

# Kinetics and Mechanisms of Oxidation of 4-hydroxy -3-methoxy benzaldehyde (Vanillin) by Bi (V) in Aqueous Alkaline medium

Parashuram Mishra

Department of Chemistry, University of Delhi, Delhi-110007, India

*Email : physicsmishra@rediffmail.com*

**Abstract:** The title reaction was investigated in aqueous alkaline medium. A first dependence in Bi (V)) concentration and a order in both Vanillin and alkali were obtained at the concentration studied. The effect of added products and the ionic strength of the reaction medium have no significant effect on the reaction rate. Effect of temperature on the rate of reaction has also been studied and Eyring's activation parameters have been evaluated. A mechanism based on the experimental results in proposed and the rate law is derived.

## 1. Introduction

Vanillin is a very popular flavouring reagent in the food industry and widely used in the synthesis of drugs; 40% of vanillin is consumed in manufacturing drugs such as Aldomet, L-Dopa (I) and Trimethaprin 2A. It is also used in the preparation of perfume and as a catalyst to polymerize methacrylate (2). 3-methoxy-4-hydroxy benzaldehyde has both phenolic and aldehyde groups and is capable of undergoing three different types of reaction those of the aldehyde groups the phenolic hydroxyl, and the aromatic nucleus. The aldehydic group undergoes condensation (3) reactions that allows substitution (4) for the aldehyde reactions, such as Canizaro's reaction. If the hydroxyl group in vanillin is protected, it undergoes oxidation [4] to vanillic acid. As a phenol, vanillin forms esters and ethers and the nucleus is easily substituted by halogen and hetero groups. In comparison with most others aldehydes, vanillin is notable for its stability. Literature reveals that no reports on the oxidation of vanillin except in one case (5) and in order to explore the mechanistic aspects of Bi(V) oxidation in alkaline medium, vanillin as a substrate.

The use of Bi(V) as an oxidant in alkaline medium and has been widely used to oxidise numerous organic and inorganic compounds. The author has

suggested that the neutral Bi(V) ion simply acts as an electron-abstracting reagent in redox reactions. However, W. J. et al. suggested (6) different path the oxidation of aldehydes, ketones and nitroparaffines. Singh et al. (7,8) while discussing the oxidations of form aldehydes, acetones and ethyl methyl ketone, have suggested that the oxidation takes place via electron transfer process resulting in the formation of a free-radical intermediate. The present work deals with the reaction to investigate the redox chemistry of Bi (V) in this medium and arrive at a suitable mechanisms for the oxidation of Vanillin by alkaline Bi(V).

## 2. Experimental

### 2.1 Materials and Methods

All chemicals used were of analytical grade. Doubly distilled water (from  $\text{KMnO}_4$  in an all glass apparatus) was used throughout the work. Solution of vanillin (s.d. fine chem) was prepared by dissolving an appropriate amount of sample in distilled water. The solution of Bi(V) was prepared by dissolving  $\text{NaBiO}_3$  (BDH) in an alkaline solution and standardized volumetrically. NaOH and  $\text{NaClO}_4$  were employed to maintain the required alkalinity and ionic strength respectively.

## 2.2 Kinetic Measurements

All kinetic measurements were performed under pseudo first order conditions where [vanillin] was always in excess over [Bi(V)] at a constant ionic strength of  $0.1 \text{ mol dm}^{-3}$  in alkaline medium at a constant temperature of  $(25 \pm 0.1)^\circ\text{C}$  respectively, unless otherwise stated. The reaction was initiated by mixing the thermostated solutions of Bi (V) and vanillin, which also contained the required concentration of NaOH and  $\text{NaClO}_4$ . The process of the reaction was followed by measuring the decrease in absorbance of Bi(V) in the reaction solution in a 1 cm quartz cell of Julabo thermostated compartment of a Hitach model 150-20 spectrophotometer at its absorbance 275 nm as a function of times where other constituted of the reaction mixture do not absorb significantly. The applicability of Beer's law for Bi (V) at 275 nm under the reaction had verified. pseudo-first order rate constant  $k_{\text{obs}}$  were obtained (Table I and II) from the slopes of plots of  $\log_{10} [\text{Bi (V)}]$  versus time; the plots were linear up to 60% completion o the reaction in alkaline medium and the  $k_{\text{obs}}$  values were reproducible to within  $\pm 5\%$  and deviation from linearity was observed above 40% of reaction due to the retarding effect of one of the products Bi (V). The results are also interpreted in terms of the initial rate of the reaction to avoid the complexation, which may arise due to interference by the

