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Liquid phase versus microwave assisted selective oxidation of volatile organic compounds involving dioxidomolybdenum(VI) and oxidoperoxidomolybdenum(VI) complexes as catalysts in the presence/absence of an N-based additive

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ABSTRACT

Four dioxidomolybdenum(VI) complexes, $[Mo^{VI}O_2(dha\text{-}bhz)(MeOH)]\cdot(H_2dha\text{-}bhz)$ (**1**), $[MoO_2(dha\text{-}inh)(MeOH)]$ (**2**), $[MoO_2(dha\text{-}nah)(MeOH)]$ (**3**) and $[MoO_2(dha\text{-}fah)(MeOH)]$ (**4**), and their corresponding oxidoperoxidomolybdenum(VI) complexes, $[MoO(O_2)(dha\text{-}bhz)(MeOH)]$ (**5**), $[MoO(O_2)(dha\text{-}inh)(MeOH)]$ (**6**), $[MoO(O_2)(dha\text{-}nah)(MeOH)]$ (**7**) and $[MoO(O_2)(dha\text{-}fah)(MeOH)]$ (**8**), with ONO tridentate Schiff base ligands derived from 3-acetyl-6-methyl-(2H)-pyran-2,4(3H)-dione (dehydroacetic acid, Hdha) and aromatic hydrazides, {benzoyl hydrazide (bhz), isonicotinoyl hydrazide (inh), nicotinoyl hydrazide (nah) and furoyl hydrazide (fah)} have been synthesized and characterized by elemental analysis, spectroscopic techniques (infrared, UV–Vis, ^1H and ^{13}C NMR) and thermogravimetric analyses. The structures of complexes **1** and **2**, confirmed by single crystal X-ray study, reveal that the tridentate ligand binds to the metal centers through the enolic oxygen (of the pyrone group), azomethine nitrogen and enolic oxygen (of the hydrazide group) atoms; methanol is coordinated at one site through the oxygen atom. The dioxidomolybdenum(VI) complexes have been tested as catalysts for the homogeneous oxidation of secondary alcohols (1-phenyl ethanol, 2-propanol and 2-butanol), using 30% H_2O_2 as an oxidant. Both microwave and conventional liquid phase oxidation methods have been tested for catalytic reactions. Various parameters, such as amount of catalyst, oxidant, solvent and temperature, of the reaction mixture have been taken into consideration for the maximum conversion of the substrates. Under the atmospheric optimized reaction conditions, secondary alcohols give high yields of the respective ketones selectively. Addition of an N-based additive reduces the time and increases the conversion of alcohols. Amongst the two methods studied, the microwave technique proves to be a time efficient system.

1. Introduction

The oxygen containing heterocycle 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid, dha) is an excellent chelating agent and possesses promising fungicidal [1], bactericidal [2], herbicidal and insecticidal activities [3,4]. It is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems [5,6]. These hydroxypyrones are also known for their versatile coordination behavior and excellent choice for the formulation of therapeutic and diagnostic metallopharmaceuticals [7]. However, no catalytic activity of such transition metal complexes has been investigated.

Volatile organic compounds (VOCs) are considered as a major source of indoor environmental pollutants both at living and working places [8,9]. Many evidences affirm that VOC's emissions can be a threat to human health [10,11]. It has been globally recognized that 2-propanol (IPA), 2-butanol and 1-phenyl ethanol, used in industry as solvents/cleaners, are toxic compounds, even at low levels, which can induce cancer in the upper respiratory tract [12,13]. It has, therefore, recently become a need to limit the emissions of volatile organic compounds [14]. Catalytic oxidation has been identified as a most efficient method to completely eliminate these compounds and generate products that are commercially valuable [15]. Various catalytic oxidations based on noble metals (e.g. Pt, Pd, Au and Ru) show excellent activity at low temperatures. However, the commercial applications of these catalysts are always limited due to their relatively higher cost [16–19]. Thin film

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catalysts [20], electrochemical oxidation [21] and plasma generated ozone flow [22] have also been applied successfully for this purpose. Photocatalytic, biological and non-thermal plasma techniques are energy-efficient, but sometimes result in low reaction rates and also are not very efficient [23].

Microwave assisted organic synthesis has been the subject of extensive investigations in recent years [24,25]. This technique has proved to be both time and energy efficient and a better substitute over conventional liquid phase methods for the acceleration of oxidation of organic substrates in the presence of a catalyst. Reactions under microwave conditions can provide pure products in high yields [26–28]. Further, microwave irradiation can reduce the reaction time as well as energy consumption and may lead to an increase in yield of the desired products [29].

Recently we were interested in the development of vanadium and molybdenum complexes based catalytic systems for the oxidation of organic substrates. The aim of this study is to develop homogenous molybdenum complexes of hydroxypyrone based ligands (Scheme 1) as catalysts for the oxidation of secondary alcohols. Microwave assisted as well as conventional liquid phase method have been applied for these catalytic reactions.

