

Estimation of Kinetic Parameters for the Catalytic Oxidation of Substituted Phenols in Liquid-phase

DANUT-GABRIEL COZMA¹, AUREL PUI^{1*}, REMY RICOUX², JEAN-PIERRE MAHY²

¹ Al. I. Cuza University, Faculty of Chemistry, 11 Carol I, Str., 700506 Iasi, Romania

² Paris Sud (XI) University, Institute of Molecular Chemistry and Materials, Laboratory of Bioorganic and Bioinorganic Chemistry, Bât 420, 91405 Orsay Cedex, France

The cobalt(II) Schiff bases complexes were used as catalysts in an oxidation reaction of substituted phenol with molecular oxygen. The kinetics parameters (reaction order, rate constants) were calculated from the van't Hoff relation and their variation limits have been subsequently statistically estimated. The dependence of the oxidation reaction rate is evaluated according to the nature of the Schiff base used as a catalyst, using statistical and probabilistic methods.

Keywords: kinetic parameters; statistical methods; oxidation reactions

Biomimetic oxygenation of organic substrates using molecular oxygen in presence of metallic complexes is used directly by oxygenase enzymes [1-3]. Preparation of bio-conjugated metal catalysts has become an important topic in bioinorganic chemistry [4-5]. In the presence of O₂, the oxidation reactions are involved in a series of chemical and biochemical processes [6]. A series of cobalt (II) complexes with Schiff bases have the capacity of reversibly binding molecular oxygen. [7,8]. They also act as catalyst in oxidation reaction [8,9].

Kinetic parameters such as rate constants and order of reaction are of particular importance in the study of the chemical reactions [10]. Deduction of these parameters can be performed using classical methods whose accuracy can be checked using statistical methods.

The present work aims to determine the kinetic parameters (reaction order, constant of reaction rate). For their validation we use a computer program Statistical Package for Social Sciences (SPSS) and establish the influence of the catalyst on the reaction rate of the oxidation of 2,6 di-tert-butyl-phenol (DTBP) with molecular oxygen in presence of cobalt(II) complexes with Schiff bases.

Experimental part

Experimental results obtained at 2,6 di-tert-butyl-phenol (DTBP) oxidation with O₂ in the presence of the cobalt complexes has been used to determine the kinetic parameters (reaction rate and reaction order). Oxidation of DTBP with molecular oxygen was made in the presence of certain cobalt(II) Schiff bases complexes acting as catalysts [11,12]. The complexes (2.5x10⁻³ mol, 5 %) were dissolved in 5 mL of dimethylformamide (DMF) under inert atmosphere of argon over which 0.1mL of pyridine (py) was poured. DTBP (5x10⁻² mol) separately dissolved in 5 mL DMF was then added. For the oxidation reaction, the inert gas was evacuated with a vacuum pump from the installation and then replaced with pure oxygen (p = 1 atm) as the stirring was initiated (T = 298K). This moment was considered as the initial one. Subsequently, at equal time intervals, the volume of consumed oxygen was measured. The reaction was considered complete and was stopped when no more oxygen was consumed for 30-60 min. The catalyst was removed by elution on a silica

column (eluent C₇H₁₆/CH₂Cl₂, 1/1 v) and after removing the volatile phases, the reaction mixture was analysed by ¹H NMR spectroscopy and gas chromatography.

Validation of the kinetic parameters was made by statistical methods using statistical program, Statistical Package for Social Sciences (SPSS, version 13.0 SPSS Inc.).

Results and discussions

The cobalt(II) Schiff bases complexes used as catalysts are presented in figure 1.

