4TH INTERNATIONAL SYMPOSIUM ON ACTIVATION OF DIOXYGEN AND HOMOGENEOUS CATALYTIC OXIDATION

ABSTRACT

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PLENARY LECTURES

(PL-1 TO PL-6)

THE SELECTIVE FUNCTIONALISATION OF SATURATED HYDROCARBONS. GIF AND ALL THAT

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Gif-type systems for the selective functionalisation of saturated hydrocarbons use pyridine and acetic acid (or other acid) as solvent. All require an ^{V}Fe oxenoid species produced by the reaction of superoxide with ^{II}Fe or of hydrogen peroxide with ^{III}Fe. Exceptionally (D.T. Sawyer) oxygen can react with an ^{II}Fe μ-oxo dimer to produce the ^{V}Fe oxenoid. All these systems convert saturated hydrocarbons selectively to ketones. For a conversion of 20-30% the yield is nearly quantitative.

Two intermediates have been identified; the first (A) has an ^{V}Fe-O sigma bond, the second (B) is an alkoxy derivative of ^{III}Fe. A plausible overall mechanism has been proposed.

Intermediate A can be captured in a preparatively useful way by a number of reagents to furnish secondary bromides, chlorides, phenylselenides, phenylsulfides, and sulfides. The bromination reaction with $BrCCl_3$ is the best reaction from the yield and utility point of view.

Gif-type chemistry seems to be closely related to the mode of action of the enzyme methane monooxygenase.

PL-2, MON

ASYMMETRIC HYDROXYLATION AND EPOXIDATION CATALYZED BY VAULTED BINAPHTHYL METALLOPORPHYRINS

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Asymmetric synthesis has emerged as a rich and rapidly developing area of chemistry, combining elements of organic synthesis, molecular recognition, metal coordination chemistry and catalysis. Of the various strategies for exploiting the available pool of chiral compounds, catalytic asymmetric induction offers the distinct advantage of chemical amplification of the asymmetry of the catalyst.

The enzymic epoxidation of simple olefins such as 1-octene has been shown to proceed with very high enantiomeric excesses, 80-100%. In such cases there can be no auxiliary, bonded interactions between the catalytic center and the substrate. Accordingly, it must be possible to develop synthetic catalysts with chirotropic cavities which can mimic this high enantioselectivity.

The discovery that iron porphyrins will catalyze alkane hydroxylation and olefin epoxidations in the presence of oxygen donors such as iodosylbenzene has provided an opportunity to use synthesis porphyrins for modelling the oxygen transfer reaction of cytochrome P-450. Chiral metalloporphyrins have been shown to mediate catalytic asymmetric oxygen transfer to afford optically active epoxides from prochiral olefins. The largest enantiomeric excess reported to date (ee=51%) has been provided by an iron porphyrin catalyst with chiral binaphtyl appendages. In this lecture we will describe the synthesis and characterization of a new, vaulted porphyrin with a chirotropic binaphthyl bridge. The iron(III) and manganese(III) derivatives of this porphyrin have proven to be robust catalysts for olefin epoxidation and sulfoxidation providing catalytic ee's as high as 72%. Most significantly, the first catalytic asymmetric hydroxylations with similarly high ee's have been observed with this catalyst. Aspects of the mechanisms of asymmetric oxygen transfer reactions will be discussed. [J.T. Groves and P. Viski, J. Am. Chem. Soc., 1989, 111, 8537; J.T. Groves and P. Viski, J. Org. Chem., 1990, 55 (in press)].

We have recently described the preparation and characterization of a trans-dioxo-ruthenium(VI) prophyrin complex which has been shown to be an efficient catalyst for the aerobic epoxidation of olefins. We have also shown that this complex will catalyze the hydroxylation of alkanes under appropriate conditions. It is now apparent that the dioxoruthenium(VI) complex is the species responsible for oxygen transfer and that an intermediate oxoruthenium(IV) complex is then reoxidized in air. We have shown that the oxidation of ruthenium(IV) to ruthenium(VI) proceeds via disproportionation to produce both ruthenium(VI) and ruthenium(II) porphyrin complexes. The ruthenium(II) complex reacts rapidly with oxygen to regenerate the oxoruthenium(IV) intermediate which then continues the catalytic cycle. Experimental results which illuminate this oxygen activation and transfer process will be described.

BIOMIMETIC BINDING AND ACTIVATION OF DIOXYGEN WITH COPPER COMPLEXES

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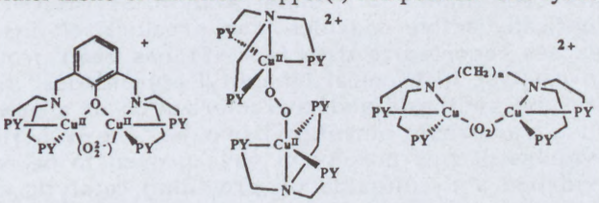
Interest in the reactivity of dioxygen (O_2) with copper ion complexes arises from (a) the general utility of this metal in oxidative processes, and (b) the occurance of Cu centers at the active sites of proteins known to interact with dioxygen and involved in processes including O_2-transport (hemocyanin), hydroxylation of aromatics (monooxygenases) and reduction of O_2 to water (oxidases). Here, we will briefly review aspects of the known protein chemistry and then summarize our attempts to model/mimic the active site structures and function, particularly those systems involving the reversible binding of O_2 and the hydroxylation of an arene substrate in a model monooxygenase system.[1,2]

Using various amine/pyridine ligating systems, we have recently descibed three types of peroxo-dicopper(II) complexes, $\{Cu_2\text{-}O_2\}^{n+}$ (**1-3**), which are formed reversibly by the addition of O_2 to either mono-or dinuclear copper(I) compounds. The syntheses, physical



1 **2** **3**

properties and O_2-binding behavior will be described. The reactivity of **1-3** with various reagents will be compared, showing that the peroxo moiety in **1** & **2** is basic or nucleophilic in character while that for **3** is the opposite, more like early transition metal peroxo compounds.

When the connecting group between tridentate moieties in **3** is a *m*-xylyl unit, hydroxylation occurs; a variety of studies indicate that an intermediate similar to **3** is involved. Reactions of copper complexes involving ligands with modified *m*-xylyl groups will also be discussed, and studies of these have helped in formulating a proposed reaction mechanism.

New ligands and complexes which may also be discussed are aimed to enhance the ability to oxidize externally added substrates or to effect the rapid four-electron reduction of O_2.

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PL-4, WED

SELECTIVE OXIDATIONS WITH DIOXYGEN CATALYZED BY RUTHENIUM AND RHODIUM COMPLEXES

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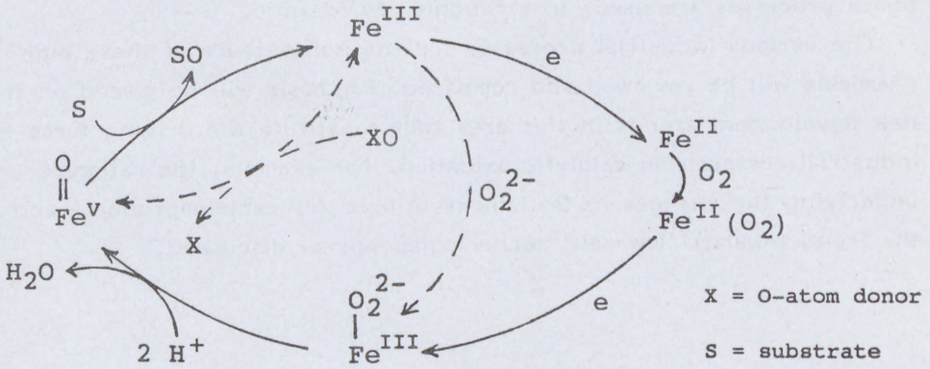
There is wide interest in using O_2 or air in processes for selective catalytic oxidations of organics because of the relatively low cost and environmental compatibility. There have been notable advances in recent years, many emanating from attempts to mimic aspects of the monooxygenase, cytochrome P-450, a heme system.



The Figure above outlines the P450 mechanism, and the various routes (addition of O_2 + 2e, O_2^{2-}, or 'O') to generate the putative $O{=}Fe^{V}$(porp) [or $O{=}Fe^{IV}$(porp$^{\bullet+}$)] species. Many groups are studying such oxidations within porpyhrin and nonporphyrin systems, and many reductants have been tested as the 2e-source in the net reductive activation of O_2;[1] such studies have led also to accidentally discovered dioxygenase systems.[1]

This lecture will present an overview of the area, incorporating also work from UBC. The latter includes : (a) O_2 -oxidations of thioethers, phenols, and alcohols using *trans*-Ru(porp)$(O)_2$ catalysts,[1,2] which can also effect O_2-oxidations of hydrocarbons, as discovered by Groves' group ;[1] (b) isolation and catalytic oxidation properties of Ru(porp)X (X = Br, Cl) species (*cf.* the Fe^{III} species in the Figure), and (c) use of H_2 as the intended sacrificial reductant ($O_2 + H_2 \rightarrow H_2O$ + 'O') with nonporphyrin Rh complexes, this leading instead to catalytic oxidation of the solvent used (N,N-dimethylacetamide) and catalytic formation of H_2O_2.

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PL-5, THU

INDUSTRIAL CATALYTIC OXIDATIONS: AN OVERVIEW

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Catalytic oxidation is the most important technology for the conversion of hydrocarbon feedstocks, such as lower olefins, aromatics and alkanes, to a variety of bulk industrial chemicals, such as ethylene oxide, propylene oxide, acrylonitrile, maleic anhydride, terephthalic acid, phenol and caprolactam. Both heterogeneous, gas phase and homogeneous, liquid phase processes are used, in a roughly 50/50 ratio.

The various industrial processes for the manufacture of these bulk chemicals will be reviewed and compared. Emphasis will be placed on the new development trends in this area that constitute the driving force for industrial research on catalytic oxidation. For example, the rationale underlying the changes in feedstocks utilized for certain products and the trend towards 'low-salt' technologies will be discussed.

PL-6, FRI

OXIDATION OF HYDROCARBONS. NEW APPROACHES.

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Selective catalytic oxidation of alkanes can involve an activation of a hydrocarbon molecule by a low-valent metal complexes with subsequent oxidation of alkyl derivative formed initially by an external oxidation agent. Oxidation of alkanes in the presence of bivalent platinum complexes is the example of such a reaction.

Another approach involves biomimetic oxidation by an iron compound which reacts first with dioxygen producing high-valent iron complex containing $Fe^{iv}=O$ fragment. Both heme and non-heme iron complexes capable to such oxidation will be considered in the lecture as well as other high-valent compounds capable to selectively oxidize hydrocarbons including methane.

Non-metal systems which may be carriers of oxygen cation and oxidize hydrocarbons will be also considered.

SESSION PLENARY LECTURES

(SP-1 TO SP-17)

SP-1, MON

NEW SYSTEMS FOR OXIDATION AND FUNCTIONALIZATION OF ALKANES

C. L. Hill, R. F. Renneke, C. M. Prosser-McCartha, and M. Faraj

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Oxidative resistant completely inorganic analogs of metalloporphyrins and other such complexes of formula, $PM_{11}(TM)O_{39}^{x-}$, where M = the d^0 ions W^{VI} or Mo^{VI}, and TM = transition metal ion, catalyze the functionalization of hydrocarbons by a range of oxygen donors.[1-5] One mechanism of several investigated to date will be discussed, that for functionalization of alkanes by *t*-butylhydroperoxide (TBHP) catalyzed by $PW_{11}(Co^{II})O_{39}^{5-}$ and related complexes. The mechanism is complex and involves oxo transfer and radical chain components. A modification of this system for the oxidative nitrogenation of alkanes will be discussed.[3]

Some early transition metal polyoxometalates catalyze a range of photochemical oxidation processes that display unusual products and mechanisms including the oxidative dehydrogenation and functionalization of saturated hydrocarbons.[6-13] Second generation systems have been developed that catalytically and selectively dehydrogenate alkanes to the nonthermodynamic and least substituted alkenes plus H_2.[13] These systems function by combining the ability of the excited states to cleave unactivated C-H bonds with the ability of the ground states to oxidize (or not oxidize) the radicals in competition with other processes. Some new polyoxometalate based photooxidation systems utilize the deactivating effect of oxygenated products to effect functionalization of unactivated C-H bonds in high conversion and high selectivity in the presence of conventionally far more reactive groups.[9] The first systems for the oxidative replacement of unactivated C-H bonds with C-C bonds and generation of the nonthermodynamic or most substituted carbanions from saturated hydrocarbons will be discussed. The latter reactions combine excited state atom abstraction with radical reduction to make the corresponding carbanions. The photooxidation capabilities of some of these systems have applications in photomicrolithography and in biotechnology.

