

KINETICS AND MECHANISM OF *O*-XYLENE OXIDATION BY Ce(IV) IN AQUEOUS ACIDIC MEDIUM

GABRIELA-CRISTINA BUCȘA*, CLAUDIA GEMMA MUREȘANU
and IOAN BÂLDEA

*Department of Physical Chemistry, Faculty of Chemistry and Chemical Engineering of "Babeș-Bolyai" University, 11 Arany Janos, 3400, Cluj-Napoca, Romania (*e-mail: gbucsa@chem.ubbcluj.ro)*

ABSTRACT. The oxidation of *o*-xylene in aqueous acidic media, using perchloric acid, has been followed spectrophotometrically. A first-order dependence on Ce(IV) concentration and a complex dependence on *o*-xylene and hydrogen ion concentrations have been established. The effect of ionic strength on the reaction rate has been studied and activation parameters were calculated. The global reaction rate is consistent with a mechanism involving the rapid formation of a complex, suffering an intramolecular electron transfer.

Keywords: cerium, *o*-xylene, kinetics and oxidation

INTRODUCTION

In acidic media, Ce(IV) is a strong oxidizing agent and is widely used in analytical and inorganic chemistry. The oxidation of different types of organic compounds is mentioned in literature and the kinetics of such reactions has been studied¹⁻²⁸. The rate laws and mechanisms for the oxidation of toluene and some substituted toluene in aqueous sulphuric acid media were reported²⁹⁻³¹, and in the case of *p*-xylene oxidation with Ce(IV), the activation energy has been determined³⁰. In order to get more details concerning the kinetic and the mechanism of *o*-xylene oxidation, we have investigated this reaction by using perchloric acid as a hydrogen ion source, where no complex formation between Ce(IV) and ClO₄⁻ is to be expected.

EXPERIMENTAL

The chemicals used in this study were of reagent grade purity, purchased from commercial sources (Reactivul Bucharest, Merck and Fluka) and employed without further purification.

Kinetic measurements were performed by means of an Able Jasco V-530 spectrophotometer, provided with a temperature jacket surrounding the cell holder.

The cuvette jacket was connected to a Lauda M-20 recirculatory water bath. Reaction mixtures were prepared directly in the quartz cell of the spectrophotometer with 5cm-path length. A rapid adding of a measured amount of cerium (IV) stock solution over the reaction mixture containing HClO_4 , NaClO_4 , *o*-xylene in twice-distilled water at desired concentration, started the reaction. The reaction progress was followed by monitoring the decrease of absorbance at 315 nm, where the UV/VIS spectrum of Ce(IV) exhibits an absorption band.

RESULTS AND DISCUSSIONS

Preliminary investigations

Check of Lambert-Beer law. The validity of Lambert-Beer law has been verified over the concentration range used, because the kinetic study consists in absorbance measurements. Figure 1 presents the linear dependence of absorbance upon Ce(IV) concentration in the absence and the presence of *o*-xylene.

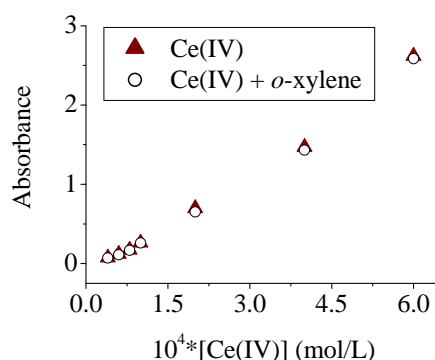


Fig. 1. Dependence prescribed by Lambert-Beer law at 315 nm
 $[\text{H}^+] = 1 \text{ mol/L}$; $\mu = 1 \text{ mol/L}$; $[\text{o-xilen}]_0 = 4 \cdot 10^{-4} \text{ mol/L}$; $t = 20^\circ\text{C}$

As it can be seen, only a slight decrease of molar absorption coefficient occurs when the mixture contains also *o*-xylene, but the linearity is maintained. Table 1 contains the values for the molar absorption coefficients for the experimental conditions. These facts suggest that a new absorbing species is formed, either in a small concentration, or it absorbs similarly to Ce(IV).