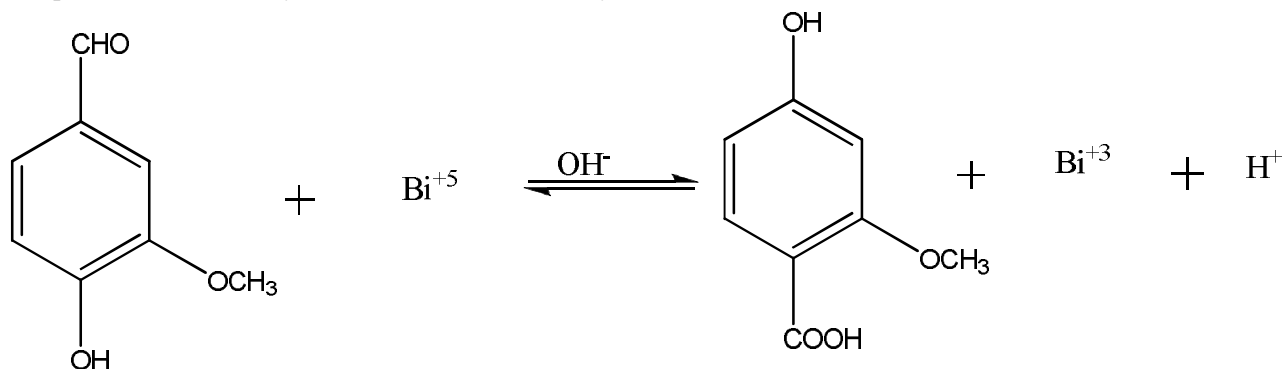
products such as Bi(V). Initial rates were obtained from the tangents at the initial stages of the concentration versus time curves by the plane mirror method (7) and were reproducible to within  $\pm 5\%$ . However, the  $k_{\text{obs}}$  values were used to interpret the results throughout the study.

The effect of dissolved oxygen on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of nitrogen. No significant difference between the results obtained under nitrogen and presence of air was observed. Always fresh solutions were used while performing the experiments.

## 3. Results and Discussion

### 3.1 Stoichiometry and Product Analysis

Reaction mixtures with different sets of concentrations of reactants where [Bi(V)] was in excess over [vanillin] at a constant ionic strength and alkali were kept for about 8 hr at  $(25 \pm 1)^\circ\text{C}$  in a thermostat reaction vessel. The remaining [Bi (V)] was assayed spectrophotometrically by measuring the absorbance at 275 nm. The results indicated that one moles of [Bi (V)] consumed one k mole of vanillin as following equation.



The stoichiometric ratio suggests that the main reaction products are vanillic acid and Bi(V). The acid was confirmed by spot test (8) and by its IR spectrum, which showed bands at  $3025$  and  $1733 \text{ cm}^{-1}$  due to OH and C=O stretching respectively.

### Reaction Order

The order with respect to [Vanillin] and [alkali] was found by  $\log k_{\text{obs}}$  versus  $\log_{10} [\text{concentration}]$  plots these orders were obtained by varying the concentration of reductant and alkali in turn while keeping constant.

### 3.2 Effect of [Co(II)]

The concentration of Bi(V) was varied in the range  $1.0 \times 10^{-4}$  to  $8 \times 10^{-4} \text{ mol dm}^{-3}$  at [vanillin];  $[\text{OH}^-]$  and ionic strength. The non-variation in the pseudo-first order rate constant at various concentration of Bi (V) indicates the order in [Bi(V)] was unity (Table I). This was confirmed by the linearity of plots of  $\log [\text{Bi (V)}]$  versus time for up to 80% completion of the reaction.

### 3.3 Effect of Vanillin

The substrate, vanillin was varied in the range of  $4.0 \times 10^{-4}$  to  $4.0 \times 10^{-2} \text{ mol. dm}^{-3}$  at  $25^\circ\text{C}$  keeping all others reactant's concentrations and conditions condition constant (Table I).

