

KINETICS OF COPPER(II) CATALYZED OXIDATION OF 2-AMINOPHENOL IN A CONTINUOUS STIRRED TANK REACTOR

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The kinetics of aerobic oxidation of 2-aminophenol catalyzed by copper (II) chloride in aqueous medium was studied using a spectrophotometric method. The proposed kinetic model obtained in a semi-batch reactor includes two active intermediates and an inactive complex and was tested in a continuous stirred tank reactor (CSTR) after a preliminary study on the efficiency of mixing in different work conditions.

INTRODUCTION

The removal and neutralization of organic pollutants from waste waters, especially of phenols, represent one of the nowadays major requirements. Oxidation processes in condensed phase are not very used even if most of organic compounds are unstable from thermodynamic point of view regarding the oxidation reaction. This is due to the fact that the oxidation reactions are kinetically limited, and the target compounds react slowly with normal oxidants, even with ozone. Phenols are very resistant at standard decontamination procedures¹ (oxidation with peroxide, ozone, auto-oxidation or catalytic oxidations in homogeneous and heterogeneous media). Despite their limitations, degradative oxidations confer an attractive perspective for the treatment of waste waters. The use of transition metal ions (copper and iron) as catalysts and oxygen from air as oxidant supplies an economical alternative method. Copper compounds in different oxidation states are especially important in the oxidation chemistry of phenols.² Aerobic oxidation of 2-aminophenol (OAP) to 2-amino-3H-phenoxazin-3-one (APX) in aqueous medium mediated by transition metal compounds was the

subject of many recent studies³⁻⁵ not only because a toxic pollutant as OAP is converted into a harmless compound, but also because APX exhibits a biological activity, including an anticancer effect.⁶ Thus, copper(II) catalyzed oxidation of OAP can be used as a synthetic model for bio mimic systems, particularly for copper containing enzymes such as tyrosinase, superoxide dismutase, phenoxazinone synthase^{4, 7} etc. Nevertheless, the study of this reaction in (semi)batch reactors is far from simulating natural conditions, especially in the case of flowing waters. A more adequate method uses reactors with a continuous feeding and evacuation such as CSTR. The present study provides a simplified model of copper-catalyzed oxidation in a CSTR.

The overall stoichiometric equation for OAP oxidation is shown in Fig. 1. Previous work on copper- and cobalt (II) catalyzed oxidation of OAP^{3, 7} as well as studies on enzymatic oxidation^{8, 9} provide a model where the formation of APX occurs through metal catalyzed oxidation of OAP to the *o*-quinone imine.

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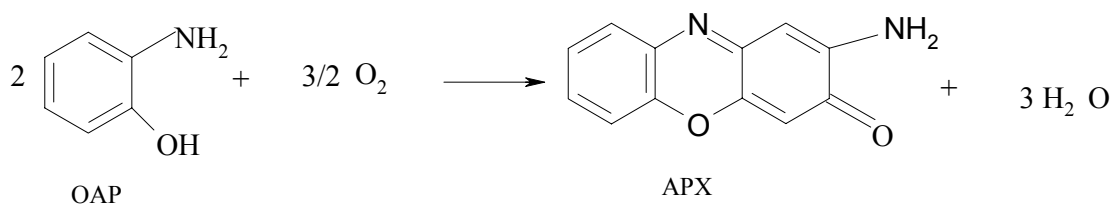


Fig. 1 – Overall equation of OAP oxidation to APX.

A simplified scheme of OAP addition to *o*-quinone imine, followed by further noncatalytic

steps^{7, 8} is given in Fig. 2:

