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Catalytic Conversion of Light Alkanes
Phase II

Topical Report
January 1990 - January 1993

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ABSTRACT

The Topical Report on Phase II of the project entitled, Catalytic Conversion of Light Alkanes reviews work done between January 1, 1990 and September 30, 1992 on the Cooperative Agreement. The mission of this work is to devise a new catalyst which can be used in a simple economic process to convert the light alkanes in natural gas to oxygenate products which can either be used as clean-burning, high octane liquid fuels, as fuel components or as precursors to liquid hydrocarbon transportation fuel.

This Topical Report documents our efforts to design, prepare, characterize and test novel catalysts for the mild selective reaction of light hydrocarbons with air or oxygen to produce alcohols directly. These catalysts are designed to form active metal oxo (MO) species and to be uniquely active for the homolytic cleavage of the carbon-hydrogen bonds in light alkanes producing intermediates which can form alcohols. Research on the Cooperative Agreement is divided into three Phases relating to three molecular environments for the active catalytic species that we are trying to generate. In this report we present our work on catalysts which have oxidation-active metals in polyoxoanions (PHASE II).

SUMMARY OF PHASE II - RESULTS TO DATE AND STATUS

We have conceived and reduced to practice catalytic principles which have encouraged us to design and to synthesize a new family of catalysts that are effective in the conversion of light alkanes to alcohols or other oxygenates. Until now, the chemical reactions needed to produce the desired oxygenates from alkanes could only be accomplished selectively by specialized enzymatic systems operating in vivo. These systems are impractical for commercial fuel production. Aided by computer-assisted molecular design techniques we have created a family of synthetic catalysts which

may operate based on fundamental principles similar to those employed by the biological systems. Our new catalysts, however, can be synthesized in the laboratory from inexpensive raw materials.

In past quarterly reports we have discussed the reductive binding of dioxygen between two iron sites, Fig 6-1 in a catalyst. As we envision oxygen activation in this hypothetical catalytic cycle, two mononuclear ironporphyrin complexes must react sequentially with dioxygen, It might indeed be better if the two metal sites were proximate in a binucleating ligand system. It appears that methane monooxygenase, MMO, an enzymatic catalyst system capable of oxidizing methane directly to methanol possesses two irons in a binucleating ligand system which are also bound by a μ-hydroxo bridge. A ligand environment that can support two iron or other oxidation-active metals in close proximity might have interesting catalytic activity. Evidence for cooperative binding of O_2 between two proximate iron centers has been obtained by Que and co-workers (J. Am. Chem. Soc., 1990). We have therefore, synthesized catalysts which have diiron sites for direct oxygen binding.

In past reports we have discussed the increased catalyst life which perhalogenation imparts to porphyrinato ligand systems. Although far more robust than the parent porphyrin complexes, the electron deficient porphyrinato ligands which we have made to date are not particularly hardy above 100°C. As we have mentioned, the polyoxometallates known as Keggin or Dawson ions have been shown to accommodate oxidation active metals and have even been called by some "inorganic porphyrins". Thus we have been using these materials as "ligands" for oxidation active first row metals. They indeed have good thermal and oxidative stablility. Polyoxometallates have also been used as structures which incorporate potentially cooperative dimetal sites and we have been using these compounds for catalytic oxidations of C_1-C_4 hydrocarbons in the liquid phase. Thus during the first three years of the Cooperative Agreement we have studied polyoxometallates having the Keggin structures $C_x[PW_9M(III)_3O_{37}]^{-x}$ where C = K^+, $(Bu_4N)^+$, H^+, and M = Fe, Cr, V(O), and Ru, and x = 6 or 7.

We have also completed synthesis and testing and reported on the structures of the new dimetal complexes: $C_x[MM'_{10}M''_2O_{36}]$ as suggested in the SOW. This entailed making the dilacunary ligand and inserting the appropriate bridged diiron species. We have done this and report on two examples of this type of complex. These complexes suffer from the same deficiency as did the polyoxometallates containing one and three oxidation-active metal centers - poor low temperature oxidation activity due to low reduction potential of the metal center.

Now having developed techniques to make and test a representative number of complexes we compared the reduction potential of iron(III) in phospho-, silico- and boro- phosphates and molybdates in an effort to systematize the effect of electron-withdrawal from the polyoxometallate ligand on the reduction potential of the iron(III). We compared reduction potential with oxidation activity of the butylammonium salts in acetonitrile solution. A correlation similar to that seen in the porphyrin series was not found. It is our belief at this time that the reason that the low-temperature oxidation activity of the polyoxometallates is inferior to that of the ironperhaloporphyrin complexes is the lower reduction potential of the iron in the polyoxometallate ligand environment. At this time, it appears that electron deficient metalloporphyrin catalysts are significantly superior to their polyoxometallate counterparts.

1.0 - 5.0 INTRODUCTION, PURPOSE, BACKGROUND, EXISTING APPROACHES TO THE PROBLEM, TECHNICAL BACKGROUND

The Phase I Topical Report should be consulted for these sections.

6.0 SUPRABIOTIC CATALYSTS

6.1. CRITERIA FOR A SUPRABIOTIC CATALYST

As was discussed in the Phase I Topical Report, a practical catalyst which operates via metal oxo intermediates for converting alkanes to alcohols must be more than biomimetic. In some ways it must be suprabiotic. When we consider how the biological systems work, we can learn some important lessons that indicate possible ways in which to activate alkanes and oxygen. One thing that we learn is that in order to activate oxygen it is necessary to bind both ends of the dioxygen molecule before cleaving and transferring it to a substrate. The enzymes use iron(II) to reductively bind one side of the dioxygen molecule and an electron and a proton to bind the other side, giving Fe-O-O-H. It is possible to do this conceptually with two Fe(II) centers instead. If two Fe(II) sites cooperate to reductively bind dioxygen, a peroxidic intermediate, Fe(III)-O-O-Fe(III), would result which could cleave to form two moles of a ferryl complex, Fe(IV)=O, which might be capable of converting an alkane to an alcohol. In this system, both oxygen atoms of O_2 would be utilized, as opposed to only one when monooxygenase enzymes are used. Water would not be formed. We have envisioned a new type of catalyst which could meet the following criteria:

a. It could generate metal oxo (M=O) from reaction of the metal center (M) with molecular oxygen ONLY. No co-reductant or external source of protons or electrons would be required.

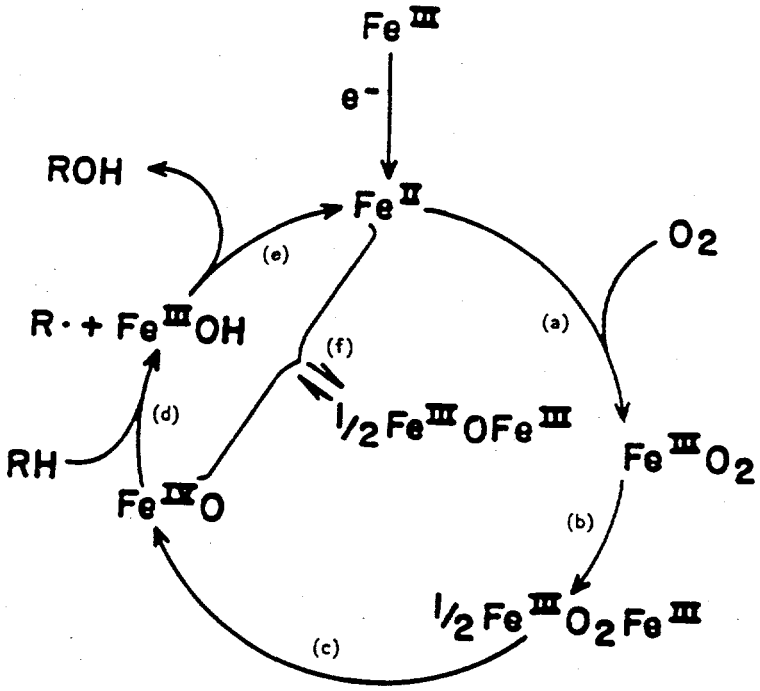
b. The metal oxo center must attract the alkane, promote facile C-H bond cleavage, but be resistant to oxidative self-destruction. The ligand system must be similarly resistant to oxidative degradation.

c. After converting the alkane to alcohol the center must expel the product from the coordination sphere and regenerate the metal center (M) for starting another catalytic cycle.

The proposed catalytic cycle shown below in Figure 6-1 indicates how these criteria could be met. Since nature uses a porphyrinic macrocycle as the ligand system this seemed to be a reasonable starting point for this research. The cycle shown below, Figure 6-1, uses elementary steps which all have precedent in inorganic chemistry.

FIGURE 6-1

ALKANE HYDROXYLATION WITH O_2 USING A SUPRABIOTIC CATALYST



Fe = (Fe) = PORPHYRINATO IRON

Oxygen reacts with the metal center to form a superoxo complex which combines with another center to form a μ-peroxo complex. Cleavage of the O-O bond in the peroxo complex leads to the metal oxo complex which oxidizes the alkane. One of the reasons why this doesn't happen readily under normal circumstances is that the highly reactive metal oxo complex combines rapidly with a metal center to form a catalytically inactive μ-oxo complex, Eq. 1.

$$M{=}O + M \longrightarrow M\text{-}O\text{-}M \qquad (1)$$

It is the goal of the catalyst design portion of this project to adjust the electronic characteristics of the ligand system about the metal center in such a way as to encourage O-O bond cleavage, and to stabilize the monomeric metal oxo relative to inactive μ-oxo intermediates.

6.2 CATALYST DESIGN CONCEPT

At the conclusion of the first three years work on the Cooperative Agreement it is instructive to re-visit the suprabiotic concept and evaluate catalyst performance relative to this idea. As we first envisioned a suprabiotic catalyst, it was one which could operate in the absence of costly stoichiometric co-reductants using only air to oxidize an alkane to an alcohol but in some respects mimic biology in that the active intermediates would be similar. It appears as though the active intermediate which oxidizes alkanes in both Cytochrome P-450 and methane monooxygenase is a ferryl species, Fe=O. We devised a possible conceptual route to active ferryl using only iron, air and substrate, Figure 6-1.

Prior to our work no success had been achieved in attempting to oxidize alkanes to alcohols with only air or oxygen in this manner. Many attempts had been made using porphyrinato complexes both with and without bulky groups which would prevent μ-oxo dimer formation, Figure

6-1f. The only successful alkane oxidations using porphyrinato complexes were achieved using costly single atom donor oxidants such as iodosylbenzene, hypochlorites, or hydroperoxides.

The problems associated with this system for air-oxidations of alkanes to alcohols were many. First, although formation of μ-oxo dimer from the iron(II) precursor is detrimental, μ-peroxo dimer formation is crucial. Secondly, access of the alkane to the active center must be good. Thirdly, the alkyl radical formed by C-H bond homolysis should remain in the coordination sphere until rebound to the alcohol occurs. Fourth, the alcohol should be expelled as quickly from the coordination sphere as possible to prevent over-oxidation. Next, μ-oxo dimer formation must be reversed or prevented. Finally, the iron(III)/(II) reduction potential must be high enough to continuously regenerate active Fe(II) from the pool of Fe(III) even in the presence of molecular oxygen. In addition, the ligand system must be robust to oxygenation, and must not have electrons readily available to reduce the high oxidation state ferryl before it can oxidize the alkane. The kind of porphyrin complexes available prior to our work did none of these things and consequently were inactive catalysts.

6.2.1 Phase I - Electron Deficient Porphyrin Complexes

Using perhaloporphyrin complexes we: a) stabilized active iron-oxygen centers to both of the kinds of decay referred to above, b) provided a lipophilic environment to attract the alkane to the active site, c) provided a hydrophilic environment to expel alcohol from the coordination sphere, d) tuned the redox potential of the metal center so that μ-oxo dimer was no longer inactive and so that iron(II) species could be continually regenerated in an oxidizing environment. Figure 6-1a suggests how our perhaloporphyrins may act as a suprabiotic catalyst for converting alkanes to alcohols.

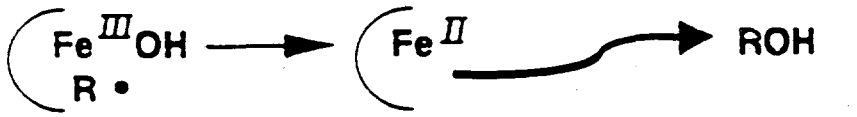
FIGURE 6-1a

PROPERTIES OF A SUPRABIOTIC CATALYST

- COOPERATIVE IRON (II) SITES

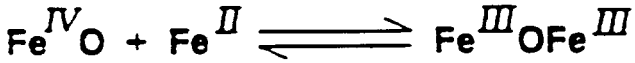
- LIPOPHILIC ENVIRONMENT *

- HIGH Fe^{III}/Fe^{II} REDUCTION POTENTIAL[I]

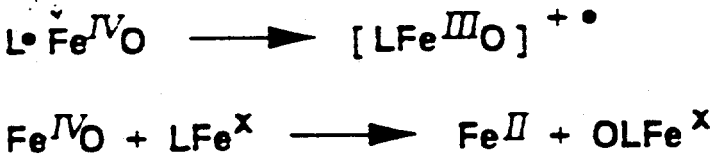


* HYDROPHOBIC ENVIRONMENT

- SUPPRESSED μ-OXO FORMATION



- STABILITY TO OXIDATION



In the Phase I Topical Report, we discussed how the electronic and steric environment about the oxidation-active metal center affects the rate and selectivity of alkane oxidation in homogeneous liquid phase oxidations. Reaction rate seems to be highly dependent on proper tuning of redox potentials. In the liquid phase we have achieved unprecedented reaction rates and have electrochemical evidence that much higher rates can still be achieved.

While steric effects influence rate as well, we are finding that their prime importance is in reaction selectivity. Ejecting formed alcohol from the coordination sphere is of great importance as we have seen in both homogeneous and heterogeneous alkane oxidation. Although our greatest gains to date are in tuning the redox potential for high activity, and although there is still room for significant improvement here, we will be also concentrating in the future on those aspects of catalyst structure that will effect selectivity to alcohol. Among all of these structural factors, a most important one is hydrophobicity of the ligand environment. Our current designs address these points and we are confident that we will continue to make significant gains in both reaction rate and selectivity until all of the light alkanes can be smoothly converted to alcohols by direct, practical, air-oxidations.

It should be noted at this point that we are proposing a completely novel solution to the 'μ-oxo dimer problem. Most efforts in the past have sought to prevent formation of this unreactive species by steric hindrance which prevents the iron centers from getting close to one another (1-2). Our approach is an electronic rather than a steric one. An implication of our approach is that even a μ-oxo complex which has been properly tuned electronically will provide a good standing concentration of active metal oxo.

An important aspect of catalyst design employed in this work is the utilization of a non-oxidizable ligand. Firstly the ligand cannot be oxidized by the very high oxidation states generated at the metal center. For example, if one attempts to form an iron(V) oxo species by treatment of tetraphenylporphyrinatoiron(III)chloride with iodosylbenzene, one forms instead the iron(IV) radical cation by electron transfer from the porphyrin ligand (3). The ligands used in this work must be resistant to this kind of electron transfer and provide a stable coordination sphere even for metals in very high oxidation states. It goes without saying that the ligands employed must be inert to autoxidation and other potentially destructive processes.

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6.3 PHASE II ALL INORGANIC SUPRABIOTIC SYSTEMS - METALS IN POLYOXOANIONS

In the Topical Report on Phase I of the Cooperative Agreement, we showed how perhalogenation of a porphyrinatometal complex resulted in oxidative stability. Still another approach to achieving oxidative stability, is to use an all inorganic catalyst ligand system. We have used heteropolytungstates and molybdates as the ligand system for oxidation-active first row transition metals. These ligands have the Keggin structure which surrounds the transition metal with

a coordination sphere of oxygen atoms yet retains an open coordination site for activating molecular oxygen. Iron(III), manganese(III) and chromium(III) are active in this environment for oxidizing alkanes in the liquid phase. Novel organic-soluble complexes of this type have been prepared and are modestly active for oxidation of methane and natural gas in the liquid phase.

6.4 POLYOXOMETALLATES CONTAINING A SINGLE OXIDATION-ACTIVE METAL CENTER

Having formulated the postulate that a stable electron-withdrawing macrocyclic ligand environment for oxidation-active first row transition metals could produce a catalyst active enough to hydroxylate a light alkane using only molecular oxygen and no coreductant, we proceded to make a large number of compounds designed to have this characteristic. One such family of compounds is the framework-substituted polyoxoanions or heteropoly acids. Table 6-1 shows that first row transition metal centers in a silicotungstate ligand system catalyze isobutane oxidation. Table 6-2 demonstrates the beneficial effect of azide ion on catalytic properties. The Keggin structure, Figure 6.2, is particularly suited for metal incorporation and gives an all-inorganic analog to the porphyrin systems.

FIGURE 6.2

POLYOXOANION, $[PM_{12}O_{40}]^{-3}$, OF THE KEGGIN STRUCTURE

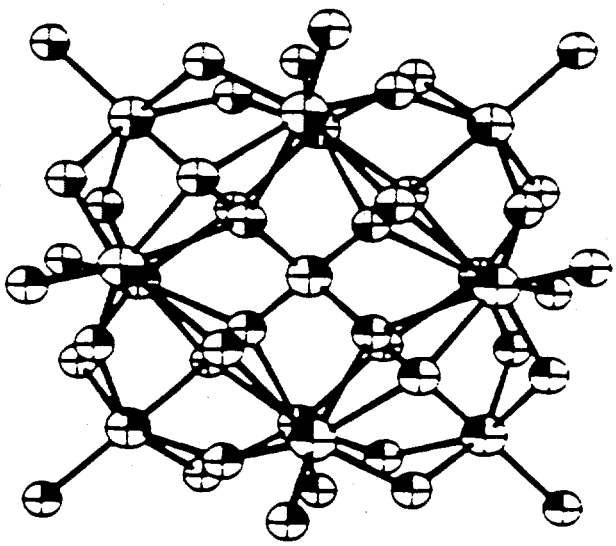


Table 6-1 Isobutane Oxidations Catalyzed by First Row Transition Metal Centers in Polyoxoanions Having the Keggin Structure[a]

Complex	mmoles Catalyst	Catalyst Turnovers
$K_4SiMo_{12}O_{40}$	0.025	0
$K_6SiMo_{11}FeO_{39}$	0.025	70
$K_5SiMo_{11}CrO_{39}$	0.025	140
$K_6SiMo_{11}MnO_{39}$	0.025	0

[a] Isobutane 7g dissolved in benzene, 15 ml, containing the catalyst stirred at 80°C under 100 psig of O_2 for 6 hours.

Table 6-2. Effect of Azide on Propane Oxidation Activity of First Row Transition Metal Centers in Polyoxoanions Having the Keggin Structure[a]

Complex	mmoles Catalyst	Catalyst Turnovers	Isopropyl Alcohol/ Acetone
$K_3PW_{12}O_{40}$	0.025	> 20	na
$K_4PW_{11}CrO_{39}$	0.010	40	na
$K_5PW_{11}CrO_{39}N_3$	0.010	2290	1.0
$K_5PW_{11}VO_{40}$	0.010	60	na
$K_5PW_{11}VO_{40}N_3$	0.010	2090	0.8

a Propane, 1.36 moles, was added to a solution of the catalyst in a solution of aqueous acetic acid and o-dichlorobenzene (48 ml) which was stirred 3 hours at 150°C under 100 psig of air. Liquids and gases were analyzed by gc.

6.4.1 Synthesis Of Polyoxometallates Containing a Single Oxidation Active Metal Center

6.4.1.1 **Preparation of $K_4[PW_{11}Fe0_{39}]$**

15.0g of $H_3[PW_{12}0_{40}]$, 12-tungstophosphoric acid, is dissolved in 35 ml of H_20. With stirring the pH is adjusted to 5.2 with potassium bicarbonate. After heating to 70°, 2.14g of iron nitrate nonahydrate is added. After 15 minutes the solution is filtered, then cooled and 1.0g of KCl is added to aid in precipitation of the product. The ppt is filtered and dried in vacuo at 110°.

6.4.1.2 **Preparation of $K_4[PW_{11}Cr0_{39}]$**

15.0g of $H_3[PW_{12}0_{40}]$ is dissolved in 35 ml of H_20. With stirring the pH is adjusted to 5.2 with potassium bicarbonate. After heating to about 70°, 2.02g of chromium triacetate monohydrate is added with stirring. After 15 minutes the solution is filtered, then cooled and 1.0g of KCl is added to precipitate the product which is filtered and dried in vacuo at 110°.

These syntheses are patterned after the pioneering work of Louis Baker (1) and Timothy Weakley (2).

6.4.2 Preparation Of Heteropolyacids From Polyoxoanions

The isolation of the acid form of polyoxoanions has not been accomplished in many instances. Only those heteropolyacids which are stable at very acidic pH's as low as one can be isolated by the usual "etherate" (3) techniques. Polyoxoanions containing oxidation active metals such as Fe, Cr, Mn, and Co do not have sufficient stability in water at low pH to form HPA's by the addition of strong acid that can be extracted with ether. Therefore, a new technique was needed to find a non-aqueous technique for preparation of the acid forms of these materials. We, therefore, developed a pyrolytic technique for converting alkylammonium salts of POA's directly to the HPA form.

