



Oxovanadium Complex of 2-((2-aminophenyl) iminomethyl) 6-methoxy phenol, Preparation, Characterization and Catalytic activity in the oxidation of Benzoin

Bushra K. Al-Salami, Samah A. Jahad and Kahtan A. Asker
University of Basra, Collage of Science, Department of Chemistry, Basra, Iraq

Available online at: www.isca.in, www.isca.me
Received 29th February 2016, revised 13th March 2016, accepted 18th March 2016

Abstract

The oxovanadium complex derived from Schiff base ligand namely [2-((2-aminophenyl) iminomethyl) 6-methoxyphenol] result from condensation of 1, 2-phenylenediamine and o-vanillin was synthesized and characterized by elemental analysis, IR, ¹HNMR and EI-mass. The ligand acts as tridentate towards vanadyl ion via the azomethine nitrogen, phenolic oxygen and the lone pair of nitrogen atom of NH₂. The thermogravimetric (TG) analysis confirm high stability of the complex. Their catalytic activity properties in H₂O₂ promoted oxidation of the benzoin to benzil was investigated.

Keywords: Schiff base, Oxidation, Vanadyl Complexes.

Introduction

Schiff base are the compounds containing azomethine group (-HC=N-). They are condensation products of ketone or aldehydes with primary amines were first report by Hugo Schiff in 1864. Formation of Schiff base generally takes place under acid or base catalysis or in refluxed solvents¹. Condensation products of aldehyde with only one amine group of diamine compounds give half units which can react with another aldehyde or ketones giving unsymmetrical Schiff base²⁻⁴.

Schiff base of azomethine nitrogen donor heterocyclic ligands are well known due to their wide range of applications in pharmaceutical and industrial fields⁵, also Schiff base derived from aromatic amine and aromatic aldehyde have wide variety of application such as biological activity, catalytic activity as well used as ligands to obtain metal complexes⁶.

Oxidation of benzoin to benzil has been extensively studied for the production of fine chemicals⁷⁻¹⁰. In this paper we report the preparation a new Schiff base derived from o-phenylenediamine and o-vanillin and oxovanadium complex as catalyst in the oxidation of benzoin to benzil.

Methodology

Materials: 1,2-phenylene diamine (Merck). O-vanillin and vanadyl sulfate, were obtained from Fluka, all solvents used were of analytical grade and were used without further purification.

Instruments: The IR spectrum was recorded as KBr pellets on

Shimadzu FT-IR. The HNMR spectra were recorded on a Bruker (400 MHz), the spectra recorded in the DMSO-d₆. TMS was used as internal standard and referenced to 0.0 ppm. Mass spectrum scanned by EI-technique at 70eV using Agilent Technologies 5975C spectrometer.

Molar conductances were obtained using conductmeter- corning model 441 at room temperature – Elemental analysis (CHN) was performed using CHNS-932 LECO Apparatus.

Synthesis of Schiff base: Quantity of 20 mmol (0.216 gm.) of 1,2- phenylenediamine was dissolved in 20 mL of hot absolute ethanol, to this an ethanolic solution 1 mmol (0.152 gm.) of ethanolic solution of o-vanillin was add drop wise with constant stirring

The solution was acidified by concentrated acetic acid and then the mixture was refluxed for three hours, the orange solid product that formed after cooling was filtered, washed with hot water and recrystallized from water – ethanol (1:1) and dried in an oven at 70°C. Yield 75%. M.P. 264- 266°C.

Synthesis of Vanadyl complex A₁VO: Vanadyl Sulfate 1 mmol (0.163g.) was dissolved in hot water and the aqueous vanadyl sulfate solution was add drop wise into hot ethanolic solution of Schiff base ligand 1mmol (0.243 gm.).

The above mixture was reflux for one hour. Green precipitate formed which was filtered, washed several times with hot water and dried at 80°C Yield 88%. M.P. 298°C. The observed physical properties are given in Table-1.

Table-1
Analytical and physical data of ligand and their Vanadyl complex

Compound	Formula	Color	M.P c°	Elemental analysis found (calc.)			(ohm ⁻¹ . cm ² .mol ⁻¹)	Yield%
				C%	H%	N%		
A ₁	C ₁₄ H ₁₄ N ₂ O ₂	Orange	264-269	69.4 (69.74)	5.7 (5.2)	11.57 (11.8)	-	75
A ₁ V _O	C ₁₄ H ₁₄ N ₂ O ₂ VO	Green	298dec	51.70 (51.36)	4.34 4.43	8-61 (8.82)	8	88

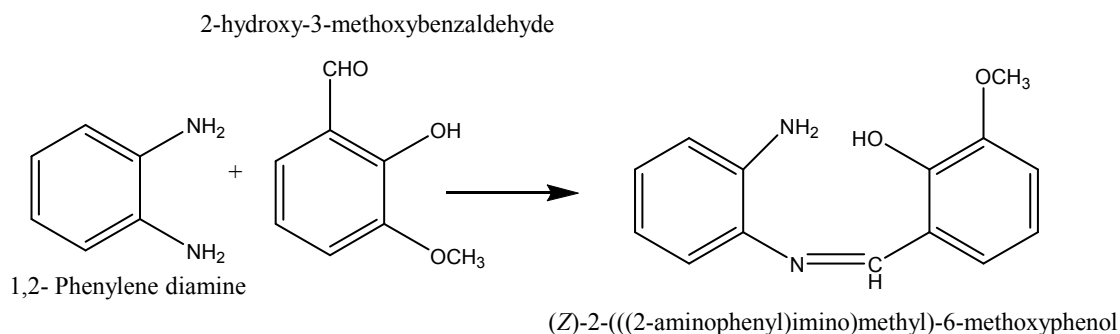
Results and Discussion

Scheme-1 shows the steps of synthesis of the Schiff base. The Schiff base (A₁) and oxo vanadium (IV) complex are subjected to elemental analysis. The result obtained is in good agreement with those calculated for suggested formula the Schiff base complex is soluble in DMF, DMSO. The analytical data indicate that the metal to ligand ratio is (1:1). The low conductivity (8 Ω⁻¹ cm² mol⁻¹) in 10⁻³m DMF solution indicates that is non-electrolytic nature. The value suggests that no anions are present outside the coordination spheres¹¹.

