

**UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI- 110 002**

**Annual / Final Report of the work done on the Major Research Project**

<b>S. No</b>	<b>Particulars</b>	<b>Details</b>
1.	Project report No. 1 <sup>st</sup> /2 <sup>nd</sup> /3 <sup>rd</sup> /Final	<b>Final</b>
2.	UGC Reference No	<b>F. No. 42-349/2013 (SR) dated 31-03-2013</b>
3.	Period of report	<b>From 01/06/2013 to 23/03/2017</b>
4.	Title of research project	<b>Spectral and electrochemical characterization and applications of heteropoly acids and their derivatives as Eco-friendly redox catalysts</b>
5 a)	Name of the Principal Investigator	<b>Dr. P. SAMI</b>
b)	Dept and /College where work has progressed	<b>Department of chemistry VHNSN College, Virudhunagar Tamil Nadu-626001</b>
6	Effective date of starting the project	<b>01/06/2013</b>
7.	Grant approved and expenditure incurred during the period of the report	
a)	Total amount approved:	<b>Rs 8,29,800.00</b>
b)	Total expenditure	<b>Rs 7,97,914.00</b>

7. c) Report of the work done

(i) Brief objective of the project

**The project work aims to explore the catalytic and redox abilities of heteropoly acids, their salts and substituted heteropolyoxometalates, in the following aspects**

- 1) Understanding the possible mechanism for the anti-oxidant characteristics of selected organic compounds present in biological systems using heteropolyoxometalates as electron transfer reagents**
- 2) Development of a green and eco-friendly synthetic route for the synthesis of variety of biologically important organic compounds using heteropolyoxometalates supported on clay materials as green catalyst.**

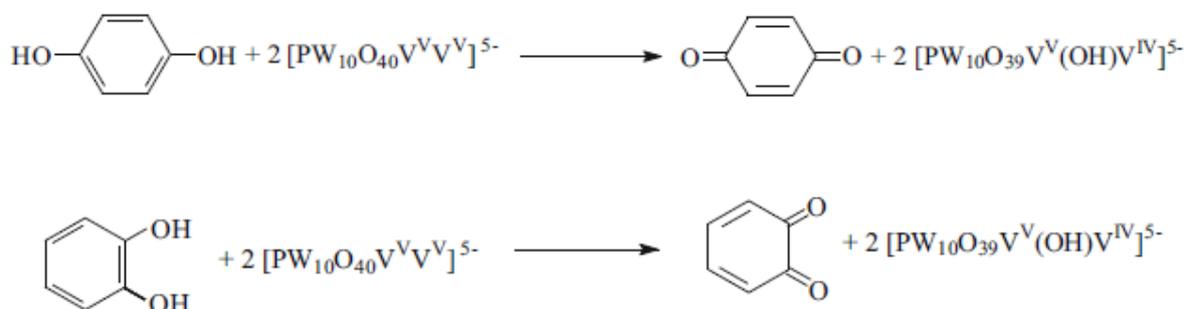
- (ii) Work done so far and result achieved and publications, if any, resulting from the work:

### **I. Studies on electron transfer reactions: oxidation of dihydroxybenzenes by heteropoly 10-tungstodivanadophosphate in aqueous acidic medium**

