STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, L, 1, 2005

KINETICS AND MECHANISM OF *P*-XYLENE OXIDATION BY CE(IV) IN AQUEOUS ACID MEDIUM. LFER AS AN ARGUMENT TO THE OXIDATION MECHANISM

GABRIELA-CRISTINA BUCŞA and IOAN BÂLDEA

Department of Physical Chemistry, Faculty of Chemistry and Chemical Engineering of "Babeş-Bolyai" University, 11 Arany Janos,400028, Cluj-Napoca, Romania (e-mail:ibaldea@chem.ubbcluj.ro)

ABSTRACT*.* The oxidation of *p*–xylene in aqueous acidic media, (using perchloric acid), has been followed spectrophotometrically. The process proceeds in parallel with the water oxidation. This reaction follows a first-order kinetics and has been taken into consideration by subtracting its contribution to the consumption of Ce(IV) A first-order dependence on Ce(IV) concentration and a complex dependence on *p*-xylene and hydrogen ion concentrations have been established for the organic substrate oxidation. 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 that suffers an intramolecular electron transfer. The linear free energy relationship of Hammett type has been obtained for the oxidation of various substituted toluenes with a negative and small reaction constant, which argues the suggested mechanism.

Keywords*:* cerium, *p*-xylene, toluene derivatives, kinetics, oxidation, LFER.

INTRODUCTION

Cerium (IV) is a strong one-equivalent oxidising agent for a large number of organic or inorganic substrates, due to the high standard oxidation-reduction potential of Ce(IV)/Ce(III) couple [1]. Various aromatic hydrocarbons have been oxidised [2-4]. A review of the literature shows that some of these electron-transfer reactions were approached from the kinetic point of view [1-28] The rate laws and mechanisms for the oxidation of toluene and some substituted toluene in aqueous sulphuric acid media were reported [29-31], and in the case of *p*-xylene oxidation with Ce(IV), the activation energy has been determined [30]. Perchloric, nitric, sulphuric and acetic acids were used as hydrogen ion sources and involvement of hydroxo-, nitrate, sulphate or acetate cerium(IV) complexes were described.

We have undertaken kinetic studies on the oxidation of toluene [31] and *o*-xylene in sulphuric and perchloric media and gave some evidence of an adduct intermediate species between Ce(IV) and aromatic hydrocarbons [32]. On the other hand, at high perchloric acid concentration and temperatures higher than 35^0C, Ce(IV) oxidises water along with the hydrocarbon reaction, a process that should be taken into consideration.

In order to get more details concerning the kinetic and the mechanism, we have investigated the electron-transfer reaction Ce(IV)- *p*-xylene by using perchloric acid as the hydrogen ion source, 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, purchased from commercial sources (Chimopar, Reanal, Merck, Aldrich and Fluka) and employed without further purification.

The various substrates were dissolved into boiled and cooled twice-distilled water under the solubility limits by using an ultrasonic bath. It ensured the elimination of dissolved air. The solutions were freshly prepared before each set of runs. Stock solutions of $Ce(ClO_4)_4$, $HClO_4$ and $NaClO_4$ were prepared and standardised spectrophotometrically and by acid - base titration, respectively. Aliquots of $NaClO_4$ solution were passed through an ion-exchange resin (Purolite C 110 H) and resulted $HClO_4$ was titrated against NaOH standard solution.

Kinetic measurements were performed by means of a Jasco V-530 spectrophotometer, provided with a temperature jacket surrounding the cell holder. The cuvette jacket was connected to a Lauda M-12 thermostat. Reaction mixtures were prepared directly in the quartz cell of the spectrophotometer having a 5 cm path length. A rapid adding of a measured amount of cerium perchlorate stock solution, kept in thermostat, over the reaction mixture containing $HClO_4$, $NaClO_4$, *p*-xylene or various substituted toluenes at desired concentration, started the reaction. The reaction progress was followed by monitoring the decrease of optical absorbance at 315 nm, where the UV/VIS spectrum of Ce(IV) exhibits an absorption band. Under each set of conditions, the water oxidation has been monitored in separate experiment. Each experiment has been carried out at least three times and the mean values of observed rate constants have been calculated.

