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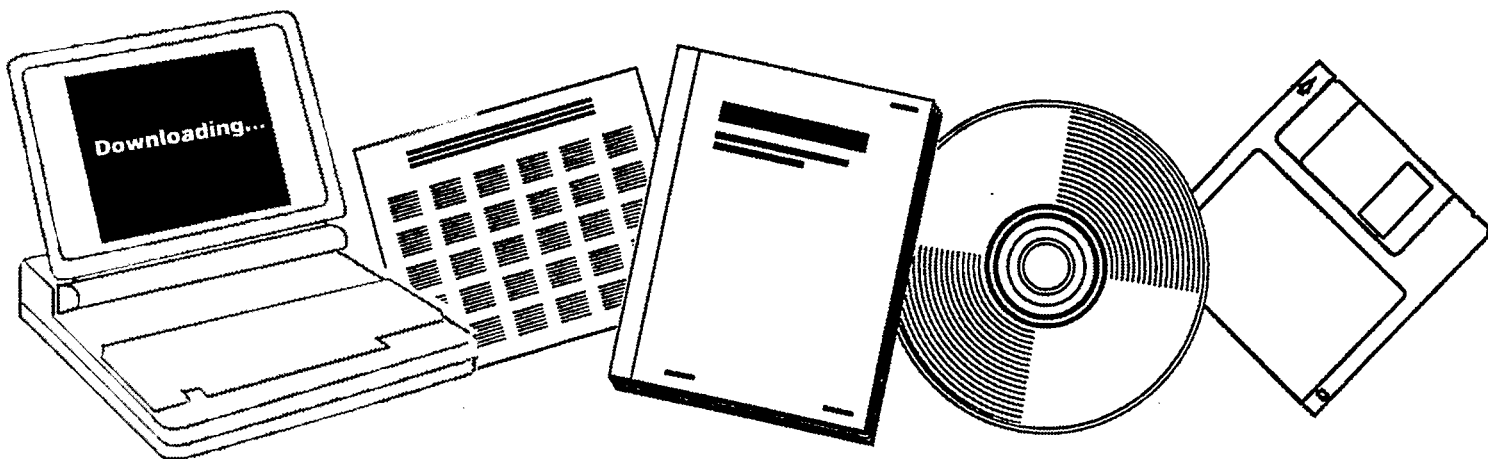
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**FUNDAMENTAL RESEARCH IN HOMOGENEOUS  
CATALYSIS AS RELATED TO U. S. ENERGY  
PROBLEMS. PROCEEDINGS OF A WORKSHOP HELD  
AT STANFORD UNIVERSITY, STANFORD,  
CALIFORNIA ON DECEMBER 4-6, 1974**

STANFORD UNIV., CA. DEPT. OF CHEMISTRY

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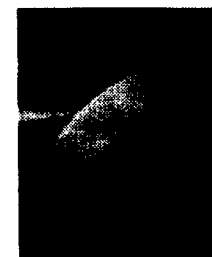
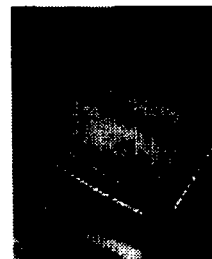
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WORKSHOP ON FUNDAMENTAL RESEARCH  
IN  
HOMOGENEOUS CATALYSIS  
AS RELATED TO U.S. ENERGY PROBLEMS

Organizing Committee

James Collman

Jack Halpern

Jack Norton

James Roth

Held at

Department of Chemistry  
Stanford University  
Stanford, California  
December 4-6, 1974

Sponsored by

National Science Foundation

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<b>REPORT DOCUMENTATION PAGE</b>	<b>1. REPORT NO.</b> NSF-RA-N-74-454	<b>2.</b>	<b>3. Recipient's Accession No.</b> PB80 157365		
<b>4. Title and Subtitle</b> Fundamental Research in Homogeneous Catalysis as Related to U.S. Energy Problems, Workshop on (Stanford University, December 4-6, 1974)		<b>5. Report Date</b> December 6, 1974			
<b>7. Author(s)</b> J. Norton, ed.		<b>6.</b>			
<b>9. Performing Organization Name and Address</b> Stanford University Department of Chemistry Stanford, California		<b>8. Performing Organization Rept. No.</b>			
<b>12. Sponsoring Organization Name and Address</b> Engineering and Applied Science (EAS) National Science Foundation 1800 G Street, N.W. Washington, D.C. 20550		<b>10. Project/Task/Work Unit No.</b>			
<b>15. Supplementary Notes</b>		<b>11. Contract(C) or Grant(G) No.</b> (C) (G)			
<b>16. Abstract (Limit: 200 words)</b> Efforts to identify solutions to energy problems by homogeneous catalysis and to recommend areas for fundamental research are reported. Homogeneous catalysts are metal complex catalysts which usually function at milder reaction conditions and often provide greater selectivity than metal or metal-oxide catalysts. A potential research area is the reduction of carbon monoxide with hydrogen over transition metal complexes. Implications of this reaction are discussed for coal gasification, methanation, methanol, the Fischer-Tropsch synthesis, and the synthesis of C <sub>2</sub> molecules from C <sub>1</sub> molecules. Another important research area is the application of homogeneous catalysis to the conversion of hydrogen, coal, and nitrogen into desirable fuels and chemicals through activation of hydrocarbons, nitrogen, and oxygen. The activation of oxygen for selective oxidation and for fuel cells is described. A section on specific catalysts for individual processes considers the possibility of designing homogeneous catalysis systems to effect specific chemical transformations. Another deals with photochemical energy storage and catalyst activities. Finally, new forms of catalysts are described.		<b>13. Type of Report &amp; Period Covered</b>  <b>14.</b>			
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<b>18. Availability Statement</b> NTIS		<b>19. Security Class (This Report)</b>	<b>21. No. of Pages</b>		
		<b>20. Security Class (This Page)</b>	<b>22. Price</b>		

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## Preface

The written report of this Workshop was derived from crude manuscripts submitted by the working subgroups (Appendix C). These manuscripts were then combined and revised by a group consisting of the organizing committee and the subgroup chairmen. The final manuscript was edited by Jack Norton with advice from the entire organizing committee. The recommendations were arrived at in a general session of the Workshop participants (Appendix B) and each recommendation received a majority vote of those present.

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## I. Introduction

The major objectives of this Workshop were to identify opportunities for the solution of energy problems by homogeneous catalysts and to formulate recommendations for fundamental research in this area that could accelerate these solutions.

The desire of the United States to attain a high degree of energy self-sufficiency is well known. It is widely recognized that achieving this goal will require a much greater utilization of coal in the production of gaseous and liquid fuels and of petrochemicals. Important contributions can also be made by new technology that provides energy conservation in ways such as more energy-efficient chemical production processes or more efficient energy conversion processes, e.g., fuel cells. Finally, harnessing solar energy to produce fuels (such as hydrogen generated from water) or feedstocks for petrochemicals could be of enormous value.

In our current technology for processing crude oil to fuels and petrochemicals, almost every step requires the use of a specific catalyst. In addition, catalysis is involved in the emerging technologies for: (1) production of synthetic natural gas and synthetic crude oil from coal; (2) routes to petrochemicals using synthesis gas derived from coal either directly via coal gasification or indirectly via the steam reforming of hydrocarbons produced from coal liquifaction; (3) fuel cell electrodes. One can also envision discoveries in catalysis permitting heretofore unknown or greatly improved processes for the activation and utilization of abundant and inefficiently used substances such as oxygen, nitrogen, carbon dioxide and paraffins. Clearly, catalysis will play a key role in the future production, utilization and conservation of energy.

Most of our existing catalytic technology is based on so-called "heterogeneous" catalysts. Historically, these heterogeneous catalysts have consisted mainly of metals or metal oxides and, in many applications, require relatively high reaction temperatures. Often these catalysts provide limited selectivity to the desired products and are characterized by energy-intensive, capital-intensive processes.

Another interesting and important class of catalysts are the so-called "homogeneous" catalysts which consist mainly of metal complexes. While for a long time metal complexes were used and studied mainly homogeneously in the liquid phase, work in recent years has shown that many of these complexes can be prepared and used in the form of a variety of heterogeneous analogs and often provide properties similar to those observed in homogeneous liquid phase systems. Their most important distinction is that they consist of metal complexes rather than metals or metal oxides. In this report the terminology homogeneous catalysts shall be synonymous with metal complex catalysts.

Metal complex catalysts usually perform at milder reaction conditions and often provide greater selectivity than is commonly found with metal/metal oxide catalysts. Greater selectivity has an important impact on energy and resource utilization in several ways. Product separation and purification is simplified and process energy requirements are significantly reduced. Byproducts may be useless or of low value and this material-value loss can be translated to an equivalent energy loss. Poor selectivity can also raise capital requirements significantly and, increasingly, capital as well as energy is regarded as a critical national resource.

An illustration of the utility of homogeneous catalysis is provided by the new process recently commercialized on a large scale for the manufacture of acetic acid from methanol and carbon monoxide. As natural gas and petroleum prices rise, the preferred raw material for acetic acid (and other petrochemical products) will become synthesis gas derived from coal. The new acetic acid process will enjoy a raw material advantage since both methanol and carbon monoxide are obtainable from synthesis gas. In addition to a favorable raw material cost, the high selectivity in this process results in low process energy and capital requirements. These advantages were made possible by the discovery and development of a highly specific homogeneous catalyst that functions at mild reaction conditions.