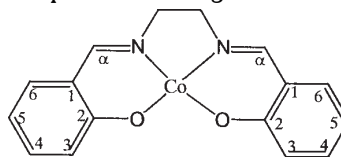
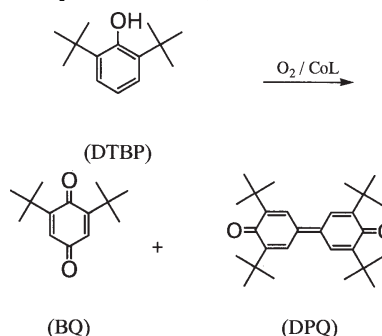


Fig. 1. General structured formula of the cobalt complexes (II)

- bis(salicylaldehyde)ethylenediamine cobalt (II), CoSalen (1);
- bis(α,5-dimethyl salicylaldehyde)ethylenediamine cobalt (II), CodMeSalen, (2);
- bis(α-ethylaldehyde)ethylenediamine cobalt (II), CoEtSalen, (3);
- bis(α- ethyl, 3,5-diiodine salicylaldehyde) ethylenediamine cobalt (II), CodIEtSalen, (4);
- bis(5-nitro salicylaldehyde)ethylenediamine cobalt (II), CoNSalen, (5).

Oxidation of the 2,6 di-tert-butyl-phenol (DTBP) with molecular oxygen, using cobalt(II) complexes as catalyst give mainly two products: 2,6-di-tert-butyl-1,4-benzoquinone (BQ) and 2,6,2',6'-tetra-tert-butyl-1,1'-diphenbenzoquinone (DPQ) [13,14], scheme 1.



Scheme 1. Oxidation reaction of 2,6-di-tertbutylphenol (DTBP) with molecular oxygen in the presence of cobalt (II) complexes (CoL)

* email: aurel@uaic.ro

When the reaction is over, the products obtained are separated and analysed. The intensity and area of the peaks, available from both ¹H NMR spectra and chromatograms, permits the evaluation of the transformation degree of DTBP, as well as of the QN and DPQ contents [11].

Formation of QN, DPQ or QN + DPQ mixture depends on the nature of the metallic ions present in the complex and ligands which may influence the development of the reaction. The mechanism of this oxidation, was thoroughly studied [15-18].

Thus, according to the reaction mechanism, the oxygen is consumed in the first step of the reaction for the formation of a [L(py)Co-O₂] adduct [19-21]. The oxygen volumes consumed at various times for the five cases of oxidation under study are presented in figure 2.

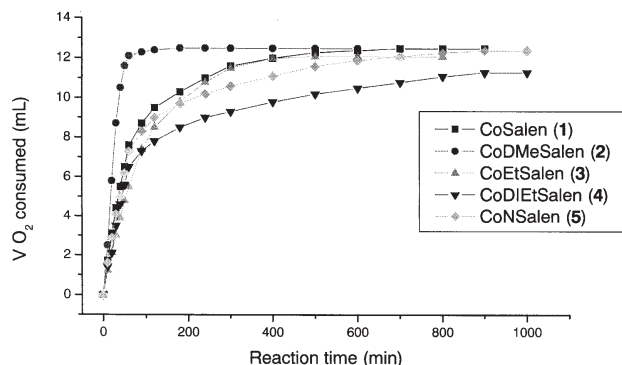


Fig. 2. Volume of O₂ consumed (mL) in function of the reaction times (min)

The consumed oxygen volumes were used for calculating the number of oxygen moles consumed at time *t* under constant working conditions (i.e. 785 mmHg and 25°C).

Determination of the reaction order and of rate constants for DTBP oxidation with molecular oxygen

The values of the number of oxygen moles (*n*) are obtained with the relation:

$$n = pv/RT \quad (1)$$

From which the kinetics parameters are determined by the differential method introduced by Van't Hoff [22] based on the utilization of the differential equation:

$$\frac{dc_s}{dt} = kc_{\text{catal}}c_s^n c_{\text{DO}} \quad (2)$$

where:

DO = dissolved oxygen in the liquid;
S = substrate

The expressions for oxygen diffusion in the liquid and mass balance for the substrate consumption are presented within equation 3 and 4 [23].

$$r_{\text{O}_2} = \frac{dc_{\text{DO}}}{dt} = (K_L a)(c_{\text{DO}}^* - c_{\text{DO}}) \quad (3)$$

$$r_s = \frac{dc_s}{dt} = kc_{\text{catal}}c_s^n c_{\text{DO}} \quad (4)$$

where:

K_La = overall gas-liquid mass transfer coefficient (usually between 0.04-0.001 L s⁻¹ [24]).

c_{DO}^{*} oxygen saturation (equilibrium) concentration in liquid phase, in mg m⁻³.