RESULTS AND DISCUSSIONS

Preliminary investigations. *Check of Lambert-Beer law.* Lambert-Beer law's validity, over the concentration range used, was verified. A linear dependence of absorbance on Ce(IV) concentration in the absence and the presence of *p*-xylene has been obtained. A slight **decrease of molar** absorption coefficient occurs when the mixture contains *p*-xylene, but the linearity is maintained. Table 1 contains the values of the molar absorption coefficients under the given experimental conditions. This coefficient is about 7.5 % smaller in the presence of the aromatic hydrocarbon.

Table 1

Molar absorptivities in the absence and the presence of p-xylene

Reaction mixture	$[H^+]$=1 mole.L^{-1}; $[ClO_4^-]$=1 mole.L^{-1}; μ=2.0; t=20^{0}C			
	Ce(IV)		Ce(IV) -*o*-xylene $4{\cdot}10^{-4}$mole.L^{-1}	
λ, nm	315	320	315	320
ε L.mole^{-1}cm^{-1}	4039±198	4047±207	3713±202	3690±206

Check for an intermediate species formation. By recording the spectra of the reaction mixture immediately after mixing at various increasing concentrations of organic hydrocarbon at 20^{0}C, where both the oxidation of water and organic substrate are slow, a small but systematic decrease of the intensity of Ce(IV) absorption band and the occurrence of an isosbestic point located at 276 nm have been noticed. This is brought about by the presence of a new absorbing species besides Ce(IV). It may be a complex involving Ce(IV) and substrate.

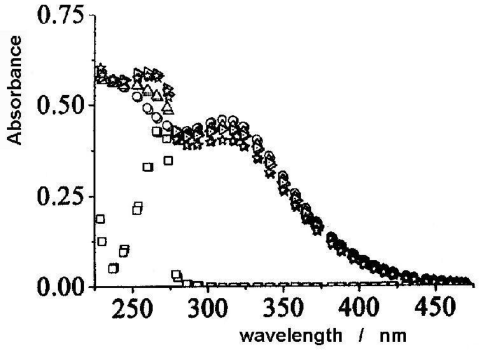


Fig. 1. Spectra recorded immediately after mixing of Ce(IV) 10^{-4}mole.L^{-1}, and *p*-xylene $2.8\cdot10^{-3}$ mole.L^{-1} and mixtures of various concentration of substyrate ($8.0\cdot10^{-5}$ to $2.8\cdot10^{-3}$ mole.L^{-1})

Stoichiometry determination. The stoichiometry of the reaction has been determined by a spectrophotometrical titration [32]. Various mixtures having increasing ratios of [*p*-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 the absorbance difference between blank probes and those with *p*-xylene shows two lines with an intersect and a turning point at the ratio 0.5, as in the case of toluene and *o*-xylene [32]. It predicts a ratio of 2 Ce(IV) ions to a molecule of *p*-xylene, indicating that the oxidation yields *p*-methylbenzylic alcohol as the main oxidation product.

Kinetics. An experiment consists in monitoring the optical absorbance against time. According to the shape of the absorbance- time curve, which looks like a bi-phasic plot, the oxidation of *p*-xylene by Ce(IV) consists of two consecutive stages of the type:

$$\mathrm{p-CH_3C_6H_4CH_3 + Ce(IV)} \xrightarrow{k_{obs1}} \mathrm{Adduct} \xrightarrow{k_{obs2}} \mathrm{Products}$$