## II. Summary

- |                            |   |
|----------------------------|---|
| One<br>Carbon<br>Chemistry | The conversion of coal to synthesis gas (carbon monoxide and hydrogen) is an important aspect of increased coal utilization in the production of gaseous fuels and of petrochemicals. In the use of synthesis gas as a raw material, a recurring chemical reaction is the reduction of carbon monoxide with hydrogen. Fundamental research is necessary on the catalysis of this reaction. The identification and study of possible intermediates will be necessary to devise both homogeneous and new heterogeneous catalysts. More knowledge of the interaction of CO and H <sub>2</sub> with metal complexes is clearly indispensable. The lack of examples of homogeneously catalyzed reductions of CO offers an important challenge. Why do CO reductions occur heterogeneously, but not homogeneously?  |
| Fischer-<br>Tropsch        | A homogeneously catalyzed synthesis of methane, for example, might provide greater resistance to sulfur poisoning, more facile heat removal and less catalyst deactivation than occurs with present heterogeneous catalysts. A homogeneous catalyst for methanol synthesis could function at lower temperatures and provide greater conversion per pass at lower reaction pressures. A homogeneous catalyst in the Fischer-Tropsch synthesis might provide higher selectivity for important products such as higher terminal olefins and alcohols. Improvements in the formation of ethanol from methanol appear readily attainable by homogeneous catalysis. Finally, the water-gas shift reaction could also benefit from homogeneously catalyzed systems that operated at lower temperatures.  |
| Hydrocarbon<br>Activation  | Homogeneous catalytic activation of the hydrocarbons produced in Fischer-Tropsch processes or otherwise available is also an area of major scientific challenge. C-H bond activation in alkanes is not now well established for soluble catalysts, except for relatively nonspecific electrophilic and free radical processes. Such a reaction would be the first step in the catalysis of both the interconversion (e.g. the isomerization of normal paraffins to branched products in petroleum refining) and the functionalization of hydrocarbons. A particularly useful type of functionalization would be selective oxidation (see below). In all such reactions the increased selectivity to be expected of homogeneous catalysts would be of vital importance in the petroleum refining and petrochemical industries. Higher yields of desirable products would not only directly decrease crude hydrocarbon consumption but also save the process energy involved in separation. |
| Nitrogen<br>Activation     | Activation of atmospheric nitrogen also merits increased attention. However, catalysis of direct ammonia synthesis is not nearly as important a goal as is the synthesis of hydrazine, nitrates, and organic amines directly from nitrogen.   |

Selective  
Oxygenation

Selective oxygenation of organic substrates remains a largely unresolved challenge to synthetic chemistry. Direct use of oxygen itself, the least energy-intensive functionalizing agent, would be ideal. In this respect there is a great deal to be learned from nature, where metalloenzymes (natural homogeneous catalysts) incorporate one or both atoms of molecular oxygen into saturated organic substrates with great selectivity. Recent developments with main group systems offer promise and suggest that these elements should have less tendency than transition metals to promote undesired, nonselective free radical oxygenations.

Oxygen  
Cathode in  
Fuel Cells

There is also need for more effective catalysis of the total oxidation of organic substrates used as fuels. The energy of combustion of fuels by  $O_2$  cannot now be converted efficiently to electrical or mechanical energy at useful rates. It would be possible to do so if the fuel could be oxidized and oxygen reduced at separate electrodes in an electrochemical cell. To reduce  $O_2$  rapidly, energetically unfavorable intermediates must be avoided or stabilized. Catalysts capable of providing multi-centered, multi-electron reaction paths or of stabilizing the intermediates of stepwise paths are needed. Information needed to aid their design will come from synthesis, properties, and chemical behavior of several types of metal compounds, and from study of pertinent enzymes. The anodic oxidation of carbonaceous fuels, including the important case of methanol, poses analogous problems with energetically unfavorable intermediates.

Catalyst  
Selectivity

It is clear from the foregoing that specificity is an important general aspect of homogeneous catalysis. There are important potential industrial applications of highly specific catalysis in the production of chiral substances (asymmetric catalysis) and other naturally occurring substances (stereospecific and regio-specific catalysis) for use as foodstuffs, drugs, vitamins, fragrances and flavorings. Further development of this area could result in new techniques for oxidation reactions and in catalytic reactions of  $SO_2$ ,  $NO_x$  and CO useful in control of pollution from stack gases.

Photo-  
chemistry

There are also many potential applications of homogeneous catalysis to the storage and use of light energy. Two are: 1) the production of high-energy substances (such as hydrogen) by energy transfer from sunlight via metal complexes to optically transparent substrates (such as water); 2) the photochemical formation of novel homogeneous catalysts, or the formation of known ones under mild conditions.

Supported Catalysts

Study of homogeneous type metal complex catalysts supported on insoluble carriers or employed in solvents in multiphase systems has the potential to eliminate or reduce problems associated with the use of soluble catalysts. More importantly, study of a variety of supports, including those able to act synergistically with the supported complex, is likely to lead to new and useful types of catalysts.

Supportive Fundamental Research

While the types of research cited above are directly linked to energy-related objectives, the effective pursuit of such research also requires a strong supportive research effort in a variety of fields of underlying basic science. Among the research themes underlying most or all of the above areas are 1) the need for new ligands resistant to severe reaction conditions, ligands capable of manifesting variable oxidation states, and ligands capable of stabilizing metals in unusual oxidation states; 2) the catalytic potential of the relatively neglected early transition elements (titanium, molybdenum, tungsten, etc.); 3) the need for fundamental research on the kinetics and mechanisms of organometallic reactions; 4) the many potential uses of multi-metallic systems; 5) the importance of the stabilization of high-energy reaction intermediates.

### III. Recommendations

#### A. High Priority Research Areas

There are many ways in which homogeneous catalysis is capable of contributing to the solution of energy problems, and thus many areas of research are recommended in subsequent more detailed sections on particular problems. However, the Workshop recognized the following areas of research as particularly important, relatively neglected at present, and potentially fruitful:

- 1) The homogeneous catalytic activation of saturated hydrocarbons.
- 2) Selective oxidation of organic substances and the activation of oxygen, including electrode surface studies.
- 3) The reduction of carbon monoxide, especially by hydrogen, including studies on the mechanism of Fischer-Tropsch synthesis and on homogeneously catalyzed analogs of the latter.
- 4) Studies on multi-metal catalyst systems, including polynuclear complexes as well as multi-function catalysts involving combinations of different metal ions. (Successful examples of the latter include the use of Cu(II) - Pd(II) couples in the Wacker reaction and Hg(II)-Pd(II) for coupling aromatics).

5) Production of high energy substances such as hydrogen from water, and carbon monoxide from carbon dioxide, especially through photo-assisted processes.

6) Catalytic complexes involving unusual metal environments, including new ligands, supported metal complexes and unusual media such as fused salts and solvents of low nucleophilicity for highly electrophilic catalysts.

#### B. Needs and Programs of Support

In recognition of certain special needs and obstacles to progress in the field, the Workshop recommended the following programs to further fundamental research in homogeneous catalysis related to energy problems:

1) A program of internships or senior postdoctoral fellowships to support sabbatical leaves (especially by young academic scientists) in laboratories where they would obtain training and experience in fields related to homogeneous catalysis and thereby be in a position to more effectively direct their research efforts.

Justification. Among the factors that warrant the assignment of a high priority to such a program in this particular field are (i) the young and rapidly expanding character of the field of homogeneous catalysis; (ii) the relatively small number of academic laboratories already working in the field and the consequently inadequate rate of training of new scientists at the postgraduate and postdoctoral levels; (iii) the multidisciplinary nature of the field, as a result of which there should be considerable contributions from scientists with prior training in other fields; (iv) the demonstrated interest of many young scientists in other fields (especially organic chemists) in undertaking research programs in homogeneous catalysis and (v) the absence of adequate programs of support of advanced postdoctoral training and sabbatical leaves in many academic institutions.

2) National and regional services to provide access to large instrumental facilities that are important for the implementation of much research in homogeneous catalysis (such as Mössbauer spectroscopy, multinuclear NMR spectroscopy, precise magnetic measurements, analytical services, ESCA, and specialized mass spectrometric analyses, etc.).

Justification. Such facilities are of crucial importance to much of modern research in the field of homogeneous catalysis and are not now accessible to many research workers. At the same time it is not practical for all the institutions where such research is being carried out to possess such facilities because of the relatively small size of many research groups. Cooperative facilities and services thus seem to be the most effective way of filling this urgent need. In recommending such a program, the Workshop

participants also recognized the limitations of such centralized facilities and stressed the importance of ensuring high quality performance and service.

3) Programs (such as contractual arrangements with commercial or academic laboratories that are qualified to undertake such tasks) for the synthesis of recognizably important classes of ligands (for example phosphine phosphites, macrocyclic ligands, chiral ligands, ligands with special substituents, etc.) to be made available to workers in the field of homogeneous catalysis through some appropriate mechanism such as a "ligand bank."

Justification. The importance of access to a wider range of ligands than is presently available to many workers in the field of homogeneous catalysis was recognized in many of the recommended areas of research. Because of the difficulty of synthesis of many desired ligands, and because such syntheses are frequently outside the areas of expertise of the research workers involved, the availability of ligands is often a limiting factor in the successful conduct of research in the field of homogeneous catalysis. In many cases (e.g. phosphine ligands) the need for specific classes of ligands (in a wider range than presently available) is sufficiently widespread and recognizable that a program to make such ligands more readily available in a systematic manner seems both feasible and desirable.

### C. Other Recommendations

In response to other problems and needs that were recognized, the Workshop recommends:

- 1) More effective interaction between academic and industrial research workers in the field of homogeneous catalysis.
- 2) More effective interaction between research workers in the fields of homogeneous and heterogeneous catalysis.
- 3) The development of more effective procedures than are presently available for the evaluation of catalytic properties of coordination and organometallic compounds that are synthesized in academic laboratories.

## IV. Production and Use of Carbon Oxides and Hydrogen

In identifying potential research areas for the utilization of 1 carbon molecules, a recurring problem is the reduction of carbon monoxide with hydrogen over transition metal complexes. A very high priority should be attached to fundamental research on the reactions between metal complexes and CO and H<sub>2</sub> mixtures. The identification of the intermediate and studies of the reactions of such species, in particular the study of 'insertion' of CO into metal hydride bonds, would be of benefit in devising both homogeneous and heterogeneous catalysts.

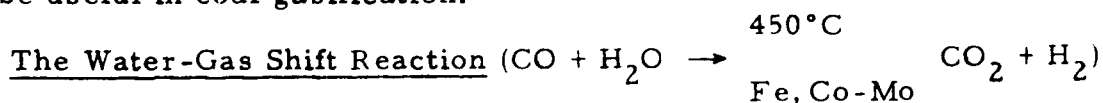
## Introduction

At present, natural gas or petroleum is used to make synthesis gas and synthesis gas in turn is used to make fuels and chemicals. Because methane is in very short supply in this country and petroleum feedstocks are becoming scarce, we must turn to our vast and indigenous reserves of coal and to other available carbon sources for the production of synthesis gas.

## Coal Gasification

The conversion of coal to synthesis gas with steam and oxygen is a well-known process. The Koppers-Totzek process operating at atmospheric pressure produces synthesis gas from coals in many plants (about 30) around the world; this gas is used mostly to produce methanol and ammonia. The well-established Lurgi process operating at 300-350 psi produces methane along with synthesis gas and is used in the Sasol plant in South Africa to produce liquid fuels and chemicals via the Fischer-Tropsch process.