As an example, we prepared a sample of $K_5[PW_{11}VO_{40}]$, dissolved it in H_20 and precipitated the tetrabutylammonium salt by the addition of $(n\text{-}Bu)_4NBr$. The product, $[(n\text{-}Bu)_4N]_5[PW_{11}VO_{40}]$ was recrystallized in acetonitrile. A TGA experiment was performed under N_2 flow and the temperature raised from ambient to 659°C. Table 6-3, and Figure 6-3 show the accumulative weight loss and corresponding molecular weight loss. This shows the loss of the five tetrabutylammonium groups between 290° - 450°C. This material is initially black due to surface carbon. The true green color of the HPA can be obtained by extraction of the solid into acetonitrile filtration, and evaporation of the solvent. Bulk samples can be pyrolyzed by heating under N_2 flow at 450°C for one hour using a glass tube and clamshell heater setup. IR spectroscopy also confirms the loss of the tetrabutylammonium groups with no adverse effect on the Keggin structure. In Figure 6.4 the top spectrum is $H_3PW_{12}0_{40}$, the middle spectrum is $[n\text{-}Bu_4N]_5[PW_{11}VO_{40}]$, and the bottom spectrum is the pyrolyzed $H_5[PW_{11}VO_{40}]$ product. The IR confirms the loss of the C-H stretches associated with the butyl ammonium cations in the 1400 cm^{-1} region with no effect on the P-O, V-O, W-O stretching region from 800-1100cm^{-1}.

TABLE 6-3

TGA OF $(Bu_4N_5)[PW_{11}VO_{40}]\cdot 3H_2O$ MW = 4010

Temp (°C)	Wt. Sample (mg)	Wt Loss (mg)	MW Loss	MW Left	Group Loss
RT	43.8	0	0	4010	
125	43.2	0.6	55	3855	$3\cdot H_2O$
290	37.0	6.2	568	3387}	
				}980	4 Bu_4N = 970
350	32.5	4.5	412	2975}	
450	29.7	2.8	256	2719*	1 Bu_4N = 242.5

* $(PW_{11}VO_{40})$ = 2744

FIGURE 6.3 TGA of $(Bu_4N)_5[PW_{11}VO_{40}]\cdot 3H_2O$

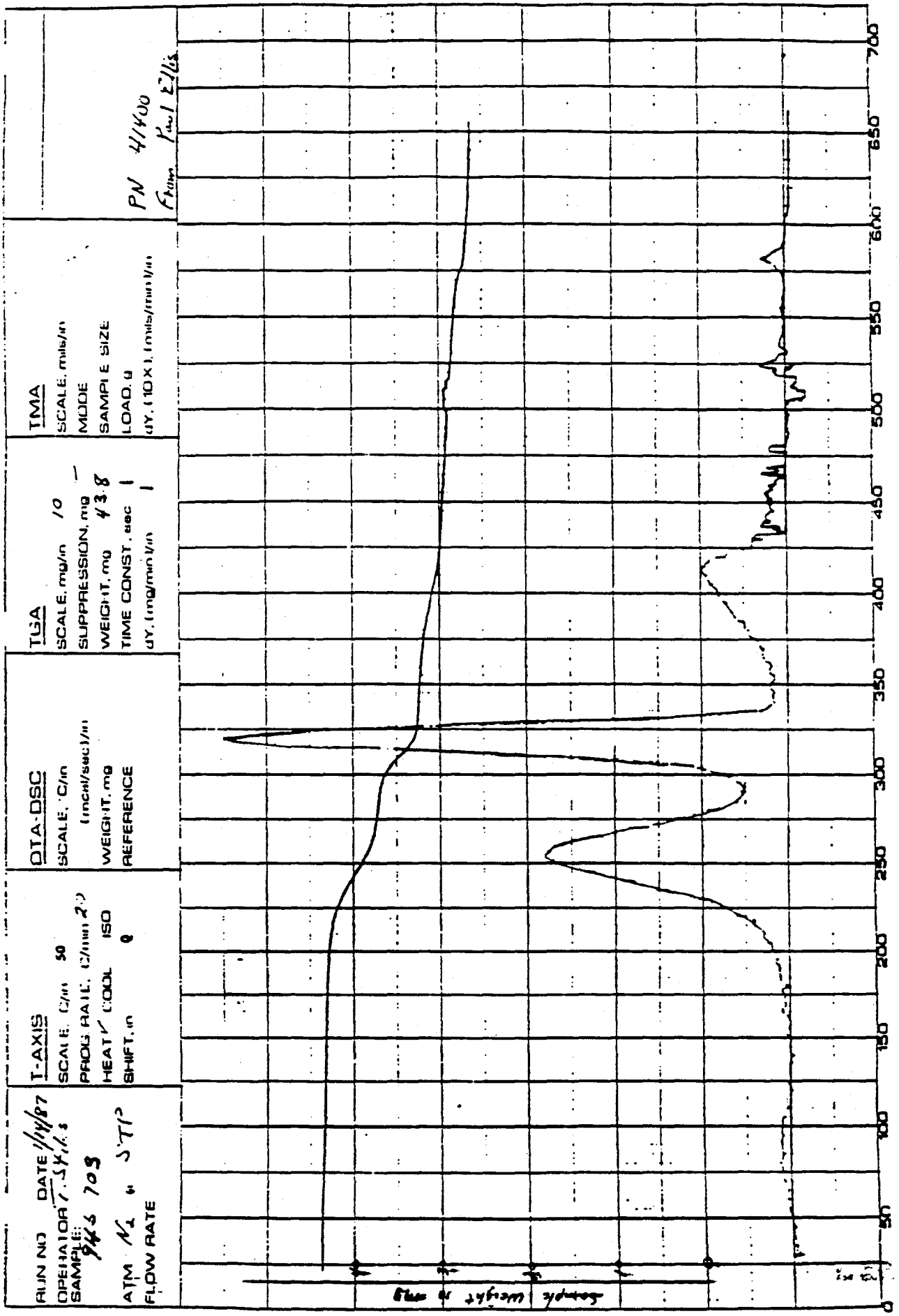
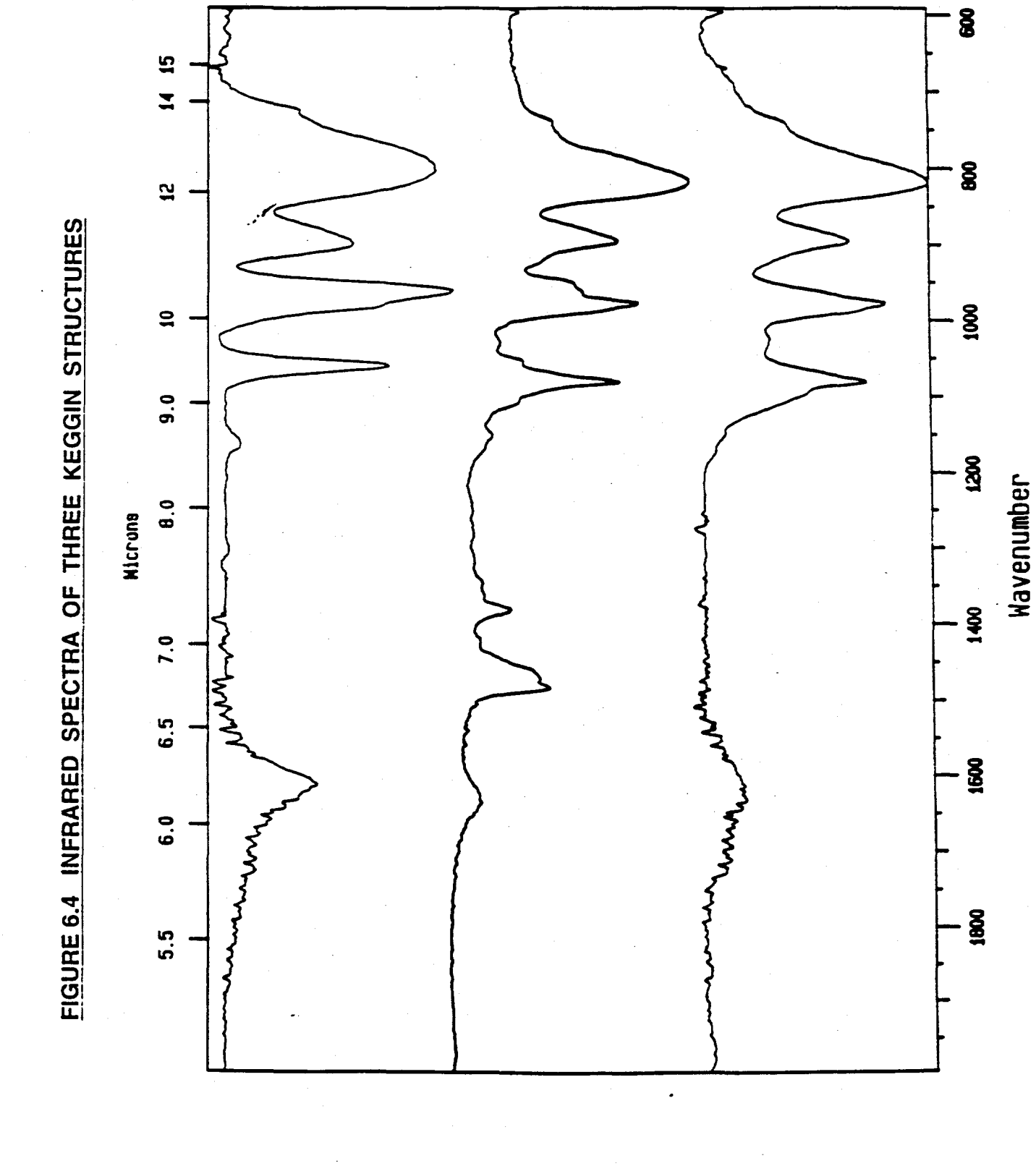


FIGURE 6.4 INFRARED SPECTRA OF THREE KEGGIN STRUCTURES



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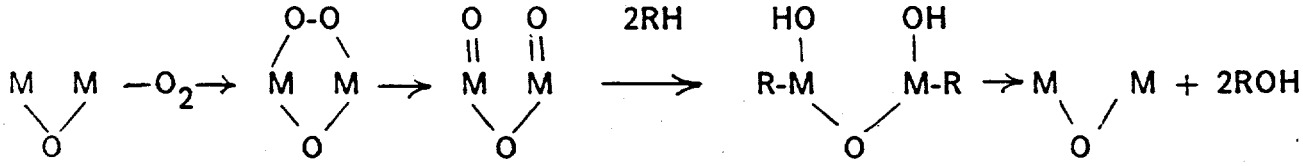
6.5 EFFECTS OF PROXIMATE METALS

As was mentioned in the Topical Report - Phase I, methane monooxygenase has proximate metal sites. On contemplating various roles for the proximate iron atoms in catalytic oxidation, the direct formation of a diiron-peroxo species seemed possible. Using the same principles as discussed for the macrocyclic systems, the μ-peroxo species could cleave to give adjacent iron oxo sites which could activate an alkane, Eq. 2 (schematically).



We have synthesized a Keggin structure with three iron atoms in close proximity separated by only oxide bridges. The triiron structure demonstrated unique catalytic activity in both liquid and vapor phase. It may be critical that the metal centers be proximate for vapor phase activity of the type that we envision. In solution, μ-peroxo species can form readily, in some instances Figure 4.1. On a surface an immobile iron center cannot readily do this unless it is already proximate to another iron center, Eq. 2.

6.5.1 Catalyst Deisgn Stragegy

Cytochrome P-450 hydroxylates carbon-hydrogen bonds in the liver by reductively binding oxygen between an iron and a protic center. It requires two electrons to accomplish this and so consumes coreductant stoichiometrically. In Fig. 6.1 we show how one might accomplish the reductive activation of dioxygen using two (Fe(II) centers to furnish electrons, bind the O_2 and cleave it. This requires that at some point the irons come into close enough proximity to form a peroxo complex. Methane monooxygenase, a non-heme biocatalyst accomplishes the very same thing. Two iron centers seem to work cooperatively to accomplish catalytic methane hydroxylation, but electrons and protons are still stoichiometrically consumed, Figure 6.5. Thus we conclude that an effective suprabiotic catalyst might benefit from having proximate iron centers as well. Figure 6.6 shows another way in which two proximate iron centers could cooperate to activate dioxygen and catalytically oxidize alkanes. Recent work by Que and coworkers (J. Am. Chem. Soc., 1990), Figure 6.7 has shown that a MMO model reductively binds dioxygen to form a peroxo species in just the way that is suggested by our hypothetical suprabiotic pathway, Eq. 2.

FIGURE 6.5

PROPOSED MECHANISM FOR MMO ACTIVITY, DALTON, 1992

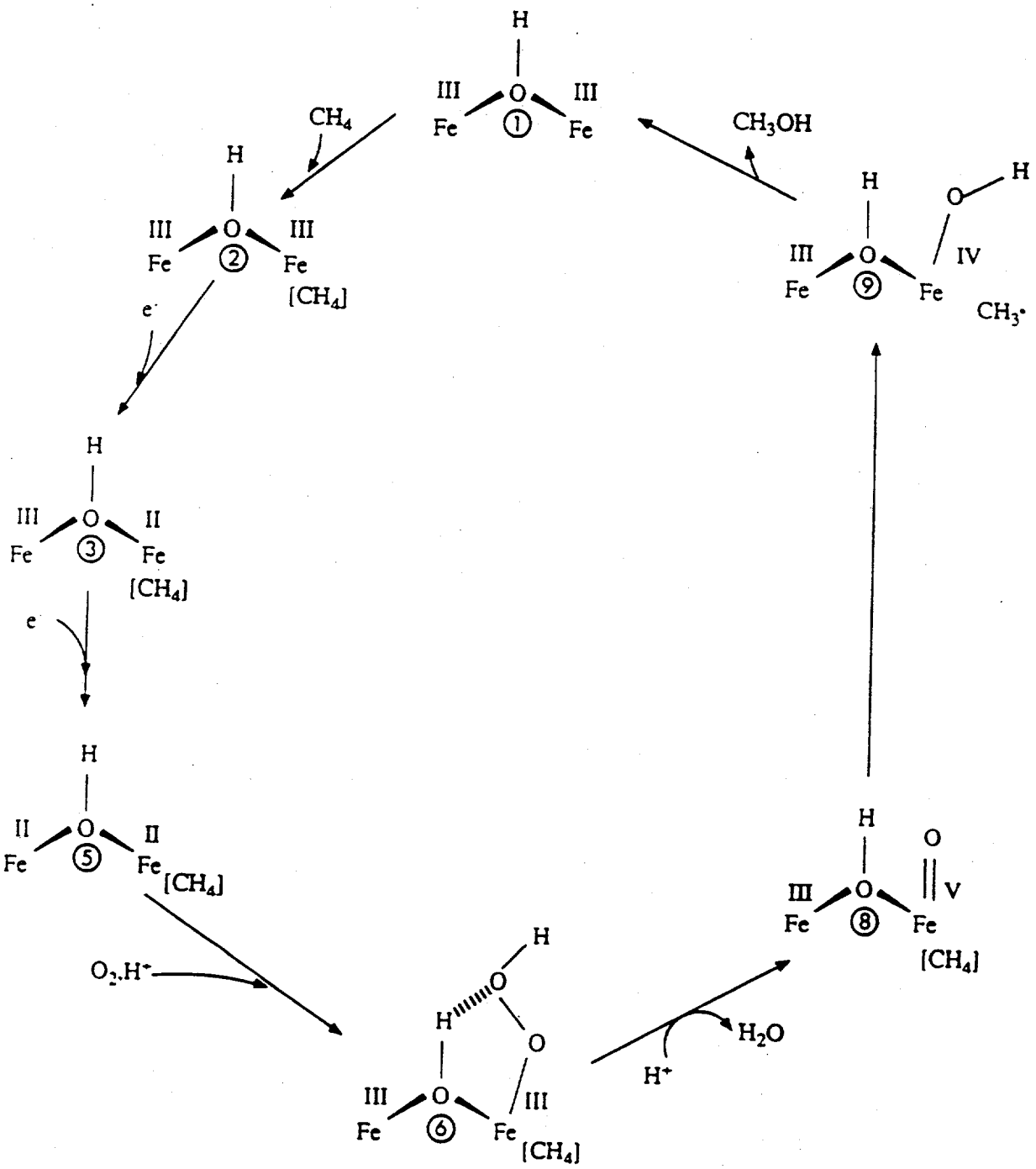


FIGURE 6.6

A SUPERIOR SUPRABIOTIC CATALYST MIGHT HAVE PROXIMATE IRON CENTERS

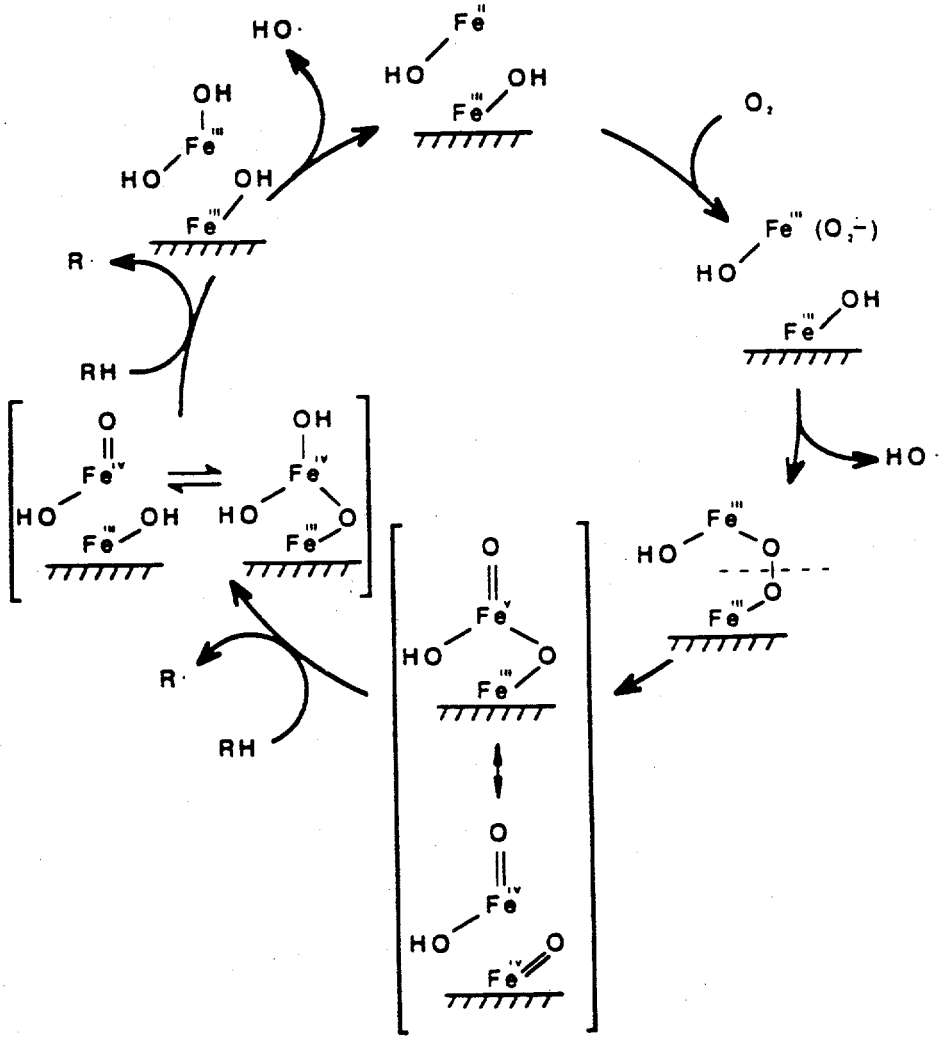
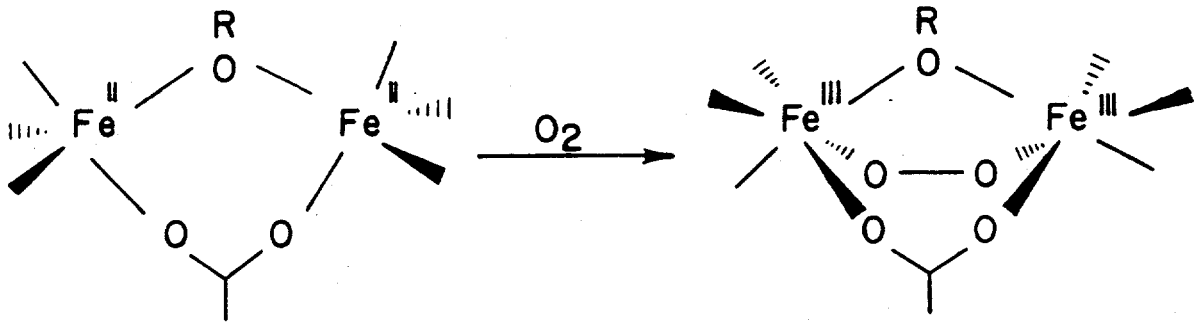


FIGURE 6.7

REDUCTIVE BINDING OF DIOXYGEN ACROSS A BINUCLEAR DIRON CENTER



QUE , 1990

This thought process coupled with the desire for more thermally and oxidatively stable ligand systems for oxidation-active metal centers led to the suggestion that polyoxometallates could be used as both soluble or surface catalysts for liquid or vapor phase hydrocarbon oxidations. Extended oxidic arrays which support proximate metal sites could also be used for vapor phase oxidations, Figure 6.8. Thus, we have studied two sets of PHASE II catalysts. These are polyoxometallates having the structures: $C_6[PW_9M(III)_3O_{37}]^{-6}$, where C = K^+, $(Bu_4N)^+$, H^+, and M = Fe, Cr, V(O), and Ru; and $C_7[PW_9Fe(III)_2M'(II)O_{37}]^{-7}$ where C = K^+, $(Bu_4N)^+$, H^+, and M = Fe, Zn, Ni, Co, Mn.