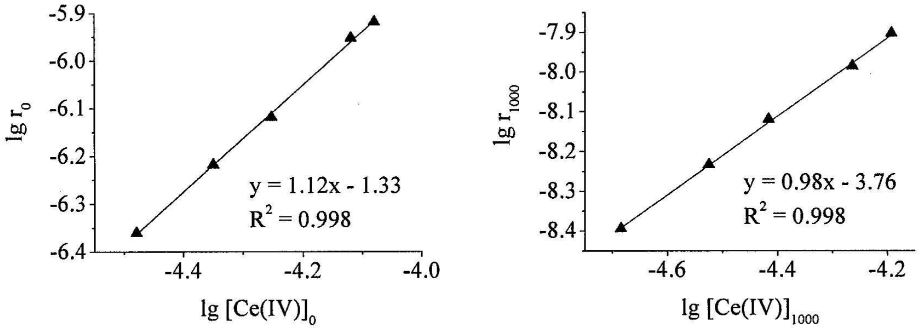
The first stage consists of a steep decline in absorbance at the beginning of the reaction. It could be attributed to the formation of an adduct between Ce(IV) and *p*-xylene. The second stage, perceptible at higher degrees of transformation, may be associated with the redox process consisting of an inner electron transfer within the complex, that finally yields the products of the reaction.

The reaction order with respect to Ce(IV) was determined from the dependence lg (r) = f (lg[Ce(IV)]). As it can be seen in figure 3, first-order with respect to cerium has been found for both stages of the reaction. The experimental curves, A = f (t), were subjected to derivation, at the initial moment and at t = 1000s, while the reaction rates (mole Ce(IV)/L.s) and the corresponding concentrations of cerium were calculated by taking $\varepsilon = 4039$ M^{-1} cm^{-1}.

Once first-order dependence 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:

$$A - A_\infty = C_1 \exp(-k^0_{obs1} \cdot t) + C_2 \exp(-k^0_{obs2} \cdot t) \qquad (1)$$

which describes the decay of the absorbance of the limiting component in a first-order series of reactions. 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 absorptivities and Ce(IV) initial concentration; k^0_{obs1} and k^0_{obs2} are apparent rate constants of the two reaction steps for the overall reduction of Ce(IV) Good fit has been achieved. Table 2 contains these pseudo-first-order rate constants at various concentration of *p*-xylene. Replicate runs yielded close values of pseudo-first-order rate coefficients.



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

Fig. 2. Determination of reaction order with respect to cerium in the two stages of the above described reaction.

Table 2

Apparent first-order rate coefficients of overall oxidation reaction as a function of p-xylene concentration: [H$^+$] = 1.0 mole.L^{-1},[Ce(IV)]= 8.0.10^{-5}, μ = 2.0 and 40^{0}C

[p-xilene]x10^4 mole.L^{-1}	$10^3 k^0_{obs1}$ s^{-1}	$10^3 k^0_{obs1}$ s^{-1} mean	$10^4 k^0_{obs2}$ s^{-1}	$10^4 k^0_{obs2}$ s^{-1} mean
4.0	3.10	3.00	3.73	3.68
	2.92		3.67	
	3.01		3.57	
6.0	4.60	4.60	4.65	4.55
	4.50		4.48	
	4.70		4.52	
7.0	5.00	5.01	5.04	4.96
	5.11		4.84	
	4.94		5.01	
8.0	5.88	5.80	5.30	5.25
	5.74		5.23	
	5.78		5.22	

[p-xilene]x10^4 mole.L^{-1}	10^3 k^0_{obs1} s^{-1}	10^3 k^0_{obs1} s^{-1} mean	10^4 k^0_{obs2} s^{-1}	10^4 k^0_{obs2} s^{-1} mean
9.0	6.76	6.70	5.60	5.59
	6.64		5.58	
	6.70		5.59	
10.0	7.53	7.50	5.90	5.88
	7.48		5.88	
	7.49		5.86	

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

$$2Ce^{4+} + H_2O \xrightarrow{k^0_{obs}} 2Ce^{3+} + 2H^+ + 1/2\ O_2$$

The kinetics of this reaction obeys a first-order dependence on Ce(IV) for the whole duration of the reaction. It has been deduced by the same procedure as for the overall process that has been described before.