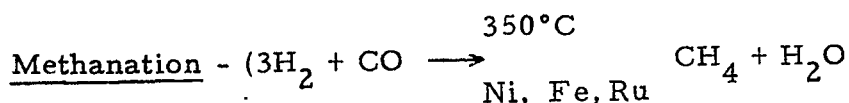
There are several so-called second generation gasification processes now in the pilot stage in the U.S. (the Hygas process, the Synthane process, the CO<sub>2</sub>-acceptor process and the Bigas process); all operate at elevated pressures (to 1000 psi) and yield synthesis gas and methane. They will have greater throughputs than existing technology permits (although efforts are under way to operate the Koppers-Totzek process at about 350 psi). All these gasification plants must operate at 700-1400°C because of thermodynamic limitations. Thus it is unlikely that homogeneous catalysts will be useful in coal gasification.



The water-gas shift reaction is a way of increasing the 1:1 H<sub>2</sub>:CO ratio or of producing pure H<sub>2</sub>. Pure H<sub>2</sub> is needed for the ammonia synthesis, 2H<sub>2</sub>:1CO is needed for the methanol synthesis and 3H<sub>2</sub>:1CO is necessary for the synthesis of substitute natural gas (SNG). A great potential benefit of a homogeneously catalyzed water-gas-shift reaction could be the production of pure H<sub>2</sub> but the use of such a catalyst to shift to 3:1 gas for methanation might become very important as SNG plants are built throughout the country. The desired products are favored by lower temperatures and we already know of homogeneous catalysts that function at <200°C.

There should be mechanistic investigations leading to new and superior homogeneously catalyzed systems for the water-gas shift.

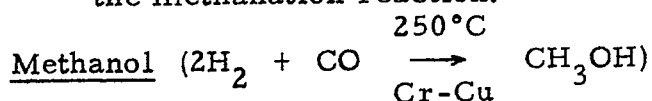




The methanation of synthesis gas is presently accomplished over heterogeneous Ni, Fe or Ru catalysts with Ni being the preferred catalyst. Surprisingly, little is known concerning the mechanism of this reaction. At present, there are no known homogeneous catalysts for the methanation of synthesis gas. Heterogeneous catalysts deactivate with time; this may be due to sulfur poisoning, sintering, carbide formation or coke formation due to the very large exothermicity of the reaction. Homogeneous catalytic systems would probably not be affected by sulfur compounds and could well avoid the other problems mentioned above.

This is an area in which homogeneous catalysts may do much to explain what is happening in the heterogeneous case. Fundamental studies should be aimed at the discovery of homogeneous catalysts or at the elucidation of the elementary steps of conceptualized pathways to methanation.

More knowledge of the interaction of  $\text{CO} + \text{H}_2$  with metal complexes, of formyl metal complexes, of hydroxymethyl metal compounds, of metal-carbene complexes, and of metal alkyls appears necessary for an understanding of the methanation reaction.



One of the great and mysterious differences (which appears again and again throughout this report) between heterogeneous and homogeneous catalysis involving  $\text{CO} + \text{H}_2$  is the ability of the heterogeneous system to catalyze the reduction of  $\text{CO}$  by  $\text{H}_2$ . Such a process is involved in the initial stage of methanation, the methanol synthesis and the Fischer-Tropsch synthesis. At present, no homogeneous catalysts are known which accomplish this. Once an initial methyl group, olefin, alcohol, etc., is formed over a heterogeneous catalyst, homogeneous catalysts are then quite effective in carrying out further reactions. Is a metal surface absolutely necessary for the initial formation of the organic entity, substrate or compound or will it be possible to find a homogeneous catalyst which will catalyze the reaction of  $\text{CO} + \text{H}_2$  to form an organic moiety such as  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ , etc. If the latter were possible, that is, if we could synthesize  $\text{CH}_3\text{OH}$  homogeneously, it would not only have great intrinsic importance, it would be significant in attempts to devise new routes to petrochemicals and fuels.

A homogeneously catalyzed methanol synthesis might show great selectivity, could be resistant to sulfur poisoning, and would remove excessive heats of reaction. This should be a primary aim of research in homogeneous catalysis.

Homogeneous catalysts for methanol would probably operate at lower temperature than the presently used heterogeneous catalysts and this would

greatly increase the methanol conversion per pass. The low pressure methanol synthesis now used operates at 150 atmospheres and 200-250°C over chromia-copper catalysts.

#### Utilization of 1-Carbon Molecules by the Fischer-Tropsch Synthesis

In the Fischer-Tropsch synthesis CO is hydrogenated on heterogeneous Fe, Co, Ni and Ru catalysts at 150°-400°C and moderate pressures. This process yields a wide array of paraffins, olefins and alcohols with a wide carbon number distribution. Changes of catalysts, feed gas, and operating conditions generally only shift these distribution curves. Production of a single molecular species or molecular weight fraction in large yields, except for CH<sub>4</sub>, has not been achieved. These catalysts are poisoned by sulfur compounds and virtually all of the sulfur must be removed from the feed. The large Sasol plant in South Africa has been operating successfully for 25 years producing a mixture of fuels and chemicals.

As noted earlier, currently known homogeneous processes do not initiate chains and generally extend them by only one carbon atom.

Homogeneous counterparts to the Fischer-Tropsch synthesis steps should be investigated to provide an understanding of these steps and to provide control of these processes to yield high selectivity in producing selected products, eg., C<sub>7</sub> to C<sub>9</sub> terminal olefins or alcohols.

Removal of the heat of reaction from the exothermic reactions would seem simpler in a homogeneous system and homogeneous reactions should be relatively insensitive to poisoning by sulfur compounds.

Again, the most crucial problem for homogeneous catalysis is to synthesize the CH<sub>3</sub> moiety from CO + H<sub>2</sub>, in other words to reduce CO with H<sub>2</sub> to a one carbon intermediate.

#### Synthesis of C<sub>2</sub> Molecules from C<sub>1</sub> Molecules

A particularly useful application of Fischer-Tropsch type chemistry could be to produce ethanol or ethylene selectively. Ethylene and ethylene based materials constitute the largest volume of organic materials produced in the world. Present methods for ethylene production are based on petroleum and natural gas. The possibility of stopping Fischer-Tropsch type synthesis at the C-2 level is attractive; this requires control of the chain termination step. The ability to fine tune homogeneous catalysts by ligand variation and the mild conditions potentially possible might allow the development of such a catalytic process. There are reactions now known in which CH<sub>3</sub>OH + CO + H<sub>2</sub> react to give ethanol in the presence of a homogeneous catalyst. A one-step process directly from CO is more desirable.

In the short run improvements in the conversion of  $\text{CH}_3\text{OH} \rightarrow \text{EtOH}$  appear attainable by homogeneous catalysis. In particular, the reduction of operating pressure and the elimination of corrosive halogen promoters are highly desirable.

A one step synthesis of ethylene from CO and  $\text{H}_2$  is a highly desirable goal. Investigation of the possibility of synthesizing and coupling potential intermediates such as methylene (or carbon) metal complexes formed from CO and  $\text{H}_2$  is desirable. Controlled chain extensions to three to six carbon molecules would lead to important industrial intermediates

### Carbon Dioxide

The synthesis of metal complexes containing  $\text{CO}_2$  as a ligand has only recently been achieved and the study of the coordination chemistry of  $\text{CO}_2$  is in its infancy. Research on such complexes is considered desirable because of the potential role that such complexes may play in the development of new and improved processes (listed in order of decreasing priority from the standpoint of energy-related importance) for 1) the oxidation of CO and  $\text{CH}_3\text{OH}$ , especially in the context of utilization for fuel cells (Note:  $\text{CO}_2$  complexes have been identified as intermediate in the oxidation of CO by metal ions); 2) the production of CO by reduction of  $\text{CO}_2$  through photo-synthetic processes involving homogeneous catalysis; 3) the utilization of  $\text{CO}_2$  as a reagent for functionalizing hydrocarbons (e. g. to carboxylic acids).

### V. Activation of Hydrocarbons

In view of the dwindling supply and increasing cost of natural gas and petroleum, the prime sources of energy for our society and feedstocks for the chemical industry, it is essential that we use them with maximum efficiency. A major contribution can be made by improving the selectivity with which industry carries out transformations of saturated hydrocarbons. Even slight improvements in petroleum refining can produce large quantitative savings in crude hydrocarbon consumption. Substitution of coal for petroleum as a feedstock or energy source would prolong the availability of this valuable resource.

One promising approach to achievement of these advantages is through more extensive application of homogeneous catalysis to the conversion of hydrocarbons, coal and nitrogen into desirable fuels and chemicals. In its limited use to date, homogeneous catalysis (defined here as use of soluble metal complexes to promote desired reactions) often has shown advantages in yield improvement, process simplification, and lower energy consumption.

In order to obtain the advantages of homogeneous catalysis in hydrocarbon and coal conversion, a substantial improvement is needed in our knowledge of the interactions between transition metal complexes and these raw materials. In the following pages, we outline some desirable goals in three process areas together with areas of study which should be useful in attainment of these goals.

#### A. Interconversion and Syntheses of Hydrocarbons

The ability to rearrange and to synthesize hydrocarbons to specific structures can have a tremendous effect on energy consumption and its efficient use. Some goals for energy-saving through increased catalytic specificity are:

1) To reduce energy consumption in energy-intensive reactions such as styrene synthesis from benzene and ethylene, dealkylation of alkylbenzenes, and dehydrocyclization of alkanes and olefins.

2) To improve conversion and selectivity efficiencies and thus save energy by the use of smaller equipment, less feedstock, and less heating and cooling in recycle. For example, potential savings can be made in the oligomerization and disproportionation of olefins.

3) To produce hydrocarbons which have higher octane number values than the hydrocarbons now produced for use in gasoline. By making isomers with higher octane numbers (o.n.) the compression ratio of automotive engines can be increased to obtain improved efficiencies and a reduction in fuel consumption of 10-15%. Some target reactions are dimerization of olefins to highly branched products such as 2,3-dimethylbutane (101 o.n.), isomerization of paraffins to isoparaffins, and alkylation of alkanes with olefins and other alkanes.

The above reactions require improvement of catalysts for alkane activation, hydride abstraction, selective addition to olefins and selective group removal. Heterogeneous catalysis has provided limited effectiveness; research in homogeneous catalysis is a possible means for obtaining increased activity and selectivity. In no case is a transition metal complex used today as a catalyst in any of the above reactions and activation of paraffins by such complexes is rare.

