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# Kinetics and Mechanism of the Oxidation of Citric and Glyoxylic Acids by Cerium(IV) Ion

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The mechanism proposed by Waters (*J. Chem. Soc.*, **1955**, 217) for the oxidation of $\alpha$-hydroxy acids by manganic pyrophosphate accounts for the kinetics of oxidation of citric acid by cerium(IV) ion. The oxidation appears to proceed through the initial formation of complex and subsequently through free radicals.

According to Benrath and Ruland,[1] the reaction between citric acid and cerium(IV) is a complicated one and does not follow the simple kinetic order. Willard and Young[2] oxidized citric acid by ceric sulphate with an idea to find a new method for the quantitative estimation of the hydroxy acid. They oxidized the hydroxy acid up to formic acid. The method described by them was tedious and hence Duke and Smith[3] developed a simpler method using cerium(IV) perchlorate as oxidant. In a more recent communication, Ghosh and Mehrotra[4] showed that the above reaction is a bimolecular one when reactants were of equimolar quantities. According to them both formic acid and formaldehyde are the products of oxidation. It has already been shown that formaldehyde[5] is very sensitive to cerium(IV) ion and two equivalents of cerium(IV) ion were needed per mole of formaldehyde, and so we were suspicious about its existence in the solution specially when it was stored in excess cerium(IV) for several days. Moreover, the stoichiometry of the oxidation reaction reported by different workers was different and the mechanism up to formic acid is not yet known. It was, therefore, intended to reinvestigate the reaction in details. Since glyoxylic acid is one of the possible intermediates of citric acid oxidation, the kinetics of the oxidation of glyoxylic acid has also been studied, the data for which are not available in the literature. A possible mechanism up to formic acid has been suggested.

## Experimental

Ceric ammonium sulphate was of E. Merck's (G.R.) grade and the solution of the salt in sulphuric acid was directly made. Ceric ammonium nitrate which was used for the preparation of cerium(IV) perchlorate was of 'AnalaR' grade. Cerium(IV) perchlorate was prepared by the electrolytic oxidation of Ce(III) perchlorate by the method suggested by Smith[3] and finally stored in an ice box until ready for use. Cerium(IV) ion was standardized by the iodometric method.[6] Citric acid was of 'AnalaR' grade whereas glyoxylic acid (Fluka) was purified by recrystallisation. The organic acids were standardized against standard caustic soda. The details of other reagents and experimental set up have been describede lsewhere.[7-9] The reactions have been followed volumetrically and an aliquot part of the reaction mixture was withdrawn at suitable intervals and analysed for residual cerium(IV) by the iodometric method.

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[1] A. Benrath and K. Ruland, *Z. Anorg. Allgem. Chem.*, **114**, 267 (1920).

[2] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 130 (1930).

[3] F. R. Duke and G. F. Smith, *Ind. Eng. Chem.* (*Anal. Ed.*), **15**, 120 (1943).

[4] S. Ghosh and R. N. Mehrotra, *Z. Physik. Chem.*, **1/2**, 56 (1963).

[5] G. Hargreaves and L. H. Satcliffe, *Trans. Faraday. Soc.*, **51**, 1105 (1955).

[6] G. Charlot and D. Bezier, "Quantitative Inorganic Analysis," John Wiley & Sons, New York (1957), p. 60.

[7] K. K. Sen Gupta, S. Aditya and B. N. Ghosh, *J. Ind. Chem. Soc.*, **40**, 823 (1963).

[8] K. K. Sen Gupta, *Indian J. Chem.*, **2**, 267 (1964).

[9] K. K. Sen Gupta and S. Aditya, *J. Electro-Chem. Soc., Japan*, **32**, 200 (1964).

The stoichiometry was determined by allowing reaction mixtures containing a large excess of Ce(IV) ion to stand for several days at 30°C. The excess Ce(IV) ion was then estimated as described previously. It has been found that 14.0 and 2.0 equivalents of cerium(IV) reacted per mole of citric and glyoxylic acids respectively.

The oxidations have been studied mainly in the presence of excess cerium(IV) ions (up to 10 fold excess in the case of citric and 2 fold excess in the case of glyoxylic acids) and the rate was found to be first order in both cases.