Oxidation of phenolic compounds plays a very important role in biological systems. Examples are provided by the oxidation of tyrosine in photosystem II and the redox cycling of hydroquinone in photosystems I and II and in the mitochondrial bc1 complex. Several biological phenols act as antioxidants, due to the consecutive two-electron oxidation of the catechol ring of flavonoids to give the corresponding quinones. Polyoxometalates are anionic clusters containing  $d^0$  metal ions [W(VI), Mo(VI)] and oxygen anions formed by sharing corners and edges of  $MO_6$  octahedra. By replacing W(VI) from the Keggin  $[PW_{12}O_{40}]^{3-}$  anion with V(V), heteropoly 10-tungstodivanadophosphate ( $[PV^V V^V W_{10}O_{40}]^{5-}$ ) can be obtained. This anion consists of  $WO_6$  and  $VO_6$  octahedra. There are terminal W(VI) = O and V(V) = O, as well as corner- and edge-shared oxygen atoms in the cluster. These anion acts as an outer-sphere electron transfer reagent. One may expect an ET-PT or s-CPET mechanism for the oxidation of hydroquinone and catechol. On the other hand, if any one of the oxoanions (basic site) acts as proton acceptor and V(V) acts as electron acceptor, a HAT mechanism is possible. We report herein the results of kinetic studies of the oxidation of hydroquinone and catechol by heteropoly 10-tungstodivanadophosphate anion.

Kinetic studies on the oxidation of hydroquinone and catechol by the heteropoly 10-tungstodivanadophosphate anion,  $[PV^V V^V W_{10}O_{40}]^{5-}$ , have been carried out in aqueous acidic medium at 25° C by UV-visible spectrophotometry. The oxidation of hydroquinone shows simple second-order kinetics overall, with first-order dependence of the rate on both [oxidant] and [hydroquinone] at constant  $[H^+]$ . For catechol oxidation, the order of the reaction with respect to [oxidant] is unity, while the order with respect to [catechol] is variable; this reaction shows Michaelis-Menten-type kinetics at constant  $[H^+]$ . The rate of the reaction is insensitive to  $[H^+]$  in the pH range 1.2–1.7. Rate retardation for deuterated hydroquinone and catechol ( $C_6H_4(OD)_2$ ) in  $D_2O$  indicates breaking of the –OH bond in the rate-limiting step. Based on the observed kinetic isotope effect and calculated ground-state free energy change ( $\Delta G^0$ ) values, a hydrogen atom transfer mechanism is suggested for the reaction; i.e., in the rate limiting step, one electron and one proton are transferred from the reductant to the oxidant in a concerted manner. Rates of oxidation of hydroquinone by this oxidant in neat

acetonitrile at 25° C have also been measured. By applying the Marcus equation, the self-exchange rate constant of the oxidant  $V^V V^{IV}OH / H^\bullet$  in acetonitrile has been evaluated.

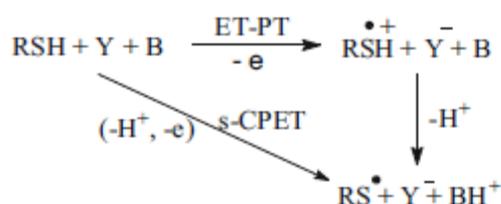


**Scheme 1 Reaction stoichiometry**

**\*This work has been published in *Transition Metal Chemistry*, 40, 197–205 (2015).**

## II. Studies on electron transfer reactions: Oxidations of 2-mercaptoethanol and 2-mercaptoethylamine by heteropoly 11-tungsto-1- vanadophosphate in aqueous acidic medium

The one-electron oxidation of aliphatic thiols (RSH) generates a thiyl radical, which undergoes dimerization to form disulphide. This is an important reaction in biological systems. For example, oxidation of the thiol side chain of L-cysteine forms disulphide linkages that are critical to the proper folding of many peptides. The thiol/disulphide couple (RSH/RSSR) acts as a redox buffer. This couple modulates the activity of biological sites and regulates metabolism, gene expression, protein conformation and enzymatic activity. Thiol-containing compounds are effective antioxidants and act as scavengers for reactive oxygen species (ROS) and thus protect cells, DNA and proteins from the destructive effects of ROS and other free radicals. There are diverse mechanisms for the generation of reactive oxygen species is given in Scheme 2.



**Scheme 2: Electron transfer pathways of aliphatic thiols**

This work aims to understand the mechanism of these electron transfer reactions using the oxidation of 2-mercaptoethanol and 2-mercaptoethylamine in aqueous medium using heteropoly 11-tungsto-1- vanadophosphate anion,  $[\text{PV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$ , as a model reaction.