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SP-2, MON

A PERSPECTIVE OF CATALYTIC OXIDATION

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An understanding of *how* and *why* an event has occurred is as important to the true scientist as the observation of the event itself. In this matter chemists exercised in the challenge of homogeneous catalytic oxidation are no exception. In many studies in this branch of chemistry the wish to understand the mechanism is evident yet, surprisingly often, mechanistic proposals appear in the literature on the back of the most limited of evidence.

This talk uses some results of mechanistic studies from the author's laboratory to illustrate generalities frequently ignored in contemporary work on metal catalysed oxygenations. It will first outline how basic evidence can be easily obtained, exemplifying this point with some findings on ruthenium catalysed oxidations of Ph_3P. A study of the oxidative decomposition of $[\{RhCl(cyclo\text{-}octene)_2\}_2]$ will be used to show how complicating factors should not always provide the excuse for lack of supporting mechanistic evidence. Finally, aspects of the mechanism of a novel oxygenative carbon-carbon bond cleavage reaction will be discussed to illustrate how evidence for the mechanistic pathway of a minor reaction may point to unsuspected reactions of major significance.

SP-3, MON

COMPLEX ACTIVATION OF O_2 FOR SELECTIVE OXIDATIONS

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Strategies that can be employed to utilize complexes to activate O_2 for selective hydrocarbon oxidations will be discussed. Our ruthenium 2,9-dimethyl, 1,10-phenanthroline (dmp) complex is one of the few systems that utilizes oxygen at near ambient conditions without the need of an external reducing agent to carry out the selective oxidation of hydrocarbons[1]. The mechanism of these reactions have implications for the understanding of biologically related iron based systems. Theoretical[2] and experimental[1] investigations of ruthenium-oxo complexes have been used to study the mechanism of oxygen atom transfer reactions and those metal properties that facilitate transfer. Ruthenium complexes also provide the basis for catalytic systems that carry out the homogeneous catalytic oxidation of methane. Studies of this system will be described.

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SP-4, MON

INTRAMOLECULAR REACTIVITY OF OXO-ALKYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Henri Arzoumanian*, Heinz Krentzien** and Helena Teruel**

* ENSSPICAM, URA 1410 du CNRS, Univérsité Aix-Marseille III, France

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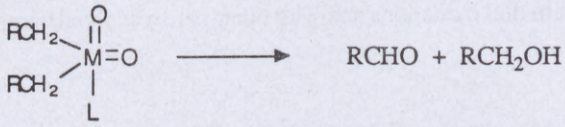
In most metal catalyzed oxydation reactions, one essential step is the oxygen transfer from metal to substrate. The nature of the oxygen can be either peroxydic or oxydic. When organic substrates are oxidized it is generally assumed that the organic moiety is coordinated to the metal center.

In order to better understand this transfer process the controlled "decomposition" of dialkyldioxo group(VI) metal complexes has been studied.

Recent results on the reactivity of dialkyldioxo molybdenum(VI) and tungsten(VI) complexes will be presented. The controlled "decomposition" yields the corresponding aldehyde and alcohol.



RCH_2 = Methyl, Isopropyl, Isoamyl, Neopentyl, Benzyl, Tolyl

L = Bipyridyl

M = Mo, W

This reaction has been followed spectroscopically ; various mechanistic pathways have been envisaged and tested and will be discussed.

OXIDATION OF ALCOHOLS AND DIOLS BY PEROXOMETAL COMPLEXES

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Anionic peroxomolybdenum and peroxotungsten complexes have been shown to behave as oxidants of the alcoholic function.[1-3] The oxo-diperoxo molybdenum complex containing the picolinate *N*-oxido ligand and the tetrabutylammonium cation as counterion, MoO_5PICO,[4] allows the oxidation of both primary and secondary alcohols to the corresponding carbonyl compounds[4] in non polar solvents, under relatively mild conditions and with a high degree of selectivity. Thus, the oxidation of the OH groups may be carried out for molecules where other groups, either oxidizable or sensitive to the reaction conditions adopted with other oxidants, are present.[5]

Although the synthetic scope of MoO_5PICO may be considered well established on the basis of several examples which will be presented, the oxidation mechanism has yet to be elucidated. Both the role of the ligand and the intimate nature of the oxidation step which, in priciple, may be either a homolytic or a heterolytic process, will be discussed also by comparing the results obtained for alcohol oxidations by MoO_5PICO with those obtained with the same oxidant in diol oxidations and with other peroxomolybdenum complexes.

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KINETICS AND THERMODYNAMICS OF DIOXYGEN INTERACTION WITH COPPER

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In contrast with the considerable amount of kinetic data and mechanistic insight on the autoxidation of low molecular Cu(I) complexes, thermodynamic parameters on copper/dioxygen interaction have been restricted to the biological oxygen carrier hemocyanin until recently.

Binding and activation of dioxygen by copper complexes has long been based purely on kinetic evidence for low molecular systems. This situation has fundamentally changed with the development and characterization[1] of quasireversible μ-peroxo copper complexes which made it possible to obtain the thermodynamic and kinetic parameters of dioxygen binding. In addition, oxygenation of organic substrates now can be studied starting from these well defined compounds, greatly reducing the speculative aspects of some kinetics studies. Enthalpies of formation of such adducts are close to those of iron complexes and of biological dioxygen carriers, i.e. roughly 60 kJ/mol, reaction entropies being responsible for their low stability constants at room temperature. Experimental evidence is indicating a strong electrophile as the oxygenating species. Dioxygen activation occurs both thermally and photochemically.

Exceptionally detailed insight into dioxygen binding is obtained with tris-(2-pyridyl-)ethylamine as ligand for which the stepwise formation of 1:1 dioxygen adduct and its subsequent transformation into the binuclear μ-peroxo complex could be followed for the first time.

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PREPARATION AND REACTION OF μ-PEROXO COMPLEXES OF COPPER AND IRON AS MODELS FOR TYROCINASE AND METHANE MONOOXYGENASE

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A series of peroxo copper which are relevant to monooxygenase were successfully synthesized by use of hindered tripod nitrogen ligands. the complexes include μ-η^2; η^2 peroxo copper(II), alkyl- and acylperoxo mononuclear copper(II) complex.[1-3] The structures, physicochemical properties and reactivities of these species provide clear insight on the structure of active site and activation mechanism of dioxygen of the corresponding monooxygenase, tyrocinase.[4]

By use of a hindered tris(pyrazolyl)borate, we succeeded to prepare a mononuclear iron(II) complex which binds dioxygen reversibly at -20° C in toluene.[5] The resonance Raman studies on the dioxygen adduct clearly demonstrated that the formed species is μ-peroxo binuclear iron(III) complex.

As a plausible function model for methane monooxygenase which contains a binuclear iron site as hemerythrin, we developed a catalytic system composed of a μ-oxo μ-carbonato binuclear iron(III) complex, Zn powder (electron donor) and acetic acid (proton donor).[6] The system is active for dioxygen oxidation of not only adamantane but also pentane and benzene with turnover numbers of more than 10.[7]

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SP-8, TUE

QUERCETIN 2,3-DIOXYGENASE MIMICKING COPPER CHEMISTRY

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Recent interest in metal-assisted oxygenation reactions is motivated by the desire to disclose new synthetic ways for the introduction of oxygen atoms into organic substrates and by the hope that such studies will give us insight into the mechanism of biological oxygenation reactions catalyzed by metalloenzymes.

Quercetin 2,3-dioxygenase, a copper-containing metalloenzyme, catalyzes the degradation of quercetin (3',4',5,7-tetrahydroxyflavonol) into a depside (phenolic carboxylic acid ester) and carbon monoxide.

We are studying the copper mediated oxygenation reactions of flavonol using several copper complexes in various solvents leading to different oxygenated products. From these mixtures copper flavonolate complexes could be isolated.

The isolation and structural characterization of copper(I) and copper(II) flavonolate compounds established the possible mode of coordination of quercetin to the copper in the enzyme. A series of flavonolato copper complexes are good catalysts for flavonol oxygenation. Oxygenation studies on copper flavonolate compounds give evidence for the possible mode of the reaction between the coordinated flavonolate ligand and dioxygen.

SP-9, TUE

IRON- AND COBALT-INDUCED ACTIVATION OF HOOH AND OF DIOXYGEN FOR THE KETONIZATION OF METHYLENIC CARBONS, AND THE DIOXYGENATION OF ARYLOLEFINS AND CATECHOLS

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In pyridine/acetic acid solvent (2:1 molar ratio) (DPA)$Fe^{III}OFe^{III}$(DPA) (DPA = 2,6-dicarboxylato-pyridine) catalyzes hydrogen peroxide for the selective ketonization of methylenic carbons ($>CH_2 \longrightarrow >C=O$), and the dioxygenation of acetylenes to α-diketones and arylolefins to aldehydes.[1] Cyclohexane is transformed with 76% efficiency (c-C_6H_{12} oxidized per two HOOH) to give >97% cyclohexanone and <3% cyclohexanol, and n-hexane with 55% efficiency to give 53% 3-hexanone, 46% 2-hexanone, and <2% 1-hexanol.

With this same py_2(HOAc) solvent $Fe^{II}(DPAH)_2$ is autoxidized by O_2 to $(DPAH)_2Fe^{III}OFe^{III}(DPAH)_2$ via a reactive intermediate, $(DPAH)_2Fe^{III}OOFe^{III}(DPAH)_2$ (1). The latter, when formed in the presence of excess substrate, reacts (about 10-30% efficient for a 50-fold excess of substrate relative to catalyst) to ketonize methylenic carbons, and to dioxygenate arylolefins [c-PhCH=CHPh → 2 PhCH(O)] and catechols [1,2-$Ph(OH)_2$ → HOC(O)CH=CH-CH=CH(O)OH (muconic acid)]. With the use of reductants [PhNHNHPh, H_2NNH_2, $PhCH_2SH$, and H_2S] stoichiometric turnovers are achieved via the reduction of $(DPAH)_2Fe^{III}OFe^{III}(DPAH)_2$ to $Fe^{II}(DPA)_2$ [e.g., 3 mM $Fe^{II}(DPAH)_2$, O_2 (1 atm, 3.4 mM), 1 M c-C_6H_{12}, and 100 mM PhNHNHPh reacts to yield 21 mM c-C_6H_{10}(O), 21% efficient)].

Analogous chemistry is facilitated by related cobalt complexes and solvent systems via activation of HOOH. Work in progress extends these systems to the monoxygenation of hydrocarbons (reaction mimics for the *methane monooxygenase* and *cytochrome P-450* enzymes).

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SP-10, WED

TITANIUM-PROMOTED ENANTIOSELECTIVE OXIDATION OF THIOETHERS AND SYNTHETIC APPLICATIONS

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The asymmetric oxidation of thioethers to sulfoxides has a theoretical and practical interest because of the simplicity of the model, the easyness of the reaction and the great importance of homochiral sulfoxides in organic synthesis[1].

Only recently methods to obtain enantiomerically pure sulfoxides by direct oxidation have been discovered[2,3,4]. However, the efficiency of such methods is still strongly dependent on the structure of the thioethers.

Studies are in progress in several laboratories as well as in our own both to improve the efficiency of the oxidation and to define the structural effects on the enantioselectivity with the available methods.

The results obtained in our group with the titanium-(R)-diethyltartrate-alkylperoxide promoted oxidation will be reported and discussed.

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SP-11, WED

DIOXYGEN ACTIVATION AND HOMOGENEOUS CATALYTIC OXIDATIONS USING METAL CYCLIDENE COMPLEXES

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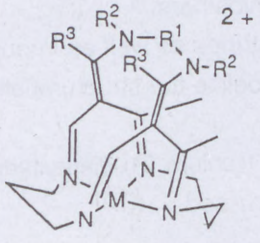
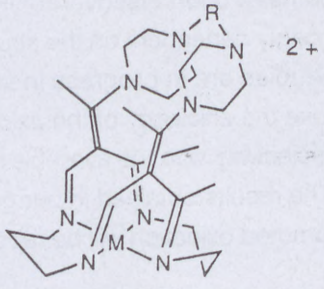
The transition metal cyclidene complexes, in their lacunar forms (structure I), are exceptional dioxygen carriers, and structural modification provided expanded cavity space to encompass a potential organic substrate in addition to dioxygen (structure II). Studies have now been made on (1) the activation of dioxygen in



I



II

cyclidene complexes and on (2) the oxidation of organic substrates using cyclidene complexes and oxygen surrogates. Several routes lead to the formation of peroxide complexes, including the direct reduction of bound dioxygen; however, subsequent substrate oxidations have not been confirmed for these species. The usual surrogate oxidizing agents oxygenate substrates and the active site (intracavity *vs* external) may be dependent on solvation properties.