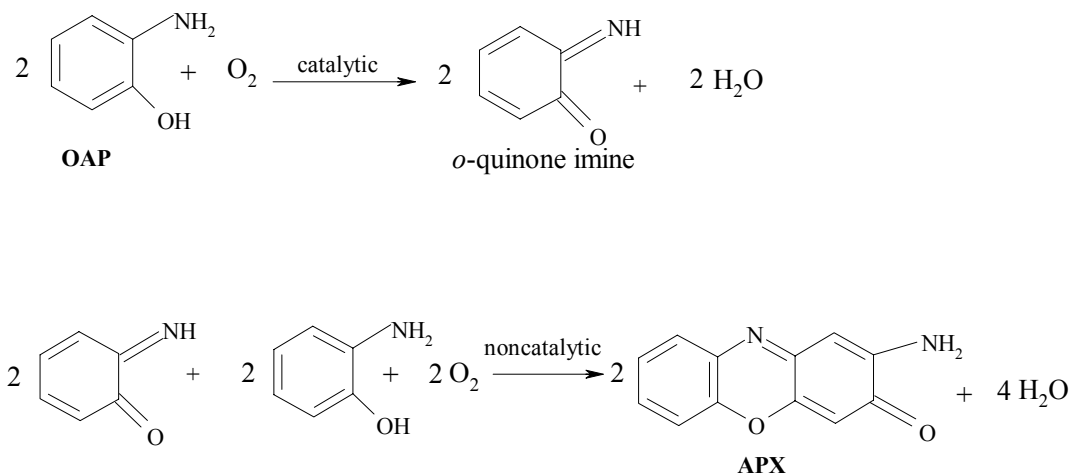


Fig. 2 – Simplified models of kinetically significant oxidation steps of OAP.

EXPERIMENTAL

Materials: OAP was obtained from Aldrich Chemical Co. and APX (m.p. = 216-217°C) was prepared according to literature methods.^{10, 11} IR spectrum of solid APX in KBr was compared to similar spectra from literature⁷ observing absorption peaks at $\tilde{\nu}(\text{cm}^{-1})$: 3320(m), 3215(w), 1590 (vs), 1572(vs), 1210(m) and 1174(m). Argon from Linde was 99.9% and copper chloride (II) was of the highest purity grade from Fluka. UV-VIS spectra were measured on a JascoW530 spectrophotometer equipped with kinetic software.

The efficiency of mixing in CSTR was tested in different work conditions (input volume flow rate, frequency of stirring). Operating parameters of CSTR (space time, residence time, spread of residence time of fluid element, spread density and intensity function) were calculated in absence of chemical reaction, using malachite green as marker and measuring the absorbance at 582 nm¹² of samples collected from the output stream. The oxidation was followed in the aqueous medium in a continuous stirred tank reactor using dioxygen from the bubbling air as oxidizing agent. The concentrations of bulk solutions of OAP and CuCl₂ were 5mM and 1mM, respectively, for all experimental sets. Both substrate and catalyst were simultaneously fed into reactor, at the following input volume flow rates: $q_{\text{OAP}}^0 = 0.1 \text{ mL}\cdot\text{s}^{-1}$ and $q_{\text{CuCl}_2}^0 = 0.083 \text{ mL}\cdot\text{s}^{-1}$; $q_{\text{OAP}}^0 = 0.083 \text{ mL}\cdot\text{s}^{-1}$ and $q_{\text{CuCl}_2}^0 = 0.066 \text{ mL}\cdot\text{s}^{-1}$; $q_{\text{OAP}}^0 = 0.066 \text{ mL}\cdot\text{s}^{-1}$ and $q_{\text{CuCl}_2}^0 = 0.05 \text{ mL}\cdot\text{s}^{-1}$; $q_{\text{OAP}}^0 = 0.05 \text{ mL}\cdot\text{s}^{-1}$ and $q_{\text{CuCl}_2}^0 = 0.033 \text{ mL}\cdot\text{s}^{-1}$; $q_{\text{OAP}}^0 = 0.05 \text{ mL}\cdot\text{s}^{-1}$

and $q_{\text{CuCl}_2}^0 = 0.033 \text{ mL}\cdot\text{s}^{-1}$ (in this last experimental set the 0.4 mM CuCl₂ solution was previously fed into reactor and maintained constant during the oxidation). The limiting 5 mM concentration of OAP was chosen due to lower solubility of OAP and APX in water. The air stream was bubbled through two thermostated saturation vessels containing water to avoid the evaporation of the solvent from reactor. Under these conditions the solution was saturated with air. All kinetic assays were run at 30°C. The stability of OAP in the absence of oxygen was tested by passing an argon stream through the reaction mixture, when no transformation of OAP occurred. APX formation was monitored measuring the absorbance at 434 nm (where OAP has no significant absorption) of the output sample ($\epsilon = 23200 \text{ cm}^{-1}\cdot\text{M}^{-1}$ for APX). The pH in the reaction mixture was also measured in the output stream, but no significant deviation from the initial value was noticed.