#### Research Strategy

Conceptually, alkane activation appears to be possible through the oxidative addition of C-H or C-C bonds to very electron-rich metal centers or by electrophilic attack upon the C-H  $\sigma$ -bond by a metal center to produce a metal-alkyl and a proton. Both mechanisms have precedent in heterogeneous catalysis but are difficult to accomplish using catalytic sites composed of a single metal atom. However, the reactivity of simple

monometallic complexes might be enhanced by providing a means for irreversible ligand dissociation and by operating in an extremely non-nucleophilic solvent system. The tactic of providing irreversible ligand dissociation might be solved by diffusion of the dissociated ligand through a semipermeable membrane into a "sea" of solvent, by tight complexation of the ligand at another atom or by using a self destructive ligand.

On an a priori basis one might expect catalysts which have two or more metal centers anchored to a small multivalent ligand to promote synergistic oxidative addition and/or heterolytic reactions. Complexes having metal-metal interactions are known in metal carbonyl clusters, metallocenes and metallocarboranes. Superior catalysts based on the polymetal concept would be best served by an imaginative synthesis program aimed at new ligands which position two metal centers (alike or different) in close proximity in a well defined molecular geometry.

### B. Functionalization of Hydrocarbons

A major petrochemical operation is the conversion of hydrocarbons to functionally substituted derivatives such as nitriles, carboxylic acids and vinyl compounds which serve as intermediates for plastics, fibers and detergents. Although homogeneous catalysis is used extensively for these conversions, especially for olefin reactions (hydroformylation, carboxylation, hydrocyanation, and epoxidation), considerable energy savings could be realized through more efficient use of feedstocks.

Our knowledge of homogeneous catalysis of olefin reactions is well developed but much less is known about mechanisms and control of selectivity in reactions of aromatic and paraffinic hydrocarbons. Because of this discrepancy in background information, it appears that priority should be given to fundamental studies on C-H and C-C bond activation in the sequence: alkanes>arenes>olefins. However, we should point out that important goals remain in olefin reactions such as anti-Markovnikov addition of water to give primary alcohols, addition of ammonia to give amines, and selective oxidations with oxygen.

Some of the reactions which might be achieved more selectively if a non-radical mechanism for activation of alkanes were found include 1) oxidation to alcohols, olefins or carboxylic acids, 2) oxidative carbonylation to ketones or carboxylic acids, and 3) chlorination to economically desirable isomers. Similarly with aromatic substrates, direct oxidation to phenols, carboxylation to acids, and control of polysubstitution to give wanted isomers are desirable objectives.

In order to develop catalysts for reactions of alkane and arene C-H bonds, an imaginative exploration of highly reactive complexes for interaction

with these substrates is required. A wide range of metals and new ligand types should be considered. Much work is needed to synthesize ligands that are stable to a wide range of reaction conditions and reagents. This consideration is particularly important in the reactions of alkanes where the ligands should not contain the same bonds as the alkane, i. e. C-H or C-C. Ligands stable to oxidation are also needed. It is suggested that when new ligands and complexes are prepared that they should be sufficiently characterized to indicate their possible suitability for consideration as catalysts. Minimum characterization should include determination of their thermal, hydrolytic and air stability.

Since bimetallic systems and metal clusters offer the promise of another degree of freedom for condensation and functionalization reactions, the study of their formation and properties should be encouraged. In particular, the transfer of a reacting organic ligand from one metal atom to another is potentially important.

In addition to the catalyst system, the choice of solvent is an important consideration, for solvents can act as ligands and influence the nature of the nucleophilicity and electrophilicity of the metal atom. These considerations are likely and particularly important in the case of alkane functionalization where electrophilicity of the metal should be very important.

### C. Homogeneous Catalysis for Coal Liquefaction

The conversion of coal, which can be regarded as a mixture of solid organic compounds, to sulfur-free liquid fuels offers some opportunities for homogeneous catalytic approaches. It is known that Lewis acids such as molten zinc halides are efficient catalysts for hydrogenation of coal to gasoline. Hydroliquefaction is also achieved with  $\text{SnCl}_2$ , Sn or  $\text{PbCl}_2$  although these catalysts are not effective for N or S removal. Volatile metal carbonyls, especially  $\text{Co}_2(\text{CO})_8$ , catalyze hydrogenation of coal to liquid products by hydrogen transfer from hydroaromatic compounds. However, practical application in liquid fuel synthesis would require complete metal removal because of economic and environmental considerations. The mechanism of action of these various catalysts provides an interesting fundamental research problem.

Another challenge in this area is development of a small, mobile catalyst molecule which could "tunnel" into coal or oil shale kerogen to break down the matrix structure to give a fluid product. No catalyst candidates are obvious but some hope for this approach is provided by the anomalously high permeability of coal to certain gases such as  $\text{CO}_2$ .

Low ranked coals, our largest energy resource, contain much oxygen and do not liquefy well under hydrogenation conditions. Nonetheless they react with  $\text{CO-H}_2\text{O}$  at  $>400^\circ\text{C}$  and  $>2000$  psig in the absence of added

catalyst to produce a heavy fuel oil. Basic materials such as  $\text{Na}_2\text{CO}_3$  and  $\text{NaOOCH}$  catalyze this reaction but are seldom needed because these coals usually contain enough basic mineral matter to catalyze the liquefaction. Soluble formates are considered the active reducing agents and thus constitute a homogeneous system. A combination of this means of reducing low ranked coals along with a volatile and recoverable hydrogenation catalyst, such as mentioned in the previous paragraph, could provide an improved means of converting lignite and subbituminous coals to fuel oil. Since these coals generally contain much water (>25%) and mineral matter (>10%) and have a low TBu value (8,000 to 10,000 BTu/lb) conversion to water-free, mineral-free fuel oil having a higher heating value (>14,000 BTu/lb) would be of considerable interest.

Coal is a reactive system even at low temperatures, but we do not know how to convert it cheaply at low temperatures into desirable products. For example, it can be reductively alkylated at room temperature to benzene-soluble material without altering the carbon structure. Perhaps new reaction systems can be devised, making use of homogeneous catalytic systems, so that specific carbon-heteroatom linkages can be broken to produce phenolic or nitrogen base compounds useful in the chemical industry. Coal-derived chemicals making use of existing functional groups could prove quite valuable.

#### Recommendations

The following research topics appear to have the greatest potential for scientific and technical impact.

1) C-H bond activation, especially in alkanes. This step is a critical first step in both interconversion and functionalization of hydrocarbons. It is not now well established for soluble catalysts, except for relatively non-specific electrophilic and radical processes.

2) Selective oxidation of hydrocarbons by air or oxygen. Oxidation processes with  $\text{O}_2$  efficiently make use of the energy potential in C-H bonds but are largely unselective (see VII).

In order to achieve these objectives, the following types of research are desirable.

1) Fundamental studies on metal-ligand interaction as it influences the finding and activation of hydrocarbons and nitrogen. Physical studies of metal-ligand bonds and metal-substrate interactions should include thermochemistry, a broad range of spectroscopic techniques, and crystal structure determination. Rate and mechanism studies of hydrocarbon substitution and of nitrogen reactions are needed.

2) Synthesis programs to prepare more active and more selective soluble catalysts, especially for selective oxidation of hydrocarbons.

New ligand types may be necessary to activate transition metals to the point that they will attack C-H or C-C. Photochemical activation, metal atom evaporation, and electrolytic reduction may give highly reactive complexes. Polymetallic complexes may simulate the role of metal surfaces in activation of alkanes.

3) Evaluation of new complexes as catalysts for energy-conserving processes.

A mechanism (possible via contract research) should be developed to insure that new metal complexes are tested for hydrocarbon activation as well as in more conventional catalytic processes.

## VI. Activation of Nitrogen

Although catalytic reduction of  $N_2$  to  $NH_3$  has been carried out industrially with a heterogeneous catalyst for over fifty years, no efficient homogeneous catalyst for  $N_2$  fixation is now known. Several reducing systems which stoichiometrically convert  $N_2$  to  $N_2H_4$  or  $NH_3$  have been developed, but they have not been well characterized with respect to specific reaction intermediates. Many transition metal dinitrogen complexes have been isolated, but few have been investigated in terms of their potential catalytic activity for reactions other than reduction to ammonia or hydrazine.

The development of homogeneous catalysts for the conversion of  $N_2$  and  $H_2$  to  $NH_3$  under mild conditions would offer potential energy savings in production and transportation. In addition to  $NH_3$  synthesis, catalytic processes utilizing  $N_2$  as a substrate for oxidative fixation of nitrogen to nitric acid and fertilizers, for organic amine and heterocycle synthesis, and even for the direct synthesis of amino acids from  $N_2$  should be explored, since such one-step syntheses also offer obvious energy savings. As noted elsewhere, development of an economical direct synthesis of hydrazine from  $N_2$  would open the way to utilization of highly efficient hydrazine fuel cells. Increasing the scope and efficiency of biological nitrogen fixation would have major impact.

### Studies Required

The characterization of new and existing dinitrogen complexes in terms of their chemistry and the structural features which determine such chemistry should receive increased emphasis. The synthesis of very reactive complexes and the chemistry available to  $N_2$  in the presence of these complexes should be explored. Studies of the coordination chemistry of ligands representative of suspected high energy intermediates in  $N_2$  fixation (e.g.  $-N=NR$ ,  $RN=NR$ ,  $-NR-NR_2$ , etc.) should be investigated as new



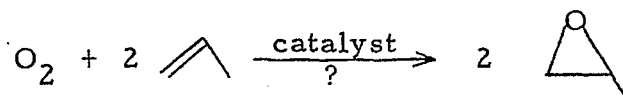
approaches to the problem. An increased effort should be made to elucidate the structure of the nitrogenase enzyme, since even a low resolution structure could provide guidelines for research in homogeneous catalysis. There appears to be merit in further theoretical calculations of the bonding in metal  $N_2$  complexes and in suspected intermediates in oxidative and reductive  $N_2$  fixation, since these often provoke new lines of research.

Finally, reactions of coordinated  $N_2$  other than  $NH_3$  synthesis should receive increased attention. Direct synthesis of  $N_2H_4$ ,  $NO_3$ , and organic amines from  $N_2$  would have large energy-saving impact but is receiving little current study.

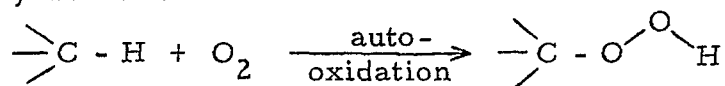
## VII. Activation of Oxygen for Selective Oxidations

Selective, direct oxygenation of organic substrates remains a largely unresolved challenge to synthetic chemistry. Autoxidations of organic molecules usually involve peroxidic intermediates in chain-radical processes mediated by a multivalent metal catalyst. Such direct oxygenations are difficult to control since they lack stereo- or regioselectivity and often cannot be halted at intermediate oxidation stages. Indirect methods for introducing oxygen atoms into organic substrates are much more selective but need further improvement. Such indirect methods necessarily are energy intensive and thus wasteful processes. Furthermore, there are very few methods of any kind for selectively oxygenating saturated hydrocarbon substrates (see V above).

