

## FT/ICR MASS SPECTROMETRY OF MOLYBDENUM-OXYGEN CLUSTERS: THE POLYOXOMOLYBDATES

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**Introduction:** The polyoxometallates are compounds that have retained the interest of chemists throughout the last century because of their applications to various biological and catalytic processes. Recently studies of such compounds have been extended to include their behavior in non-aqueous solvents where the choice of the cation influences the size of the associated anion, which in turn influences their relative solubilities in such solvents. An interesting question that arises in the ESI of such inorganic species concerns the relative nature of the ions present in the associated solid, solution and gas phases of the compound. In this study we know the structures of the ions in the solid phase (*x-ray crystallography*) and the composition of those in the gas phase (*FT-ICR mass spectrometry*) and we attempt to draw conclusions about their structures in the gas and solution phases.

**Methods and Instrumentation:** The following pure compounds have been studied by ESI-FT/ICR mass spectrometry using methanol and acetonitrile as solvents:-  $(\text{Ph}_4\text{P})_2\text{Mo}_2\text{O}_7$ ,  $(\text{Ph}_4\text{P})_2\text{Mo}_6\text{O}_{19}$ ,  $(\text{Bu}_4\text{N})_4\text{Mo}_8\text{O}_{26}$ ,  $(\text{Ph}_4\text{P})_2\text{Na}_2\text{Mo}_8\text{O}_{26}$  and  $(\text{Bu}_4\text{P})_2(\text{NH}_4)_2\text{Mo}_8\text{O}_{26}$ .

The mass spectra were measured on a *Bruker-Daltonics* high field 7T FT/ICR mass spectrometer equipped with an *Analytica* electrospray ionization source. Collision-induced-dissociation (*CID*) was used to investigate the relative bonding in the various oxo-metal anions. The gas phase reactions of selected molybdate anions with  $\text{H}_2\text{S}$ ,  $\text{CO}$  and  $\text{C}_2\text{H}_2$  are also examined.

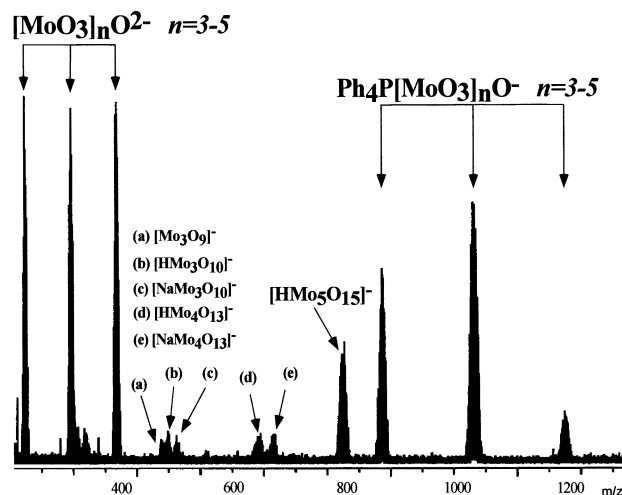
**Results and Discussion:** No anions observed thus far carry a charge of greater than two minus and for the positive-ion mass spectra, only simple cations assigned to counter-ions in the polyoxomolybdates are observed.

For the smaller molybdates,  $(\text{Ph}_4\text{P})_2\text{Mo}_2\text{O}_7$  and  $(\text{Ph}_4\text{P})_2\text{Mo}_6\text{O}_{19}$ , the anions remain intact in solution since anions containing  $\text{Mo}_2\text{O}_7$  and  $\text{Mo}_6\text{O}_{19}$  groups are observed in their ESI-mass spectra.

For the larger molybdates incorporating the  $\text{Mo}_8\text{O}_{26}$  anions only the  $(\text{Bu}_4\text{N})_4\text{Mo}_8\text{O}_{26}$  compound produces anions containing the  $\text{Mo}_8\text{O}_{26}$  moiety. In this case loss of one of the  $\text{Bu}_4\text{N}^+$  cations results in the production of the anion,  $[(\text{Bu}_4\text{N})_3\text{Mo}_8\text{O}_{26}]^-$ . The tetraphenylphosphonium and tetrabutylphosphonium salt solutions produce no gas phase species containing the  $\text{Mo}_8\text{O}_{26}$  anion. (See Fig. 1)

For the larger molybdate salts the major gas phase ions observed in the CID experiments depend strongly on the applied capillary-skimmer voltage that induces CID. The CID mass spectra indicate that the bonding in these species is not a simple ion pair interaction.

In aqueous solutions the molybdates are known to react with  $\text{H}_2\text{S}$  but, in the gas phase, we observe that only a few gas phase molybdate anions react with  $\text{H}_2\text{S}$  and  $\text{CO}$  and none with  $\text{C}_2\text{H}_2$ . For example,  $[\text{Mo}_3\text{O}_9]^-$  reacts by addition of  $\text{H}_2\text{S}$  to give  $[\text{H}_2\text{S}+\text{Mo}_3\text{O}_9]^-$  but  $[\text{HMo}_3\text{O}_9]^-$  is unreactive under the same reaction conditions.  $[\text{HMo}_4\text{O}_{13}]^-$  reacted in the presence of  $\text{CO}$  to form  $[\text{HMo}_3\text{O}_9]^-$ .



**Figure 1** Negative-ion FTICR mass spectrum of  $(\text{Ph}_4\text{P})_2\text{Na}_2[\text{Mo}_8\text{O}_{26}]^-$ .