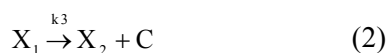
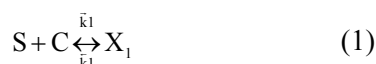
RESULTS AND DISCUSSION

The obtained characteristics of CSTR indicated a quasi ideal mixing, *i.e.* chemostat operating regime.¹² The constant density flow yields equal input and output volume flow rates and consequently, equal space and residence times ($\tau_{\text{SP}} = \bar{t}$). It was previously shown¹³ that the overall non-catalyzed oxidation process in air-saturated solution is a pseudo-first order one, having an

apparent rate constant $k' = 4 \cdot 10^{-7} \text{ s}^{-1}$. The differential equations of transformation rates of OAP and APX in CSTR should also contain the corresponding term of the pseudo - first order reaction. The rate equation of copper (II) chloride catalyzed oxidation in air saturated solution was previously obtained in a semi-batch reactor¹⁴ starting from the following experimental observations: The linear increase of initial oxidation rate towards catalyst initial concentration showed a first order dependence;

The peak shaped form of oxidation rate plot towards initial concentration of OAP suggested a possible inhibition step similar to enzymatic substrate inhibition.

A sequence involving two active intermediates, in accord with literature data^{7,9} and with theoretical models for catalytic reactions was proposed. This model includes several single reactions obtained lumping the elementary steps into one composite process. The simplified reaction sequence is:



where S represents the substrate OAP, X_1 and X_2 are the active intermediates (substrate - catalyst complex and *o*-quinone imine, respectively) and P_2 represents the final reaction product APX; “ \leftrightarrow ” indicates a bilateral reaction far from equilibrium.

The obtained kinetic model (using the steady-state assumption for X_1 and X_2 species and conservation equation of catalytic centres) was improved by adding a new step in order to explain the lowering of the reaction rate for increased concentrations of substrate:



where P_1 represents an inactive ternary complex, substrate-catalyst-substrate; “ \leftrightarrow ” indicates a bilateral reaction close to equilibrium. A new

kinetic equation was obtained by adding the quasi-equilibrium condition for step (4):

$$r_r = \frac{a_0 \cdot [S]}{1 + a_1 \cdot [S] + a_2 \cdot [S]^2} \quad (5)$$

with the followings significances: $a_0 = \frac{\bar{k}_1 \cdot k_3 \cdot [C_0]}{\bar{k}_1 + k_3}$

$$a_1 = \frac{\bar{k}_1 \cdot K_2}{\bar{k}_1 + k_3}, \quad a_2 = \frac{\bar{k}_1}{\bar{k}_1 + k_3}$$

The function (5) was fitted to experimental data initial rates towards initial concentration of OAP. A smoothing algorithm using a polynomial interpolation was applied because its simplicity and safety in preserving data features¹⁵. The smoothed data provided the followings values: $a_0 = (1.3 \pm 0.7) \cdot 10^{-5} \text{ s}^{-1}$, $a_1 = 0.0454 \pm 919 \text{ L} \cdot \text{mol}^{-1}$, $a_2 = (1.227 \pm 0.415) \cdot 10^6 \text{ L}^2 \cdot \text{mol}^{-2}$, with $r = 0.955$ and $F_{\text{stat}} = 31$ (for a significance level $\alpha = 0.05$), exceeding the critical value of $F_{\text{stat}} = 8.88$. The larger errors that affect the parameter a_1 , are due to the small number of experimental points used for fitting a model with three parameters. In order to improve the goodness of fit, a convenient function ($y^{-1} = a + b \cdot x^2 \cdot \ln x + c \cdot \ln x / x^2$) was fitted on experimental points $r_{t_0} = f([S]_0)$. This function was chosen taking into account the following statistical features: correlation coefficient, random distribution of residuals, standard deviations of parameters. A number of 100 generated points was obtained for x ranging within 0.445 – 4.45 mM. Function (5) was fitted on the generated data, yielding $a_1 = 211 \pm 39 \text{ L} \cdot \text{mol}^{-1}$, the other parameters preserving their values within the experimental errors. However, the sensitivity analysis proved that a_1 has the slightest contribution to the rate equation.