We have determined the influence of different parameters on the oxidation of water and both water and substrate. Because the literature [33] stipulates, and we have also found [34] that Ce(III) diminishes the rate of the water oxidation reaction, we introduced Ce(III) into the reaction mixture

Table 3

Several first-order rate constants at the oxidation of water [Ce(IV)] = 8.0x10^{-5}

Temp ^{0}C	[Ce(III)]x10^5 mole.L^{-1}	[H$^+$] mole.L^{-1}	μ	10^{4}k$^0_{obs}$ s^{-1}
40.0	0.0	1.0	2	2.06
	0.4			1.54
	0.8			1.41
	1.0			1.28
	1.2			0.95
	1.6			0.77
40.0	0.8	0.5	3	0.92
		1.0		1.32
		1.5		1.96
		2.0		2.29
		2.5		2.60
35	0.8	1.5	3	1.20
40				2.02
45				3.65
50				6.75
55				9.00
60				16.3

from the beginning in a ratio 1:1 ([Ce(IV)]:[Ce(III)]).The experimental curves for the water oxidation reaction were determined by a fitting method with the equation:

$$A - A_\infty = C_3 \exp(-k_{obs}^0 \cdot t) \tag{2}$$

Several rate constants are presented in table 3. The activation parameters were calculated.

Once we had all the first-order rate constants, we proceed by subtracting the rate constant of the oxidation of water from the rate constants of the overall reaction as follows:

$$\mathrm{k_{obs1} = k^0_{obs1} - k^0_{obs}} \tag{3}$$

$$\mathrm{k_{obs2} = k^0_{obs2} - k^0_{obs}} \tag{4}$$

where: k_{obs1} and k_{obs2} are the observed first-order rate constants of the xylene oxidation reaction for the first and the second step and k_{obs}^0 is the observed first-order rate constant for the water oxidation reaction under the same acidity or ionic strength conditions employed.

The effect of *p*-xylene concentration, always in a large excess, upon the apparent rate constant is presented in figure 3. Observed rate constants were obtained using equation (3) and (4).

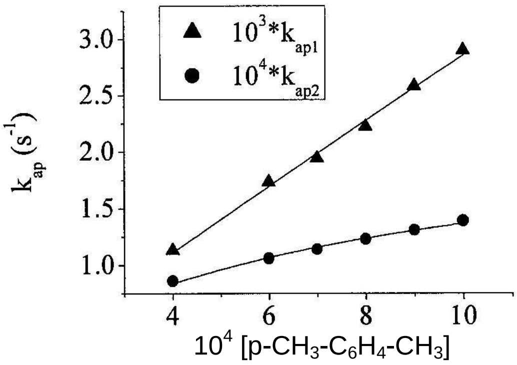


Fig. 3. The effect of *p*-xylene on the first and the second stage of the reaction: [Ce(IV)] = [Ce(III)] =$8 \cdot 10^{-5}$ mole.L^{-1}; [H^+]=1 mole.L^{-1} μ =2.0; t=40^0C

The best fit has been obtained with the equations:

$$\mathrm{k_{obs1} = (-1.0 \cdot 10^{-5} \pm 7.2 \cdot 10^{-5}) + (7.3 \pm 0.2)[p-xylene]_0} \tag{5}$$

with R^2= 0.9910, χ^2= $2.0 \cdot 10^{-8}$ for N = 18, and respectively

$$\mathrm{k_{obs2} = \frac{(13.8 \pm 0.5)[p-xylene]_0}{1 + (139 \pm 90)[p-xylene]_0}} \tag{6}$$

with $R^2 = 0.9800$, $\chi^2 = 7.50 \cdot 10^{-9}$ for N = 18. It is easy to recognise that the first stage of the reaction obeys also a first-order dependence on *p*-xylene, while the second stage follows a Michaelis – Menten pattern. A fractional sub-unitary order is obtained, suggesting also the involvement of an intermediate species.