Table 1

Molar absorptivities in the absence and the presence of *o*-xylene

Reaction mixture	$[\text{H}^+] = 1 \text{ mol.L}^{-1}$; $[\text{ClO}_4] = 1 \text{ mol.L}^{-1}$; $\mu = 2 \text{ mol.L}^{-1}$; $t = 20^\circ\text{C}$			
	Ce(IV)		Ce(IV) + <i>o</i> -xylene $4 \cdot 10^{-4} \text{ mol.L}^{-1}$	
λ , nm	315	320	315	320
$\epsilon \text{ L.mol}^{-1}\text{cm}^{-1}$	4039 ± 198	4047 ± 207	3958 ± 209	3898 ± 201

Check for an intermediate species formation. By recording the spectra of reaction mixture immediately after mixing at 20°C and various increasing concentration of organic hydrocarbon, a small but systematic decrease of the intensity of Ce(IV) absorption band and the occurrence of an isosbestic point located at 375 nm have been noticed (fig. 2). This is brought about by the presence of a new absorbing species besides Ce(IV). It can be a complex involving Ce(IV) and the substrate.

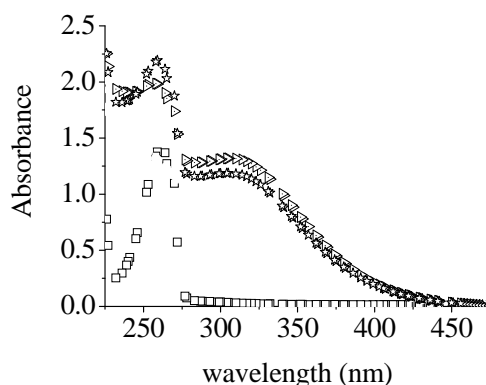


Fig. 2. Some spectra recorded immediately after mixing of Ce(IV) and o-xylene at various concentration (8.0×10^{-5} to 1.0×10^{-3}) of o-xylene

Stoichiometry determination. The stoichiometry of the reaction has been determined by a spectrophotometrical titration. Various mixtures having increasing ratios of [o-xylene]:[Ce(IV)] were allowed to react to completion at constant acidity. The absorbance values of the unreacted Ce(IV) were determined. Part of the Ce(IV) was consumed by the water molecule oxidation. Nevertheless, the mixture reacted the same period of time, and comparison has been done to the blank probe. The plot of absorbance difference between blank probe and those with o-xylene shows a turning point at the ratio 0.5, as can be seen in fig. 3. It predicts a ratio of 2 Ce(IV) ions to a molecule of o-xylene, indicating the oxidation yields o-methylbenzylic alcohol as the main oxidation product.

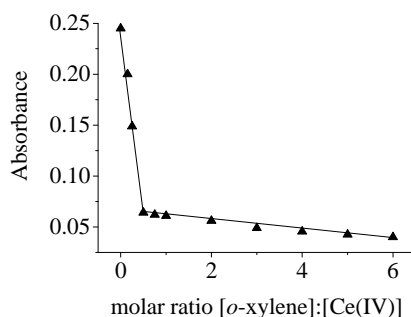
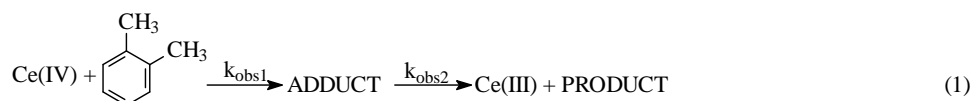


Fig. 3. Remainder absorbance difference at various molar ratios.

Kinetics

Experimental measurement consists in absorbance readings against time.

According to the shape of the experimental curve absorbance versus time, which looks like a biphasic plot, the oxidation of *o*-xylene by Ce(IV) consists in two consecutive stages of the type:



The first stage, perceptible at low degrees of transformation, could be attributed to the formation of an adduct between Ce(IV) and *o*-xylene. The second stage, perceptible at higher degrees of transformation, may be associated with the redox process consisting of an inner electron transfer within the complex, yielding the products of the reaction.

The reaction order with respect to Ce(IV) was determined from the dependence $\lg(r) = f(\lg[\text{Ce(IV)}])$. As can be seen in the figure 4, first-order with respect to cerium has been found for both stages of the reaction.