The system of kinetic differential equations for CSTR contains the following parameters: k , a_0 , a_1 , a_2 , τ_{SP} (where a_0 is the ratio of a_0 and the initial concentration of catalyst in the semi-batch reactor, namely 6.25 mM), initial concentrations of substrate and catalyst, $[S]_0$ and $[C]_0$, respectively:

$$\frac{d[S]}{dt} = -k' \cdot [S] - 2 \cdot [C] \cdot \frac{a'_0 \cdot [S]}{1 + a_1 \cdot [S] + a_2 \cdot [S]^2} + \frac{([S]_0 - [S])}{\tau_{\text{SP}}} \quad (6)$$

$$\frac{d[P_2]}{dt} = \frac{k' \cdot [S]}{2} + [C] \cdot \frac{a'_0 \cdot [S]}{1 + a_1 \cdot [S] + a_2 \cdot [S]^2} - \frac{[P_2]}{\tau_{\text{SP}}} \quad (7)$$

$$\frac{d[C]}{dt} = \frac{[C]_0 - [C]}{\tau_{\text{SP}}} \quad (8)$$

The system was solved by numerical integration using an ODE solver for stiff systems.¹⁶ All calculations were performed with a FORTRAN program which required the following input data: values of k' , a_0 , a_1 , a_2 , τ_{SP} , $[S]_0$, $[C]_0$ and the jacobian matrix of the system. Simulated curves APX vs. time were compared with the experimental ones:

- set 1 $[S]_0 = 2.72$ mM, $[C]_0 = 0.45$ mM, $\tau_{SP} = 4.04 \cdot 10^2$ s (fig. 3);

- set 2 $[S]_0 = 2.77$ mM, $[C]_0 = 0.44$ mM, $\tau_{SP} = 4.93 \cdot 10^2$ s (fig. 4);

- set 3 $[S]_0 = 2.86$ mM, $[C]_0 = 0.43$ mM, $\tau_{SP} = 6.34 \cdot 10^2$ s (fig. 5);

- set 4 $[S]_0 = 3.00$ mM, $[C]_0 = 0.40$ mM, $\tau_{SP} = 8.88 \cdot 10^2$ s (fig. 6);

- set 5 $[S]_0 = 3.00$ mM, $[C]_0 = 0.40$ mM, $\tau_{SP} = 8.88 \cdot 10^2$ s (fig. 7) with catalyst previously added in the reactor.

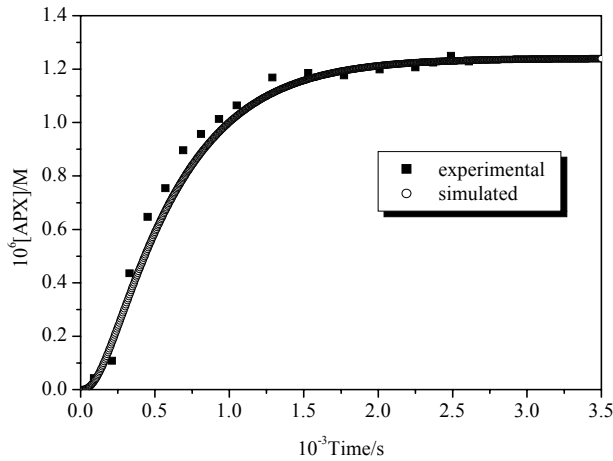


Fig. 3 – Kinetic curves [APX] vs. time
 $q_{OAP}^0 = 0.1$ mL·s⁻¹, $q_{CuCl_2}^0 = 0.083$ mL·s⁻¹

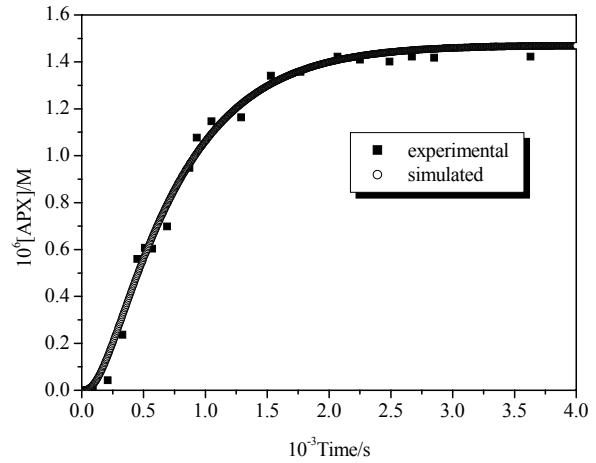


Fig. 4 – Kinetic curves [APX] vs. time
 $q_{OAP}^0 = 0.083$ mL·s⁻¹, $q_{CuCl_2}^0 = 0.066$ mL·s⁻¹