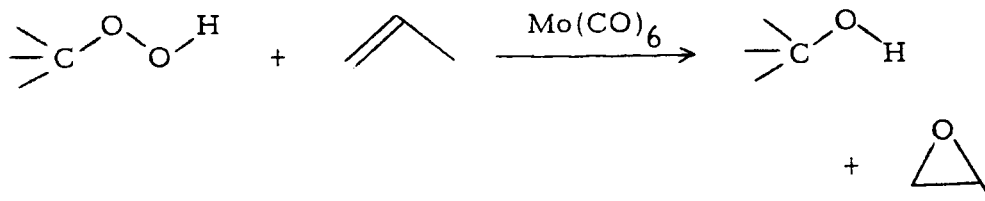
As an example, one would like to be able to transfer oxygen atoms selectively to an organic substrate employing molecular oxygen as the oxygen source. A reaction of special interest is the epoxidation of olefins; unfortunately there is no direct method for effecting the following transformation:



Such a direct use of molecular oxygen is possible for ethylene using a silver catalyst but with larger olefins allylic oxidation is the predominant path. Although selective direct epoxidations using oxygen are not yet possible, indirect routes of high selectivity have recently been discovered. In fact, one of these is now used industrially for the synthesis of propylene oxide. The oxygen is first reduced to the peroxide level by interaction with a reactive hydrocarbon:



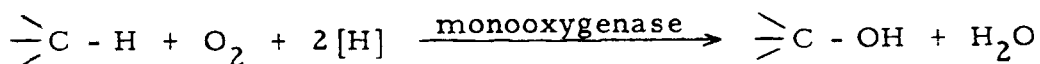
The resulting hydroperoxide is then used to epoxidize the olefin in the presence of certain (e. g. Mo and V) transition metal catalysts:



It may be significant that this method of dealing with oxygen bears a strong resemblance to the process effected by mixed-function oxygenases discussed below. In both instances the oxygenating reagent is generated by prior partial reduction of oxygen. This is unfortunate since half of the oxidizing potential is lost in these indirect processes. Furthermore, a reducing agent is consumed. The discovery and development of selective oxygenations which employ both of the atoms of the oxygen molecule should be an important goal for research in this area.

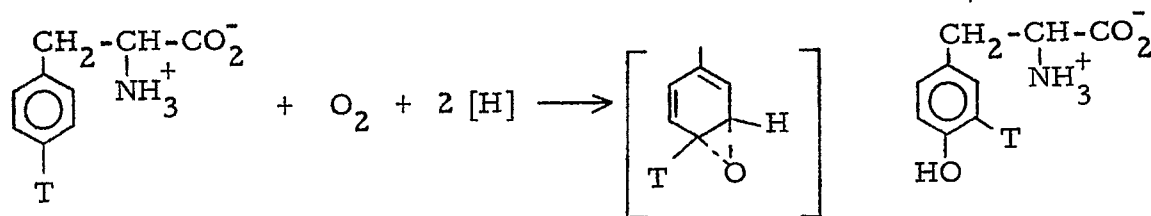
Nature carries out the direct incorporation of one or both atoms of the oxygen molecule into saturated organic substrates with great selectivity by means of the mono and dioxygenases. In the majority of cases these oxygenases are metalloenzymes and activation of molecular oxygen is known or thought to involve coordination of dioxygen to the transition metal center(s) (iron and copper). Undoubtedly there is a great deal to be learned from Nature in mimicing these sorts of reactions.

The monooxygenases (also called the mixed-function oxygenases or monohydroxylases) are much better understood and may serve as an example of approaches which should be explored. These enzymes catalyze the reaction between oxygen, a hydrocarbon substrate and two reducing equivalents affording the hydroxylated product and water. Although not



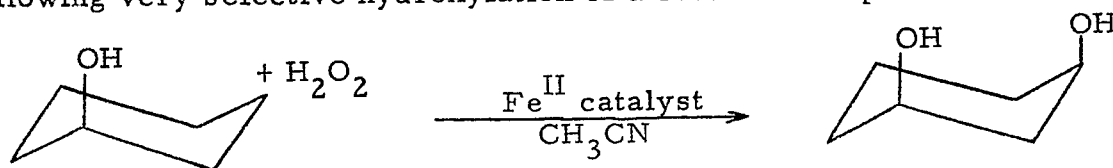
unique, a ubiquitous and important class of such enzymes are the so-called cytochrome P<sub>450</sub> hydroxylases.

Several experiments suggest that the active oxygenating site in the P<sub>450</sub> system is electrophilic ("oxenoid") and not free radical in character. For example, olefinic groups are converted to epoxides by steroidal P<sub>450</sub> hydroxylases. The hydroxylation of aromatic rings involves an "arene epoxide" intermediate further illustrating the parallel character of the active oxygenating site in P<sub>450</sub> hydroxylases. This intermediate was deduced through the discovery of the so-called "NIH shift" in which a substituent (T, Cl, etc.) in the para position of phenylalanine migrates to the adjacent (meta) position in the product (tyrosine).



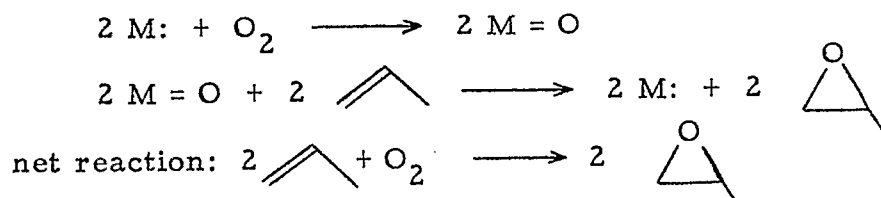
A recent report describes a model iron complex which catalyzes the autoxidation of *p*-deuteroanisole forming hydroquinone monomethyl ether and giving the "NIH shift"--again, apparently an electrophilic oxygenation. This catalyst is easily poisoned and the system is at present ill-resolved; nevertheless this reaction points the way to inventing and understanding synthetic systems which may mimic the efficient and selective biological oxygenases.

Another recent model study, also a remarkable imitation of the oxygenations effected by the natural iron oxygenases, has found the following very selective hydroxylation of a saturated aliphatic substrate:



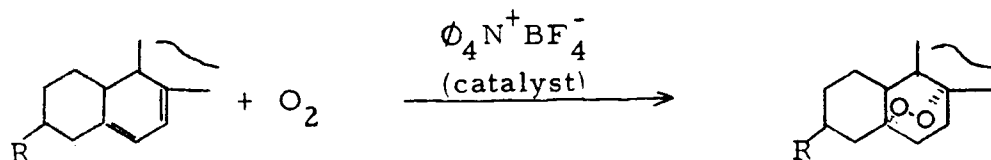
This example illustrates the importance of intramolecular reactions in discovering new chemical steps.

There is evidence that oxoiron species ( $\text{Fe}=\text{O}$ ) may be the active oxidants in the  $\text{P}_{450}$  dependent oxygenases. The detailed mechanisms and further synthetic aspects of oxygenations of organic molecules by oxo-transition metal and oxo-main group species should be further investigated. If an oxo-reagent ( $\text{M}=\text{O}$ ) can be found which cleanly transfers its oxygen atom to organic substrates, one could try to generate this same oxospecies directly from molecular oxygen so that an overall process such as that shown below for the epoxidation of propylene could be realized:

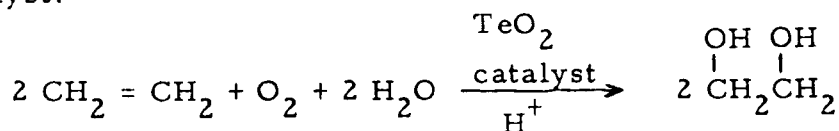


When thinking of schemes for activating oxygen, transition metal catalysis is usually the first thing to come to mind. However there are several indications that non-metal systems ought to be considered as well.

A singlet oxygen type reaction can be realized with ground state oxygen in the presence of catalytic amounts of certain radical cations:



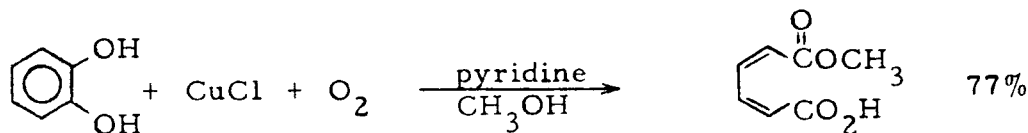
There is also a new industrial process for making ethylene glycol from ethylene and molecular oxygen which depends on tellurium dioxide as a catalyst:



It would appear that tellurium and other metalloids (e.g. selenium, iodine, and bismuth) in the lower right hand area of the periodic table are worthy of further investigation in hopes of finding similar types of catalytic oxygenations. Main group systems should have less tendency than transition metal ones to promote undesired, nonselective free radical oxygenations.

Considerable progress has been made in the area of asymmetric reductions; however, asymmetric oxidations are virtually unknown. This is an important area for investigation since one could imagine making synthetic foods if efficient methods for chiral oxygenations and other asymmetric transformations could be found.

Little is known about natural processes introducing two oxygen atoms. A recent stoichiometric example suggests the value of model studies to develop catalytic processes which introduce both oxygen atoms into organic substrates.



However, further information from the natural dioxygenases may be essential to guide the development of model systems.

There are several examples of another route for selective oxidations. In this class, a metal compound oxidizes the substrate in a two-electron process, the oxygen moiety introduced comes from the medium instead of  $\text{O}_2$ ,

and the reduced catalyst is re-oxidized by  $O_2$ . The oxidation of ethylene to acetaldehyde in aqueous medium by mixed palladium and copper salts (Wacker Process) is the classic example. Though it has been extensively studied, the possibilities of this class of oxidations are far from exhausted.

### Recommendations

The foregoing analysis leads to recommendations of research on:

- 1) The redox properties and the kinetics and mechanisms of reactions of coordinated dioxygen species leading to high volume oxychemicals.
- 2) The structure and mechanisms of reaction of enzymes which catalyze selective oxidation of organic substrates by  $O_2$ , and synthesis and reactions of model systems which mimic them.
- 3) Reactions in which an oxygen atom, neutral or charged, is transferred selectively.
- 4) Reactions in which organic substrates are selectively oxidized by species which are regenerated by reducing  $O_2$ .