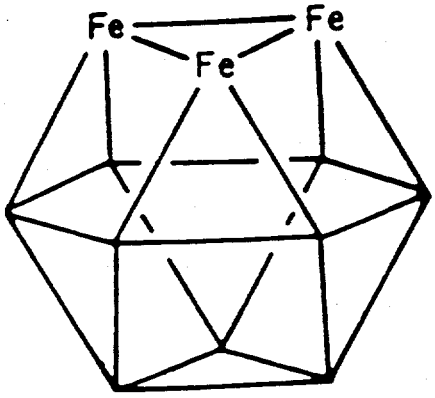
6.5.2 Catalyst Synthesis Strategy

Figure 6.9 outlines the synthetic strategy employed to prepare the PHASE II catalysts which are being investigated during the first two years of the program. Homo or heteronuclear trimetal acetates are prepared from their nitrate salts in acetic acid solution. The nonatungstate receptor is prepared from tungstate and phosphate precursors at the required pH and the timetal acetate is inserted into the receptor. The molecule "heals" into a Keggin-like structure which can be converted to the tetrabutylammonium form and then pyrolyzed to the corresponding heteropolyacid.

FIGURE 6.8 PHASE II, III, CATALYSTS

- ALL INORGANIC FOR GREATER THERMAL AND OXIDATIVE STABILITY
- HAVE PROXIMATE METAL CENTERS FOR OXYGEN ACTIVATION

POLYOXOMETALLATES



$B\text{-}K_7[PW_9Fe_3O_{37}]$

FRAMEWORK SUBSTITUTED ZEOLITES

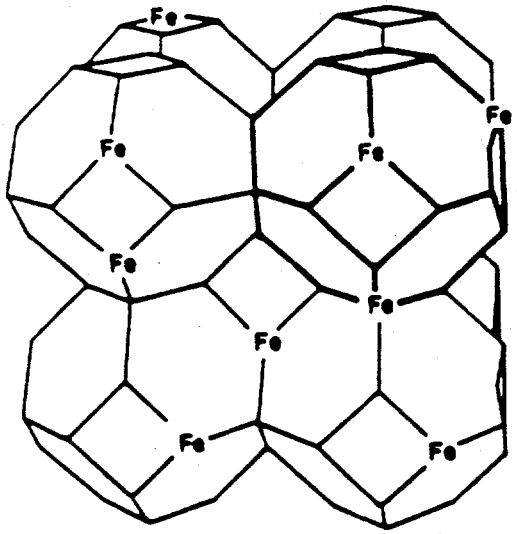


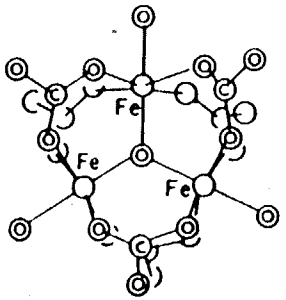
FIGURE 6.9

Synthesis of Multi-Nuclear First Row Group VIII Centers in Keggin Structures

$3M(NO_3)_3 + XS\ HOAc\ (aq.) \rightarrow [M(III)_3O(OAc)_6(H_2O)_3]^-$ or

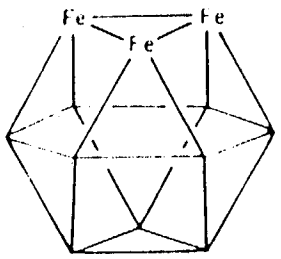
$2Fe(NO_3)_3 + M'(NO_3)_2 + XS\ HOAc\ (aq.) \rightarrow [Fe_2M(II)O(OAc)_6(H_2O)_3]$

Na_2WO_4
Na_2HPO_4 —HCl, pH = 1.0→ B–$Na_9[PW_9O_{34}]$ "TRILAC"



Trimetalacetate

KOAc, KCl, pH = 6.0, 50°



B-$K_7[PW_9Fe_3O_{37}]$
(I)

(I) + $(Bu_4N)Br \rightarrow$ ß-$(B_4N)_7[PW_9Fe_3O_{37}]$ $\xrightarrow{\Delta\Delta}$ B-$H_7[PW_9Fe_3O_{37}]$

6.6 TRIMETAL SUBSTITUTED KEGGIN IONS

Trilacunary polyoxoanions have been prepared, Figure 6.9 as a ligand for oxo-bridged triiron units. Polyoxoanions of the formulas $K_6[PW_9Fe_3O_{37}]$ and $[(C_4H_9)_4N]_6$ $[PW_9Fe_3O_{37}]$ were prepared in this manner. The tetrabutylammonium salt was pyrolyzed at 450°C to give the dry acid form: $H_6[PW_9Fe_3O_{37}]$ which had acceptable solubility in organic solvents such as acetonitrile. A trichromium complex was synthesized in a similar manner. Propane was air-oxidized at a far faster rate in the presence of the triiron complex than when the parent phosphotungstate catalyst was used. The triiron cluster was also much more active in the Keggin structure than was the oxo-bridged triiron hexa-acetate complex from which it was made. The triiron Keggin acid was also more active than a monoiron derivative. It was superior to a trichromuim Keggin acid as well. Azide ion made a 1:1 complex with these polyoxoanions and the azide further enhanced catalytic activity. The triiron species showed low but noticeable methane oxidation activity.

6.6.1 Synthesis of Trimetal Substituted Keggin Ions

6.6.1.1 **Preparation of $K_6[PW_9Fe_30_{37}]$**

8.49g of the "trilacunary" complex $Na_8H[PW_90_{34}]$ (48) is dissolved in 200 ml of H_20 buffered with sodium acetate and acetic acid to the proper pH = 6.0. This material is then treated with stirring, with 1.69g of $Fe_3(CH_3CO_2)_6(OH)Cl$ (49) dissolved in 50 ml of H_20. The orange-brown solution is heated and stirred at 50°C for 15 minutes. After cooling to room temperature, 10g of KCl is added and the solution is placed in a refrigerator overnight. The material is purified by passing a 0.005 M solution over 10"X1" Amberlyst 15 ion-exchange resin in the K^+ form then reducing the volume until ppt occurs. $K_7[SiW_9Fe_30_{37}]$ has been prepared by Ortega (50) by a similar procedure. The crystals are filtered and vacuum dried at 125° for 3 hours. The infrared spectrum $K_6[PW_9Fe_30_{37}]$ is given in Figure 6.10a,b. The tetrabutylammonium salt can be prepared

by dissolving the $K_6[PW_9Fe_3O_{37}]$ in a minimum of hot H_2O (T=60°) and adding an equal volume of a saturated solution of $(n\text{-}Bu)_4NBr$. After cooling overnight, orange crystals are filtered which can be recrystallized from hot acetonitrile.

6.6.1.2 Preparation of $K_6[PW_9Cr_3O_{37}]$

8.49g of $Na_8H[PW_9O_{34}]$[51] is dissolved in 200 ml of H_2O buffered to pH=6 with sodium acetate and acetic acid. This solution is treated with a solution containing 1.81g of $Cr_3(CH_3CO_2)_7(OH)Cl$[52] dissolved in 50 ml of H_2O. The blue-green solution is stirred and heated to 50°C for 15 minutes. After cooling, 10g of KCl is added and the solution is refrigerated overnight. After filtration the product $K_6[PW_9Cr_3O_{37}]$ is obtained. The material is purified by passing a .005 M solution 10"X1" over Amberlyst 15 ion-exchange resin column in the K^+ form then reducing the volume until ppt occurs. An infrared spectrum of this product is shown in Figure 6-11a,b. It is vacuum dried at 125°C for three hours. Yield 6.76g IR (included) shows the characteristic metal oxygen stretching region characteristic of these trisubstituted poloxoanions. The tetrabutylammonium salt, $[(n\text{-}Bu)_4N]_6[PW_9Cr_3O_{37}]$ is prepared as before by metathesis in H_2O with $(n\text{-}Bu)_4NBr$ followed by recrystallization in hot acetonitrile.

FIGURE 6.10a

INFRARED SPECTRUM OF $K_6[PW_9Fe_3O37]$

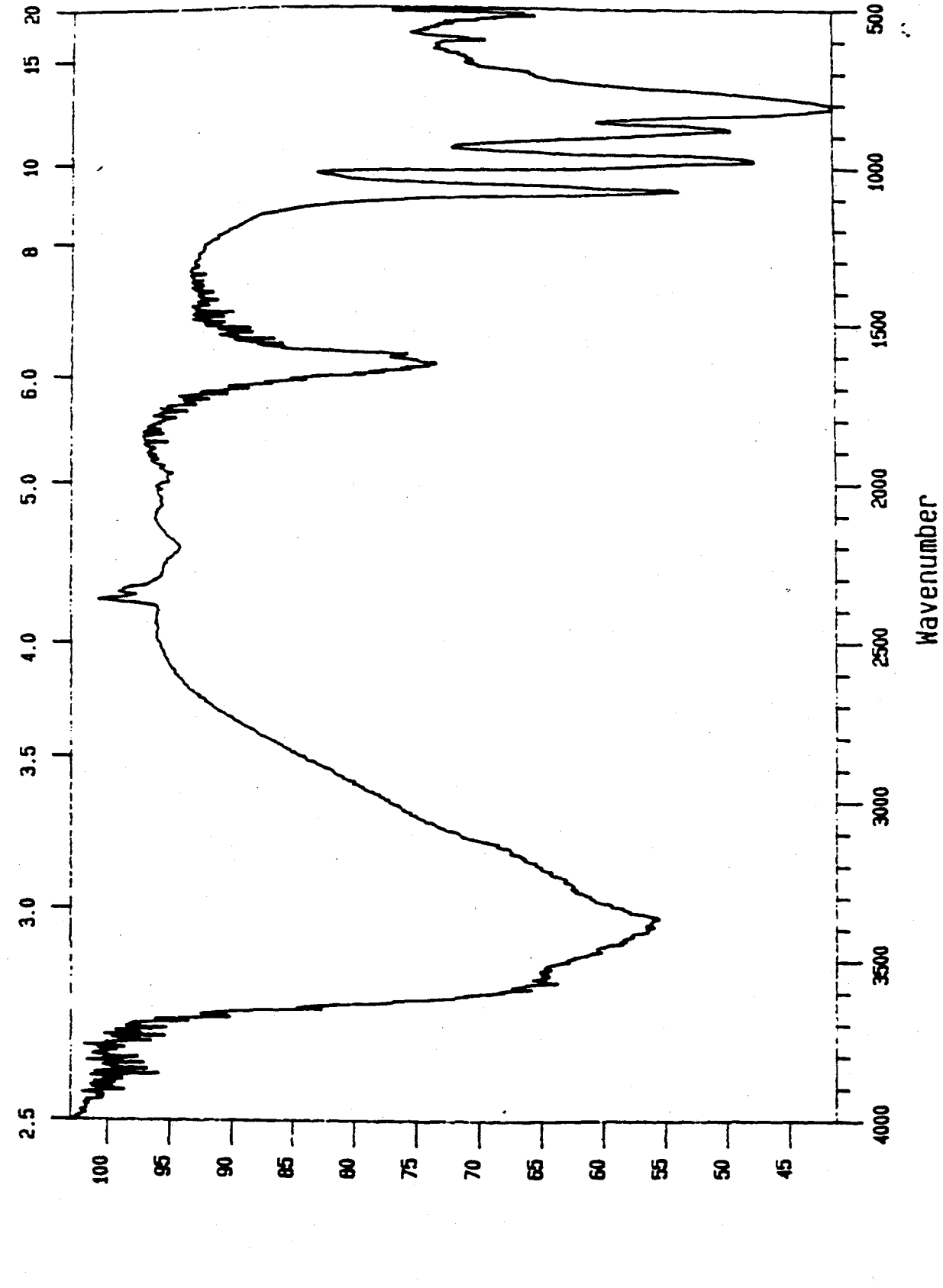


FIGURE 6.10b

INFRARED SPECTRUM OF β-K [$PW_9Fe_3O_{37}$] IN THE POA FINGERPRINT REGION (1500-500) cm^{-1}

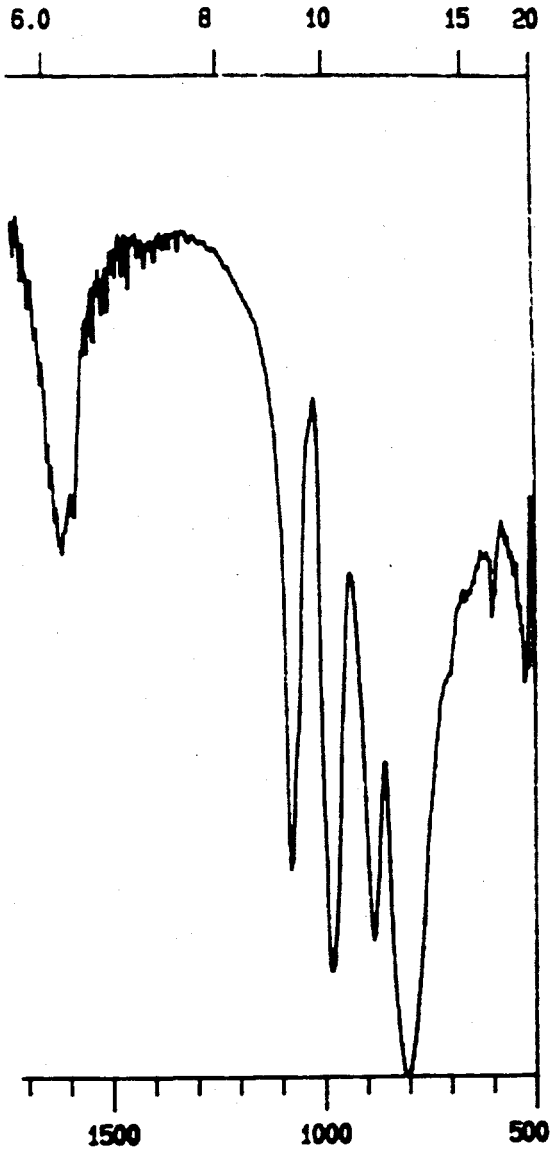


FIGURE 6.11a INFRARED SPECTRUM OF $K_6[PW_9Cr_3O_{37}]$

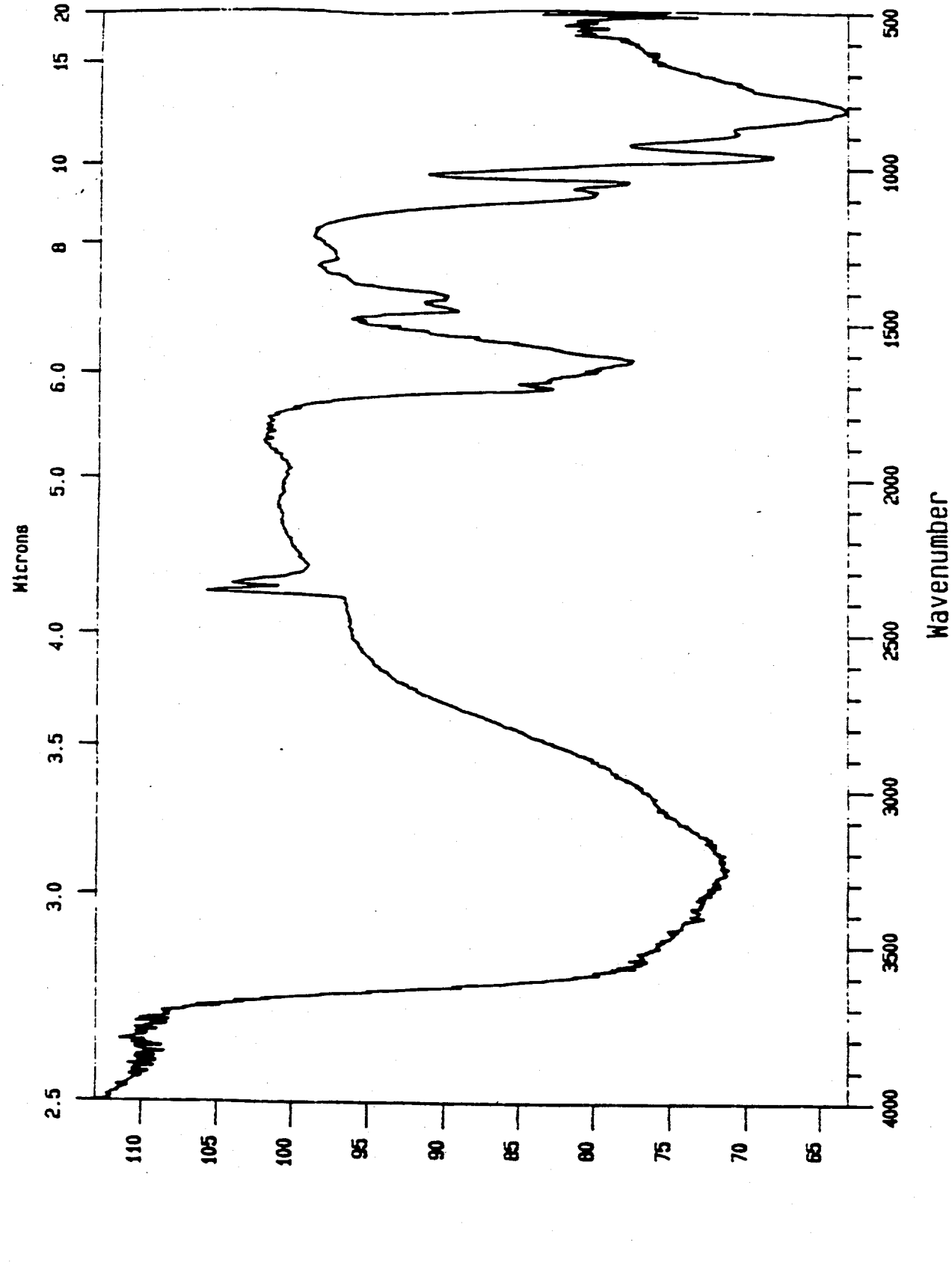
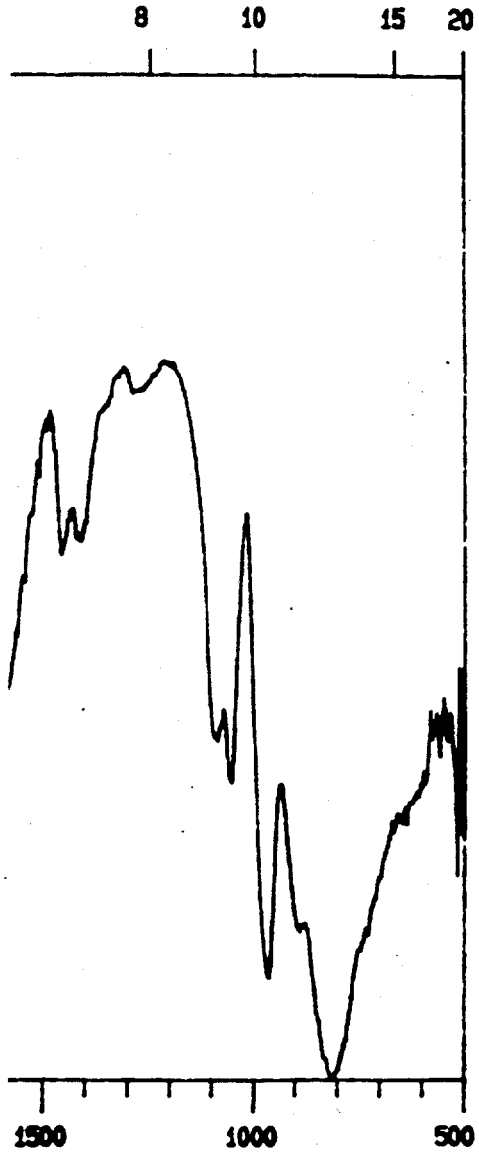


FIGURE 6-11b

INFRARED SPECTRUM OF β-$K_6[PW_9Cr_3O_{37}]$ IN THE POA FINGERPRINT REGION (1500-500 cm-1)



6.6.1.3 Preparation of 1,4,9-$K_6[PW_9V_3O_{40}]$

This complex is prepared by the method of Domaille and Watunya*. 2.0 g of $NaVO_3$ is powdered then dissolved in 100 ml of water with stirring. Slowly, 3MHCl is added to reduce the pH to 0.8. Any V_2O_5 formed at this point is removed by filtration. 15.0 g of B-$Na_9[PW_9O_{34}]$ is added to the stirring solution in small portions. The red solution is heated to 90° and 10 g of KCl is added, then the volume reduced to 670 ml by evaporation. Cooling the solution to 40-60° sometimes produces some yellow precipitate which is removed by filtration. the filtrate is cooled overnight in the refrigerator to produce red-orange crystals. Yield 10.1 g. IR examination, Figure 6.12 reveals the 600-1200 cm^{-1} metal-oxygen stretching region to be identical to that found by Domaille.

6.6.1.4 Preparation of $[Ru_3O(CO_2CH_3)_6(H_2O)_3](CO_2CH_3)$

The following materials are charged to a flask with condenser:

2.0 g. of $RuCl_3 \bullet XH_2O$
4.0 g. of Sodium Acetate
50 ml of Glacial Acetic Acid
50 ml of Ethanol

This solution is refluxed for 4 hrs. The mixture is cooled in a dry ice/acetone bath for 2 hrs., then filtered cold. The filtrate is rotovapped to dryness and redissolved in methanol, filtered then evaporated to dryness again. the material is dried in vacuo over P_2O_5 with no heat.