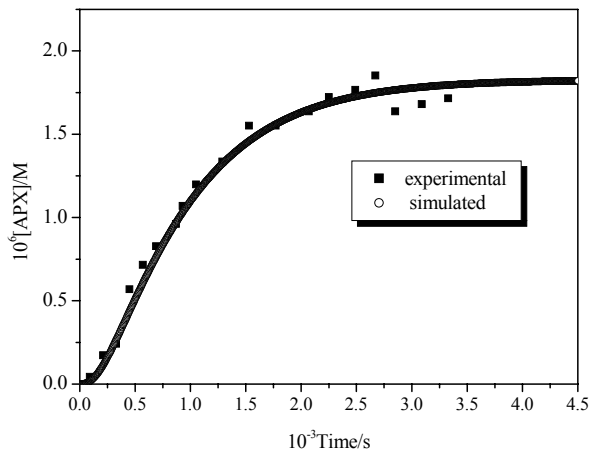


Fig. 5 – Kinetic curves [APX] vs. time
 $q_{OAP}^0 = 0.066$ mL·s⁻¹, $q_{CuCl_2}^0 = 0.05$ mL·s⁻¹

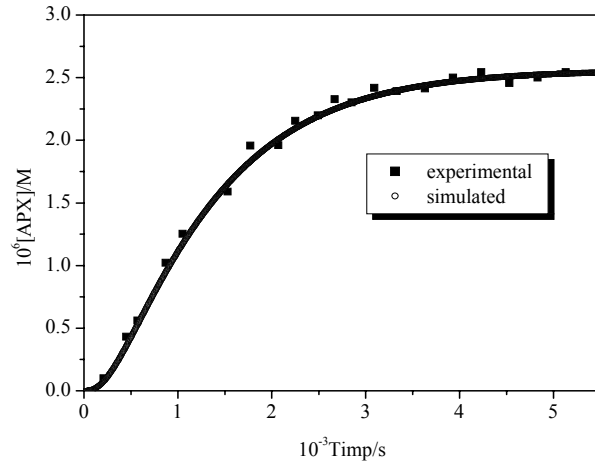


Fig. 6 – Kinetic curves [APX] vs. time
 $q_{OAP}^0 = 0.05$ mL·s⁻¹, $q_{CuCl_2}^0 = 0.033$ mL·s⁻¹

The system of differential equations used to simulate experimental data of set 5 when the

concentration of catalyst was maintained constant, becomes:

$$\frac{d[S]}{dt} = -k' \cdot [S] - 2 \cdot [C]_0 \cdot \frac{a'_0 \cdot [S]}{1 + a_1 \cdot [S] + a_2 \cdot [S]^2} + \frac{([S]_0 - [S])}{\tau_{SP}} \quad (9)$$

$$\frac{d[P]}{dt} = \frac{k' \cdot [S]}{2} + [C]_0 \cdot \frac{a'_0 \cdot [S]}{1 + a_1 \cdot [S] + a_2 \cdot [S]^2} - \frac{[P_2]}{\tau_{SP}} \quad (10)$$

A reasonable agreement between simulated and experimental kinetic curves was obtained as can be observed in figs. 3-6. Comparing experimental sets for equal input volume flow rates (figs. 6 and 7) it was observed that APX had reached a stationary

concentration faster when the catalyst was previously added in the reactor (2270 s as compared to 5000 s). For each experimental set the reaction rates in stationary regime were calculated as:

$$r_r = \frac{[P_2]_{\text{output}} - [P_2]_0}{\tau_{\text{SP}}} = -\frac{1}{2} \cdot \frac{[S]_{\text{output}} - [S]_0}{\tau_{\text{SP}}} \quad (11)$$

