AN ABSTRACT OF THE THESIS OF

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The absorbance maxima of the reduction products for the heteropoly compound potassium 1:12 dodecatungstosilicate seventeen hydrate, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$, with isopropyl alcohol and sulfuric acid have been studied using a Bausch and Lomb Spectronic 20 photometer, and GCA McPherson ultraviolet-visible spectrophotometer. The position of absorbance maxima and maximum absorbance depend on the concentrations of the heteropoly compound and isopropyl alcohol, irradiation time and deaerated mixtures with nitrogen. The rate of photooxidation of organic substrates and related compounds with the heteropoly compound occurring in an ultraviolet photochemical reactor was studied and reported. The rate of photooxidation of alcohols and amine with the heteropoly compound is secondary $\geq$ primary $\approx$ amine $>$ tertiary. Amino acids, except glycine, and saccharides such as glucose, maltose, and sucrose, also are photooxidized by the heteropoly compound. The rate of the photooxidation of saccharides is glucose $>$ sucrose $\geq$ maltose. The proposed reactive functional

group in the photooxidation of the alcohols and amine is either a -CH(OH) or a -CH(NH) moiety. The proposed mechanism for the photocatalyzed oxidation of alcohol by the heteropoly anion is consistent with these results.

OXIDATION OF ALCOHOLS AND RELATED COMPOUNDS
WITH HETEROPOLY TUNGSTATE

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I love my family.

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CHAPTER I. INTRODUCTION

I-1. Definition of Iso- and Heteropoly Acids or Anions

Numerous compositions of oxo acids or oxo anions exist which are suggestive of being derived from one or more of the acid anhydrides by dehydration and condensation. A polyacid or a polyanion can be based either on a single type of anhydride that is called an isopoly or on more than one type of anhydride that is called a heteropoly[1]. Isopoly species are characteristic of both certain non-metals (e.g., S, P, As) and certain *d*-transition metals (e.g., V, Mo, W). Heteropoly species are characteristic of certain *d*-transition metals in combination with other elements that are called heteroatoms.

Much of the chemistry of molybdenum (Mo) and tungsten (W) involves the formation of numerous polymolybdate(VI) and polytungstate(VI) acids and their anions. Vanadium (V^{5+}), niobium (Nb^{5+}), tantalum (Ta^{5+}), and uranium (U^{6+}) show comparable behavior, but the chemistry of these is more limited. For the examples of molybdenum and tungsten, the isopoly acids and their related anions contain only molybdenum or tungsten along with oxygen and hydrogen, and the heteropoly acids and their related anions contain one or two atoms of another element in addition to molybdenum or tungsten along with oxygen and hydrogen[2].

The isopoly anions and heteropoly anions of molybdenum and tungsten have been known for well over a century. In recent years, considerable interest has been shown in the heteropoly compounds (HPC) of molybdenum and tungsten, not only in the structure and characterization of such compounds, but also in those aspects of their chemistry that are generating increasing attention because of important industrial applications such as oxidation of unsaturated aldehydes or methacrolein or the hydration of propene or *iso*-butene, *etc*. In general, heteropoly compounds of molybdenum and tungsten are used as catalysts in a variety of commercially important chemical processes such as hydrocracking, hydrogenation, isomerization, and polymerization[3 and 4].

The blue reduction products of heteropoly compounds are called heteropoly blues (HPB). Heteropoly blues are a class of mixed valance complexes that are obtained by reaction of isopoly and heteropoly compounds of molybdates, tungstates, vanadates, *etc*. These are used in analytical chemistry in the colorimetric determination of several elements such as phosphorus (P), silicon (Si), arsenic (As), and germanium (Ge) and in the biochemical determination of compounds such as uric acid, adrenalin, phenol, and sugar[5].

Migration of the electrons within the crystal lattice can be influenced by applying an external potential[4]. For example, when a heteropoly compound is oxidized in an externally applied electric field, the heteropoly compound becomes blue. The blue color disappears when the polarity is reversed. Hence the electrochromism on the heteropoly compounds is of interest in industry because of the possibility of use in digital display devices[6]. The characterization of heteropoly compounds in photochemical research began in the early 1900's[7] and has been patented for possible use in photography[8].

Heteropoly compounds and isopoly electrolytes constitute large categories of coordination type salts and free acids with each member containing a complex and high molecular weight anion. In heteropoly and isopoly anions of molybdenum and tungsten, two to eighteen hexavalent molybdenum or tungsten atoms surround one or more central atoms or heteroatoms. Their general formula can be presented as:

$[M_mO_y]^{p-}$ ($y \geq m$) for isopoly anions, and

$[X_xM_mO_y]^{q-}$ ($x < m$) for heteropoly anions[9].

Here X is a heteroatom or a central atom that can be one of 69 elements which belong to various groups of the Periodic Table except the noble gases. These heteroatoms or central atoms are listed Table I. While isopoly and heteropoly anions have been prepared with heteroatoms or central atoms from 69 elements, the suitability of elements as peripheral metal atoms appears to depend on the ionic radius and charge as well as the ability to form a peripheral metal-oxygen pi bond[10]. The M is the so-called addenda atom or a polyatom in a heteropoly anion or isopoly anion. Usually M is molybdenum or tungsten, and to a lesser extent vanadium, niobium, tantalum, or a mixture of these elements. The transition metals of M are in high oxidation states (d^0, d^1). Mixed polyoxometalates also exist with formulae $[M_mM'_nO_y]^{p-}$ for isopoly anions and $[X_xM_mM'_nO_y]^{q-}$ for heteropoly anions. Here M′ represents a secondary addenda atom or polyatom that can be one of the above listed metals or other metals[4]. The O is oxygen. Oxygen atoms in the isopoly and heteropoly anion are found in three kinds of bonding environments (see Figure 1): (a) four of these atoms interconnect the central atom and the peripheral metal atoms; (b) other oxygen atoms bridge the peripheral metal atoms; and (c) twelve terminal oxygen atoms are each bound only to the peripheral atoms and protrude from the anion[10].

I-2. Nomenclature of Heteropoly Compounds

Various methods of nomenclature for heteropoly compounds have been proposed during the last several decades. According to the International Union of Pure and Applied Chemistry (IUPAC)[11], a heteropoly compound is named with an Arabic numeral designating the simplest ratio of molybdenum or tungsten atoms to the central atom. This system is followed by the prefix "molybdo" or "tungsto" and then by the name of the simple anion or acid that contains the central atom in the corresponding oxidation state. In case of ambiguity, Roman numerals may be used to designate the oxidation state of the central atom. For example, Pope[9 and 12] gives the name of $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ as potassium 1:12 alpha dodecatungstosilicate 17 hydrate and the name of $[H_6CrMo_6O_{24}]^{3-}$ as hexahydrogenhexa-μ-oxohexa-μ_3-oxo-7-chromium(III)-hexakis(dioxomolybdate)(3-).

I-3. Background of Heteropoly Compounds

I-3-1. General Historical Background of Heteropoly Compounds

In 1826, Berzelius prepared and analyzed the yellow precipitate of ammonium dodecamolybdophosphate, $(NH_4)_3[PMo_{12}O_{40}]\cdot xH_2O$, from the reaction of molybdate with phosphate[12]. Struve described the heteropoly molybdates of Cr^{3+} and Fe^{3+} in 1854; however, he postulated these as double salts. Marignac first discovered 12-tungstosilicic acid in 1862 and he recognized such compounds as a distinct class rather than as double salts. Miolati and Pizzighelli made the first attempt to understand the composition of heteropoly compounds in 1908. They suggested structures of these heteropoly compounds on the basis of ionic theory and Werner's coordination theory[3]. Their suggestion was further developed and applied by Rosenheim. This model is now called the Miolati-Rosenheim theory (MR theory)[9]. According to MR theory, heteropoly acids are based on six-coordinate heteropoly atoms with MO_4^{2-} or $M_2O_7^{2-}$ anions as ligands or bridging groups coordinated to the central atom. Formulae derived from the Miolati-Rosenheim theory and from modern theory result in different formulae for the heteropoly compounds. For example, the Miolati-Rosenheim formula is given as $H_8[Si(W_2O_7)_6]$, but $H_4[SiW_{12}O_{40}]$ is the modern formula for this compound. Note that the silicon (Si) to tungsten (W) ratios are the same, but the number of oxygen (O) atoms and the number of acidic hydrogen (H) atoms are different in the above formulae. However, until recently, the Miolati-Rosenheim formula was still frequently used to interpret some of heteropoly structures when modern structural information was lacking[3].

Pauling proposed a structure of heteropoly compounds having a ratio of the number of the central atoms (X) to the addenda atoms (M) of 1:12 in 1929. According to the structure proposed by Pauling, the molybdenum (Mo^{6+}) and tungsten (W^{6+}) were octahedrally coordinated by oxygen and by corner sharing of twelve MO_6 octahedra surrounding a central XO_4 tetrahedron[9 and 13]. In Pauling's structure, 42 oxygens are required. Keggin reported the structure of the heteropoly acid $H_3[PW_{12}O_{40}] \cdot 6H_2O$ by analysis of 32 powder X-ray crystallography lines in 1933[14]. His structure was a more compact corner shared polyhedron than that proposed by Pauling[12]. This structure today is called the "Keggin structure". The general formula of Keggin is $[X^{n+}M_{12}O_{40}]^{(8-n)-}$. The Keggin structure is shown in Figure 1 using polyhedra. In Figure 1, the corners of the twelve octahedra and of the one tetrahedron represent the oxygen atoms. The Keggin structure was confirmed by Bradly and Illingworth using $H_3[PW_{12}O_{40}]\cdot 29H_2O$ by analysis of powder photographs in 1936[9]. At that time, analytical methods other than X-ray crystallography could not distinguished between $[SiW_{12}O_{40}]^{4-}$ and $[SiW_{12}O_{42}]^{8-}$. At about the same time, Anderson suggested a structure for the para(or hepta)molybdate anion, $[Mo_7O_{24}]^{6-}$[15]. Using a new X-ray crystallographic structure, a heteropoly anion, $[TeMo_6O_{24}]^{6-}$, was reported by Evans in 1948[16]. The formula of $[X^{n+}Mo_6O_{24}]^{(12-n)-}$ is now called the "Anderson structure"[16 and 17].

Only a few researchers were working on heteropoly research in Europe and the United States in 1950, but since then the number of researchers has grown. As development of X-ray crystallographic hardware and software advanced, the number of different reported structures has increased. During the last 20 years, spectroscopic methods have been developed and combined with precise electrochemical measurements and new analytical techniques, such as fast atom bombardment mass spectrometry (FABMS)[18], to further study the bonding, structures, and uses of these heteropoly compounds. Some papers of catalysis by solid state and photocatalytic oxidation of organic substrates by polyoxometalates of heteropoly compounds were reported by several chemists in the 1980's and 1990's[9 and 19-24].

I-3-2. Historical Background of 1:1:11 Heteropoly Anions

In 1962, Simmons and Baker reported the preparation of the first heteropoly anion which contained two different heteroatoms, cobalt and silicon, in combination with tungsten[25]. Figgis and Baker in 1970 reported that the species of Simmons really was a 1:1:11 heteropoly anion[26]. Their heteropoly anion was shown to contain two non-acidic hydrogen atoms and was formulated as $K_6[SiW_{11}O_{39}CoH_2O]$, not as $K_6H_2[SiCoW_{11}O_{40}]$ as had Simmons. According to Figgis, the silicon atom is the heteroatom (X) of the Keggin structure, has tetrahedral coordination, and is located at the center of the anion structure. This heteroatom is attached to four oxygen atoms. Figgis showed that this anion should be formulated as $[H_2OCoO_5W_{11}O_3SiO_4]^{6-}$. Following this report, other researchers reformulated their results using the 1:1:11 formulae.

Corigliano and Di Pasquale reported the transfer of a vanadium isopoly into non-polar organic solvent in 1974[27]. Landis further substantiated the 1:1:11 formulation for analogous "dumbbell" complexes with bridging pyrazine in 1977[28]. Landis studied the octahedral trans effect of cobalt in a series of these 1:1:11 diheteropoly tungstate salts. He analyzed and characterized 32 potassium salts of dihetero-11-tungsto anions. For example, a typical formula of these dihetero-11-tungsto anions is the pyrazinecobalt(III)-11-tungstogermanate, $[N_2C_4H_4CoO_5W_{11}O_{30}GeO_4]^{5-}$ and

$N_2C_4H_4(CoO_5W_{11}O_{30}GeO_4)_2]^{10-}$. Kazanskii and co-workers measured magnetic susceptibility of $K_6[SiM_{11}Fe^{III}(OH)O_{39}]\cdot H_2O$ in a low spin Fe^{III} for the molybdate and a high spin Fe^{III} for the tungsten in 1980[29].

I-4. Structures and Characteristics of Heteropoly Anions

I-4-1. Structures of Heteropoly Anions in the Solid State

Heteropoly compounds in the solid state are composed of heteropoly anions, cations (protons, metal ions, or onium ions), and water of crystallization. Sometimes in addition they contain neutral or protonated organic molecules. Metal atoms in the polyanions occupy interstitial positions in close-packed arrays of the oxide ions. In metal oxides, these arrays appear as infinite chains, sheets, or three-dimensional lattices. Polyanions are limited in size and appear as discrete units. Commonly polyanions have high symmetry[1]. X-ray crystallographic structural determinations have been made on several heteropoly compounds and on related isopoly molybdates and tungstates. The simplest way to represent the heteropoly anions is by polyhedra that share corners, edges or faces with one another. For the heteropoly molybdates or tungstates, each Mo or W is at the center of an octahedron, and an oxygen atom is located at each vertex of the octahedron. The ionic radii for Mo^{6+} and W^{6+} are 0.62 and 0.65 angstrom, respectively, and that for O^{2-} is 1.40 angstrom. A MoO_6 or WO_6 octahedron can share corners, edges or both with other MoO_6 or WO_6 octahedra[30]. When two octahedra share an edge, two oxygen atoms form part of each octahedron. The central atom (X) is located at the center of an XO_4 tetrahedron or an XO_6 octahedron. In a limited number of cases (e.g., X=Ce, Th), icosahedrally coordinated XO_{12} heteropoly anions are present. For each structure having a central atom, this atom is generally surrounded by MoO_6 or WO_6 octahedra. Also each MoO_6 or WO_6 octahedron is directly attached to a central atom through a shared oxygen atom. The structures of the octahedra actually are frequently distorted[31-34].

I-4-2. Structures of Heteropoly Anions in Solution

In aqueous solution, two forms of the Keggin structure exist: α form and ß form. The α form that is the well-known Keggin structure was suggested by Baker and Figgis[26] in the previous section **I-3-2**. The ß form was suggested by Sasaki and co-workers[35 and 36]. The ß form has one edge shared M_3O_{13} group which is rotated by 60 degrees relative to the α form. Both forms can exist, but once prepared they do not readily interconvert.

The fundamental structure of heteropoly anions can be separated into five series distinguished by the coordination number of the heteroatoms[37 and 38]:

Series I. This series contain tetrahedrally coordinated heteroatoms, particularly the 1:12, 1:11 and related heteropoly anions. The 1:12 heteropoly anions are the most easily formed, and have been the most widely studied[39]. Three compact symmetrical clusters of MO_6 exist: (a) a tetrahedron (*Td*), (b) an octahedron (*Oh*), and (c) an icosahedron (*Id*). The structure of a 1:12 tetrahedron species was elucidation by Keggin[14]. Therefore, the 1:12 heteropoly anions are the so-called "Keggin structure"[14 and 17]. Numerous other papers have verified and revealed details of the structure[3, 4 and 9]. The general formula of Keggin structure was previously mentioned as $[X^{n+}M_{12}O_{40}]^{(8-n)-}$. The Keggin structure is shown in Figure 1. Some examples of heteropoly anions having the Keggin structure are $[PMo_{12}O_{40}]^{3-}$, $[PW_{12}O_{40}]^{3-}$, $[SiMo_{12}O_{40}]^{4-}$, $[FeW_{12}O_{40}]^{4-}$, $[SiW_{12}O_{40}]^{4-}$, and $[BW_{12}O_{40}]^{5-}$. The Keggin structure commonly has an overall tetrahedron (*Td*) symmetry that consists of an XO_4 (coordinated heteroatom) tetrahedron surrounded by twelve MO_6 octahedra that usually contain molybdenum or tungsten atoms. These octahedra are organized in four groups of three fused MO_6, written as M_3O_{13}. The MO_6 units are joined to members of the same group through shared edges, and to the MO_6 units of other groups and the XO_4 tetrahedron through shared corners. In terms of bonds, the Keggin structure is distinguished by twelve quasilinear M-O-M bonds, twelve M-O-M angular bonds, four X-O-M bonds, and twelve M=O bonds with terminal O atoms[4]. Within each octahedron, the longest W-O distance, 2.49 angstrom, occurs between the tungsten and an oxygen atom in the interior of the complex; whereas, the W-O distance involving the peripheral oxygen atoms which are not shared by other tungsten atoms is only 1.43 angstrom[40]. The second symmetrical clusters of MO_6 octahedra (*Oh*) have not been observed for a discrete polyoxometalate. However, several derivatives, such as the mixed-valence mineral sherwoodite, $[AlV_{14}O_{40}]^{9-}$, are known[12]. This cluster is based on edge sharing MO_6 octahedra and may be considered as fragments of a cubic closest packing of oxygen atoms[41]. The icosahedron (*Id*) symmetry is known only for a handful of heteropoly molybdates of tetravalent lanthanide and actinide cations[12]. Usually the molybdenum compounds are yellow, and the tungsten compounds are very pale yellow or colorless in solution and in most crystals. The 1:11 heteropoly anions can be formed at high pH conditions. For example, the 1:11 molybdogermanate anion exists in solution at pH above 4.8 in equilibrium with germanate, molybdate, and 1:12 molybdogermanate[3].

The formula of the 1:11 structure is generally $[X^{n+}M_{11}O_{39}]^{(12-n)-}$ where heteroatom (X) is boron(III), phosphorus(V), arsenic(V), and germanium(IV). The 1:11 heteropoly anions appear to differ in properties from the 1:12 heteropoly anions. The formula of 1:11 heteropoly anions can subsequently incorporate a secondary addenda atom (M′) to form complexes of the type $[XMM'O_{40}]^{q-}$. The structural units of 1:12 and 1:11 heteropoly anions are two or three edges shared MO_6

octahedra.

Series II. Tetrahedrally coordinated 2:18 and 2:17 heteropoly anions belong to this series that are structurally related to series I. The basic unit of the 2:18 heteropoly anions was elucidated by Dawson in 1953 for $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$[42]. The 2:18 heteropoly anions are now called the "Dawson structure"[17 and 42]. The formula of the Dawson structure is $[X_2^{n+}Mo_{18}O_y]^{(2y-108-2n)-}$ or $[X_2^{n+}W_{18}O_{62}]^{(16-2n)-}$ where heteroatom (X) is phosphorus(V), arsenic(V), and beryllium(II). The Dawson structure is shown in Figure 2. Examples of the Dawson structure are $[P_2W_{18}O_{62}]^{6-}$, $[As_2W_{18}O_{62}]^{6-}$, and $[P_2Mo_{18}O_{62}]^{6-}$. The 2:18 molybdenum compounds are a darker orange color, and the analogous tungstates are a yellow color. The two heteroatoms (X) are not joined together through O. The symmetry of the Dawson structure is D_{3h} and is of ellipsoid shape. Two groups of six MO_6 octahedra are located near the poles of the long axis, and a group of twelve metal oxides is located in the equator. The bonds of the 2:18 heteropoly anions of the Dawson structure are distinguished by eighteen M-O-M quasilinear bonds, eighteen M-O-M bent bonds, eight X-O-M bonds, and eighteen M=O bonds with terminal O atoms[4].