IR spectra: The IR spectra of the complex were compared with the Schiff base as in Table-2. In order to know the coordination sites that may be involved in chelating. The position and intensities of these peaks are expected to be changed on chelating. The IR spectrum of ligand showed a strong band at 3369 cm⁻¹ attributed to NH₂. Group of 1-2-phenylene diamine. The IR of ligand show in Figure-1. The absence of band at

1693cm⁻¹ due to C=O of the aldehyde. Instead a new band at 1612 cm⁻¹ due to azomethine (HC=N) linkage appeared¹¹. Indicating that the condensation between 1-2-phenylene diamine and o-vanilin has taken place resulting in to formation of the desired ligand A₁, on complex the band of azomethine group shift to lower wave number in the range 1605 cm⁻¹ indicating the coordination of the azomethine nitrogen atom to the vananyl ion¹².

The ligand show a broad band at 3466 cm⁻¹ characteristic of stretching of OH group, this band disappear in the complex spectrum Figure-2. Suggest the involvement of phenolic oxygen with metal after deportation, also a strong band at 1253cm⁻¹^{13,14} attributed to the C=O in the IR spectrum of the ligand attributed to C-O gets shifted to a lower wave number in the complex to 1248cm⁻¹ and this is indicative of banding through phenolic oxygen.



Scheme-1
Synthesis the Schiff base

Table-2
Important IR spectral data cm⁻¹ of Schiff base and their complex

Compound	N-H str.	O-H str.	O-H H ₂ O	C-H aromatic	C-H alipatic	HC=N str.	V=O
A ₁	3369	3466	-	3079	2950	1612	-
A ₁ V _O	3504	-	3558	3058	2930	1605	981

HNMR: HNMR spectrum of Schiff base ligand in DMSO-d₆ is shown in Figure-3. The spectrum show three singlet signal one of them at δ 3.8ppm (3H) attributed to methoxy group (OCH₃)¹⁴, and the other signal at δ 8.9 ppm assigned to the proton of the

azomethine (HC=N)¹⁵, a signal at δ 13.2 ppm attributed to phenolic proton¹⁶. The multiple signal in the rang δ 6.96-7.64 ppm attributed to aromatic proton¹⁵.

