with increasing  $[\text{thiol}]$  indicates that the higher thioglycerol-Ce(IV) complexes are more resistant to disproportionation.

$$\frac{1}{k'} = \frac{[\text{CO}_3^{2-}]}{k_1 K_1 [\text{RS}^-]} + \frac{1}{k_1} \quad \dots(8)$$

 TABLE 7 — ACTIVATION PARAMETERS AT DIFFERENT  $[\text{MONOTHIOGLYCEROL}]$ 
 $\{10^4[\text{Ce(IV)}]=1.6M; \text{pH}=10.17\}$ 

$10^2[\text{Thio- glycerol}]$ (M)	$\Delta E^\ddagger$ ( $\pm 0.5$ kcal mole <sup>-1</sup> )	$\Delta G^\ddagger$ ( $\pm 0.5$ kcal mole <sup>-1</sup> )	$\Delta S^\ddagger$ ( $\pm 2$ cal deg <sup>-1</sup> mole <sup>-1</sup> )
0.2	8.5	23.0	-49
0.4	14.0	23.0	-31
0.8	21.0	25.6	-7
1.2	22.0	22.6	-4
1.6	27.5	22.3	15

The interesting observation made in this study is that the energy of activation ( $\Delta E^\ddagger$ ) increases and the entropy of activation ( $\Delta S^\ddagger$ ) becomes more positive with increasing  $[\text{thiol}]$  (Table 7). The plot between  $\Delta E^\ddagger$  and  $\Delta S^\ddagger$  was linear.

The entropy of activation at  $35^\circ$  was calculated from relation (1) where  $A$  is the frequency factor. The energy of activation was calculated from the slopes of linear Arrhenius plots.

$$\Delta S^\ddagger = 4.576 \log A - 60.58 \quad \dots(1)$$

The isokinetic temperature ( $\beta$ ), calculated from the slope of the linear plot between  $\Delta E^\ddagger$  and  $\Delta S^\ddagger$  is found to be  $27^\circ$ . It may be noted that for the calculation of  $\beta$  it is usually  $\Delta H^\ddagger$  which is plotted against  $\Delta S^\ddagger$ , but in solutions there is hardly any difference (the difference is not more than the uncertainty found in the value of energy of activation itself) in the values of  $\Delta E^\ddagger$  and  $\Delta H^\ddagger$ .

**Mechanism** — In the proposed mechanism, the complex formation between reactive Ce(IV) species and monothioglycerol is anticipated which is supported by the change in colour of Ce(IV) solution on the addition of thiol solution. It is also to be noted that the extrapolated value of the absorbance at zero time changes with the change in  $[\text{thioglycerol}]$  at a given  $[\text{Ce(IV)}]$ . Further support in favour of the complex formation is provided by the observed fractional order in thioglycerol (Table 5).

The retardation in  $k'$  with increasing  $[\text{CO}_3^{2-}]$  is also consistent with the proposed inner sphere mechanism in which substrate (thioglycerol) displaces the ligand (carbonate ion) from the coordination sphere of the metal ion in an equilibrium or a number of equilibria prior to the rate limiting disproportionation of the complex. The mechanism is further supported by the linear plot between  $1/k'$  and  $[\text{CO}_3^{2-}]$  in conformity with Eq. (8).

The equation (8) indicates that the values of disproportionation constant  $k_1$  and the formation constant  $K_1$  could be calculated from the linear plots of  $1/k'$  versus  $[\text{thioglycerol}]^{-1}$  and  $1/k'$  versus  $[\text{CO}_3^{2-}]$  respectively. The values of  $k_1$  were found to be 0.0143, 0.0018 and 0.0006  $\text{sec}^{-1}$  in 0.0, 0.75 and 1.9M carbonate solutions respectively. Similarly the values of  $K_1$  were found to be 7.7, 165 and 1160 in the respective carbonate solutions. The value at zero concentration of carbonate ion was obtained by extrapolation.