The Dawson structure is closely related to the Keggin structure. If three adjacent corner-linked MO_6 octahedra are removed from the Keggin structure, a half-Dawson structure fragment is formed with a set of three octahedra over a ring of six octahedra. Two identical half-units that are related by a plane of symmetry perpendicular to the three-fold rotation axis can be formed from the XM_{18} anion. These two halves are linked by corner sharing. As with the 1:12 heteropoly anions, two structural isomers of the 2:18 can be prepared. The 2:18 heteropoly anions also can form 2:17 heteropoly anions in a similar way to the formation of 1:11 heteropoly anions from 1:12 heteropoly anions by a suitable adjustment of pH. The 2:17 heteropoly anions can incorporate a second heteroatom to form a ternary heteropoly anion.

Series III. The 1:6 heteropoly anions belong to this series. The structure of 1:6 heteropoly anions consists of only octahedral coordination of the metals. There are two types of 1:6 heteropoly anions: type I and II. (a) For the type I, Evans first classified this series complexes such as $[TeMo_6O_{24}]^{6-}$[16 and 31]. However the 1:6 heteropoly anions today are called the "Anderson structure"[15 and 17]. The general formula of Anderson structure is mentioned section **1-3-1** such as $[X^{n+}M_6O_{24}]^{(12-n)-}$ where heteroatom (X) is tellurium(VI) and iodine(VII). The Anderson structure is shown in Figure 3. In the structure of $[TeMo_6O_{24}]^{6-}$, the Anderson structure involves an octahedrally coordinated tellurium atom and surrounded by a planar annulus of MoO_6 octahedra sharing edges. Usually the tungsten complex of heteropoly anions has an unstable Anderson structure, although $[IW_6O_{24}]^{5-}$ appears nalogous to $[IMo_6O_{24}]^{5-}$. (b) For type II, the general structure of 1:6 heteropoly anions is $[X^{n+}M_6O_{24}H_6]^{(6-n)-}$. Where heteroatom (X) is aluminum(III), chromium(III), iron(III), cobalt(III), rhodium(III), gallium(III), nickel(II)(with molybdenum), nickel(II), and gallium(III)(with tungsten)[3]. The complexes of nickel for 1:6 heteropoly anions have been prepared such as $(NH_4)_4[H_6NiMo_{6-n}W_nO_{24}]$. Where n is from 0 to 6[43]. Type II is distinguished from type I in that three molecules of water of constitution are required so that the total number of oxygen atoms within the anion are twenty four. The 1:6 heteropoly anions of each central atom have characteristic colors in the solid state and solutions. For example, aluminum, iron, and gallium are colorless, chromium is dark pink, cobalt is green blue, rhodium is amber, and nickel is blue in heteropoly molybdates[3].

Series IV. This series contains octahedrally coordinated 1:9 heteropoly anions. The 1:9 heteropoly anions are called the "Waugh structure"[17, 38 and 44]. The general formula of Waugh structure is $[X^{n+}M_9O_{32}]^{(10-n)-}$. The Waugh structure is shown in Figure 4. From the right in Figure 4, this structure is composed of octahedra of oxygen atoms with a metal atom in the center of each octahedron. From the left in Figure 4, the structure of Waugh has been exploded along the three-fold axis that is joined by the twelve oxygen atom. The typical example of this series is $[MnMo_9O_{32}]^{6-}$ which is oranged-red colored.

e structure of $[MnMo_9O_{32}]^{6-}$ is an octahedrally coordinated anganese atom partially surrounded by edge sharing MoO_6 ctahedra[1 and 44]. The formation of 1:9 heteropoly anions is expected to be unfavorable with tungsten.

Series V. Icosahedrally coordinated 1:12 heteropoly anions can be formed by two octahedra sharing a face that is also shared with a corner of a neighboring unit and with the central atom or heteroatom. Usually the 1:12 heteropoly anions having icosahedral coordination are called the "Silverton structure"[17 and 38]. The general formula of Silverton structure is $[X^{n+}M_{12}O_{42}]^{(12-n)-}$. The Silverton structure is shown in Figure 5. The Silverton structure provides an icosahedral set of 12 oxygen ligands for the hetero-cation in Figure 5. A species of M^{4+} ions from the lanthanides and actinides (e.g., Ce^{4+}, Th^{4+}, and U^{4+}) can be found in such a structure. An example of icosahedrally coordinated 1:12 is $(NH_4)_2H_6[CeMo_{12}O_{42}]\cdot 12H_2O$ which has a light yellow color[45].

I-5. General Formulae of Heteropoly Anions

The type of heteropolies of interest in this study is typically two kinds of formulae. Commonly these formulae of heteropoly anions are according to the possible ratios of heteroatom (X) to addenda atom (M). The principal formulae of heteropoly molybdate anions and tungstate anions are as[3, 4 and 9]:

(a) heteropoly molybdate anions

$[X^{n+}Mo_{12}O_{40}]^{(8-n)-}$ for 1:12 ratio of X and Mo

$[X_2^{n+}Mo_{18}O_y]^{(2y-108-2n)-}$ for 2:18 ratio of X and Mo

(b) heteropoly tungstate anions

$[X^{n+}W_{12}O_{40}]^{(8-n)-}$ for 1:12 ratio of X and W

$[X_2^{n+}W_{18}O_{62}]^{(16-2n)-}$ for 2:18 ratio of X and W.

Examples of these formulas are as $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, and $[FeW_{12}O_{40}]^{4-}$ for Keggin structure, and $[P_2W_{18}O_{62}]^{6-}$, $[As_2W_{18}O_{62}]^{6-}$, and $[P_2Mo_{18}O_{62}]^{6-}$ for Dawson structure. These structures are shown in Figures 1 and 2.

I-6. Properties of Heteropoly Anions

The general properties of heteropoly anions are the following[3, 4, 9 and 17]:

1. Heteropoly anions have high molecular weights. The range of molecular weight is from 2,000 to 40,000.

2. Free acids and their salts with small metal ions are very soluble in water; however, salts with large ions (e.g., Cs^+, Ag^+, Ti^+, Hg^{++}, Pb^{++}, NH_4^+, K^+, Rb^+, and the larger alkaline earth salts) are insoluble or slightly soluble in water. Also many of the free acids and a few of the salts for heteropoly anions are very soluble in organic solvents, especially if the latter contains oxygen. Ethers, alcohols and ketones are generally the best organic solvents for heteropoly anions.

3. The crystalline free acids and salts of heteropoly anions are almost always highly hydrated. Sometimes acids and

salts of heteropoly anions can be formed as solid hydrates.

4. Many heteropoly anions become highly colored when the heteropoly anions are crystallized. The colors range through the spectrum and occur in many shades.

5. Heteropoly anions have multielectron reductions, and those having Mo and V as polyatoms are strong oxidizing agents. Usually the reduction products are colored an intense deep blue. In solution, the blue substances obey Beer's Law. The reduced products can in turn act as reducing agents, and the original colors of the anions are restored upon oxidation.

6. Free acids of heteropoly anions are very strong Bronsted acids. Generally tungstens are stronger acids than molybdates; therefore, heteropoly tungstates are hydrolytically more stable than heteropoly molybdates. From the literature[46-48], tungstate acids that are both the oxidized and the two-electron reduced species are dissociated in aqueous solution; however, molybdate acids are protonated on reduction. The strong acidity is caused by: (a) dispersion of the negative charge over many atoms of the polyanion, and (b) the fact that the negative charge is less distributed over the outer surface of the polyanion owing to the double bond character of the addenda atom (M) and of the terminal oxygen bond which polarizes the negative charge of terminal oxygen toward addenda atom (M). The acid strengths estimated from the formation constants for complexes of polyanions with chloral hydrate are in the order[49]:

$PW_{12} > PMo_{12} > SiW_{12} \approx GeW_{12} > SiMo_{12} \approx GeMo_{12}$.

he general trends of the acid strengths of heteropoly anions re W > Mo > V for polyatoms, and $P^{5+} > Si^{4+}$, Ge^{4+} for heteroatoms.

7. All heteropoly anions, especially Mo and W, are decomposed by strongly basic solutions. For example, final decomposition products for heteropoly molybdates and heteropoly tungstates are molybdate or tungsten ions and either an oxyanion or a hydrous metal oxide of the central atom as:

$$[PW_{12}O_{40}]^{3-} + 23OH^- \text{--->} HPO_4^{2-} + 12WO_4^{2-} + 11H_2O$$

$$[CrMo_6O_{24}H_6]^{3-} + 9OH^- \text{--->} Cr(OH)_3 + 6MoO_4^{2-} + 6H_2O.$$

A limited number of heteropoly molybdates exist only in very acidic solutions.

8. In aqueous solution, heteropoly anions are stable at a low pH, but they tend to be hydrolyzed at a high pH. The stability of heteropoly anions is greater in organic media.

9. The reduction-oxidation (redox) chemistry of heteropoly anions is characterized by their ability to accept and subsequently release a certain number of electrons without decomposition. The methods of reduction-oxidation reaction of heteropoly anions are potentiometric titration (using Cr^{2+}, Fe^{2+}, Eu^{2+}, *etc.*), polarography, photoredox reactions, and high energy radiation through formation of reducing free radicals. Typical redox properties of heteropoly anions can be classified into ten types. (a) The electrochemical reduction

XM_{12} generally proceeds reversibly by one to six electron, pending on the applied potential, solvent, *etc.* (b) The xidation potentials of polyanions containing Mo and V are igh since these anions are easily reduced. One-electron and three-electron reduced polyanions tend to disproportionate to ven-electron reduced species that involve 0, 2 and 4 electrons. In the case of two-electron reduced species, polyanions with n x M^{4+} and 2n x M^{5+} are possible. (c) On reduction, heteropoly anions are mainly colored blue. The so called heteropoly blue has a broad absorption at about 700 nm because the heteropoly anions contain metal ions in different oxidation states. Therefore, the heteropoly anions are assigned to the category of mixed valence compounds[50]. (d) The oxidative ability or oxidation potential of heteropoly anions decreases in the order V > Mo > W containing heteropoly anions. The oxidation potential energy or oxidation ability decreases linearly with increasing valence of the central atom or the increasing negative charge of the polyanions. The order of oxidation ability is as: PW_{12}^{3-} > GeW_{12}^{4-} > SiW_{12}^{4-} > FeW_{12}^{5-} > BW_{12}^{5-} > $Co(II)W_{12}^{6-}$ > $H_2W_{12}^{6-}$ > CuW_{12}^{7-}. For polyanions with mixed polyatoms, the redox potentials have been reported to be $PMo_{10}V_2$ > $PMo_{11}V$ > $PMo_{12} \approx PMo_6W_6$ > PMo_{12}[17]. Sometimes it is not certain whether a heteropoly anion with mixed polyatoms is a single species or not. In the case of mixed polyatoms and heteropoly anions of Mo-V, W-V, and Mo-W, the reduced poly anions can be reoxidized by oxygen molecules. (e) Reduction of heteropoly anions is often accompanied by protonation; that is, the corresponding potential is pH dependent. An increasing pH shifts the redox potentials to more negative values and often splits the two electron polarographic waves into two of one-electron pH independent waves. Also reduction potentials of heteropoly anions shift to more negative values with increasing negative charge on heteropoly anions[46 and 47]. (f) Molybdates are more easily reduced than tungstates[48]. (g) The 2:18 heteropoly anions are reduced at slightly positive potentials and retain their structure on addition of more electrons than the corresponding 1:12 heteropoly anions. (h) The reduced heteropoly anions usually are more stable in basic solution than the non-reduced heteropoly anions. (i) Additional annexations of electrons by heteropoly anions can result in distortion of the structure, in formation of d^2 electronic configuration, and in increasing metal-metal bond character[51]. (j) In mixed heteropoly anions, the added electrons are localized on the more electronegative metal[52-54].

10. Non-reduced heteropoly anions are characterized by oxygen to addenda atom (M) charge transfer bands in the near visible and ultraviolet region. Absorbance of molybdates generally occurs at higher wavelengths than that of tungstates. According to studies by electron spin resonance (ESR), nuclear magnetic resonance (NMR), and several other methods, the reduced electron of heteropoly anions is

localized onto one metal ion at low temperatures. Pope and Prados have suggested that, with two electrons, the electrons are located on adjacent metal ions[55]. Heteropoly molybdates do not show an ESR signal[56]; however, they do show a two-electron reduction by polarography. Reduction of a heteropoly blue can reduce the O-M charge transfer band and produce the formation of an intervalence charge transfer (IVCT) band in the visible and near infrared (IR)[16, 40, 42 and 50]. The near IR and visible bands are assigned in order of increasing energy to intervalence charge transfers that involve metal ions in the same M_3O_{13} group of the Keggin structure and *d-d* transitions[57].

I-7. Applications

The applications of heteropoly compounds are primarily dependent on their unique properties: molecular weight, color, solubility, electron transfer, proton transfer, ability to store electrons, thermal stability, lability of lattice oxygen, basicity, and acid strength. An advantage of heteropoly acids is that they can be separated and enriched by extraction into organic solvents[3 and 12]. In this section, applications of heteropoly compounds are described in three different areas: (a) analytical chemistry, (b) clinical chemistry, and (c) catalysis.

I-7-1. Analytical Chemistry

Analysis of heteropoly compounds have been based on properties such as: (a) their high molecular weights, (b) their electro-chemical activity and reducibility to form colored species, and (c) the variety of elements. Also phosphate (PO_4^{3-}), silicate (SiO_3^{2-}), arsenate (AsO_4^{3-}), and germinate (GeO_3^{2-}) ions have been determined by either gravimetric methods or physical methods (e.g. colorimetric analysis) after reduction to heteropoly blues in solution. By incorporating into the heteropoly compound, the elements of P, Si, As, and Ge have been determined by differential-pulse anodic voltametry[58], and high performance liquid chromatography (HPLC) separations[59]. The measurement of nanomolar (10^{-9} molar) concentrations of silica in seawater has also been reported[60].

I-7-2. Clinical Chemistry

Many pharmaceutical and biological samples are routinely determined using heteropoly compounds[61]. Recently, the abilities of heteropoly compounds to coagulate proteins and to precipitate organic molecules like alkaloids have been used in clinical chemistry and in the analysis of drug preparations, pesticides, and other biologically active molecules. The methods of uric acid determination[62] and Lowry protein determination involve reduction to mixed valence heteropoly blue solutions[63]. Separations of cholesterol, low density lipoprotein (LDL), and high density lipoprotein (HDL), involve the same heteropoly blue solutions[64]. The usage of polytungstates for electron microscopy has been improved as organic derivatives of heteropoly anions have been developed[65 and 66]. The heteropoly anions permit highly selective labeling.

I-7-3. Catalysis

Heteropoly anions are broadly used as oxidation catalysts as well as acid catalysts. The basic reversible redox reactions with substrate oxidations can be represented by the following equations[12]:

$$[\mathrm{HPA}]_{ox} + \mathrm{S} + (x)\cdot\mathrm{H} \longleftrightarrow \mathrm{H}_x[\mathrm{HPA}]_{red} + \mathrm{OS}$$

$$[\mathrm{HPA}]_{red} + (x/4)\cdot\mathrm{O} \longleftrightarrow [\mathrm{HPA}]_{ox} + (x/2)\cdot\mathrm{H_2O}$$

Where $[\mathrm{HPA}]_{ox}$, and $[\mathrm{HPA}]_{red}$ are the oxidized and reduced forms of a heteropoly anions, respectively. The S is substrate, and the OS is oxidized substrate. For example, such catalysts can be used to form carboxylic acids from the corresponding aldehydes, and to form C=C and C=O bonds from the dehydrogenation of alcohols, aldehydes, and carboxylic acids. The photocatalytic action of the heteropoly compounds has been demonstrated for the oxidation of a variety of organic compounds[19 and 22]. It has been shown that heteropoly compounds undergo multielectron photoreduction in the near-visible and ultraviolet region with concomitant oxidation of the organic compound[24].

Heterogeneous catalytic oxidation processes have been involved in the commercial vapor-phase oxidation of methacrolein to methacrylic acid[67] and methane oxidation[68]. Currently, researchers are developing the synthesis of new bifunctional catalysts from heteropoly compounds[69].

The homogeneous oxidative catalytic activity was studied by Russian workers for mixed metal polyanions $[PV_xMo_{12-x}O_{40}]^{n-}$ with palladium (Pd^{2+}) salts[70 and 71]. Recently, heteropoly compounds have been used in the sensitization of semiconductor[72] and sensitization of electrodes[73]. Hill and his co-worker studied oxygen transfer to alkanes in homogeneous catalytic oxidation[22].

I-8. Purpose of the Research

The goals of this research were to investigate the reactivity of one kind of heteropoly anion, $[SiW_{12}O_{40}]^{4-}$, upon changing the substrate and acid content. Various alcohols and related compounds were to be investigated in order to determine the range of compounds which could be oxidized. Also the effects of substrate concentration and relative acidity were to be studied.

Initial attempts to preform these studies using a simple spectrophotometer indicated that more precise data were necessary. Hence this paper is generally divided into three areas: (a) results for the absorbance of the heteropoly compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$ at several concentrations with isopropyl alcohol and acid at several concentrations using both a Bausch and Lomb Spectronic 20 photometer and a GCA McPherson ultraviolet-visible spectrophotometer, (b) results for the photooxidation of organic and biochemical substrates with the heteropoly compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$, and (c) a proposed reactive functional group of the alcohols and amine, and a proposed mechanism for the photocatalyzed oxidation of alcohol by the heteropoly anion, $[SiW_1O_{40}]^{4-}$.

CHAPTER II. EXPERIMENTAL

II-1. Equipment

II-1-1. Photochemical Reactor

A microscale, immersion well photochemical reactor from ACE Glass, model 7880 reaction assembly, was used. The photochemical reactor was designed in 1989 by John H. Penn and Richard D. Orr[74]. The photochemical reactor is shown in Figure 6, and is designed for carrying out reactions on a small scale such as volumes of 5-15 mL. The photochemical reactor consists of an immersion well that has a water jacket and O-ring cap seal, and of an outer jacket that has a glass frit disc and side arm. The immersion well is constructed from quartz with an inside diameter of 11 mm inside the water jacket. The immersion well is placed in a water-cooled jacket to minimize thermal effects on the reaction. The effects of temperature on a photochemical reaction can easily be studied. The ultraviolet lamp used was a Pen-Ray, UVP Model 11-SC-1 mercury lamp with a SCT-1 power supply. The mercury lamp was made of double bore quartz and placed inside the immersion well. The outer body of the reactor was fabricated of borosilicate glass. A glass frit (glass filter disc) of 4-8μm porosity provides a gas inlet for the reaction vessel. This frit (filter disc) also allows the introduction of an inlet gas to remove oxygen from the solution and the agitation (mixing) of the small solution volume. The small porosity size creates a large number of small bubbles which enhances the rate of equilibration. This is necessary to ensure a uniform irradiation of the reaction solution in a shorter time. Further usage of the glass frit is for collection of solid products which precipitate from solution. An O-ring cap for sealing the immersion well to the outer jacket allows for maximum flexibility of solution volumes. The solution volumes are adjusted simply by changing the depth of the immersion well. In this experiment, the total volume was kept at 10 mL.

II-1-2. Bausch and Lomb Spectronic 20 Photometer

The Bausch and Lomb Spectronic 20 photometer measures the intensity of visible light after passage through a sample. A small replica grating provides the dispersion and, in conjunction with fixed slits, provides a band pass of 20 mμ[75]. The Spectronic 20 photometer has a monochromatic source of light vibrating at a single frequency. The Spectronic 20 photometer must be adjusted to zero the meter each time a reading is made. Distilled water was used as a solvent blank. It was necessary to rezero the meter using distilled water in order to obtain more precise absorbance data because of fluctuations in the electronic components. The cover of the instrument always was closed to exclude stray light.