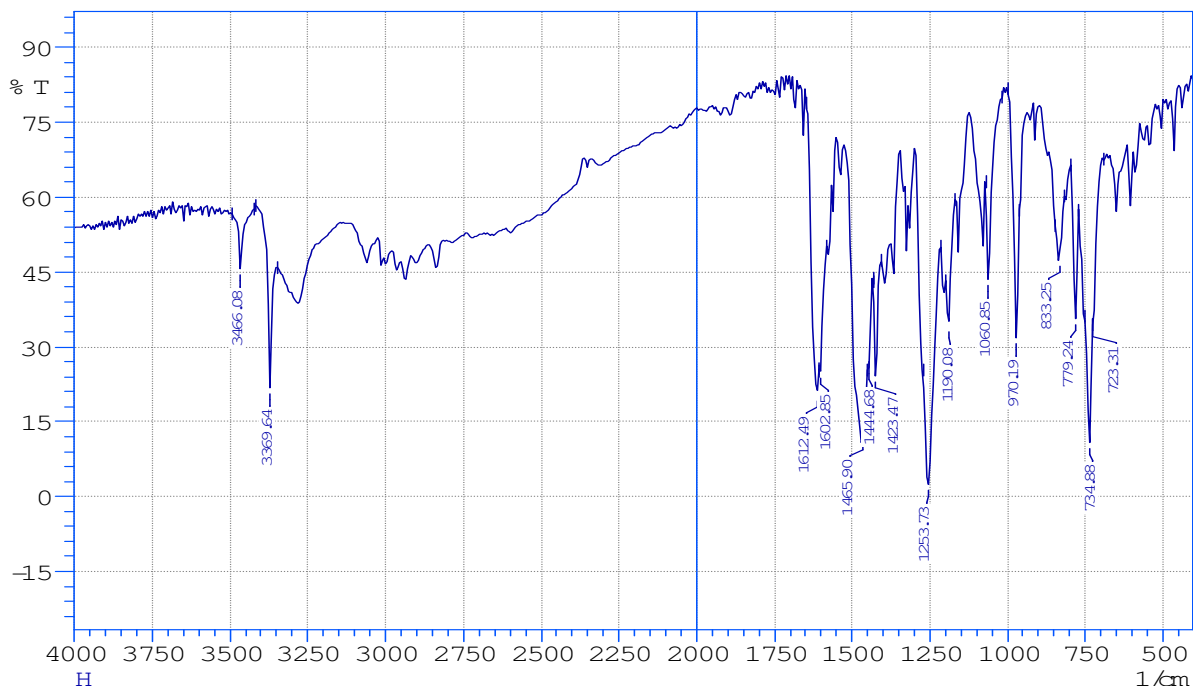


Figure-1
 IR Spectrum of 2-(2-aminophenyl) iminomethyl 6-methoxy phenol

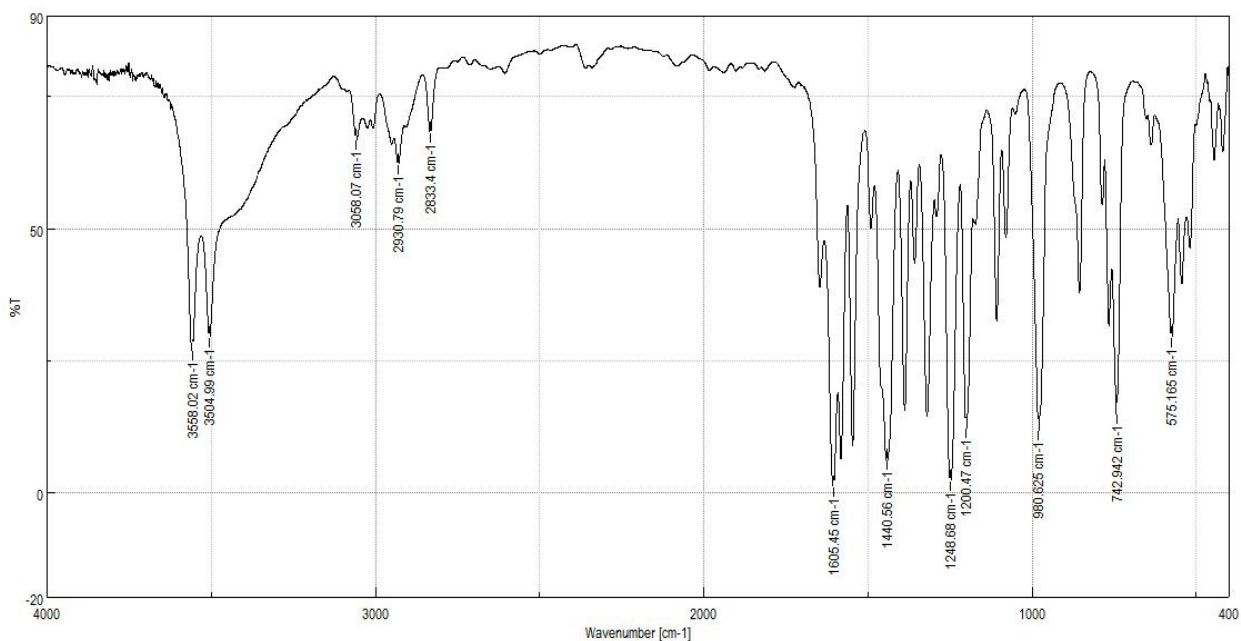


Figure-2
 IR Spectrum of Vanadyl Complex

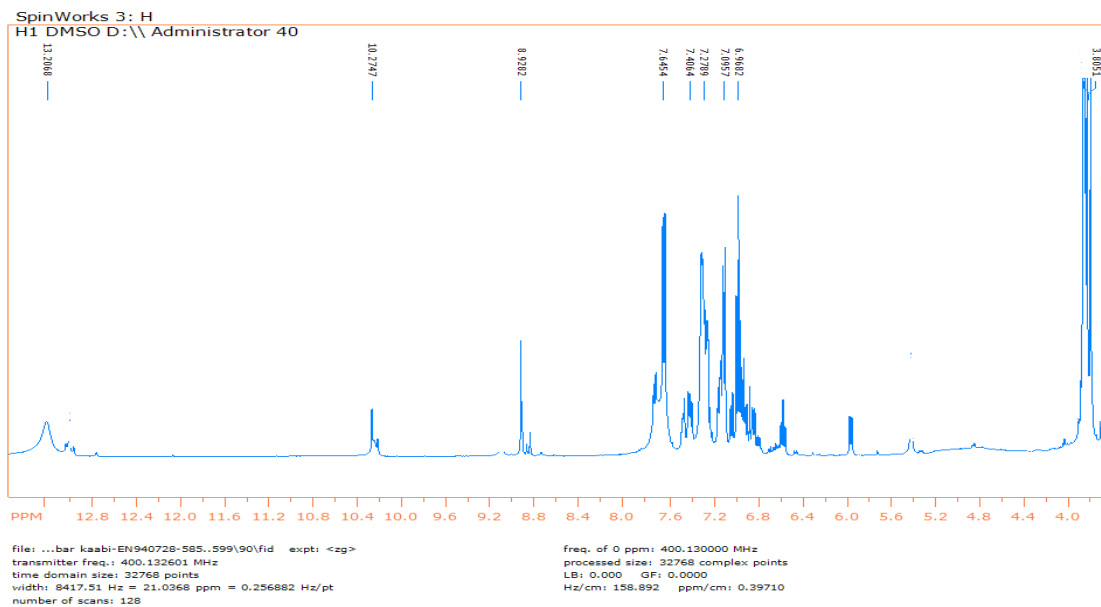


Figure-3
¹H NMR Spectrum of 2-(2-aminophenyl) iminomethyl 6-methoxy phenol

EI-Mass: The mass spectrum of ligand Figure-4. Shows the exact molecular ion at m/z242 with relative abundance 52% this peak indicate that the condensation between aldehyde and amine has take place resulting into the formation of the Schiff base ligand with the ratio (1:1) which agreement with the formula

and its molecular ion. Also the spectrum shows a peak at m/z 241 with relative abundance 85% corresponds to the ion $[M - H]^+$, while the base peak appear at m/z 119 which attributed to the ion $[C_7H_7N_2]$.