Representation of this differential equation in logarithmic coordinates gives the following expression:

$$\ln \left| \frac{dc_s}{dt} \right| = \ln k c_{\text{catal}} + n \ln c_s + \ln c_{\text{DO}} \quad (5)$$

The catalyst and the substrate concentration remanent were introduced into a *k_n* constant and the logarithm reaction rate becomes:

$$\ln r = \ln k_n + n \ln c_{\text{DO}} \quad (6)$$

Thus, both the reaction order and the constant of reaction rate may be obtained in one simple determination. The number of moles calculated from relation (1) will be considered as concentration and the reaction rate will be calculated with relation:

$$r = \Delta c / \Delta t, \quad (7)$$

The Δ variations were considered for two consecutive times. The *r* and *c* values have been then looked up respectively in the logarithm of the *e* base. The results are presented in figure 3.

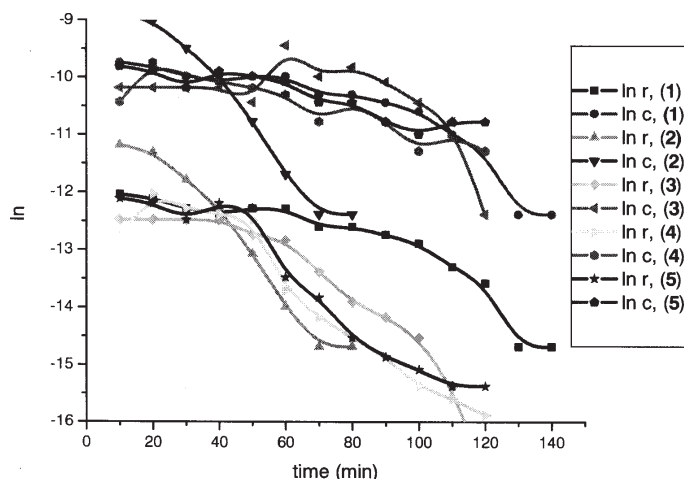


Fig. 3. Variation of ln *r* and ln *c* function of time for oxidation reaction

The equation. 7 is applicable for only isothermal data, only for observable variable of the model, and for a constant experimental error. Such a rule is applicable to a category of approximate methods for kinetic model estimation (i.e. discretization methods); we have to mention that precise estimation rule is usually used for such purpose [25]. For instance, the least squares (LSQ) estimator minimize the sum of squares of residuals $e_{j,u} = c_{j,u} - \hat{c}_{j,u}$ between the experimental concentration $c_{j,u}$ and concentration $\hat{c}_{j,u}$ predicted by the integrated kinetic model (3, 4) for every recorded species 'j' in the experimental point 'u' at the time *t_u*.

Furthermore, the parameters of the linear regression line between the *x* = ln *c* independent variable and the *y* = ln *r* dependent variable have been calculated according to the regression equation (6). A simple linear regression model can be written as follow:

$$Y = \alpha + \beta X + eu \quad (8)$$

where:

Y is the dependent variable;
X the independent variable and *e_u* the simple variable (residue) and $e_u = y_u - \hat{y}_u$. The parameters of the regression equation are:

α = y-coordinate, or the value of the Y variable when X=0;

β = line slope, also known as the regression coefficient.

The sign of the β regression parameter indicating the direction of the linkage between the two correlative variables is:

$-\beta > 0$ direct, positive linkage

$-\beta = 0$ no linkage

$-\beta < 0$ inverse, negative linkage

Parameters α and β are not known, but the parameters of a regression model are estimated on the basis of the data of an analysed sample by using the following estimator:

$$\hat{y} = a + bx \quad (9)$$

in which a and b are estimates of the α and β parameters. The values of residuals between experimental value and kinetic model prediction are estimated with (eq. 8):

$$e_i = y_i - (a + bx_i) \quad (10)$$

and it represents the distance of any (x_i, y_i) point, given the $\hat{y} = a + bx$ regression line. Estimates **a** and **b** are presented in table 1 but the e_i estimate is not the object of this study.