SP-12, WED

COBALT SCHIFF BASE COMPLEX CATALYZED EPOXIDATION OF OLEFINS WITH NaOCl

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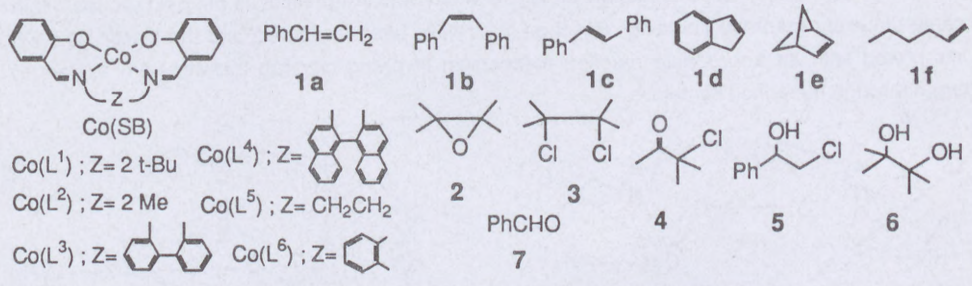
Cobalt Schiff base complexes [Co(SB)] are interesting because of their characteristic behavior as artificial oxidoreductases: dioxygenations in aprotic solvents, monooxygenations in alcohols, and dehydrogenations.[1] However, no information has been available about catalytic activity of Co(SB) for epoxidation. We report here that Co(SB) catalyze the oxidation of olefins with NaOCl mainly to give epoxides. The oxidation was examined with olefins **1a - 1f**. A solution of **1** in dichloromethane containing Co(SB) was stirred with a solution of NaOCl in a borate buffer (pH 10) at room temperature. Products **3 - 7** were isolated in addition to epoxides**2** from the resulting mixture. No reaction takes place without the catalyst. The nature and distribution of the chlorinated products depend on the



structure of **1**. On the other hand, the structure of Co(SB) does not afffect the product distribution but the reaction rate. Since both cis- and trans-stylbenes give only trans-stilbene oxide, the present oxidation should involve a radical process. Nonplanar $Co(L^1)$-$Co(L^4)$ are more effective than planar $Co(L^5)$ and $Co(L^6)$ in the present catalysis. Product and kinetic analyses of the oxidation suggest a mechanism involving rate controlling homolysis of $Co^{III}(SB)(OCl)$ under the interaction with the substrate, different from the mechanism proposed for the Mn(TPP)Cl catalyzed epoxidation.[2]

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SP-13, WED

REACTIONS BETWEEN COORDINATED DIOXYGEN AND COORDINATED SUBSTRATES IN BINUCLEAR MACROCYCLIC COMPLEXES

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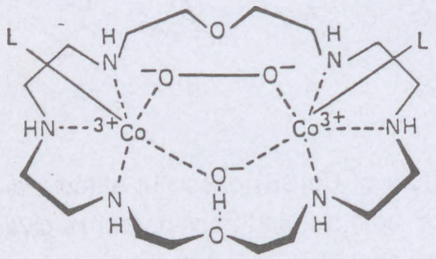
The use of a dicobalt(II) macrocyclic complex as host for the coordination and activation of secondary bifunctional bridging ligands as guests is described. The macrocycle 1,4,10,13,16,11-hexaaza-7,19-dioxacyclotetracosane (BISDIEN) coordinates two Co(II) ions to form a dinuclear complex which is greatly stabilized by bridging ligands such as hydroxide, oxalate, and mesoxalate anions, as well as dioxygen. Equilibrium constants for the formation of the corresponding mono-bridged dinuclear Co(II)-BISDIEN complexes have been determined potentiometrically.[1] It was found that the dioxygen complex also contains a bridging hydroxide ion, as well as two coordinated water molecules, indicated by L in formula **1**, which are converted to hydroxide ions at high pH. When a third bridging bifunctional donor such as oxalate is present, it occupies the coordination sites indicated by L in **1** to give **2**, a triply-bridged dinuclear macrocyclic cobalt(II) complex (formally indicated as Co^{3+} with dioxygen as a μ-peroxo bridge. The equilibrium constants controlling the formation of **2** have been determined and conversion to this species is about 65% complete under an atmosphere of pure dioxygen at 25.0°C in aqueous solution at pH 8.5 with initial concentrations of 1.0×10^{-3} M BISDIEN, 1.0×10^{-3} M oxalate and 2.0×10^{-3} M Co(II). The dioxygen is sufficiently activated by metal ion coordination that it readily oxidizes oxalate at 45.0°C when both are present as bridging groups within the same dinuclear macrocyclic cavity. Reaction rates have been measured, and the kinetic data will be interpreted with an appropriate reaction mechanism involving electron transfer from oxalate to dioxygen through the cobalt centers.[1]



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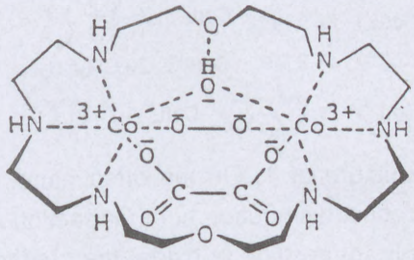

2

A similar investigation[2] has been carried out with mesoxalate (ketomalonic acid) in place of oxalate, and similar mixed singly-, doubly-, and triply-bridged dicobalt BISDIEN complexes are formed. In this case, however, the redox reaction within the macrocyclic cavity occurs in a catalytic mode in the presence of excess mesoxalate, with the reductant being converted completely to carbon dioxide, rather than a mixture of carbon dioxide and carbon monoxide. A cyclic reaction scheme will be proposed showing regeneration of the starting polybridged binuclear complex, followed by oxygenation and oxidation of the substrate to carbon dioxide.

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SP-14, WED

SINGLET OXYGEN AND ELECTRON-TRANSFER IN PHOTOOXIDATIONS

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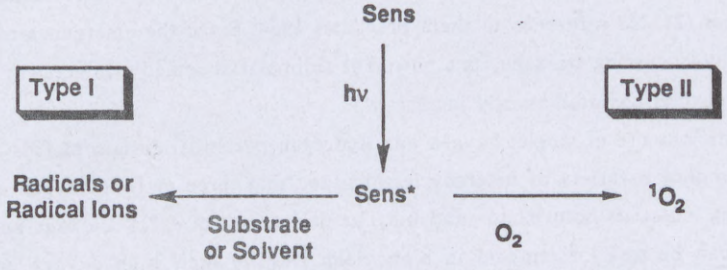
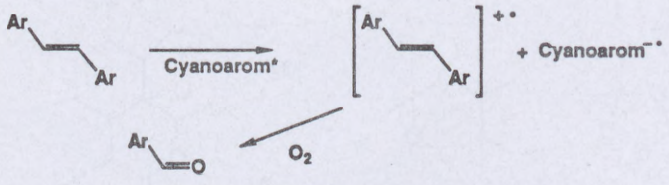
Photosensitized oxidations involve absorption of light by a sensitizer, followed by oxidation of a substrate. Two basic reactions of the excited sensitizer occur. Sens* can either react directly with the substrate (Type I) or with oxygen (Type II). The Type II reaction leads mainly to singlet molecular oxygen by an energy transfer mechanism.



The cyanoaromatic-sensitized photooxidation of aromatic alkenes such as *trans*-stilbene is a prototype for the Type I electron-transfer reaction. The radical cation and anion intermediates have both been detected spectroscopically. However, we have previously shown that both Type I and Type II processes compete in reactions with this sensitizer. In this paper we show how contibutions from each process can be assessed.



The "monomol" luminescence at 1270 nm can be used for direct measurement of both the absolute amount of singlet oxygen produced and its lifetime. The quantum yield of singlet oxygen ($^1O_2$) production by 9,10-dicyanoanthracene (DCA) has been redetermined by this method in benzene and acetonitrile; $^1O_2$ is produced from both singlet and triplet states of DCA. Direct preparation of ^{3}DCA by enhanced intersystem crossing with 2,5-dimethyliodobenzene (DMIB) allowed determination of the individual contributions of ^{3}DCA and ^{1}DCA to $^1O_2$ production. Substrate-enhanced intersystem crossing can make the triplet pathway a major route under some conditions. Flash spectroscopic detection can be used to measure the amount of radical ions and triplet DCA. The quantum yield of singlet oxygen ($^1O_2$) production from DCA in the presence of *trans*-stilbene (TS) was also determined. The formation of $^1O_2$ is quenched by TS in acetonitrile, but enhanced in benzene. Exciplex emission is observed in both solvents. These observations suggest that exciplex formation in benzene leads to enhanced intersystem crossing in DCA, but that ion-pair separation in acetonitrile is too rapid to allow this process. These observations emphasize the complexity of some photochemical oxidation reactions but show how they may be successfully probed by a combination of physical methods.

SP-15, WED

1,2,3-TRIOXANES. THE CHEMISTRY OF A NEW CLASS OF SATURATED HETEROCYCLES

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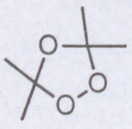
CH-1211 Geneva 4, Switzerland

Secondary ozonides or 1,2,4-trioxolanes (1) occupy an important place in the annals of classical chemistry. In contrast, little has been reported of their higher homologues, the 1,2,4-trioxanes (2). No reference to them pre-dates 1954. Since the emergence of arteannuin (3), a naturally-occurring trioxane, as a powerful antimalarial remedy, interest in this class of oxygen heterocycles has dramatically increased.

By the judicious use of singlet oxygen and hydrogen peroxide, certain olefins can be oxygenated to produce a variety of heterocycles incorporating three or four oxygen atoms. From simple starting materials both mono- and bicyclic derivatives of 1,2,4-trioxane and 1,2,4-trioxan-5-one can be easily assembled in high yield. Despite their high oxygen content, they are surprisingly stable, often occurring as crystalline solids, so enabling their structures to be determined by X-ray. We will present new mechanistic, structural, and chemical results dealing with the formation of these poly-oxygenated products, their potential as synthetic intermediates, and their role as oxidants.



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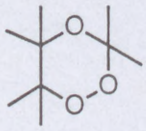

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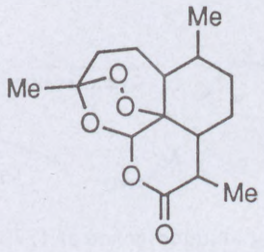

3

NITRATE AND NITRITE LIGANDS AS MEDIATORS IN PALLADIUM CATALYZED OXIDATION OF OLEFINS

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Data about oxidation reactions of organic and inorganic substrates (olefins and sulphides, aromatic compounds) catalyzed chiefly with palladium complexes involving the NO_x ligands (x = 2,3) are represented in the paper.

Mechanism of nitratoxilation processes (formation of the ethylene-glycol nitrates) and of acetoxilation (formation of the ethylene-glycol acetates) of ethylene, being conducted in solutions of the palladium salts in concentrated nitric and acetic acids correspondingly, is investigated, as well as that of reaction of oxidation of dialkylsulphides to dialkylsulphoxides.

Nature of the key intermediates of stoichiometric oxidation of ethylene with NO_x ligands in the complexes $L_2PdX_{2-n}(NO_x)_n$, where n = 1+2, X = 2, 3, L - CH_3CN, to various products: acetaldehyde, vinylacetate, nitroethylene, ethylene-glycol monoacetate, ethyledendiacetate, - is studied in details by application of the method of NMR- and IR-spectroscopy. Problems of influence of nature of the NO_x ligand and solvent on the direction of the ethylene oxidation process, are discussed.

Catalytic compositions on the basis of nitrito- and nitrato-complexes of palladium for realization of the processes of co-oxidation of carbon monoxide and olefins to various compounds containing carboxyl groups, are developed.

Additional introduction of ferric compounds to palladium complexes made it possible to increase sharply the rate of re-oxidation of the palladium nitroso complexes by dioxygen, the first being the products of reduction of the nitrite and nitrate complexes. As a whole, presence of ferric compounds allowed to increase the activity of the palladium-nitrite complexes in reactions of oxidation and nitration into ring of the benzene derivatives.

Heterogenized analogues of the palladium-nitrite systems were obtained: anchored on the fixed nitrile ligands; adsorbed on SiO_2 and active carbon, dispersed metal particles of palladium supported on SiO_2, TiO_2, active carbon and treated with nitric acid were produced. Behaviour of these systems when contacting with carbon monoxide, ethylene, propylene, was studied by a wide set of physical methods of investigation being applied. Information on a mechanism of heterogenized systems, which in general terms is similar to that of homogeneous analogues, was obtained.