II-1-3. GCA McPherson Ultraviolet-visible Spectrophotometer

The ultraviolet (UV) and visible spectra were obtained using a GCA McPherson spectrophotometer, model EU-707-11, with an IBM computer and monitor. The instrumental parameters used are listed Table II. The source of radiation used depended on the region of the spectrum. In the visible and near infrared (IR) regions, the source was a tungsten bulb which emits continuous radiation between 2500 and 350 nm[76]. In the ultraviolet region, a high pressure deuterium gas discharge lamp was used as the source. This source emits continuous radiation from 380 to 180 nm[76].

II-1-4. Operation of the GCA McPherson Ultraviolet-visible Spectrophotometer

The GCA McPherson ultraviolet-visible spectrophotometer was allowed to warm up for 30 minutes and stabilize prior to use. Baseline spectra of the instrument were obtained using distilled water in both sample cell and reference cell. Distilled water was used in the reference cell when the spectra of the heteropoly solutions were collected. The sample cells were rinsed several times with distilled water before use. Then, the sample cell was rinsed with and filled with the heteropoly solution. Care was taken to remove air bubbles. In these experiments, the light source was adjusted to the tungsten lamp to collect the spectra in the visible region. The computer automatically collected absorbance data of mixtures, heteropoly compound, isopropyl alcohol, acid, and distilled water, onto a floppy disk. Then, a Quattro Pro spreadsheet program was used to import the absorbance data from the diskette to make the graphs. Before a graph was plotted, the absorbance of the reference water was subtracted from the measured absorbance of the sample. This corrected for a slightly slopping baseline.

II-1-5. Cells of the GCA McPherson Ultraviolet-visible Spectrophotometer

Quartz ultraviolet-visible spectrophotometer cells were used to obtain all spectra. The path length of the cells is 1.00 cm.

II-1-6. Balance

Masses of the heteropoly compounds and solid chemicals were determined using a Sartorius GMBH, type 1207 MP2, analytical balance. The sensitivity of the balance is given as 1×10^{-4} g.

II-1-7. Glassware and Other Apparatus

Volumetric and graduated pipettes of 2.0 mL, 3.0 mL, and 5.0 mL were used and were obtained from Pyrex, Alpha, Kimax and Fisher, respectively. Test tubes and volumetric flasks purchased from Kimax and Pyrex were used. Also a plastic spatula was used to measure the heteropoly compound and solid chemicals; this was necessary to prevent reduction of the heteropoly by reaction with the metal of the spatula. Other standard general laboratory apparatus and glassware were used as needed.

II-2. Chemicals

Except for the reagents listed below either ACS grade or reagent grade chemicals were used. Various vendors were used. These were Fisher, Matheson Coleman and Bell, J. T. Baker, Mallinckrodt, Eastman, Aldrich, Sigma, and JWH. Technical grade sodium silicate solution from Fisher was used in the preparation of the 12-tungstosilicate anion. Commercial sugar (sucrose) was used in some photocatalysis experiments.

II-3. Conditions in the Laboratory

During these studies, the mixtures were at ambient laboratory temperature and pressure. These were generally between 19 and 25 degree of Celsius and 740 to 780 mm Hg pressure.

II-4. Preparation of the Heteropoly Compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$

For the preparation of the heteropoly compound, potassium 1:12 alpha-dodeca-tungstosilicate 17 hydrate, $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O$ (molecular weight : 3337), the literature rocedure of Ginsberg[77] was used. The overall chemical quation for the preparation is:

$$12[WO_4]^{2-} + [SiO_3]^{2-} + 22H_3O^+ + 4K^+ \text{ -----> } K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 17H_2O(s) + 16H_2O$$

The salt was precipitated from solution at pH 2 and room temperature. The potassium 1:12 alpha-12-tungstosilicate 17 hydrate is a white solid which is soluble in water and is stable as polyanion below pH 4.5. This ion can be characterized by polarography of the fresh solution in 1 *M* sodium acetate. The polarogram should have two one-electron and one two-electron waves at -0.24, -0.48, and -0.95 V respectively versus the saturated calomel electrode (SCE). The ultraviolet spectrum in aqueous solution shows a maximum of molar absorptivity (ϵ^{max}_{258}) of 47,000 and minimum of molar absorptivity (ϵ^{min}_{232}) of 19,200[77]. The polarogram was not determine in the current work.

CHAPTER III. RESULTS

This section is divided into three kinds of results. These are: (a) the use of a Bausch and Lomb Spectronic 20 spectrophotometer to measure the absorbance for several concentrations of heteropoly compound at several concentrations of isopropyl alcohol, (b) the use of a GCA McPherson ultraviolet-visible spectrophotometer to measure absorption spectra for several concentrations of heteropoly compound at several concentrations of isopropyl and acid, and (c) the photooxidation of organic and biochemical substrates by the heteropoly compound.

III-1. Using a Bausch and Lomb Spectronic 20 Photometer for Absorbance Measurements of Several Concentrations of Heteropoly Compound at Several Concentrations of Isopropyl Alcohol and 1.00 x 10^{-3} M Acid

Mixtures of various concentrations of heteropoly compound and isopropyl alcohol, and 1.00 x 10^{-3} M sulfuric acid were prepared as given in Table III. When the sample is blanketed with nitrogen gas rather than exposed air, the absorbance increases (see Figures 7 and 12). For samples 2, 3 and 6 (see Figure 8) the highest absorbance was shifted a little towards shorter wavelengths as the concentrations of heteropoly compound were increased. Sample 5 exhibited its highest absorbance around 750 nm (see Figure 9). The result is similar to sample 3 (see Figure 8). When the irradiation time was 25 minutes, the highest absorbance appeared around 800 nm (see Figure 10). Several concentrations of isopropyl alcohol, 4.70×10^{-3} M and 2.35×10^{-3} M, with 1.99×10^{-6} M heteropoly after 60 and 25 minutes of irradiation are shown in Figure 11. Absorbance of the less concentrated isopropyl alcohol and the longer irradiation time has a greater peak height than that of the more concentrated isopropyl alcohol and the shorter irradiation time for samples 1, 2, and 4 (see Figure 12). The absorbance of the less concentrated isopropyl alcohol deaerated with nitrogen gas has a greater peak height than that of the more concentrated isopropyl alcohol exposed to air.

III-2. Using a GCA McPherson Ultraviolet-visible Spectrophotometer for Measuring Absorption Spectra of Several Concentrations of Heteropoly Compound at Several Concentrations of Isopropyl Alcohol and of Acid

The concentrations of mixtures of heteropoly compound, isopropyl alcohol, acid and distilled water ranged from 9.17×10^{-6} M to 1.81×10^{-5} M heteropoly compound, from 1.18×10^{-3} M to 7.05×10^{-3} M isopropyl alcohol, and from 1.00×10^{-3} M to 6.00×10^{-3} M acid. The concentrations for the ten samples (sample numbers from 8 to 17) are given in Table IV. A reference sample was scanned using distilled water versus distilled water (see Figure 13). Before irradiation, the mixture of 1.81 x 10^{-5} M heteropoly compound, 4.70 x 10^{-3} M isopropyl alcohol, 1.00 x 10^{-3} M acid, and distilled water was colorless (see Figure 14). The highest absorbance is around 830 nm. This mixture appeared colorless to the eye. The absorbance spectrum of the solution before irradiation is small compared with the spectrum after irradiation. The absorbance spectra of samples 8, 9, 10, and 11 after irradiation for 30 minutes are given in Figure 15. This mixture appeared blue after irradiation. Usually the blue color changed slowly after 20 minutes. Below 800 nm, the more concentrated acid usually resulted in a lower absorbance. When the irradiated blue solutions are left on the table exposed to air, changes occur. The solution slowly changes to colorless from blue. This colorless solution was scanned again with the spectrophotometer (see Figure 16). A small decrease in the absorbance spectrum is observed for each concentration of acid as compared to Figure 15. Note that sample 10 (2.00 x 10^{-3} M acid) has the lowest absorbance among the samples. Therefore, concentration of acid influences the absorbance of the blue solutions (see Figure 15). The data for various concentrations of isopropyl alcohol for samples 8, 12, 13, and 14 ranging from 7.05 x 10^{-3} M to 1.18 x 10^{-3} M are given in Figures 17 and 18. Results similar to sample 10 were tained. The blue solutions are shown in Figure 17 and the lorless solutions after exposure to the air are shown in igure 18. Except for sample 12, the absorbance increases etween 600 nm and 775 nm as the concentration of alcohol ecreases. A maximum in the absorbance appeared around 675 nm or sample 13 (1.18×10^{-3} M isopropyl alcohol) in Figure 17. he absorbance of the lower concentration of isopropyl alcohol (sample 13) is shifted from around 650 nm to around 730 nm (see Figure 18). From these results (see Figures 17 and 18), except sample 13, there are no absorbance maxima exhibited in the visible region. For samples 8, 15, 16, and 17 (see Figures 19 and 20) higher concentrations of heteropoly compound, except sample 15, have higher absorbances in the visible region. These results are very similar to the results of the samples 8, 9, 10, and 11 (see Figures 15 and 16).

III-3. Photooxidation of Organic and Biochemical Substrates by Heteropoly Compound

A mixture of alcohol, heteropoly compound, and acid was irradiated in the reactor until the color was judged to have become blue. When isopropyl alcohol was used, three minutes were required for the blue color. Replacing the isopropyl alcohol with methyl alcohol resulted in a color change after 4 minutes. Ethyl alcohol required 3 minutes; *n*-propyl and *iso*-pentyl alcohols each required 2 minutes. The *n*-propyl alcohol was darker blue than the *iso*-pentyl alcohol. Two cohols, *n*-octyl and *n*-octadecyl, were not miscible with the teropoly / acid mixture and were still colorless after 15 inutes.

Four secondary alcohols were studied. Each of these econdary alcohols turned blue within 5 minutes. Tertiary utyl alcohol did not react or only slightly reacted after 22 inutes. These data are summarized in Table V. Also included in the table are data for two dicarboxylic acids and diethylamine. The amine turned blue within 4 minutes. The carboxylic acids did not react or turn color. Irradiation was stopped after 20 minutes.

The results of the of the biochemical substrates with the heteropoly compound ($K_4[SiW_{12}O_{40}]\cdot17H_2O$), acid, and distilled water are given in Table VI. Five of the six amino acids tested turned light blue between 15 and 23 minutes. Glycine did not turn color after irradiation for 20 minutes. The reaction of the amino acids is very slow compared with the alcohols and amine. Four carbohydrates were tested. Between the monosaccharides and the disaccharides, the disaccharides resulted in more color intensity than the monosaccharides. The reaction time of the glucose, which is a monosaccharide, is shorter than that of the disaccharides. Fructose required a very long time for reaction, 28 minutes.

CHAPTER IV. DISCUSSION

This discussion chapter is divided into three parts : (a) interpretations of the results for the absorbance of the heteropoly compound, $K_4[SiW_{12}O_{40}] \cdot 17H_2O$, with several concentrations of the isopropyl alcohol and of the acid using both a Bausch and Lomb Spectronic 20 photometer and a GCA McPherson ultraviolet-visible spectrophotometer; (b) interpretations of the results of the photooxidation of organic and biochemical substrates with the heteropoly compound $K_4[SiW_{12}O_{40}] \cdot 17H_2O$; and (c) a proposed reactive functional group and a proposed reaction mechanism for the photooxidation of organic and biochemical substrates with the heteropoly anion $[SiW_{12}O_{40}]^{4-}$. The emphasis in this chapter is mainly on sections (b) and (c).

IV-1. Interpretations of the Absorbance Results

IV-1-1. The Heteropoly Compound at Several Concentrations with Several Concentrations of Isopropyl Alcohol and 1.00 x 10^{-3} M Acid Using a Bausch and Lomb Spectronic 20 Photometer

The effect of air on the reaction is apparent from the results of samples 1 and 2. The nitrogen gas blanketed sample has a higher absorbance. One explanation is that the absorbance is caused by the reduced-substrate complex, and that the nitrogen gas excludes oxygen gas. The oxygen gas reoxidizes some of the reduced complex in the mixture. Hence the absorbance of the unblanketed mixture is less than the blanketed mixture.

Higher concentrations of the heteropoly compound have only a small effect on the absorbance (see Figures 8 and 9). The peak maxima of the reduced heteropoly compound also is dependent on the concentrations of the heteropoly compound. For example, sample 3 has a higher absorbance than sample 6 (see Figure 8). The peak maxima shifted to around 750 nm from around 800 nm (see Figures 8 and 9). One of the principal reasons for this shift is that the irradiation time influences the number of electrons gained by the heteropoly which changes the absorption spectrum[4]. Normally the longer irradiation time causes a longer wavelength at absorbance maximum.

Increasing the concentration of isopropyl alcohol decreases the position of the absorbance maximum (see Figures 11 and 12). The highest absorbance peak of the reduced heteropoly compound exists as a broad band between 700 nm and 800 nm. These results are not exactly the same as the literature[4 and 78]. These authors however have not differentiated among the various heteropoly anions. Perhaps this is due to the fact that PW_{12} and SiW_{12} have slightly different spectra.

From the literature[4 and 78], the spectra of the non-reduced heteropoly compounds of both tungstates and molybdates are characterized by oxygen-to-metal charge transfer bands in the near visible and ultraviolet regions and no absorption in the visible region. All metals are W^{6+} or Mo^{6+} with d^0 configuration. The blue reduction products have a broad peak around 700 nm according to these authors.

These bands around 700 nm and 800 nm are attributed to metal to metal charge transfer ($M^{5+} \dashrightarrow M^{6+}$, here M is addenda atom, W or Mo.) which is responsible for the blue color of the compound, and to *d-d* transitions of the d^1 metal ions. The reduced heteropoly compounds are not photosensitive at wavelengths greater than 500 nm in the presence of organic additives; therefore, the above absorption bands around 700 nm are not responsible for the photochemistry.

IV-1-2. The Heteropoly Compound at Several Concentrations with Several Concentrations of Isopropyl Alcohol and of Acid Using a GCA McPherson Ultraviolet-visible Spectrophotometer

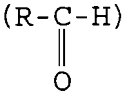
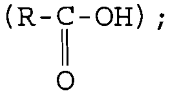
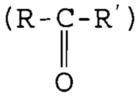
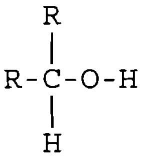
The ultraviolet absorbance spectra of the non-reduced forms of the heteropoly compound show very minor changes upon addition of the alcohols (see Figure 14). From this one can conclude that the change of the ultraviolet absorbance spectra of the heteropoly compound depends on the ultraviolet light used in the reactor. The position of the peak absorbance maxima for the reduced heteropoly compound generally decreases at higher concentrations of the acid (see Figure 15), lower concentrations of the heteropoly compound (see Figure 19), and higher concentrations of the isopropyl alcohol (see Figure 17). These results are similar to those obtained using the Spectronic 20 photometer.

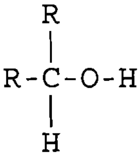
The absorbance of the blue solutions decreases and becomes almost colorless upon standing. The spectra obtained by the GCA McPherson ultraviolet-visible spectrophotometer (see Figures 16, 18 and 20) show decreased absorbances compared with the absorbance maxima of the blue solutions. The reason is that the heteropoly compound probably is oxidized by air in the mixture. These results are similar to the previous results with the Spectronic 20 photometer.

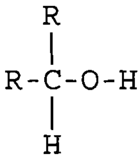
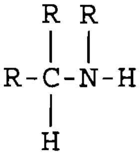
Comparing the absorbance between literature[4, 46, and 56] and the experimental data, the absorbance peak for photooxidation of the heteropoly compound with isopropyl alcohol indicates a two-electron blue. Pope and Varga[46 and 56] determined the number of electrons accepted by five types, reduced forms of Keggin structures. In the reduced forms of five *iso*-structural polytungstates (the heteropoly anions, $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[Fe^{III}W_{12}O_{40}]^{5-}$, $[Co^{II}W_{12}O_{40}]^{6-}$, and the *iso*-polymetatungstate anion, $[H_2W_{12}O_{40}]^{6-}$) have accepted two electrons without decomposition. These conclusions were determined by polarography and potentiometric titrations[46].

IV-2. Interpretations of the Results for the Photooxidation

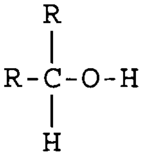
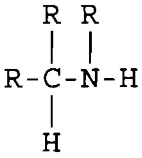
IV-2-1. Organic Substrates with the Heteropoly Compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$

Primary alcohols having a chain structure and secondary alcohols including linear and ring structures react rapidly (within 5 minutes) with the heteropoly compound (see Table V). The heteropoly compounds are photosensitive in near visible and ultraviolet regions of the spectrum in the presence of organic substrates[4, 9 and 19]. Primary alcohols are converted to aldehydes  $(R\text{-}\underset{\underset{O}{\|}}{C}\text{-}H)$ or carboxylic acids  $(R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH)$; whereas, secondary alcohols form ketones  $(R\text{-}\underset{\underset{O}{\|}}{C}\text{-}R')$ after photooxidation with heteropoly compounds in aqueous solution[19, 78 and 79]. Between primary and secondary alcohols, primary alcohols have a higher color intensity than secondary alcohols; however, the reaction time of secondary alcohols with the heteropoly compound is a little faster than that of primary alcohols. The reason is the stability of carbocations. That is tertiary > secondary > primary > methyl[80]. Both primary and secondary alcohols contain the bonding arrangement of  $R\text{-}\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}\text{-}O\text{-}H$ at the reactive site which reduces the heteropoly compound. Even though *n*-octyl and *n*-octadecyl alcohols are primary alcohols, they do not react via photooxidation with the heteropoly compound. The noneactivity is probably because they are immiscible in water.

The structures of the organic substrates used are given n Figure 21. Note that the tertiary alcohol does not react ith the heteropoly compound. The reason is that tertiary alcohols do not contain a  $\mathrm{R-\underset{H}{\overset{R}{C}}-O-H}$ bonding arrangement at the reactive site in the photooxidation of the heteropoly compound even though the tertiary carbocation is very stable[80]. If a tertiary alcohol does react with the heteropoly compound, the reaction time of the tertiary alcohol with the heteropoly compound is very long, and a very light color intensity is produced (see Table V). The color produced may be due to an impurity in the alcohol.

Carboxylic acids do not react photochemically with the heteropoly compound because the carbon atom of the carboxylic acid can not be further oxidized[80] and the structure of carboxylic acids does not contain a  $\mathrm{R-\underset{H}{\overset{R}{C}}-O-H}$ bond grouping. However the amine does react to photoreduce the heteropoly compound. The amine contains a reactive site and photoreduces the heteropoly compound[17]. The bond between nitrogen and hydrogen of amine is the reactive site of photooxidation with the heteropoly compound. The structure of the amine also ontains a  $R-\underset{H}{\overset{R}{C}}-\overset{R}{N}-H$ bond grouping. In order for the photo-

xidation of alcohols and amine with the heteropoly compound o occur in aqueous solution, the alcohols and amine should

ontains either  $R-\underset{H}{\overset{R}{C}}-O-H$ or  $R-\underset{H}{\overset{R}{C}}-\overset{R}{N}-H$ bond arrangement. The

proposed reactive functional group of alcohols and amine with the heteropoly compound will be discussed in section **IV-3-1**.