The kinetics of oxidation of 2-mercaptoethanol and 2-mercaptoethylamine by the heteropoly 11-tungsto-1- vanadophosphate anion,  $[\text{PV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$ , have been studied spectrophotometrically in aqueous perchloric acid at 25° C. EPR and optical studies show that  $[\text{PV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{4-}$  is reduced to the one-electron reduced heteropoly blue,  $[\text{PV}^{\text{IV}}\text{W}_{11}\text{O}_{40}]^{5-}$ , whilst the thiols are oxidized to the corresponding disulphides, RSSR. Spectrophotometric titrations show that the stoichiometry of both reactions is 1:1. At constant pH, the reactions show simple second-order kinetics with first-order dependence of rate on both [oxidant] and [thiol]. At constant [thiol], the rate of the reaction increases with increasing pH. Plots of  $k_{\text{obs}}/[\text{thiol}]t$  versus  $1/[\text{H}^+]$  are linear with finite intercepts, showing that both the undissociated thiol (RSH) and thiolate ion ( $\text{RS}^-$ ) are reactive species. Generation of  $\text{RS}^{\bullet}$  from RSH proceeds via a separated concerted proton–electron transfer mechanism. The reaction of thiolate ion is a simple outer-sphere electron transfer reaction. By applying the Marcus theory, the self-exchange rate constants for the couples  $\text{HOCH}_2\text{CH}_2\text{S}^{\bullet}/\text{HOCH}_2\text{CH}_2\text{S}^-$  and  $\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{S}^{\bullet}/\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{S}^-$  were evaluated as  $3 \times 10^9$  and  $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at 25° C.

- **This work has been published in Transition Metal Chemistry 41, 77–85 (2016).**

### **III. Studies on electron transfer reactions: Oxidation of thiourea by heteropoly $\alpha_2$ -17-tungsto-1-vanadodiphosphate anion**

Kinetics of the oxidation of thiourea (tu) by heteropoly- $\alpha_2$ -17-tungsto-1-vanadodiphosphate anion,  $\alpha_2\text{-}[\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$ , have been studied spectrophotometrically in aqueous acidic medium at 25° C. At low pH (2.4– 3.0), the neutral form of tu is the only reactive species. At higher pH (4.2–4.9), both neutral and deprotonated forms of tu participate in the reaction. The observed mixed-order kinetics suggest two parallel reactions: one in which the order in [tu] is unity, and a second in which it is two. In both cases, the order in  $[\alpha_2\text{-}[\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}]$  is unity. Based on the kinetic studies, a mechanism is proposed, in which a second-order proton-coupled electron transfer involving  $\text{NH}_2\text{CSNH}_2$  and  $\alpha_2\text{-}[\text{P}_2\text{V}^{\text{V}}\text{W}_{17}\text{O}_{62}]^{7-}$  proceeds through a sequential electron transfer, followed by proton transfer such that the reaction is an “activation-controlled” outer-sphere electron transfer process. By

applying the Marcus equation, the self-exchange rate constants for the couples  $\text{NH}_2\text{CSNH}_2^+ / \text{NH}_2\text{CSNH}_2$  and  $\alpha_2\text{-[P}_2\text{V}_V\text{W}_{17}\text{O}_{62}]^{7-} / \alpha_2\text{-[P}_2\text{V}^{\text{IV}}\text{W}_{17}\text{O}_{62}]^{8-}$  were evaluated.