SP-17, FRI

SELECTIVE FUNCTIONALISATION OF SATURATED HYDROCARBONS BY OXO RUTHENIUM COMPLEXES

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Selective functionalization of saturated hydrocarbons has become a subject matter of much current interest.[1,2] Cytochrome P450 models involve the use of macrocyclic complexes of Fe, Mn, Cr, Ru in the presence of oxidants such as NaOCl, C_6H_5IO, ICH_5O_5 and amine oxides for the oxidation of saturated hydrocarbons.[3-5] Ru(III)-EDTA catalyzes the oxidation of saturated hydrocarbons in the presence of molecular oxygen[6] or NaOCl[7] as oxidants. The nature of the products depend on the oxidant.

In the oxidation of hydrocarbons by molecular oxygen catalyzed by Ru(III)-EDTA, the products of oxidation are those of a P450 radical cage type.[3] Cyclohexane gives 8% conversion to cyclohexanol[6] and 1% cyclohexanone, adamantane[7] gives 4% of 1-adamantol with 0.2% of 2-adamantone The ratio of $C_2/C_3 \approx 0.05$. Ru(III)-EDTA can be oxidized by NaOCl to Ru^{V}=O(EDTA) which catalyzes the oxidation of cyclohexane, tetrahydrofuran and adamantane in the presence of NaOCl. The reaction proceeds by a Gif type[1] of product selectively. Cyclohexane gives 7% yield of pure cyclohexanone; tetrahydrofuran gives 10% yield of γ-butyrolactone and adamantane, 3% of 2-adamantone and 0.5% of 1-adamantol ($C_2/C_3 \approx 6$).

The mechanism of these reactions will be discussed.

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MICROSYMPOSIUM LECTURES

(M-1 TO M-6)

CATALYSED OXIDATIONS USING PEROXYGEN REAGENTS

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Catalytic oxidation is an important process type widely in current use in the chemical industry. One technique enables low cost oxidants to be used for a wide range of functional group oxidations.

Hydrogen peroxide is particularly suitable to catalytic activation. Under neutral conditions at ambient temperature it is not very reactive. It may be converted "in situ" to a wide range of active species which will perform specific oxidations. It may also be used to re-oxidise other active oxidants within a process giving an overall catalytic effect. Other peroxygen reagents such as persulphates or percarboxylic acids are generally more reactive than Hydrogen Peroxide.

The presentation will review the many active oxidant species generated by peroxygen compounds. Species covered include oxygen transfer, oxygen radical and other redox species:-

- Epoxidation
- Bayer Villiger oxidation of ketones
- Aromatic side-chain oxidations

M-2, THU

CATALYTIC Cu(II) INDUCED REACTIONS

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One of the great challenges of the chemical industry is the development of selective catalytic oxidations with O_2. There is considerable interest at the present time in Cu-catalysed oxidation reactions from very different points of view[1,2,3].

A lot of scientific and industrial chemical research has been done on the Cu-catalysed polymerisation of 2,6-dimethyl phenol[4,5,6], especially on the organic chemical aspects of the growing polymer chain. However mechanistic studies on the operating catalytic system were relatively scarce untill 1985.

At DSM therefore a study was started to eluicidate the role of Cu, the 2 substrates (phenols and O_2), ligands and solvents, in the polymerisation of phenols . The DSM system consisted of simple Cu-carboxylates in the corresponding carboxylic acid, phenol and oxygen.

It was shown that in the catalytic cycle of Cu-carboxylates at least 3 Cu-complexes are involved.

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M-3, THU

NEW METAL COMPLEX SORBENTS FOR THE RECOVERY OF OXYGEN

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Oxygen is produced in large tonnage quantities for the most part by the distillation of air at cryogenic temperatures. In recent years alternative methods for the separation of air have emerged. These include pressure-swing processes using zeolites as nitrogen-selective adsorbents, molecular sieve carbons as kinetically selective adsorbents for oxygen, and very recently polymer membranes.

Reversibly oxygen binding metal complexes, principally of cobalt and iron have been studied as potentially highly selective sorbents for the separation of oxygen from air. Ideally, a solid state metal complex is required which has an appropriate reversible oxygen affinity and capacity, a low heat of reaction and is stable in use. This last requirement has been the most difficult to realize. In this paper we will describe the synthesis, and characterization and basic properties of a new family of solid state complexes that show an unprecedently facile oxygen absorption and desorption at ambient conditions.

M-4, THU

SELECTIVE OXYGEN-DRIVEN DECARBOXYLATIONS OF N-SUBSTITUTED AMINO ACIDS.

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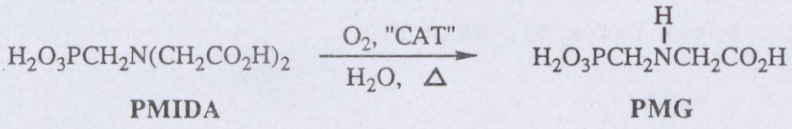
Cobalt(II) ion in aqueous solution has been found to catalyze very selectively the molecular oxygen driven oxidation of ((N-phosphonomethyl)imino)diacetic acid (PMIDA) to (N-phosphonomethyl)glycine (PMG):



PMIDA **PMG**

This homogeneous catalytic conversion is novel and represents, in effect, an oxidative dealkylation of one carboxymethyl moiety yielding the N-substituted glycine. This oxygen-driven reaction is extremely selective to the desired product PMG when carried out to high conversions (>99%) at the natural pH of the free acid substrate (~1-2) and when carried out at substrate loadings less than 5% by weight. In addition, the catalytic system is very selective for the PMIDA substrate; i.e., other closely related ligands show no reactivity; e.g., NTA, EDTA, etc. The results of kinetic and mechanistic studies on dilute systems are presented and discussed with special emphasis on how an understanding of the mechanism can make it possible to generate a catalyst system which gives very high yields even with very high substrate loadings. This Co catalyzed reaction is first-order in substrate and $[Co]_{tot}$. The oxygen pressure dependence exhibits saturation kinetics, while the selectivity increases as oxygen pressure increases. The rate is also inversely proportional to $[H^+]$. Product and labeling studies as well as the kinetic studies support a mechanism in which Co(III) ion is generated from the reaction of O_2 with a Co^{II}(PMIDA) complex producing hydrogen peroxide and a Co^{III}(PMIDA) complex. Co(III) is the oxidant of a bound PMIDA, followed by the decarboxylation of the resultant radical and the subsequent trapping of the $NCH_2\cdot$ radical with oxygen. The ultimate fate of the oxygenated radical is to the N-formyPMG, **1**, which hydrolyzes to the PMG product.

WHY NOT OZONE ?

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75 321 Paris Cedex 07. FRANCE.

Industrial applications of ozone are strongly dependent upon the economics of its generation. Recently, significantly reduced energy costs were achieved by using oxygen feeded ozone generators associated with an oxygen-ozone separation device. The economics of this new technology will be compared with the air operated ozone generation.

Potential applications of this large source of cheap ozone in several fields like chemical synthesis, water treatment, pulping,... will be illustrated.

M-6, THU

TITANIUM SILICALITE CATALYZED OXIDATIONS

B.NOTARI

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Oxygen of the air is undoubtedly the cheapest and most widely used oxidant.In quite a few cases however the desired products cannot be obtained with the use of oxygen and more expensive oxygen sources must be used: hydrogen peroxide,hydroperoxides, peracids. Hydrogen peroxide is very attractive because of the low cost per oxygen atom,absence of by-products and ease of operations,but its use has been limited by the relatively low yields of useful products that could be obtained with respect to other oxidants.

It has recently been discovered that Titanium Silicalite (TS-1), a crystalline microporous solid having the structure of silicalite but containing Ti(IV) in framework positions, acts as a highly selective oxidation catalyst for many different reactions in which H_2O_2 is the oxidant: epoxidation of olefins and diolefins,oxidation of alcohols to aldehydes or ketones, hydroxylation of aromatics,ammoximation of ketones. New processes and technologies making use of H_2O_2 have been made possible by TS-1 unique properties.

The hydroxylation of phenol with H_2O_2 for the production of catechol and hydroquinone proved competitive with existing processes and an industrial plant for the production of 10.000 T/Y of diphenols has been built and is succesfully operating since 1986 in Ravenna,ITALY.

Evidence concerning the structure of the material and the mechanism by which it acts as a selective oxidation catalyst are discussed.

CONTRIBUTED PAPERS

(O-1 TO O-21)

OVER-OXIDATION OF CYCLOHEXANE BY THE GIF SYSTEM IN AN ATMOSPHERE OF PURE OXYGEN

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The Gif system has been shown to be very selective for the oxidation of secondary CH_2-groups to the corresponding ketones.[1] Under an atmosphere of pure oxygen, cyclohexane is oxidized with more than 85% selectivity to cyclohexanone with turnover numbers as high as 100/h.[2] With prolonged reaction times the cyclohexanone and cyclohexanol formed are further oxidized.[2] We have now studied the oxidation of these compounds separately and identified some of the products formed. Under the same reaction conditions (20°C, 4 h, pure oxygen) oxidation of cyclohexanol and cyclohexanone is slower. Cyclohexanol is further oxidized with a turnover number of 23/h, but cyclohexanone was only 23% of the oxidation products. Cyclohexanone is further oxidized with the rate of 20/h and forms mainly a cyclohexanedione, which is presently being identified by comparison with an authentic sample. No adipic acid is formed under the reaction conditions. Similar results have been reported by Barton et al.,[1] who found that the Gif system oxidizes cyclohexanol only slowly, giving cyclohexanone in 14% yield, and that adamantanone is further oxidized to adamantanediones with 10.2% yield.

This work was financed by Nitrocarbono S.A. Fellowships from CNPq and UNICAMP are acknowledged.

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Transformation of Fe(III)TMP N-Oxide to a Two Electron Oxidized Equivalent of Fe(III)TMP Complex

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The reaction of Fe(III)TMP N-oxide (**1a**, TMP: tetramesitylporphyrin)[1] with an excess amount of trifuluoroacetic acid (TFA) in toluene at ca -30°C gave a new species (**4a**), whose soret band appears at 412 nm, via the transient formation of an intermediate (**3a**). A titration of **1a** with TFA indicates one mole of the acid being required to complete the formation of **3a**. Upon the addition of an acid scavenger such as pyridine immediate reproduction of **1a** was observed. Further, red shifted soret band of **3a** (437 nm) indicated its structure to be a protonated form of **1a** at the N-oxide oxygen. Addition of a larger amount of TFA to **3a** accelerated to form **4a**. A very similar reaction was also observed in the reaction of Fe(III)TDCPP N-oxide (TDCPP: tetrakis-2,6-dichlorophenyl-porphyrin). In addition, slow reduction of **4a** to Fe(III)TMP$^{+\bullet}$ at -30°C and to Fe(III)TMP at room temperature were observed. It is consistent with the chemical reduction of **4a** to Fe(III)TMP by 2 equiv. amount of iodide. The UV-Vis spectrum of **4a** is very different from that of Fe(IV)TMP and Fe(IV)TMP$^{+\bullet}$,[2] but very similar to porphyrin dication complexes of Zn, Mg, and Ni.[2] The EPR spectrum of **4a** at -150°C showed two broad absorptions at g=4.2 and 2.05, similar to Fe(III)TPP(ClO_4). Based on these results, we assigned **4a** to be an Fe(III)TMP dication complex.

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METALLOPORPHYRIN - CATALYZED EPOXIDATION OF PROPYLENE

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Selective oxidation of hydrocarbons has been the subject of a great interest and investigations. Especially, model systems based on metalloporphyrins used as catalysts have been intensely explored. Here we report the results of the investigations on the reaction of epoxidation of propylene with LiOCl as the oxygen source and porphyrins of such transition metals as Mn(III), Fe(III), Ni(II), Cu(II), and Zn(II) as the catalysts. The yield in propylene oxide as well as the selectivity appeared to be dependent not only on the character of the metal centre but also on the structure of the porphyrin ligand.

From among the investigated porphyrins the one with manganese centre and 2,6-dichlorotetraphenylporphyrin ligand (ClMnTDCPP) shows the highest activity: 5 cycles per minute and selectivity which exceeds 90%. Smaller selectivity ca. 60% is observed for manganese (III)-tetramesitylporphyrin (ClMnTMP) while manganese (III)-tetratolyloporphyrin (ClMnTTP) gives very poor results. Corresponding iron(III) porphyrins show smaller activity and selectivity in the investigated process, however, the influence of the character of the porphyrinic ligand is similar.

The addition of imidazole increases the yield of propylene oxide in the reactions catalyzed by manganese porphyrins while its effect on the reactions catalyzed by iron porphyrins is negative.

Nickel, copper and zinc tetratolyloporphyrins appeared practically inactive.

In contrast to the results described above, when propylene was epoxidized by molecular oxygen in the presence of aldehyde as the reducing agent, ClMnTTP appeared to be more effective catalyst than ClMnTDCPP.