Even under high acid concentration, the hydrolysis of Ce(IV) ion takes place and complicates the kinetics. 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 4.

Table 4

Effect of hydrogen ion concentration on the apparent rate constant; $[Ce(IV)] = 8 \cdot 10^{-5}$ mole.L^{-1}; $[Ce(III)] = 8 \cdot 10^{-5}$ mole.L^{-1}; [*p*-xylene]= $4.0 \cdot 10^{-4}$ mole.L^{-1}; $\mu = 3.0$ and temperature of 40^0C

$[H^+]$ (mole.L^{-1})	$10^3 \cdot k_{obs1}$ (s^{-1})	$10^4 \cdot k_{obs2}$ (s^{-1})
0.5	11.9	2.58
1	6.60	3.16
1.5	5.38	4.07
2	4.43	5.08
2.5	3.39	5.98

A comparison with the oxidation of *o*-xylene under similar conditions reveals rate constants [32] larger than in that case, probable due to the absence of steric effects. As it can be seen from the table 3, the concentration of hydrogen ion has an opposite effect on the two stages of the reaction. It diminishes the rate constants of the first step, according to equation below, and reveals the loss of the proton:

$$k_{obs1} = \frac{(3.30 \cdot 10^{-2} \pm 4.5 \cdot 10^{-4})}{1 + (3.67 \pm 1.90)[H^+]} \tag{7}$$

with $R^2 = 0.9569$, $\chi^2 = 1.74 \cdot 10^{-6}$ for N = 15. It causes a linear increase of the rate constant of the second stage according to:

$$k_{obs2} = (1.6 \cdot 10^{-4} \pm 1.1 \cdot 10^{-5}) + (1.7 \cdot 10^{-4} \pm 7.6 \cdot 10^{-6})[H^+] \tag{8}$$

with $R^2 = 0.9750$, $\chi^2 = 4.4 \cdot 10^{-10}$, N = 15.

The influence of ionic strength on the reaction rate was also studied. As it can be seen from table 5, ionic strength has a positive effect on both the

Table 5

Influence of ionic strength on the rate constants for both processes $[Ce(IV)] = [Ce(III)] = 8.0x10^{-5}$ mole.L^{-1}; [p-xilene]= $4.0x \cdot 10^{-4}$ mole.L^{-1}mol.L^{-1}; t = 40^0C

μ	10^3 k_{obs1} (s^{-1})	10^4 k_{obs1} (s^{-1})
0.5	2.14	0.57
1	3.29	1.13
1.5	4.43	1.51
2	5.58	2.09
2.5	6.38	2.91
3	7.77	3.31

first and the second stage of the reaction. Although Debye – Hückel relation for activity coefficients could be applied only at lower ionic strengths ($\approx 10^{-2}$) we have plotted the equation of the form

$$\lg k_{\mu} = \lg k_{\mu=0} + \frac{\mathrm{Const}\sqrt{\mu}}{1+\sqrt{\mu}} \tag{9}$$

and have obtained a linear dependence for both stages of the oxidation process

$$\lg k_{obs1} = (-3.72 \pm 0.04) + (2.51 \pm 0.09)\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \tag{10}$$

with $R^2 = 0.9830$, $\chi^2 = 3.6 \cdot 10^{-3}.013$, N = 18 and

$$\lg k_{obs2} = (-5.89 \pm 0.06) + (3.43 \pm 0.13)\frac{\sqrt{\mu}}{1+\sqrt{\mu}} \tag{11}$$

with $R^2 = 0.983$, $\chi^2 = 6.5 \cdot 10^{-3}$, N = 18., respectively. 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 seems to involve ions of like charges (positive slopes).

Activation parameters were determined for both stages of the reaction from the Arrhenius and from the Eyring plots. The effect of the temperature is presented in table 6, and activation parameters in Table 7 along with those for the water oxidation.