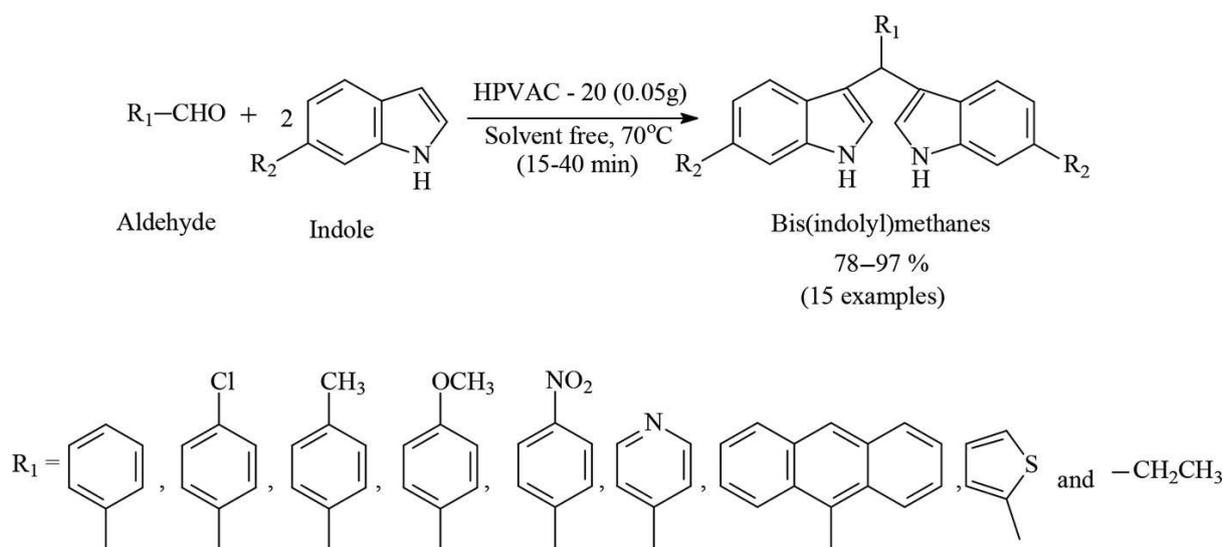
\* This work has been published in *Transition Metal Chemistry*, 42 95-103 (2017).

#### **IV \*One-pot three-component synthesis of bis(indolyl)methanes under solvent-free condition using heteropoly-11-tungsto-1- vanadophosphoric acid supported on natural clay as catalyst**

Multi-component reactions (MCRs) play an important role in combinatorial chemistry because of its ability to synthesize small drug-like molecules with several degrees of structural diversity. A MCR is defined as a reaction in which three or more compounds react in a single operation to form a single product that contains essentially all of the atoms of the starting materials (with the exception of condensation products, such as  $\text{H}_2\text{O}$ ,  $\text{HCl}$ , or  $\text{MeOH}$ ). This reaction tool allows compounds to be synthesized in a few steps and usually in a one-pot operation. Another typical benefit from these reactions is simplified purification, because all of the reagents are incorporated into the final product. In this project we aimed to perform MCRs in the presence of heteropolyoxometalates supported on clay material as catalyst.

For that we synthesized new catalytic material, hetero-poly-11-tungsto-1-vanadophosphoric acid,  $\text{H}_4[\text{PV}^{\text{V}}\text{W}_{11}\text{O}_{40}]$  (HPV) supported on activated natural clay by incipient wetness impregnation method. The characterizations of the HPV (20%) supported on natural clay (HPVAC-20) was done with the aid of instrumental methods such as Fourier transform infrared spectroscopy, powder XRD, SEM, EDX and XRF methods.

The catalytic ability of this catalyst was checked towards the one-pot three-component condensation reaction of two moles of indole and one mole of aromatic aldehyde for the synthesis of bis(indolyl)methanes under solvent-free reaction condition. The reaction pattern is given in Scheme 3.



**Scheme 3.** Synthesis of bis(indolyl)methanes using HPVAC-20 as catalyst.

In this manner we have reported the synthesis of fifteen derivatives and characterize them with the help of elemental analysis, melting point measurements,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectral methods. Solvent-free heterogeneous reaction condition, simple workup procedure, short reaction time, high yield of products, and reusability of the catalyst are the advantages of the protocol.