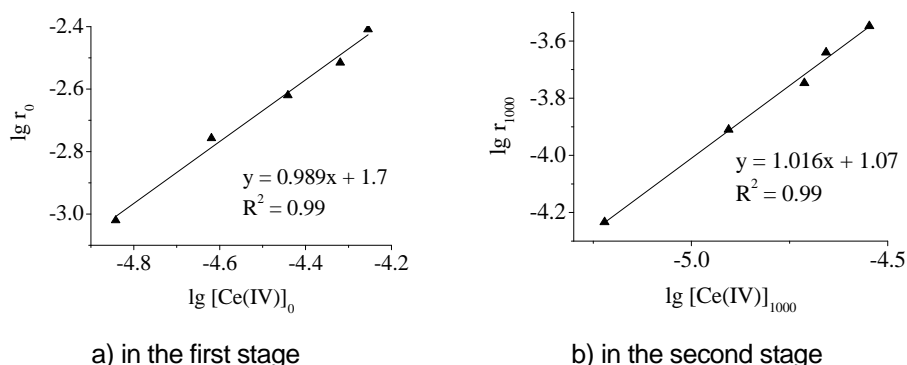


Fig. 4. Determination of reaction order with respect to cerium (IV) in the two stages of the reaction described above

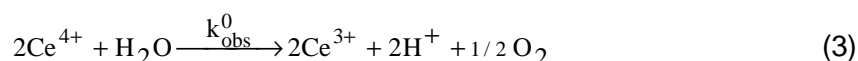
The experimental curves, $A = f(t)$, were the subject of derivation, at the initial moment and at $t = 1000\text{s}$, while the reaction rates and the corresponding concentrations of cerium were calculated by taking $\varepsilon = 4039 \text{ M}^{-1} \text{ cm}^{-1}$.

Once it has been established, we preferred to determine the rate constants by a non-linear fitting of the experimental $A = f(t)$ curves, with the bi-exponential equation:

$$A - A_{\infty} = C_1 \exp(-k_{\text{obs}1}^0 \cdot t) + C_2 \exp(-k_{\text{obs}2}^0 \cdot t) \quad (2)$$

which describes the decay of the absorbance of the limiting component in a first order follow up reaction. A and A_{∞} stand for the absorbance at actual time and at the end of the reaction respectively. The parameters C_1 and C_2 are constants including the molar absorbance coefficients and Ce(IV) initial concentration. k_{obs1}^0 and k_{obs2}^0 are apparent rate constants of the two reaction steps.

Parallel to the oxidation of *o*-xylene, oxidation of water by Ce(IV) takes place, according to the stoichiometry:



The kinetics was of a first-order. We determined the influence of different parameters over the oxidation of water. Because in the literature³² we found that Ce(III) (which is a product of the reaction) diminishes the rate of the water oxidation reaction we put it in the reaction mixture in equal concentration to Ce(IV). The experimental curves for the water oxidation reaction were determined by a fitting method with the equation:

$$A - A_{\infty} = C_3 \exp(-k_{obs}^0 \cdot t) \quad (4)$$

Once we had all the rate constants, we subtract the rate constants for the oxidation of water from the rate constants of the overall reaction as follows:

$$k_{obs1} = k_{obs1}^0 - k_{obs}^0 \quad (5)$$

$$k_{obs2} = k_{obs2}^0 - k_{obs}^0 \quad (6)$$

where: k_{obs1} and k_{obs2} are the observed first-order rate constants of the xylene reaction for the first and the second step and k_{obs}^0 is the observed first-order rate constant for the water oxidation reaction.

The effect of *o*-xylene excess concentration upon the apparent rate coefficient, at constant hydrogen ion concentration and ionic strength, is presented in Table 2. Observed rate constants were obtained using equation (5) and (6).

In order to find the reaction order with respect to the *ortho*-xylene concentration, the logarithm of the apparent rate constants were plotted against the logarithm of *ortho*-xylene concentration excess.

