

Thermal and Photochemical Reactivity of the Alkyl Phosphomolybdates  
 $P_3O_9MoO_2OR^{2-}$  in Solution: Oxidation, Dehydration, and Isomerization

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Final Seminar

August 13, 1987

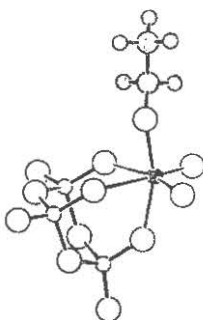
Catalytic selective organic oxidation over metal oxides produces some very important chemicals such as formaldehyde, acrolein, and maleic anhydride [1-3]. Although these heterogeneous catalytic reactions have been the subject of mechanistic studies for many years, the mechanisms involved in these catalytic cycles are still largely unclear. Studies on molecular complexes as models of the local structure of the heterogeneous systems provide insight into the fundamental chemistry involved in the catalytic reactions and afford opportunities to explore novel reactions not observed in heterogeneous systems.

Here we would like to report the synthesis and the thermal and photochemical reactivity study of  $P_3O_9MoO_2OCH_2CH_3^{2-}$  and  $P_3O_9MoO_2OCH_2CH=CH_2^{2-}$ . This study provides more details of alcohol oxidation by oxomolybdenum(VI) compounds and reports a new metal alkoxide photoreaction.

The compounds  $P_3O_9MoO_2Cl^{2-}$  and  $P_3O_9MoO_2OCH_3^{2-}$  were prepared according to eq. 1 and 2.

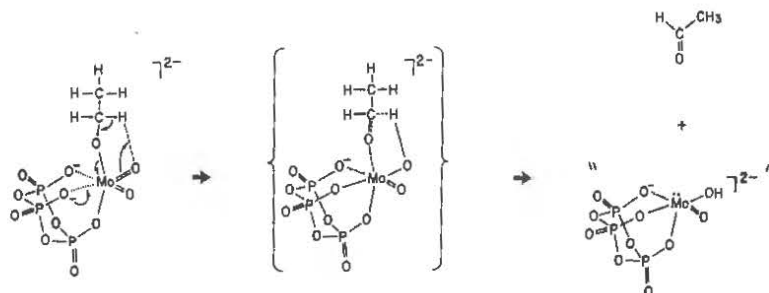


The ethyl ester  $P_3O_9MoO_2OCH_2CH_3^{2-}$  and allyl ester  $P_3O_9MoO_2OCH_2CH=CH_2^{2-}$  were prepared by alcohol exchange of  $P_3O_9MoO_2OCH_3^{2-}$  with excess ethyl or allyl alcohol. Single crystal structural analysis of the ethyl ester by Professor Victor Day at the University of Nebraska revealed that the ethyl ester is composed of discrete  $P_3O_9MoO_2OCH_2CH_3^{2-}$  anions and  $[(n-C_4H_9)_4N]^+$  cations. The ball and stick drawing of the ethyl ester anion is shown below.