Estimates **a** and **b** correspond to the values from the "Parameter Estimates" columns, as follows:

-For **a**: this estimate allows finding out of the $\ln k_n$ value (rate constants);

-For **b**: this estimate allows finding out of the n value (reaction order).

Reaction order and influence of the magnitude of the "R square" factor

In the case of complexes **1** and **2**, the "R square" value is equal to one, which indicate that the linkage between the two variables is total. On the other hand, the last three ones present high values of the reaction order. Also, the values of the rate constants raise many problems. The first two values are very low, the third is moderate, and the penultimate is high while the last one records an exceptional value.

The "R square" value shows the variation ratio of the dependent variable explained by the regression model i.e. it is used for evaluating the quality of the selected regression model. The decreasing order of the "R square" values of the five studied coordinate complexes with a catalytic role is: **1 = 2 > 5 > 4 > 3**. The lowest reliability on the quality of the values obtained by the performed linear regression is found in the case of complex **3**, and the highest possible one in the case of complexes **1** and **2**.

The reaction order and the influence of the significance degree ("P value") are obtained using the analysis of variance (ANOVA) [26-29]. The values of the significance coefficient lower than 0.05 shows the rejection of the null hypothesis ($\beta = 0$) at a coefficient of risk equal to 0.05. Such conditions are in favour of the alternative hypothesis that is, of the existence of a significant linkage between the two variables defined by the equation (4). The coefficient of risk, chosen here to be 0.05, expresses the existence of a threshold of significance, assuming that the occurrence of an error of type I should take place. In this case, it means the rejection of the H^0 null hypothesis when it is valid [30]. The results of the ANOVA test are summarized presented in table 2.

Considering the results presented in table 2, the Sum of Square due to the Regression is $\sum_{u=1}^N (\hat{y}_u - \bar{y})^2$, Sum of Square of Residuals $\sum_{u=1}^N (y_u - \hat{y})^2$, and Total Sum of Squares of Residuals $\sum_{u=1}^N (y_u - \bar{y})^2$ it is to mention that a rough index to characterize the model adequacy is the standard derivation

$$\text{of the model, which is: } S = \sqrt{\frac{\sum_{u=1}^N (y_u - \bar{y})^2}{Nr - p}}$$

where:

N= no of the experimental points (between 7 and 13 here);

r = no. of observable variables (=1 here, that is the substrate rate);

p = no. of model p = no. of model parameters (=2 here).

Table 1
RESULTS OF THE LINEAR REGRESSION FOR THE CALCULATION OF THE "a" AND "b" ESTIMATES IN REGARDS TO OBTAIN THE KINETIC PARAMETERS

Complexes	Parameters						
	Model Summary*					Parameter Estimates	
	R Square	F**	df1	df2	Sig.***	a	b
1	1	0	1	12	0	-2.30259	1
2	1	0	1	6	0	-2.30259	1
3	0.61077	15.692	1	10	0.00268	2.21263	1.53521
4	0.86837	65.972	1	10	1E-05	13.8188	2.62972
5	0.90185	91.889	1	10	2.3E-06	18.3256	3.09533

*Dependent Variable: $\ln v$ (for complexes **1, 2, 3, 4, 5**), 785 mmHg and 25 ° C.

**F = the Fischer – Snedecor statistics

*** Sig. = degree of significance

The oxidation condition: p = 785 mm Hg and t = 25 ° C

Table 2
DATA OF THE ANALYSIS OF THE VARIANCE (ANOVA) FOR
THE FIVE CASES OF OXIDATION

Complexes	Parameters	Sum of Squares	df*	Mean Square	F	Sig.
1	Regression	9.934	1	9.934	0	0
	Residual	0	12	0		
	Total	9.934	13			
2	Regression	14.622	1	14.622	0	0
	Residual	0	6	0		
	Total	14.622	7			
3	Regression	13.562	1	13.562	15.692	0.0027
	Residual	8.643	10	0.864		
	Total	22.205	11			
4	Regression	19.212	1	19.212	65.972	1E-05
	Residual	2.912	10	0.291		
	Total	22.124	11			
5	Regression	18.148	1	18.148	91.889	2E-06
	Residual	1.975	10	0.197		
	Total	20.123	11			

*df = degree of freedom

Predictors: (Constant), ln c (for complexes 1, 2, 3, 4, 5), 785 mmHg and 25 ° C.