IV-2-2. Biochemical Substrates with the Heteropoly Compound, $K_4[SiW_{12}O_{40}]\cdot17H_2O$

The amino acids, except glycine, slowly react to photoreduce the heteropoly compound. The color produced by the amino acids is light blue (see Table VI). One reason for this reactivity is that the carboxylate ion, COO^-, acts via an inductive effect, donating electron density through the sigma bonds of the molecule to destabilize the carbocation intermediate[80]. A second reason is the stability of carbocation as mentioned in the previous section **IV-2-1**. A third reason is that photoreduction of the heteropoly compound with amino acids may be dependent on the R group. The structures of the amino acids used (given in Figure 22) contained a R group other than hydrogen atom. However glycine has a single hydrogen atom as the R group. The hydrogen atom the glycine is too small to influence the high degree of olarity of the α-amino and α-carboxyl groups in aqueous olution[81]. Therefore glycine does not photoreduce the eteropoly compound.

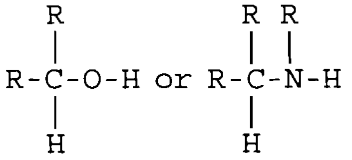
Monosaccharides are called simple sugars and are classified according to the chemical nature of their carbonyl group and the number of their carbon atoms[82]. If the carbonyl group is an aldehyde, as in glucose, the sugar is an aldose. If the carbonyl group is a ketone, as in fructose, the sugar is a ketose. Cyclic and linear forms of aldoses and ketoses interconvert readily. So these sugars undergo reactions typical of aldehydes and ketones. Mild oxidation of an aldose, either chemically or enzymatically, results in the conversion of its aldehyde group to a carboxylic acid function thereby yielding an aldonic acid[81 and 82]. Glucose and fructose have the same molecular weight (180.16) and formula ($C_6H_{12}O_6$); however, the structures are different. The structure of glucose has a six membered ring that is called a pyranose because it can be considered as a derivative of the heterocyclic compound pyran. The structure of fructose is a five membered ring that is called furanose because it can be considered as a derivative of the heterocyclic compound furan[82]. The linear forms and the Haworth projections of glucose and fructose are shown in Figure 23[83]. Usually five membered rings are less stable than six membered rings because the five membered rings have more strain than the six membered rings[81]. Different rates of reaction for monosaccharides may be due to the different values of the torsional deformation energies. Values of these energies were calculated using an Alchemy II program which yield numbers in kcal/mol. Fructose has higher values of torsional deformation energy than glucose. Glucose has 0.5 kcal/mole of torsional deformation energy; whereas, fructose has 1.8 kcal/mole of torsional deformation energy. Therefore one would predict that fructose will have a longer reaction time and less intense color than glucose. This corresponds to the observed order of reaction rates. Glucose reacts faster in the photooxidation and produces greater color intensity than fructose.

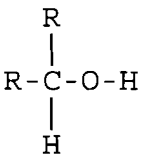
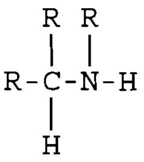
The disaccharides, sucrose and maltose, consist of two monosaccharides joined by a glycosidic linkage[81]. The structure of sucrose, commonly called cane sugar, is a disaccharides of glucose and fructose. Sucrose is linked as ß-D-fructofuranosyl-α-D-glucopyranoside (or glucose α(1,2)-ß-fructose)[81 and 82]. Maltose is formed as an intermediate product of the action of amylases on starch and contains two D-glucose residues. The structure of maltose is linked as 4-α-glucopyranosyl-D-glucose (or glucose α(1,4)-glucose)[81 and 82]. Sucrose and maltose have the same molecular weight (342.30) and formula ($C_{12}H_{22}O_{11}$); whereas, the structures are different. The Haworth structures of these disaccharides are shown in Figure 24[83]. The rate of reaction of sucrose is a ittle faster than that of maltose. The reason is that ucrose has 6.1 kcal/mol of torsional deformation energy; hereas, maltose has 7.1 kcal/mol of torsional deformation nergy as calculated using Alchemy II. So one could expect that sucrose will have a slightly shorter reaction time than maltose. This is the same reasoning as used with the monosaccharides. Note that the difference between the maltose and sucrose is smaller than between glucose and fructose. The rates of monosaccharides and disaccharides also show similar differences.

IV-3. Photooxidation of the Organic and Biochemical Substrates with the Heteropoly Anion, $[SiW_{12}O_{40}]^{4-}$

IV-3-1. Proposed Reactive Functional Group for the Reaction

The photosensitivity of the heteropoly anions with organic substrates and related compounds, especially alcohols and biochemical substrates, results in oxidation of the above substrates and reduction of the heteropoly anions. Primary and secondary alcohols and the amine react via photooxidation with the heteropoly anions. These alcohols and amines contained either $R\text{-}\overset{R}{\underset{H}{C}}\text{-}O\text{-}H$ or $R\text{-}\overset{R}{\underset{H}{C}}\text{-}\overset{R}{N}\text{-}H$ bond grouping. Therefore, in order to photooxidize organic and related compounds, the



reactive site  $\mathrm{R\text{-}\overset{R}{\underset{H}{C}}\text{-}O\text{-}H}$ or  $\mathrm{R\text{-}\overset{R}{\underset{H}{C}}\text{-}\overset{R}{N}\text{-}H}$ must be contained in the molecule[17]. The hydrogen atoms of the reactive site probably move to heteropoly anion in the oxidation reaction. A sketch of the proposed reactive functional group for photooxidation of alcohols and amine with the heteropoly anions, $[SiW_{12}O_{40}]^{4-}$, is shown in Figure 25. The oxidation reactions with heteropoly anions are oxidative dehydrogenation to produce aldehydes, carboxylic acids, ketones, nitriles from primary alcohols, secondary alcohols and amines[17]. A mechanism for the photocatalyzed oxidation of alcohol by the heteropoly compound is proposed in the next section.

IV-3-2. Proposed Mechanism for the Reaction

Photoexcited heteropoly anions react with alcohols mainly by hydrogen atom or electron transfer[4]. This results in reduction of the heteropoly anions and oxidation of alcohols through formation of radicals. The mechanism of hydrogen atom transfer is deduced from the alcohol. The mechanism of the photooxidation of alcohols with various heteropoly compounds has been studied previously[21, 22, 84 and 85]. The mechanism of photooxidation of an alcohol with heteropoly compounds has a step to from a preassociated complex. Therefore the mechanism proposed here for the photocatalyzed oxidation of alcohols by the heteropoly compound show that a primary alcohol forms an aldehyde or a carboxylic acid and secondary alcohol forms a ketone. This corresponds with literature[19, 78 and 85]. The proposed mechanism for photooxidation of a secondary alcohol upon irradiation in the presence of the 12-tungstosilicate anion, $[SiW_{12}O_{40}]^{4-}$, is shown in Figure 26. From the figure, the heteropoly anion and alcohol make preassociated complex before irradiation. This involves hydrogen bonding to the oxygens of the heteropoly anion. And then one of hydrogen atoms with its electron moves to one of the terminal oxygen atoms of the heteropoly substrate. Therefore the alcohol has become a radical after irradiation by photochemical reactor. At this time the blue color appears. The other hydrogen atom now immediately moves to another one of the terminal oxygen atoms of the heteropoly anion. The secondary alcohol rearranges to form the ketone in the mechanism. The heteropoly substrate having hydrogen atoms is converted back to the oxidized form of the heteropoly anion again by dehydrogenation or by oxygenation.

CHAPTER V. CONCLUSIONS

From the results of this research, several conclusions about the reaction of alcohols and related compounds with the heteropoly compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$ can be deduced. These conclusions are briefly stated in the following paragraphs.

1. The position of the absorbance maxima increases as the concentrations of the heteropoly compound is increased; as the concentrations of the isopropyl alcohol is decreased; as the irradiation time is increased, and upon deaerating the mixtures with nitrogen.

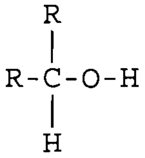
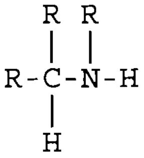
2. The rate of the photooxidation of the alcohols with the heteropoly compound is : Secondary ≥ Primary > Tertiary.

3. Amines can be photooxidized with the heteropoly compound. Also the rate of photooxidation of amines with the heteropoly compound is very similar to primary alcohols.

4. Amino acids containing R groups with an -OH or delocalizing groups are slowly photooxidized with the heteropoly compound. Glycine is an exception.

5. Carbohydrates (saccharides) that contain six membered rings are photooxidized with the heteropoly compound. The rate for the carbohydrates is : Glucose > Sucrose ≥ Maltose.

6. The proposed reactive functional group of the alcohols

and amines are either a  $R-\overset{R}{\underset{H}{C}}-O-H$ or a  $R-\overset{R}{\underset{H}{C}}-\overset{R}{N}-H$ moiety respectively in the molecule.

7. The proposed mechanism for the photocatalyzed oxidation of alcohols by the 12-tungstosilicate anion, $[SiW_{12}O_{40}]^{4-}$, is consistent with above.

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Appendix A

Figures

Figure 1

Keggin Structure (*Td*)
of a
1:12 Heteropoly Anion

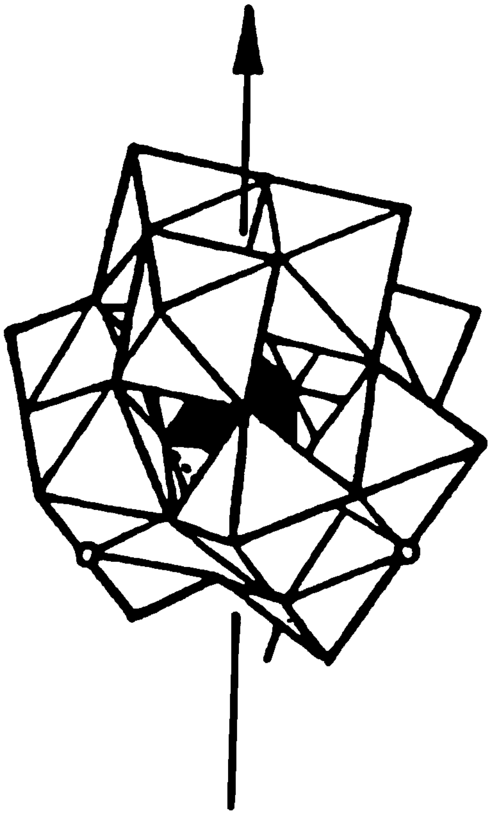


Figure 2

Dawson Structure
of a
2:18 Heteropoly Anion

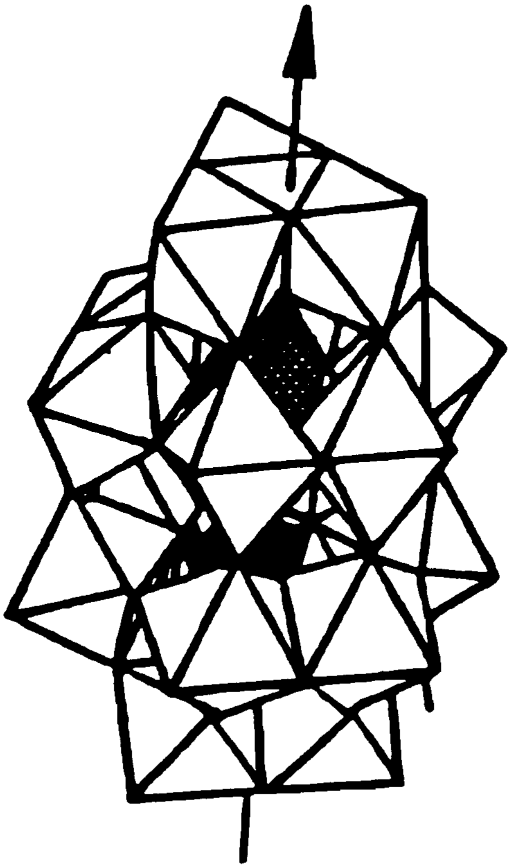


Figure 3

Anderson Structure
of a
1:6 Heteropoly Anion

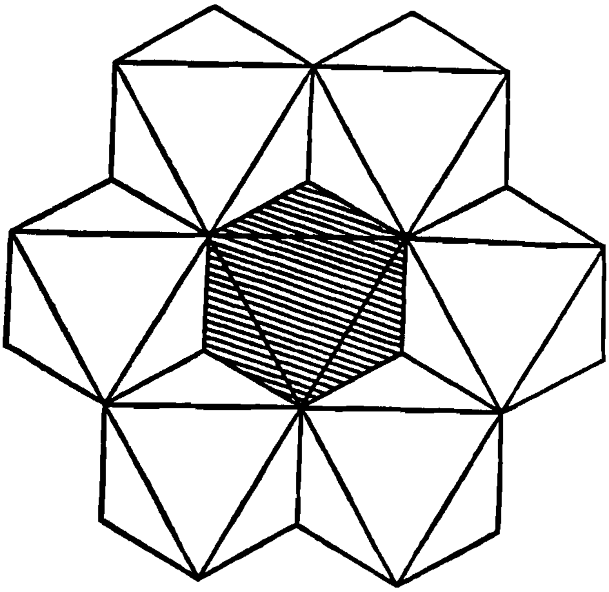


Figure 4

Waugh Structure
of a
1:9 Heteropoly Anion

(Left : an exploded view of the ion)
(Right : the oxygen framework of the ion)

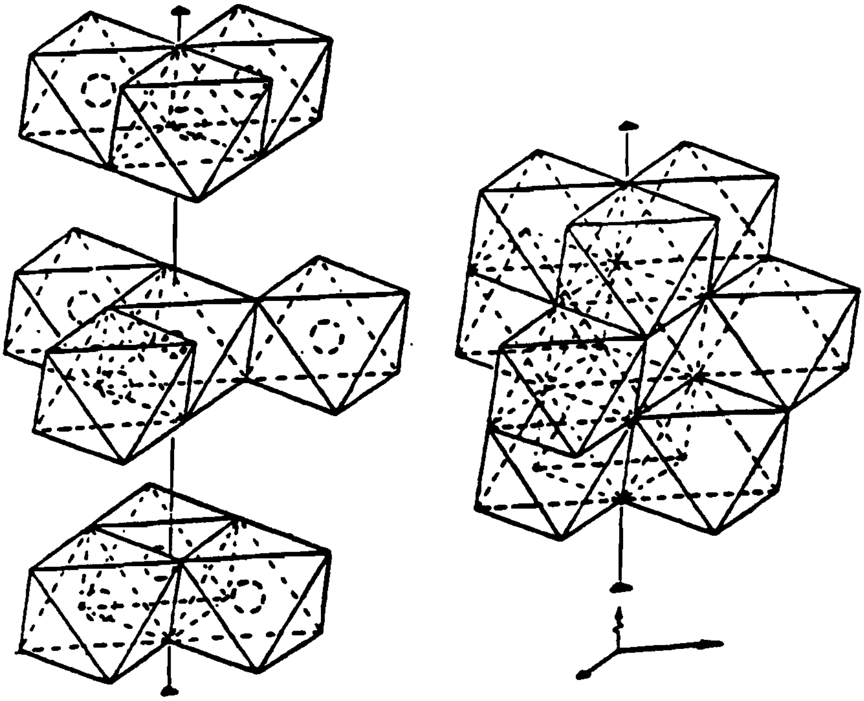


Figure 5

Silverton Structure
of an
Icosahedrally Coordinated
1:12 Heteropoly Anion

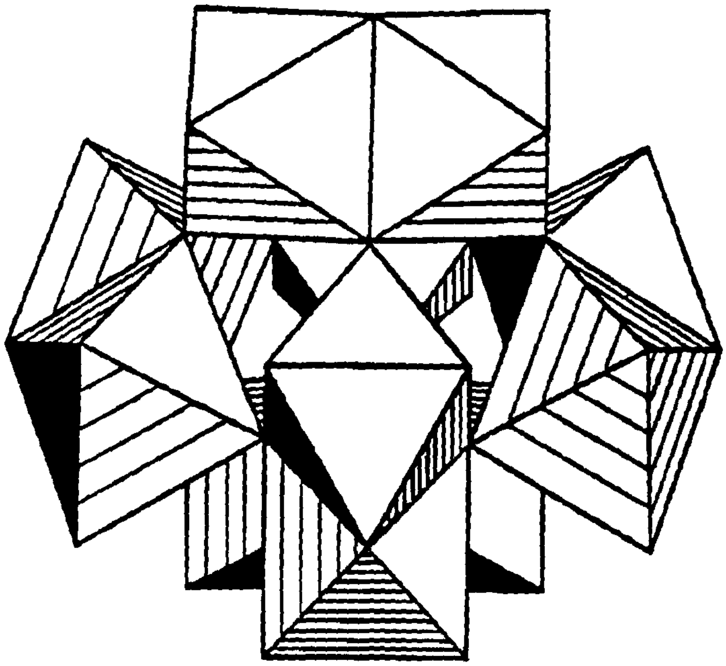


Figure 6

Immersion Well Photochemical Reactor

(ACE glass, Model 7880)

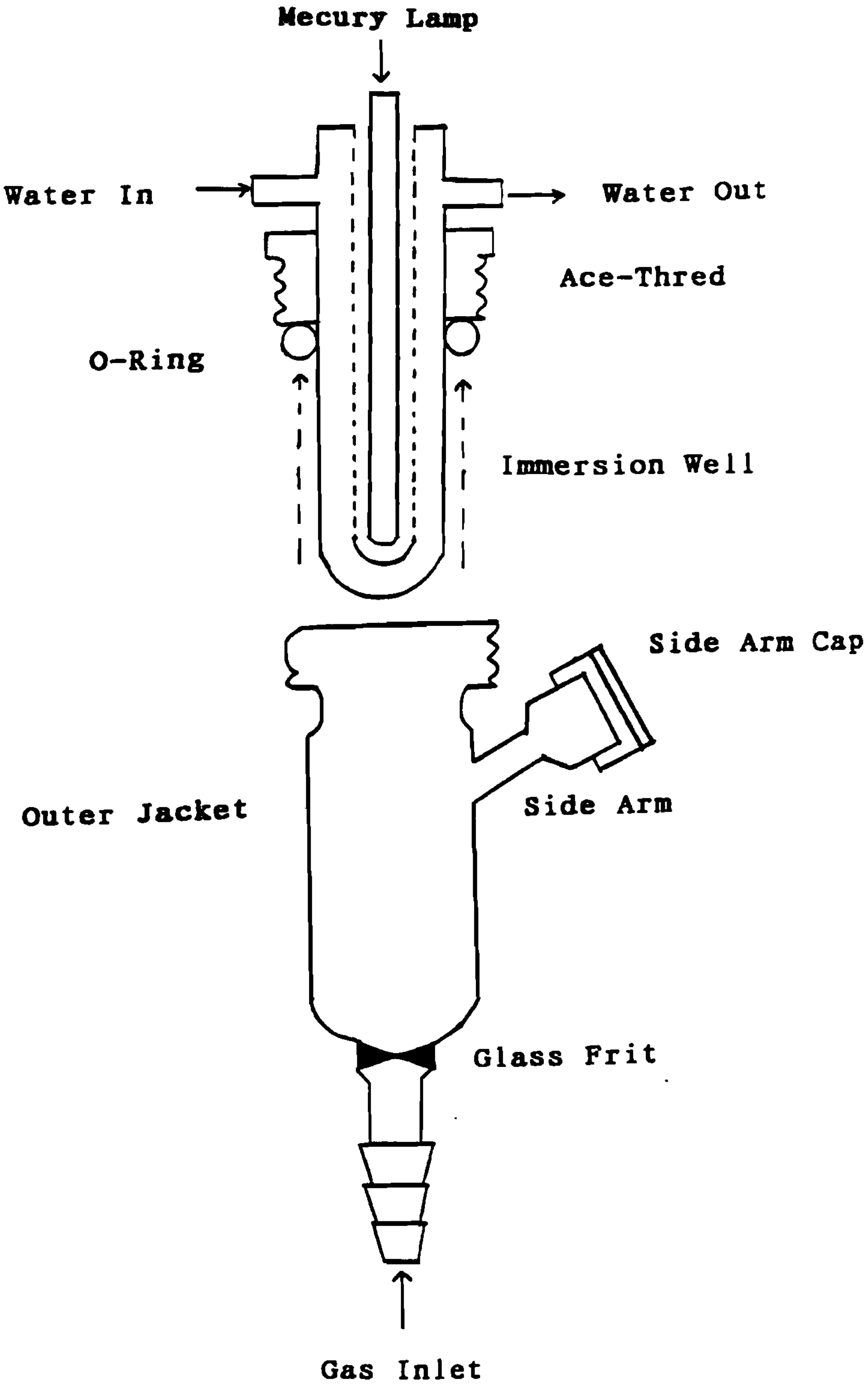

Mecury Lamp
Water In
Water Out
Ace-Thred
O-Ring
Immersion Well
Side Arm Cap
Outer Jacket
Side Arm
Glass Frit
Gas Inlet