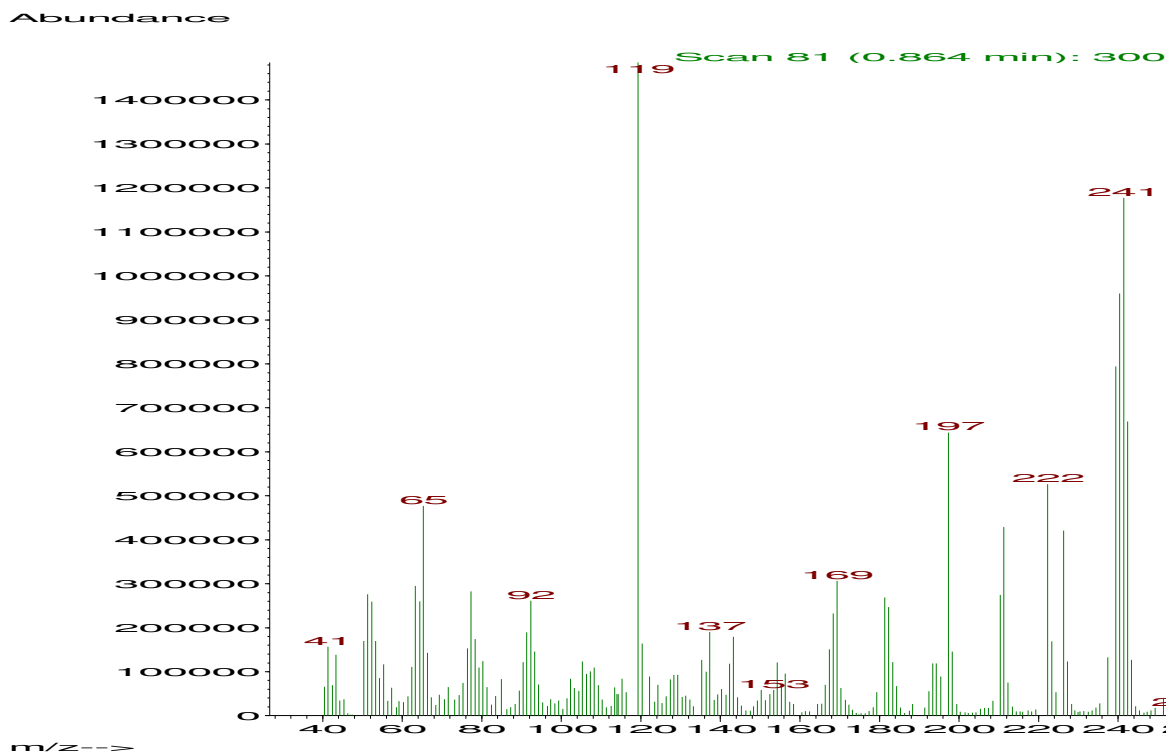


Figure-4
Mass Spectrum of of 2-(2-aminophenyl) iminomethyl 6-methoxy phenol

Thermal analysis: The thermal investigation was carried out from room temperature to 600°C under nitrogen atmosphere (20 mL/min) with heating rate 10°C/min. The thermo gram of compound complex Figure-5. Indicate no mass loss up to 120°C which indicate the totally absence of lattice water¹⁶. The curve show a mass loss between (130 – 220°C) 5.5% which equivalent to loss of one coordinated water molecule (theoretical 5.53%)¹⁶.

Catalytic activity: The catalytic activity of complex in oxidation of benzoin to benzil was carried out in a 25ml R.B.F filed with condenser, aqueous solution (28%) of H₂O₂ as an oxidized agent. MeCN and CCl₄ were used as solvent. The

catalytic activity study was carried out in 30°C and 50°C, the effect of time was studied. The product was monitored by UV-Visible Spectroscopy using 1cm quartz cell, the λ_{max} of benzil 290 nm. (Figure-6).

Figure-7 shows that the absorbance at 290 nm increases with reaction time as an indication of the catalysts, namely A₁VO.

The influence of time on the oxidation was found to increase (3.7 folds) as increasing the time from 1hr. to 25 hr. at 30°C in CCl₄ (Figure-8).

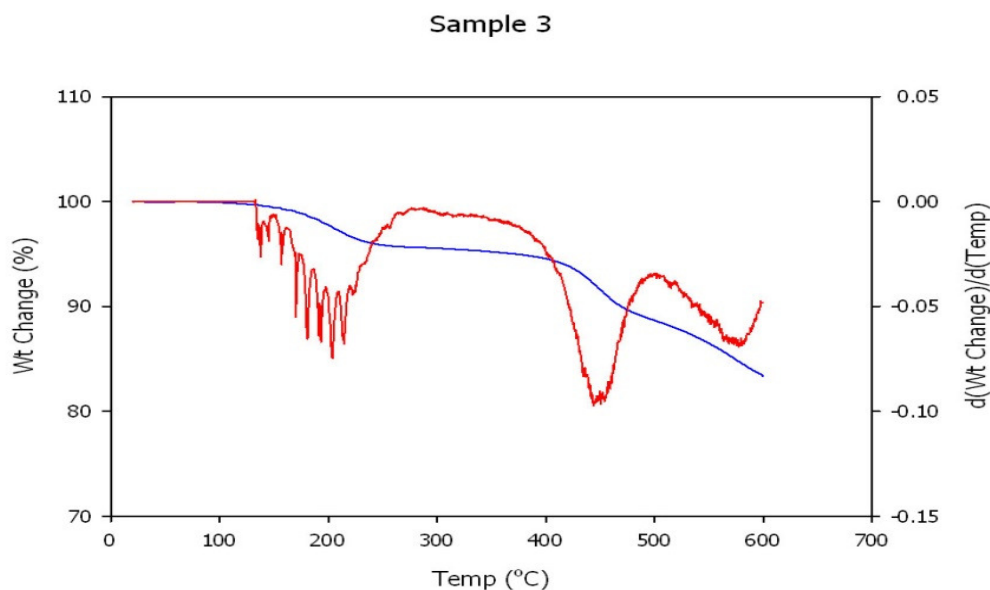
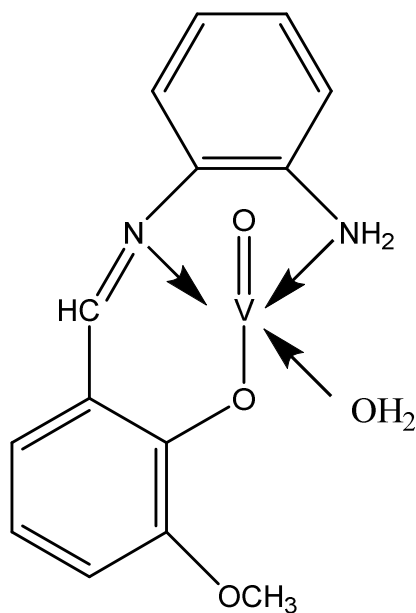