Dependent Variable: ln v (for complexes 1, 2, 3, 4, 5), 785 mmHg and 25 ° C.

So, for instance looking at catalyst **3**, $S = 0.98$. Comparatively to the average $|y| = 13.5$, the approximate prediction error is in the range $\hat{y} \pm s = 13.5 \pm 0.98$, that is ca. 7% relative error, which is acceptable. For the other catalysts model variance "s" is between zero and 0.46. The relative errors are in the range: for catalyst **1**, $\hat{y} \pm s = 9.9 \pm 0.0 = 0\%$; for catalyst **2**, $\hat{y} \pm s = 14.6 \pm 0 = 0\%$; for catalyst **4**, $\hat{y} \pm s = 19.2 \pm 0.57 = 3\%$; for catalyst **5**, $\hat{y} \pm s = 18.1 \pm 0.46 = 2.5\%$.

With the exception of case **3**, the other situations indicate null or very low values of the significance degree, although even case **3** presents this value under the 0.05 thresholds. Therefore, the independent variable explains the variation of the dependent variable, assuming a risk coefficient of 0.05. The order of the oxidation reaction is one for complexes **1** and **2**, one and a half for complex **3**, two and a half for complex **4** and three for complex **5**. The independent variable ($x = \ln c$) explains the variation of the dependent variable ($y = \ln v$) in all cases of oxidation analysed, assuming a risk coefficient of 0.05.

Kinetic significances of the reaction order values

The oxidation of the DTBP organic substrate is a solution-gas reaction, which implies that a series of intermediary processes may be observed, such as the diffusion of the gas (the molecular oxygen) at the level of the solution, fixation of the molecular oxygen on the

complex, etc. A fractional reaction order expresses the competition between the physical and chemical processes taking place in the studied system. Actually, order one is a "pseudo-one" as, being a catalytic reaction; the reaction rate is proportional to the concentration of the catalyst according to the relation:

$$\frac{dx_s}{dt} = k c_{\text{catal}} c_{s,0} (1 - x_s) \quad (11)$$

where, x = substrate conversion and c_{catal} is the concentration of catalyst.

Apparently, the reaction is of order one since the order is affected by the participation of the solvent (DMF) and by the catalyst whose concentration did not change. The influence of the solvent is explained both by a "cage effect" (with a certain value of the energy barrier) and by a viscosity effect. Also, the effect of the solvent can be thermodynamically predicted by the differences between the solvation degrees of the various species of the reacting substances and those of the reactive complex. If the solvent has a selective solvation action, then an increase of the activation energy will be reached. On the other hand, recognition of an endothermic solvation and a decrease of the activation energy means that the reactive complex solvates better.

Influence of the catalyst nature on the reaction rate

The influence exerted by the nature of the complex used as a catalyst on the reaction rate is studied using the variance analysis (ANOVA). The values of the average oxidation rate for catalysts 1-6 are given in table 3.

Table 3
INFLUENCE OF THE CATALYST ON THE OXIDATION RATE

Complexes	N*	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum	Oxidation rate average
				Lower Bound	Upper Bound			
1	14	1.797E-06	4.802E-07	2.223E-06	4.298E-06	4.000E-07	5.900E-06	3.261 E-06
2	8	5.432E-06	1.921E-06	7.42E-07	9.825E-06	4.000E-07	1.390E-05	5.284 E-06
3	12	1.558E-06	4.498E-07	1.074E-06	3.054E-06	0.000E+00	3.800E-06	2.064 E-06
4	17	1.975E-06	4.789E-07	4.72E-07	2.503E-06	1.000E-07	5.900E-06	2.062 E-06
5	17	2.149E-06	5.212E-07	5.64E-07	2.774E-06	0.000E+00	5.500E-06	2.337 E-06
Total	68	2.767E-06	3.355E-07	1.777E-06	3.116E-06	0.000E+00	1.390E-05	