On the basis of the obtained results important mechanistic conclusions may be drawn.

MOLECULAR OXYGEN AS OXIDANT IN HETEROPOLYANION CATALYSED OXIDATIONS

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Two modes of heteropolyanion (HPA) catalysed oxidations using molecular oxygen as the primary oxidants are presented. In the first mode use of heteropolymolybdates enables the oxidative dehydrogenation of alcohols to aldehydes, of amines to nitriles and aromatization of dienes in high selectivity and in quantitative yields by electron transfer from the organic substrate to the heteropolyanion The reduced heteropolymolybdate is then reoxidized by molecular oxygen coupled with formation of water. The entire catalytic cycle may be summarized by equation 1.

(1) HPA_{ox} + Substrate $\longrightarrow$ $2H^+$ + HPA_{red} + Product

$2H^+ + HPA_{red} + 1/2O_2 \longrightarrow HPA_{ox} + H_2O$

The presentation will focus on two types of heteropolymobybdates that are active in such reactions and discuss the synthetic and mechanistic aspects of the reactions. In particular emphasis will be placed on the identity of the reduced species and the manner of reoxidation by dioxygen.

In the second reaction mode transition metal substituted heteropolyanions of the general formula $SiM(H_2O)W_{11}O_{39}$ (M = Mn, Cu, Ru, Rh etc) are used together with reducing agents such as sodium borohydride, sodium dithionite or hydrogen and colloidal platinum to oxidize alkenes to epoxides and alcohols. Depending on the reducing agent and type of heteropolyanion used several reaction pathways are implicated including allylic autoxidation, high valent metal oxo mediated epoxidation and formation alcohols with anti-Markownikoff orientation perhaps via decompostion of organoboranes formed by catalytic hydroboration.

Novel Oxidation of Phenols by Copper(II) Complex Catalyst / O_2 System.

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We previously reported that $CuCl_2 \cdot 2H_2O$ coupled with amine, hydroxylamine, or oxime catalyzes the oxygenation of 2,3,6-triemthylphenol to trimethyl-*p*-benzoquinone(TMQ) with dioxygen in alcoholic solvent in the presence of hydrochloric acid.[1&2] Here, we report the oxygenations of 2,6-dimethylphenol(2,6-DMP) and 2,4,6-trimethylphenol (2,4,6-TMP) by the similar reaction system.

2,6-DMP, which affords mainly diphenoquinone or poly(phenylene oxide) in usual copper(II) catalyzed oxidation, was oxygenated selectively to 2,6-dimethyl-*p*-benzoquinone(2,6-DMQ)(90% yield) in the present oxidation. This oxygenation was favoured by the presence of hydrochloric acid and the most preferable catalyst system was $CuCl_2 \cdot 2H_2O$-hydroxylamine hydrochloride, similarly to the case of the oxidation of 2,3,6-TMP to TMQ.

2,4,6-TMP was selectively converted to 3,5-dimethyl-4-hydroxybenzaldehyde (DMHBA)(95 % yield) by $CuCl_2 \cdot 2H_2O$-acetone oxime / O_2 system. A presence of hydrochloric acid rather caused the formation of 2,6-DMQ as a by-product. In 2,4,6-TMP oxidation, a substantial amount of 2,6-dimethyl-4-alkoxymethylphenol was detected as an intermediate to DMHBA, and therefore 3,5-dimethyl-4-hydroxybenzaldehyde dialkyl acetal is most likely the precursor of DMHBA. It is thus considered that oxygen atom incorporated into aldehyde group of DMHBA is derived from water, while that incorpoated into *p*-benzoquinones is from oxygen molecule. The latter incorporation is accelerated by the presence of proton acid. This may arouse interest in the oxidation mechanism because a hydroperoxo species can be formed by protonation of activated dioxygen and considered as the active species in the biomimetic oxidation by dicopper(I) complex as a model of Type 3 copper protein.[3]

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O-6, WED

RUTHENIUM OXO COMPLEXES AS ORGANIC OXIDANTS

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As part of our continuing work on platinum group oxo complexes as catalysts for organic oxidations we report a number of new carboxylato complexes of ruthenium(VI) and (V). Their reactions have been investigated as oxidants for alcohols, phosphines, sulphides and activated halides.

Ruthenium(VI). Reaction of RuO_4 with acetic acid in the presence of tetra-arylphosphonium chlorides gives the acetato species $[RuO_2(OAc)Cl_2]^-$; propionato, butyrato and other carboxylato complexes have also been isolated. The X-ray crystal structure of the acetato complex is reported as are its reactions with organic substrates. The new complexes are effective, selective oxidants for primary alcohols to aldehydes and secondary alcohols to ketones; halides to aldehydes, sulphides to sulphoxides and sulphones and phosphines to phosphine oxides. In the presence of N--methylmorpholine-N-oxide (NMO) and other co-oxidants they function as efficient catalysts for the above reactions, and unsaturated substrates do not suffer competing double bond cleavage.

Ruthenium(V) and osmium(V). Reaction of $(R_4N)[RuO_4]$ (R = ^{n}Pr, ^{n}Bu) or $(Ph_4P)[OsO_4]$ with tertiary α-hydroxycarboxylic acids H_2L gives the salts $(R_4N)[RuOL_2]$ and $(Ph_4P)[OsOL_2]$ (L = $\{OC(O)C(O)Et_2\}^{2-}$ (ehba); $\{OC(O)C(O)Me_2\}^{2-}$; $\{OC(O)C(O)MeEt\}^{2-}$; $\{OC(O)C(O)MePh\}^{2-}$). We have already reported the X-ray crystal structure[2] of $(^nPr_4N)[RuO(ehba)_2]$; it is analogous to that of the chromium(V) species $Na[CrO(ehba)_2]$,[3] with the oxo ligand occupying an equatorial position in a distorted trigonal bipyramid. Reactions of these complexes are reported; they are mild oxidants for alcohols and phosphines.

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SELECTIVE OXIDATION OF ALCOHOLS BY DIOXIRANES

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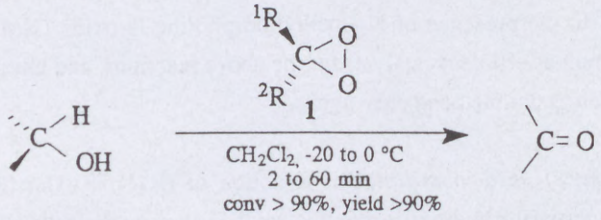
Once it became estabilished[1] that the reaction of peroxomonosulfate HSO_5^- (caroate) with ketones generates dioxiranes,[2] the feat of isolation of a few volatile species such as dimethyldioxirane (**1a**) (in **1**: $^1R=^2R=CH_3$)[3,4] and methyl(trifluoromethyl)dioxirane (**1b**)[5] (in **1**: $^1R=CH_3$; $^2R=CF_3$) precipitated an intensive utilization of these unique oxidants in synthetic applications.[2] Among these, the most remarkable to-date appears to be the O-atom insertion into "unactivated" C-H bonds of alkanes.[2,6] In these reactions, the data collected and scout runs had indicated that - in most of the cases - the secondary alcohols initially formed are further oxidized to the corresponding ketones.[6] We have now carried out a detailed study demonstrating that a variety of cyclic and alicyclic secondary alcohols can be cleanly transformed into ketones using **3b** under extraordinary mild conditions and in high yield. within very short reaction times.



Dioxirane **1b** was found to be over 200 times more reactive than **1a** in the conversion of cyclohexanol into cyclohexanone. And yet, with **1b** remarkable selectivities attain, allowing - e.g. - the clean transformation of epoxyalcohols into epoxyketones ; *endo*-norborneol was found to be over 40 times more reactive than its *exo* stereomer. Cyclobutanol is transformed by **1b** into cyclobutanone only, and an isotope effect k_H/k_D of ca. 1.6 has been measured using cyclohexanol and cyclohexanol-d_{12}. These and other pieces of evidence suggest that a radical or radical-chain mechanism is unlikely for the title reaction.

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REGIOSELECTIVITY OF SINGLET OXYGEN ENE REACTIONS. THE NON-BONDING LARGE GROUP EFFECT.

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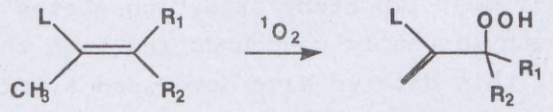
The ene reaction of singlet oxygen[1] with alkyl or aryl substituted alkenes shows a general preference for hydrogen abstraction from the group which is geminal to the larger substituent of the double bond. These results, like the previous observations[2], require that non-bonding interactions be the dominant factor that controls the relative stabilities of the transition states leading to isomeric products.



major product

L	R_1	R_2	% major prod.
Neopentyl	H	H	100
"	H	CH_3	83
"	CH_3	CH_3	78
^{t}Butyl	H	CH_3	66
$(CH_3)_3Si$	CH_3	CH_3	100
Isobutyl	CH_3	isobutyl	97
"	isobutyl	CH_3	97
x-Phenyl	H	CH_3	75 (aver.)

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O-9, THU

A FUNDAMENTAL KINETIC MODEL FOR AMOCO'S CO/MN/BR LIQUID PHASE OXIDATION CATALYST

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A homogeneous mixture of cobalt acetate, manganese acetate and hydrobromic acid is a highly efficient catalyst for oxidizing alkylaromatic groups, via dioxygen, to their corresponding aromatic carboxylic acids. The most important commercial example is the oxidation of p-xylene to terephthalic acid.

We have measured the rate constants of all of the catalyst components in their most important oxidation states with each other, with the methylaromatic compounds and with the solvent acetic acid. From this data we have developed a model to explain why addition of bromide to a cobalt catalyst greatly enhances the rate of oxidation and reduces the amount of solvent decarboxylation. The model also correctly predicts the effect of manganese addition to the Co/Br catalyst.

As time permits, we will discuss the active catalytic species. Hammett studies reveal that these oxidations do not proceed via Co(III) or the bromine atom but rather by a manganese-bromine complex.

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INTERACTION OF MOLECULAR OXYGEN WITH TRANSITION METAL CENTERS IN ELECTROCATALYTIC SYNTHESIS OF PEROXO SPECIES

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Transition metal complexes are widely used as models, either of oxygen carriers or of dioxygen activators in catalytic oxidations. The key factors determining the oxygen carrying or the catalytic properties are the thermodynamic and kinetic features of the interaction of molecular oxygen with the metal center, possibly yelding an oxygen adduct.

The catalytic mechanism does not require extensive amounts or stability of the product of the interaction between molecular oxygen and the transition metal complex. On the other hand, enhanced reactivity of coordinated dioxygen is essential.

It is thus difficult to provide direct evidence for the formation of an oxygen adduct or of an interaction product which should be very reactive and present in even minute amounts.

We have used extensively the electrochemical tecniques to investigate the reduction of molecular oxygen in the presence of metal complexes and the mechanism of catalytic oxidations which can be observed in the presence of substrates.

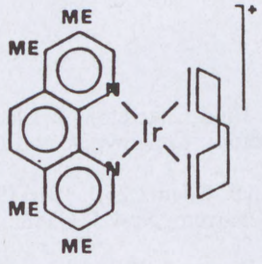
The essential (overall) reactions are the following:

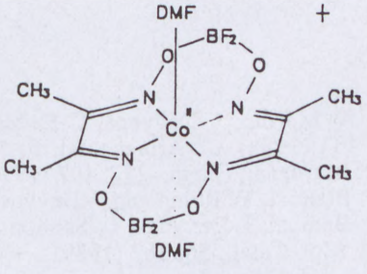
$$ML_n^{(x)} + e \longrightarrow ML_n^{(x-1)}$$
$$ML_n^{(x-1)} + O_2 \longrightarrow ML_n - O_2$$
$$ML_n - O_2 + \text{substrate} \longrightarrow ML_n^{(x)} + \text{oxidation products}$$

The main requirement is the regeneration of the $ML_n^{(x)}$ species (whithout extensive irreversible oxidation of the ligands) ; the critical point for the catalytic efficiency is the M - O_2 interaction.

We have found that the reversible formation of a *very reactive and electrochemically active interaction product at the electrode* can be documented even in cases of instability of the dioxygen adduct in the bulk.

As examples the cases of the following complexes are reported





The relationships between the reactivity of the interaction product, the electrocatalytic reduction of dioxygen and electrocatalytic synthesis of peroxo species are discussed.

ELECTROASSISTED OXIDATION OF HYDROCARBONS BY MOLECULAR OXYGEN CATALYZED BY POLYPYRROLE MANGANESE PORPHYRIN FILMS.