6.6.1.5 Preparation of $K_6[PW_9Ru_3O_{37}]\bullet XH_2O$

This material is prepared in an identical fashion to $K_6[PW_9Fe_3O_{37}]$, (cf. First Quarterly Report) however, 2.36 g $Ru_3O(CO_2CH_3)_6(H_2O)_3](CO_2CH_3)$ is substituted for $Fe_3(CO_2CH_3)_6(OH)_2Cl$ in the preparation. The green complex is purified as with the Fe complex by ion-exchange chromatography. IR analysis reveals a trisubstituted Keggin ion metal-oxygen stretching region from 800-1200 cm^{-1}(Figure 6.13).

*P. J. Domaille and G. Watunya, Inorg. Chem., 25, 1239 (1986).

FIGURE 6-12

INFRARED SPECTRUM OF 1,49-$K_6[PW_9V_3O_{37}]$ IN THE POA FINGERPRINT REGION (1500-500 cm^{-1})

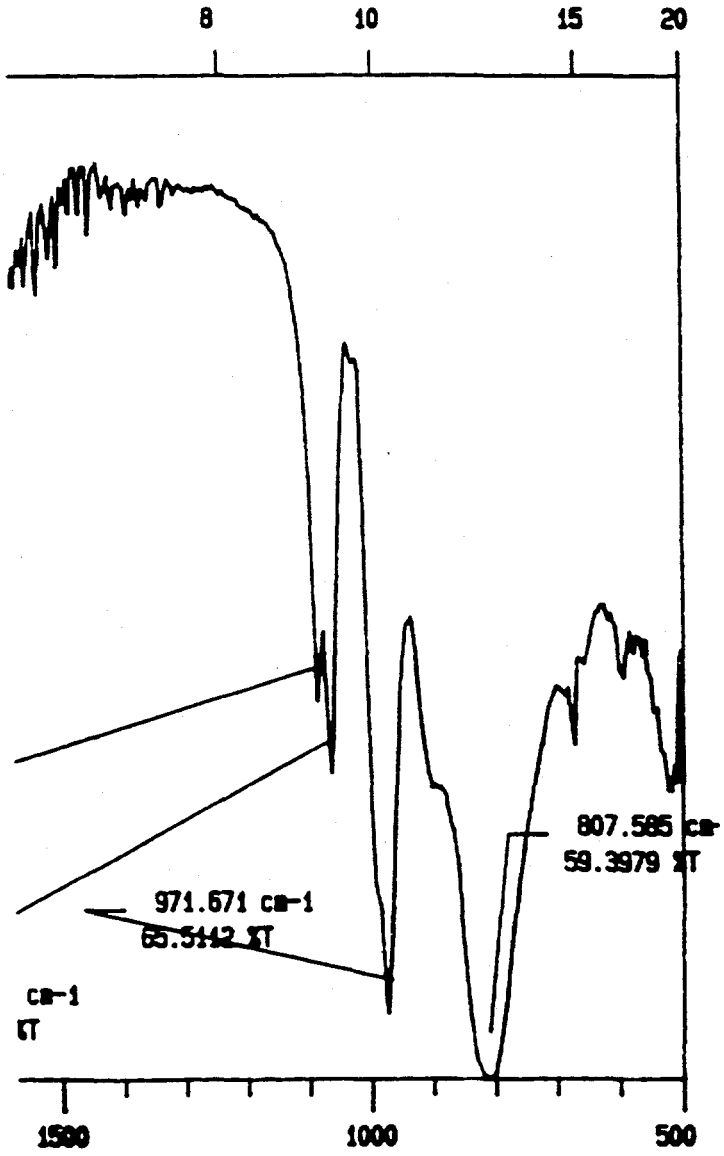
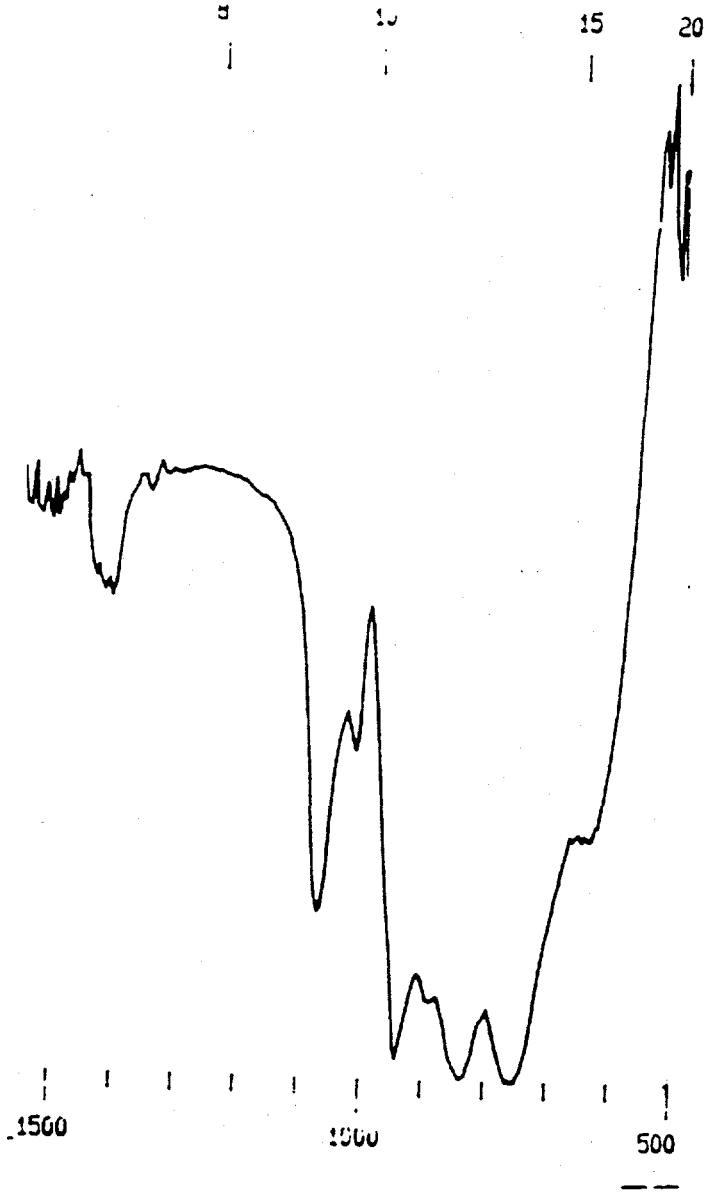


FIGURE 6-13

INFRARED SPECTRUM OF β-$K_6[PW_9Ru_3O_{37}]$ IN THE POA FINGERPRINT REGION (1500-500 cm^{-1})



6.6.2 Testing of Trimetal Substituted Keggin Ions

The goal of the 1990 PHASE II work plan was to prepare, characterize and test six soluble transition metal substituted Keggin structures having the formula:$[Bu_4N]_6[PW_9M_3O_{37-40}]$ wherein M = V, Cr, Mn, Fe, Ru, and M' (M' = an unspecified transition metal. It became evident after synthesizing and testing four of the six planned complexes that the tetrabutylammonium $[Bu_4N]$ moiety was not stable to oxidation. We then converted the tetrabutylammonium complexes to the acid forms: $H_6[PW_9M_3O_{37-40}]$ wherein M = V, Cr, Fe, and Ru and found that they are active catalysts in acetonitrile.

Synthesis of all of the tri-metal framework substituted Keggin structures have been reported in earlier Quarterly Reports. In this report we will disclose the results of the isobutane and propane test reactions done on these complexes.

6.6.2.1 Oxidation of Isobutane

As we discussed in the Third Quarterly Report, it was necessary for us to modify our isobutane screening procedure for polyoxometallates due to problems associated with catalyst solubility. We are now conducting isobutane oxidations catalyzed by polyoxometallates in acetonitrile at 80-125°C using 0.005 mg of catalyst. The porphyrin catalysts were screened in benzene at 25-60°C using a higher catalyst concentration.

Table 6-4 shows the results of the oxidation of isobutane at 100 and 125°C in the presence of azide-promoted $H_6[PW_9Fe_3O_{37}]$ as catalyst. The striking difference which is noted between these runs and the metalloporphyrin catalysts, Table 6-5, is that whereas $Fe(TPPF_{20}\beta\text{-}Br_8)$ produced almost exclusively (93 mole %) tert-butyl alcohol (TBA) with only traces of tert-butyl hydroperoxide (TBH), $H_6[PW_9Fe_3O_{37}]$ produced a mixture of both TBA and TBH in major amounts. Although the mechanism of C-H bond cleavage may be similar, subsequent steps are quite different for these two catalyst types.

TABLE 6-4

OXIDATION OF ISOBUTANE CATALYZED BY $H_6(PW_9Fe_3O_{37})$[a]

	REACTION TEMP., °C	
	125	100
Molar Selectivity to TBA, %	53	43
Conversion of i-Butane, %	19.9	14.8
Product[b] Anal., Wt. %		
Isobutane	1.00	0.98
Di-t-Butyl Peroxide	0.51	0.34
Acetone	2.98	1.05
t-Butyl Alcohol	15.48	10.40
i-Butyl-t-Butyl Peroxide	0.12	0.02
Acetonitrile	68.16	72.18
2-Methyl-1-Propanol	0.12	0.09
t-Butyl Hydroperoxide	11.45	14.83
Isobutyric Acid	0.16	0.09
	99.98	99.98

a Propane, 1.36 moles was added to a solution of 5μ moles catalyst in 38 ml acetonitrile containing 100 mg of NaN_3 and heated under 1000 psig air for 3 hrs.

b Analysis of liquid reactor effluent after gases had been stripped at room temperature.

TABLE 6-5

LIQUID REACTOR EFFLUENT FROM ISOBUTANE OXIDATION[a]
CATALYST=Fe(TPPF$_{20}$β-Br$_8$

PEAK	COMPOUND	WT. %
1	Isobutane	3.36
2	t-Butylisopropylether	0.28
3	Methyl Formate	0.33
4	Di-t-Butyl Peroxide	1.99
5	Isorpopyl-t-Butyl Peroxide	0.19
6	Acetone	3.89
7	t-Butyl Formate	0.09
8	t-Butyl Alcohol	86.66
9	Isobutyl-t-Butyl Peroxide	0.38
10	Isopropyl Alcohol	1.28
11	Isobutyl Formate	0.05
12	Isobutyl Alcohol	1.23
13	t-Butyl Hydroperoxide	0.09
14	Isobutyric Acid	0.14
	TOTAL	99.96

a Isobutane was oxidized by an oxygen-containing gas mixture (75 atm. diluent = N_2) in the liquid phase (180 ml) for 3 hours. Oxygen added as consumed.

6.6.2.2 Oxidation of Propane

We oxidized propane at 150°C, Table 6-6, made several runs on methane and ethane using PHASE II catalysts. Methane was oxidized in the presence of $H_6 PW_9Fe_3O_{37}$ but rates and yields were low.

Table 6-6

Liquid Phase Oxidation Of Alkanes Using Heteropolyacid Catalysts

SUBSTRATE	CATALYST	T°C	T.O'S[a]	IPA/A[c]
Propane[b]	None	150	0	--
	$H_3PW_{12}O_{40}$	150	750	0.85
	$H_6PW_9Fe_3O_{37}$	150	2240	0.65
	$H_6PW_9Fe_3O_{37}\bullet NaN_3$	150	8110	0.61
	$H_4PW_{11}FeO_{39}\bullet NaN_3$	150	2034	0.52
	$Fe_3O(OAc)_6(OH)_3$[c]	150	20	na
	$Fe_3O(OAc)_6(OH_3$[c]$\bullet NaN_3$	150	190	0.53
	$H_6PW_9Cr_3O_{37}$	150	4420	0.47
	$H_6PW_9Cr_3O_{37}\bullet NaN_3$	150	5550	0.52
Methane	$H_6PW_9Fe_3O_{37}$	280	50	

a Moles propane / mole catalyst used.

b Propane, 1.36 moles was added to a solution of 5μ moles catalyst in 38 ml acetonitrile and heated under 1000 psig air for three hours.

c 44μ mole catalyst used.

6.7 MIXED TRIMETAL SUBSTITUTED KEGGIN IONS

Thus, we have found superior routes to triiron and trichromium Keggin ions and compared their oxidation activity with the corresponding monoiron and monochromium compounds. The trimetal species were clearly the superior catalysts for light alkane oxidation. The trimetal Keggin systems were of interest because they possessed M-O-M bonding similar to that in MMO. We were curious whether the Keggin structure could participate in electron withdrawal similar to that found in the haloporphyrin ring, and if metal oxo species could be formed which could give active oxidation catalysts.

It became of interest to us to prepare and test trimetal systems in which two of the metals were iron and the third could be varied. In other words we were interested in the effect of the third substituted metal on the Fe-O-Fe system in a trimetal Keggin complex. In the following sections we present the synthetic methods and alkane oxidation test data on these complexes.

6.7.1 Synthesis of New Keggin Structures

We report here the synthesis of a number of Keggin structures for use as light alkane oxidation catalysts. In the last quarterly report we described the synthesis of $K_6[PW_9Fe_3O_{37}]$ and $K_6[PW_9CrO_{37}]$. The POA fingerprint region for these complexes is shown in Figures 6.11a and 6.11b for purposes of comparison with those complexes whose spectra we will describe for the first time in subsequent sections of this report.

We have synthesized $[Bu_4N]_7[PW_9MFeIII_2O_{37}]$ wherein M = Mn(II), Fe(II), Ni(II), Zn(II) and Co(II). For the reasons given above, these complexes were converted to their acid form and screened for isobutane and propane activity in acetonitrile. The results of these reactions are disclosed in this Report. A limited amount of ethane and methane screening was also performed.

Two of the azide forms of these catalysts, were also prepared.

6.7.2 Preparation of the Acid Forms of "Fe_2M" POA's

In Section 6.4.2, we reported a novel method for converting the sodium or potassium salts of the trimetal framework substituted POA's to their acid salts by converting them to the corresponding tetrabutylammonium salts which were then pyrolyzed to the heteropolyacid. New oxidation-active complexes were prepared from the "Fe_2M" POA's (M = Zn, Mn, Ni, Co) by this method.

6.7.2.1 Preparation of $Fe_2M^{II}(CH_3CO_2)_6(H_2O)_3]\bullet XH_2O$ $M^{II} = Mn^{II}, Zn^{II}, Co^{II}, Ni^{II}$

These complexes are prepared by the method of Blake*, et.al. As an example the detailed synthesis of the Mn^{II} complex is shown here.

A solution of 42.0 g of sodium acetate in 70 ml of H_2O is added to a filtered, stirring solution of 2.87 g (.01 mole) of $Mn(NO_3)_2\bullet 6H_2O$ and 8.0 g (0.02 mole) of $Fe(NO_3)_3\bullet 9H_2O$ in 70 ml of H_2O. A precipitate forms which is filtered, washed with H_2O and ethanol then dried at room temperature. The other complexes are made from their respective nitrate salts in a similar manner.

6.7.2.2 Preparation of $K_7[PW_9Fe_2M^{II}O_{37}]\bullet XH_2O$ $M^{II} = Mn^{II}, Zn^{II}, Co^{II}, Ni^{II}$

As an example, the preparation of $K_7[PW_9Fe_2Mn^{II}O_{37}]\bullet XH_2O$ will be described. 9.74 g of β-$Na_9[PW_9O_{34}]$ is dissolved in 100 ml of a warm (40-50°) aqueous solution buffered to pH of 6 with potassium acetate/acetic acid. When the solution clears 2.56 g of $Fe_2Mn^{II}(CH_3CO_2)_6(H_2O)_3]$

dissolved in 50 ml of H_2O is added with stirring. After cooling 10 g of KCl is added as the solution is reduced in volume until precipitation starts to occur. After overnight refrigeration, the precipitate, in this case yellow is filtered. Yield 7.60 g. This material can be recrystallized from warm water at pH = 2-3. IR analysis of these complexes are similar to those reported for $K_6[PW_9Fe_3O_{37}]$. The infrared spectrum of $K_6[PW_9Fe_2NiO_{37}]$ is shown in Figure 6.14.

* A.B. Blake, A. Yavari, W.E. Hatfield, and C.N. Sethulekshmi, J. Chem. Soc., Dalton Trans., 2509 (1985)

6.7.2.3 Synthesis of $H_7[PW_9Fe_2NiO_{37}]$

The tetrabutyl ammonium salt of $K_7[PW_9Fe_2NiO_{37}]$ - the prep of which was given earlier is prepared by dissolving the potassium salt in a minimum of water then saturating the aqueous solution with tetrabutylammonium bromide. The $(n\text{-}Bu_4N)_7[PW_9Fe_2NiO_{37}]$ is precipitated, filtered and recrystallized from acetonitrile.

$(n\text{-}Bu_4N)_7[PW_9Fe_2NiO_{37}]$, 2.5 g., was placed in the center of a one inch diameter quartz tube vertically held in a tube furnace with quartz wool and ceramic spacers. Nitrogen flowed upward through the quartz tube at 50 ml/min. The material was heated under nitrogen flow for 60 min at 400°C then cooled under flowing nitrogen to ambient conditions. The red-orange starting material had turned into a greyish-orange solid (1.2 gram recovery). The greyish carbonaceous material could be removed if desired by placing the material in Soxhlet thimble and extracting the colored soluble product into refluxing acetonitrile then evaporating the solution to dryness. The infrared spectrum of this product is shown in Figure 6.15.

FIGURE 6-14

INFRARED SPECTRUM OF β-$K_7[PW_9Fe_2NiO_{37}]$
THE POA FINGERPRINT REGION (1500-500 cm^{-1})

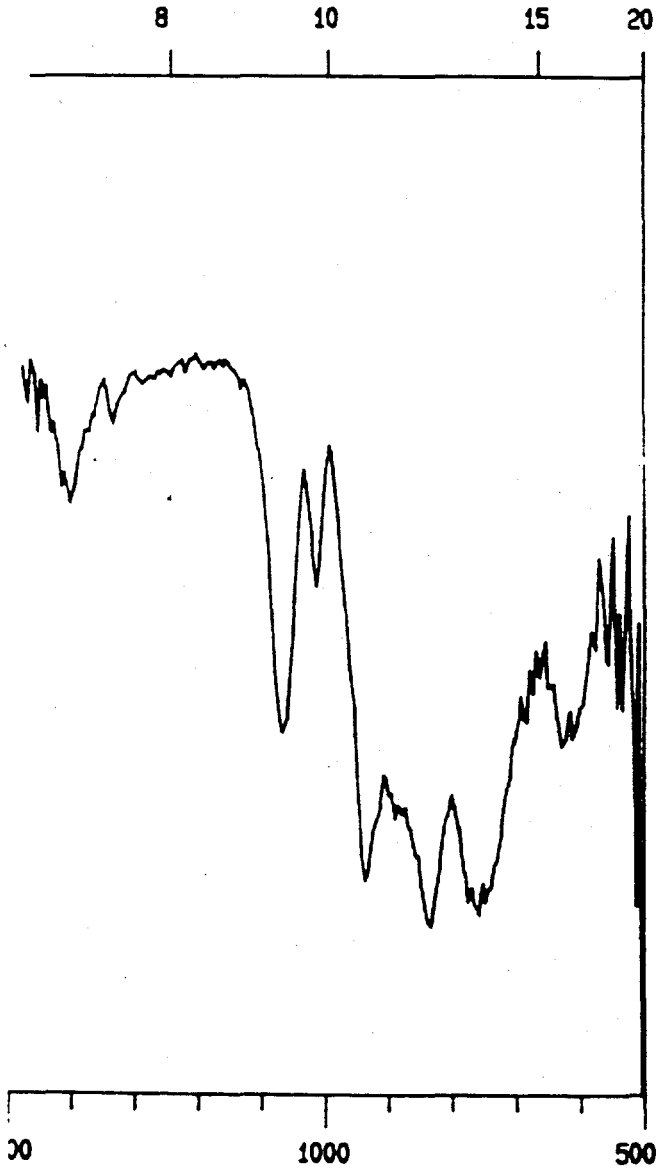
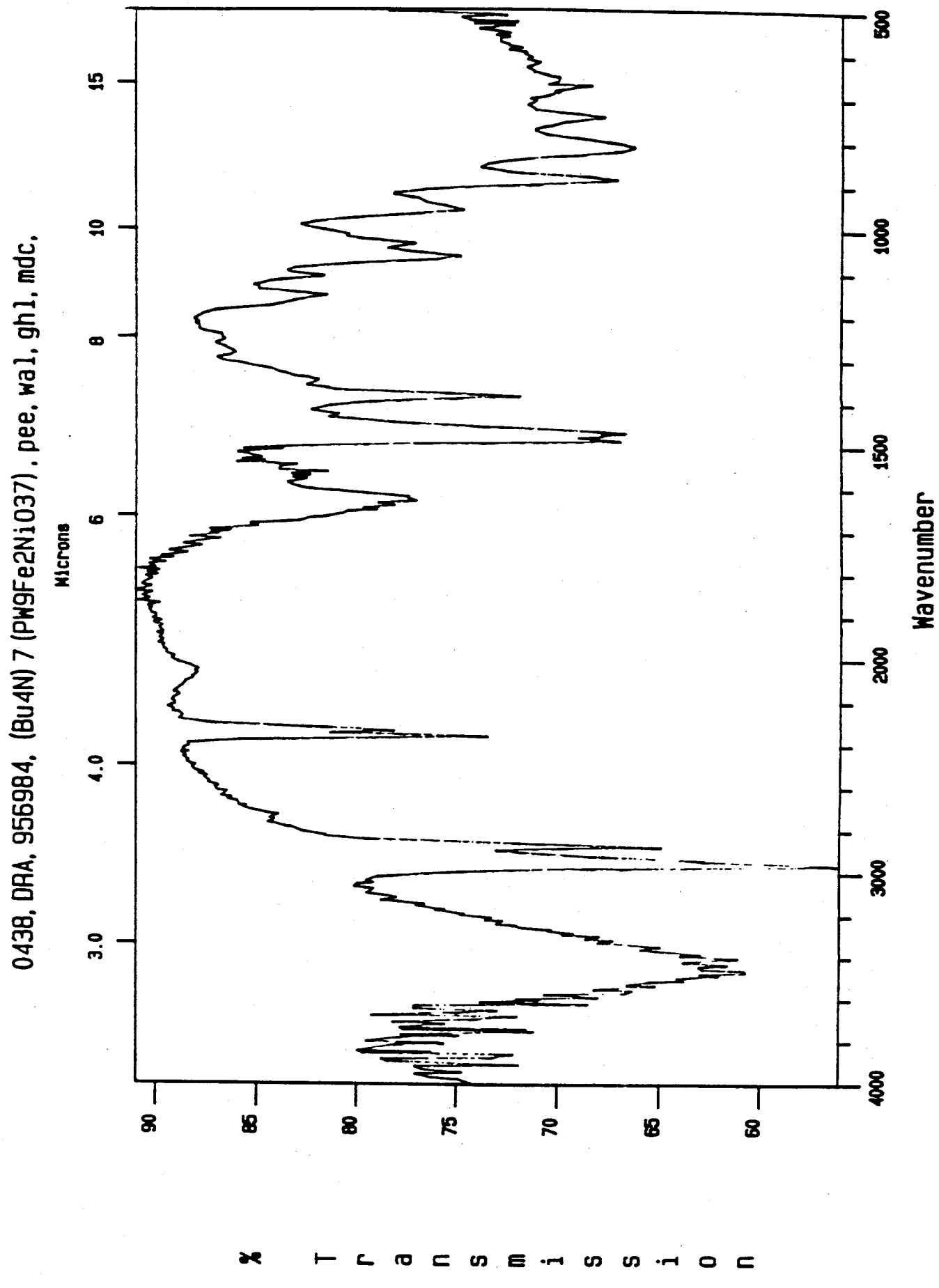