* N = number of cases

Table 4
THE ANOVA PARAMETERS OF THE INFLUENCE OF THE CATALYST ON THE OXIDATION RATE

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.000	4	0.000	3.878	0.007
Within Groups	0.000	63	0.000		
Total	0.000	67			

Table 5
TEST OF THE HOMOGENEITY OF THE VARIANCES – CONDITION FOR ANOVA – IN THE STUDY OF THE VALUES OF THE OXIDATION RATES FOR THE 5 CASES OF CATALYSIS

Levene Statistic	df1	df2	Sig.
10.397	4	63	0.000

For such mean values, there exist the confidence intervals presented in table 3 assuming a risk coefficient of 0.05. Namely, there exists a risk of 5% that the real value of the mean should not be covered by the interval of the values [Lower Bound, Upper Bound], table 4.

The value of the confidence degree is lower than the assumed risk coefficient (0.05). This means that the null hypothesis of equality of the means for the five oxidation rates is rejected. Therefore, from a statistical point of view, the oxidation rates do significantly differ as a function of the catalyst nature. The Fischer statistics, (F), is calculated with the relation:

$$F = S_E^2 / S_R^2 \quad (12)$$

in which the numerator represents the estimator of the "Between Groups" variance, which is calculated as a mean of the squares of the mean deviation of each group versus the mean recorded for all groups, showing the influence of the grouping factor (nature of catalysts, fig. 1). The denominator represents the estimator of the group variances showing the variance within each group (catalyst).

Even if the restriction illustrated in table 5 does not appear, no differentiation could be made at the population level among the five types of Schiff bases with a catalytic role. Therefore, only influences at the sample level are possible.

By using the test for homogeneity of variances, Levene test, the value of the level of significance is of 0.000, which is, lower than the used risk coefficient. Therefore, the variances of the five cases of oxidation are not equal so the condition of homogeneity of variances (homoscedasticity) required for applying the ANOVA analysis is thus accomplished, table 6.

In all the five cases of oxidation, the normality test (Kolmogorov-Smirnov) gives values of the level of significance higher than of the assumed risk coefficient. Therefore, we can say with a 0.95 probability that the values, representing the oxidation rates/ reaction rate with molecular oxygen, for the catalysts **1**, **2** and **3**, are normally distributed, but not for the catalysts **4** and **5** (in the Gauss-Laplace direction). The distribution of the oxidation rate versus catalysts is presented in figure 4.

Thus, complex **2** which, according to figure 4., assures the highest oxidation rate, shows:

Table 6
KOLMOGOROV-SMIRNOV (KSL) TEST FOR THE DECISION OF NORMAL LAPLACE-GAUSS DISTRIBUTION OF THE VALUES OF THE OXIDATION RATES (MOL/L . min)

Complexes	N	Normal Parameters (a, b)		Most Extreme Differences			KSL	Sig. (2-tailed)
		Mean	Std. Deviation	Absolute	Positive	Negative		
1	14	3.261 E-6	1.797 E-6	0.137	0.095	-0.137	0.514	0.954
2	8	5.284 E-6	5.432 E-6	0.220	0.220	-0.185	0.623	0.832
3	12	2.064 E-6	1.558 E-6	0.201	0.186	-0.201	0.697	0.716
4	17	1.488 E-6	1.9747 E-6	0.301	0.301	-0.239	1.242	0.091
5	17	1.669 E-6	2.149 E-6	0.296	0.296	-0.225	1.221	0.101