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Attachment of transition metal complexes, and especially porphyrins to polymeric support has been researched extensively over the past several years. The electroactive thin films described here have been obtained from direct anodic oxidation of pyrrole substituted metalloporphyrins[1] to obtain modified electrodes. These new electrodes are aimed at catalysing redox and organic reactions, and can be involved in efficient biomimetic systems for hydrocarbon and/or hindered phenol oxidation by molecular oxygen, using supported manganese porphyrins as catalysts. The complete catalytic processes requiere the electrochemical reduction reduction of Mn(III)porphyrin to obtain the catalytic species [2].

We report the electrochemical preparation and behaviour of a poly(pyrrole-Mn(III)porphyrin) film modified electrodes, and we note that porphyrin linkage to polypyrrole does not modify the redox system of manganese (E° (Mn(III)/Mn(II)) = -0.3V/SCE). Thus, the catalytic activity towards oxidation by molecular oxygen can be examined. Results for the electroassited oxidation reactions of cis-cyclooctene, adamantane and 2, 6-diterbutylphenol by dioxygen, under atmospheric pressure, in organic solutions using the manganese porphyrin coated electrodes as catalyst are described. One of the remarkable aspects of these results is the large activity of the porphyrin catalyst when it is fixed on the electrode [2,3]. The relation between the catalytic activity of the supported porphyrin and the material of the electrode is discussed. In addition, these results confirm the stability of such polypyrrole films.

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O-12, THU

REACTIVITY OF ORGANOPALLADIUM COMPOUNDS TOWARDS EARLY TRANSITION METAL PEROXIDES: O-INSERTION *vs.* C-X-COUPLING

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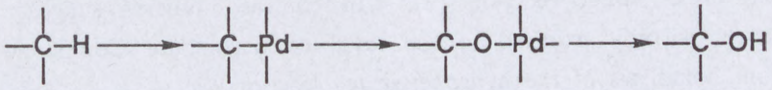
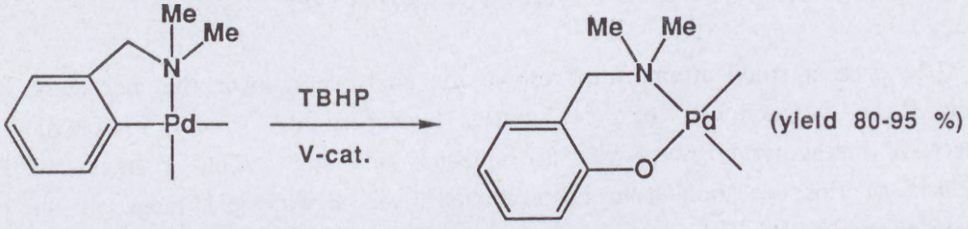
Oxygen insertion into the Pd-C bond is of interest as it offers a route for the oxy-functionalisation of a C-H bond:



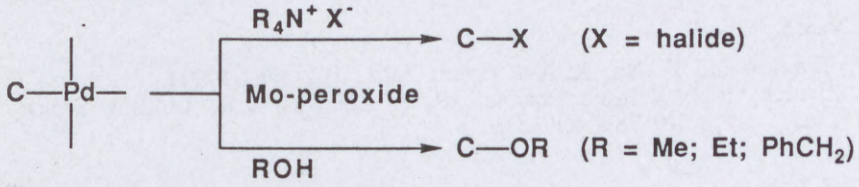
We have studied reactions of early transition metal peroxides with organopalladium compounds and found marked differences in reactivity, depending on the nature of the peroxo species and the reaction conditions.

The expected oxygen insertion could be achieved by using TBHP (*tert*.butylhydroperoxide) and a vanadium catalyst (*e.g.* $VO(acac)_2$):



By variation of the ligand X in cyclopalladated complexes of the type $Pd(C_6H_4CH_2NMe_2\text{-}2)X$ it was shown that the reactivity is strongly enhanced by increasing the nucleophilicity of the Pd-centre.

In contrast to vanadium peroxo species, the molybdenum peroxide $MoO(O_2)_2.HMPT.H_2O$ displays a totally different chemistry. Oxygen insertion in the Pd-C bond is only of minor importance for this reagent. Instead, this Mo-peroxide couples halide- or alkoxide-nucleophiles to the palladated carbon atom:



The alkoxylation is of special interest as it offers a one-pot conversion of a C-H bond into a C-OR function with very high selectivity.

THE REACTIONS OF IRON(III) PORPHYRINS WITH TERTIARY-BUTYL HYDROPEROXIDE IN AQUEOUS SOLUTION

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It is generally agreed that the reaction of peroxyacids with iron(III) porphyrins results in the formation of an oxo-iron(IV) porphyrin π cation radical, (a peroxidase Compound I model), reaction (1). However, there is disagreement over the corresponding reactions of alkyl hydroperoxides. Some studies[1] provide evidence that hydroperoxides behave similarly to peroxyacids and oxidise iron(III) porphyrins in an initial 2-electron step with heterolytic cleavage of the O-O bond, reaction (2). In contrast, others[2] suggest the iron(III) porphyrin is only oxidised to the level of peroxidase Compound II with concomittant homolysis of the hydroperoxide, reaction (3).

$$Fe(III)P + R\overset{\overset{O}{\|}}{C}O_2H \longrightarrow O{=}Fe(IV)P^{+\bullet} + RCO_2H \qquad (1)$$

$$Fe(III)P + RO_2H \longrightarrow O{=}Fe(IV)P^{+\bullet} + ROH \qquad (2)$$

$$Fe(III)P + RO_2H \longrightarrow O{=}Fe(IV)P + RO^{\bullet} + H^{+} \qquad (3)$$

The present study attempts to resolve the controversy over the mechanism using the reaction of t-butyl hydroperoxide with iron(III) tetra(4-*N*-methylpyridyl)porphryin in aqueous solution. The kinetics and products of this reacation have been studied over a wide pH range in the presence and absence of efficient chemical traps for the short-lived oxidising species. The intermediates have been characterised by uv-vis and resonance Raman spectroscopy and by stopped-flow e.s.r. methods. The role of the axial ligands in influencing the course of the reaction has also been investigated. The results are discussed in terms of heterolytic and homolytic cleavage of hydroperoxides by iron(III) porphyrins and they reveal the difficulties in distinguishing between the two mechanisms.

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O-14, THU

RUTHENIUM CATALYZED OXIDATION OF NITROGEN-CONTAINING HETEROAROMATIC COMPOUNDS

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Nitrogen-containing aromatic heterocyclic compounds such as quinoline, isoquinoline, acridine et al., were oxidized to corresponding aromatic o-dicarboxylic acids at high yields remaining pyridinic structure in the product molecules by hypochlorite ion in the presence of ruthenium catalyst at ambient temperatures in alkaline aqueous solution. Quinoline was oxidized to pyridine-2,3-dicarboxylic acid (yield=84%) when the initial concentration of OH^- was fixed as 1.1 M[1]. The concentration of OH^- in aqueous solution was found to play an important role on the selectivity of the reaction. The major product in the oxidation of quinoline was changed to oxalic acid or CO_2 depending on the OH^- concentration. The spectrophotometric study indicates that the active species for selective oxidation of quinoline into the pyridinedicarboxylic acid may be $(Ru(VII)O_4)^-$ (perruthenate ion) which shows its absorption maximum at 385 nm.

When the oxidation of quinoline was carried out using two-phase reaction system, such as CCl_4-H_2O or $CHCl_3$-H_2O, the rate of oxidation was drastically decreased. On the contrary, the oxidation proceeded more rapidly compared with the case of the absence of an organic phase, when acetonitrile was used as an organic phase instead of CCl_4 or $CHCl_3$. The result shows that the two-phase system composed of CH_3CN-H_2O is very convenient for a substrate being oxidized whose solubility in aqueous alkaline solution is limited.

Acridine was oxidized using CH_3CN-H_2O solution system. Pyridine-2,3,5,6-tetracarboxylic acid was formed at the yield of 82% at 3 h when relatively higher initial OH^- concentration (1.1 M) and 30°C were used as reaction conditions. On the other hand, quinoline-2,3-dicarboxylic acid (acridinic acid) was formed at the yield of 23% in addition to pyridinetetracarboxylic acid (yield=55%) when lower initial OH^- concentration (0.55 M) and lower reaction temperature (10°C) were used. Acridinic acid is the reaction intermediate to pyridinetetracarboxylic acid in the ruthenium catalyzed oxidation of acridine.

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O-15, THU

"ENHANCED ELECTRONIC DELOCALIZATION IN FACE-TO-FACE DIPORPHYRINS. IMPLICATION IN THE UNIQUE REACTIVITY OF THE COBALT DERIVATIVES TOWARDS DIOXYGEN AND IN THE 4-ELECTRON REDUCTION MECHANISM OF O_2."

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In the search for electrocatalysts for the oxygen cathode of fuel cells, dicobalt cofacial diporphyrins capable of reducing O_2 directly to H_2O through the 4-electron mechanism have been synthesized[1]. A complete electrochemical and spectroscopic (UV-vis, EPR) reinvestigation of these families of dimers, first with non-electroactive metal derivatives, and afterwards with the cobalt ones anew, turned out to be necessary to interpret the particular redox properties and oxygen reactivity of the cobalt derivatives[2,3]. This study emphasizes a strong "diporphyrin effect"[4]. It is mainly electronic and is generated by strong π-π couplings between the two porphyrin rings, independently of the metal centers: it induces an enhancement of the electron density in the neutral form and a two-rings-extended electronic delocalization in the oxidized forms of these dimers. Their special geometry also introduces a steric hindrance to axial ligation. The complete description of the "diporphyrin effect" allows an interpretation of the remarkable reactivity of the cobalt derivatives towards dioxygen. Its unicity originates in that both the electrons of the rings and those of the cobalt(II) participate in the O_2 fixation through intramolecular ring-cobalt-oxygen electron transfers. A μ-superoxo and a μ-peroxo dicobalt complex are reversibly formed by reaction of O_2, respectively with the monooxidized $[Co(II)P \cdot Co(II)P]^+$ and dioxidized $[Co(II)P- - -PCo(II)]^{2+}$ forms of the cobalt dimers in the absence of any strong axial ligand, whereas surprisingly the neutral one [Co(II)P Co(II)P] does not fix O_2. The two oxygenated forms can be reversibly interconverted electrochemically. These results will be discussed in terms of their possible implication in the mechanism of the 4-electron reduction of O_2.

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O-16, THU

OXIDATION OF ALCOHOLS BY RUTHENIUM(II) COMPLEXES

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Although many valid procedures are available for the preparation of carbonyl compounds by the oxidation of alcohols, catalytic alternatives to well established methods are still attractive. Among the various transition metal, ruthenium-based catalysts have been widely tested in conjunction with a number of oxidants.[1]

In this paper we report the ruthenium-catalyzed oxidation of alcohols, using LiClO or $KHSO_5$ as the stoichiometric oxidants, in water-dichloromethane double phase. Fast oxidation (up to 30 turnovers/min) of secondary alcohols to ketones and of primary alcohols to aldehydes (and to a lesser extent to carboxylic acids) are achieved with almost quantitative yields to the oxidants. The catalysts examined are a representative choice of ruthenium(II) complexes $[RuX_2(L)_4]$, containing phosphorus, sulfur, oxygen or nitrogen donors.[2] Also commercial ruthenium trichloride was tested for comparison purposes.

The reactions are first order in ruthenium, but zero order in alcohol, as shown by varying the substrate concentrations over the range 0.1-1 M. Clearly worth noting are also the almost absent D-effects for the oxidation of various deuterated forms of 1-butanol, whereas cyclobutanol is mostly converted into cyclobutanone, thus suggesting a 2-e^- transfer.

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LACTONIZATION OF CYCLIC KETONES WITH HYDROGEN PEROXIDE CATALYZED BY PLATINUM(II) COMPLEXES.

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The Baeyer-Villiger oxidation of ketones to esters is an interesting synthetic reaction that is generally performed with organic peroxy acids[1]. However being the reaction slower than the related epoxidation of olefins, acidic conditions are usually required, peroxytrifluoroacetic acid being the reagent of choice[2].

The use of hydrogen peroxide as primary oxidant for this reaction has been occasionally reported in the literature associated with As[3], Mo[4] or Se[5] as catalysts. With the exception of some arylseleninic acids the above catalysts are effective only using 90% H_2O_2, their use being somehow impractical for larger scale operations. In this communication we report a very straightforward method for the lactonization of cyclic ketones with commercial 32% H_2O_2 solutions under very mild conditions. This oxidation is based on the use of some Pt(II) complexes as catalysts which proved useful also in the selective epoxidation of terminal olefins under mild conditions[6].