Figure 7

Absorbance of
1.81×10^{-5} M Heteropoly Compound,
4.70×10^{-3} M Isopropyl Alcohol and
1.00×10^{-3} M Acid
after 60 minutes Irradiation
in Air Used with
the Bausch and Lomb Spectronic 20 Photometer

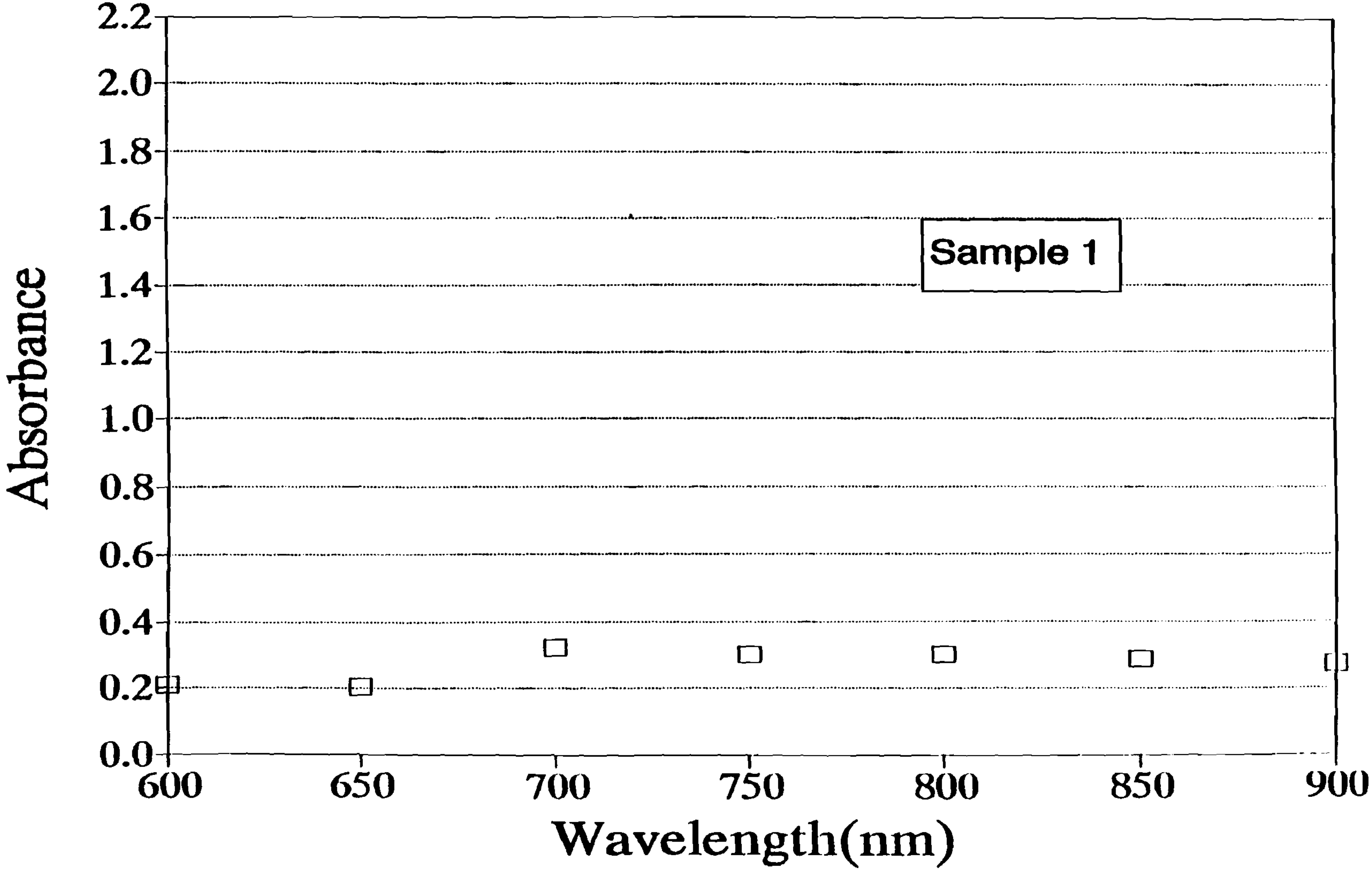

2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)
Sample 1

Figure 8

Absorbance of
1.81×10^{-5} M, 1.99×10^{-6} M, and
3.33×10^{-6} M Heteropoly Compound,
4.70×10^{-3} M Isopropyl Alcohol and
1.00×10^{-3} M Acid
after 60 minutes Irradiation
in Deaerated with Nitrogen Gas Used with
the Bausch and Lomb Spectronic 20 Photometer

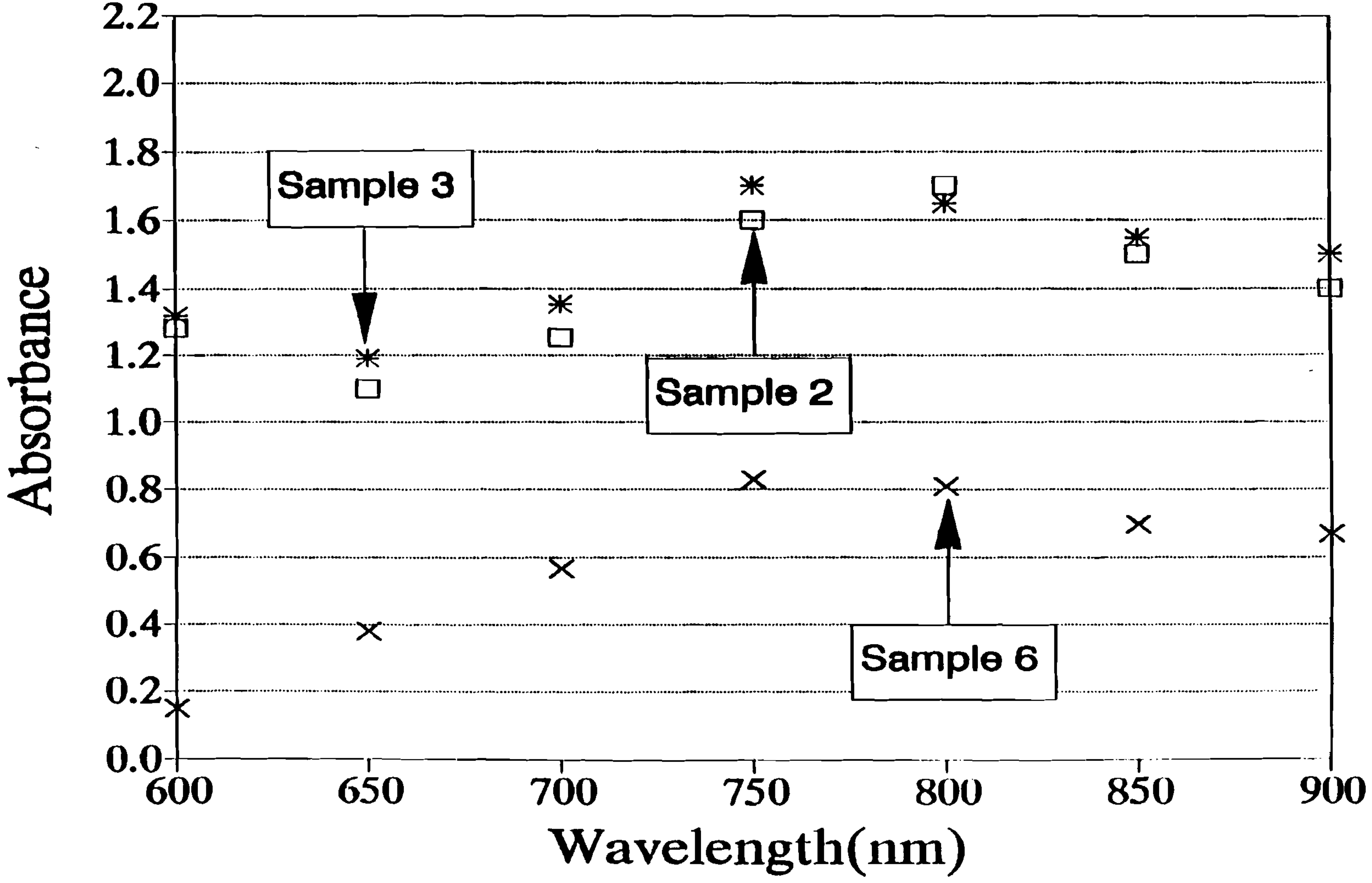

Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
600
650
700
750
800
850
900
Wavelength(nm)
Sample 3
Sample 2
Sample 6

Figure 9

Absorbance of
1.81 x 10^{-5} M, and 1.99 x 10^{-6} M Heteropoly Compound,
2.35 x 10^{-3} M Isopropyl Alcohol and
1.00 x 10^{-3} M Acid
after 60 minutes Irradiation
in Deaerated with Nitrogen Gas Used with
the Bausch and Lomb Spectronic 20 Photometer

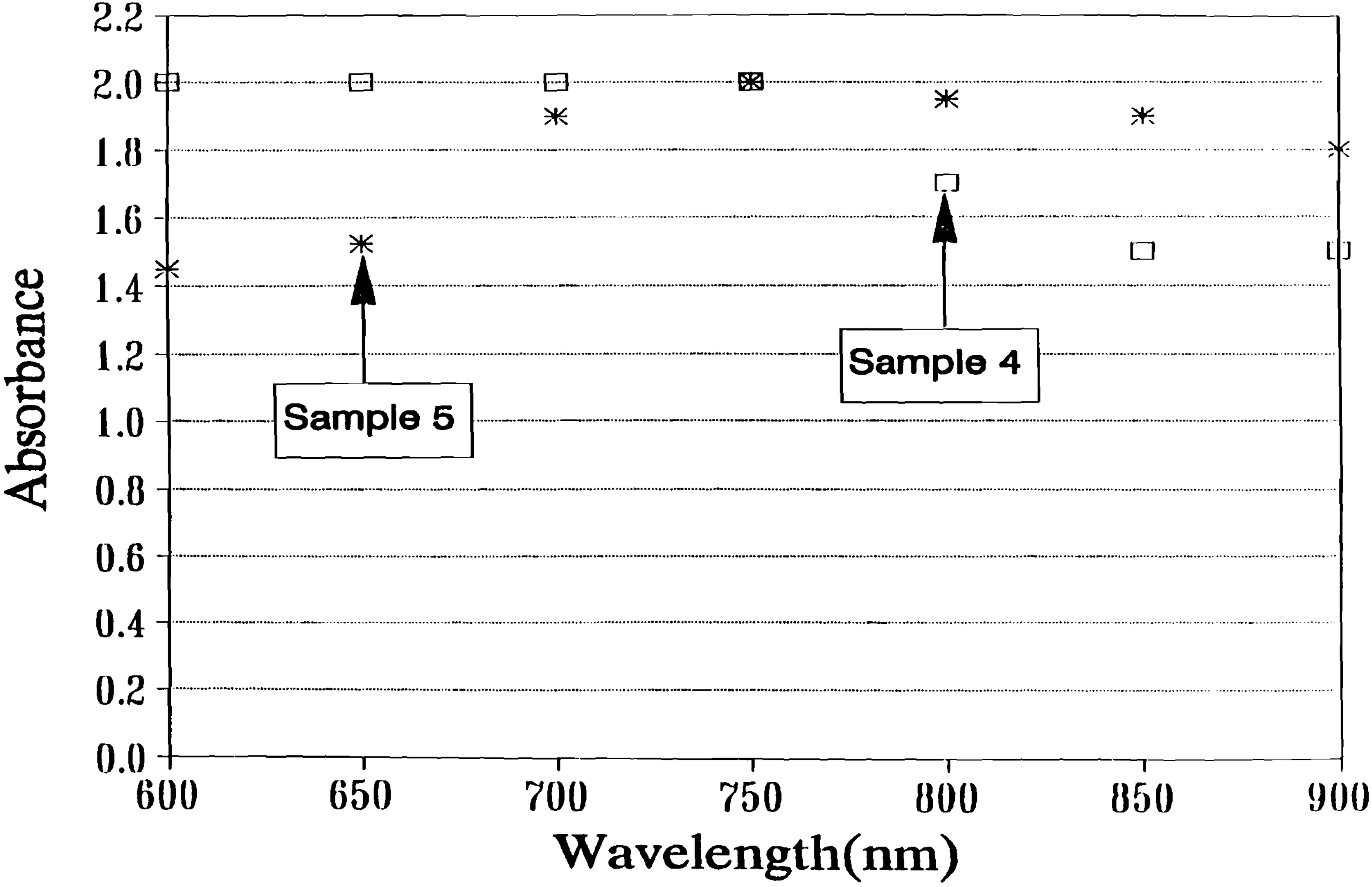

Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
600
650
700
750
800
850
900
Wavelength(nm)
Sample 5
Sample 4

Figure 10

Absorbance of
1.99 x 10^{-6} M Heteropoly Compound,
4.70 x 10^{-3} M Isopropyl Alcohol and
1.00 x 10^{-3} M Acid
after 25 minutes Irradiation
in Deaerated with Nitrogen Gas Used with
the Bausch and Lomb Spectronic 20 Photometer

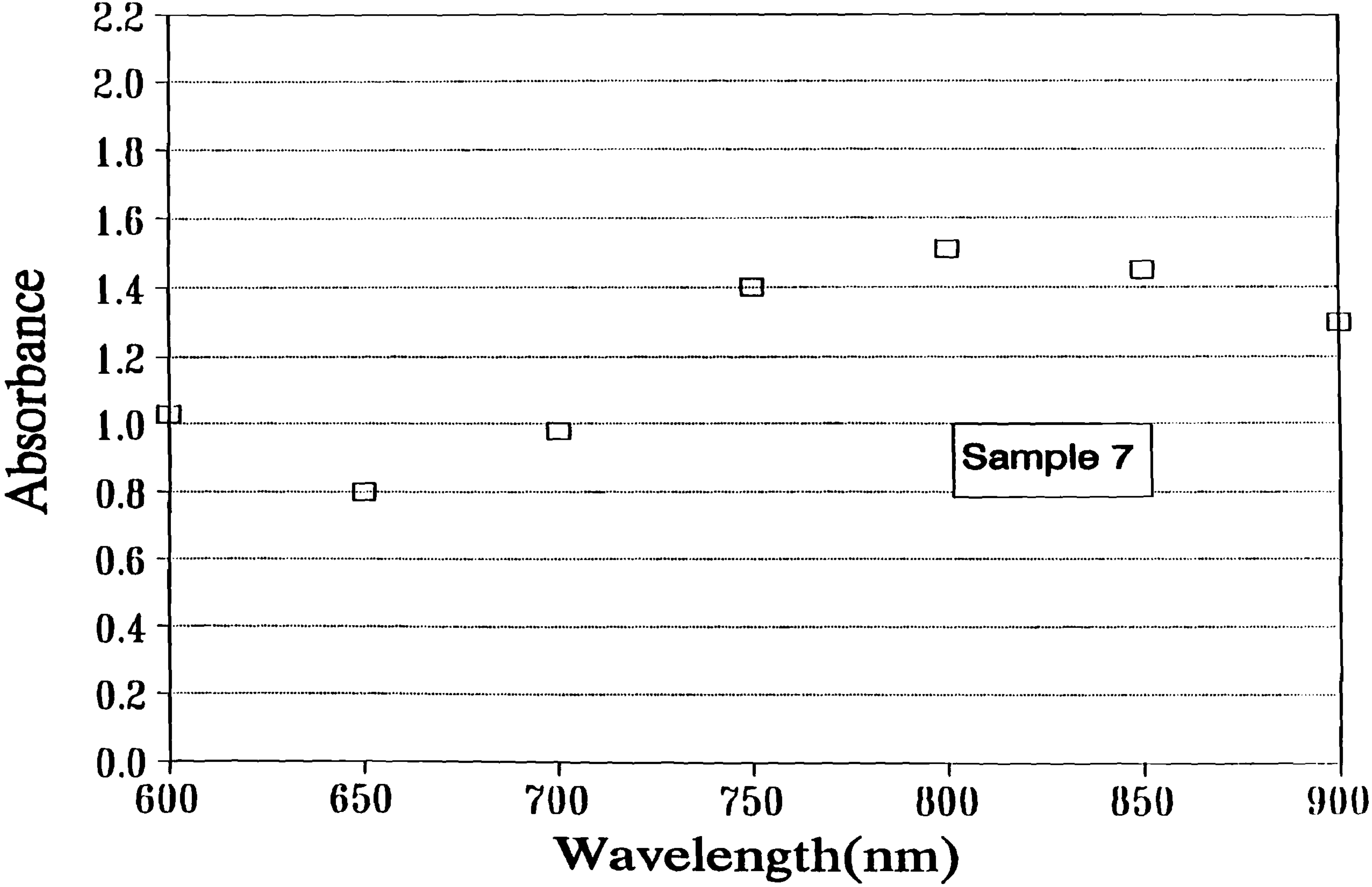

Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
600
650
700
750
800
850
900
Wavelength(nm)
Sample 7

Figure 11

Absorbance of
1.99 x 10^{-6} M Heteropoly Compound,
4.70 x 10^{-3} M, and 2.35 x 10^{-3} M Isopropyl Alcohol and
1.00 x 10^{-3} M Acid
after 60 and 25 minutes Irradiation,
Deaerated with Nitrogen Gas Used with
the Bausch and Lomb Spectronic 20 Photometer

