

Synthesis and Reactivity of Iso- and
Hetero-polyoxotungstates Containing Organic Subunits

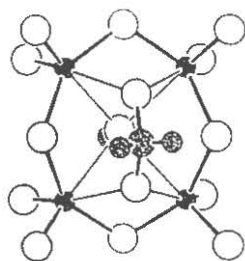
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Final Seminar

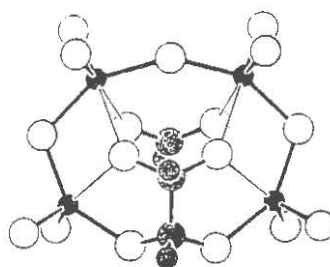
August 10, 1987

The selective oxidation of hydrocarbons, which is catalyzed by molybdenum, tungsten, and vanadium oxides, is a major industrial process [1]. There has thus been considerable interest in understanding the detailed nature of the interaction between small organic moieties and metal oxide surfaces [2]. Little information concerning the surface-bound organic species is available, however, due to the difficulty of studying solid oxide surfaces. An alternative method of investigation is to synthesize molecular metal oxide clusters containing hydrocarbon units. These compounds can serve as useful models for the structure and reactivity of surface-bound intermediates. During the past decade, several carbomolybdates have been prepared and structurally characterized [3]. However, since many of these carbomolybdates are unstable in solution, we were prompted to synthesize the structurally analogous carbotungstates and investigate their chemistry. Three classes of carbometallates were synthesized as tetra-n-butyl ammonium salts: (a) acetal complexes, $\text{RCHMo}_4\text{O}_{15}\text{H}^{3-}$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}$; $\text{M} = \text{Mo}, \text{W}$), (b) diacetal complexes, $\text{HCCHMo}_4\text{O}_{15}\text{X}^{3-}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{HCOO}, \text{F}$), (c) alkoxide complexes, $(\text{P}_3\text{O}_9)\text{WO}_2\text{OR}^{2-}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{CH}_2\text{CHCH}_2$).

The acetal complexes $\text{RCHMo}_4\text{O}_{15}\text{H}^{3-}$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}$) were prepared by reaction of $\text{Mo}_2\text{O}_7^{2-}$ with large excess amount of aldehydes, RCHO [4]. The $\text{CH}_2\text{-Mo}_4\text{O}_{15}\text{H}^{3-}$ anion shown in a was prepared at ambient temperature and isolated as a pure crystalline solid. However, the other two compounds $\text{CH}_3\text{CHMo}_4\text{O}_{15}\text{H}^{3-}$ and $\text{CH}_2\text{CHCHMo}_4\text{O}_{15}\text{H}^{3-}$ were purified by reprecipitation from CH_2Cl_2 with ether at 0°C due to their instability in solution. The tungstate analogues $\text{RCHW}_4\text{O}_{15}\text{H}^{3-}$ ($\text{R} = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}$) were prepared by treatment of aldehydes with WO_4^{2-} plus equimolar acids and isolated as pure crystalline solids. All of these compounds are assumed to have isostructural anions based on spectroscopic data. The relative thermal stabilities of these compounds in CD_3CN solution were examined by measuring their ^1H NMR spectra under several different conditions. This study shows that the tungstates are generally more stable in solution than the molybdate analogues.



a



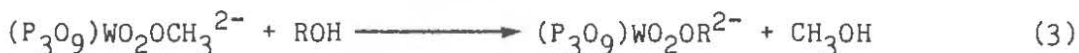
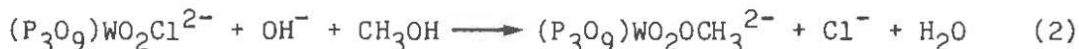
b