Figure-5
Tg/DTg thermogram of complex



Structure of complex

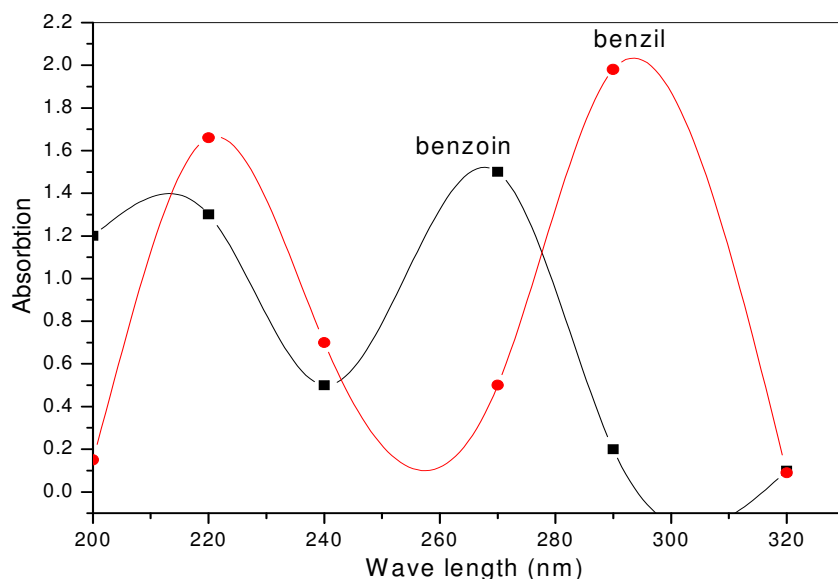


Figure-6
Absorption spectra of benzoin and benzil in acetonitrile

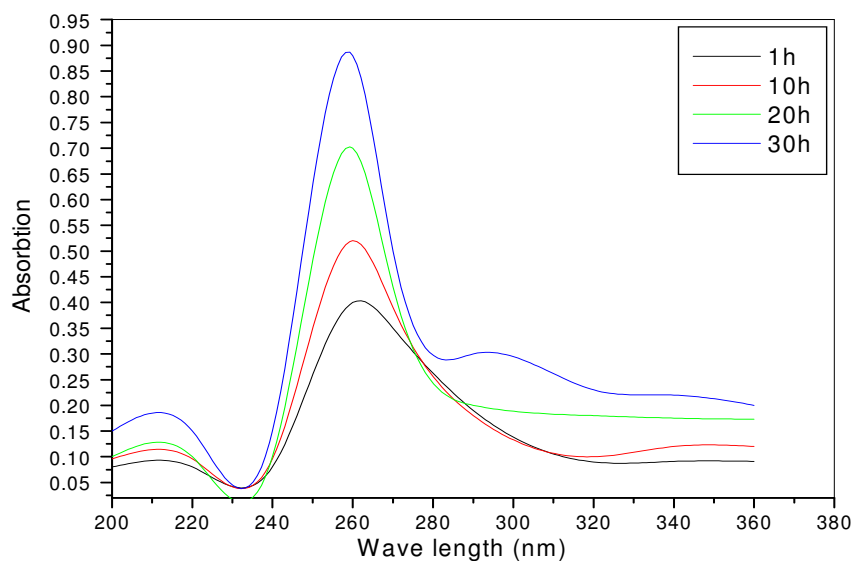


Figure-7
Change in the absorption spectra with time using A₁VO

But no significant effect of time was observed at 50 °C with increasing time. it means that the temperature effect is predominate. Figure-9.

The effects of temperature was investigated at two temperatures 30°C and 50°C in CCl₄ after 6 hrs the catalytic activity increased with increasing temperature (1.498 folds), Figure-10.

The influence of time on the oxidation was found to increase (1.485 folds) as increasing the time from 1 hr. to 7 hr. at 50°C in MeCN. (Figure-11).