The values of activation energy and enthalpy for the first stage are quite small. The negative activation entropy is in agreement with the involvement of the adduct formation pre-equilibrium. The reaction of electron-transfer claims a little bit higher activation energy. The entropy modification in this stage is also negative, suggesting a bimolecular process namely the proton assisted formation of Ce(III) and an uni-equivalent oxidised product.

Concerning the second step, by taking into consideration all the effects of concentrations, the rate law takes of the form:

$$r = k_2 \frac{a\,[\mathrm{p-xylene}]_0\,[H^+]\,[\mathrm{Ce(IV)}]}{1 + b\,[\mathrm{p-xylene}]_0} \tag{12}$$

A reaction mechanism can be suggested, based on recorded spectra, the stoichiometry, rate law of the two stages and the effect of ionic

Table 6

Temperature effect on the first-order rate constants.$[H^+]$=1.5 mole.L^{-1}
μ=2.0; [Ce(IV)]= [Ce(III)]=$8.0x \cdot 10^{-5}$ mole.L^{-1}; [p-xylene]=$4.0x \cdot 10^{-4}$ mol.L^{-1}

Temp. (K)	308	313	318	323	328	333
$10^{2*}k_{ap1}$ (s^{-1})	0.86	0.84	1.12.	1.58	2.74	3.56
10^4*k_{ap2}(s^{-1})	1.22	1.25	2.01	3.39	5.94	6.90

Table 7

Activation parameters for the two stages of oxidation of o-xylen*e.*

Stage	E_a (kJ/mol)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta S^{\neq}$ (J/K)
1	58.4±4.4	57.1±4.4	-102.6±8.6
2	73.2±5.6	70.64±5.7	-92.6±7.2
Water oxidation	88.6±3.4	86.0±3.5	-40.9±2.6

strength. It involves the formation of an adduct between *p*-xylene and the hydroxo-complex of Ce(IV), followed by the oxidation of the adduct by an inner electron transfer. t is presented in the scheme below:

$$\begin{aligned}
&\mathrm{Ce^{4+} + H_2O \Longleftrightarrow Ce(OH)^{3+} + H^+} && \mathrm{k_1, k_{-1},\quad K_1}\\
&\mathrm{Ce(OH)^{3+} + CH_3C_6H_4CH_3 \Longleftrightarrow Adduct} && \mathrm{k_2, k_{-2},\quad K_2}\\
&\mathrm{Adduct + H^+ \longrightarrow [CH_3C_6H_4(H)CH_2^{\bullet}]^+ + Ce(III)} && \mathrm{k_3\quad rds}\\
&\mathrm{[CH_3C_6H_4(H)CH_2^{\bullet}]^+ + Ce^{4+} \xrightarrow{fast} CH_3C_6H_4CH_2^+ + Ce(III)} &&\\
&\mathrm{CH_3C_6H_4CH_2^+ + H_2O \xrightarrow{fast} CH_3C_6H_4CH_2OH + H^+} &&
\end{aligned}$$

The species $\mathrm{[CH_3C_6H_4(H)CH_2^{\bullet}]^+}$ is a free radical cation. The rate-determining step involves a proton assisted electron transfer, to stabilise the formed free radical. It is difficult to assign the position of this hydrogen ion. It may be bound either to the nucleus (π electron system conjugated with the free electron on metylene group) or to the side group [36]. The subsequent steps - the oxidation to carbenium ion and its hydrolysis - are very rapid leading finally to the major oxidation product, which is *p*-methylbenzylic alcohol.

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

$$\mathrm{Ce^{4+} + p - CH_3C_6H_4 - CH_3 \Longleftrightarrow Adduct + H^+} \qquad \mathrm{K = K_1K_2}$$

than the rate equation determined from the mechanism suggested by us will have the form of equation (13)

$$\mathrm{r = k_3K_1K_2\,\frac{[Ce(IV)]\,[H^+]\,[p-xylene]_0}{1 + K_1[H^+] + K_2[p-xylene]_0}} \tag{13}$$

that is in agreement with the kinetic and extra-kinetic data we have obtained, provided that the second term in the denominator is not too important.