As a continuing effort to study polyoxometallate-aldehyde interactions, the glyoxal dialdehyde adduct $\text{OHCCHMo}_4\text{O}_{15}\text{H}^{3-}$ was prepared by reaction of 2,3-dihydroxy 1,4-dioxane with $\text{Mo}_2\text{O}_7^{2-}$ plus a stoichiometric amount of HCl . Similarly, the tungstate $\text{OHCCHW}_4\text{O}_{15}\text{H}^{3-}$ was obtained by treatment of 2,3-dihydroxy 1,4-dioxane with WO_4^{2-} plus equimolar HCl . These compounds are also assumed to be isostructural with the $\text{RCHMo}_4\text{O}_{15}\text{H}^{3-}$ anions on the basis of the spectroscopic data. Reaction of $\text{OHCCHMo}_4\text{O}_{15}\text{H}^{3-}$ with acids such as formic acid and hydrofluoric acid according to equation (1) gave the diacetal adducts $\text{HCCHMo}_4\text{O}_{15}\text{X}^{3-}$ ($\text{X} = \text{HCOO}, \text{F}$) [5]. The $\text{HCCHMo}_4\text{O}_{15}\text{HCOO}^{3-}$ anion structure is shown in **b**. The

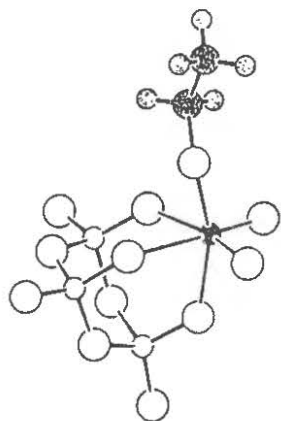
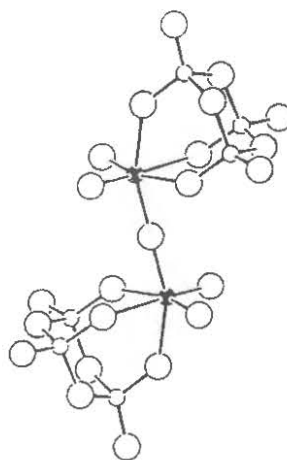


tungstates $\text{HCCHW}_4\text{O}_{15}\text{X}^{3-}$ ($\text{X} = \text{HCOO}, \text{F}$) were prepared by a similar method to that used to prepare $\text{HCCHMo}_4\text{O}_{15}\text{X}^{3-}$. All of these compounds were characterized spectroscopically. The spectroscopic results suggest that all of the anions have a common structure. The relative thermal stabilities of the diacetal adducts were also examined in CD_3CN solution. Surprisingly, the molybdates show greater stability in solution than the tungstate analogues.

The tungsten dioxo chloride adduct of the trimetaphosphate anion (P_3O_9)- $\text{WO}_2\text{Cl}^{2-}$ was obtained by treatment of WO_2Cl_2 with $\text{P}_3\text{O}_9^{3-}$. Reaction of (P_3O_9)- $\text{WO}_2\text{Cl}^{2-}$ with $(n\text{-C}_4\text{H}_9)_4\text{NOH}$ in methanol gave the methyl ester (P_3O_9) $\text{WO}_2\text{OCH}_3^{2-}$ according to equation (2). The ethyl, isopropyl, and allyl esters (P_3O_9) $\text{WO}_2\text{OR}^{2-}$ ($\text{R} = \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{CH}_2\text{CHCH}_2$) were obtained by transesterification as shown in equation (3). The structure of the ethyl ester shown in **c** was determined by a



single crystal X-ray diffraction study [6]. Hydrolysis of the esters resulted in the formation of the anhydride, $[(\text{P}_3\text{O}_9)\text{WO}_2]_2\text{O}^{4-}$ whose structure is shown in **d** [6]. All of these compounds were isolated as pure crystalline solids and

**c****d**

characterized spectroscopically. The acid $(P_3O_9)WO_2OH^{2-}$ was not isolated but identified by ^{31}P NMR spectroscopy. Thermal and photochemical degradations of the esters were investigated and compared with the corresponding molybdophosphate esters. The tungstates gave different decomposition products in both the thermolysis and photolysis than those observed from the corresponding molybdates [7].

References

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7. Klemperer, W. G.; Wang, R. C. unpublished results.