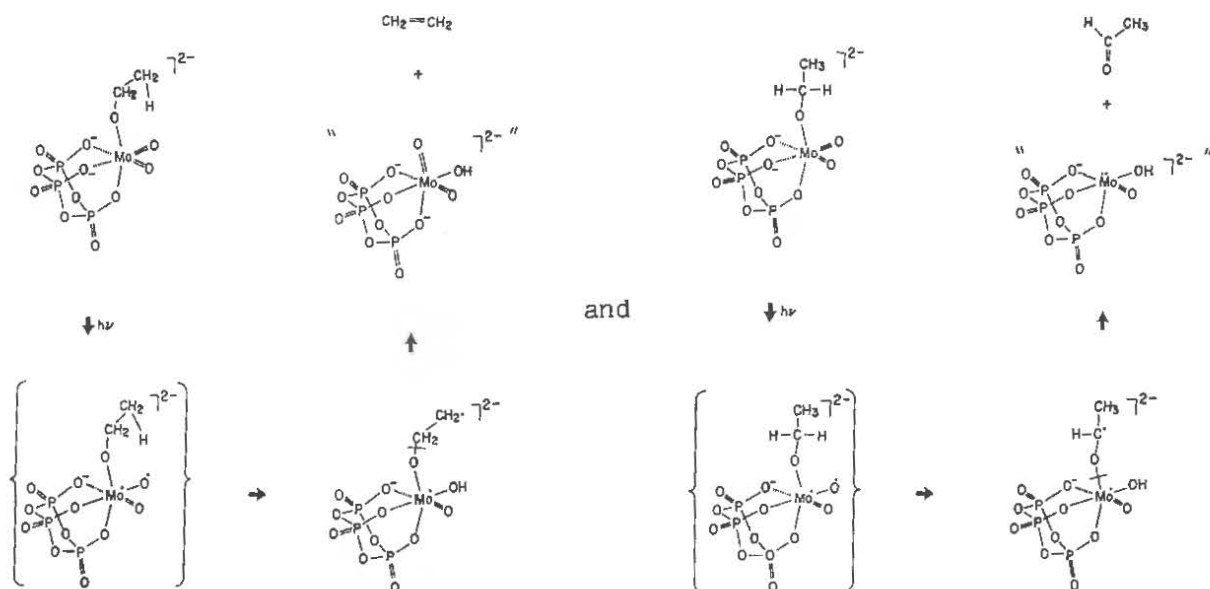


Upon thermolysis at 180°C, the ethyl ester produces  $CH_3CHO$ ,  $CH_3CH_2OH$ , and unidentified soluble inorganic product(s). Deuterium labeling at the methylene group of the ethyl ester results in an isotope effect  $k_H/k_D = 5.4$  for the formation of acetaldehyde. Addition of pyridine to the reaction solution enhances the formation rate of acetaldehyde by a factor of 5.2. These observations clearly indicate that the rate-determining step of this ethyl ester thermolysis is the removal of a methylene hydrogen as  $H^+$ . Based on the kinetic observations

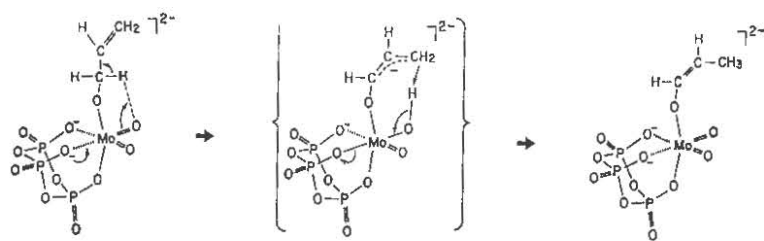
and the short contact between the methylene hydrogen and the Mo=O oxygen found in the structure, an intramolecular mechanism for the thermolysis of the ethyl ester is proposed:



When the ethyl ester is photolyzed,  $\text{CH}_3\text{CHO}$ ,  $\text{CH}_2=\text{CH}_2$ , and  $\text{CH}_3\text{CH}_2\text{OH}$  are liberated in addition to unidentified soluble inorganic product(s). Deuterium labeling at the methylene group gives a primary isotope effect  $k_{\text{H}}/k_{\text{D}} = 1.3$  for acetaldehyde formation and an inverted isotope effect  $k_{\text{H}}/k_{\text{D}} = 0.7$  for ethylene formation. Labeling at the methyl group has virtually no effect on the acetaldehyde formation rate and has an isotope effect  $k_{\text{H}}/k_{\text{D}} = 2.6$  on the formation of ethylene. From this deuterium labeling experiment, mechanisms similar to the well-known organic Norrish Type II reaction [4] are proposed for the photolysis of the ethyl ester:



The allyl ester isomerizes to form  $\text{cis-P}_3\text{O}_9\text{MoO}_2\text{OCH}=\text{CH}-\text{CH}_3^{2-}$  upon heating. A kinetic study revealed that this isomerization is a first order reaction and that the rate-determining step of this reaction is the cleavage of the  $\beta$  C-H bond ( $k_{\text{H}}/k_{\text{D}} = 10.1$ ). Crossover experiments further indicated that the isomerization is intramolecular. An intramolecular mechanism is proposed as shown below.



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