Figure 12 shows the influence of solvent on oxidation rate at 50°C it is clear that the non polar solvent [CCl₄] shows a significant effect¹⁶.
MeCN < CCl₄

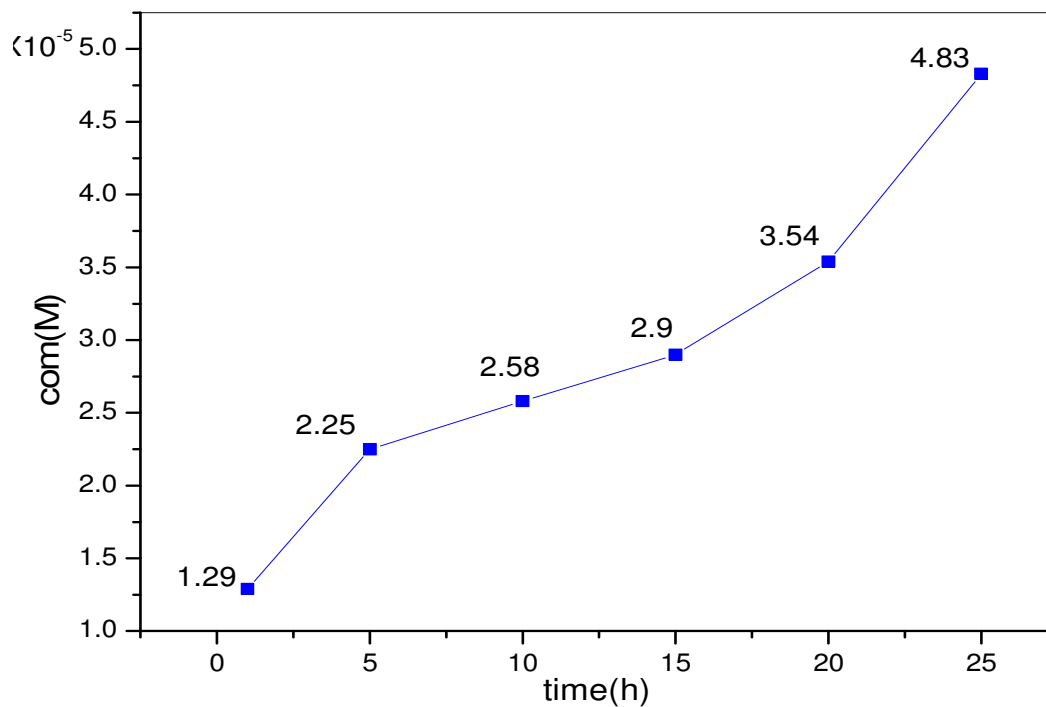


Figure-8
Catalytic activity with time for the formation of benzil in CCl_4 at $30^\circ C$

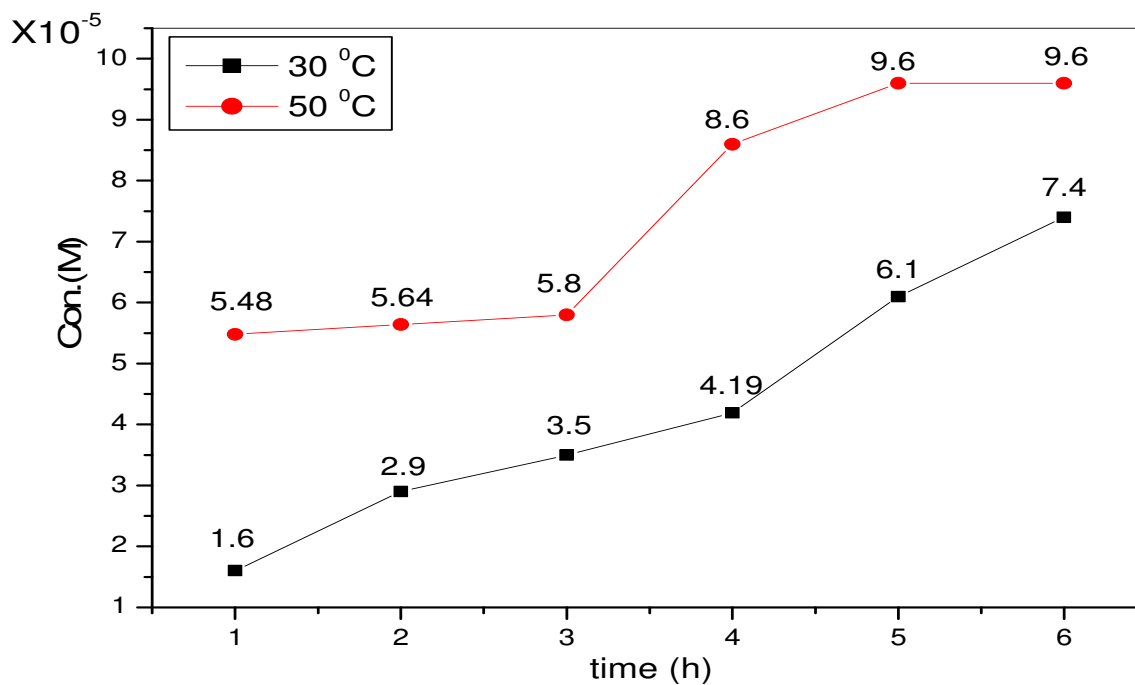


Figure-9
Catalytic activity in two reaction temperatures in MeCN after 6 h reaction time

Conclusion

Oxovanadium complex of tridentate Schiff base resulted from condensation o-phenylenediamine and o-vanillin in 1:1 mole

ratio have been prepared and characterized by IR, HNMR, Mass and thermal analysis. The catalytic activity for oxidation of benzoin to benzil was investigated in different temperatures and different solvents.