FIGURE 6.15


0438, DRA, 956984, (Bu4N) 7 (PW9Fe2Ni037), pee, wal, ghl, mdc,
Microns
3.0
4.0
6
8
10
15
Wavenumber
4000
3000
2000
1500
1000
500
% Transmission
90
85
80
75
70
65
60

6.7.2.4 Synthesis of $H_7[PW_9Fe_2CoO_{37}]$

$(n\text{-}Bu_4N)_7[PW_9Fe_2CoO_{37}]$ was prepared from $K_7[PW_9Fe_2CoO_{37}]$ in the manner described previously for the diiron-nickel complex. The tetrabutylammonium salt of the diiron-cobalt compound, 1.28 grams, was pyrolyzed in a quartz tube as described above at 400°C for one hour. After cleanup, 0.89 g of blue-green material was recovered.

6.7.2.5 Synthesis of $H_7[PW_9Fe_2MnO_{37}]$

The title complex was a brown solid, 0.95 grams, prepared from 1.48 grams of $(n\text{-}Bu_4N)_7[PW_9Fe_2MnO_{37}]$ in an analogous manner to the above preps.

6.7.2.6 Synthesis of $H_7[PW_9Fe_2ZnO_{37}]$

The title complex was a tan solid, 0.92 grams, prepared from 1.42 grams of $(n\text{-}Bu_4N)_7[PW_9Fe_2ZnO_{37}]$ in an analogous manner to the above preps.

6.7.2.7 Synthesis of $H_7[PW_9Fe_2VO_{38}]$

The title complex was an orange solid, 0.72 grams, prepared from 1.20 grams of $(n\text{-}Bu_4N)_7[PW_9Fe_2VO_{38}]$ in an analogous manner to the above preps.

6.7.2.8 Synthesis of $[Fe(III)_2Fe(II)(CH_3CO_2)_6(OH)_2{\bullet}4H_2O]$

A solution consisting of 30 grams $FeCl_2{\bullet}4H_2O$, 55.5 grams of $Ca(OAc)_2$ and 170 ml of glacial acetic acid is heated with stirring to 70°C while air was bubbled through the solution. After seven hours the brown solution was cooled and filtered giving 18.9 grams of dark brown powder (3).

6.7.2.9 Synthesis of $K_7[PW_9Fe(III)_2Fe(II)O_{37}]$

B-$Na_9[PW_9O_{34}]$ was dissolved in 300 ml of a buffered potassium/acetic acid solution at pH=6. To this solution we added 4.14 grams of $Fe(III)_2Fe(II)(CH_3CO_2)_6(OH)_2 \bullet 4H_2O$ in 150 ml of water. The solution was stirred for 15 min. at 50°C then cooled and excess powdered KCl added to help precipitation to occur. After refrigerating the solution overnight, a brown-black crystalline solid was obtained which yielded 5.80 grams of the title compound on filtration.

6.7.3 Testing of New Keggin Structures

As mentioned above, and in the first quarterly report, a number of sodium and potassium polyoxoanionic complexes were prepared with either one, two, or three oxidation active transition metals regioselectively substituted into the polyoxoanionic framework. Initial screening of these complexes while relatively successful, was complicated by the insolubility of these materials in most organic solvents. Elaborate solvation schemes were devised to study oxidations of light alkanes. Reactions were not convenient to carry out.

As we reported Section 6.4.2, we have devised a novel method for preparing the corresponding transition metal substituted heteropolyacids which have at least limited solubility in some polar aprotic solvents. Although we are still in the process of acquiring characterization data, we find that the framework-substituted heteropolyacids derived from "Fe_2M" complexes can be studied in acetonitrile solution and that they are active for the air-oxidation of propane in this medium. Ethane and methane are also oxidized in solutions of these complexes but rates are slow and selectivities low.

It is clear from the results obtained that the third metal in a "Fe_2M" framework exchanged system has a significant effect on the activity of the catalyst for alkane oxidation. The effectiveness of M decreases in the order: Ni>Fe>Zn~Mn>Co.

6.7.3.1 Oxidation of Isobutane

The screening reactors used for testing the perhaloporphyrin complexes for oxidizing isobutane in benzene proved to be inadequate for screening metallo Keggin catalysts for oxidizing isobutane in acetonitrile due to the solubility problems alluded to earlier. Although a number of runs were conducted and isobutane was oxidized at 80°C, these results may be misleading because of poor solubility and will not be reported here. We have now modified our testing procedure, and, though more laborious, the new procedure will circumvent the solubility problems experienced previously for reactions carried out at or above 80°C. Although our screening process was planned for 25-60°C, it became desirable to carry out PHASE II isobutane screening from 80-125°C.

Table 6-7 shows that when multi-nuclear first row group VIII metal centers are inserted into Keggin structures, active catalysts are formed for isobutane oxidation, but that hydroperoxides are major reaction products together with tert-butyl alcohol, TBA, acetone, and other by-products. Table 6-7 also indicates that, although the tri-metal substituted Keggin complexes are active high temperature catalysts (>100°C), they are not nearly as active as the perhaloporphyrin complexes at low (<100°C) temperatures. We suspect that the difference in the catalytic performance of the tri-metal Keggin catalysts and the perhaloporphyrin complexes is due to the greater ease with which the metalloperhaloporphyrins return to a low oxidation state and activate molecular oxygen. We believe

that the presence of binuclear metal sites is beneficial but that these catalysts would be even more active if *their reduction potential were higher. The reduction potential of the iron(III) sites in the tri-iron Keggin ion:* $K_6[PW_9Fe_3O_{37}]$ is quite low having a half wave potential of about -0.2 for the simultaneous reduction of all three Fe(III)'s to Fe(II). This is not much above the value obtained for the un-halogenated porphyrin and if plotted on the graph of oxidation activity versus Fe(III)/Fe(II) reduction potential would predict relatively low oxidation activity.

Table 6-7 shows the results of the oxidation of isobutane using a number of Keggin ion catalysts both with and without azide promotion. We have found that although virtually no hydroperoxides were found among the products of metalloporphyrin-catalyzed isobutane oxidations, polyoxometallate-catalyzed isobutane oxidations gave large amounts of tert-butyl hydroperoxide together with tert-butyl alcohol. The yield of di-tert-butyl peroxide though small, was higher in the oxidations catalyzed by polyoxometallates than in reactions catalyzed by metalloporphyrin complexes. This suggests that either the polyoxometallates catalyze alkane oxidations by a different mechanism than do the metalloporphyrins, or that the metalloporphyrins convert tert-butyl hydroperoxide to TBA far more rapidly than do the polyoxometallates. the polyoxometallates used so far have extremely low or no activity at 60°C or lower. At this time, the perhaloporphyrins appear to be superior to the polyoxometallates examined to date for the low temperature oxidation of isobutane to tert-butyl alcohol both from the standpoint of rate and reaction selectivity. The polyoxometallates, however, have superior high temperature stability and may prove to have advantages in oxidizing the more refractory alkanes, methane and ethane.

6.7.3.2 Oxidation of Propane

Table 6-8 shows the results of the low temperature oxidation of propane catalyzed by five of the polyoxoanions synthesized during 1990 on PHASE II of the Cooperative Agreement. Oxidations were carried out both with and withoutaddition of sodium azide as a promoter.

TABLE 6-7

ISOBUTANE OXIDATIONS CATALYZED BY POLYOXOMETALLATES[a]

Catalyst - μMoles		Temp (°C)	t, hrs	Products, MMoles			$i\text{-}C_4$ Conv. %	TBA Sel., %	TON Moles Pro Mole Cat
				Acetone	TBA	TBH			
Azide Promoted:[b]									
$H_6(PW_9Fe_3O_{37})$	- 5	125	2.5	24	102	62	19	54	37,670
	- 5	100	7.0	8	62	72	14	44	<8,340
	- 2	80	3.0	1	11	4	2	64	3,320
$H_6(PW_9Fe_2VO_{38})$	- 5	125	4.6	23	97	66	20	50	39,180
	- 5	100	6.0	13	63	31	11	55	22,940
	- 5	80	6.0	1	3	7	1	21	2,480
$H_7(PW_9Fe_2CoO_{37})$	- 5	125	2.5	24	107	61	21	52	41,260
	- 5	100	6.0	5	13	35	6	22	11,860
	- 5	80	6.0	2	8	12	2.5	32	5,000
$H_7(PW_9FeMnO_{37})$	- 5	125	2.3	21	76	56	16	46	32,720
	- 5	100	6.3	36	108	22	18	61	35,230
	- 5	80	6.0	na	3	3.5	na	na	na
$H_5(PW_{10}V_2O_{40})$	- 5	125	2.3	21	93	29	17	56	33.060
	- 5	100	7.0	19	105	37	17	61	34,180
	- 5	80	6.0	2	2	1	1	23	1,580
$H_7(PW_9Cr_3O_{37})$	- 5	125	3.2	31	103	6	15	67	33,060
	- 5	100	6.0	20	101	36	16	61	32,770
	- 5	80	6.0	2	2	2	1	22	1,500
No Azide Added:									
$H_6(PW_9Fe_2VO_{38})$	- 5	100	6.5	4	7	24	4	20	7,080
$H_7(PW_9Fe_2CoO_{37})$	- 5	100	6.0	3	5	22	3	17	6,000
$H_7(PW_9Fe_2MnO_{37})$	- 5	100	6.0	4	8	22	3.5	23	2,000
$H_7(PW_{10}V_2O_{40})$	- 5	100	6.2	4	10	22	4	28	7.200
$H_7(PW_9Cr_3O_{37})$	- 5	100	6.0	23	132	45	20	66	40,000

[a] Isobutane, 1.0 mole, was added to the catalyst in 37.7g of acetonitrile and 1500 psig of air added to the reactor. The reaction mixture was heated for the designated time cooled and analyzed by GC.

[b] Sodium azide, 0.10g, was added to the reaction mixture before heating.

TABLE 6-8

PROPANE OXIDATIONS CATALYZED BY POLYOXOMETALLATES[a]

CATALYST	ADDED AZIDE, GMS	/PA/ ACETONE	TON[b]
$H_7(PW_9Fe_2MnO_{37})$	0.1	0.4	154
	0.0	0.4	84
$H_7(PW_9Fe_2CoO_{37})$	0.1	0.3	126
	0.0	0.3	96
$H_7(PW_9Fe_2VO_{38})$	0.1	0.4	134
	0.0	na	~40
$H_5(PW_{10}V_2O_{40})$	0.0	0.3	123
$K_7(PW_9Cr_3O_{37})$	0.0	0.5	141

a Propane, 60gms, was added to the catalyst and sodium azide in acetonitrile and 1500 psig of air admitted to the reactor. The reaction mixture was heated at 125°C with stirring for 6 hours then cooled and analyzed by GC.

Comparison of the turnover numbers reported in Table 6-8 with those using perhaloporphyrin complexes shows that the metalloporphyrins are more active catalysts. In addition, the alcohol/ketone ratio was higher (0.8-1.0) when metalloporphyrins were used as catalysts than when polyoxometallates were used (0.3-0.5). On the other hand porphyrins begin to decompose over 150°C whereas the polyoxometallates exhibit high catalytic activity at this elevated temperature, Table 6-9. The polyoxometallates exhibit low methane and ethane oxidation activity at elevated temperatures.

6.7.3.3 Ethane Oxidations Catalyzed by Polyoxoanions

We have noted that polyoxoanions having the Keggin structure into which has been incorporated one or more oxidation-active first or second row transition metals have been active high temperature catalysts for oxidizing isobutane and propane. These catalysts did not have the low temperature catalytic activity that the metalloporphyrins exhibited nor did they give alcohols in as high selectivity. Ethane and methane can also be oxidized with the polyoxoanion catalysts since they are more robust at the higher temperatures (>200°C) than the porphyrin catalysts. Although methanol selectivity was not high, interesting selectivity was noted in the case of ethane oxidations, Table 6-10 carried out in benzonitrile (PhCN) or acetonitrile (ACN). Ethane can be oxidized using cobalt salts or other conventional catalysts or initiators used in high concentration at temperatures in the neighborhood of 200°C. Selectivity to ethanol (5%) is extremely low in these cases however. The majority of the products are C_1 compounds formed from cleavage of intermediate C_2 radicals. Thus, methanol, formaldehyde, formates, CO and CO_2 are formed with very low yields of methanol or acetaldehyde. We have found, Table 6-10, however, that when tetrabutyl ammonium salts of iron substituted Keggin complexes are used under the same conditions, ethanol is the predominant oxidation product. Investigations of light alkane oxidations using these complexes was, therefore, continued.

TABLE 6-9

LIQUID PHASE OXIDATION OF ALKANES USING HETEROPOLYACID CATALYSTS

SUBSTRATE	CATALYST	T,°C	T.O'S[a]	IPA/A[c]
Propane[b]	None	150	0	-
	$H_3PW_{12}O_{40}$	150	750	0.85
	$H_6PW_9Fe_3O_{37}$	150	8110	0.61
	$H_4PW_{11}FeO_{39}$	150	2034	0.52
	$Fe_3O(OAc)_6(H_2O)_3Cl$	150	190	0.53
	$H_7PW_9Fe_2NiO_{37}$	150	9730	0.71
	$H_7PW_9Fe_2ZnO_{37}$	150	5640	0.65
	$H_7PW_9Fe_2MnO_{37}$	150	5570	0.65
	$H_7PW_9Fe_2CoO_{37}$	150	3290	0.70
	$H_7PW_9Fe_2MnO_{37}$	125	158	0.30
	$H_7PW_9Fe_2CoO_{37}$	125	125	0.40
Ethane	$H_7PW_9Fe_2NiO_{37}$	200	240	
Methane	$H_6PW_9Fe_3O_{37}$	280	50	

a Moles propane/mole catalyst used.

b Propane, 1.36 moles was added to a solution of 5μ moles catalyst in 38 ml acetonitrile and heated under 1000 psig air for 3 hours.

c 44μ molar catalyst used.

TABLE 6-10

LIQUID PHASE OXIDATION OF ETHANE CATALYZED BY METAL-SUBSTITUTED KEGGIN STRUCTURES[a]

Catalyst-mmole	T °C	t, Hrs.	Pair psi	Solvent-g.	C_2 Chg.-g.	Products, mmoles EtOH	MeOH	CH_3CHO	CO	CO_2	T.O.	Ethane Conv.
None	200	3	180	PhCN-76	11	0.57	0	0	0	1.1		
$H_7[PW_9Fe_2NiO_{37}]$-0.018	200	3	170	PhCN-76	11	4.35	na	1.35	0.8	2.0	470	1.9
	225	3	170	PhCN-76	11	4.97	na	1.50	2.8	4.0	740	2.7
	250	3	170	PhCN-76	11	5.86	3.21	0.81	2.3	3.2	850	3.0
None	200	3	170	ACN-59	9.1	0.68	0	0	0	2.0		
$H_7[PW_9Fe_2NiO_{37}]$-0.018	200	3	170	ACN-59	11	5.19	1.40	0.58	1.6	3.2	660	2.4
None	200	3	170	ACN-59	46	0.51	0	0	0	1.8		
$H_7[PW_9Fe_2NiO_{37}]$-0.018	200	3	170	ACN-59	39	3.19	3.49	0.47	0.7	1.9	540	2.0
$H_6[PW_9Fe_3O_{37}]$-0.018	200	3	170	ACN-59	47	5.46	2.27	0.75	1.4	3.4	660	2.7
$H_6[PW_9Fe_3O_{37}]$-0.018	200	3	500	ACN-59	45	7.73	2.53	0.58	2.8	9.0	1130	4.2
Co(II)Naphthenate-0.2	200	3	483	ACN-59	39	0.59	10.67	tr	1.4	11.0	120	3.3
	200	3	170	ACN-59	44	0.75	8.12	tr	0.5	5.0	72	2.1

[a] Ethane was oxidized in a glass lined, stirred autoclave under the conditions given in the table. Gas and product analysis by g.c.

6.8 t-BUTYLAMMONIUM SALTS OF KEGGIN ION CATALYSTS

During the first year of the Cooperative Agreement we synthesized and tested a series of soluble polyoxometallates into which one or more oxidation-active transition metal centers had been inserted. These materials were more oxidatively and thermally stable than porphyrins but had lower organic solubility and were more prone to decomposition by solvolytic processes. Complexes were generated having adjacent metal centers for possible cooperative binding of dioxygen. One of these centers could be in the divalent oxidation state necessary to bind O_2. Nonetheless, we found that the low temperature oxidation activity of the polyoxometallate complexes was not as high as that of the metalloporphyrins. To circumvent the organic solubility problems, we prepared a series of tetrabutyl ammonium salts of the Keggin-ion catalysts: $(Bu_4N)_6(PW_9Cr_3O_{37})$, $(Bu_4N)_6(PW_9Fe_3O_{37})$, and $(Bu_4N)_7(PW_9Fe_2NiO_{37})$. These complexes had excellent solubility in acetonitrile. Despite the oxidative instability of the tetrabutylammonium cation, we attempted oxidations of isobutane at 80°C in relatively concentrated acetonitrile solutions. This work showed that the activity of the tetrabutylammonium salts was less than that of the Phase I iron perhaloporphyrin complexes.

6.8.1 Synthesis of Tetrabutylammonium Salts of Keggin Ions

In past quarterly reports we have synthesized the potassium salts of Keggin ions and used them as catalysts for alkane oxidations. As we have noted, however, the solubility of these complexes makes it difficult to find suitable media in which to use them as homogeneous catalysts. Increased solubility can be obtained using the protic form, but the catalysts are strong acids with somewhat different properties. The protic form of Keggin ions having proximate oxidation-active metal centers were active for isobutane oxidation but gave very poor TBA selectivity and produced the

alkylhydroperoxide as a major reaction product. We have synthesized a number of tetrabutylammonium salts of the same Keggin ions. They have good acetonitrile solubility and can be used conveniently as homogeneous catalysts for alkane oxidation.

6.8.1.1 Synthesis of $(Bu_4N)_6[PW_9Fe_3O_{37}]$

The potassium salt, $K_6[PW_9Fe_3O_{37}]$, 3.0 grams, was dissolved in 20 ml water (HPLC grade) with warming and the acidity of the clear green solution adjusted to pH = 1.0 with 3M HCl. An aqueous solution of tetrabutyl ammonium chloride (9.1% by weight), 11 ml, was added to the green solution of Keggin ion and a mint green precipitate immediately formed. This solution was filtered and the solid washed with 150 ml of an acidic aqueous solution of pH = 1. The solid was recovered and dried in vaccuo. A hot, saturated solution in acetonitrile was filtered free of a white solid and the volume of the green solution reduced by standing in an evaporating dish. A green solid slowly formed which was recovered (0.600 grams) and dried.