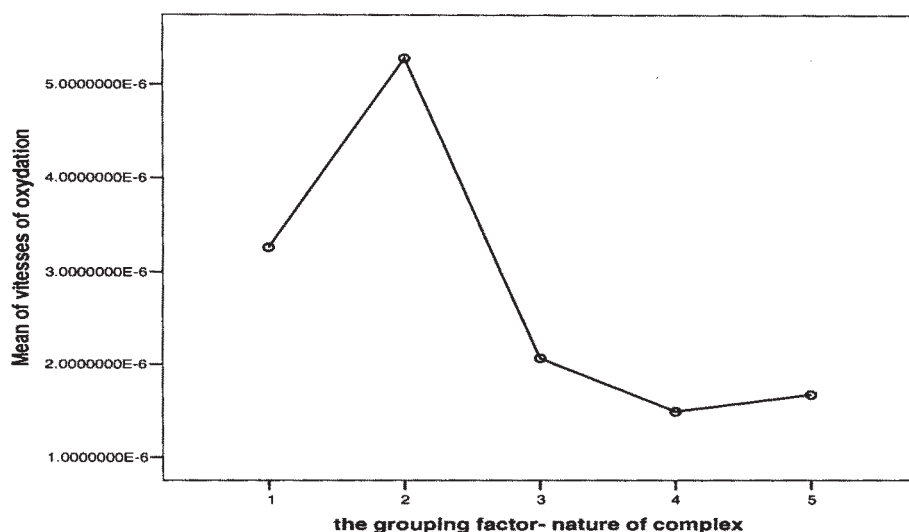


Fig. 4. The distribution of the oxidation rates depending on the nature of the catalyst

-the lowest probability among the studied samples that the oxidation rate should be lower than the lower bound of the variation interval of the mean oxidation rate per sample, calculated with a 0.05 risk coefficient;

-the highest probability of the studied samples that the oxidation rate should be lower than the upper bound of the variation interval of the mean of the oxidation rate per sample, established with a 0.05 risk coefficient.

Correspondingly, complex 4 which, according to figure 3, assures the lowest oxidation rate evidences:

-the highest probability from all studied samples that the oxidation rate should be lower than the lower bound of the variation interval of the mean oxidation rate per sample established with a 0.05 risk coefficient;

-the lowest probability from all studied samples that the oxidation rate should be lower than the upper bound of the variation interval of the mean oxidation rate per sample, established with a 0.05 risk coefficient.

We can not assume whether the reaction rate of any oxidation reactions, developed during heterogeneous catalysis with molecular oxygen involving catalysts with the above mentioned structures, are statistically arranged in the established order depending on the nature of the complex playing the role of catalyst. In other words, assuming an acceptable degree of risk, one cannot anticipate whether complex 2 will allow the highest oxidation rate in similar oxidation reactions or, on the contrary, whether complex 4 will allow the lowest oxidation rate in similar oxidation reactions.

For that reason only the catalytic behaviour of the complexes used in this oxidation reaction will be mentioned.

Influence of the steric hindrance nature from cobalt(II) complex – (catalyst) on the oxidation reaction rate of DTBP with molecular oxygen

The oxidation rate agrees with the structures of the complexes. Thus, complex 2, which has two methylenic groupings in azomethynic and para positions versus to the phenolic oxygen, presents an increase of the electrons density on the metallic centre compared to complex 1. This means that the metallic ion is more electronegatively charged and becomes more oxidized, thus increasing the reaction rate. Complex 3 has an ethyl grouping in azomethynic position that also leads to an increase of electrons density on the metallic ion, yet the reaction rate significantly decreases compared to complex 2. For complex 4, the donor effect of the electrons of the ethyl grouping from the azomethynic position is compensated by the attraction effect of the iodine ions; a decrease of electronic density on the metallic ion takes place making it more difficult to oxidize. This means that the reaction rate will implicitly decrease.

In the case of complex 5, the nitro grouping from the para position versus the phenolic oxygen with an effect of electrons attraction also leads to a significant decrease of the electronic density of the metallic ion, which leads to a diminished reaction rate.

Conclusions

The experimental data have been processed for the calculation of the kinetic parameters and of the confidence intervals. Statistical modelling allows evidencing the dependency of the catalyst nature on the reaction rate of the oxidation reaction with molecular oxygen for reaction catalysed by Schiff bases complexes. Certain correlations between the Schiff base structure with a catalytic role and the oxidation rates for the particular cases investigated have been confirmed.