### VIII. Activation of Oxygen for Fuel Cells

If they were more efficient and less expensive, electrochemical cells would be the basis for major advances in the conversion of fuels to electrical energy and in the reversible electrolysis of water to hydrogen and oxygen for energy storage and transportation. Most of our electrical and mechanical energy is now produced from the energy of reduction of atmospheric oxygen by fuels. At present, useful reaction rates (power), can be achieved only by free radical chain reactions, from which the energy can be collected only as heat. The efficiency with which the heat can be converted to electrical energy or work is thermodynamically limited to a maximum of ca. 40% with present materials.

Direct conversion of chemical to electrical energy in electrochemical cells would avoid the Carnot inefficiency. But, to be economical, the oxygen-fuel reaction must be rapid enough to produce a current of ca. 1 ampere per square centimeter of electrode surface. If the catalytic sites were spaced 10 Å apart on this surface, each would have to transfer 60,000 electrons per second between the electrode and the reacting molecules. (Roughening the surface can increase the number of sites per geometrical surface area ten-fold at most.) For maximum efficiency, the electrons which reduce oxygen to water must be drawn from a surface very reluctant to release them (i. e. at a potential close to 1.2 volts more oxidizing than the standard hydrogen electrode). To avoid carbonate accumulation from

atmospheric CO<sub>2</sub> or carbonaceous fuels, the medium in which the O<sub>2</sub> is reduced should be CO<sub>2</sub> rejecting.

No catalysts now exist which are capable of effecting electron transfer at the needed rates and potentials. The best are only 50-60% efficient at 1 ampere/cm<sup>2</sup>, are expensive, and have other deficiencies. They are heterogeneous, and the structure of their active sites is unknown.

Several very significant advantages would be possible if the conductive solid at the electrode-electrolyte interface had an internal texture with cavities connected by ports, as in zeolites. The effect would be to replace the roughly two-dimensional interface by a three-dimensional zone whose thickness would be limited by mass transfer. The number of sites per square centimeter of planar electrode could be increased by 10<sup>2</sup> to 10<sup>3</sup>. Homogeneous catalysts could be assembled and retained within the cavities from components small enough to diffuse through the ports. Alternatively, homogeneous catalysts could be strongly adsorbed on, or chemically bound to, other conductive supports whose internal texture was analogous to that of graphite intercalation compounds.

Chemical factors which must be considered in a search for useful catalysts are discussed in Appendix A.

#### Anodic Oxidation of Carbonaceous Fuels

The anodic oxidation of carbonaceous fuels, notably methanol, is not specifically treated in other sections of this report. The problems involved are closely analogous to those in the cathodic reduction of O<sub>2</sub>. The net change, as in  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$  must deliver six electrons to an electrode reluctant to accept them (potential close to that of the hydrogen electrode). The intermediates in the oxidation path are energetically unfavorable. Therefore, catalysts must be found which are capable of stabilizing intermediates in sequential steps, or of providing concerted paths avoiding them.

There are two fuels for which satisfactory anodic catalysts already exist: hydrogen and hydrazine. If an inexpensive synthesis of the latter were discovered, it would allow important advances in fuel cell technology.

#### Recommendations

The foregoing analysis (including that encompassed by Appendix A) leads to recommendation of research on:

- 1) The detailed nature, including thermodynamic properties and theoretical description, of interactions and bonding between metal compounds and members of the series: O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>2-</sup>, O<sup>-</sup>, O<sup>2-</sup>, with and without protons.

2) The synthesis, redox properties, and reactions with  $O_2$  of compounds capable of providing several electrons from orbitals extending over several atoms, as in metal complexes with redox ligands, bi- and polynuclear metal complexes, metal macrocycles and dimers thereof.

3) The details of reactions in which oxygen is reduced or water oxidized by metal compounds to define better the chemical requirements which must be met to achieve high rates.

4) The structure and mechanisms of reactions of enzymes which reduce oxygen to water, and synthesis and reactions of model systems which mimic them.

5) Methods for and chemical effects of linking catalytic molecules to surfaces, including conductive surfaces and carbons.

6) Synthesis of conductive electrocatalyst supports with internal zeolite-like cavities and parts or with structures similar to graphite intercalation compounds.

## IX. More Specific Catalysis of Industrial Processes

### A. Introduction

It is possible to design homogeneous catalysis systems to carry out extremely specific chemical transformations. Specificity may arise in the functional groups or molecules which react, in product selectivity, stereochemistry, regiochemistry or in asymmetric induction. Comparable specificity has not been achieved with heterogeneous catalysis. Homogeneous catalysis can be made specific because the catalyzed reactions usually occur under mild conditions and are promoted by discrete molecular entities whose properties may be changed through modifications of the ligands. It is thus possible to obtain a good fundamental understanding of how catalysis occurs using a particular metal complex and to apply this understanding to design of better catalysts. A spectacular success has already been achieved in the commercial synthesis of the anti-Parkinsonism drug L-Dopa using catalytic asymmetric hydrogenation. Many other examples of stereoselective, regioselective and asymmetric catalysis are known including additions to  $C = C$ ,  $C = O$  and  $C = N$  bonds, diene oligomerizations and olefin dimerizations. Some other types of selective catalysis, however, are largely unexplored. These include selective oxidations and reactions of tetra-substituted olefins.

The potential is great for selective catalysis to transform the nature of organic synthesis leading to advanced industrial processes, a goal of Project Independence. Asymmetric and other selective catalysis such as regioselective dimerization of isoprene could lead to lower costs or make available for the first time useful substances in the areas of food additives,

drugs, vitamins, flavorings and fragrances. Uses in preparing artificial food are also conceivable. Initial energy savings will be modest but artificial food stuff production might eventually lead to large savings of energy now used to grow, store, preserve and prepare food. Improvements in the quality of life can, moreover, be expected on a much shorter time scale.

Detailed fundamental studies of asymmetric and regioselective catalytic processes can also be expected to lead to discovery of principles of homogeneous catalysis which are useful in a broad range of applications.

#### B. Recommendations

Some areas of stereospecific, regiospecific and asymmetric catalysis which merit study are the following:

1) The use of new ligand systems in conjunction with known catalytic processes. (Many otherwise useful catalytic reactions do not have mechanisms compatible with high specificity. Analogous and more specific reactions may be found through systematic study of metal-ligand combinations.) The duplication of known catalytic chemistry of the noble metals with other transition elements, notably Ti, Zr and Hf. The search for new types of catalytic reactions.

2) Applications of regiospecific olefin dimerizations of isoprene to synthesis of  $C_{10}$  (e.g. myrcene),  $C_{15}$  and  $C_{20}$  head-to-tail type oligomers as intermediates for synthesis of vitamins A and E, squalene, phytol, etc.

3) Applications of asymmetric catalysis to synthesis of chiral molecules needed for drugs, vitamins, flavorings and fragrances. Worthwhile specific targets would be chiral amines, hydrocarbons and alcohols.

Fundamental studies directed towards any of these goals in field of oxidation chemistry would be desirable (see VII above):

1) Replacement of organic hydroperoxides with molecular oxygen of air in the conversion of olefins to epoxides, e.g., propylene to propylene oxide, butadiene to butadiene monoepoxide.

2) Replacement of expensive heterogeneous catalysts of relatively poor selectivity with homogeneous catalysts of improved selectivity. Replacement of the solid silver catalysts for oxidizing ethylene to ethylene oxide with a homogeneous catalyst operating at lower temperatures where overoxidation could be avoided.



- 3) Use of transition metal complexes to concentrate and activate oxygen from the air for use in selective oxidation of hydrocarbons to intermediates such as alcohols, aldehydes, and ketones. If the functionality can be introduced at the end of a long paraffin chain a new route to fatty acid derivatives will have been achieved, freeing the natural products (fats) for use in food.
- 4) Finding catalytic analogs of stoichiometric oxidation reactions of metal complexes, e.g., selenium, thallium, silver, chromium, and manganese compounds.
- 5) Identifying the relationships between metal and ligands that affect the selectivity of free radical oxidations catalyzed by metal complexes.
- 6) Determining how homogeneously catalyzed oxidative dehydrogenations may be run to high conversion - e.g. in converting ethylbenzene to styrene - to reduce the energy required to separate product.

The principles identified in the above studies on improved homogeneous oxidation catalysts may find application in advanced systems for selective electrolytic oxidation of organic compounds or in fuel cells using organic substrates.

Homogeneous catalysts also appear to have the potential to complex selectively with gaseous air pollutants and catalyze their conversion to inert or even useful products. Fundamental studies are required to establish the scope of this concept and follow up the leads that have been studied so far on complexes of  $\text{SO}_2$  and  $\text{NO}_x$ . Complexes containing CO have been investigated much more intensively.

Stack gas scrubbing to remove  $\text{SO}_2$  often generates a calcium sulfate sludge that is difficult to dispose of without environmental insult. Alternate processes under study require an absorbing medium containing citrate or formate and produce sulfur as the product, using  $\text{H}_2\text{S}$  or CO as the reducing agent in a separate reactor.

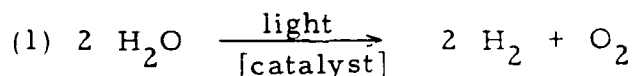
We suggest that basic studies on chemistry of complexes of  $\text{NO}_x$ ,  $\text{SO}_2$ , and CO emphasize reactions which can be carried out in aqueous systems and, when sulfur is produced, at temperatures where it could be handled as a liquid. These in turn might lead to advanced stack gas scrubbing systems where CO would be the reducing agent with sulfur and/or nitrogen and  $\text{CO}_2$  as environmentally acceptable products.

Alternatively, means of obtaining complexes  $\text{SO}_2$  or  $\text{NO}_x$  so that they could be reacted with hydrocarbons to form useful industrial compounds would be desirable, but probably the demand for the product would not justify widespread installation.

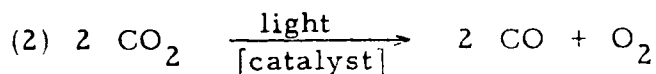
## X. Photochemical Energy Storage and Catalyst Activation

### A. Potential Photoproduction of High Energy Materials

Conversion of solar energy into chemical energy in the form of high energy substances (fuels) is an attractive goal since it would utilize the fundamental external energy source. A desirable reaction would be



It would also be attractive to be able to use reactions such as (2) to produce CO. Recovery of carbon in this way could become important when present sources of carbon containing fuels are depleted.