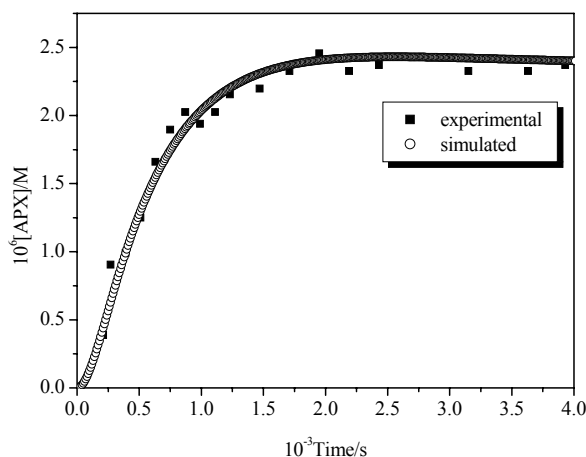


Fig. 7 – Kinetic curves [APX] vs. time

$$q_{\text{OAP}}^0 = 0.05 \text{ mL}\cdot\text{s}^{-1}, q_{\text{CuCl}_2}^0 = 0.033 \text{ mL}\cdot\text{s}^{-1}, [\text{CuCl}_2]_{\text{reactor}} = 0.4\text{mM}$$

Table 1

Reaction rates in stationary conditions for several space times

	$\tau_{\text{SP}}/\text{s}$	$10^9 \cdot r_{\text{exp}}/\text{M}\cdot\text{s}^{-1}$	$10^9 \cdot r_{\text{sim}}/\text{M}\cdot\text{s}^{-1}$
1	404	2.92	3.06
2	493	2.91	2.98
3	634	2.73	2.89
4	888	2.85	2.86
5	888	2.33	2.72

Experimental and simulated reaction rates are summarized in Table 1.

The tabulated data indicate a good agreement between experimental and simulated velocities.

CONCLUSIONS

The kinetic study of copper (II) catalysed oxidation of OAP to APX in a semi-batch reactor suggests an inhibitory effect of OAP on the catalyst. The formation of a substrate - catalyst - substrate ternary complex is a possible step since OAP can function as a bidentate ligand. The quasi-ideal efficiency of mixing in the CSTR and the kinetic model resulted in a reasonable agreement between simulated and experimental data. The

stationary regime was reached much faster when the catalyst was previously added in reactor.

The study of OAP catalyzed oxidation in CSTR provides a model of degradation in natural conditions. Copper ions, as well as copper-containing enzymes, are species constantly present in waste waters. Their use allows the development of a natural efficient method of degradation of pollutants to less toxic compounds.

REFERENCES

1. L. Gianfreda, F. Sannino, M. A. Rao and J. M. Bollag, *J. Water Res.*, **2003**, *37*, 3205-3215.
2. A. Puzari and J.B. Baruah, *J. Mol. Cat. A*, **2002**, *187*, 149-162.

3. J. Kaizer, R. Csonka and G. Speier, *J. Mol. Cat.*, **2002**, *180*, 91-96.
4. T. Horvath, J. Kaizer and G. Speier, *J. Mol. Cat. A*, **2004**, *215*, 9-15.
5. M. Puiu and D. Oancea, *An. Univ. Buc.*, **2004**, *XIII*, 263-268.
6. G. Fukuda, N. Yoshitake, Z.A. Khan, M. Kanazawa, Y. Notoya, X.F. Che, S. Akiyama, A. Tomoda, S. Chakrabarti and M. Odawara, *Biol. Pharm. Bull*, **2005**, *28*, 797-801.
7. L. Prati and M. Rossi, *J. Mol. Cat*, **1992**, *75*, 347-355.
8. O. Toussaint and K. Lerch, *Biochemistry*, 1987, *26*, 8567-8571.
9. C. E. Barry, G. N. Parmesh and T. P. Begley, *Biochemistry*, **1989**, *28*, 6323-6333.
10. V. Stuzka, E. Sinderlarova, *Collection Czech. Chem. Commun.*, 1977, *42*, 13333-1337.
11. T. Nogami, T. Hishida, M. Yamada, H. Milkawa and Y. Shiota, *Bull. Chem. Soc. Jpn.*, **1975**, *48*, 3709-3714.
12. M. Puiu, *PhD Thesis*, Cinetica unor reacții de oxidare în soluție. Univ. Buc., 2004.
13. D. Oancea and M. Puiu, *Central Eur. J. Chem*, **2003**, *3*, 233-241.
14. M. Puiu and D. Oancea, *Prog. Cat.*, **2004**, *12*, 75-81.
15. W. S. Cleveland, *J. Amer. Statst. Assoc.*, **1979**, *74*, 829-836.