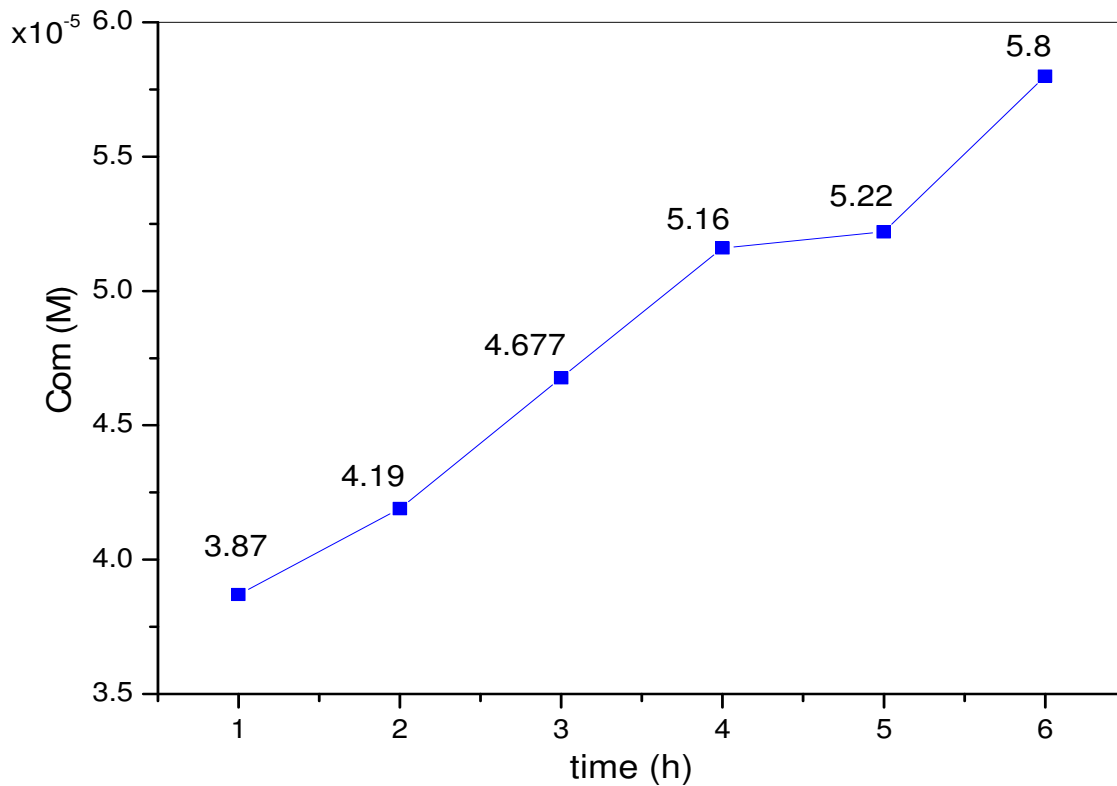


Figure-10
Catalytic activity with time in CCl_4 at 50°C

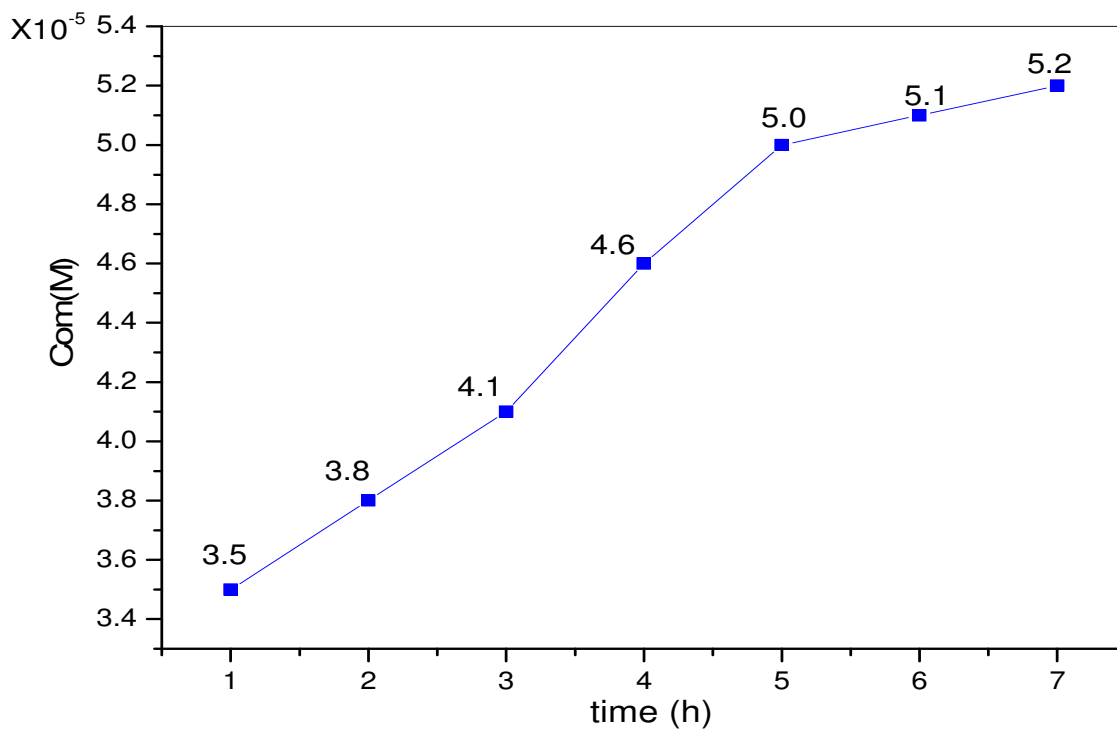


Figure-11
Catalytic activity with time in MeCN at 50°C

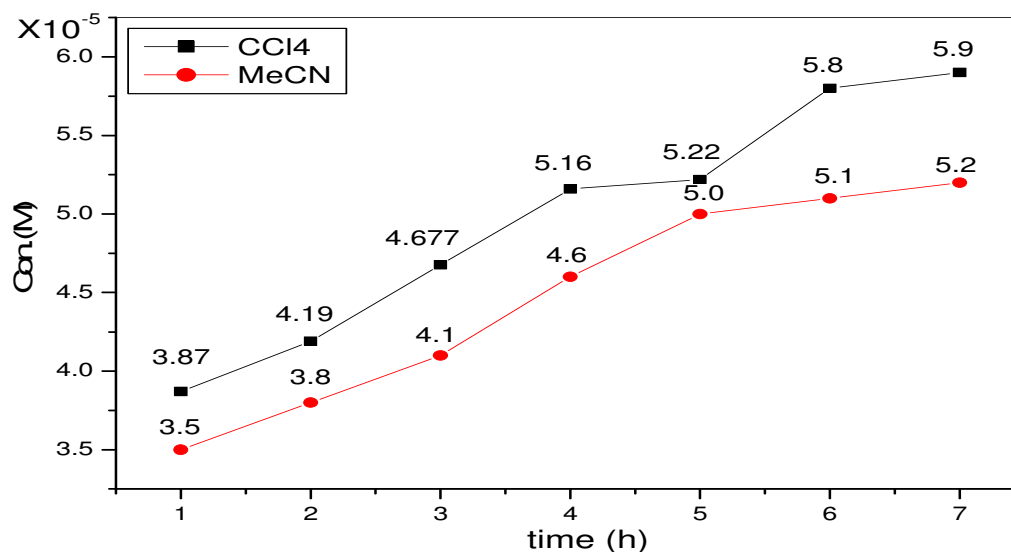


Figure-12
Effect of solvent on % yield of benzil at 50°C

References

- Pati (1970). The chemistry of Carbon-Nitrogen double bond John Wiley and Sons Ltd.
- Boghaei D.M and Lashanizadegan M. (2000). Template synthesis, characterization of highly unsymmetrical tetradentate Schiff base complex of Nickel (II) and copper (II), *J. Sci. I. R. Iran*, 11(1), 301-308.
- Munde A.S., Shelke V.A., Jadhav S.M. Kirdant. A.S., Vaidya S.R., Shankarwar S.G and Chondhekar T.K. (2012). Synthesis, Characterization and Antimicrobial Activities of some Transition metal complex of Biologically Active Asymmetrical Tetradentate Ligand, *Advance in Applied Science Research*, 3(1), 175-182.
- Munde A.S, Jagdar A.N., Jadhav S.M. and Chondhekar T.K. (2009). Synthesis and Characterization of Some Transition Metal Complex of Unsymmetrical Tetradentate Schiff Base Ligand, *Journal of Korean Chemical Society*, 53(4), 407 – 414.
- Jeena Pearl A. and T.F Abbs Fen Reji. (2013). Synthesis, Characterization, antimicrobial and DNA Cleavage Studies on some metal complexes incorporating 4-chlorobenzaldehyde and 4- aminoantipyrine, *Journal of chemical and Pharmaceutical Research*, 5(1), 115-122.
- Shelk V.A., Jadhav S.M., Shankarwar S.G. and Chondhekar T.K. (2013). Synthesis, Spectroscopic Characterization and Antimicrobial Activities of some Rare Earth Metal Complexes of Biologically Active Asymmetrical Tetradentate ligand. *J. of Chem. Sci. and Technology*, 2(2). 61 – 69.
- Thaseen A., Alsalam Jabbar S, Hadi Omar, N. Ali, Hanan S. Abbo and Salam J.J. titnchi (2010). Oxidation of benzoin catalyzed by oxovanadium (IV) Schiff base complexes, 7(3), 1-8.