Table 2

Effect of *o*-xylene concentration on the apparent rate constants.
 $[\text{Ce(IV)}] = [\text{Ce(III)}] = 8 \cdot 10^{-5} \text{ mol.L}^{-1}$; $[\text{H}^+] = 1 \text{ mol.L}^{-1}$; $\mu = 1 \text{ mol.L}^{-1}$; $t = 40^\circ\text{C}$

$10^4 \cdot [\text{o-xylene}]$ (mol/L)	$10^3 \cdot k_{\text{obs1}}$ (s ⁻¹)	$10^4 \cdot k_{\text{obs2}}$ (s ⁻¹)
4	1.13	0.86
6	1.73	1.06
7	1.94	1.14
8	2.22	1.23
9	2.58	1.31
10	2.9	1.39

For the first stage of reaction, we found first-order dependence with respect to *o*-xylene and sub-unit fraction order for the second stage. The best fit, we could find for the data from table 1 was obtained by using the equations:

$$k_{\text{obs1}} = (-3 \cdot 10^{-5} \pm 6 \cdot 10^{-5}) + (2.89 \pm 0.08)[\text{o-xylene}]_0 \quad (7)$$

$$k_{\text{obs2}} = \frac{(0.32 \pm 0.06)[\text{o-xylene}]_0}{1 + (1308 \pm 484)[\text{o-xylene}]_0} \quad (8)$$

It is easy to recognize in the dependence of the second stage a Michaelis – Menten pattern, suggesting also the involvement of an intermediate.

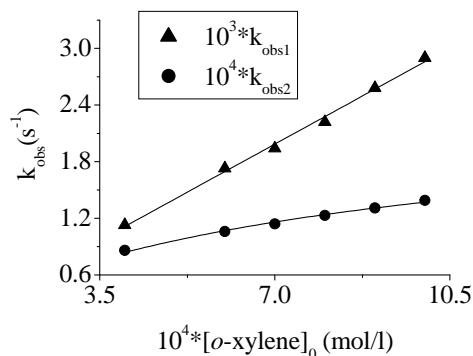


Fig. 5. The effect of *o*-xylene for the first and the second stage of the reaction;
 $[\text{Ce(IV)}] = [\text{Ce(III)}] = 8 \cdot 10^{-5} \text{ mol/L}$; $[\text{H}^+] = 1 \text{ mol/L}$; $\mu = 2 \text{ mol/L}$; $t = 40^\circ\text{C}$

Even under high acid concentration, the hydrolysis of Ce(IV) ion, and the formation of polynuclear ions complicate the kinetics of Ce(IV) reaction. It is revealed from the influence of hydrogen ion concentration on the rate constant that it is quite complex, investigated in the limits presented in the Table 3.

Table 3
Effect of hydrogen ion concentration on the apparent rate constant; $[Ce(IV)] = 8 \cdot 10^{-5} \text{ mol.L}^{-1}$;
 $[Ce(III)] = 8 \cdot 10^{-5} \text{ mol.L}^{-1}$; $[o\text{-xylene}] = 4 \cdot 10^{-4} \text{ mol/L}$; $\mu = 3 \text{ mol.L}^{-1}$; $t = 40^\circ\text{C}$

$[H^+]$ (mol.L ⁻¹)	$10^3 \cdot k_{\text{obs1}}$ (s ⁻¹)	$10^4 \cdot k_{\text{obs2}}$ (s ⁻¹)
0.5	11.39	0.99
1	8.37	2.25
1.5	6.9	3.09
2	5.87	4.22
2.5	5.12	5.34

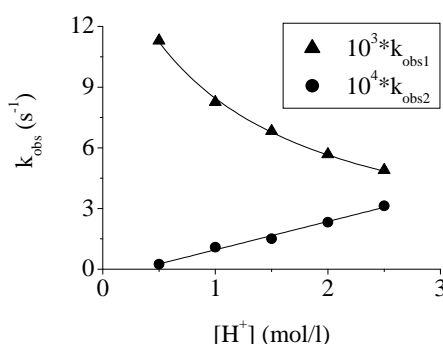


Fig. 6. Dependence of rate constant upon the hydrogen ion concentration;
 $[Ce(IV)] = [Ce(III)] = 8 \cdot 10^{-5} \text{ mol.L}^{-1}$; $[o\text{-xilen}] = 4 \cdot 10^{-4} \text{ mol.L}^{-1}$; $\mu = 3 \text{ mol/L}$; $t = 40^\circ\text{C}$.