**Table-1: Effect of variations of [Bi (V)], [Vanillin] and [OH<sup>-</sup>] on the oxidation of vanillin by [Bi (V)] at 25°C, I =1.0 mol dm<sup>-3</sup>**

| [Bi(V)]×10 <sup>4</sup> (mol. dm <sup>-3</sup> ) | [Vanillin]×10 <sup>3</sup> mol.dm <sup>-3</sup> | [OH <sup>-</sup> ] mol.dm <sup>-3</sup> | k <sub>obs</sub> × 10 <sup>3</sup> s <sup>-1</sup> |
|--------------------------------------------------|-------------------------------------------------|-----------------------------------------|----------------------------------------------------|
| 0.8                                              | 3.0                                             | 0.4                                     | 5.33                                               |
| 1.0                                              | 3.0                                             | 0.4                                     | 5.35                                               |
| 2.0                                              | 3.0                                             | 0.4                                     | 5.39                                               |
| 6.0                                              | 3.00                                            | 0.4                                     | 5.33                                               |
| 8.0                                              | 3.00                                            | 0.4                                     | 4.25                                               |
| 5.0                                              | 4.00                                            | 0.4                                     | 5.45                                               |
| 5.0                                              | 2.00                                            | 0.7                                     | 6.20                                               |
| 4.0                                              | 8.00                                            | 0.1                                     | 4.03                                               |
| 4.0                                              | 8.00                                            | 1.0                                     | 2.73                                               |
| 6.0                                              | 8.00                                            | 0.2                                     | 6.45                                               |
| 6.0                                              | 8.00                                            | 0.2                                     | 0.55                                               |
| 6.0                                              | 8.00                                            | 0.2                                     | 1.65                                               |

### 3.4 Effect of alkali concentration

The effect of [alkaline] on the rate of reaction was studied at constant concentration of vanillin and ionic strength at 1.0 mol dm<sup>-3</sup> at 25°C. The rate constants increased with increases ion [alkali]

### 3.5 Effect of Ionic Strength and solvent Polarity

The effect of ionic strength was studied by varying the [NaClO<sub>4</sub>] in the reaction medium. The ionic strength of the reaction medium was varied from 1.0–3.0 mol·dm<sup>-3</sup> at constant [Bi(V)], [Vanillin] and [OH]. It was found that as ionic strength increases, the rate of the reaction increases (slope = 0.6).

### 3.6 Effect of Initially Added Products

The effect of initially added products, vanillin acid and Bi(V), on the rate of reaction was also studied in the range of 1.0×10<sup>-4</sup>, 1.0×10<sup>-3</sup> and dm<sup>3</sup> at 25°C at constant [Bi(V)], [vanillin], [OH] and ionic strength. The added vanillic acid did not alter the rate of reaction. However,

Bi (V) was shown to have a retarding effect on rate of reaction (Table II).

### 3.7 Effect of temperature

The kinetics were also studied at 30, 40 and 50°C at [Bi (V)] = 2.0×10<sup>-4</sup> dm<sup>-3</sup>, [vanillin] = 2.0×10<sup>-3</sup> mol·dm<sup>-3</sup> [OH<sup>-</sup>] = 6.0 mol·dm<sup>-3</sup>, I =0.6 mol. dm<sup>-3</sup> and the resulting k<sub>obs</sub> values were 2.25 × 10<sup>-3</sup>, 2.45 × 10<sup>-3</sup> and 2.65×10<sup>-3</sup>s<sup>-1</sup>. The corresponding Eyring's parameters are shown in Table 2 which can be evaluated with the following relations

$$\Delta H^* = \Delta E^* - RT$$

$$\Delta S^* = 2.3031 \log \left[ \frac{Ah}{kT} \right]$$

$$\Delta G^* = \Delta H^* - T \Delta S^*$$

where h is Plank's constant A is frequency factor and k is Boltzman constant

**Table 2: Effect of Temperature**

| Temp ° C | k × 10 <sup>2</sup> s <sup>-1</sup> |
|----------|-------------------------------------|
| 30       | 3.54                                |
| 40       | 4.97                                |
| 50       | 8.69                                |