- Ebitani K., Ji H-B, Mizugaki T. and Kaneda K. (2004). Highly active trimetallic Ru/ CeO₂/CoO(OH) catalyst for oxidation of alcohols in the presence of molecular oxygen. *J. mol. Catal. A: chem.*, 212, 161-170.
- Makwana V.D., Son Y.C. Howell A.R. and Sub S.L. (2002). The role of lattice oxygen in selective benzyl alcohol Oxidation using OM5-2 catalyst: A Kinetic and isotope-labeling study. *J. catal.*, 210, 46-52.
- Kobayashi S, Miyamura H, Akiyama R. and Ishid T. (2005). Highly active, immobilized ruthenium catalysts for oxidation of alcohols to aldehydes and Ketones, Preparation and use in both batch and flow systems. *J. Am. chem. Soc.*, 127, 9251-9254.
- Bushra K. Al-Salami, Amel H. Mohammad and Kahtan A. Askar (2014). Synthesis and characterization of new Schiff Bases Derived From 2-hydroxybenzaldehyde and Amino Acid and their Vanadyl complexes. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 5(4), 1457-1472.
- Har Lal Singh J and Bhadur Singh. (2012). Synthesis, spectral 3D molecular modeling and antibacterial studies of dibutyltin (IV) Schiff base complexes derived from substituted isatin and amino acids, *Natural Science*, 4(3), 170-178.
- Suman Malik, Saparna Ghosh and Bhari Jain. (2010).

- Synthesis characterization and antimicrobial studies of Zn(II) complexes of chemotherapeutic importance. *Archives of Applied Science Research*, 2(2), 304-308.
14. Bushra K. Alsalami, Rehab G. Abood, Handi M. Jarallah and Zuhair A. Abdalnabi (2015). Synthesis, spectral and thermal properties of complexes derived from 2-(2-hydroxyphenylimino) methyl-6-methoxyphenol. *Journal of chemical and pharmaceutical Research*, 7(2), 917-923.
15. Chaisab K., Bhkakh and Jabbar S. Hadi. (2015). New unsymmetrical Schiff base as Inhibitor of carbon steel corrosion and Antibacterial Activity. *Research Journal of chemical Sciences*, 5(1), 64-70.
16. Skobridis K, Theodorou V and Weber E. (2006). A very simple and chemoselective air oxidation of benzoin to benzil using alumina. *Arkivoc*, 10, 102-106.