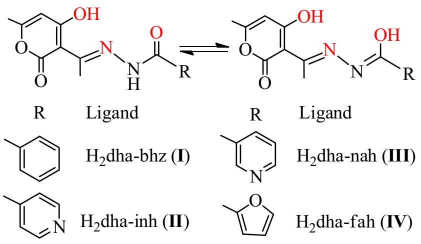
2. Experimental

2.1. Materials

Ammonium molybdate tetrahydrate, isonicotinic acid hydrazide (inh) and nicotinic acid hydrazide (nah) (Loba Chemie, India), 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid, dha) (purity ⩾98.0%), 2-furoic acid hydrazide (fah), acetylacetone (Hacac), 1-phenyl ethanol (98%) (Aldrich, U.S.A.) and 30% aqueous H_2O_2 (Renkem, India) were used as supplied. 2-Propanol and 2-butanol (AR grade) were purchased from Qualigens Pvt. Ltd., India. Benzohyrazide (bhz) was prepared by the reaction of a twofold excess of hydrazine hydrate with ethyl benzoate. $[Mo^{VI}O_2(acac)_2]$ was prepared using the method reported in the literature [30]. Other solvents used were of analytical reagent (AR) grade.

2.2. Instrumentation and characterization procedures

Elemental analysis (C, H and N) of the ligands and complexes was carried out on an Elementar Analyser Vario-El-III. Thermogravimetric analysis of the complexes was carried out using an EXSTAR TG/DTA 6300, having a weight sensitivity of 0.2 µg under an oxygen atmosphere. Alumina powder was used as a reference and the temperature increment rate was fixed at 10 °C/min. Infrared spectra were recorded as KBr pellets on a Nicolet 1100 FT-IR spectrometer after grinding the sample with KBr. UV–Vis spectra of the ligands and complexes were recorded on a Shimadzu single beam spectrophotometer in methanol. ^1H NMR spectra were obtained in DMSO-d_6 on a Bruker Avance 500 MHz spectrometer. The residual DMSO-d_6 in conventional 99.8% DMSO gives a signal at $\delta = 2.50$ ppm, which was used for the calibration of the chemical shift scale. Microwave catalytic reactions were carried out in an Anton paar Monowave 300 synthesis reactor, where the reaction mixture was continuously stirred in a sealed tube during microwave irradiation (25 W). The microwave was set initially to raise the temperature to 65 °C within 1 min and then to attain 80 °C. Microwave experiments were carried out at 80 °C for a specific period of time. The oxidation products were analyzed with a Shimadzu 2010 plus gas-chromatograph fitted with an Rtx-1 capillary column (30 m × 0.25 mm × 0.25 µm) and a FID detector, and the identity of the products was confirmed by checking against the GC–MS Shimadzu QP-5000.



Scheme 1. The ligands derived from 3-acetyl-6-methyl-2H-pyran 2,4(3H)-dione used in this study.

2.3. X-ray crystal structure determination

Three-dimensional X-ray data were collected on a Bruker Kappa Apex CCD diffractometer at room temperature for **1** and **2** by the ϕ–ω scan method. Reflections were measured from a hemisphere of data collected from frames, each of them covering 0.3° in ω. Of the 22782 for **1** and 22151 for **2** reflections measured, all were corrected for Lorentz and polarization effects and for absorption by multi-scan methods based on symmetry-equivalent and repeated reflections, 5952 and 3589 independent reflections, respectively, exceeded the significance level $(|F|/\sigma|F|) > 4.0$. After data collection, in each case an empirical absorption correction (SADABS) [31] was applied, and the structures were solved by direct methods and refined by full matrix least-squares on F^2 data using the SHELX suite of programs [32]. In **1**, hydrogen atoms were located in the difference Fourier map and left to refine freely, except for C(3), C(6), C(9), C(15), C(16A), C(16B), C(20), C(25) and C(31), which were included in calculation positions and refined in the riding mode. In **2**, hydrogen atoms were located in the difference Fourier map and left to refine freely, except for C(4), C(8), C(12) and C(15), which were included in calculation positions and refined in the riding mode. Refinements were done with an allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference Fourier map showed a high residual density in **1** and no residual density in **2**; 3.104 and −0.525 e Å^{-3} for **1** and 0.361 and −0.463 e Å^{-3} for **2**. The weighting schemes $w = 1/[\sigma^2(F_o^2) + (0.075700P)^2 + 1.879700P]$ for **1** and $w = 1/[\sigma^2(F_o^2) + (0.035100P)^2 + 0.577300P]$ for **2**, where $P = (|F_o|^2 + 2|F_c|^2)/3$, were used in the latter stages of refinement. The crystal of **1** presents an important disorder on the methyl group of the coordinated methanol ligand. The disorder has been refined and two atomic sites have been observed and refined with anisotropic atomic displacement parameters. The site occupancy factor was 0.62207 for C(16A). The high residual density has its origin in this disorder. Further details of the crystal structure determinations are given in Table 1.

2.4. Preparations

2.4.1. H_2dha-bhz (**I**), H_2dha-inh (**II**), H_2dha-nah (**III**) and H_2dha-fah (**IV**)

All ligands were prepared following essentially the same method. The preparation of one representative ligand is presented here. 3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione (0.840 g, 0.005 mol) and benzoyl hydrazide (0.680 g, 0.005 mol) were dissolved separately in 50 mL of methanol each in a flask. Both solutions were mixed with stirring and the reaction mixture was refluxed on a water bath for 4 h. After cooling the reaction flask at room temperature for 3 h, the separated white solid was collected by filtration, washed with methanol and dried in a vacuum desiccator over silica gel.

*H_2dha-bhz (**I**):* Yield: 1.30 g (90%). *Anal.* Calc. for $C_{15}H_{14}N_2O_4$ (286.28): C, 62.93; H, 4.93; N, 9.79. Found: C, 62.7; H, 4.8; N, 9.7%.