

Photocatalytic Oxidations by Polytungstate Anions

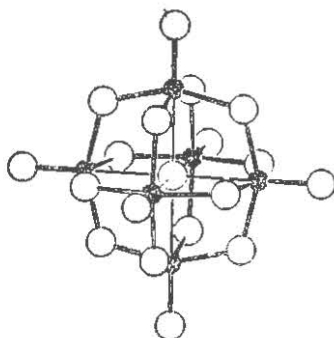
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As early as 1916 [1] it was recognized that solutions of polytungstate anions are capable of photochemically oxidizing certain organic molecules. In the last ten years, several research groups have begun to reinvestigate this area [2], with most of the work focusing on photocatalytic reactions in aqueous solutions. In an effort to understand some of the fundamental photochemical processes involved in these types of reactions, a systematic investigation of a series of hexametallate polytungstate ions was initiated, using the oxidation of isopropanol to acetone as a model reaction. All of the complexes were used as their tetra-n-butyl ammonium salts and studied under identical conditions.

Hexametallates are a relatively simple and well characterized class of compounds [3], the simplest member being the $W_6O_{19}^{2-}$ anion shown below. Derivatives can be prepared in which one or more early transition metals have been substituted for the tungsten atom(s), or by replacing one of the oxygen atoms with some other ligand.



The first part of this investigation involved the synthesis of new titanium-containing anions that would not undergo photochemical degradation. The only known titanium containing compound of this type is the $C_5H_5TiW_5O_{18}^{3-}$ anion [4], which is not expected to be stable towards loss of C_5H_5 [5]. The compounds $ClTiW_5O_{18}^{3-}$ and $ROTiW_5O_{18}^{3-}$ ($R = CH_3, C_2H_5,$ and $(CH_3)_2CH$) were all prepared by a similar method to that used to prepare $C_5H_5TiW_5O_{18}^{3-}$. Reaction of $ClTiW_5O_{18}^{3-}$ with OH^- or hydrolysis of $ROTiW_5O_{18}^{3-}$ resulted in formation of $(TiW_5O_{18})_2O^{6-}$. All of these compounds were prepared as analytically pure, crystalline salts and characterized spectroscopically.

The electronic structure of the series of hexametallates $W_6O_{19}^{2-}$, $VW_5O_{19}^{3-}$, $NbW_5O_{19}^{3-}$, $TaW_5O_{19}^{3-}$, $ROTiW_5O_{18}^{3-}$, and $(TiW_5O_{18})_2O^{6-}$ was probed using electronic spectroscopy and cyclic voltammetry. The major conclusion reached from the cyclic voltammetry data was that, with one exception, reduction occurs at a tungsten atom and is dependent primarily on the overall charge of the anion. The exception is the $VW_5O_{19}^{3-}$ anion in which reduction is known to occur at the vanadium atom. The electronic absorption spectra are more difficult to understand. All of the anions have a strong absorption between 250-280 nm with a small, low energy shoulder. In an attempt to understand these spectra, a calculation was done for the $W_6O_{19}^{2-}$ anion using the $X\alpha$ method. Although it was not possible to arrive at complete assignments of the spectra due to the large

number of allowed transitions, the calculation did suggest that the strong band near 275 nm arises from a combination of several allowed bridging oxygen to tungsten charge transfer transitions with the lower energy shoulder assigned to a terminal oxygen to tungsten charge transfer.

Photolysis of these anions in a mixed solvent containing equal parts acetonitrile and isopropanol results in photochemical formation of acetone. The reaction is catalytic with respect to polytungstate anion and no other products could be detected by ^1H NMR. Quantum yields for production of acetone were measured and compared with other systems.

References

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