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Dedicated to Professor Ionel Haiduc
on the occasion of his 65th birthday

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

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ABSTRACT. The oxidation of p-xylene by Ce(IV) in aqueous acidic media has been followed spectrophotometrically in a reaction mixture containing $HClO_4$ and $NaClO_4$. The effects of p-xylene and hydrogen ion concentration on the reaction rate have been studied. The kinetic study revealed a two-stage process. The experimental rate law exhibits a first-order dependence on Ce(IV) concentration and a complex dependence on p-xylene and hydrogen ion concentrations. Apparent activation parameters were also calculated. A reaction mechanism involving the formation of an adduct between p-xylene and Ce(IV) in the first step was suggested. The adduct is the subject of an inner electron transfer, in the next step, in order to yield the products.

Keywords: cerium, p-xylene, kinetics

Cerium is a strong oxidizing agent due to its relatively high oxidation potential in acidic media[1]. Although it is a widely used as oxidizing agent in analytical and inorganic chemistry, less attention has been given to its use to oxidize in organic compounds[2]. Nevertheless, the oxidation of different types of organic compounds is mentioned in literature and the kinetics of such reactions has been studied.[3-19] The rate laws and mechanisms for the oxidation of toluene and some substituted toluenes in aqueous sulphuric acid media are reported [20, 21, 22], and in the case of p-xylene oxidation with Ce(IV), the activation energy has been determined [21]. In order to get more details concerning the kinetic and the mechanism of p-xylene oxidation, we have investigated this reaction in perchloric acid medium, where no complex formation between Ce(IV) and ClO_4^- is to be expected.

EXPERIMENTAL

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

Kinetic measurements were performed by means of a V-530 Able Jasco spectrophotometer, provided with a temperature jacket surrounding the cell holder. The jacket was connected to a Lauda M20 recirculatory water bath. Reaction mixtures were prepared directly in the quartz cell of the spectrophotometer with the path length of 5 cm. The reaction was started by adding a measured amount of cerium stock solution over the reaction mixture ($HClO_4$, $NaClO_4$, p-xylene and twice-distilled water). The reaction was followed by monitoring the decrease of absorbance at 315 nm, where the UV/VIS spectrum of Ce(IV) exhibits a maximum.

RESULTS AND DISCUSSIONS

The stoechiometry of the reaction has been determined by a spectrophotometrical titration.

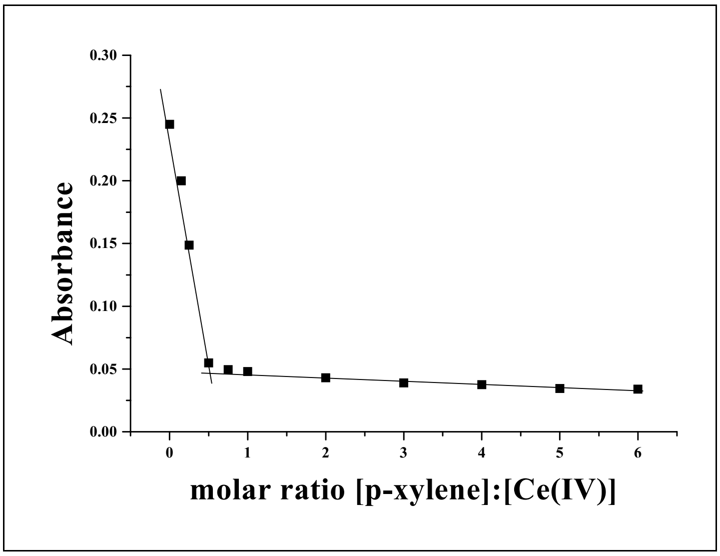


Figure 1. Determination of reaction stoechiometry

Various mixtures having increasing ratios of [p-xylene]:[Ce(IV)] were allows to react to completion at a constant acidity. The absorbance of the unreacted Ce(IV) were determined. The plot of absorbance difference between blank probe and those with p-xylene shows a turning point at the ratio 0.5, as can be seen in figure 1. It predicts the stoechiometry of 2 Ce(IV) for a molecule of p-xylene, indicating the oxidation to p-methylbenzylic alcohol.

Absorbance readings were processed according to the integrated form of a first-order rate law:

$$\ln(A - A_{\infty}) = k_{obs2}t \qquad (1)$$

where: A_{∞} ,A are the measured values of absorbance at the end and at different time moments of the reaction.