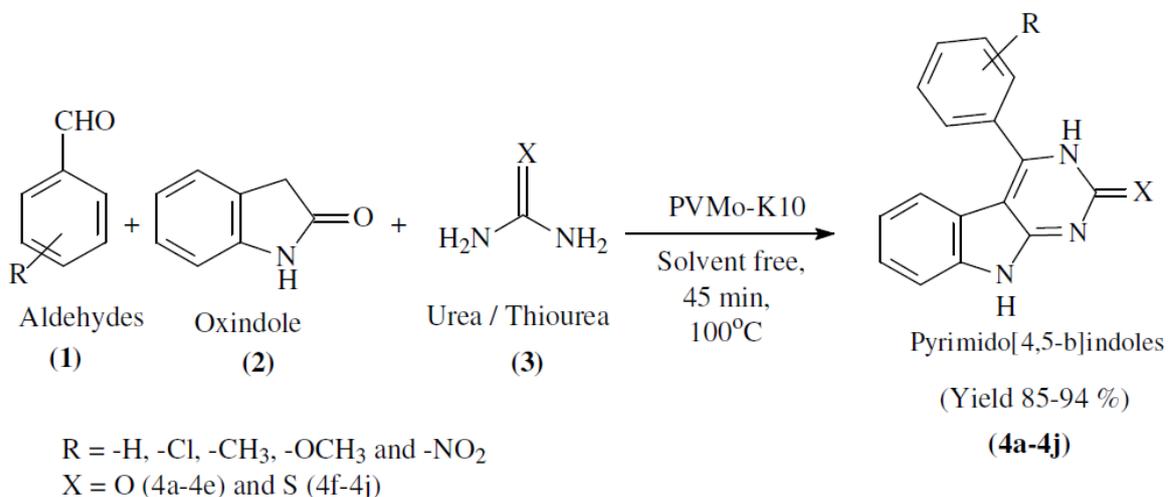
\* This work has been published in *Synthetic Communications* **47**, 913–927 (2017), DOI: [10.1080/00397911.2017.1296159](https://doi.org/10.1080/00397911.2017.1296159)

**V Synthesis of pyrimido [4,5-b] indoles using heteropoly-11-molybdo-1-vanadophosphoric acid supported on montmorillonite K10 clay as catalyst: A Green Approach**

We also synthesized another one catalytic material, heteropoly-11-molybdo-1-vanadophosphoric acid,  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]\cdot 32\text{H}_2\text{O}$  supported on montmorillonite K10 clay for about 10 % (PVMo-K10) by incipient wetness impregnation method. The characterization of the catalytic material was done with the aid of instrumental methods such as Fourier transform infrared spectroscopy, powder XRD, SEM, EDX and XRF methods.

A method for synthesis of pyrimido [4,5-b] indole derivatives has been developed through the one-pot, three-component reaction of aldehyde, oxindole, urea (or) thiourea derivatives in the presence of catalytic amount of Keggin-type heteropoly acid, heteropoly-11-molybdo-1-vanadophosphoric acid,  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]\cdot 32\text{H}_2\text{O}$  supported on montmorillonite

K10 clay for about 10 % (PVMo-K10) as catalyst. The general reaction stoichiometry is given as Scheme-4.



#### Scheme 4: General synthetic scheme of indoles

In this manner we have synthesized sixteen derivatives and characterize them with the help of elemental analysis, melting point measurements,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectral methods. Solvent-free heterogeneous reaction condition, simple workup procedure, short reaction time, moderately yield and reusability of the catalyst are the advantages of this protocol.

\* **This work has been published in *Materials Today: Proceedings* 4 (2017) 12437–12447**

7.c iii) Has the progress been according to original plan of and towards achieving the objective:

**Yes. Work progress as per plan**

iv) Please indicate the difficulties, if any, experienced in implementing the project

**No difficulties**

v) If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the commission on a separate sheet

**Not applicable**

vi. If the project has been completed, please enclose a summary of the findings of the study. One bound copy of the final report of work done may also be sent to University Grants Commission.