6.8.1.2 Synthesis of $(Bu_4N)_6[PW_9Cr_3O_{37}]$

The potassium salt, $K_6[PW_9Cr_3O_{37}]$, 14 grams, was dissolved in 250 ml water and the pH adjusted to unity using conc. HCl. A solution of 14 grams of tetrabutylammonium chloride in 50 ml HPLC grade water was prepared and added to the original solution of the Keggin ion. A light blue precipitate immediately formed. After stirring the suspension of blue solid for one hour it was filtered and washed with 150 ml of an acidic aqueous solution of pH = 1. The blue solid was recovered and dried in vacuuo. Acetonitrile, 10 ml, was then added to the solid and the suspension stirred at reflux and the suspension filtered hot to give a clear green filtrate. The filtrate was poured into an evaporating dish and the liquid volume was reduced by evaporation at room temperature until dark green solid appeared. A dark green solid was recovered in this manner (0.800 gram) and dried.

6.8.1.3 Synthesis of $(BuN_4)_7[PW_9Fe_2NiO_{37}]$

The potassium salt, $[K[PW_9Fe_2NiO_{37}]$, 15 grams, was dissolved in 200 ml of water and the acidity adjusted to pH = 1.0 by adding conc. HCl to give a tan colored solution on gentle warming. A solution of 15 grams tetrabutylammonium bromide in 40 mls water was then added and a yellow-green solid precipitated. The solid was washed with aqueous acid and recrystallized from hot acetonitrile as above giving 1.3 grams of a greenish-tan solid.

6.8.2 Isobutane Oxidations Using Phase II Catalysts

In an earlier quarterly report a comprehensive study of the use of the acid form of a number of Keggin structures showed that although active above 100°C, these catalysts performed poorly as catalysts for low temperature oxidation of isobutane. At 80°C rates of oxidation were slower than when perhaloporphyrin catalysts were used and at all temperatures reaction selectivity was low. Catalysts were used in their acid form because in this form they had greater organic solubility. We wondered, however, whether the low selectivity might be due to the strong acid character of these materials. As mentioned above, we have now synthesized a number of Keggin ions in their tetrabutylammonium form and find that they have even greater solubility in polar organics than the heteropoly acids. These catalysts dissolve readily in acetonitrile and homogeneous catalytic oxidations of isobutane can be conveniently carried out. Table 6-11 shows, however, that rates are comparable to the acid forms and selectivities are no better. Large amounts of the hydroperoxide are formed and cleavage to acetone is a major reaction pathway.

TABLE 6-11

ISOBUTANE OXIDATIONS CATALYZED BY POLYOXOMETALLATES[a]

CATALYST - mmoles	t HRS.	PRODUCT, mmoles TBA	TBH	ACETONE	iC_4 Conv.%	TBA SEL.,%	TON moles PROD/mole CAT
$(Bu_4N)_6(PW_9Cr_3O_{37})$ - 6	6	6	11	2	2	32	3,200
$H_6(PW_9Cr_3O_{37})$ - 5	6	2	2	2	1	22	1,500
$(Bu_4N)_6(PW_9Fe_3O_{37})$ - 6	6	2	5	1	1	22	1,300
$H_6(PW_9Fe_3O_{37})$ - 2	3	11	4	1	2	64	3,300
$(Bu_4N)_6(PW_9Fe_2NiO_{37})$ -6	6	6	8	2	2	37	2,700
$H_6(PW_9FeNiO_{38})$ - 5	6	8	12	2	2.5	32	5,000
$(Bu_4N)_6(PW_9FeNiO_{38})$ - 6[b]	6	9	10	9	3	33	4,700

[a] Isobutane, 1.0 mole, was added to the catalyst and sodium azide, 0.10 g in 37.7 g of acetonitrile and 1500 psig of air was added to the reactor. The reaction mixture was heated for the designated time colled, and analyzed by gc.

[b] No sodium azide added to this run.

To date we have been able to prepare no polyoxometallate catalysts which are as efficient or as selective for the low temperature oxidation of isobutane to tert-butyl alcohol as are the iron perhaloporphyrins. As we noted in the last quarterly report, we believe that one of the problems with the low temperature activity of the polyoxometallates is the relatively low M^{+3}/M^{+2} reduction potential of metals in the framework. If we are to create a truly active homogeneous catalytic polyoxometallate, this problem must be solved.

6.9 DI-METAL SUBSTITUTED KEGGIN IONS

In past sections we have disclosed the preparation, characterization and testing of complexes of polyoxometallates containing either one oxidation-active metal center or three proximate active metal centers. It was one of the major goals of this phase of the Cooperative Agreement to prepare, characterize and test polyoxometallate complexes that have two proximate metal centers. We therefore prepared and characterized complexes having the structure: $K_6[M_2SiW_{10}O_{38}]$. We have prepared the dilacunar precursor: $K_8[SiW_{10}O_{36}]$, and reacted it with di-iron and di-chromium complexes to form the novel complexes: $K_6[Fe_2SiW_{10}O_{38}]$ and $K_6[Cr_2SiW_{10}O_{38}]$ for the first time. We then converted these complexes to their organic-soluble tetrabutylammonium forms and tested their activity for the oxidations of light alkanes, (C_1-C_4). It has long been our goal to prepare and test complexes having two proximate oxidation-active metal centers in a polyoxoanionic ligand system for light alkane oxidation but until recently synthetic routes for their synthesis have not been available.

6.9.1 Synthesis of Diiron Substituted Keggin Ions

6.9.1.1 Preparation of $[(acac)_2Fe(OC_2H_5)]_2$

The ethoxy-bridged diiron complex was prepared according to the method of Wu et. al. Inorg. Chem. 11, 990 (1972). To 50 ml of ethanol was added 1.0 gram of $Fe(acac)_3$. To this stirred slurry was added 0.192 grams of sodium ethoxide at 0°C. Orange solids precipitated and were filtered at 0°C then air-dried to provide the title complex, 0.756 grams.

6.9.1.2 Preparation of $Cr_2(OH)(O_2CH)_2(H_20)](TxO)_3 \bullet 6H_2O$

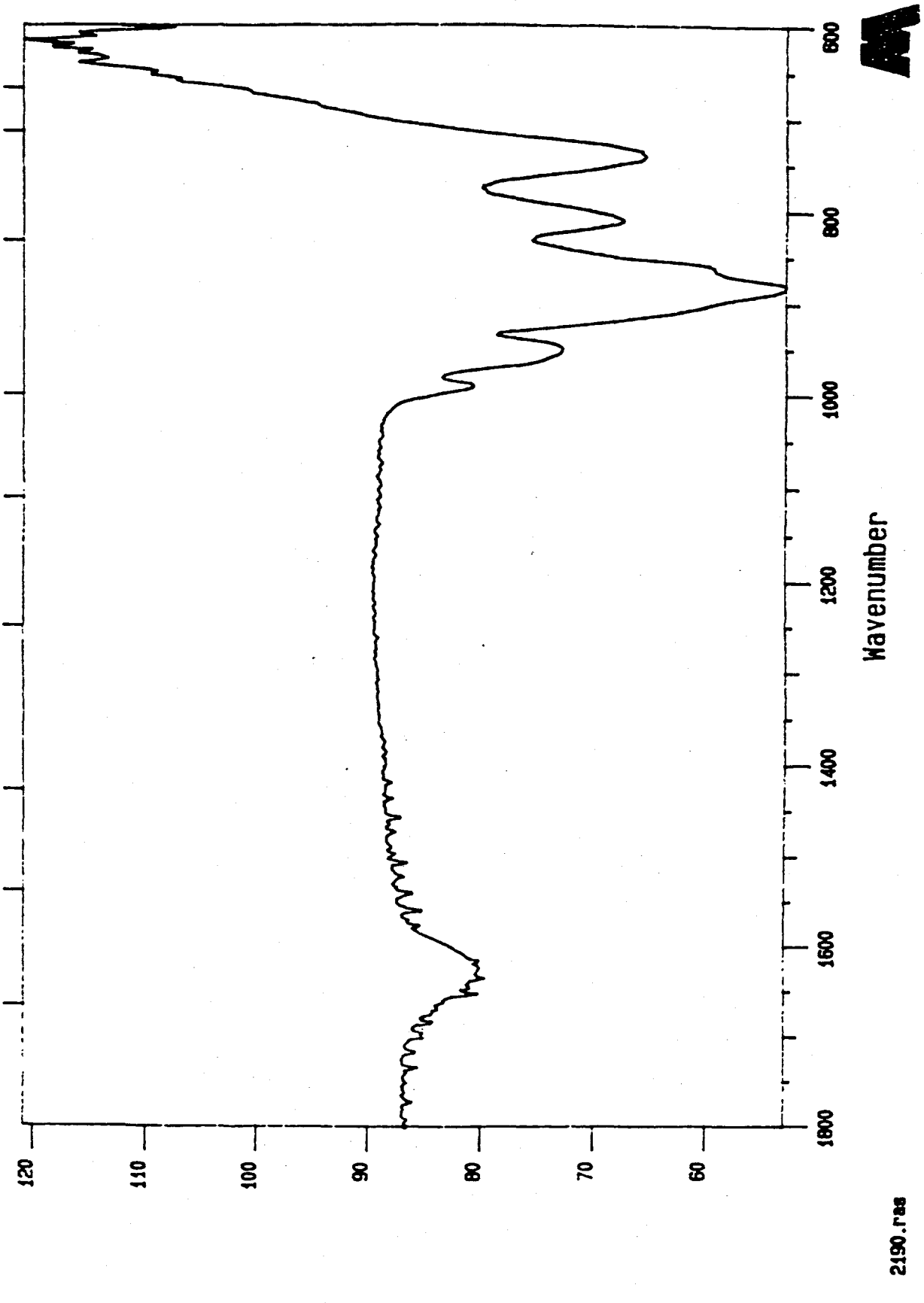
A solution of 1.20 grams of CrO_2 in 10 ml of H_20 was added dropwise to 100 ml of formic acid, the color changing from red to blue. this solution was diluted with 100 ml of water and added to a 6"X1" Dowex 50X2-200 ion-exchange column, then eluted with 0.5M p-toluenesulfonic acid. The cut containing the desired product was evaporated until violet crystals emerged. The crystals were filtered and washed with acetone giving 0.47 grams of the title compound.

6.9.1.3 Preparation of $K_8[\beta_2\text{-}SiW_{11}O_{39}] \bullet 14H_2O$

The monolacunar polyoxometallate was prepared according to the method of A. Teze and G. Herre, J. Inorg. Nucl. Chem., 39, 999 (1977). Sodium tungstate (91 g) was dissolved in 150 ml of water. To this vigorously stirred solution was slowly added 82 ml of 4NHCl over 10 min. A solution of 5.5 g of sodium metasilicate in 50 ml of water was added at this point and the pH was maintained between 5 and 6 by incremental addition of 4N HCl. After 2 hours 45 g of KCl was added with stirring. After 1 hour the precipitate was filtered and reprecipitated in H_2O with KCl addition as before. The product was washed with 2M KCl and air-dried. The infrared spectrum of this complex is given in Figure 6.16.

FIGURE 6.16

IR SPECTRUM OF $K_8[B2\text{-}SiW_{11}O_{39}]$



6.9.1.4 Preparation of β-$K_8SiW_{10}O36.12H_2O$

The dilacunar polyoxometallate was prepared according to the method of J. Canny, A. Teze, R. Thourenot and G. Herre, Inorg. Chem. 25, 2114 (1986). The pH of a solution of 15 g of β_2-$K_8SiW_{11}O_{39}$ in 150 ml of water was adjusted to 9.1 with 2M K_2CO_3. After 20 min., 20 g of KCl was added while maintaining the pH at 9.1 with K_2CO_3. The solid which is formed on standing overnight was air dried. The infrared spectrum of this complex is given in Figure 6.17.

6.9.1.5 Preparation of $K_8[SiCr_2W_{10}O_{36}]$

$K_8[SiW_{10}O_{36}]$, 1.0 g, was dissolved in 3.5 ml of 1NHCl. The pH was 3.8 when 0.277 grams ($3.33X10^{-4}$ mole) of $[Cr_2(OH)(O_2CH)](TsO)_3$ was added. The color changed at this point to pale blue and the pH was recorded as 3.28. Cesium chloride (0.5g) was added to precipitate the pale blue-grey product. This crude material was redisolved in 4 ml of 0.5N HCl and 0.5g of CsCl was added to reprecipitate the product. Yield = 0.89 g. The infrared spectrum of this complex is given in Figure 6.18. Figure 6.19 shows the changes in the POA infrared fingerprint region during dichromium complex formation.

6.9.1.6 Preparation of $K_8[SiFe_2W_{10}O_{36}]$

$K_8[SiFe_2W_{10}O_{36}]$, 2.0g, was dissolved in 10 ml of 1N HCl. To this solution was added 0.7g of $[(acac)_2Fe(OC_2H_5)]_2$. The orange solution changed to red as the pH stabilized at 1.21. At this point 10 grams of CsCl was added to precipitate the product. After filtering and drying in vacuo the title compound was recovered in 2.05 grams. Figure 6.20 gives the infrared spectrum of this compound. Figure 6.21 compares the changes in the POA infrared fingerprint region during diiron complex formation.

6.9.1.7 Preparation of $(Bu_4N)_8[SiFe_2W_{10}O_{36}]$

β-$K_8[Fe_2SiW_{10}O_{36}]$, 1.95 grams was stirred for 30 minutes with warming at 70 C. The solution was filtered warm to remove a small amount of undissolved solid. To the warm well-stirred solution was added an equal volume of a saturated solution of tetrabutyl ammonium bromide and a flocculent solid immediately precipitated. The mixture stirred for an additional 30 minutes after which it was chilled at 6°C overnight. A pale yellow-green solid was filtered from the mixture and washed with 150 ml of cold water. The solid was dried in vacuuo giving 100 mg of recovered product.

FIGURE 6.17

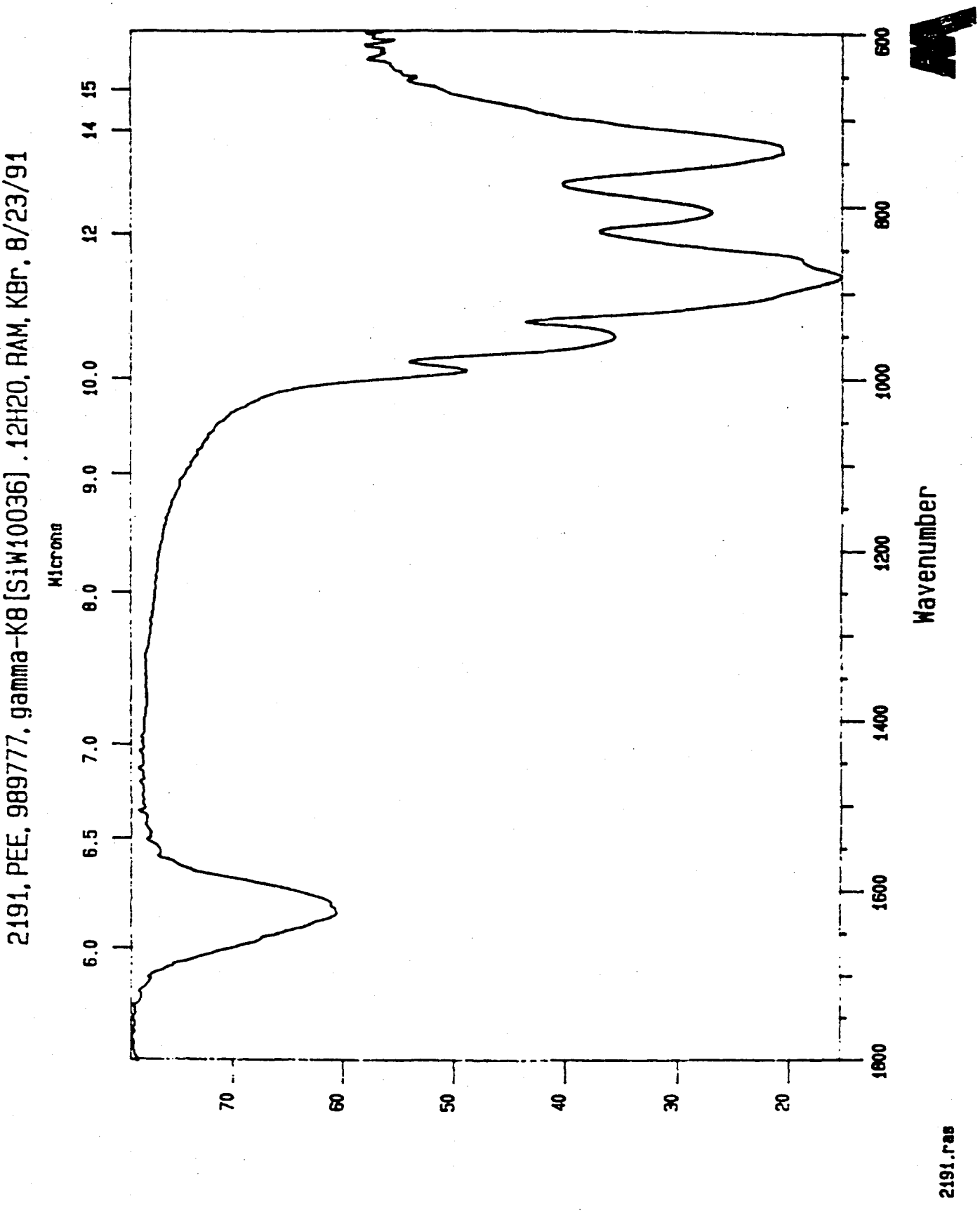

2191, PEE, 989777, gamma-K8 [SiW10036] . 12H2O, RAM, KBr, 8/23/91
Microns
6.0
6.5
7.0
8.0
9.0
10.0
12
14
15
% Transmission
70
60
50
40
30
20
1800
1600
1400
1200
1000
800
600
Wavenumber
2191.ras

FIGURE 6.18

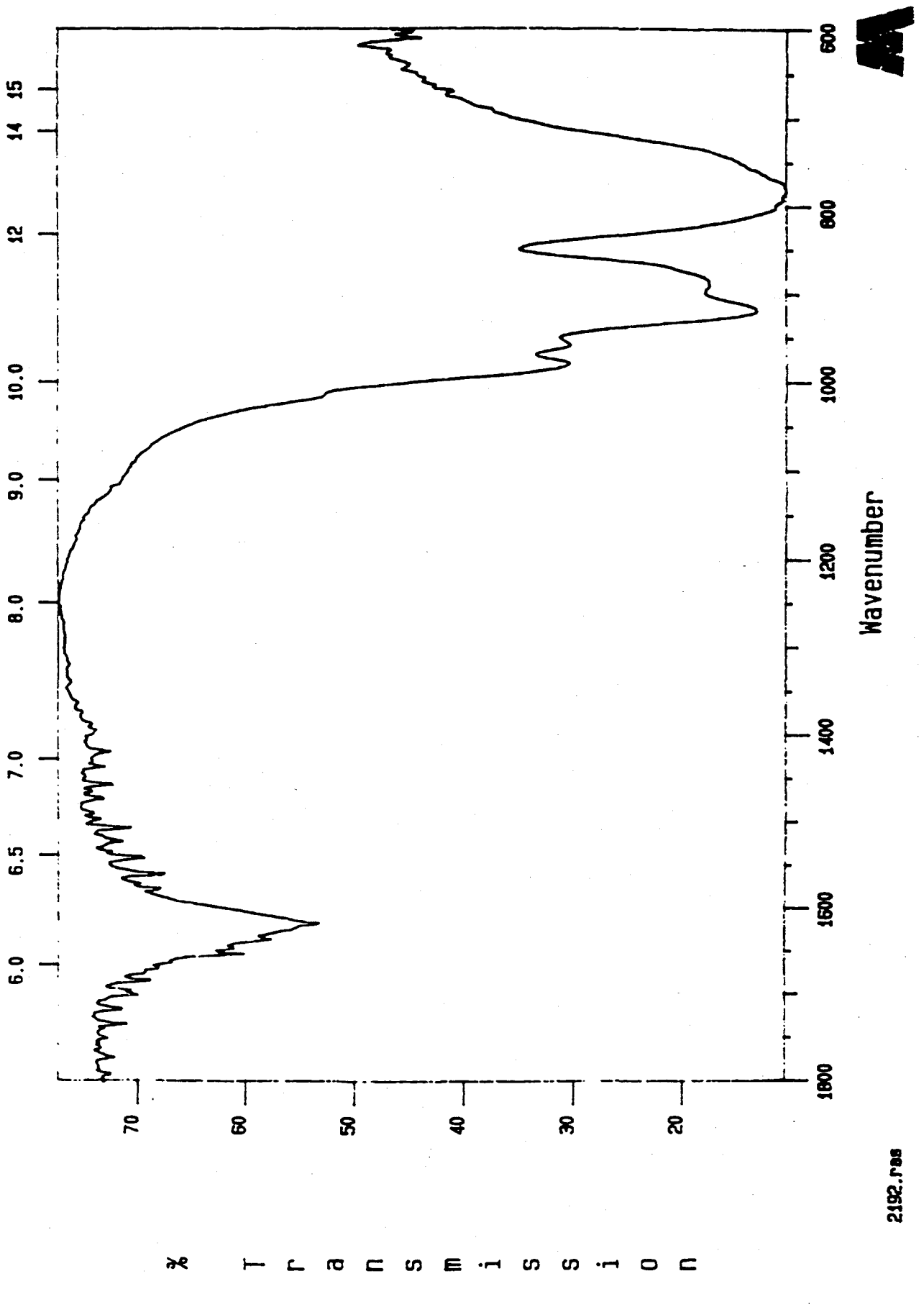

2192, PEE, 989782, K6 [Cr2Si3W10O38], RAM, KBr, 8/23/91
Microns
6.0
6.5
7.0
8.0
9.0
10.0
12
14
15
% Transmission
70
60
50
40
30
20
Wavenumber
1800
1600
1400
1200
1000
800
600
2192.rss