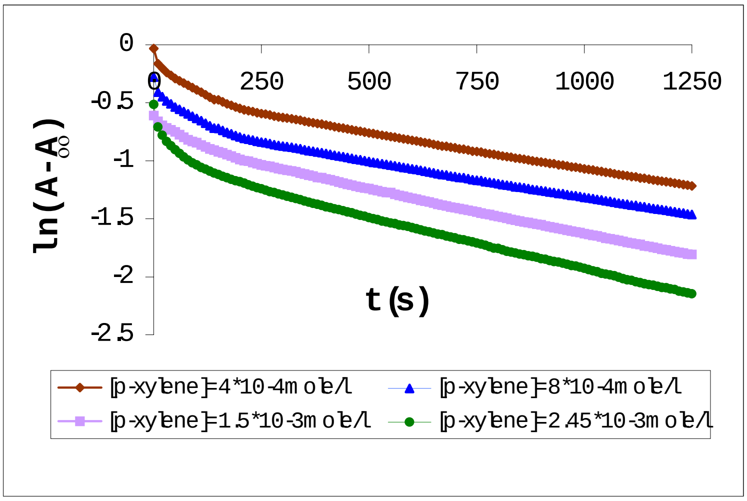
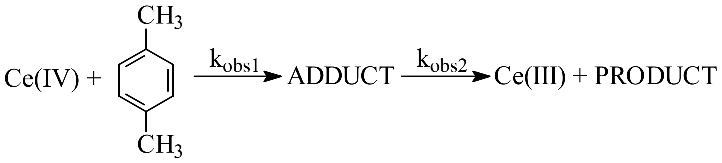


Figure 2. First order dependence for the oxidation reaction between p-xylene and Ce(IV); [Ce(IV)] = $8*10^{-5}$ mol/l; [H^+] = 1 mol/l; j = 2 mol/l; t = 40^0C

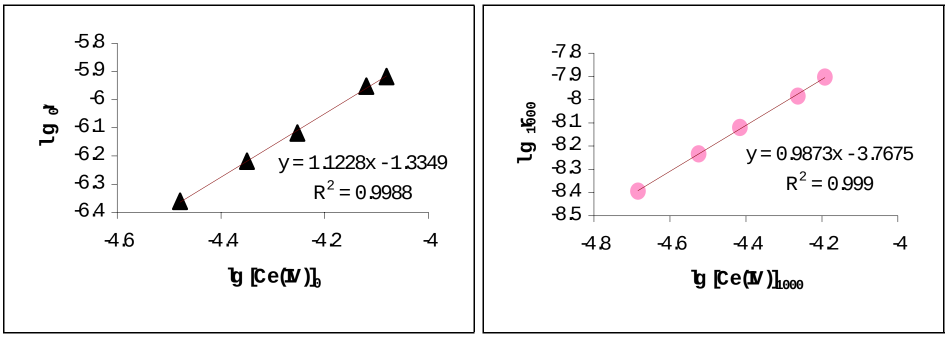
First – order semilogarithmic plots obtained, in the presence of an excess of p-xylene, at constant hydrogen ion concentration and constant ionic strength, are presented in figure 1. The initial part of the plots exhibits a curvature, followed by a linear dependence, characteristic to a first – order process, up to 90% of reaction. The bi-phasic character of the plot may be associated with the presence of two first-order successive stages.



(2)

The first stage, perceptible at the beginning of transformation, could be attributed to the formation of an adduct between Ce(IV) and p-xylene. The second stage, perceptible at higher degrees of transformation, may be associated with oxidation by inner electron transfer yielding the products of the reaction.

As can be seen from the linear dependence lg (r) = f lg([Ce(IV)]) (Fig. 3), the reaction order with respect to Ce(IV) is one, either for the first or the second stage of the reaction.



a) in the first stage b) in the second stage

Figure 3. Determination of reaction order with respect to cerium in the two stages of the reaction described above

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

Once it was established, that both stages are first-order, we preferred to determine the rate constants by a non – linear fitting of the A = f (t) curves, with the biexponential:

$$A - A_{\infty} = C_1 \cdot \exp(-k_{obs1} \cdot t) + C_2 \cdot \exp(-k_{obs2} \cdot t) \qquad (3)$$

which describes the decay of the absorbance of the limiting component in a first order follow up reaction. A and A_{∞} have the same meaning as in relation (1), C_1 and C_2 are constants including the molar absorbance coefficients of the absorbing species and k_{obs1} and k_{obs2} are apparent rate constants of the two reaction steps.

The effect of p-xylene concentration, always in large excess, upon the apparent rate constant at constant hydrogen ion concentration and ionic strength is presented in Table 1.

Table 1

Effect of p-xylene concentration on the apparent rate constants.
$[Ce(IV)]=8 \cdot 10^{-5}M$; $[H^+]=1M$; j =1M; $t=40^0C$

$10^4 \cdot [p\text{-xylene}]_0$ (mol/l)	4	6	8	10	15	24.5
$10^3 \cdot k_{obs1}$ (s^{-1})	4.50	5.24	6.21	6.60	7.79	10.05
$10^4 \cdot k_{obs2}$ (s^{-1})	3.69	4.92	5.50	6.29	7.37	8.00

In order to find the reaction order with respect to the p – xylene concentration, the logarithms of the apparent rate constants were plotted against the logarithms of p – xylene excess.