## Summary of the Project work

Electron transfer reactions of vanadium (V) substituted heteropolyoxometalates have been studied towards the oxidation of substrates such as hydroquinone, catechol, thiourea, 2-mercaptoethanol and 2-mercaptoethylamine and possible mechanisms have been evolved with the help of experimental and theoretical tools. These works have been highly useful to understand the mechanism of electron transfer reaction reactions of these compounds in biological systems.

Further heteropolyoxometalates supported clay catalysts have been prepared, characterized and utilized as green catalysts in the multi component synthesis of organic compounds such as bis-indolylmethanes, indoles and imidazoles. Green and solvent free synthetic routes have been evolved.

vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as

**Work done during the course of the project has been published in reputed journals.**

a) Manpower trained :

**Nil**

b) Ph.D. awarded:

**Mr.K. Selvakumar worked in this project registered for his Ph.D., Degree in Madurai Kamaraj University and submitted his thesis**

c) Publication of results:

**Seven papers have been published.**

## List of Papers Published

1. Proton-coupled electron transfer reactions: kinetic studies on the oxidation of dihydroxybenzenes by heteropoly 10-tungstodivanadophosphate in aqueous acidic medium, T. Shanmugaprabha, K. Selvakumar, M. Vairalakshmi, K. Rajasekaran, **P. Sami**, Transition Met. Chem. **40**, 197–205 (2015).
2. A kinetic study of the oxidations of 2-mercaptoethanol and 2-mercaptoethylamine by heteropoly 11-tungsto-1- vanadophosphate in aqueous acidic medium, T. Shanmugaprabha, K. Selvakumar, K. Rajasekaran, **P. Sami**, Transition Met. Chem. **41**, 77–85 (2016).

3. Kinetics of the outer-sphere oxidation of thiourea by heteropoly  $\alpha$ 2-17-tungsto-1-vanadodiphosphate anion, T. Shanmugaprabha, K. Selvakumar, M. Vairalakshmi, K. Rajasekaran, **P. Sami**, *Transition Met. Chem.* **42**, 95-103 (2017).
4. One-pot three-component synthesis of bis(indolyl)methanes under solvent-free condition using heteropoly-11-tungsto-1- vanadophosphoric acid supported on natural clay as catalyst, K. Selvakumar, T. Shanmugaprabha, R. Annapoorani, and **P. Sami**, *Synth. Commun.*, **47**, 913–927 (2017), DOI: 10.1080/00397911.2017.1296159
5. Synthesis of pyrimido [4,5-b] indoles using heteropoly-11-molybdo-1-vanado phosphoric acid supported on montmorillonite K10 clay as catalyst: A Green Approach, M.Kumaresan, K.Selvakumar and **P.Sami**, *Materials Today: Proceedings* **4** (2017) 12437–12447
6. One-pot multi-component synthesis of *N, N'*- alkylidene bisamides and imidazoles using heteropoly-11-tungsto-1-vanadophosphoric acid supported on natural clay as catalyst:A green approach, K. Selvakumar, T. Shanmugaprabha, M. Kumaresan, **P. Sami**, *Synth. Commun.*, **47**, 2115–2126, (2017). DOI: 10.1080/00397911.2017.1366524
7. Heteropoly acid supported on activated natural clay-catalyzed synthesis of 3,4-dihydropyrimidinones/thiones through Biginelli reaction under solvent-free conditions, K. Selvakumar, T. Shanmugaprabha, M. Kumaresan, **P. Sami**, *Synth. Commun.*, **48**, 223–232 (2018), DOI: 10.1080/00397911.2017.1396614

d) Other impacts, if any:

Nil

**SIGNATURE OF THE PRINCIPAL**

**INVESTIGATOR**  
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