**Dependence of Rate on Ho in $H_2SO_4$.** The reactions were studied at different sulphuric acid concentrations which retarded the rate of reaction. The plot $\log K$ against $-H_0$ ($H_0$=Hammett acidity) was linear which was confirmed from two sets of experiments at two different temperatures. (Fig. 1), where the rate constant of first order was denoted by $K$ in sec.$^{-1}$ The values of $H_0$ at different sulphuric acid concentrations have been taken from the tables of Paul and Long.[10]

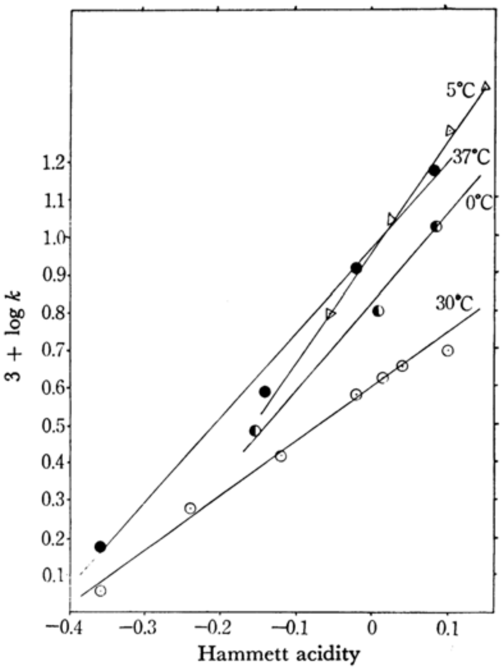

Fig. 1. Variation of $\log k$ against Hammett acidity.

⊙ ● Citric acid

◐ △ Glyoxylic acid

**Influence of Salts on the Rate Constants.** The reactions have been investigated in the presence of different salts, *e. g.*, potassium chloride, sodium perchlorate, sodium sulphate and magnesium sulphate. Sodium perchlorate had no influence on the rate constant. But there was a slight decrease of rate constant in the case of potassium chloride possibly because of the fact that chloride ion complexes[11] with cerium(IV) thereby decrease the concentration of active species of cerium(IV). Thus no effect of ionic strength has been found on the overall kinetics of the reaction. As usual both sulphate and bisulphate ions retarded the rate of reaction (Tables 1 and 2) and the plots $[SO_4]^{2-}$ against $1/K$ have been shown in Fig. 5. The inhibiting effect of addition of sulphates or sulphuric acid can be explained in the light of the complex nature of ceric sulphate in the solution. This has been discussed in previous communications.[7-9]

TABLE 1. OXIDATION OF CITRIC ACID BY Ce(IV) SULPHATE

[Ce(IV)]=0.0095 M, [Citric]=0.00376 M, $[H_2SO_4]$=0.251 M, Temp. 30°C

| Salt and its concentration | $K \times 10^3$ (sec$^{-1}$) |
|---|---|
| 0 | 16.32 |
| 0.333 M $NaClO_4$ | 16.32 |
| 0.333 M $MgSO_4$ | 15.35 |
| 0.333 M $Na_2SO_4$ | 9.212 |
| 0.333 M $KHSO_4$ | 10.45 |

TABLE 2. OXIDATION OF GLYOXYLIC ACID BY Ce(IV) SULPHATE

[Ce(IV]=0.01912 M, [Glyoxylic]=0.0144 M, $[H_2SO_4]$=0.7963 M, Temp.=2°C

| Salt and its concentration | $K \times 10^2$ (sec$^{-1}$) |
|---|---|
| 0 | 2.11 |
| $8 \times 10^{-2}$ M $NaClO_4$ | 2.11 |
| $8 \times 10^{-2}$ M $K_2SO_4$ | 1.23 |

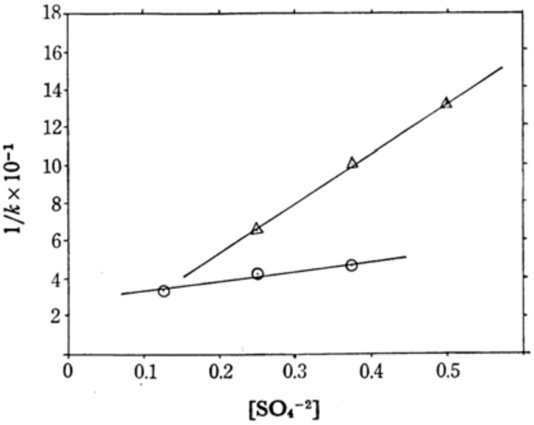

Fig. 5. Oxidation of citric acid by $Ce^{IV}(SO_4)_2$.