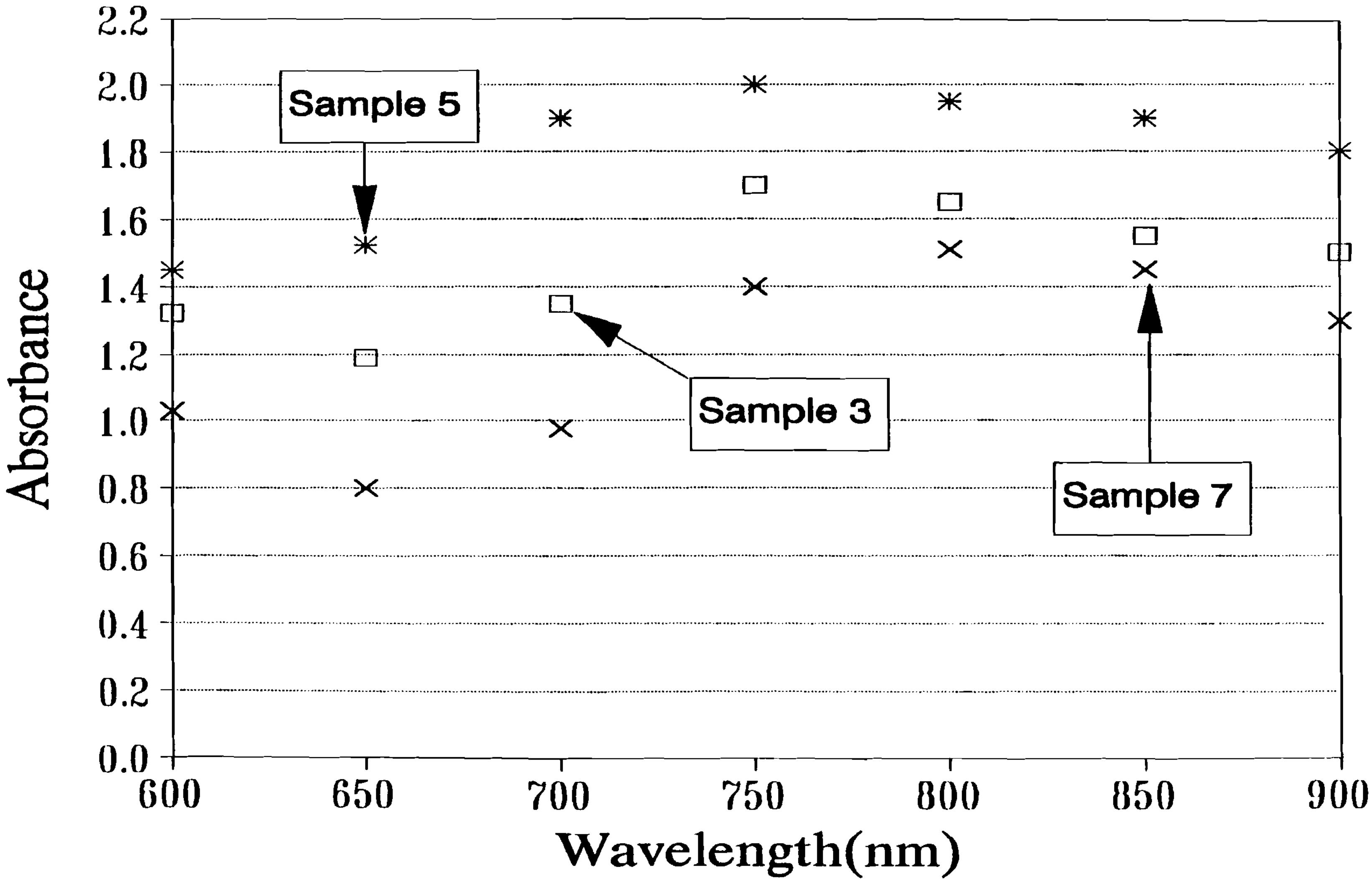
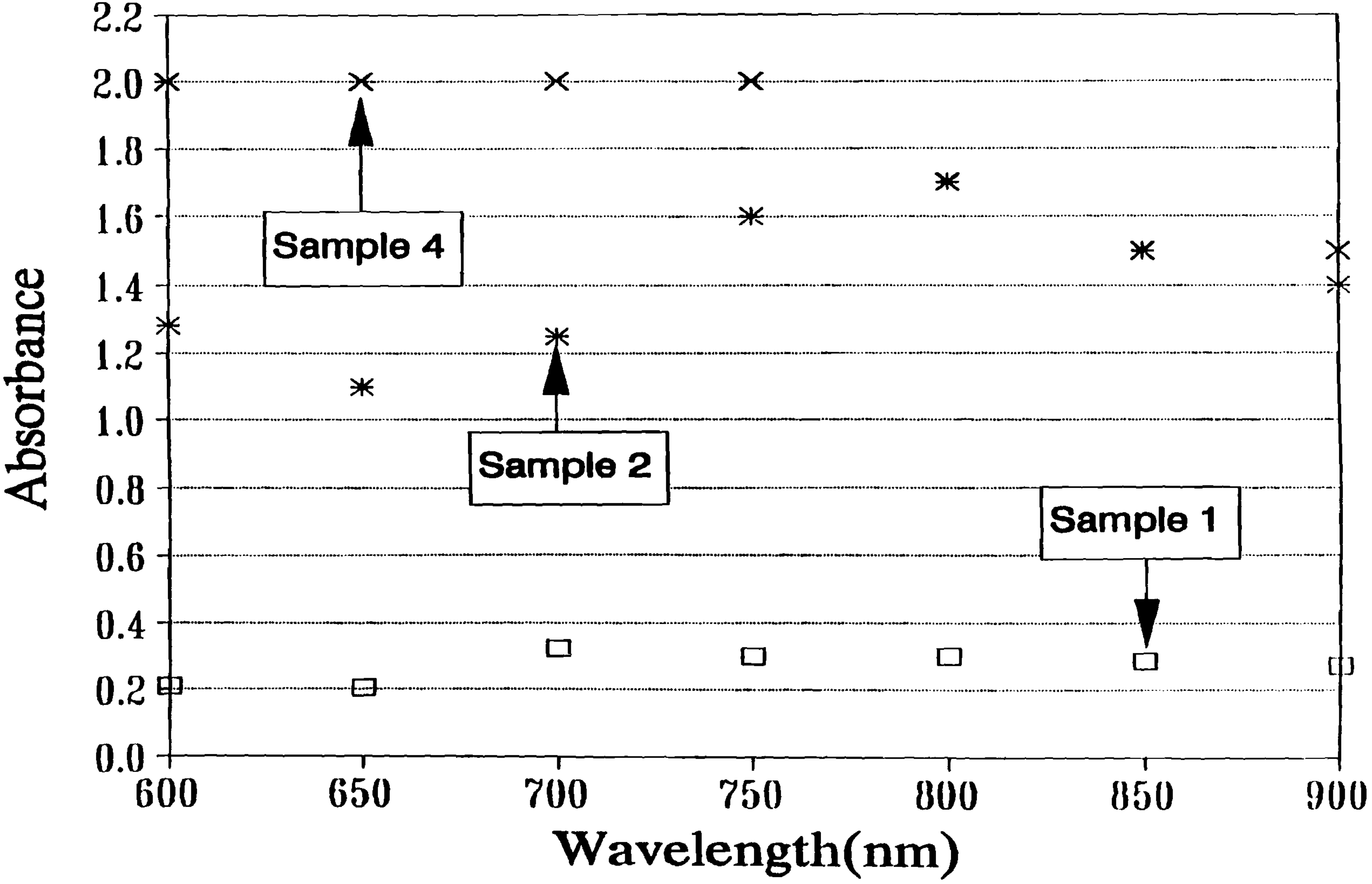

Sample 5
Sample 3
Sample 7
Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
600
650
700
750
800
850
900
Wavelength(nm)

Figure 12

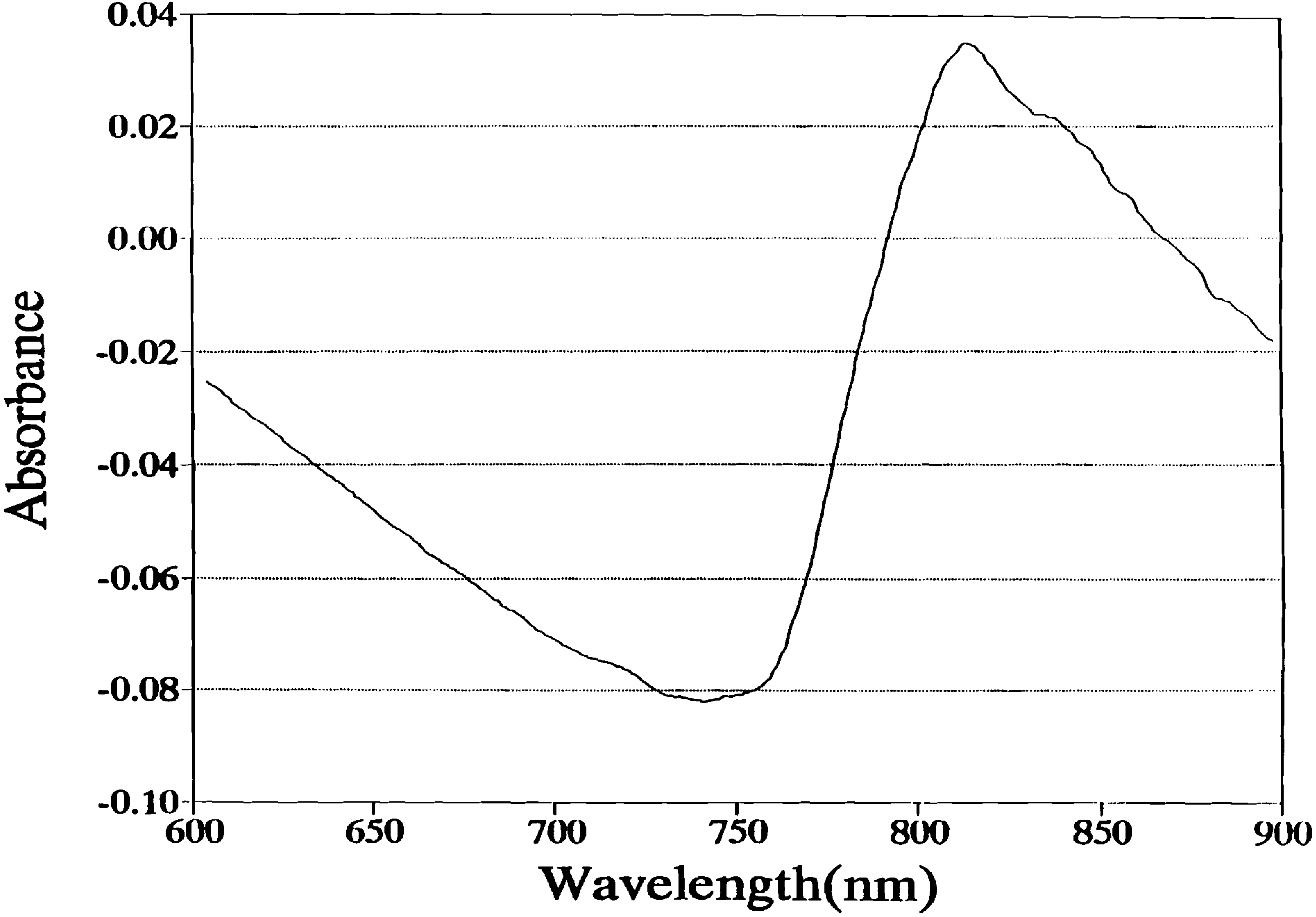
Absorbance of
1.81×10^{-5} M Heteropoly Compound,
4.70×10^{-3} M, and 2.35×10^{-3} M Isopropyl Alcohol and
1.00×10^{-3} M Acid
after 60 minutes Irradiation,
Deaerated with Nitrogen Gas (Samples 2 and 4)
and in Air (Sample 1) Used with
the Bausch and Lomb Spectronic 20 Photometer



Absorbance
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
600
650
700
750
800
850
900
Wavelength(nm)
Sample 4
Sample 2
Sample 1

Figure 13

Baseline of
the Distilled Water versus Distilled Water
Used with the GCA McPherson Ultraviolet-visible
Spectrophotometer



0.04
0.02
0.00
-0.02
-0.04
-0.06
-0.08
-0.10
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)

Figure 14

Absorption Spectra of
Colorless Solution for
1.81×10^{-5} M Heteropoly Compound,
4.70×10^{-3} M Isopropyl Alcohol, and
1.00×10^{-3} M Acid
before Irradiation Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer

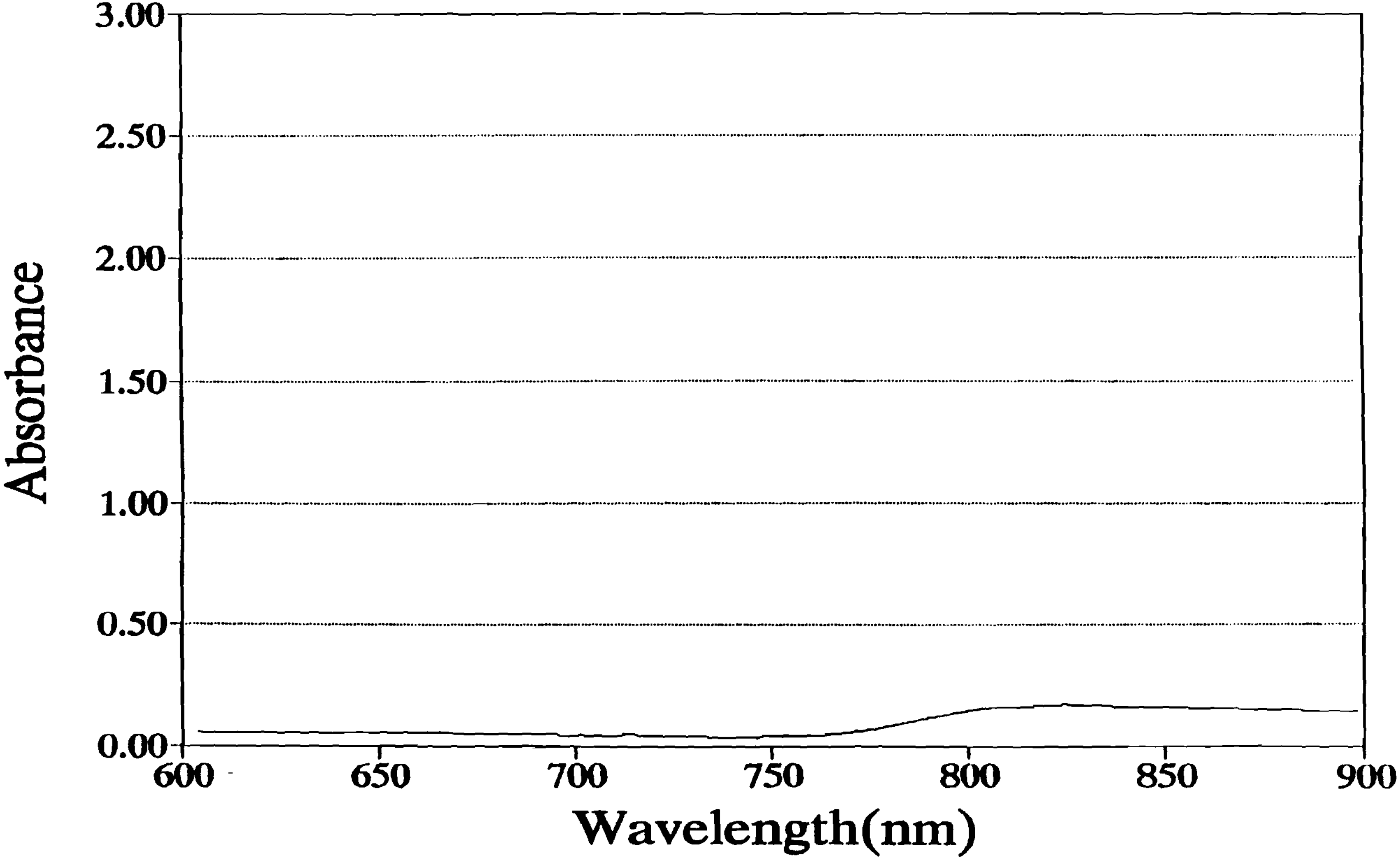
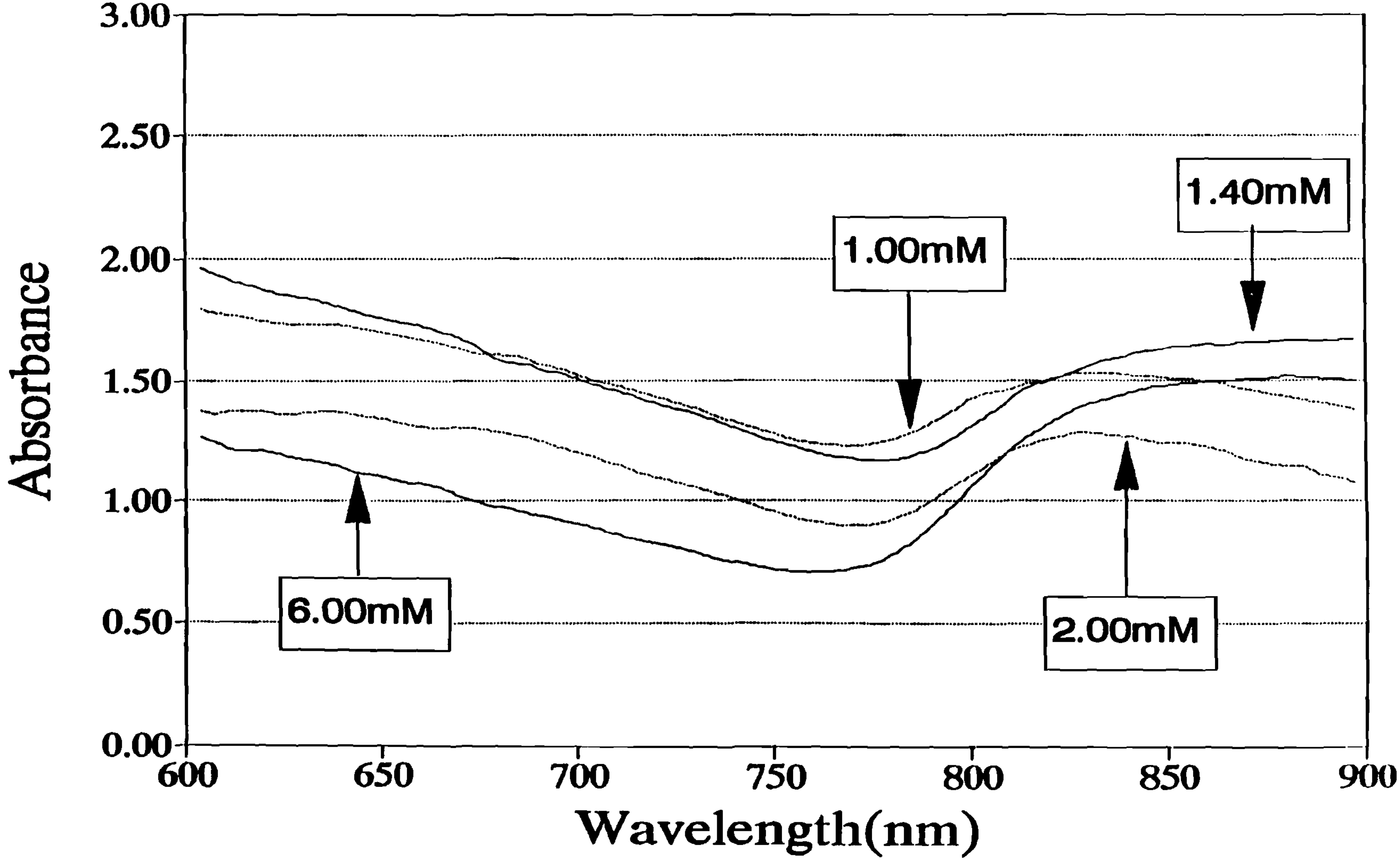

3.00
2.50
2.00
1.50
1.00
0.50
0.00
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)

Figure 15

Absorption Spectra of
Blue Solution for
1.81 x 10^{-5} M Heteropoly Compound,
4.70 x 10^{-3} M Isopropyl Alcohol, and
1.00 x 10^{-3} M, 6.00 x 10^{-3} M, 2.00 x 10^{-3} M, and
1.40 x 10^{-3} M Acid
after 30 minutes Irradiation Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer



Absorbance
3.00
2.50
2.00
1.50
1.00
0.50
0.00
600
650
700
750
800
850
900
Wavelength(nm)
1.40mM
1.00mM
6.00mM
2.00mM

Figure 16

Absorption Spectra of
Colorless Solution for
1.81 x 10^{-5} M Heteropoly Compound,
4.70 x 10^{-3} M Isopropyl Alcohol, and
1.00 x 10^{-3} M, 6.00 x 10^{-3} M, 2.00 x 10^{-3} M, and
1.40 x 10^{-3} M Acid
after Scanned Blue Solution Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer

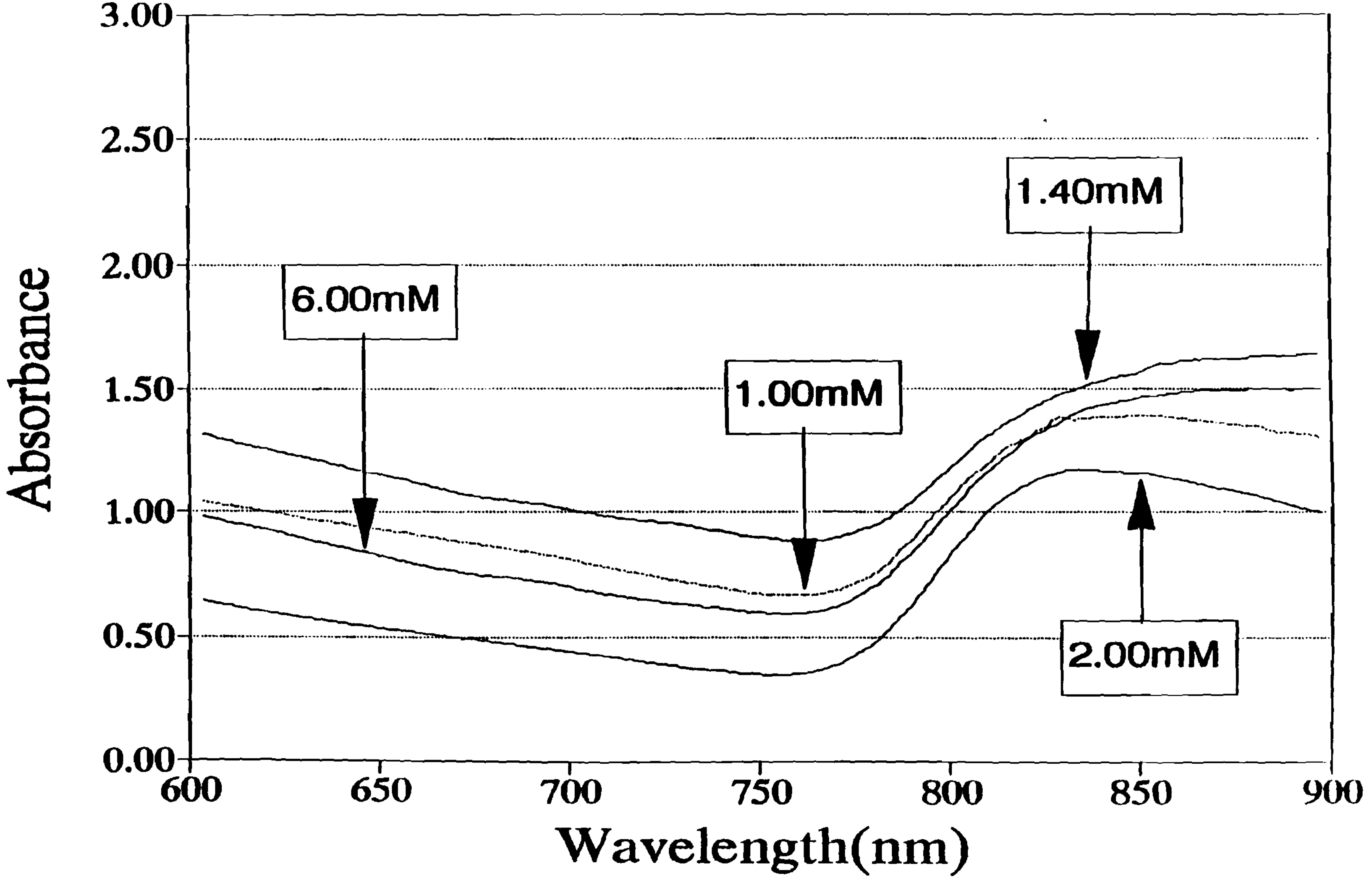

3.00
2.50
2.00
1.50
1.00
0.50
0.00
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)
6.00mM
1.00mM
1.40mM
2.00mM

Figure 17

Absorption Spectra of
Blue Solution for
1.81 x 10^{-5} M Heteropoly Compound,
4.70 x 10^{-3} M, 2.35 x 10^{-3} M, 1.18 x 10^{-3} M, and
7.05 x 10^{-3} M Isopropyl Alcohol, and
1.00 x 10^{-3} M Acid
after 30 minutes Irradiation Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer

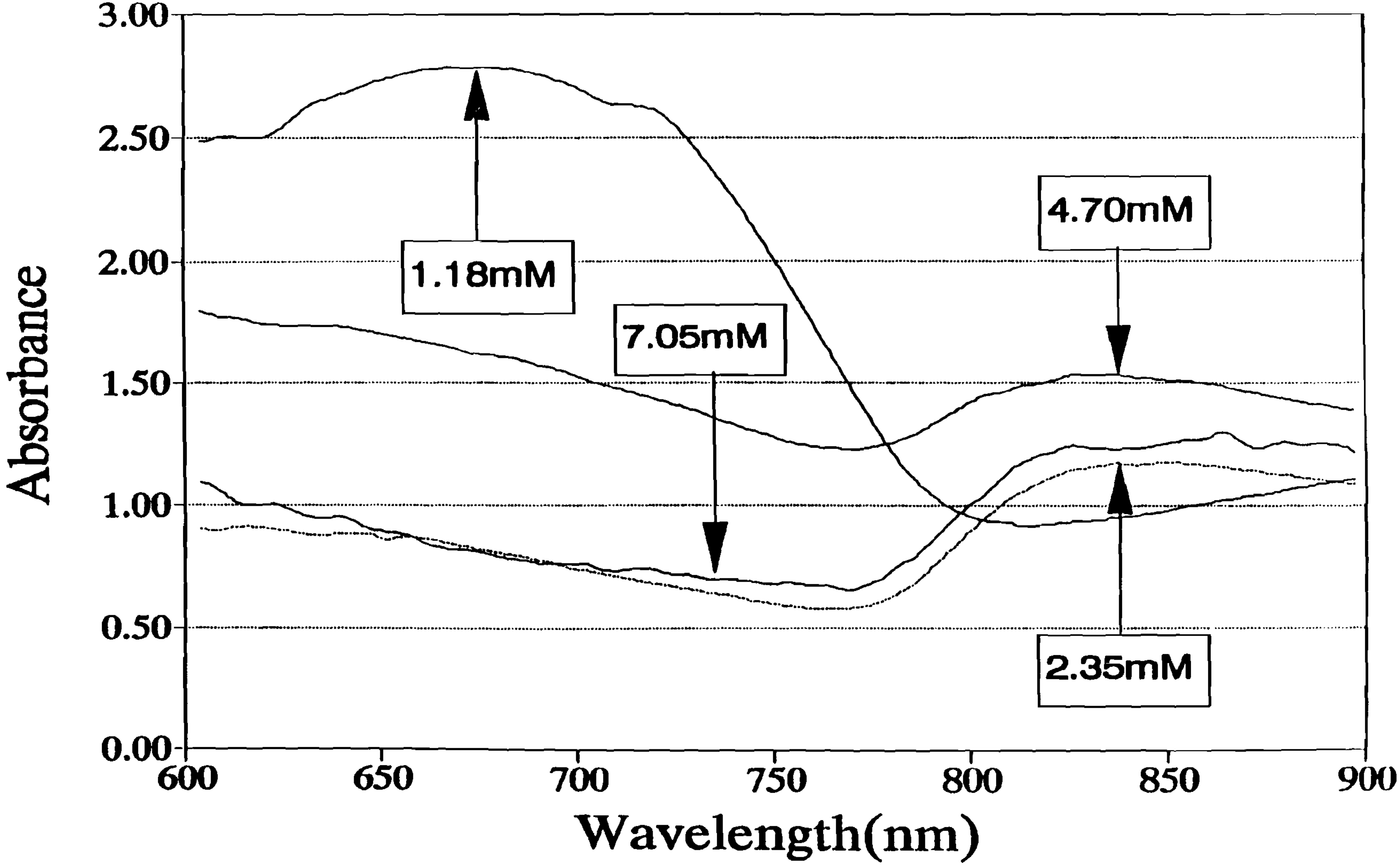

3.00
2.50
2.00
1.50
1.00
0.50
0.00
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)
1.18mM
4.70mM
7.05mM
2.35mM

Figure 18

Absorption Spectra of
Colorless Solution for
1.81 x 10^{-5} M Heteropoly Compound,
4.70 x 10^{-3} M, 2.35 x 10^{-3} M, 1.18 x 10^{-3} M, and
7.05 x 10^{-3} M Isopropyl Alcohol, and
1.00 x 10^{-3} M Acid
after Scanned Blue Solution Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer

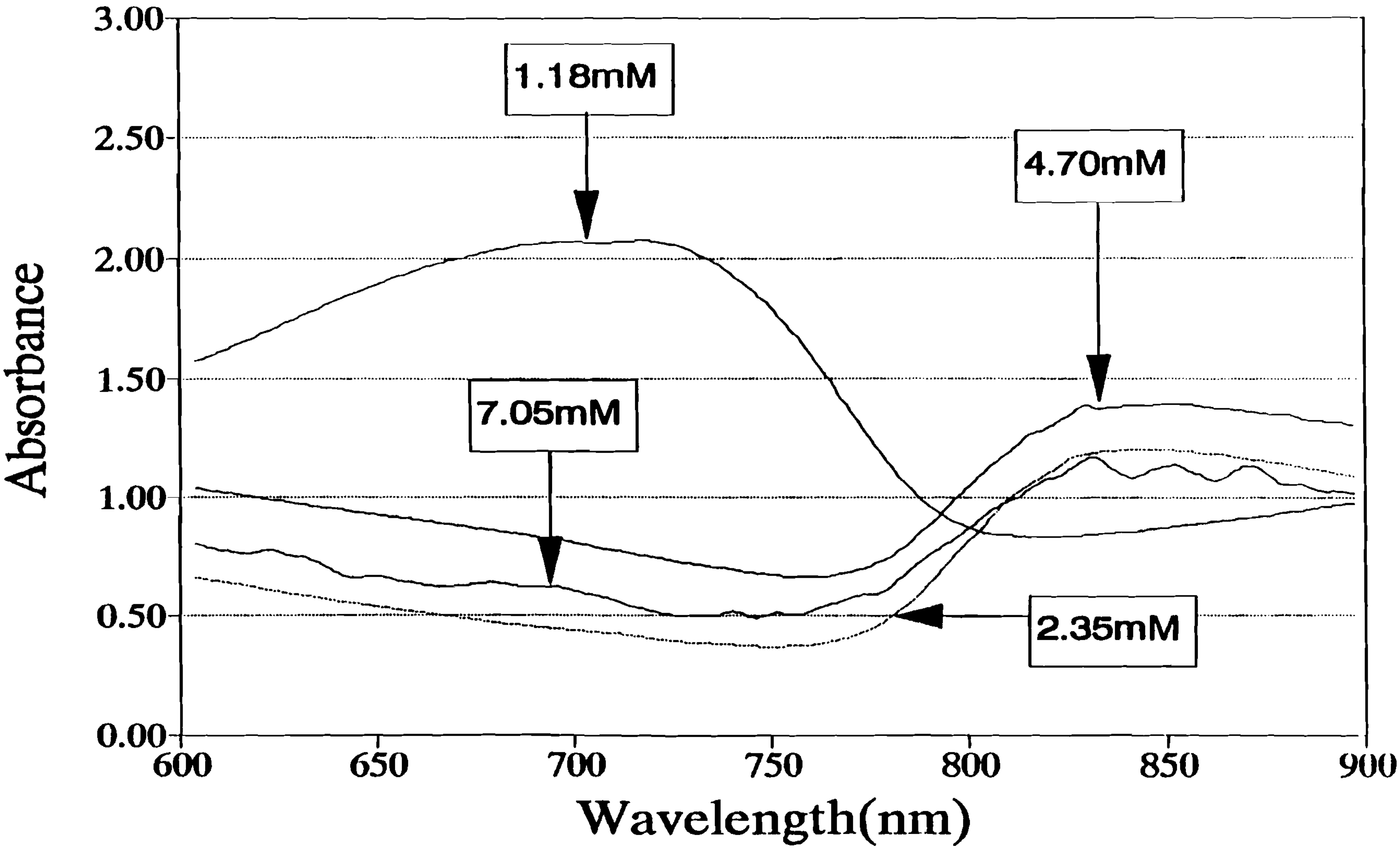
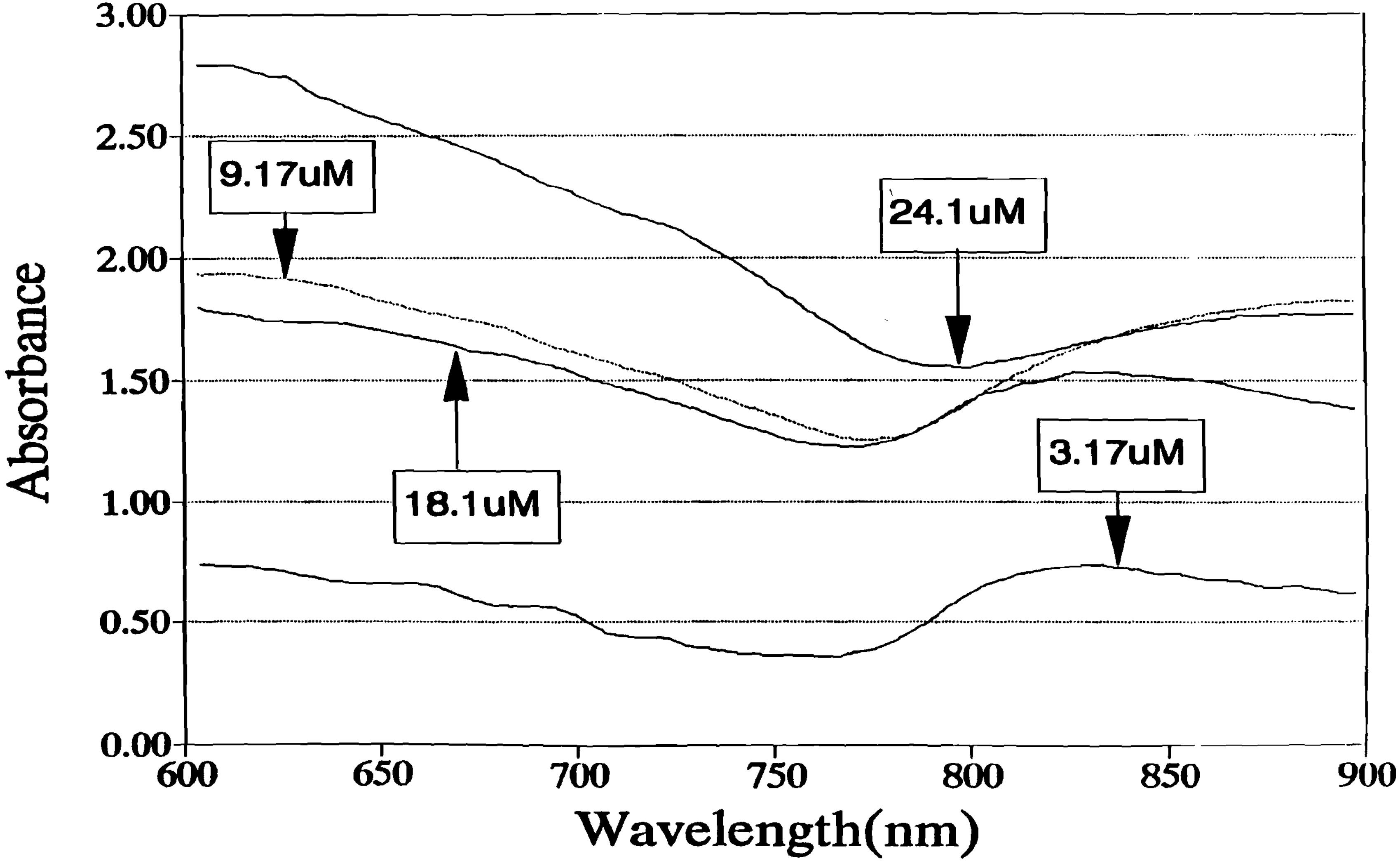

3.00
2.50
2.00
1.50
1.00
0.50
0.00
Absorbance
600
650
700
750
800
850
900
Wavelength(nm)
1.18mM
4.70mM
7.05mM
2.35mM

Figure 19

Absorption Spectra of
Blue Solution for
1.81×10^{-5} M, 9.17×10^{-6} M, 3.17×10^{-6} M, and
2.41×10^{-5} M Heteropoly Compound,
4.70×10^{-3} M Isopropyl Alcohol, and
1.00×10^{-3} M Acid
after 30 minutes Irradiation Used with
the GCA McPherson Ultraviolet-visible
Spectrophotometer



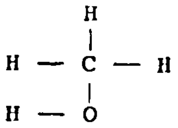
3.00
2.50
2.00
1.50
1.00
0.50
0.00
600
650
700
750
800
850
900
Absorbance
Wavelength(nm)
9.17uM
24.1uM
18.1uM
3.17uM

Figure 21

Structures of Organic Substrates

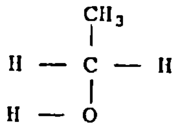
Primary Alcohols

Tertiary Alcohol



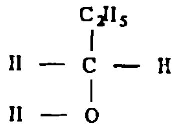
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

Methyl



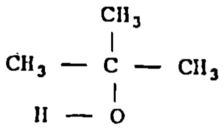
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

Ethyl



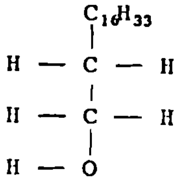
$$\begin{array}{ccccc} & & C_2H_5 & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

n-propyl



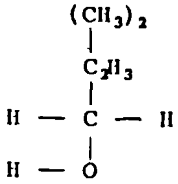
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & CH_3 \\ & & | & & \\ H & - & O & & \end{array}$$

tert-butyl



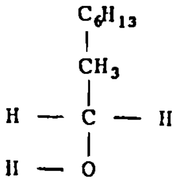
$$\begin{array}{ccccc} & & C_{16}H_{33} & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

n-octadecyl



$$\begin{array}{ccccc} & & (CH_3)_2 & & \\ & & | & & \\ & & C_2H_3 & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

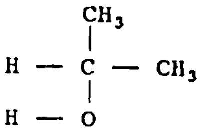
iso-pentyl



$$\begin{array}{ccccc} & & C_6H_{13} & & \\ & & | & & \\ & & CH_3 & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

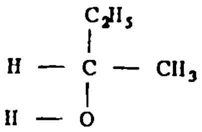
n-octyl

Secondary Alcohols



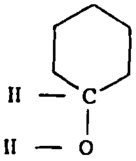
$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H & - & C & - & CH_3 \\ & & | & & \\ H & - & O & & \end{array}$$

iso-propyl

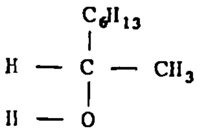


$$\begin{array}{ccccc} & & C_2H_5 & & \\ & & | & & \\ H & - & C & - & CH_3 \\ & & | & & \\ H & - & O & & \end{array}$$

sec-butyl



cylco-hexyl

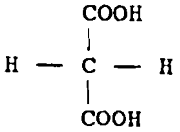


$$\begin{array}{ccccc} & & C_6H_{13} & & \\ & & | & & \\ H & - & C & - & CH_3 \\ & & | & & \\ H & - & O & & \end{array}$$

sec-octyl

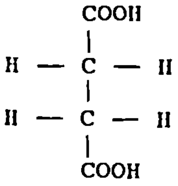
Carboxylic Acids

Amine



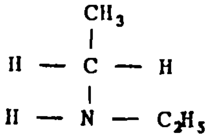
$$\begin{array}{ccccc} & & COOH & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & COOH & & \end{array}$$