### Eyring's Parameters

| $E^*/\text{Jmol}^{-1}$ | $\text{Log } A/\text{sec}^{-1}$ | $\Delta S^* \text{ JK}^{-1}\text{mol}^{-1}$ | $\Delta H^* \text{ KJ mol}^{-1}$ | $\Delta G^* \text{ kJmol}$ |
|------------------------|---------------------------------|---------------------------------------------|----------------------------------|----------------------------|
| 54.23                  | 7.4                             | 5.113                                       | 51.752                           | 14.98                      |

### Test of Free Radicals

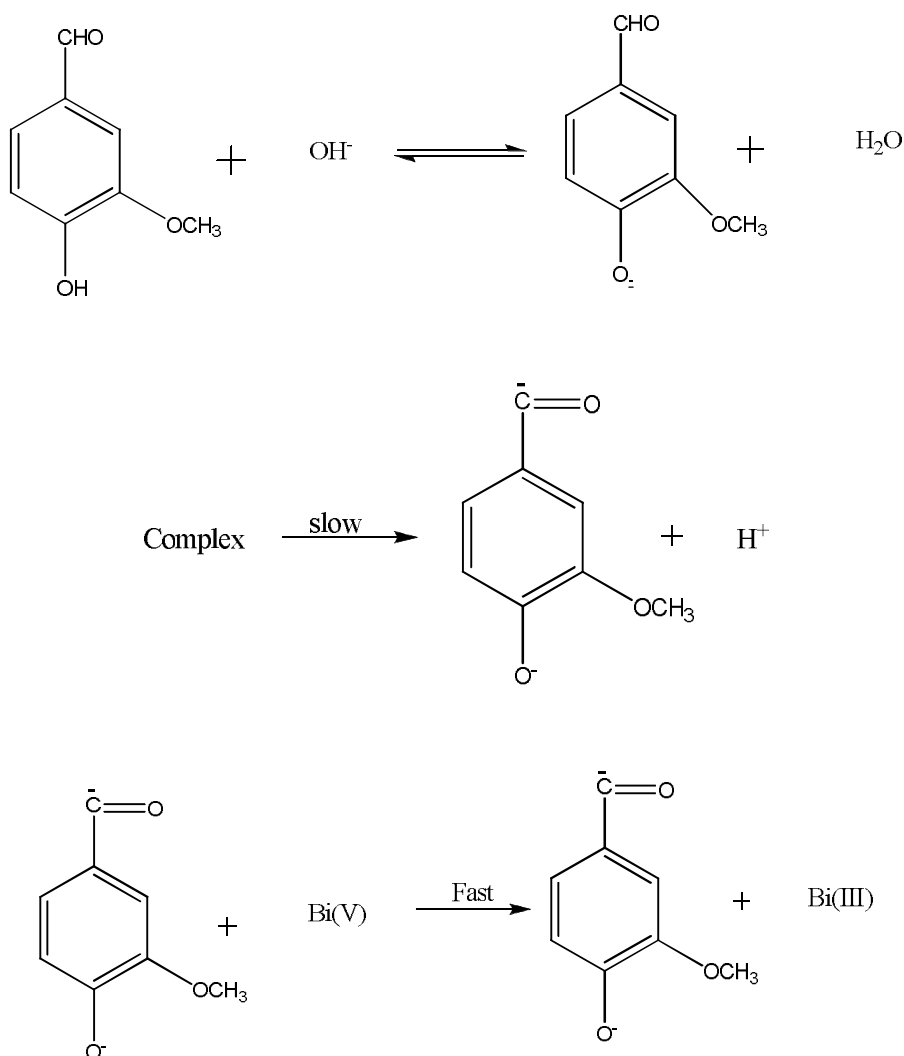
To test the intervention of free radicals, the reaction mixture was mixed with acetonitrile and kept 24 hours in an inert atmosphere, during the course of reaction and on diluting with methanol, no copious precipitate was obtained. It is contrary to expectation and discussed elsewhere.