$[Ce^{IV}]$=0.0356 M, [Citric]=0.0139 M, $[H_2SO_4]$=0.272 M, Temp=30°C

⊙ $MgSO_4$, △ $Na_2SO_4$

**Influence of Substrate Concentration.** The reaction has been studied in various substrate concentrations and the velocity of reaction increased with the increase of substrate concentration. Figure 2 represents the plot of $1/K$ against 1/[Substrate].

**Influence of Temperature.** The velocity constants have been calculated at different temperatures. Each

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[10] F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 1 (1957).

[11] K. K. Sen Gupta, S. P. Moulik and P. K. Pal, *J. Ind. Chem. Soc.*, **40**, 217, 429 and 989 (1963).

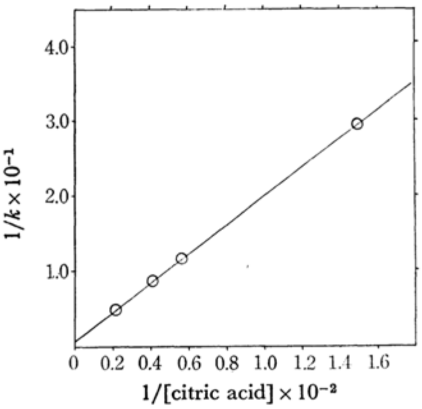


Fig. 2. Variation of substrate on the rate.

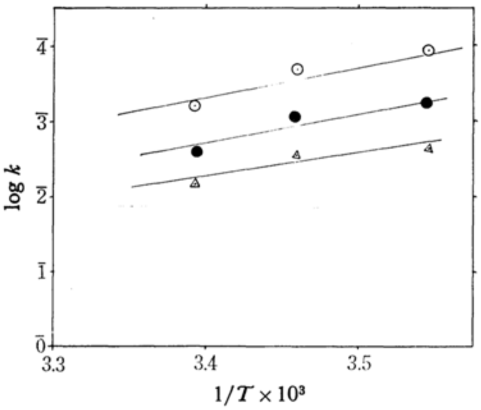


Fig. 3. Oxidation of citric acid by $Ce^{IV}$ perchlorate.

⊙ $[H_2SO_4] = 1.920$ M
● $[H_2SO_4] = 1.276$ M
△ $[H_2SO_4] = 0.869$ M

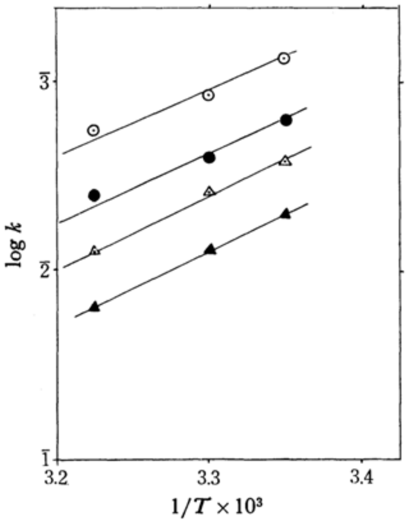


Fig. 4. Oxidation of citric acid by $Ce^{IV}(SO_4)_2$.

⊙ $[H_2SO_4] = 1.280$ M △ $[H_2SO_4] = 0.587$ M
● $[H_2SO_4] = 0.863$ M ▲ $[H_2SO_4] = 0.447$ M

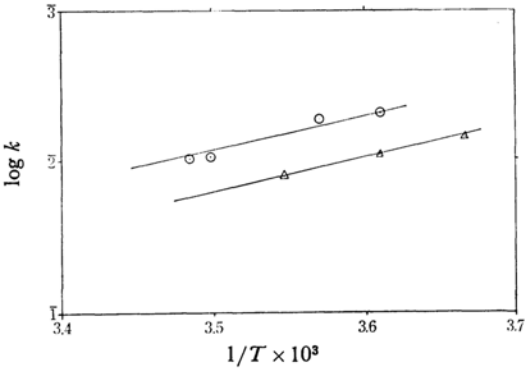


Fig. 6. Oxidation of glyoxylic acid by $Ce^{IV}(SO_4)_2$.