Catalysts in reactions (1) and (2) would have to be the primary photo-receptors as the substances are transparent to the solar spectrum. They must also provide pathways to use the absorbed light energy for the desired chemical conversion. Transition metal complexes capable of complexing  $\text{H}_2\text{O}$  or  $\text{CO}_2$  are potential candidates to catalyze reactions (1) or (2). This is a very speculative area but the potential payoff is very high.

Another mechanism for solar energy utilization would be provided by devices which convert light energy directly into electrical energy. In principle, this can be accomplished by photoinduced processes which are thermally reversible and involve electron transfer.

### B. Photoinitiation of Catalysis

Photoinitiation of catalysis involves photoproduction of a reactive substance which operates as a conventional catalyst. Photoinitiated catalysis can potentially generate under mild conditions catalysts of unique structure and high selectivity, reducing side reactions, catalyst decomposition and energy consumption. Applications of photoinitiated catalysis might also lead to development of new imaging systems and optical switches.

### C. Recommendations

Successful use of light in conjunction with catalysts will require a sophisticated understanding, not now available, of the absorption of light and its chemical consequences in transition metal complexes. Fundamental studies of transition metal complex photochemistry are, therefore, recommended in the following areas:

1) Spectroscopic work should be carried out to characterize accessible excited states in metal complexes, with emphasis on correlation of excited states with chemical reactivity. Competitive photophysical processes should be identified and understood so that they can be controlled or exploited.

2) Characterization of photochemical primary products and other photogenerated intermediates such as metal radicals, coordinatively unsaturated species and strongly oxidizing or reducing excited complexes by spectroscopic and chemical methods is essential to realize the goal of producing high energy and/or catalytically active species photochemically.

3) A broad effort should be made to uncover new reaction pathways of excited metal complexes, including photoreactions of coordinated ligands, examples of reductive elimination, creation of multiple coordinative unsaturation with one quantum, utilization of multiple photon reactions, and bimolecular reactions of excited complexes such as nucleophilic attack, electron transfer, addition, etc.

## XI. New Forms of Catalysts

### A. Introduction

Attachment of soluble type catalysts to insoluble supports could potentially combine desirable features of homogeneous and heterogeneous catalysts and obtain catalysts with entirely new properties. Such hybrid catalysts may offer advantages such as ease of recovery of catalyst and its separation from product, as well as increased catalyst lifetime and increased resistance to solvolytic, oxidative and photochemical decompositions and to conversion into active or insoluble forms as sometimes observed for homogeneous catalysts. Combining homogeneous type catalysts with supporting phases also offers opportunities for useful synergistic interactions between the metal complex and the support. Some of the possibilities deserving mention are creation of catalysts having two different metals bound to the support, catalysts wherein the support and the supported metal complex engage in cooperative binding with substrates and catalysts (e. g. for fuel cells) wherein metal complexes are found to electrically conductive supports. Soluble catalysts consisting of larger polynuclear molecular entities also may have properties quite different from simpler mononuclear systems. Study of catalysis in immiscible liquid phases, use of phase transfer techniques as well as fundamental studies of structure--activity relationships and mechanism of supported catalysts also may lead to new types of catalysts.

### B. Recommendations

New synthetic organic, biopolymer and inorganic supports for soluble type catalysts should be designed to incorporate and provide such features

as high chemical, physical and light stability, controlled loading of catalyst and synergists, controllable substrate and product diffusion properties and solvent compatibility. Physical properties of the supported catalysts-- e.g. pore size, texture, surface polarity, etc.-- should be determined. Consideration and use of polymer technology will be important. Studies which relate the influence of structural variables in supported catalysts to catalytic activity should lead to an improved understanding and usefulness of both the supported and classical heterogeneous catalysts.

Development of electrically conducting supports such as graphite would be desirable for fuel cell applications.

Synthetic efforts in this field would benefit from development of new methods to attach catalysts to supports.

Study of polynuclear metal complexes and of substances such as water-soluble aggregates of metal oxides similar to the heterogeneous metal oxide catalysts should be undertaken to search for new specific catalytic reactions.

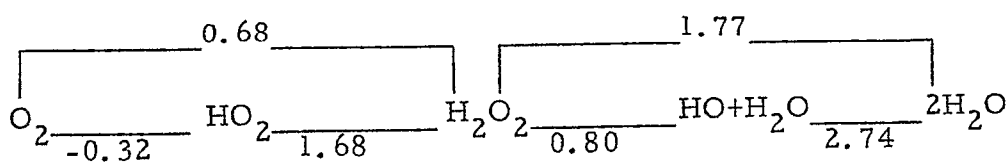
Investigation is recommended of novel media for "homogeneous" catalysis by supported or free metal complexes. Some possibilities are multiphase liquid systems (e.g. micelles), use of phase transfer agents or polyfunctional ligands to solubilize complex catalysts, use of fused salt solvent systems and use of semi-permeable membranes.

Problems and possibilities discussed above are essentially multi-disciplinary in character and cooperative efforts should be encouraged.

## APPENDIX A

Chemical Factors in Oxygen Activation and UtilizationProblem of Stability of Intermediates

The cathodic reduction of  $O_2$  at 1 atmosphere in a strong acid at unit activity taking place as an equilibrium process generates 1.23 volts measured against the hydrogen electrode also operating as an equilibrium process at standard conditions. Equilibrium can be achieved if the reaction is allowed to proceed infinitely slowly, thus allowing time for intermediates in the reaction sequence leading from  $O_2$  to  $H_2O$  to reach equilibrium with respect to their disproportionation reactions. For a practical process taking place at a finite rate, we must be concerned with the steady state concentrations of the intermediates which are involved in the steps of the reaction. Increasing the rate of oxygen reduction causes these to rise above their equilibrium values, thus reducing the potential developed by the electrode. A serious limitation on the practical reduction of oxygen by a reversible process arises from the fact that the overall reduction involves a multi-particle change: conversion of  $O_2$  to the stable product water requires the addition of 4 electrons and 4 protons. Apart from whatever enthalpy barrier there is to a process that requires the attachment of eight particles onto an oxygen molecule, 4 protons from the solution and 4 electrons from, say, the electrode, there is the inherent improbability of such an event. In any case, in almost all reductions of oxygen which have been studied the reactions take place stepwise. In the limit of 4 independent reduction steps, the intermediates which have been identified are  $HO_2$ ,  $H_2O_2$  and  $OH$ . The values of the standard reduction potentials associated with each of the steps (these are accurate only for the  $2e^-$  stages  $O_2 - H_2O_2$  and  $H_2O_2 - H_2O$ ) are:

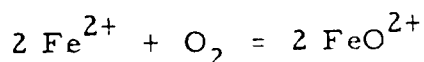


It can be seen that the potential for  $O_2$  being reduced to the intermediate  $HO_2$  is only -0.3 volt, and in a  $2e^-$  process, to  $H_2O_2$ , it is only 0.68 as compared to 1.23 for the overall process. The diminished potentials for the reactions producing the intermediates of course reflect the fact that the intermediates are unstable, at least in the thermodynamic sense. Although in actual process the concentrations of the intermediates might well be less than those corresponding to unit activity, finite times are associated with their further reduction or decomposition. As a consequence, it is questionable whether in a practical system a potential near the reversible value can be achieved even if the less stable stage,  $HO_2$ , is bypassed as long as the reactions are required to pass through the stage  $H_2O_2$ .

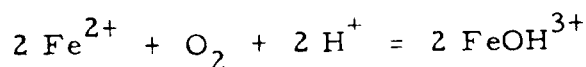
In what has gone before it has been tacitly assumed that the electrode material has no chemical individuality and that it serves only as a source of electrons, with the positive charge needed to stabilize the negative charge deposited on the oxygen coming from protons from acidic solution. The reaction barriers will be modified by the interaction of the intermediates with the electrode surface. The question arises: can the affinities of  $\text{HO}_2$  or  $\text{H}_2\text{O}_2$  for a metal species at an electrode be sufficiently great to alter the barriers significantly? The possibility that the negative charge on the intermediates  $\text{O}_2^-$  or  $\text{O}_2^{2-}$  (or  $\text{HO}_2^-$ ) is stabilized by the interaction of those species with metal ions on the surface needs also to be considered. It is not obvious that metal ions can stabilize the intermediate ions much more than do protons, but the possibility cannot be ignored.

#### Possible Ways to Avoid Intermediates

We are led by the foregoing considerations to search for processes which bypass the intermediates  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$ , and which involve 4 electron reduction of  $\text{O}_2$ . Several kinds of such processes can be imagined: (a) two metal centers cooperating in the reduction process, each metal then undergoing a  $2e^-$  change. The charge stabilization on the reduced oxygen can occur by its interaction with the metal ion as in



and by involving protons also



(b) reductions taking place on a single metal center, the source of the electron being the metal center itself or some other center (which need not be a metal but might be a ligand) which is in communication with it. Again, the possible involvement of protons must be considered.

To be adaptable to electrode use, the reaction systems in question need to satisfy other stringent conditions. Thus in the specific example of  $\text{Fe}^{2+}$  being oxidized to  $\text{FeO}^{2+}$ , the species  $\text{FeO}^{2+}$  must be strongly oxidizing. It must be readily reducible by an electrode, and moreover whatever reduction takes place must produce  $\text{Fe(II)}$  rather than  $\text{Fe(III)}$ . It is clear that fundamental work on the mechanism of reduction of oxygen by metal ions is required, including work with multicenter systems, and work in which the reactivity of the metal ions is modified by the ligands, particularly "non-innocent" ligands. Interest is by no means limited to the reduction of oxygen, and it is clear that the study of the mechanism of oxidation of water is of equal significance.

An important question that arises is whether the four-equivalent reduction of dioxygen to water can be accomplished in an outer-sphere

reaction. Although not many outer-sphere reductions of dioxygen are known, there is good evidence that the reactions of  $O_2$  with  $Cr(CN)_6^{4-}$  and with  $Ru(NH_3)_6^{2+}$  to produce peroxide make use of this pathway. This is an important result, for it shows that coordination of dioxygen to a metal center may not be required for its rapid reduction. Since a substitution step is not required in an outer-sphere reaction, such reactions can in principle proceed more rapidly than inner-sphere reactions. This may be of importance when rapid reduction and turnover of dioxygen is required.

Several metalloenzymes are able to carry out a "direct" four-equivalent reduction of dioxygen; these include cytochrome c oxidase, laccase, ascorbate oxidase, and ceruloplasmin. All of these enzymes have at least four metal centers. For laccase, which contains four copper atoms per enzyme, there is some evidence to indicate that a binuclear  $Cu(I)---Cu(I)$  center is the site of  $O_2$  reduction. Rapid delivery of four electrons (two from the active site and two from the other two  $Cu(I)$ 's) and four  $H^+$  to the  $O_2$  is presumably accomplished at this site, but the exact nature of the electron/proton steps is not at all understood at this time.