FIGURE 6.19

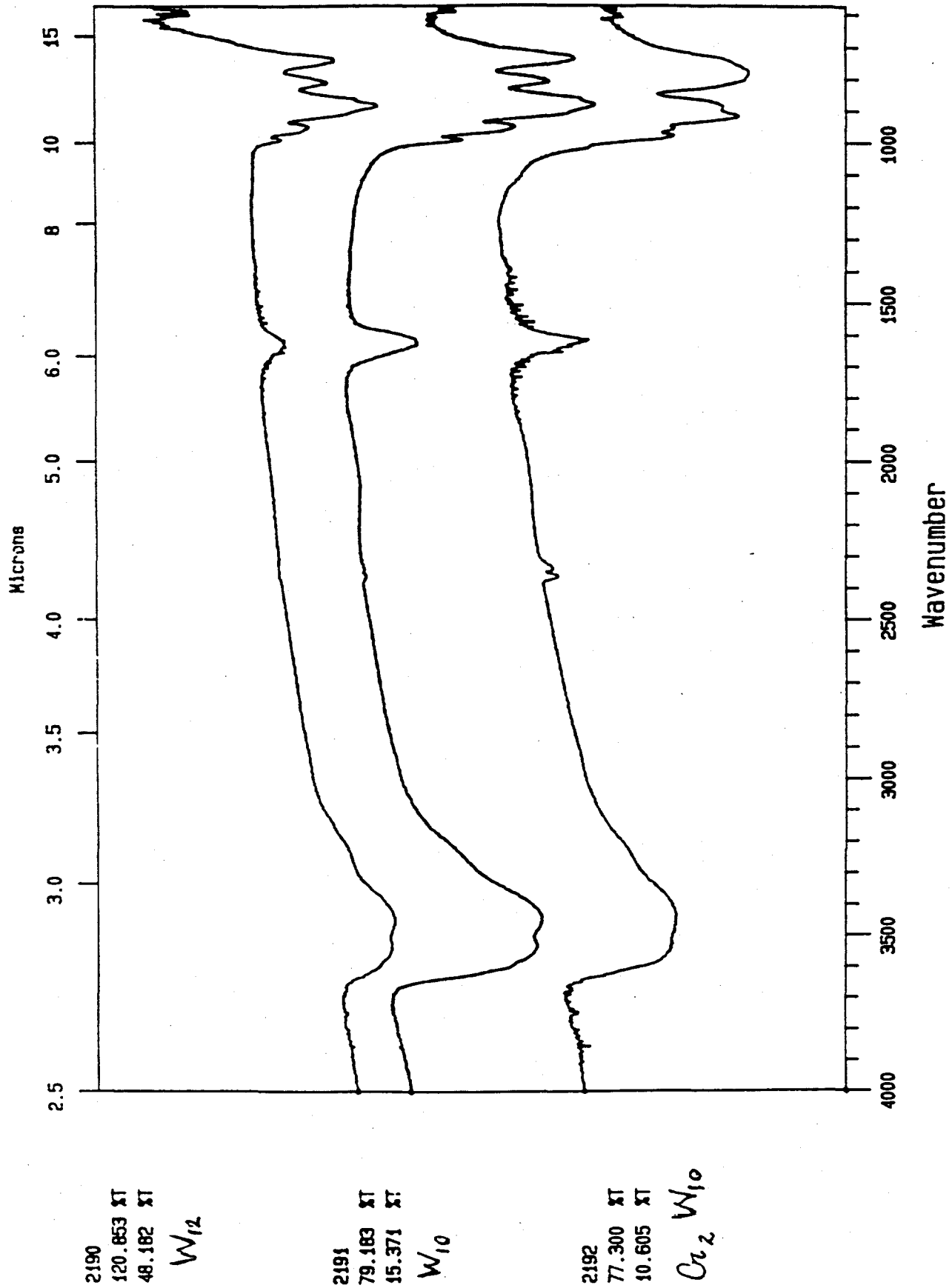

Microns
2.5
3.0
3.5
4.0
5.0
6.0
8
10
15
Wavenumber
4000
3500
3000
2500
2000
1500
1000
2190
120.853 %T
48.182 %T
W_{12}
2191
79.183 %T
15.371 %T
W_{10}
2192
77.300 %T
10.605 %T
Cr_2 W_{10}

FIGURE 6.20

IR SPECTRUM OF $K_8[SiFe_2W_{10}O_{36}]$

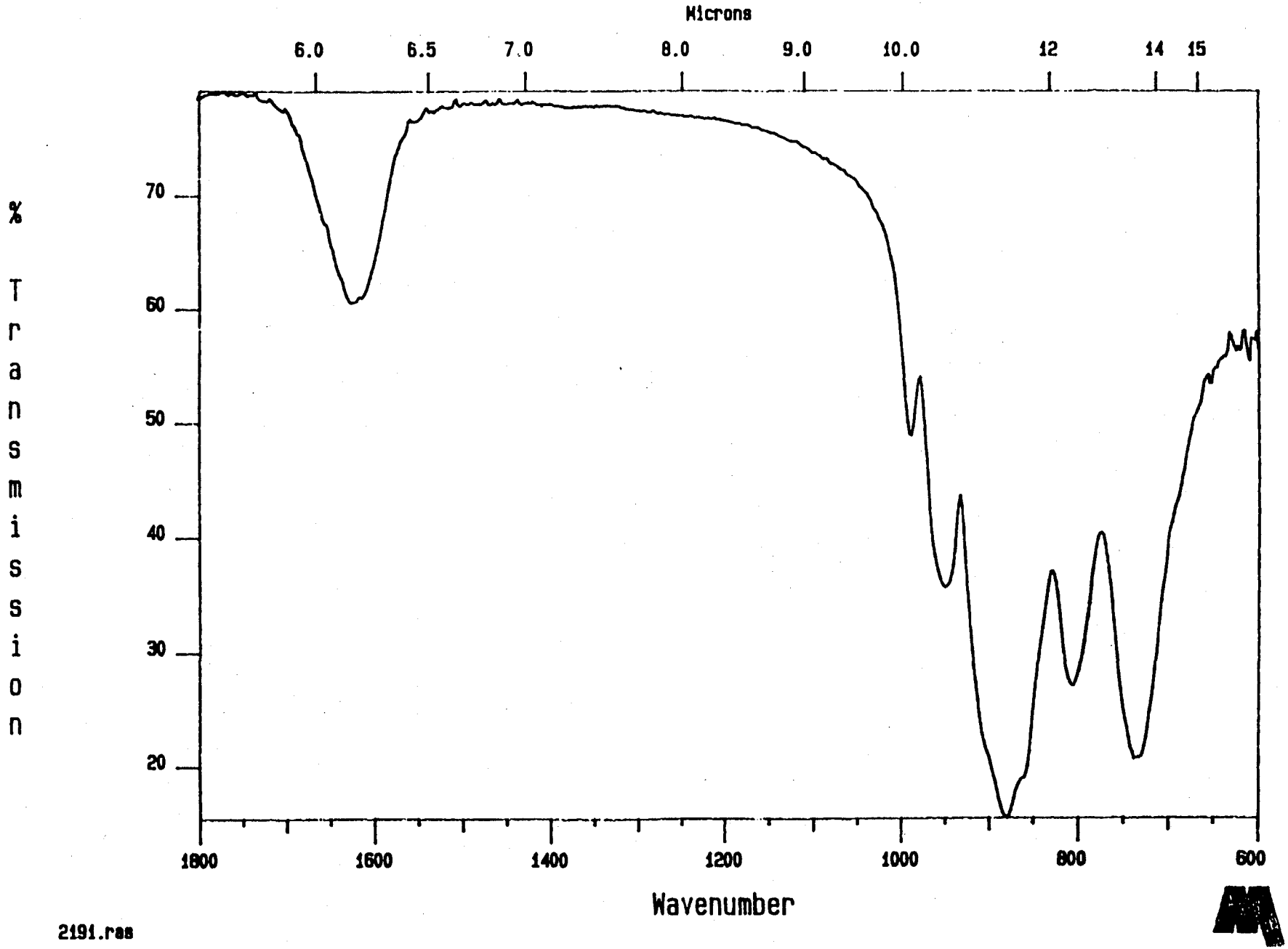
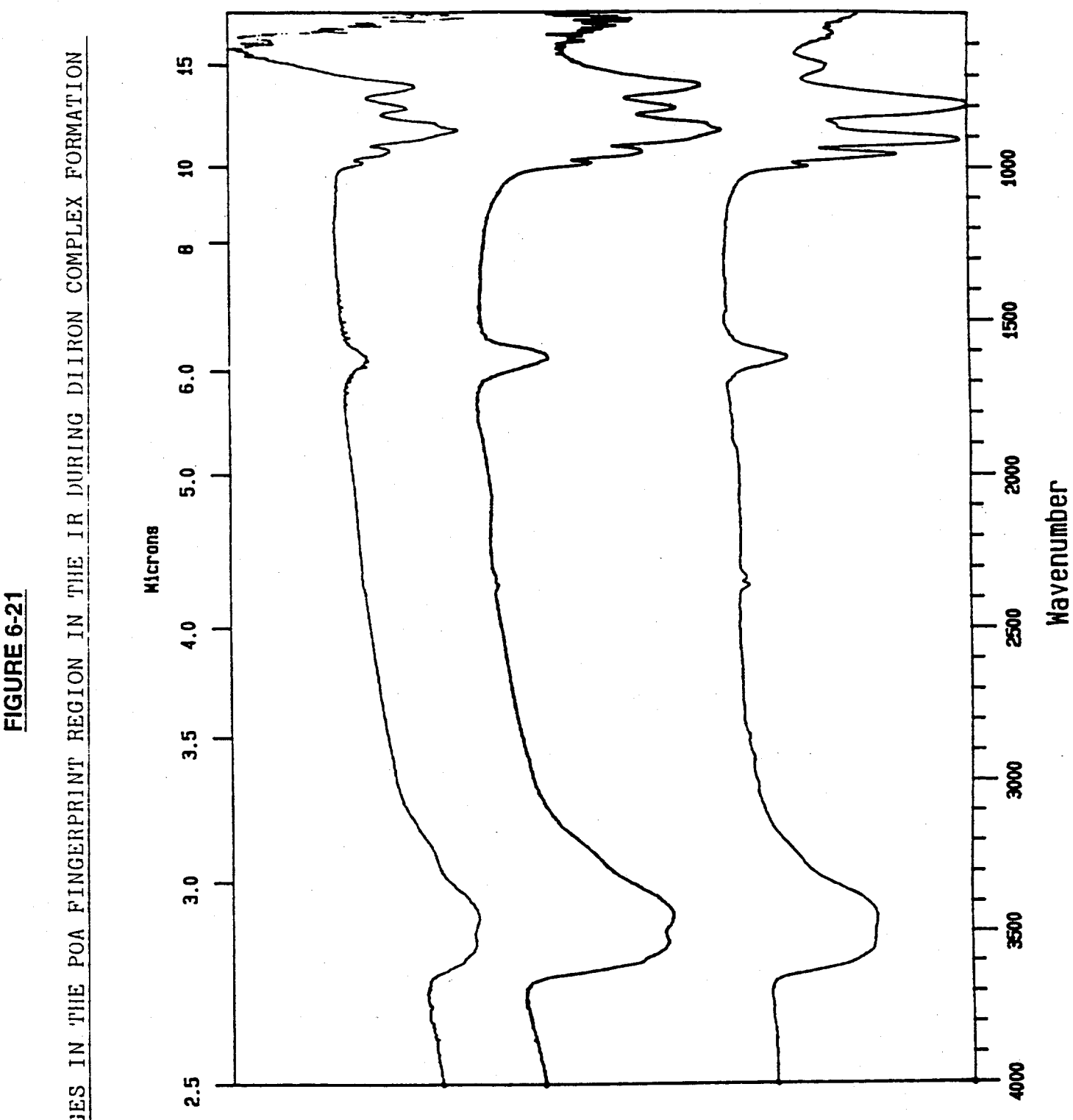


FIGURE 6-21

CHANGES IN THE POA FINGERPRINT REGION IN THE IR DURING DIIRON COMPLEX FORMATION



6.9.2 Testing of Diiron Polyoxoanions for Light Alkane Oxidation

We have used the diiron polyoxometallate system: $(Bu_4N)_8[SiFe_2W_{10}O_{36}]$ as a catalyst for the air oxidation of isobutane, butane, and propane at 125°C in acetonitrile. Initial results indicate that, as expected, isobutane is oxidized rapidly at this temperature giving 2600 moles product/mole catalyst in a 3 hour period. As was the case when other polyoxoanion catalysts were used for this reaction, TBA selectivity was not high (~55%) and a large amount of tert-butyl hydroperoxide was formed among the oxidation products. n-Butane reacted sluggishly, producing slightly more than 1100 moles product/ mole catalyst in a 19 hour period. Again selectivity was much lower than obtained with the perhaloporphyrin catalysts. MEK was made in slightly over 50% selectivity with large (>40%) quantities of acetic acid also formed. Propane was nearly unreactive at 125°C using this complex. As was discussed above, these catalysts have poor low-temperature activity relative to the perhaloporphyrin complexes, and are not effective in decomposing tertiary hydroperoxides. Thus either high temperatures or long times are required resulting in poorer selectivities. We, therefore, oriented our research in this area to attempts to improve low temperature oxidation activity by finding ways to increase Fe(III)/Fe(II) reduction potential in polyoxometallate systems.

6.10 TUNING THE POLYOXOANION REDUCTION POTENTIAL

We have noted that methane monooxygenase has a **hydroxo-bridged diiron non-heme active center** which, with the help of electrons and protons from NADH, is capable of binding and cleaving the dioxygen molecule and slowly converting methane to methanol even at room temperature. For this reason we are interested in attempting to tune the redox potential of similar small model complexes having bridged diiron in non-porphyrin ligands the same as we have in the porphyrin

series. Polyoxoanionic complexes such as Keggin systems seemed to be a good model for reasons listed in previous sections. In addition to their electronic properties and the possibility of incorporation more than one iron into this "ligand" system, these compounds would be expected to have very high thermal and oxidative stability and, if active, one would expect long catalyst life even at elevated temperatures.

Polyoxometallates have been used as structures to incorporate potentially cooperative dimetal sites in a thermally and oxidatively stable ligand environment. We have been using these compounds for catalytic oxidations in the liquid phase. Thus during the first three years of the Cooperative Agreement, we have studied many polyoxoanionic catalysts including three particular sets of PHASE II catalysts. These are polyoxometallates having the Keggin structures: $C_x[PW_{11}(M)O_{39}]^{-x}$, $C_y[PW_{11}M_2O_{38}]^{-y}$, and $C_z[PW_9M(III)_3O_{37}]^{-z}$ where C = K^+, $(Bu_4N)^+$, H^+, and M = Fe, Cr, V(O), and Ru. In this section, we present the results of synthesis characterization and testing of select members of this series in which C = $(Bu_4N)^+$.

During the first three years of the Cooperative Agreement, we have completed essentially the entire program of synthesis and testing of these complexes which was transmitted in the SOW at the outset of this work. While having interesting high-temperature activity in promoting alkane autoxidation, the same lower-temperature activity for selective alcohol formation that was observed for the porphyrin complexes was not observed for the polyoxoanionic complexes of oxidation-active transition metals when introduced in either their +2 or +3 oxidation states. It is necessary to exceed 100°C to achieve oxidation even of isobutane, and although the entire range of substrates tested: methane, ethane, propane, isobutane and synthetic natural gas - was oxidized, the selectivity to alcohols was not high.

The area of work reported in this Section is that of catalyst characterization. Early work on the electrochemsitry of the materials which we have prepared showed that the first row metals did not have a very high M(III)/M(II) reduction potential. Analytical results showed that the materials which we produced contained a great number of water and other hydroxylic molecules of solvation. It is known that solvation of this type contributes to lower reduction potential and that by producing very "dry" materials higher M(III)/M(II) reduction potentials result. For this reason we are currently engaged in making two series of polyoxometallates as their organic soluble tetrabutyl ammonium salts in the dry form: $ZM_{11}M'O_{39}$ (Z = B,Si,P; M = Mo,W; M' = Fe,Mn, Cr,Co) and $ZM_9M'_3O_{37}$ (Z = B,Si,P; M = Mo,W; M' = Fe). We have obtained high quality crystalline materials whose electrochemistry was studied. In this work we are looking for a correlation between M(III)/M(II) reduction potential as a function of either the central atom, Z, or the surrounding non-active metal system, M.

6.10.1 Synthesis of Metal Substituted Polyoxoanions

6.10.1.1 Synthesis of $(nBu_4N)_4H[SiW_{11}Fe(H_2O)O_{39}]$

- $K_8[SiW_{11}O_{39}] \sim 14H_2O$ (32.0 g, 9.0 mmol) was suspended in 65 ml of deionized water at ~90°C. $Fe(NO_3)_3 \bullet 9H_2O$) (4.2 g, 10.4 mmol) was added to above suspension in small portions to get bright orange solution, which upon further heating at 90-2°C produced brown-red turbidity. The solution was cooled down to room temperature and filtered from the brown turbidity to get a lemon-yellow solution. A yellow precipitate was formed by the addition of 36.5 mL of 1.0 M solution of n-Bu_4NBr to the above solution with vigorous stirring. The crude product was collected on a medium

frit, washed with 50°C water (3 x 10 mL), aspirated to dryness, and allowed to air dry at room temperature to get 11.1 g of dried product which contained moisture and was observed by Infrared Spectroscopy. 4.8 g of crude product was dissolved in a minimum vol of slightly warmed HPLC grade CH_3CN and filtered to remove any turbidity to get a yellow solution. Enough anhydrous Et_2O was added to the above solution to the point of incipient precipitation and then refrigerated at 5°C overnight to get a yellow microcrystalline product. Repeated the above procedure once more to obtain homogeneous crystalline material. The final product was dried under vacuum at 60°C for 4-5 hrs. yield: 60%. Infrared (KBr, cm^{-1}): 1000 (w), 960 (s), 910 (vs), 880 (m), 790 (vs), 750 (shoulder).

Analysis calculated for $C_{64}H_{147}N_4SiW_{11}O_{40}$: C, 20.67; H, 3.99; N, 1.50; Fe, 1.50; Si, 0.76; W, 54.39. Found: C, 19.97; H, 3.79; N, 1.45; Fe, 1.56; Si, 44
0.68; W, 54.19.

TGA (weight loss at 550°C under N_2). Calculated for 4 n-Bu_4N^+: 26.08%. Actual: 23.42%.

6.10.1.2 Synthesis of (n-$Bu_4N)_4[PFe(H_2O)W_{11}O_{39}]$

$K_7PW_{11}O_{39}$ was prepared in-situ by following the literature procedure: $K_3PW_{12}O_{40}.xH_2O$ (18.8 g, 6.28 mmol) was suspended in hot deionized water (95°C). 25mL of 1.0 M of $KHCO_3$ solution was added slowly with vigorous stirring as to keep the pH of solution below 5. The white suspension dissolved upon complete addition of base to give clear solution and pH was maintained at 4.8 0.1 at 85°C. The temperature was raised to 95°C over hot-plate and $Fe(NO_3)_3.9H_2O$ (2.57g,

6.4 mmol) was added slowly while stirring. The solution became yellow and after complete addition of iron nitrate, a brown turbidity persisted. The solution was cooled down to room temperature and filtered to get a yellow solution. A yellow ppt was formed by the addition of solid n-Bu_4NBr (10.0 g. 31 mmol) to the solution with vigorous stirring. The crude product was collected on medium frit, washed with 50°C warm water until washings were free of bromide ($AgNO_3$ test), followed by ethanol, aspirated to dryness, and finally allowed to air dry overnight at room temperature to obtain 14.9 gm of product. This product contained water (IR Spectrum). The crystallization procedure was adopted in a similar way as explained for compound **1**. Infrared (KBr, cm^{-1}): 1070 (s), 970 (vs), 895 (vs), 820 (vs, bread), 750 (w, shoulder).

Analysis calculated for $C_{64}H_{146}N_4FeO_{40}PW_{11}$: C, 20.64; H, 3.95; N, 1.51; Fe, 1.50; P, 0.83; W, 54.35. Found: C, 20.54; H, 3.87; N, 1.47; Fe, 1.35; p. 0.77; W, 53.14.

TGA (weight loss at 500°C under N_2). Calculated for 4 n-Bu_4N^+: 26.04%. Found: 26.73%.

6.10.1.3 Synthesis of $(n\text{-}Bu_4N)_4H_2[BFe(H_2O)W_{11}O_{39}]$

The starting material $BW_{11}O_{39}^{9-}$ was prepared in situ by the following procedures: $Na_2WO_4.2H_2O$ (18.2 G, 0.11 mol) was dissovled in 75 mL of deionized H_2O and its pH adjusted to 6.0•H_3BO_3 (1.25 g, 20.0 mmol) was added and with the addition of 4M HCl, the pH was readjusted to 6.0. $Fe(NO_3)_3$ $9H_2O$ (4.2 g, 10.0 mmol) was dissolved in 50 mL of deionized H_2O and solution was heated to 90-95°C. To this hot solution, the $BW_{11}O_{39}$ solution was added immediately to get a yellow solution and stirred for five minutes. The insoluble material [hydrolyzed excess Fe(III) and

paradodecatungstate, a common impurity in $BW_{11}O_{39}^{9-}$] was removed after rapidly cooling the filtrate. The yellow solution was treated with solid n-Bu_4NBr(16.0 g, 50.0 mmol) under vigorous stirring to get a pale-yellow precipitate. The precipitate was washed with CH_3OH (30 mL) followed by ether and air dried. The precipitate was placed in a vacuum oven and dried overnight at room temperature, to get 5.2 g of microcrystalline product. Recrystallization was unsuccessful due to some decomposition to a white powder. Infrared (KBr, cm^{-1}): 955 (vs), 880 (s), 810 (vs), 760 (br, should).