To get more arguments about the suggested mechanism, we have followed the oxidation reaction of substituted toluene, and tried to see if a Hammett correlation holds. Such LFER might be used to diagnose mechanism by determining the extent of bond formation or breakage in the transition state or by assessing the electronic and polar effects on the rate. As presented before, the apparent first-order rate constant for the second

Table 8

Observed first-order rate constants for the oxidation process (k_{obs2}) and substituent constants at $[Ce(IV)]_0 = [Ce(III)]_0 = 8\cdot10^{-5}$ mole.L^{-1}; [*p*-xylene]= $1.0\cdot10^{-3}$ mole.L^{-1}; μ = 2.0 and temperature of 40^{0}C[37,38]

Substrate	σ	$10^4 k_{obs2}$ (s^{-1})
p-Xylene	-0.31	7.80
m-Xylene	-0.07	4.02
Toluene	0.0	3.92
p-Chlorotoluene	0.11	3.46
p-Bromotoluene	0.15	3.30
p-Toluenesupphonic acid	o.32	2.12
m-Chlorotoluene	o.37	1.95
m-Nitrotoluene	0.71	0.68
p-Nitrotoluene	o.78	0.45

stage (by allowing for the water oxidation) were calculated for nine compounds. Data are presented in table 8 and the line in figure 4. The Hammett equation in the form $\lg k_{obs2} = \lg k_0 + \rho\sigma$ by using the data in the table is:

$$\lg k_{obs2} = -(3.38 \pm 0.03) - (1.08 \pm 0.04)\sigma \qquad (14)$$

with R^2= 0.951, $\chi^2 = 2.1\cdot10^{-3}$, N = 9. It suggests a common mechanism. As the equation stipulates (ρ< 0) the electron-releasing substituents increase the oxidation rate, while the electron-withdrawing substituents have the opposite effect. The reaction constant, negative and close to unity, suggests a free radical mechanism [39]. The ρ = - 1.08 is in agreement with the one of the oxidation in acetic acid with perchloric acid addition of ρ = -1.7 [39]. Here, because of lower dielectric constant as compared to water, the field effects are more important and a higher reaction constant value should be expected.

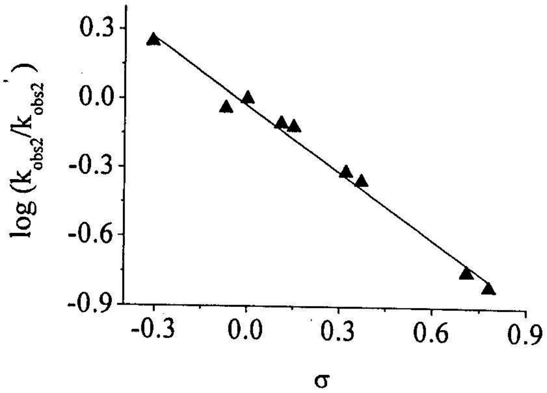


Fig. 4. Hammett plot of the second stage first-order rate constant

ACKNOWLEDGEMENT. This work was supported by the National Research Council of the Ministry of Education and Research (CNCSIS) under Grant.33374/2004, no. 60 Code 164, for which the authors wish to acknowledge.