| | $[Ce^{IV}(SO_4)_2]$ | [glyoxylic] | $[H_2SO_4]$ |
|---|---|---|---|
| ⊙ | 0.0196 M | 0.0184 M | 1.575 M |
| △ | 0.0191 M | 0.0144 M | 1.301 M |

TABLE 3. OXIDATION OF THE ACIDS BY Ce(IV) SULPHATE

| Acid | $E$ (kcal) | $-\Delta S$ ($e.\ u.$) |
|---|---|---|
| Citric | 18.4 | 6.1 |
| Malonic | 16.1 | 16.5 |
| Glyoxylic | 10.6 | 29.6 |

TABLE 4. OXIDATION OF THE ACIDS BY Ce(IV) PERCHLORATE

| Acid | $E$ (kcal) | $-\Delta S$ ($e.\ u.$) |
|---|---|---|
| Citric | 16.1 | 13.3 |
| Malonic | 9.2 | 38.6 |

experiment was carried out at identical concentrations of sulphuric acid and the reactants. The results have been plotted (Figs. 3, 4 and 6). From the plot of log $K$ *vs.* $1/T$, the activation energy has been calculated. The values of the activation energy and entropy of activation for the different cases of oxidation have been recorded in Tables 3 and 4.

## Discussion

On oxidation of citric acid by cerium(IV) ion, $CO_2$ is evolved and formic acid remains in solution. When large excess of cerium(IV) ion was present (about 20 times excess) a total of about 14 equivalents of cerium(IV) was destroyed per mole of citric acid and this confirms the observation of Smith,[3)] and 1.95 mol of formic acid were produced per mole of the citric acid. When Ce(IV) perchlorate was used as oxidant, the reaction was completed within an hour at 30°C up to formic acid which remained unaffected even in excess of cerium(IV) ion. Therefore,

$$C_6H_8O_7 + 14Ce(IV) + 5H_2O \longrightarrow 4CO_2 + 2HCOOH + 14H + 14Ce\ (III)$$

would represent the stoichiometry of the equation. The presence of formic acid was confirmed by chromotropic acid reaction which was estimated by the usual procedure.[12] Finally, an attempt was made to distinguish between mechanisms (a) and (b).

$$\text{(a)}\quad \text{Ce(IV)} + \text{HCl} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Ce(IV)}\cdot\text{HCi}.$$

$$\text{Ce(IV)}\cdot\text{HCi} \xrightarrow{K'} \text{Ce (III)} + \text{product}$$

(subsequent steps fast)

$$\text{(b)}\quad \text{Ce(IV)} + \text{HCi} \xrightarrow{K_2} \text{Ce (III)} + \text{product}$$

(subsequent steps fast)

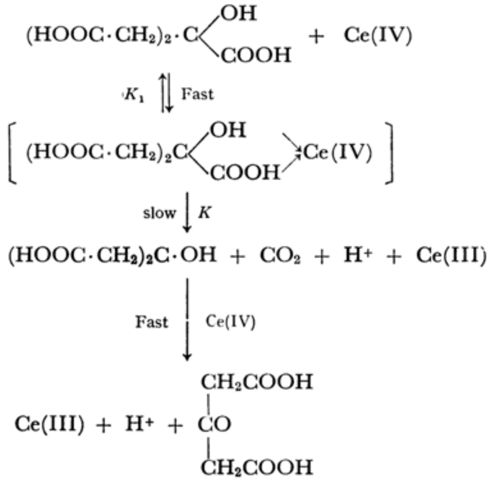
The immediate change in colour from orange to red (the colour was more prominent when ceric perchlorate was used as oxidant) which again changes to its original colour clearly shows the occurrence of an unstable chelate at the initial stage. A few attempts were made to investigate the complex by Job's method of continuous variation but failed owing to its highly unstable character. The kinetic evidence only indicates that citric acid is oxidized *via* complex formation and the plot $1/K$ against 1/[substrate] labels[13] the corresponding $1/K$ axis indicating information of a complex. This shows that the rate dependence is according to (a)

$$\frac{-\mathrm{d}[\text{Ce(IV)}]}{\mathrm{d}t} = \frac{K'K[\text{Ce(IV)}][\text{HCi}]}{1+K[\text{HCi}]}$$

and not the simple dependence (b)

$$-\frac{\mathrm{d}[\text{Ce(IV)}]}{\mathrm{d}t} = K[\text{Ce(IV)}][\text{HCi}]$$