Analysis calculated for $C_{64}H_{148}N_4BFeO_{40}W_{11}$ = C, 20.75; H, 4.03; N, 1.51; Fe, 1.51; W, 54.61. Found = C, 18.21; H, 3.61; N, 1.39; Fe, 1.44; W, 44.21.

TGA (wt. loss at 150-500°C under N_2). Calculated for 4 n-Bu_4N^+: 25.3%. Found: 26.0%.

6.10.1.4 $\underline{(n\text{-}Bu_4N)_4[As\ Fe(H_2O)W_{11}O_{39}]}$

$Na_2HAsO_4.7H_2O$ (1.56 g, 5.0 mmol) and $Na_2WO_4.2H_2O$ (18.15 g, 55 mmol) were dissolved separately in 40 mL deionized water each at 80°C. The hot solutions were mixed together and heated to 90°C. The mixture was acidified with 6.2 mL of 13.8 M HNO_3 and maintained the pH at 2.92. $Fe(NO_3)_3.9H_2O$ (2.02 g, 5.0 mmol) was added to the above hot solution in small portions to obtain a yellow solution. The solution was cooled down to room temperature and filtered to remove some hydrolyzed excess $Fe(NO_3)_3$. n-Bu_4NBr (20 mL, 1.0 M). The solution was then added to above yellow filtrate under vigorous stirring to get yellow precipitate. Filtered, washed with 50°C water (3 x 100 mL) until washings were free from Br^- ions ($AgNO_3$ test), aspirated to dryness and allowed to air dry overnight at room temperature to get 11.6 g of product. Took 1.0 g of the product and crystallized in a similar way as described for compound 1. Infrared (KBr, cm^{-1}) = 970 (s), 900

(vs), 865 (m), 800 (vs).

Analysis Calculated for $C_{64}H_{146}N_4AsFeO_{40}W_{11}$: C, 20.42; H, 3.91; N, 1.49; As, 1.99; Fe, 1.48; W, 53.71. Found: C, 19.76; H, 3.72; N, 1.44; As, 1.71; Fe, 1.32; W, 52.51.

TGA (wt. loss at 500°C under N_2). Calculated for 4 n-Bu_4N^+:25.76%.

6.10.1.5 $\underline{(n\text{-}Bu_4N)_4[PFe(H_2O)Mo_{11}O_{39}]}$

The starting material $PMo_{11}O_{39}^{7-}$ was prepared in situ by the following method:

First, $H_3PMo_{12}O_{40}$ was prepared by dropwise addition of H_3PO_4 (10.0mL, 1.0M) under vigorous stirring to a mixture of 29.03 g of $Na_2MoO_4.2H_2O$ dissolved in 120 mL of deionized water and 100 mL of dioxane which was acidified with 18.0 mL of 13.0 M HNO_3. The color of the solution became golden yellow at pH 1.6. 200 mL of the golden solution from above was heated to 85°C and 1.0 M $KHCO_3$ solution was added at intermittent interval until pH of solution became 4.3. This pH was maintained for 15 minutes, and then $Fe(NO_3)_3.9H_2O$ (3.0 g, 7.4 mmol) was added in small portions keeping the temperature constant at 80-5°C to get yellow solution. The mixture was cooled down to room temperature, filtered to remove excess hydrolyzed $Fe(NO_3)_3$ and then n-Bu_4NBr was added (12.0 g, 37.2 mmol) to the above filtrate under vigorous stirring to obtain a yellow precipitate. The solid was filtered, washed with water (2 x 50 mL), EtOH (2 x 50 mL), Et_2O (2 x 50 mL), aspirated to dryness and allowed to air dry overnight to get 22.5 g of product. Recrystallization was carried out in an analogous manner as described for compound **1**. Infrared

(KBr, cm^{-1}): 1068(s), 955 (vs), 880 (s), 815 (vs), 755 (w, shoulder).

Analysis calculated for $C_{64}H_{146}N_4FeMo_{11}O_{40}P$: C,, 27.91; H, 5.34: N, 2.03; Fe, 2.03; Mo, 38.32; P, 1.12. Found: C, 26.82; H, 5.07; N, 1.95; Fe, 1.66; Mo 38.85; P, 1.09.

TGA (wt. loss at 550°C under N_2). Calculated for 4 n-Bu_4N+: 35.2%. Found: 33.22%.

6.10.1.6 $\underline{(n\text{-}Bu_4N)_4H[SiFe(H_2OMo_{11}O_{39}]}$

The starting material, $SiMo_{11}O_{39}^{8-}$, was prepared insitu by following the literature preparation: $Na_2SiO_3.5H_2O$ (4.25 g, 20 mmol) was dissolved in 275 mL deionized water and brought to boiling on a heating mantle in 500 mL, 3-N flask fitted with condenser. In a single addition, MoO_3 (23.03 g, 160 mmol) was added and the mixture was kept stirring at 72-3°C for 3 days to obtain a clear yellowish-green solution. A 100 mL solution of $Na_2MoO_4.2H_2O$ (14.5 g, 60 mmol) was then added drop-wise to the above solution and heated at 72-3°C for an additional day without stirring. The yellowish-green solution was cooled down to room temperature and filtered to remove silicic acid impurity. Took 92.5 mL of above yellowish-green solution and added dropwise to 2.02 g Fe $(NO_3)_3.9H_2O$ dissolved in 50 mL of deionized H_2O at 90°C. During addition of $SiMo_{11}O_{39}^{8-}$, the color of the solution became orange-brown with suspended brown precipitate. Heated at 90°C for an additional five minutes. Cooled down the solution to room temperature, filtered to remove brown suspension and then added n-Bu_4NBr (7.0 g, 20.0 mmol) under vigorous stirring to get greenish-yellow precipitate. This product was washed with 50°C H_2O until washings were free of Br^- ions ($AgNO_3$ test), EtOH (2 x 50 mL) followed by Et_2O (2 x 50 mL) and aspirated

to dryness to obtain 3.6 g of product. Recrystallization was done in an analogous manner as described for compound 1.Yield 70%. Infrared (KBr, cm^{-1}): 955 (s), 930 (w, shoulder), 910 (vs), 860 (w, shoulder), 810 (vs), 740, (s, shoulder), 675 (m).

6.10.1.7 $\underline{(nBu_4N)_4H_3[SiW_9\{Fe(H_2O)\}_3O_{37}]}$

The sodium salt of $[SiW_9\{Fe(H_2O)_3\}_3O_{37}]^{7-}$ was prepared according to a literature procedure. In a 500 mL round bottoms Flask, β-$Na_9SiW_9O_{34}H.23H_2O$ (8.54 g, 3.0 mmol) was dissolved in 200 mL solution of sodium acetate-acetic acid buffer of pH 6. This colorless solution was then treated with $[Fe_3O(OAc)_6(H_2O)_3]Cl$ (1.38 g, 3.0 mmol) suspended in 25 mL of deionized water. Not all of the iron complex was dissolved. The mixture was warmed to 50°C in an oil-bath for 15 minutes. The iron complex dissolved and gave a light greenish brown solution. At room temperature, 0.5 g KCl was added and stirred to dissolve. The mixture was cooled down to 14°C in an ice-bath, filtered to remove a rusty brown precipitate and then added n-Bu_4NBr (10.28 g, 42.4 mmol) under vigorous stirring to get a yellow-green precipitate. The precipitate was washed with water, EtOH, Et_2O and aspirated to dryness to get 1.7 gm of product. Recrystallized according to the procedure as mentioned for compound 1. Yield: 50% Infrared (KBr, cm^{-1}): 100 (w), 955 (s), (905 (vs), 810 (vs), 775 (s, shoulder).

Analysis calculated for $C_{64}H_{153}N_4Fe_3O_{40}SiW_9$: C, 22.26: H, 4.45; N, 1.6l; Fe, 4.83; Si, 0.81; W, 47.7. Found: C, 21.85; H, 4.21; N, 1.54; Fe, 4.36; Si, 0.67; W, 45.4.

TGA (wt. loss at 550 C under N_2). Calculated for 4 n-Bu_4N^+L 27.96%. Found: 28.22%.

6.10.2 Electrochemistry of Metal Substituted Polyoxoanions

It has recently been reported that the Fe(III)/Fe(II) reduction potential of iron in a Keggin ion complex is highly dependent on the nature of the central atom (J. E. Toth Ph.D. Dissertation, Caltech, Pasadena), Table 6-12. The reduction potential increases as the central atom is varied in the order: Si(V)>Ge(IV)>P(V)>As(V). The iron(III)/(II) reduction potential varies over a span of nearly 270 mv from -0.145 to + 0.123 over this series. For this reason we synthesized the series of (tetra-N-butylammonium) complexes of the formula: $Fe(III)XM_{11}0_{39}$ wherein X = Si(IV) Ge(IV) P(V) or As(V), and M = W or Mo. We obtained electrochemical information on these complexes. We have studied the oxidation of light hydrocarbons and report results in section 6.10.3.

It is also known that the iron(III)/(II) reduction potential is sensitive both to the pH of the medium and to the counter ion used, Table 6-13. We have screened these complexes under different conditons of pH and with varying counter ions to attempt to use them under conditions favoring the highest Fe(III)/Fe(II) reduction potential.

TABLE 6-12

FORMAL POTENTIALS OF THE THREE REDOX COUPLES EXHIBITED BY $FeXW_{11}O_{39}^{z-}$ HETEROPOLYANIONS. a,b

X	Z	One-Electron wave (Fe(III)/Fe(II))	Z	First Two-Electron wave	Z	Second Two-Electron wave
Si(V)	-5	-0.145	-6	-0.580	-8	-0.720
Gel(IV)	-5	-0.065	-6	-0.557	-8	-0.666
P(V)	-4	0.039	-5	-0.560	-7	-0.706
As(V)	-4	0.123	-5	-0.537	-7	-0.655

a Entries are in volts vs. SSCE.

b Supporting electrolyte: 0.1 M NaClO4 + 0.01 M HClO4 T = 22±2°C.

TABLE 6-13

FORMAL POTENTIALS OF THE FeIII/FeII COUPLE OF $H_2OFeGeW_{11}O_{39}^{s-}$ IN VARIOUS SUPPORTING ELECTOLYTES

A. FIXED pH(5)

Counter-ion	Counter-ion Conc., M	E^f, mV	E^f, mV
Na^+	0.001	-171	-34
Na^+	0.1	-37	0
Na^+	1.1	-86	+51
Li^+	1.1	-95	+42
K^+	1.1	-77	+60
Rb^+	1.1	-62	+75

B. FIXED COUNTER-ION (Na^+)

pH	E^f,mV [Na+]=0.1M	E^f, mV [Na+]=1.1M	E^f, mV
2.0	-50	-18	+32
3.0	-102	-60	+42
4.0	-135	-92	+43
5.0	-137	-86	+51
6.0	-149	-117	+32
7.0	-172	-190	+18
8.0	-247	-220	+27

6.10.3 Redox Behavior and Oxidation Activity

First row oxidation-active transition metal complexes can be placed in the framework of polyoxometallates. Polyoxometallates are all-inorganic, thermally and oxidatively stable environments for these transition metal centers and thus we reasoned hat they might be good catalysts for oxidation of alkanes, especially at higher temperatures at which porphyrin complexes are unstable. As we discussed, first row oxidation active transition metal centers such as iron, are not as active in polyoxoanionic matrices such as Keggin ions, as they are in the perhaloporphyrinato ligand system. We speculated that one reason may be that the Fe(III)/(II) reduction potential might be too low because of the preference for Fe(III) in the framework. The limited amount of available data suggested that this was the case. On the other hand, literature data suggested that there are four factors which influence Fe(III)/(II) reduction potentials of iron in a Keggin ion: (1) the central heteroatom, (2) the ligands on the Fe center, (3) the nature of the framework metal, and (4) the pH of the solution. We have therefore set out to systematically vary these four factors to see if we can control the Fe(III)/Fe(II) reduction potential in a series of iron-containing Keggin ions and further to determine the relationship between Fe(III)/Fe(II) reduction potential and alkane oxidation activity in these catalyst systems.

In the previous section, we listed some literature data which showed that the Fe(III)/(II) reduction potential for a series of iron-containing Keggin complexes varied from -0.145 to +0.123 eV, a difference of 0.268 eV. These results, however were obtained in aqueous solution and our homogeneous catalytic oxidation reaction must be conducted in organic media. Acetonitrile has been found to be a good solvent for both tetrabutylammonium salts of Keggin complexes and the

hydrocarbons to be oxidized. We have therefore obtained electronchemical data on a large number of Keggin complexes whose synthesis was reported in the last quarterly report. We have observed large differences in Fe(III)/Fe(II) reduction potential but our results are not similar to those reported in aqueous solution.

6.10.3.1 Effects of The Central Heteroatom on The Oxidation Activity of Iron Substituted Keggin Systems

We have synthesized and characterized a series of heteroatomtungstates into which a single iron atom has been framework substituted. These complexes have the structure $[MW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H_x$ where M=B,Si,P,As,Bi,Ge, and Sb, and x=0,1,or2. Table 6-14 shows the effects of varying the heteroatom, M, on the iron(III)/(II) reduction potentital and catalytic activity. We can see that there is a general trend in decreasing oxidation activity with increasing Fe(III)/(II) reduction potential although there is an outlying point which is being reexamined. The Iron(III)/(II) reduction potentials in the Keggin ion systems were examined by cyclic voltammetry of either the corresponding potassium salts in water or the tetrabutylammonium salts in acetonitrile. Both solutions contained buffers. Because the central heteroatom oxidation state and consequently the charge on the Keggin ion varied, the correlation is expected to be a rough one at best.

The finding that the oxidation activity of iron Keggin catalysts decreased with increasing reduction potential was a very surprizing one since previous work with metalloporphyrin iron complexes has indicated that increased oxidation activity is usually observed by enhancing the Fe(III)/Fe(II) reduction potential (previous progress reports). Some unusual features of the work on the polyoxoanions deserves mention, however. Firstly, the Fe(III)/(II) reduction potentials of the

polyoxoanions determined in acetonitrile are all below -0.2 volts. This is below the value at which any catalytic activity is observed in the porphyrin systems. Secondly the electrochemical studies done in acetonitrile contained an acetate buffer to keep the pH at 4.7. The oxidations reported in Table 6-14 through 6-16 were all run in neutral acetonitrile. When small amounts of acetic acid were added to lower the pH, catalysis was completely quenched. When electrochemistry was attempted in neat acetonitrile, no Fe(III)/(II) wave was seen. Thus, electrochemistry was by necessity done under conditions at which no catalysis occurs, and catalysis was done under conditions at which no electrochemistry could be observed. More work would be needed to establish a valid correlation.

Electrochemical Studies - Electrochemical instrumentation consisted of an EG&G Princeton Applied Research (PAR) Model 273 instrument using Model 270 Electrochemical Analysis Software. Each tetrabutylammonium complex was dissolved in 0.1M $TBAPF_6$ in CH_3CN to a concentration of 2.0mM and then acetate buffer was added to pH ~4.7. Scan rates were kept constant at 200mV/s. A coil of platinum wire served as counter electrode. BAS glassy carbon electrode and Ag/AgCl were used as working and reference electrodes respectively. Between each run, the solutions were purged with N_2 for at least 5 minutes. The $E_{1/2}$ for the Fc/Fc+ couple under the above conditions was 283mV.

6.10.3.2 The Effect of the Number of Tetrabutylammonium Groups on the Oxidation Activity of Iron Substituted Keggin Catalysts

Table 6-15 shows the effect of going from three to four tetrabutylammonium groups in iron substituted silico- and phosphotungstate Keggin catalysts on the low temperature liquid phase oxidation of propane. There seems to be a significant lessening of the activity as the fourth tetrabutylammonium group is added.

6.10.3.3 The Effect of the Framework Metal on the Oxidation Activity of Iron Substituted Keggin Catalysts

The oxidation activity of two pairs of iron-substituted Keggin complexes were compared in Table 6-16. The first set of complexes are an iron-substituted silicotungstate and an iron substituted silicomolybdate. The second pair are an iron-substituted phosphotungstate and an iron substituted phosphomolybdate. In both cases the tungsten complex had slightly higher activity.

TABLE 6-14

EFFECT OF THE CENTRAL HETEROATOM, M, ON PROPANE OXIDATIONS CATALYZED BY KEGGIN CATALYSTS[a]

CATALYST	M(X) X	CHARGE ON COMPLEX, Z	FeIII/FeII V(b)	FeIII/FeII V(c)	TO	ONE/ OL[d]
$[BW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H_2$	III	6	-	-	306	4.0
$[SiW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]H$	IV	5	-0.500	-0.145	224	3.7
$[PW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4$	V	4	-0.415	+0.039	197	5.0
$[AsW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4$	V	4	-0.317	+0.123	150	3.5
$[BiW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H_2$	III	6	-	-	95	2.5
$[GeW_{11}Fe(H_2O)O_{39}][n\text{-}C_4H_9)_4N]_4H$	IV	5	-0.267	-0.065[e]	48	f
$[SbW_{11}Fe(H_2O)O_{39}][n\text{-}C_4H_9)_4N]_4H_2$	III	6	-0.217	-	0	-

[a]Air, 1500 psig, pressed on 60 g propane in 48 ml acetonitrile containing 0.023 mmoles catalyst. Heated to 125°C with stirring for 20 hours Product analysis by standardized glpc.

[b]Half wave potentials (E1/2) determined in CH_3CN (TBAPF6) with acetate buffer (pH 4.7) Ag/AgCl. Fc/Fc^+ = 283 mv.

[c]Formal Fe(III)/Fe(III) reduction potentials exhibited by $[FeMW_{11}O_{39}]^{x-}$ added as potassium salt in water. J. E. Toth, Ph.D Dissertation, Caltech, Pasadena.

[d]Acetone/isopropyl alcohol molar ratio.

[e]Outlying point in electrochemical trend. Measurement will be repeated.

[f]No isopropyl alcohol detected.

TABLE 6-15

EFFECT OF THE NUMBER OF $(n\text{-}C_4H_9)_4N$ GROUPS ON CATALYTIC ACTIVITY OF KEGGIN CATALYSTS[a]

CATALYST	M(X) X	CHARGE ON COMPLEX, Z	TO	ONE/ OL[d]
$[BiW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_3H_3$	III	6	248	3.2
$[BiW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H_2$	III	6	95	2.5
$[SbW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_3H_3$	III	6	144	3.5
$[SbW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9N]_4H_2$	III	6	0	-

[a]Air, 1500 psig, pressed on 60 g propane in 48 ml acetonitrile containing 0.023 mmoles catalyst. Heated to 125°C with stirring for 20 hours Product analysis by standardized glpc.

[d]Acetone/isopropyl alcohol molar ratio.

TABLE 6-16

EFFECT OF THE NATURE OF FRAMEWORK METAL ON OXIDATION ACTIVITY OF KEGGIN CATALYSTS[a]

CATALYST	M(X) X	CHARGE ON COMPLEX, Z	TO	ONE/ OL[d]
$[Si_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H$	IV	5	224	3.7
$[SiMo_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4H$	IV	5	199	5.6
$[PW_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4$	V	4	197	5.0
$[PMo_{11}Fe(H_2O)O_{39}][(n\text{-}C_4H_9)_4N]_4$	V	4	171	4.5

[a]Air, 1500 psig, pressed on 60 g propane in 48 ml acetonitrile containing 0.023 mmoles catalyst. Heated to 125°C with stirring for 20 hours Product analysis by standardized glpc.

[d]Acetone/isopropyl alcohol molar ratio.

7.0 CONCLUSIONS

The results of the three year study on polyoxo metallates have been assessed. Polyoxometallates such as Keggin ions have a number of desirable properties as "ligands" for first and second row oxidation-active metal centers. Firstly they are thermally and oxidatively stable. This allows one to access temperatures at which the more refractory alkanes such as methane and ethane are oxidized. Secondly, we have shown that it is possible to vary reduction potentials of framework metals by changing the nature of the Keggin ion. And finally, complexes of this type are indeed active for liquid phase oxidation of light alkanes.

On the other hand, during our investigations we have found that POA's such as Keggin ions containing oxidation active metal centers have several drawbacks as homogeneous air-oxidation catalysts. Organic solubility, especially in hydrocarbons is low. Although thermal and oxidative stability is high, solvolytic stability is low - especially to water, alcohols and carboxylic acids. Although active, the Keggin systems do not have the superb low temperature oxidation activity of the porphyrin systems nor do they give the high alcohol selectivities in alkane oxidations that metalloporphyrins do. Although it is possible to enhance reduction potentials of the oxidation-active metal centers in Keggin ions, we have not been able to create as great an enhancement in these complexes as we can in the porphyrin series. For these reasons we do not plan a major effort in POA's as catalysts for liquid phase oxidation as we enter the proof-of-concept phase. For our liquid phase work we intend to concentrate on the PHASE I porphyrin complexes or metals in related macrocycles. Utility of polyoxoanionic catalysts for vapor phase oxidations is still being explored (Phase III).