The reactions were generally performed at room temperature using in most cases $[(dppe)Pt(CF_3)(CH_2Cl_2)]\ ClO_4$ (dppe = 1,2-bis-diphenylphosphinoethane) as catalyst dissolved in neat ketone. Under these experimental conditions a variety of cyclic ketones can be oxidized. The initial rates are usually high and lead to rapid formation of significant amounts of lactone.

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O-18, FRI

A NOVEL OXIDATION OF ALKYNES WITH HYDROGEN PEROXIDE CATALYZED BY PEROXOTUNGSTOPHOSPHATES

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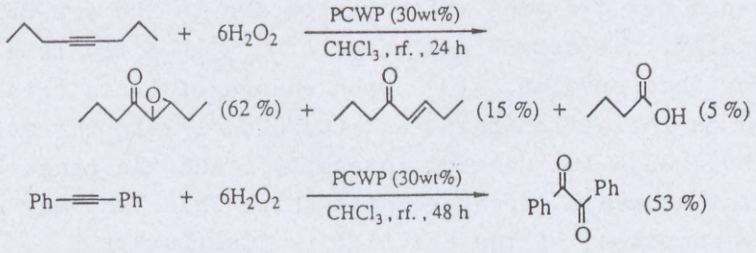
In the previous paper, we showed that treatment of $H_3PW_{12}O_{40}$ (WPA) in excess 35%-H_2O_2 with α-$C_5H_5N^+(CH_2)_{15}CH_3$ Cl(CPC) easily produced peroxotungstophosphate (PCWP) cotaining cetylpyridinium moiety as the counter cation.[1] The PCWP thus prepared was found to be similar in structure to that of the peroxocomplex prepared by Venturello and his coworkers.[2] Recently, Tomaselli et al. have reported the stoichiometric oxidation of terminal alkynes into keto aldehydes by metalperoxide like (HMPA)$MoO(O_2)_2$ in the presence of $Hg(OAc)_2$, and the catalytic oxidation with dilute H_2O_2 by $NaMO_4$ or (cetylpyridinium)$_3P_{12}M_{40}$(M : Mo or W) combined with $Hg(OAc)_2$.[3]

We now found that the PCWP catalyzes a new class of oxidation of internal alkynes to α,β-epoxy ketones with 35%-H_2O_2 under two-phase system by using chloroform as the solvent. For example, 4-octyne gave 5,6-epoxy-octan-4-one, 5-octen-4-one and a small amount of cleaved product, butyric acid. The same reaction of 4-octyne in tert-butyl alcohol in place of chloroform gave butyric acid as a principal product. The oxidation of 5-octen-4-one, which is considered to be the precursor of epoxide, afforded 5,6-epoxy-octan-4-one as expected. Meanwhile, diphenyl acetylene was oxidized to benzil under the tow-phase system, but benzoic acid was formed in tert-butyl alcohol.



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O-19, FRI

CHEMILUMINESCENCE OF SYSTEM "LUMINOL·METAL COMPLEX·H_2O_2

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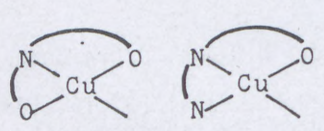
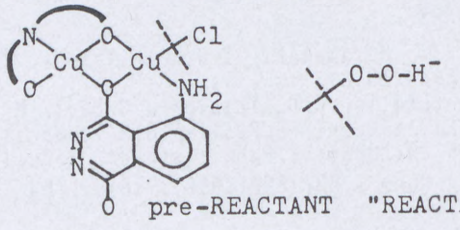
In an alkaline solution, luminol(3-aminophthaloylhydrazine, abbrev. Lu) reacts with oxidizing agents(O_2, O_3, ClO^- and H_2O_2 to emits a weak chemiluminescence with an emission max. at 424 nm.(fluorescence due to the exited state of 3-aminophthalate anion produced by the oxidation of Lu).

It has been known that metal complexes of Fe(II), Fe(III), Co(II), Co(III) and Cu(II) acts as efficient catalysts to enhance the emission intensity of this system. This paper presents to certify the existence of the "REACTANT" for this luminescent reaction. As proof of the "REACTANT", the following results have been presented using the complexes type-a and -b.

(1) The ligands which cab form efficient catalyst for this reaction possess the alkanolamine moiety which exhibit a tendency to form an O-bridge dimer itself or with other ligands (for ex. with Lu). (2) The dependence of luminescent intensity on change of pH reflects the relationship between the catalytic activity and structural change of the catalyst depends on pH. The optimum condition for this reaction was established within the limits of pH: 10.5-11. At this pH range, the CuL·Lu system displayed a new d-d band which may be due to the pre-REACTANT. Additionally, the sub-normal value of μ_{eff}(1.5 BM) is also the proof for this species. (3) Upon change of Lu in this system appeared an inflection point at [Lu]/[Cu]=1/2 in the relationship "[Lu]/[Cu]~luminescent intensity", and the range below this point showed a linear relationship. This fact may suggest that the component of the REACTANT is "CuL:Lu=2:1".



a b



pre-REACTANT "REACTANT"

THERMAL AND PHOTOCHEMICAL CATALYSIS BY POLYOXOMETALLATES. REGENERATION OF CATALYST BY DIOXYGEN.

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Polyoxometallates of molybdenum, tungsten and vanadium are effective catalysts in a variety of important industrial processes. Their catalytic activity is, generally, attributed to their: a. acid base properties, b. redox properties, and c. the "bulkiness" and flexibility of their structure [1].

Recently their photocatalytic capabilities have been recognized in: a. H_2-production, b. photogalvanic cells, c. oxidation of organic compounds[2], d. functionalization of alkanes[3], e. sensitization of semiconductors[4], and f. sensitization of electrodes[5].

Whereas molybdates are stronger reducing reagents than tungstates, their regeneration (reoxidation) requires H_2O_2, or dioxygen with active charcoal. On the other hand tungstates are poor oxidizing reagents; However, excitation in the near visible and UV regions renders tungstates (as is always the case) effective oxidizing reagents, and due to their fast reoxidation by dioxygen effective photocatalysts.

This presentation reports on the effect of the nature of polyoxometallate, redox potential, degree of reduction, ionic strength and pH in the reoxidation mechanism of reduced oxometallates by dioxygen in homogeneous solutions.

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O-21, FRI

Oxidation of Naphthalene on Palladium Based Catalysts.

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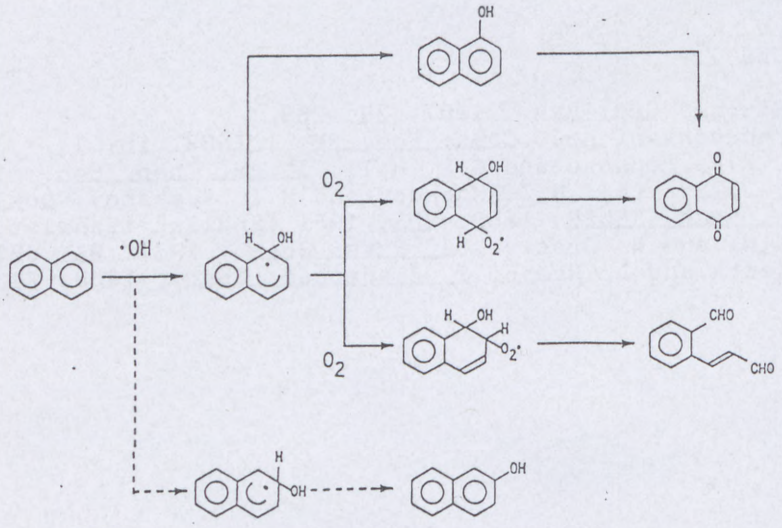
We have demonstrated[1] that some palladium catalysts supported on silica have potentialities of producing phenols directly from benzene and gaseous oxygen under ambient conditions. This paper deals with the reaction of naphthalene in comparison with the reaction of benzene. The catalyst used was basically silica supported palladium catalyst which works with the Cu(I)/Cu(II) redox couple. In contrast to benzene, which needs no solvent, naphthalene necessitates the use of solvent. Acetic acid containing some water was found to be useful. Products obtained were 1-naphthol, 1,4-naphthoquinone and (E)-2-formylcinnamaldehyde with a yield of more than 78 % in which naphthoquinone shared 40 %. The reaction mechanism for producing these products are outlined as follows.

1-Naphthol, one of the primary products, is gradually converted to naphthoquinone when copper species are in the reaction system. When, however, copper is eliminated from the system, 1-naphthol is obtained as the stable product.



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SYNTHESIS, STRUCTURE AND BIOMIMETIC CATALASE TYPE ACTIVITY OF A NOVEL OXO BRIDGED TETRANUCLEAR MANGANESE AGGREGATE EXHIBITING SHORT O···O INTERACTIONS

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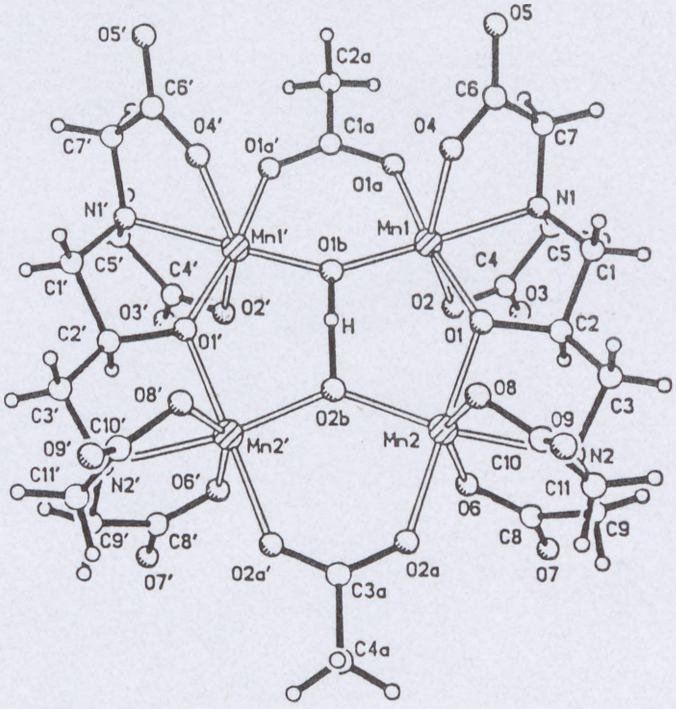
A novel oxo (hydroxo) bridged valence trapped $Mn(II)Mn(III)_3$ aggregate comprising the unprecedented $[O\cdots H\cdots O]^{3-}$ core (O-O distance 2.467(5)Å) has been synthesized and structurally characterized. Barium and calcium ions are linked to the aggregate via hydrogen bonded water molecules. This tetranuclear complex has the same oxidation level as the S_0 state of the oxygen evolving manganese center of Photosystem II. Its catalase activity parallels that of both S_0 state of PSII and manganese (pseudo) catalases.



POSTERS

(P-01 TO P-54)

ON THE MECHANISM OF IRON PORPHYRIN-CATALYZED CARBON-CARBON BOND CLEAVAGE OF 1,2-DIOLS

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As a model system mimicing the reaction of cytochrome P-450scc, we have reported successful oxidative cleavage of various 1,2-diols having aromatic substituents with dioxygen and N-benzyl-1,4-dihydonicotine amide (BNAH) as the reducing agent catalyzed by (TPP)FeCl.[1,2] Recently, we found that the catalytic system was also effective for the bond cleavage of various aliphatic 1,2-diols. The reactivity was determined by the structure of diols with the order being, approximately, 2°-$2^{\circ} > 2^{\circ}$-$3^{\circ} > 3^{\circ}$-$1^{\circ} > 3^{\circ}$-$3^{\circ} > 1^{\circ}$-2° diol. Kinetic study using several type of diols shows saturation of the rate at high concentration of diols which was an indication of the mechanism following Michaelis-Menten behavior. Km values, apparant dissociation constants, increased by the introduction of substituents at the α-positions of the hydroxyl groups, and the reactivity was influenced by the steric hindrance of substrates. The Km values were also parallel to the pKa values of corresponding alcohols, consistent with the formation of iron(IV)-diolato complex as the intermediate, which was previously proposed. Inspection of Vmax values suggests that rate-determining bond cleavage is dependent on the C-C bond energy between the carbons having hydroxy groups, that is, the stability of hydroxy carbon radicals, in accordance with the mechanism through formation of radical species.
To confirm the generation of radical species, we attempted spin trapping by DMPO in the decomposition of iron(IV)-diolato complex. EPR measurement at low temperature (-80°C) revealed the formation of two DMPO adducts, one of which was characteristic for a spin adduct of an oxy radical. The observation of the O-centered radical, which would be generated by one electron oxidation of the diol anion coordinated to iron (IV) center, is a direct evidence for the mechanism involving radical species.