The complex finally decomposes to give a free radical[14] the formation of which was tested by induced reduction of mercuric chloride. During the oxidation of citric acid by Ce(IV) ion, mercuric chloride was found to be reduced indicating the formation of a reducing intermediate,[15] *e. g.*, free radical. The reduction was more prominent in concentrated solutions of citric acid and Ce(IV) ion. The free radical further picks up Ce(IV) ion and is oxidised in the following manner.



The subsequent steps up to formic acid are also considered to be very fast and an attempt was made to investigate the initial rates of the expected intermediates under comparable conditions. The concentration of the oxidant was three times that of the substrate and the experiments were carried out at 30°C and at sulphuric acid concentration of 0.5 M. The values of $K_{\text{Citric}}$ and $K_{\text{Malonic}}$ were found to be $4.99\times10^{-3}$ ($\text{sec}^{-1}$) and $10.07\times10^{-3}$ ($\text{sec}^{-1}$) respectively. Again under the same experimental condition glyoxylic acid was instantaneously oxidized and with two fold excess of the oxidant at 5°C, $K_{\text{glyoxylic}}$ was found to be $1.84\times10^{-2}$ ($\text{sec}^{-1}$). The comparison of the values of activation energy of Table 3 also shows the following order:

$$K_{\text{citric}} < K_{\text{malonic}} < K_{\text{glyoxylic}}$$

The oxidation of expected acetone dicarboxylic acid may now take place either through acetone which is formed by the successive decarboxylations of two carboxyl groups as in the case of the oxidation of citric acid[16] by potassium permanganate or by the cleavage of C–C bond of citric acid molecule. It is interesting to examine which of the paths explains the following experimental results. In the oxidation of acetone by Ce(IV) sulphate, Hinshelwood and Shorter[12] found that 8.6 equivalents of Ce(IV) ion are required per mole of acetone even at 70°C. So if acetone dicarboxylic acid is to give acetone and then subsequently oxidized it would need only 8.6 equivalents with the overall consumption of 10.6 equivalents of the oxidant. This rules out the possibility that $CH_3$-$COCH_3$ is an intermediate. Therefore acetone dicarboxylic acid is oxidized to give one mole of malonic acid and one mole of glyoxylic acid with the overall consumption of four equivalents of Ce(IV) ions in the following way (Scheme 1.)

The formation of glyoxylic acid *via* glycollic acid is not possible as the oxidation of glycollic acid is too slow.[9] The oxidation[17] of malonic acid by cerium(IV) ion may be represented stoichiometrically by the equation:

$$\begin{aligned} CH_2(COOH)_2 + 6\text{Ce(IV)} + 2H_2O &\longrightarrow \\ 2CO_2 + HCOOH + 6\text{Ce(III)} &+ 6H^+ \end{aligned}$$

The possible mechanism of the above reaction has already been discussed in the previous communi-

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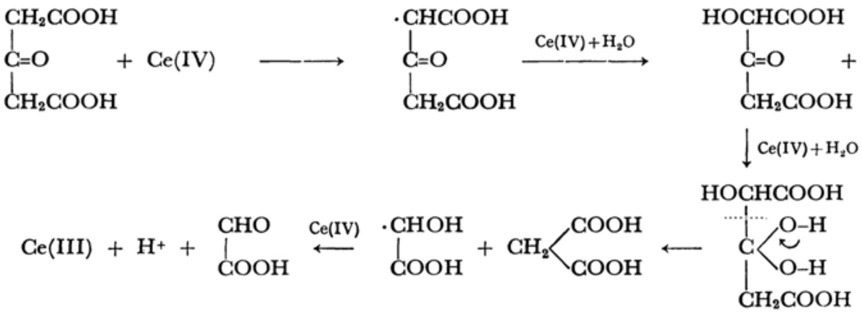
[12] C. N. Hinshelwood and J. Shorter, *J. Chem. Soc.*, **1950**, 3276.