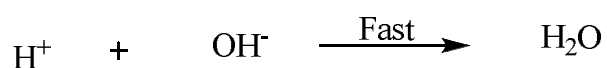
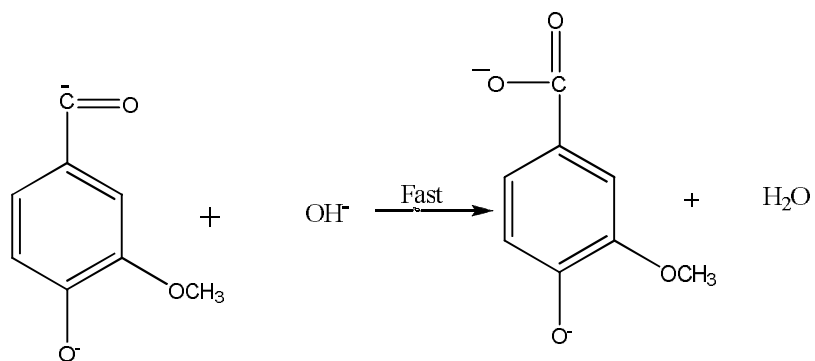
The overall reaction is approximately second order, being first order in [oxidant], fractional order in [vanillin] and  $[\text{OH}^-]$  and the retarding effect of Bi(V) can be accommodated in the following scheme I.

The oxidation of Bi(V) resembles that the with Cu(II) which reaction occurs through intervention of a free radicals with rapid oxidation [9-12]. The potential of

the Bi(V) – Bi(III) couple is greater than that for Cu(II)  $\rightarrow$  Cu(I). Hence there might be a rapid oxidation of the free radical that could mask the polymerization of acetonitrile. As found experimentally, sometimes the vinyl compounds themselves are oxidised under the experimental conditions used and the test for the radicals' foils (13, 17).

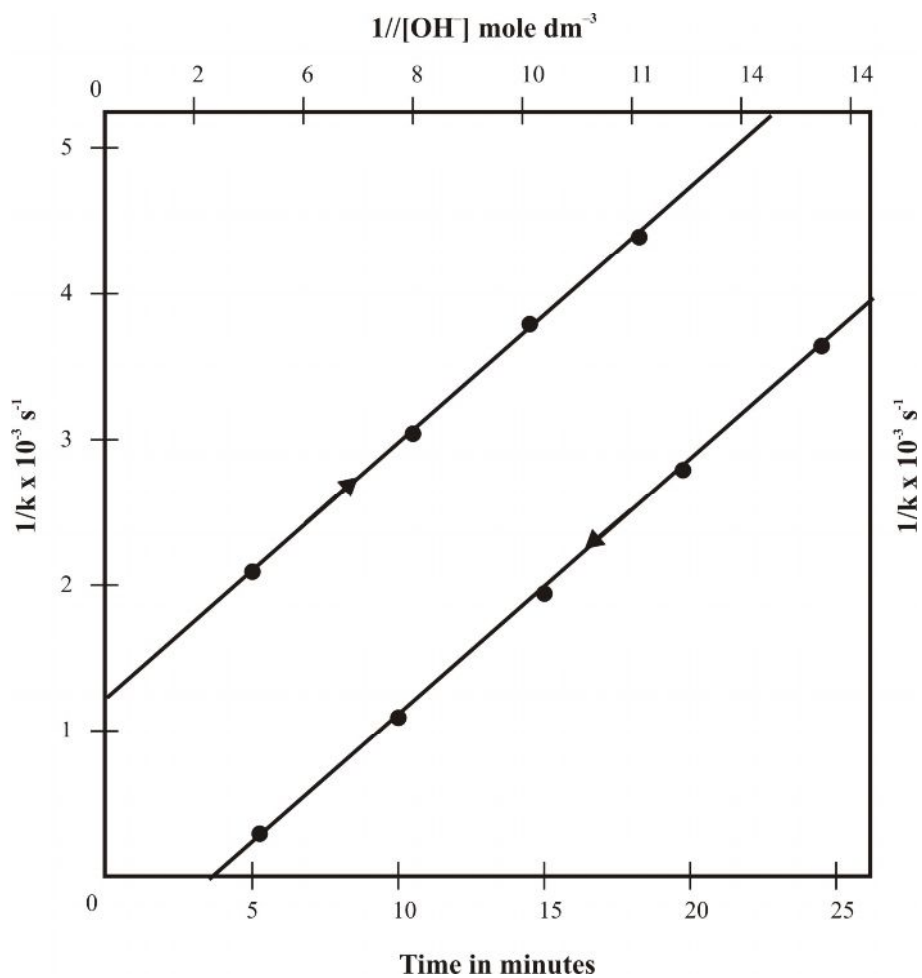
In the present study, the oxidation proceeds via the formation of the anion of vanillin, first it forms a complex with the oxidant in a prior equilibrium state. The plausible mechanisms to be proposed as