We obtained an order about 1 with respect to p – xylene for the first stage and an order near to 0.5 for the second stage of the reaction.

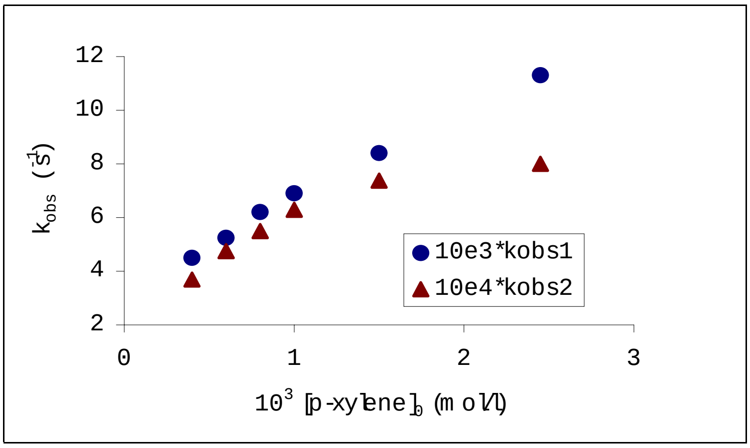


Figure 4. The effect of p-xylene for the first and the second stage of the reaction

The best fit, we could find for the data from table 1 is given by:

$$k_{obs1} = (0.38 \pm 0.02) + (262 \pm 16)[p - xylene]_0 \quad (4)$$

$$k_{obs2} = \frac{(1.5 \pm 0.08)[p - xylene]_0}{1 + (1439 \pm 129)[p - xylene]_0} \quad (5)$$

It is easy to recognize the Michaelis – Menten pattern for the electron transfer process.

The influence exerted by hydrogen ion concentration on the rate constant was investigated within the limits presented in the Table 2.

Table 2

Effect of hydrogen ion concentration on the apparent rate constant, 45^{0}C

[H^+] (mol/l)	0.5	0.6	0.7	0.8	0.9
$10^2 \cdot k_{obs1}$ (s^{-1})	1.59	1.40	1.19	1.03	0.95
$10^4 \cdot k_{obs2}$ (s^{-1})	3.14	4.30	5.15	5.70	6.44

As it can be seen the concentration of hydrogen ion has an opposite effect on the two steps of the reaction. It diminishes the rate constants of the first step according to:

$$k_{obs1} = \frac{(0.13 \pm 0.05)}{1 + (13.7 \pm 6.6)[H^+]} \qquad t = 45^0C \qquad (6)$$

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

$$k_{obs2} = (6.4 \cdot 10^{-4} \pm 7 \cdot 10^{-5})[H^+] \qquad t = 45^0C \qquad (7)$$

Activation parameters were determined for the second stage of the reaction from the Arrhenius and from the Eyring plot (Figure 5).

In order to determine the activation parameters, we employed:

$$k_2^* = k_{obs2}/([p - xylene]_0^{0.5} \cdot [H^+]) \qquad (8)$$

and obtained E_a = 62.37 kJ/mol, ΔH* = 59.77 kJ/mol and ΔS* = -89.87 J/mol·K.

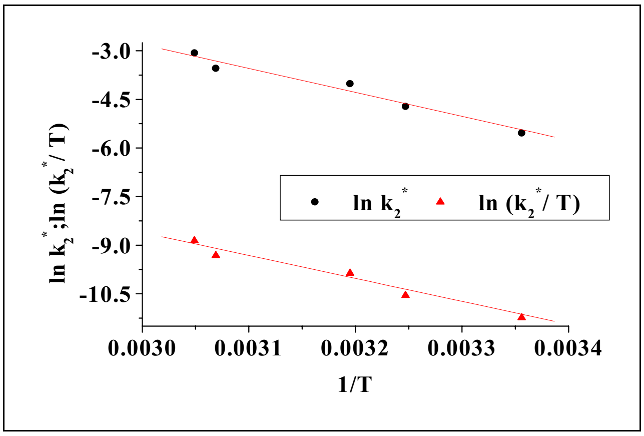
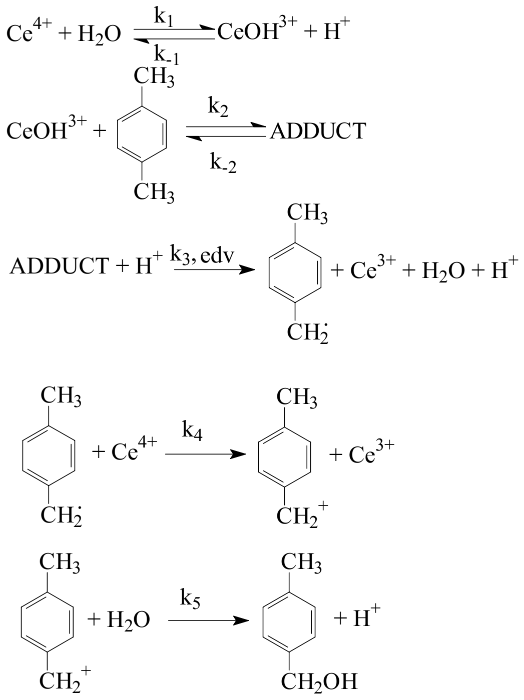