[13] H. Lineweaver and D. Burke, *J. Am. Chem. Soc.*, **56**, 81 (1934).

[14] W. A. Waters and P. Levesley, *J. Chem. Soc.*, **1955**, 217.

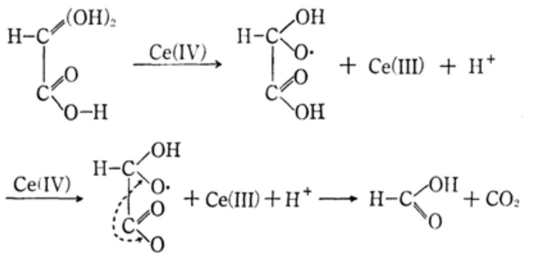
[15] A. Y. Drummond and W. A. Waters, *ibid.*, **1953**, 2836.

[16] G. V. Bakore and R. Shanker, *Indian J. Chem.*, 1963 (1693).



Scheme 1

cation.[17] Malonic acid is oxidized initially to give tartronic acid which by fast steps is further oxidized to produce glyoxylic acid. Glyoxylic acid is then hydrated and oxidized instantaneously at 30°C to give formic acid with the consumption of two equivalents of Ce(IV) ion.



The other mole of glyoxylic acid which has been obtained from acetone dicarboxylic acid has also been oxidized in the above manner to give other mole of formic acid.

While discussing the mechanism through which the reaction proceeds, it has been suggested that the first step is the formation of a complex between ceric ion and the substrate. The question that would occur is why one prefers to assume an initial complex formation and then an electron abstraction by ceric ion to give cerous ion. The possible alternative would be to assume the initiation step as in the case of the oxidation by hydrogen peroxide or a more plausible analogue than by $Co^{3+}$ salt. In cases of both these oxidation processes, formic acid is found to be oxidized, whereas in the oxidation by Ce(IV) salt, formic acid is never oxidized but constitutes one of the products of oxidation reaction. The choice, therefore, falls on the mechanism in which the initiation of the reaction through the formation of a complex and abstraction of electron by ceric ion, is a general first step. The radical would next be involved in reactions be lost, before it can be stabilized. That the reaction is not ionic is supported by the fact that ionic strength had no effect on the rate of oxidation in systems contain- ing perchlorates.

It has been observed that when the oxidant is in excess, the reaction (the consumption of ceric) follows a first order rate. This has been explained on the basis that a steady state concentration[18] of free radical is attained and this finally reacts with ceric ion.

When the organic acid is equivalent or in excess the radical will react with the complex (if it is stable) and then the reaction is apparently a second order one. This is possibly what has been observed by Ghosh and Mehrotra.[4] On the other hand, if the complex is weak the radical will react with ceric ion and the reaction will continue to be the first order. Thus if the organic acid forms a stable complex with the ceric ion, the reaction will pass to one of second order when it goes from excess oxidant to excess of the substrate. Thus stability of the complex plays a role in determining the order of the reaction.

Concerning the thermodynamic constants in the presence of different oxidants, it has been observed that the activation energy in the case of the oxidation by Ce(IV) perchlorate is less than that of the Ce(IV) sulphate. This is possibly due to the fact that sulphate ion forms strong complexes with Ce(IV) ion while perchlorate ion is a weak complex forming anion. Therefore Ce(IV) sulphate will react more slowly with the substrate than Ce(IV) perchlorate. This may also be explained in the light of oxidation potential of Ce(IV)—Ce(III) system which depends on acidity as well as on the kinds of anion present. The oxidation potential of Ce(IV) perchlorate (1 M—2 M acid) is 1.87 V whereas that of Ce(IV) sulphate in sulphuric acid (1M—2 M acid) is 1.44 V which shows that the oxidizing capacity of Ce(IV) sulphate should be less than that of Ce(IV) perchlorate. On the other hand the reaction should be retarded in Ce(IV) sulphate solution requiring a greater energy in the medium.

Thanks are due to Prof. B. N. Ghosh and Dr. M. N. Das for providing laboratory facilities.

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[17] K. K. Sen Gupta and S. Aditya, *Z. Physik. Chem.*, **38**, **1/2**, 25 (1963).

[18] M. Bodenstein, *ibid.*, **85**, 329 (1913).