As it can be seen the concentration of hydrogen ion has an opposite effect on the two stages of the reaction (fig. 6). It diminishes the rate constants of the first step, according to equation above, and revealing the loss of the proton:

$$k_{\text{obs1}} = \frac{(0.016 \pm 1.24 \cdot 10^{-3})}{1 + (0.9 \pm 0.14)[H^+]} \quad (9)$$

and causes a linear increase of the rate constant on the hydrogen ion concentration of the form:

$$k_{\text{obs2}} = (2.1 \cdot 10^{-4} \pm 1 \cdot 10^{-5}) [H^+] \quad (10)$$

The influence of ionic strength on the reaction rate was also studied. As can be seen from table 4, ionic strength has a positive effect on both the first and the second stages of the reaction. Although Debye – Hückel relation for activity coefficients could be applied only at lower ionic strengths ($\approx 10^{-2} \text{ mol/L}$) we have plotted equation of the form:

$$\ln k_\mu = \ln k_{\mu=0} + \frac{2Az_A z_B \sqrt{\mu}}{1 + Ba\sqrt{\mu}} \quad (11)$$

Table 4

Influence of ionic strength on the rate constants for both processes
 $[\text{Ce(IV)}] = [\text{Ce(III)}] = 8.0 \times 10^{-5} \text{ mol.L}^{-1}$; $[\text{o-xylene}] = 4.0 \times 10^{-4} \text{ mol.L}^{-1}$; $t = 40^\circ\text{C}$

$\mu \text{ (mol.L}^{-1}\text{)}$	$10^3 k_{\text{obs1}} \text{ (s}^{-1}\text{)}$	$10^4 k_{\text{obs2}} \text{ (s}^{-1}\text{)}$
0.5	1.39	0.28
1	2.19	0.56
1.5	2.88	0.77
2	4.08	1.03
2.5	5.28	1.25
3	6.17	1.43

which can be seen in the figure 7.

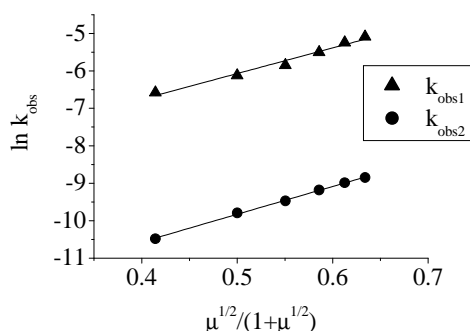


Fig. 7. Dependence of rate constant upon ionic strength. Debye – Huckel representation;
 $[\text{Ce(IV)}] = [\text{Ce(III)}] = 8.0 \times 10^{-5} \text{ mol.L}^{-1}$; $[\text{o-xylene}] = 4.0 \times 10^{-4} \text{ mol.L}^{-1}$;
 $[\text{H}^+] = 0.5 \text{ mol.L}^{-1}$ and $t = 40^\circ\text{C}$

The relation (11) lead to the following expressions with our data:

$$\ln k_{\text{obs1}} = (-9.49 \pm 0.2) + (6.83 \pm 0.36) \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad R^2 = 0.960, \chi^2 = 0.013, N = 18$$

$$\ln k_{\text{ap2}} = (-13.52 \pm 0.1) + (7.4 \pm 0.19) \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \quad R^2 = 0.991, \chi^2 = 0.0026, N = 18$$

As can be seen in the figure 6, the plots are linear for both stages. Even so, we can only say that the influence of ionic strength has a contribution of primary salt effect as well as secondary salt effect and involves ions of like charges.

Activation parameters were determined for both stages of the reaction from the Arrhenius and from the Eyring plot. The effect of the temperature is presented in table 5. The plots of the linear form of Arrhenius and Eyring equations were linear with quite good correlation coefficients. The results are presented in table 6.