REFERENCES

1. Gopal Rao G., Madhava Rao B., *Anal. Chim. Acta*, **1972**, *59(3)*, 461
2. Trahanovsky, W. S., Young L. B., *J. Org. Chem.*, **1966**, *31*, 2033
3. Syper L., *Tetrahedron Letters*, **1966**, *37*, 4493
4. Baciocchi E., Rol C., Sebastiani G. V., *J. Chem. Research(Synopsis)*, **1983**, *9*, 232
5. Das A. K., Das M., *J. Chem. Soc. Dalton Trans.*, **1994**, 589
6. Willard H. H., Young P., *J. Am. Chem. Soc.*, **1930**, *52*, 132
7. Pondit A. K., Das A. K., Banerjea D., *Transitionmet. Chem.*, **1991**, *16*, 324
8. Hintz H. L., Jhonson D. C., *J.org.chem.*, **1967**, *32*, 556
9. Duke F. R., Bremer R. F., *J. Am. Chem. Soc.*, **1951**, *73,* 5179
10. Waters W. A., Jones J. R., Litter J. S., *J. Chem. Soc.*, **1961**, 240
11. Muhammad S. S., Rao K. V., *Bull. Chem. Soc. Jpn.*, **1963**, *36*, 943
12. Ardon M., *J. Chem. Soc.*, **1957**, 1811
13. Hargreaves G., Sutcliffe L. H., *Trans. Faraday Soc.*, **1955**, *51*, 1105
14. Sankhla P. S., Mehrotra R. N., *J. Inorg. Nucl. Chem.*, **1972**, *34*, 3781
15. Rangaswamy M., San tappa M., A*cta Chim. Acad. Sci. Hung.*, **1968**, *56*, 413
16. Grover V. K., Gupta Y. K., *J. Inorg. Nucl. Chem.*, **1969**, *31*, 1403
17. Wells C. F., Husain M., *Trans. Faraday Soc.*, **1970**, *66*, 679
18. Balasubramanian T. R., Venkata subramanian N., *Indian J. Chem.*, **1970**, *8*, 305
19. Dayal R., Bakore G. V., *Indian J. Chem.*, **1972**, *10*, 1165
20. Rao G. N., *Indian J. Chem.*, **1970**, *8*, 328
21. Krishna B., Tewari K. C., *J. Chem. Soc.*, **1961**, 3077
22. Ignaczak M., Dziegiec J., Markiewicz M., *Pol. J. Chem.*, **1980**, *54*, 1121
23. Sethuram B., Muhammad S. S., *Acta Chim. Acad. Sci. Hung.*, **1965**, *46*, 115
24. Sethuram B., Muhammad S. S., *Acta Chim. Acad. Sci. Hung.*, **1965**, *46*, 125
25. Trahanovsky W. S., Young L. B., Brown G. L., *J. Org. Chem.*, **1967**, *32*, 3865
26. Paquette D., Zador M., *Can. J. Chem.*, **1968**, *46*, 3507
27. Melicherik M., Treindl L., *Chem. Zvesti*, **1981**, *35*, 153
28. Wiberg K. B., Ford P. C., *J. Am. Chem. Soc.*, **1969**, *91*, 124
29. Ignaczak M., Deka M., *Pol. J. Chem.*, **1980**, *54*, 259
30. Ramaswamy M. S., Venkatachalapathy M. S., Udupa H. V. K., *Bull. Chem. Soc. Jpn.*, **1962**, *35*, 214
31. Claudia G. Muresanu, I. Baldea, Gabriela C. Bucsa *Rev. Roum. Chem*., **2000**, *45*, 111.
32. Gabriela C. Bucsa, Claudia G. Muresanu, I. Baldea, *Studia Univ. Babes-Bolyai, Chem*., **2003,** *49(1),* 125.
33. D. Kolp, H. C. Thomas,, *J. Am. Chem. Soc.*, **1949**, *71*, 3047
34. Gabriela C. Bucsa, Claudia G. Muresanu, I. Baldea, *Studia Univ. Babes-Bolyai, Chem*., **2002,** *48(1-2),* 67..
35. D. Kolp, H. C. Thomas,, *J. Am. Chem. Soc.*, **1949**, *71*, 3047

36. G. Calvaruso, F. P. Cavasino, C. Sbriziolo, *Int. J. Chem. Kinet.,* **1981***, 13), 135*
37. H. C. Brown, Y. Okamoto, *J. Am. Chem. Soc*., 1958, 80, 4979.
38. H. Zollinger, *Helv. Chem. Acta*., 1853, 36, 1730.
39. Radhakrishna P. S., Pati S. C., *Chem. Ind.*, **1967**, *17*, 702