This decomposition in a slow step to give a free radical and in further fast steps, the anionic forms of vanillinic acid is formed as shown in Scheme I. Scheme I leads the rate law as follows.

$$\text{Rate} = \frac{d[\text{Bi(V)}]}{dt} = \frac{K K_1 K_2 [\text{Bi(V)}][\text{VAN}][\text{OH}^-]}{[1 + K_1[\text{OH}^-]](1 + K_1 K_2)[\text{VAN}][\text{OH}^-]} \dots\dots\dots 2$$



The denominator on right-hand side of equation (ii) should also contain a term  $(1+K_2[\text{Bi(V)}])$  which is neglected as it almost tends to unity due to low concentrations of Bi(V) used in the present study. The formation of the complex is proven kinetically by the non-zero intercept group of  $1/K_{\text{obs}}$  written as (Fig. 2). Equation (2) can be written as

$$K_{\text{obs}} = \frac{KK_1K_2[\text{VAN}][\text{OH}^-]}{(1+K_1[\text{OH}^-])(1+K_1K_2[\text{VAN}][\text{OH}^-])} \quad (3)$$

or

$$K_{\text{obs}} = \frac{KK_1K_2[\text{VAN}][\text{OH}^-]}{(1+K_1[\text{OH}^-])(K_1K_2[\text{VAN}][\text{OH}^-]) + (K_1K_2[\text{VAN}][\text{OH}^-])} \quad (4)$$

The term  $K_1K_2[\text{VAN}][\text{OH}^-]$  in equation (4) can be omitted due to the low concentration of vanillin and  $\text{OH}^-$ . Thus eq. (4) becomes.

$$K_{\text{obs}} = \frac{KK_1K_2[\text{VAN}][\text{OH}^-]}{(1+K_1[\text{OH}^-]) + K_1K_2[\text{VAN}][\text{OH}^-]} \quad (5)$$

Eq. (5) is verified in the following form

$$\frac{1}{K_{\text{obs}}} = \frac{1}{KK_1K_2[\text{VAN}][\text{OH}^-]} + \frac{1}{K_1K_2[\text{VAN}]} + \frac{1}{K} \quad (6)$$

The plots of  $1/K_{\text{obs}}$  versus  $1/[\text{OH}^-]$  and  $1/K_{\text{obs}}$  versus  $1/\text{Vanillin}$  were found linear shown in fig. (2). From the slopes and intercept, the constant  $K_1$ ,  $K_2$  and  $K$  were calculated as  $(4.3 \times 10^{-3} \text{ s}^{-1})$ ,  $(10.75 \times 10^{-3} \text{ s}^{-1})$  and  $(20.4 \times 10^{-3} \text{ s}^{-1})$  respectively. Using these values in eq. (5) the rate constants for various concentrations of  $[\text{Bi(V)}]$ , vanillin and  $\text{OH}^-$  were calculated.

The effect of ionic strength on the rate of the reaction is also in the expected direction as similar charged species Bi(V) and the anionic forms of vanillin is involved in the reaction. Ion pairing between Bi(V) and  $k_1$  is well known (13, 14). Thus, ion pairing between  $\text{Na}^+$  and Bi(V) appears to be reduced due to the expected value of slope (i.e. 2). Similar ion pairing is also experienced for the other reaction (14-7).

The Eyring's parameters were calculated and more ordered than the reactants. The small value of  $k$  also indicates the nature of activated complex.