Table 5

Temperature effect on the first-order rate constants. $[H^+] = 1.5 \text{ mol.L}^{-1}$; $\mu = 3 \text{ mol.L}^{-1}$; $[Ce(IV)] = [Ce(III)] = 8.0 \times 10^{-5} \text{ mol.L}^{-1}$; $[o\text{-xylene}] = 4.0 \times 10^{-4} \text{ mol.L}^{-1}$

Temp. (K)	308	313	318	323	328	333
$10^2 k_{\text{obs1}} (\text{s}^{-1})$	0.46	0.56	0.66	0.93	1.81	2.64
$10^4 k_{\text{obs2}} (\text{s}^{-1})$	0.46	0.54	1.13	1.39	2.69	3.4

The relatively small values of activation energy and activation enthalpy could be explained by the involvement of an adduct formation pre-equilibrium, and intramolecular electron transfer. Concerning the rate determining step the rate law is, depending on the concentrations of organic compound, of hydrogen ion and of oxidizing agent, of the form:

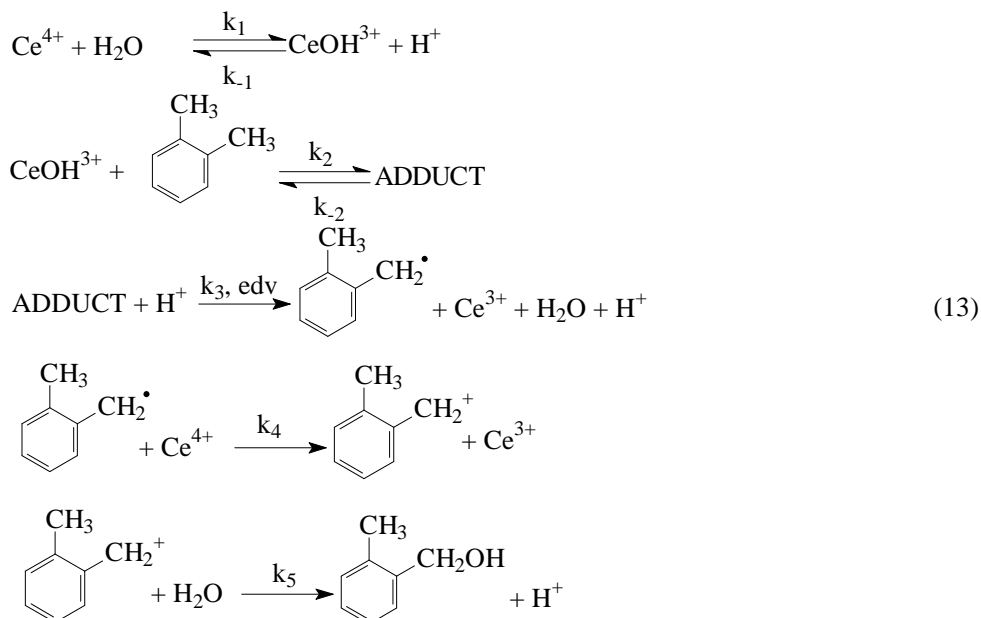
$$r = k_2 \frac{a [o\text{-xylene}]_0 [H^+] [Ce(IV)]}{1 + b [o\text{-xylene}]_0} \quad (12)$$

Table 6

Activation parameters for the two stages of oxidation of o-xylene.

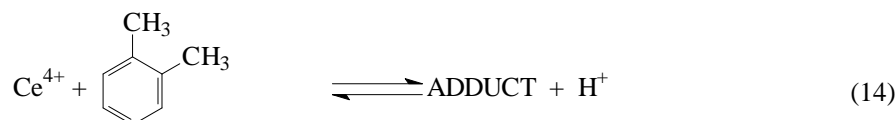
Stage	E_a (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger (J/K)
1	61.1 ± 7.8	58.5 ± 7.7	-101.6 ± 0.02
2	87 ± 4.9	84.4 ± 4.9	-55.6 ± 0.2

A reaction mechanism (13) can be suggested, based on spectral measurements, the stoichiometry, the rate law and literature data. It involves the formation of an adduct between o-xylene and the hydrocomplex of Ce(IV),



followed by the inner electron transfer. This step is the rate determining. The subsequent steps are very rapid leading finally to the major oxidation product, which is *o*-methylbenzylic alcohol.