Malonic



$$\begin{array}{ccccc} & & COOH & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & COOH & & \end{array}$$

Succinic

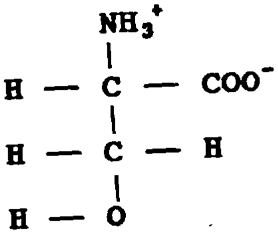


$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & N & - & C_2H_5 \end{array}$$

Diethyl

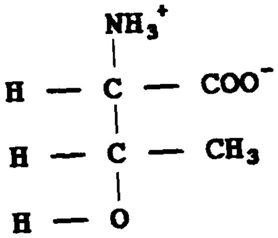
Figure 22

Structures of Amino Acids



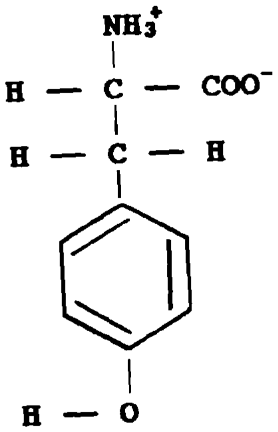
$$\begin{array}{ccccc} & & NH_3^+ & & \\ & & | & & \\ H & - & C & - & COO^- \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ H & - & O & & \end{array}$$

Serine

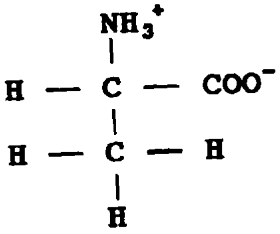


$$\begin{array}{ccccc} & & NH_3^+ & & \\ & & | & & \\ H & - & C & - & COO^- \\ & & | & & \\ H & - & C & - & CH_3 \\ & & | & & \\ H & - & O & & \end{array}$$

Threonine

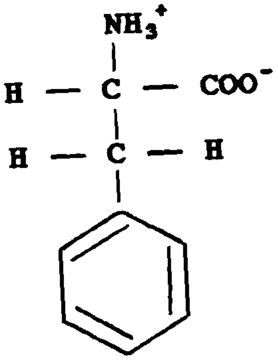


Tyrosine

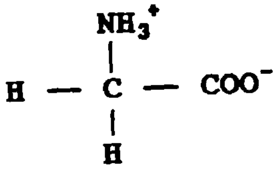


$$\begin{array}{ccccc} & & NH_3^+ & & \\ & & | & & \\ H & - & C & - & COO^- \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Alanine



Phenylalanine

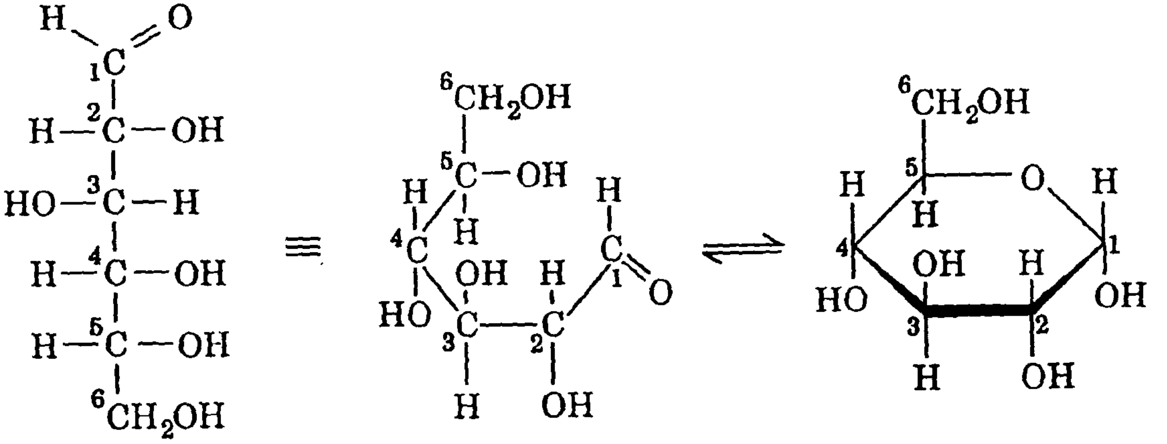


$$\begin{array}{ccccc} & & NH_3^+ & & \\ & & | & & \\ H & - & C & - & COO^- \\ & & | & & \\ & & H & & \end{array}$$

Glycine

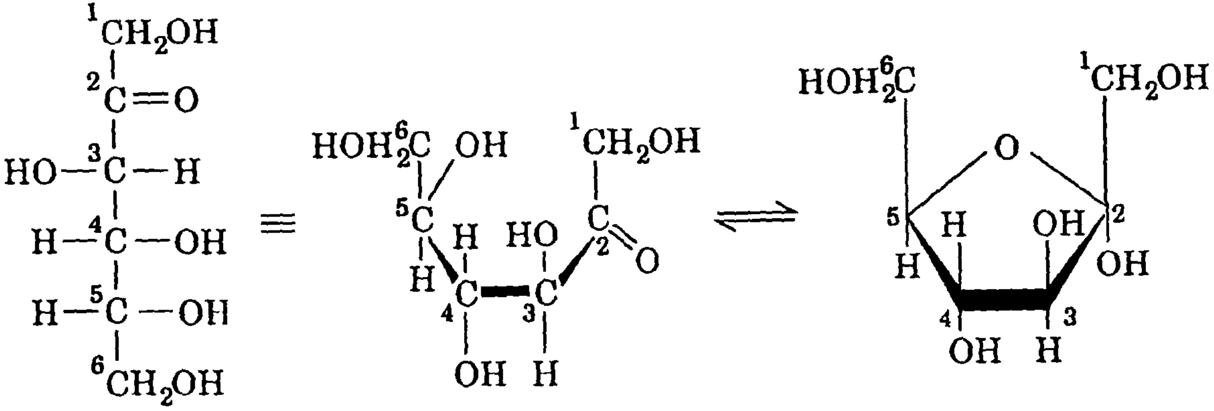
Figure 23

Structures of Glucose and Fructose



D-Glucose
(linear form)

α-D-Glucopyranose
(Haworth projection)

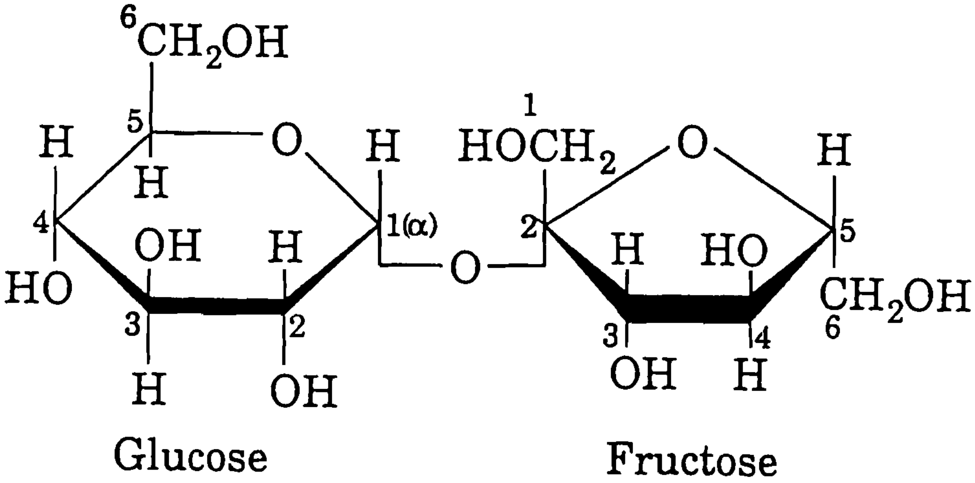


D-Fructose
(linear form)

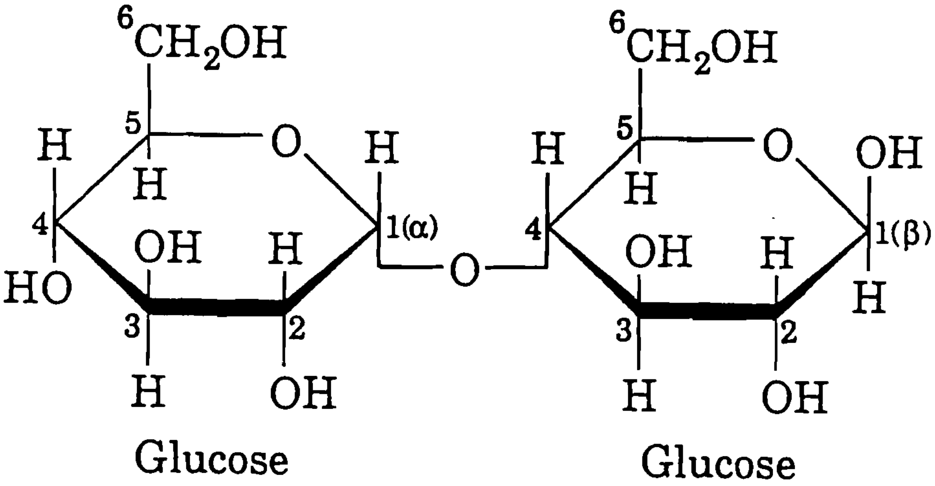
α-D-Fructofuranose
(Haworth projection)

Figure 24

Structures of Sucrose and Maltose



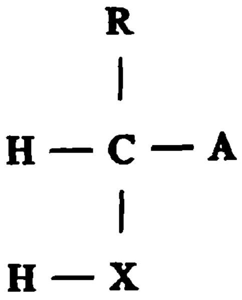
Sucrose



Maltose

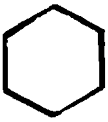
Figure 25

Proposed Reactive Functional Group for the Photooxidation of Alcohols and Related Compounds with the Heteropoly Anion, $[SiW_{12}O_{40}]^{4-}$



$$\begin{array}{ccccc} & & R & & \\ & & | & & \\ H & - & C & - & A \\ & & | & & \\ H & - & X & & \end{array}$$

X = O or N

A = H, CH_3, CH_2CH_3, or 

R = Electron donating groups
(examples : CH_3CH_2R, CHR_2, CR_3,
COO^-, O^-, *etc.*)

Figure 26

Proposed Mechanism of the Photooxidation of Alcohols and Related Compounds with the Heteropoly Anions, $[SiW_{12}O_{40}]^{4-}$

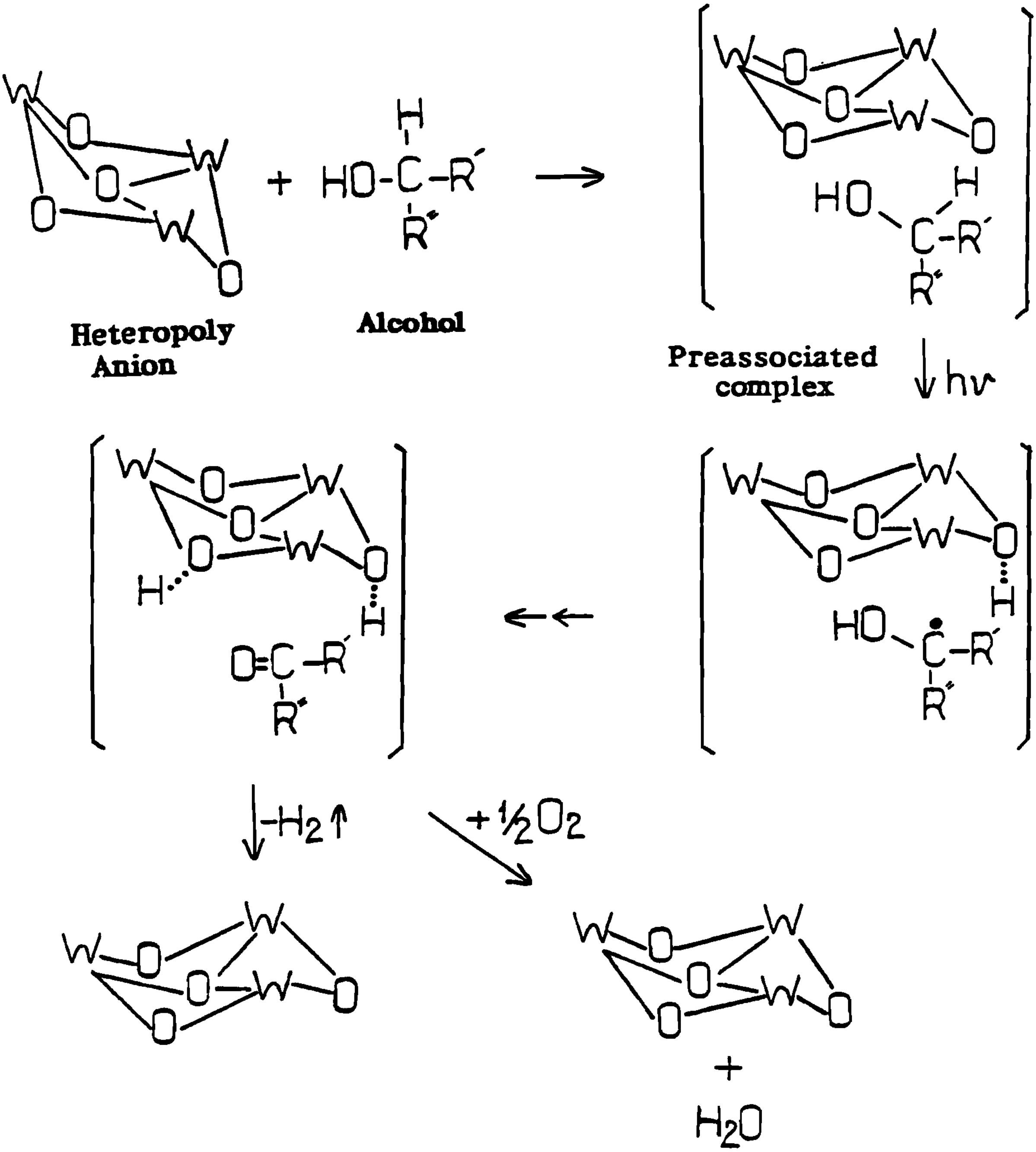

Heteropoly Anion
Alcohol
Preassociated complex
hν
$-H_2\uparrow$
$+\frac{1}{2}O_2$
$+ H_2O$

Table I

Currently Known Heteroatoms in Heteropoly Anions

1A	2A	3A	4A	5A	6A	7A	8A			1B	2B	3B	4B	5B	6B	7B
H																
Li	Be											B	C			
Na	*Mg*											Al	Si	P	S	
K	*Ca*		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	
Rb	*Sr*	Y	Zr	Nb	Mo		*Ru*	Rh		*Ag*		In	Sn	Sb	Te	I
Cs	*Ba*	La	Hf	Ta	W	Re	*Os*		Pt			Tl	*Pb*	*Bi*		
			Ce	Pr	Nd		Sm	Eu	Gd	*Tb*		Ho	Er		Yb	
			Th		U	Np	*Pu*	Am	*Cm*		*Cf*					

Note : Elements shown in italic character have been observed only as secondary heteroatoms

Table II

GCA McPherson Ultraviolet-visible Spectrophotometer Settings for Absorption Spectra

Wavelength Calibrate	:	546.07 nm
Deuterium Lamp	:	for UV Spectra
Tungsten Lamp	:	for Visible Spectra
Slit Width	:	400 microns
Sample Beam	:	Rear
Signal Averaging	:	200
Scan Recorder (NM/DIV-DIV/MIN)	:	50
Function	:	Double Beam, A
Voltage	:	1100 V
Recorder Span	:	2.0 A

Table III

Concentrations of Heteropoly Compound, and of Isopropyl Alcohol in 1.00×10^{-3} M Acid Used with the Bausch and Lomb Spectronic 20 Photometer

	Conc. of Heteropoly Compound	Conc. of Isopropyl Alcohol	Gas	Irradiation Time(min.)
Sample 1	1.81×10^{-5}M	4.70×10^{-3}M	Air	60
Sample 2	1.81×10^{-5}M	4.70×10^{-3}M	Nitrogen	60
Sample 3	1.99×10^{-6}M	4.70×10^{-3}M	Nitrogen	60
Sample 4	1.81×10^{-5}M	2.35×10^{-3}M	Nitrogen	60
Sample 5	1.99×10^{-6}M	2.35×10^{-3}M	Nitrogen	60
Sample 6	3.33×10^{-6}M	4.70×10^{-3}M	Nitrogen	60
Sample 7	1.99×10^{-6}M	4.70×10^{-3}M	Nitrogen	25

Table IV

Concentrations of Heteropoly Compound, of Isopropyl Alcohol, and of Acid Deaerated with Nitrogen Gas Used with the GCA McPherson Ultraviolet-visible Spectrophotometer

	Heteropoly Compound	Isopropyl Alcohol	Acid	Irradiation Time
Colorless Solution	1.81×10^{-5}M	4.70×10^{-3}M	1.00×10^{-3}M	0 min.
Sample 8	1.81×10^{-5}M	4.70×10^{-3}M	1.00×10^{-3}M	30min.
Sample 9	1.81×10^{-5}M	4.70×10^{-3}M	6.00×10^{-3}M	30min.
Sample 10	1.81×10^{-5}M	4.70×10^{-3}M	2.00×10^{-3}M	30min.
Sample 11	1.81×10^{-5}M	4.70×10^{-3}M	1.40×10^{-3}M	30min.
Sample 12	1.81×10^{-5}M	2.35×10^{-3}M	1.00×10^{-3}M	30min.
Sample 13	1.81×10^{-5}M	1.18×10^{-3}M	1.00×10^{-3}M	30min.
Sample 14	1.81×10^{-5}M	7.05×10^{-3}M	1.00×10^{-3}M	30min.
Sample 15	9.17×10^{-6}M	4.70×10^{-3}M	1.00×10^{-3}M	30min.
Sample 16	3.17×10^{-6}M	4.70×10^{-3}M	1.00×10^{-3}M	30min.
Sample 17	2.41×10^{-5}M	4.70×10^{-3}M	1.00×10^{-3}M	30min.

Table V

Results of the Photooxidation of Organic Substrates with the Heteropoly Compound, $K_4[SiW_{12}O_{40}]\cdot 17H_2O$

Substrates	Minute (Color)
1. Primary Alcohols	
(a) methyl	4 (light blue)
(b) ethyl	3 (blue)
(c) *n*-propyl	2 (deep blue)
(d) *iso*-pentyl	2 (blue)
(e) *n*-octyl	15 (colorless)
(f) *n*-octadecyl	15 (colorless)
2. Secondary Alcohols	
(a) *iso*-propyl	3 (blue)
(b) *sec*-butyl	3 (light blue)
(c) cyclohexyl	2 (blue)
(d) *sec*-octyl	5 (blue)
3. Tertiary Alcohol	
tert-butyl	22 (very light blue)
4. carboxylic Acids	
(a) malonic	20 (colorless)
(b) succinic	20 (colorless)
5. Amine	
diethylamine	4 (blue)

Table VI

Results of the Photooxidation of Biochemical Substrates with the Heteropoly Compound, $K_4[SiW_{12}O_{40}] \cdot 17H_2O$

Substrates	Minutes (color)
1. amino Acids	
(a) serine	15 (light blue)
(b) threonine	20 (light blue)
(c) tyrosine	23 (light blue)
(d) alanine	23 (light blue)
(e) phenyl alanine	23 (light blue)
(f) glycine	20 (colorless)
2. Monosaccharides	
(a) glucose	5 (light blue)
(b) fructose	28 (light blue)
3. Disaccharides	
(a) maltose	12 (deep blue)
(b) sucrose	11 (deep blue)

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Youngmo Yoon
Signature of Author

Dec. 15. 94
Date

Oxidation of Alcohols and Related
Compounds with Heteropoly Tungstate
Title of Thesis

Signature of Graduate Office Staff Member

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