However, in consistence with the proposed mechanism one would expect that  $k_1$  remains constant with varying  $[\text{CO}_3^{2-}]$  and only the composite rate coefficient  $k_1K_1$  should vary with  $[\text{CO}_3^{2-}]$ .

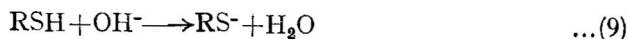
The apparent contradiction between the expected and observed results could be rationalized if one considers that a variation in  $[\text{CO}_3^{2-}]$  would simultaneously affect the reactive Ce(IV) species. Further an increase in  $[\text{CO}_3^{2-}]$  would favour the formation of dimeric Ce(IV) species<sup>8</sup>, and in this situation  $K_1$  is expected to increase and  $k_1$  to decrease as has been observed. The mechanistic scheme of the reaction thus remains unaltered and there is a change in the reactive Ce(IV) species with the variation in  $[\text{CO}_3^{2-}]$ .

The retardation in  $k'$  by the added Ce(III) is difficult to explain for there is a lack of any mathematical correlation between the observed retardation in  $k'$  and  $[\text{Ce(III)}]$ . The complex formation between Ce(III) and monothioglycerol is very much expected as Ce(III) is known to form complexes with thiols<sup>9</sup>. Such complex formation would effectively reduce the  $[\text{thioglycerol}]$  with lapse of time. This explains the observed retardation in  $k'$  and deviation from the linearity of the plots between  $\log(\text{absorbance})$  and time (Fig. 1) specially at low  $[\text{thioglycerol}]$ . However, at high concentrations of thioglycerol over Ce(IV), the complex formation

between Ce(III) and thioglycerol does not effectively decrease the  $[\text{thioglycerol}]$  until enough Ce(III) is produced in the system.

The value of the isokinetic temperature ( $\beta = 27^\circ$ ) was found to be close to the temperature range (35-50°) employed for the study of  $\Delta E^\ddagger$  and  $\Delta S^\ddagger$ , and thus it is no surprise that the free energy of activation ( $\Delta G^\ddagger$ ) was reasonably invariant.

The reactive species of monothioglycerol is considered to be  $\text{RS}^-$  where R represents  $\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}_2$  part of the thiol molecule. The  $pK_a$  value of  $-\text{SH}$  group in the thiol is not known. However, its conversion to  $\text{RS}^-$  in the basic solutions of the strength used was considered complete as shown in Eq. (9).



Eq. (9) would indicate that the rate should increase with the increase in  $p\text{H}$  of the solution as opposed to the observed effect. This could be again rationalized by accepting the formation of dimeric Ce(IV) species at higher  $p\text{H}$ , which is certainly less reactive than the monomeric Ce(IV) species. The deviation in the results associated with the increasing  $[\text{CO}_3^{2-}]$  or  $p\text{H}$  of the solution is due to a change in the nature of the reactive Ce(IV) species.

#### Acknowledgement

The authors are thankful to the UGC, New Delhi for financial assistance.

#### References

- HILL, J. & MCAULEY, A., *J. chem. Soc. (A)* (1968), 156.
- GOMWALK, U. D. & MCAULEY, A., *J. chem. Soc. (A)*, (1968), 2848.
- KAPOOR, R. C. & AGGARWAL, B. S., *Indian J. Chem.*, **10** (1972), 551.
- PANPALIA, S. S., MEHROTRA, R. N. & KAPOOR, R. C., *Indian J. Chem.*, **12** (1974), 1166.
- RICHARDSON, W. H., in *Oxidation in organic chemistry*, edited by K. B. Wiberg (Academic Press, New York), Vol. I, 1965, 243.
- DUKE, F. R. & FORIST, A. A., *J. Am. chem. Soc.*, **71** (1949), 2790.
- DUKE, F. R. & BREMER, R. F., *J. Am. chem. Soc.*, **73** (1951), 5179.
- MELLOR, J. W., *Comprehensive treatise on inorganic and theoretical chemistry*, Pt. I (Longmans, London), Vol. V, 1960, 664.
- SAKHAROVA, N. N., *Doklady Akad. Nauk SSSR*, **113** (1957), 1073.