Figure 5. Determination of activation parameters.

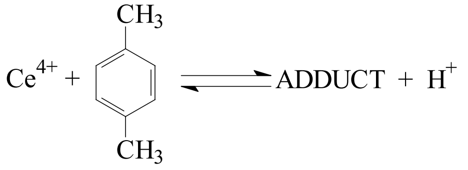
The relatively small values of activation energy and activation enthalpy and the negative and relative large activation entropy may be explained by the oxidation of the adduct by inner electron transfer.

A reaction mechanism, can be suggested, based on the stoechiometry, rate law and literature data. It involves the formation of an adduct between p-xylene and the hydrocomplex of Ce(IV), followed by the oxidation of adduct by inner electron transfer. This step is the rate-determining step. The subsequent steps are very rapid leading finally to the major oxidation product, which is: p-methylbenzylic alcohol.



(12)

The two pre-equilibria can be combined as one, eliminating a hydrogen ion:



(13)

Based on the proposed mechanism the rate of alcohol formation is of the form:

$$r = k_3 K_h^{'} K_2 \frac{[\mathrm{Ce(IV)}] \cdot [\mathrm{H}^+] \cdot [\mathrm{p-xylene}]_0}{K_h^{'}[\mathrm{H}^+] + 1 + K_2[\mathrm{p-xylene}]_0} \tag{14}$$

where: $K_h^{'} = K_1/[H_2O]$ and K_2 is the equilibrium constant for the second reaction.

REFERENCES

1. Hanna S. B., Kessler R. R., Mehrbach A., Ruzicka S., *J. Chem. Education*, **1976**, *53(8)*, 524
2. Trahanovsky W. S., Young L. B., *J. Chem. Soc.*, **1965**, 5777
3. Das A. K., Das M., *J. Chem. Soc. Dalton Trans.*, **1994**, 589
4. Willard H. H., Young P., *J. Am. Chem. Soc.*, **1930**, *52*, 132
5. Pondit A. K., Das A. K., Banerjea D., *Transition Met. Chem.*, **1991**, *16*, 324
6. Hintz H. L., Jhonson D. C., *J. Org. Chem.*, **1967**, *32*, 556
7. Duke F. R., Bremer R. F., *J. Am. Chem. Soc.*, **1951**, *73,* 5179
8. Waters W. A., Jones J. R., Litter J. S., *J. Chem. Soc.*, **1961**, 240
9. Muhammad S. S., Rao K. V., *Bull. Chem. Soc. Jpn.*, **1963**, *36*, 943
10. Ardon M., *J. Chem. Soc.*, **1957**, 1811
11. Hargreaves G., Sutcliffe L. H., *Trans. Faraday Soc.*, **1955**, *51*, 1105
12. Sankhla P. S., Mehrotra R. N., *J. Inorg. Nucl. Chem.*, **1972**, *34*, 3781
13. Rangaswamy M., Santappa M., *Acta Chim. Acad. Sci. Hung.*, **1968**, *56*, 413
14. Grover V. K., Gupta Y. K., *J. Inorg. Nucl. Chem.*, **1969**, *31*, 1403
15. Wells C. F., Husain M., *Trans. Faraday Soc.*, **1970**, *66*, 679
16. Balasubramanian T. R., Venkatasubramanian N., *Indian J. Chem.*, **1970**, *8*, 305
17. Dayal R., Bakore G. V., *Indian J. Chem.,* **1972**, *10*, 1165
18. Rao G. N., *Indian J. Chem.,* **1970**, *8*, 328
19. Krishna B., Tewari K. C., *J. Chem. Soc.*, **1961**, 3077
20. Baciocchi E., Rol C., Sebastiani G. V., *J. Chem. Research (Synopsis)*, **1983**, *9*, 232
21. Ramaswamy M. S., Venkatachalapathy M. S., Udupa H. V. K., *Bull. Chem. Soc. Jpn.*, **1962**, *35*, 214
22. Radhakrishna P. S., Pati S. C., *Chem. Ind.*, **1967**, *17*, 702