## References

1. Goddard, William A., III; Chenoweth, Kimberly; Pudar, Sanja; Duin, Adri C.T.Cheng, Mu-Jeng. Structures, Mechanisms, and Kinetics of Selective Ammonoxidation and Oxidation of Propane over Multi-metal Oxide Catalysts Materials and Process Simulation Center (139-74), Topics in Catalysis (2008), 50(1-4), 2-18.
2. Mishra, Parashuram Kinetics and mechanism of oxidation of 6-[2-amino-2-(4-hydroxyphenyl)acetyl amino]-3,3-dimethyl-7-oxo-4-thiol-1-azabicyclo[3,2,0]heptane-2-carboxylic acid (amoxicillin trihydrate) with Bi(V) in  $\text{HClO}_4$ -HCl mixture Asian Journal of Chemistry (2008), 20(4), 2539-2544
3. Haber, J.; Stoch, J.; Zazhigalov, V. A.; Bacherikova, I. V.; Cheburakova, E. V. Selective oxidation of light alkanes on transition metal promoted vanadylpyrophosphate (VPO) catalysts Polish Journal of Chemistry (2008), 82(9), 1839-1852.
4. Liu, Yuan; Liu, Huiling; Li, Yan. Comparative study of the electrocatalytic oxidation and mechanism of nitrophenols at Bi-doped lead dioxide. Applied Catalysis, B: Environmental (2008), 84(1-2), 297-302.
5. Wang, Hongsen; Alden, Laif; DiSalvo, F. J.; Abruna, Hector D. Electrocatalytic mechanism and kinetics of SOMs oxidation on ordered PtPb and PtBi intermetallic compounds: DEMS and FTIRS study Physical Chemistry Chemical Physics (2008), 10(25), 3739-3751
6. Ward Jones, Sarah E.; Zheng, Susan H.; Jeffrey, Craig A.; Seretis, Spiros; Morin, Sylvie; Compton, Richard G. Stripping voltammetry of bismuth at

- Au(111): Mathematical modeling and numerical simulation. Journal of Electroanalytical Chemistry (2008), 616(1-2), 38-44.
7. Barteau, Mark A.; Lopez, Liza; Buttrey, J. Douglas In situ studies of hydrocarbon oxidation by bismuth molybdate and vanadyl pyrophosphate catalysts Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008 (2008)
8. Dasgupta, M.; Dasgupta, S.; Mahanti, M. K. Kinetics and mechanism of oxidation of sodium tetrahydroborate by bismuth(V) Oxidation Communications (2006), 29(1), 115-119.
9. Chen, Fengqiu; Wang, Yang; Zhan, Xiaoli. Monte Carlo simulation of propylene selective oxidation and ammoxidation over  $\square$ -Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> catalyst under anaerobic condition.. Chinese Journal of Chemical Engineering (2005), 13(5), 615-622
10. Mishra, Parashuram Kinetics and mechanism of oxidation of acetophenone oximes with Bi(V) in  $\text{HClO}_4$ -HF mixture. Asian Journal of Chemistry (2005), (2006), 18(1), 176-180.
11. Golubchenko, N. V.; Moshnikov, V. A.; Chesnokova, D. B. Kinetics and oxidation mechanisms of bismuth doped polycrystalline lead selenide layers, Materialy Elektronnoi Tekhniki (2005), (1), 23-28.
12. Kohtani, Shigeru; Tomohiro, Misa; Tokumura, Kunihiro; Nakagaki, Ryoichi. Photooxidation reactions of polycyclic aromatic hydrocarbons over pure and Ag-loaded BiVO<sub>4</sub>. Applied Catalysis, B: Environmental (2005), 58(3-4), 265-272

13. Itoh, Satoshi; Ono, Junji; Hino, Mitsutaka; Nagasaka, Tetsuya. Kinetic study on recovery of antimony in anode slime from used lead batteries utilizing volatile oxide formation Materials Transactions (2005), 46(3), 658-664.
14. Mishra, Parashuram Kinetics and mechanism of oxidation of diethanolamine with Bi(V) in HClO<sub>4</sub>-HF mixture. Oriental Journal of Chemistry (2004), 20(3), 525-528.
15. Alardin, F.; Wullens, H.; Hermans, S.; Devillers, M. Mechanistic and kinetic studies on glyoxal oxidation with Bi- and Pb-promoted Pd/C Journal of Molecular Catalysis A: Chemical (2005), 225(1), 79-89.
16. Mohamed Gehad G; Sharaby Carmen M, Metal complexes of Schiff base derived from sulphonamethole and o-vanillin. Synthesis, spectral, thermal characterization and biological activity Spectrochimica acta. Part A, Molecular and biomolecular spectroscopy (2007), 66(4-5), 949-58.
17. Uherek-Straszko H; Dolinska U; Wojdylo M Urinary vanilinomandelic acid (VMA) immediately before and after operations performed under endotracheal general anaesthesia with diethyl ether, halothane and nitrous oxide, neuroleptanalgetic agents and nitrous oxide. Anaesthesia, resuscitation, and intensive therapy (1974), 2(2), 123-32.

\*\*\*\*\*