If the first two pre-equilibria from the mechanism are combined as follows:



than the rate equation determined from the mechanism suggested by us will have the form:

$$r = k_3 K_h K_2 \frac{[\text{Ce(IV)}][\text{H}^+][o\text{-xylene}]_0}{1 + K_h[\text{H}^+] + K_2[o\text{-xylene}]_0} \quad (15)$$

in accordance with the kinetic and extra-kinetic data. The complex between Ce(IV) named here adduct is formed at the interaction of Ce(OH)^{3+} and xylene, when a hydrogen ion coming from a methyl group bonds to hydroxyl ion and carbon anion bonds to Ce(IV) entering its coordination sphere. In the rate-determining step the supplementary proton seems to be necessary to stabilize the methylbenzyl free radical formed.

REFERENCES

1. Das A. K., Das M., *J. Chem. Soc. Dalton Trans.*, **1994**, 589.
2. Willard H. H., Young P., *J. Am. Chem. Soc.*, **1930**, 52, 132.
3. Pondit A. K., Das A. K., Banerjea D., *Transitionmet. Chem.*, **1991**, 16, 324.
4. Hintz H. L., Jhonson D. C., *J. Org. Chem.*, **1967**, 32, 556.
5. Duke F. R., Bremer R. F., *J. Am. Chem. Soc.*, **1951**, 73, 5179.
6. Waters W. A., Jones J. R., Litter J. S., *J. Chem. Soc.*, **1961**, 240.
7. Muhammad S. S., Rao K. V., *Bull. Chem. Soc. Jpn.*, **1963**, 36, 943.
8. Ardon M., *J. Chem. Soc.*, **1957**, 1811.
9. Hargreaves G., Sutcliffe L. H., *Trans. Faraday Soc.*, **1955**, 51, 1105.
10. Sankhla P. S., Mehrotra R. N., *J. Inorg. Nucl. Chem.*, **1972**, 34, 3781.

11. Rangaswamy M., Santappa M., *Acta Chim. Acad. Sci. Hung.*, **1968**, 56, 413.
12. Grover V. K., Gupta Y. K., *J. Inorg. Nucl. Chem.*, **1969**, 31, 1403.
13. Wells C. F., Husain M., *Trans. Faraday Soc.*, **1970**, 66, 679.
14. Balasubramanian T. R., Venkatasubramanian N., *Indian J. Chem.*, **1970**, 8, 305.
15. Dayal R., Bakore G. V., *Indian J. Chem.*, **1972**, 10, 1165.
16. Rao G. N., *Indian J. Chem.*, **1970**, 8, 328.
17. Krishna B., Tewari K. C., *J. Chem. Soc.*, **1961**, 3077.
18. Gopal Rao G., Madhava Rao B., *Anal. Chim. Acta*, **1972**, 59(3), 461.
19. Trahanovsky W. S., Young L. B., *J. Org. Chem.*, **1966**, 31, 2033.
20. Syper L., *Tetrahedron Letters*, **1966**, 37, 4493.
21. Ignaczak M., Dziegiec J., Markiewicz M., *Pol. J. Chem.*, **1980**, 54, 1121.
22. Sethuram B., Muhammad S. S., *Acta Chim. Acad. Sci. Hung.*, **1965**, 46, 115.
23. Sethuram B., Muhammad S. S., *Acta Chim. Acad. Sci. Hung.*, **1965**, 46, 125.
24. Trahanovsky W. S., Young L. B., Brown G. L., *J. Org. Chem.*, **1967**, 32, 3865.
25. Paquette D., Zador M., *Can. J. Chem.*, **1968**, 46, 3507.
26. Melicherik M., Treindl L., *Chem. Zvesti*, **1981**, 35, 153.
27. Wiberg K. B., Ford P. C., *J. Am. Chem. Soc.*, **1969**, 91, 124.
28. Ignaczak M., Deka M., *Pol. J. Chem.*, **1980**, 54, 259.
29. Baciocchi E., Rol C., Sebastiani G. V., *J. Chem. Research(Synopsis)*, **1983**, 9, 232.
30. Ramaswamy M. S., Venkatachalapathy M. S., Udupa H. V. K., *Bull. Chem. Soc. Jpn.*, **1962**, 35, 214.
31. Radhakrishna P. S., Pati S. C., *Chem. Ind.*, **1967**, 17, 702.
32. D. Kolp, H. C. Thomas, *J. Am. Chem. Soc.*, **1949**, 71, 3047.