References

1. MEUNIER, B., *Chem Rev.*, 92, 1992, p.141
2. MANSUY, D., *Pure Appl. Chem.*, 59, 1987, p.759
3. UENO, T., KOSHIYAMA, T., ABE, S., YOKOI, N., OHASHI, M., NAKAJIMA, N., WATANABE, Y., *J. Organometallic Chemistry*, 692, 2007, p.142
4. ABE, S., UENO, T., REDDY, P. A. N., OKAZAKI, S., HIKAGE, T., SUZUKI, A., YAMANE, T., NAKAYAMA, H., WATANABE, Y., *Inorg. Chem.*, 46, 2007, p.5137
5. LU Y., *Angew. Chem. Int. Ed.*, 45, 2006, p.5888
6. SIMÁNDI, L. I., *Dioxygenation activation homogenous catalytic oxidation*, Elsevier, 1991
7. VIGATO, P. A., TAMBURINI, S., *Coord. Chem. Reviews*, 248, 2004, p.1717
8. COLLMAN, J. P., ZENG, L., BRAUMAN, J. I., *Inorg. Chem.*, 43, 2004, p.2672
9. BRYLIAKOV, K. P., TALSI, E. P., *Angew. Chem. Int. Ed.*, 43, 2004, p.5282
10. NEMES, A., BAKAC, A., *Inorg. Chem.*, 40, 2003, p.746
11. PUI, A., BERDAN, I., BADARAU, I. M., GREF, A., PERRÉE-FAUVET, M., *Inorg. Chim. Acta*, 320, 2001, p.167
12. PUI, A., MAHY, J. P., *Polyhedron*, 26, 2007, p.3143
13. AMBROZIAK, K., PELECH, R., MICHERT, E., DZIEMBOWSKA, E., ROZWADOWSKI, T., *J. Mol. Catalysis A: Chemical*, 211, 2004, p.9
14. SIMÁNDI, L. J., SIMÁNDI, T. M., MAY, Z., BESENYEI, G., *Coord. Chem. Rev.*, 245 (1-2), 2003, p. 85
15. OWSIK, I., KOLARZ, B. N., JEZERSKA, J., *Catalysis Letters*, 107, 3-4, 2006, p.197
16. UENO, T., OHASHI, M., KONO, K., SUZUKI, A., YAMANE, T., WATANABE, Y., *Inorg. Chem.*, 43, 2004, p.2852
17. RIO, M. F., PUJOL, D., CHATERON, C. B., FAUVET, P. M., GAUDMER, A., *J. Chem. Soc. Perkin Trans. I*, 1984, p.1971
18. OMURA, K., *J. Org. Chem.*, 61, 1996, p.2006
19. DENG, Y., BUSCH, D. H., *Inorg. Chem.*, 34, 1995, p.6380
20. CAREY, J. R., MA, S. K., PFISTER, T. D., GARNER, D. K., KIM, H. K., ABRAMITE, J. A., WANG, Z., GUO, Z., LU, Y., *J. Am. Chem. Soc.*, 126, 2004, p.10812
21. PUI, A., *Croatica Chemica Acta*, 75, 1, 2002, 165
22. SCHNEIDER, I. A., *Cinetica Chimica*, Ed. Didactica si Pedagogica, Bucuresti, 1974
23. TRAMBOUZE P., Van LANDEGHEN H., WAUQUIER J-P., *Chemical Reactors: Design, Engineering, Operation*, Edition Technip, Paris, 1988
24. GALACTION A. I., CASCAVAL D., ONISCU C., TURNEA M., *Chem. Biochem. Eng. Q*, 19, 2005, p.87.
25. GAVRILESCU M., *Chem. Biochem. Eng. Q*, 18, 2004, p. 195
26. JABA, E., *Statistica*, third edition, Editura Economică, Bucuresti, 2002
27. KANJI, G. K., *100 Statistical tests*, Sage publications London New York Paris New Delhi, 1993
28. LANDAU, S., EVERITT, B. S. *A Handbook of Statistical Analyses Using SPSS*, CRC Press, 2003
29. DUMITRU, M., SAMIDE, A., PREDĂ, M., MOANTA, A., *Rev. Chim.*, (Bucharest), 60, no. 9, 2009, p. 957
30. GERBER S.B., FINN, K.V., *Using SPSS for Windows*, second edition, Springer, 2005

Manuscript received: 19.05.2010