### Electronic Structure of Dioxygen

Discussion of the redox chemistry of dioxygen requires knowledge of the molecular orbital description of its ground state electronic structure. The molecule possesses 12 valence electrons (each atom is  $2s^2 2p^4$ ), which are arranged in molecular orbitals in the order  $(2s\sigma_g^+)^2 (2s\sigma_u^+)^2 (2p\sigma_g^+)^2 (2p\pi_u)^4 (2p\pi_g)^2$ . The ground state is therefore a spin-triplet  $^3\Sigma_g^-$ . It is important to note that the half-filled  $\pi_g$  level is antibonding between the two oxygen atoms. As a result, introduction of electrons into this level substantially increases the bond distance:

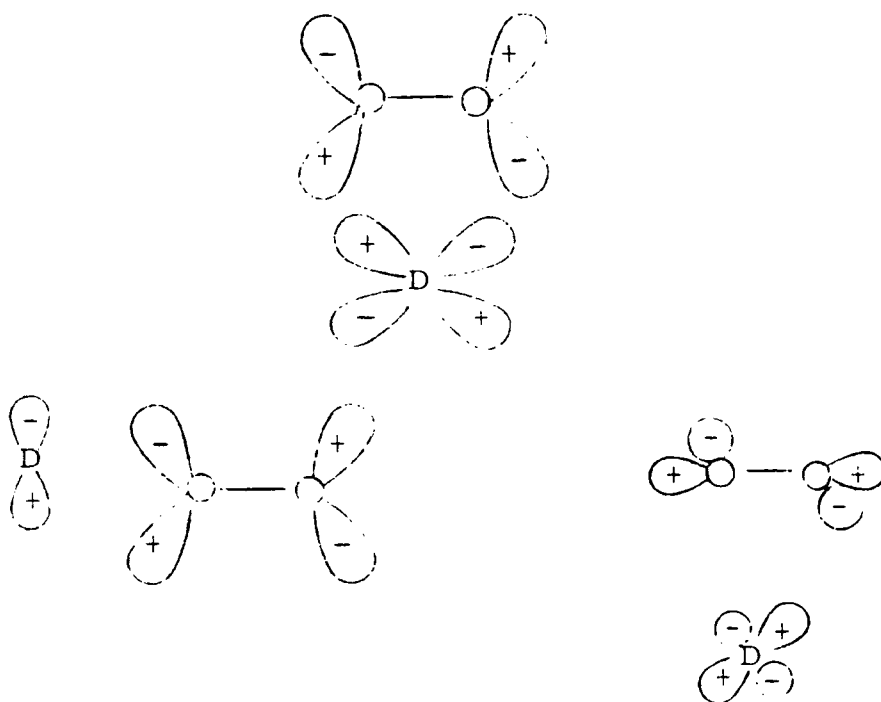
State	$r_{eq}, \text{\AA}$
$^3\Sigma_g^-(\pi_g)^2 O_2$	1.21
$^2\pi_g(\pi_g)^3 O_2^-$	1.26
$^1\Sigma_g^+(\pi_g)^4 O_2^{2-}$	1.49

### Kinetic Consequences of the Spin and Orbital Symmetry Properties

The fact that the ground state of dioxygen is a triplet can have important kinetic consequences. Hydrogen peroxide as well as most organic compounds have singlet ground states. As a consequence spin will

generally not be conserved in the two-equivalent reduction of dioxygen by an organic compound (unless the organic product has a low lying triplet state) and such reactions are likely to be slow. This spin restriction is absent when dioxygen undergoes a one-equivalent reduction with a diamagnetic organic compound (producing an organic free radical) but, as shown above, the one-equivalent reduction of dioxygen is not thermodynamically favorable. The spin restriction can also be released by the binding of the dioxygen to (or the close proximity of) a paramagnetic center such as can be provided by a transition metal ion. The reduction of dioxygen is a two-equivalent step and is likely to proceed particularly rapidly in such systems.

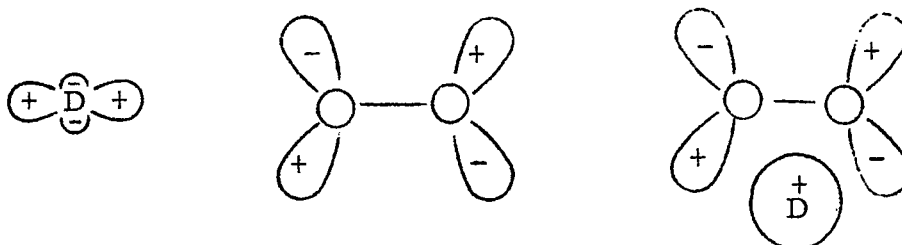
A second point of potential concern is orbital symmetry. Delivery of an electron into a  $\pi_g$  orbital could in principle be symmetry forbidden or allowed, depending on the orientation and symmetry properties of the donor orbital. The requirement of efficient overlap with these orbitals places certain restrictions on the geometry of the transition state for electron transfer. Examples of an allowed process would be



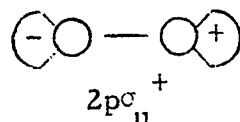
(D = donor orbital)



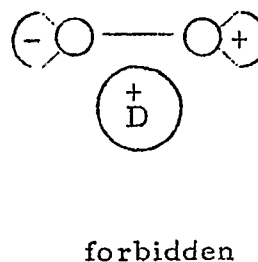
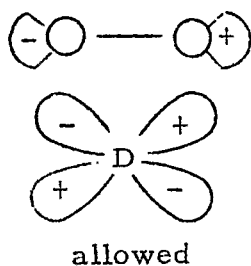
Symmetry forbidden electron transfers include:



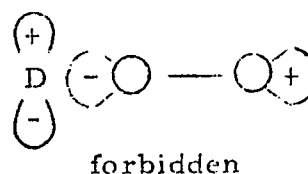
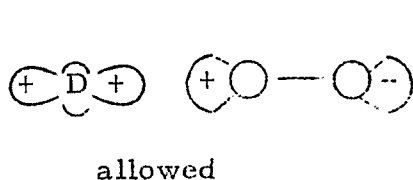
Reduction beyond the  $O_2^{2-}$  state could be viewed in terms of population of the lowest unoccupied molecular orbital of that species, namely,  $2p\sigma_u^+$ :



It is of interest to note that "side-on" electron transfer into  $\sigma_u^+$  encounters the same symmetry restrictions as those for  $\pi_g$ :



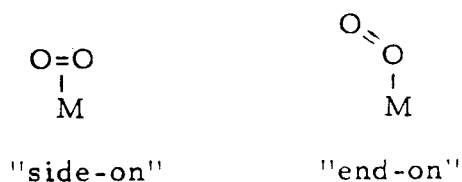
but "end-on" transfer should follow different selection rules:



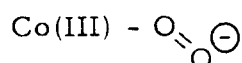
This means that "side-on" reduction of  $O_2$  could proceed all the way to O-O bond cleavage (to give OH) by utilizing donor orbitals of  $\pi$  symmetry, whereas both  $\pi$  (to  $O_2^{2-}$ ) and  $\sigma$  (to OH) donors would be needed in an end-on transition state geometry. Similar reasoning can be applied to bi- and polymetallic donors.

### Binding of Dioxygen to Metal Centers

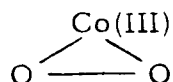
Knowledge of how metal species bind  $O_2$  is essential to design of catalysts for both the  $O_2$ - $H_2O$  couple and the selective oxidation of other substrates. Reference has already been made to the two limiting geometrical structures for coordinated dioxygen.



Of concern to us now is the question of the electronic structural description of such  $MO_2$  units. Perhaps the crucial point to make is that such units can reasonably span extremes of charge distribution from  $MO_2$  to  $M^{2+}+O_2^{2-}$ . Cobalt complexes of dioxygen have been quite thoroughly studied, and serve to illustrate some of the possibilities. There is overwhelming evidence that cobalt(II) complexes of dioxygen possess ground states of the type



whereas cobalt(I)-dioxygen adducts prefer "side-on" (bidentate) cobalt(III) coordination.

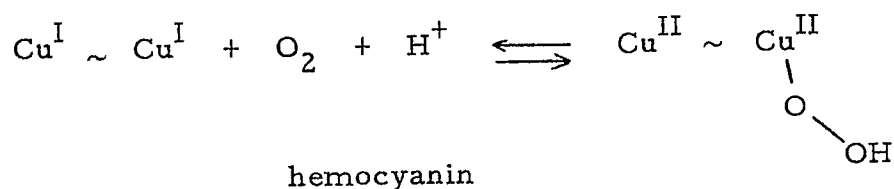
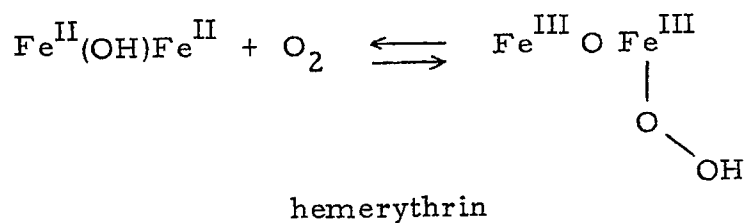


Special stability is associated with a  $^1A_{1g}(t_{2g})^6 Co(III)$ . The ground state obviously plays an important role in determining the state of bound dioxygen in these cases.

Assignment of the oxidation state of  $O_2$  is not as clear in several model complexes containing heavy metals (Ir, Rh, Pt, etc.), but in all cases there is good evidence for substantial charge withdrawal in the sense  $M^{\delta+}O_2^{\delta-}$ . The geometrical structures of these heavy metal  $-O_2$

adducts are generally consistent with the limiting formulation  $[M^{2+}O_2^{2-}]$ .

The binding of dioxygen to metal ions in blood proteins has also been the subject of intensive research. The ground states of hemerythrin and hemocyanin now appear to be well established. In both cases dioxygen binding is accompanied by two electron oxidation of a binuclear metal center:



Much blood has been shed over the nature of the iron-dioxygen bond in hemoglobin. Recent work with picket-fence porphyrin model compounds has indicated that the original Pauling formulation (low-spin  $Fe(II)$  and end-on  $O_2$ ) is in fact correct. There is thus at least one case where reduction of dioxygen does not accompany coordination to a metal center.

## APPENDIX B

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#### 3. Activation of Hydrocarbons

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M. Frederick Hawthorne  
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Eric Stern  
Mark Wrighton  
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