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Generation of Fe(III)OEP-Hydrogen Peroxide Complex by Reduction of Fe(II)OEP-oxygen Complex with Ascorbic Acid Sodium Salt

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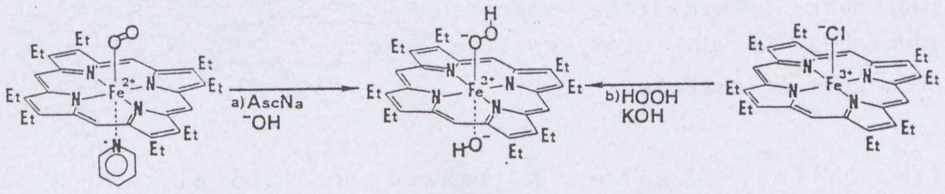
An aqueous solution of ascorbic acid sodium salt (denoted as AscNa; 0.2M, 0.02ml) was added to DMF solution of Fe(II)OEP(pyridine)-O_2 complex (1.0mM, 0.4ml) at -40 ℃, and the mixture was immediately frozen at 77 K. The observed ESR spectrum revealed formation of the ferric low-spin complex (denoted as complex (A); g_1=2.286, g_2=2.171 and g_3=1.953), with the free radical species derived from AscNa (g=2.006). On the other hand, optical spectrum recorded for the same frozen solution showed a pair of new absorption maxima at 556 and 604 nm. It is noted here, that the same ferric low-spin complex was also recorded by mixing Fe(III)OEPCl and aqueous hydrogen peroxide in the presence of KOH (Table). The observed ESR and optical parameters of these complexes agreed well with those of previously reported Fe(III)TPP($^-$OH)($^-$OOH) complex.[1] This means that the identical Fe(III)OEP($^-$OH)($^-$OOH) complex is generated by reduction of Fe(II)OEP-O_2 complex with AscNa, but also by mixing Fe(III)OEPCl and hydrogen peroxide under alkaline condition (Scheme 1).[2] The complex (A) will be the practical model for the intermediate heme-hydrogen peroxide complex of the P-450.



Complex A

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P-03, MON

Important role of Fe(III)TPP-Oxygen-Skatole Ternary Complex in Tryptophan Dioxygenase Model Reaction System

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Mechanism on the dioxygenation of 3-methylindole occurring in the presence of Fe(III)TPPCl and alkaline reagents was studied by means of the product analyses and spectroscopic measurements. The results of GC-MS measurements indicated that 3-methylindole (skatole) was converted to o-formamidoacetophenone (FA), in which two oxygen atoms derived from atmospheric oxygen were involved. Optical spectrum recorded for the mixture at -78 ℃ demonstrated the presence of new iron complex as characterized by absorption maxima at 421, 550 and 586 nm. ESR spectrum recorded for the same reaction mixture revealed formation of two types ferric low-spin complexes (g_1=2.32, g_2=2.17 and g_3=1.95; and g_1=2.24, g_2=2.16 and g_3=1.96) with anomalously small g-anisotropy. From comparison of ESR parameters of the complexes with those of previously reported heme-butyl peroxide complexes,[1,2,3] the present complexes were assumed to be the six coordinate Fe(III)TPP-peroxide complex. Therefore, these complexes were concluded to be the Fe(III)TPP($^-OCH_3$)($^-$OO-skatole) and Fe(III)TPP($^-$OO-skatole)$_2$ complex, having the 3-methyl-3-hydroperoxo-indolenine at axial position (Fig. 1).[4] The Fe(III)TPP-oxygen-substrate ternary complex will be an important intermediate species generated in the dioxygenation processes of skatole.

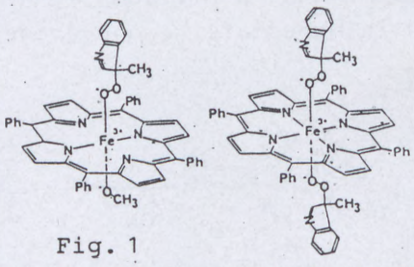

Fig. 1

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DECOMPOSITION OF CYCLOHEXYL HYDROPEROXIDE CATALYSED BY VARIOUS RUTHENIUM(II) PORPHYRINS.

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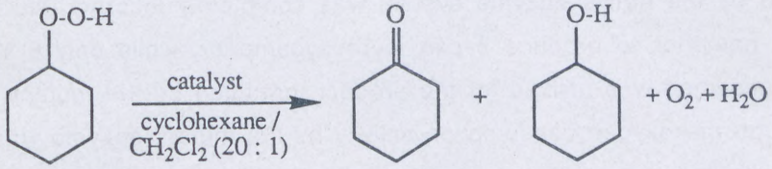
The conversion of cyclohexane to cyclohexanone is an important industrial process. An intermediate in this reaction is cyclohexyl hydroperoxide. This peroxide can be decomposed into two main products, *i.e.* cyclohexanone and cyclohexanol. Other products are oxygen and water.



The decomposition is catalysed by various metalloporphyrins. We investigated in particular manganese and ruthenium tetraarylporphyrins. A difference in behaviour of these two types of porphyrin complexes is that the former requires an axial ligand such as pyridine, whereas the latter does not.

The behaviour of five different tetraarylporphyrins will be presented: tetraphenyl-, tetramesityl-, tetrakis(2-chlorophenyl)-, tetrakis(2,6-dichlorophenyl)-, and tetrakis(2,3,4,5,6-pentachlorophenyl)porphyrinatoruthenium carbonyl.

During the reaction the ruthenium(II) porphyrin probably is converted into a *trans*-dioxoruthenium(VI) porphyrin. Under the reaction conditions a precipitate is formed. Also this precipitate is catalytically active.

The selectivity for ketone and alcohol is the same for the various ruthenium(II) porphyrins. Therefore, the mechanism of the decomposition is likely to be the same for these catalysts.

A mechanism will be proposed.

The Role of Threonine 252 in the Oxygen Activation by Cytochrome P-450cam: Mechanistic Studies by Site-directed Mutagenesis

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The fuctional role of threonine 252 in the oxygen activation by cytochrome P-450cam was examined by employing site-directed mutants of cytochrome P-450cam. The replacement of threonine 252 to alanine did not cause significant spectral changes of the ferric, ferrous and CO-ligated states. When the product analysis was combined with the oxygen consumption assay, we found that oxygen consumed by the native enzyme system was completely incorporated into the substrate camphor to produce 5-*exo* -hydroxycamphor, while only 6 % of the oxygen consumed was utilized for the product formation by the mutant enzyme even though the oxygen consumption activity by the mutant enzyme was nearly identical with that of the native enzyme. In this uncoupled reaction the remaining part of the oxygen, *i.e.*, about 85 % of oxygen consumed by the mutant enzyme was demonstrated to be directly transformed to H_2O_2 but not O_2^-. Thus, the absolute coupling of oxygen incorporation to the substrate was lost in the mutant enzyme resulting in the production of H_2O_2. Essentially the same findings were obtained for another mutant enzyme with valine 252, except that the enzymic activity reduced to one-third of that of native enzyme. These results imply that H_2O_2 is produced in the process of the second electron input to the oxygenated enzyme, and threonine 252 plays a crucial role in the oxygen activation by cytochrome P-450cam.[1)]

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P-06, MON

BIOMIMETIC DIOXYGEN ACTIVATION AND CATALYTIC OXYGENATIONS OF UNSATURATED HYDROCARBONS USING IRON PORPHYRINS

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Catalytic oxygenation of hydrocarbons by molecular oxygen using metalloporphyrin catalysts, model reactions for the function of naturally occuring monooxygenase enzymes have attracted much attention over the past years. The catalytic system usually requires a reducing agent in analogy to NADPH in enzymic systems, to cleave the oxygen-oxygen bond in the dioxygen-iron(II) porphyrin complex to form the active oxo-iron species in the cytochrome P-450 cycle.

Photoreduction of iron(III) porphyrins with visible light yields iron(II) complexes which are able to co-ordinate dioxygen and to form the oxo-porphinato iron(IV) species [1], an alternative intermediate in cytochrome P-450 reactions [2]. Although several physico-chemical data are available for this species, only few is known about its chemistry.

We studied the reactivity and chemoselectivity of different oxo(tetraarylporphinato)iron(IV) complexes toward various olefins. Depending on the structure of the olefins epoxidation and/or hydroxylation reaction products were observed. The reactivity and chemoselectivity was found to be influenced by the structure of the porphyrin and axial ligands. Similarly to the well studied reactions of oxo-iron(IV) porphyrin cation radicals with hydrocarbons the reaction mechanism involves oxygen transfer to yield epoxides and/or hydrogen abstraction from the hydrocarbons to yield finally alcohols or ketones.

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P-06, MON

HYDROXYLATION OF PHENOL CATALYZED BY METAL PHTHALOCYANINES

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The liquid phase hydroxylation of phenol to isomeric dihydroxybenzenes is catalyzed by strong mineral acids, Fenton's reagent or titanium silicalite[1-3].

In this paper phenol has been hydroxylated with hydrogen peroxide in the presence of metal phthalocyanines. Various reaction parameters including time, temperature, initial concentration of H_2O_2, ratio of reactants and nature of the catalyst were studied. Under practical reaction conditions H_2O_2 : PhOH : catalyst = 1 : 20 :0.1; 75°C ; 4 hr hydroquinone and pyrocatechol are formed in 60 - 70 % yield.

It was found that catalytic properties of metal phthalocyanines are influenced by /i/ the type of the central metal and its ligand, /ii/ mode of catalyst preparation and purification, /iii/ in the case of polymeric phthalocyanines by the size of the polymer and mutual ratio of two different metals in the complex. The best yields of isomeric dihydroxybenzenes were obtained with Bi, Sb and Sn phthalocyanines. The mixed W-Mo polymeric phthalocyanine obeys synergistic effect, whereas the bimetallic mixtures Sn-Bi, Sn-Sb and Sn-Mo antagonistic. Metal phthalocyanines deposited on anorganic carriers are less active.

The nature of metal catalyst and its concentration affect also the distribution of reaction products. Hydroquinone and pyrocatechol are formed in the ratio 2.2 : 1 to 7.0 : 1.An electrophilic substitution mechanism is proposed for hydroxylation.

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PHTHALOCYANINE DERIVATIVES AS CATALYSTS FOR SOFT PEROXIDATIVE OXIDATION

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In order to estimate the reactivity-sctructure correlation and to find the most effective catalysts for the oxidative reactions of saturated hydrocarbons such as cyclohexane by hydroperoxides we have synthesized the following substituted derivatives of cobaltous phthalocyanine: tetra-4-phenoxy-(I), tetra-4-tert-butyl-(II), tetra-3-phenylthio-5-tert-butyl-(III), tetra-3-bromo-5-tert-butyl-(IV), tetra-3-phenoxy-(V) and tetra-3-nitro-5-tert-butylphthalocyanine (VI). Using these compounds as catalysts we have investigated the kinetics of the reaction of cyclohexane oxidation by cumene hydroperoxide in mild conditions (benzene, 20 C, inert atmosphere, $t_r \leqslant 0.5h$) and of the reaction of phthalocyanine degradation in the oxidative media. The product of cyclohexane oxidation is the mixture of cyclohexanol and cyclohexanone with ratio 1.2-1.5/1, the total yield is 80-90% on hydroperoxide used.

We have established that the stability of the catalysts is much more sensitive to the nature of the substituent than its catalytic activity. Namely, the rate constants of cyclohexanol and cyclohexanone formations varied from 4.6 and $2.4 M^{-1}s^{-1}$ for (I) to 0.66 and $0.4 M^{-1}s^{-1}$ for (VI). (For the compounds II-V the values of the appropriate constants are 3.0, 1.8; 4.0, 2.1; 4.5, 2.5; 1.9, 1.1 $M^{-1}s^{-1}$, respectively). In contrast, the rate constants of oxidative degradation of catalysts I-VI (k_{ox}) varied more than 100-fold range: 2.5, 6.0, 0.8. 0.5, 0.7 and 0.015 $M^{-2}s^{-1}$, respectively, and a linear relationship between these values and one-electron oxidation potentials is observed.

HYDROPEROXIDE OXIDATION OF CYCLOHEXANE CATALYZED BY METAL COMPLEXES OF AZAPORPHINES

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The catalytic hydroxylation of saturated hydrocarbons by reduced forms of oxygen in the presence of porphine-like catalysts is now extensively investigated. However, there are only few reports concerning azaporphine catalysts which are often more available than porphyrines and more stable towards oxidants. We have discovered and investigated the reaction of cyclohexane oxidation by cumene hydroperoxide in the solutions of cobaltous and ferrous complexes of tetra-4-tert-butylphthalocyanine (^{t}PcM) and tetra-tert-butyltetrazaporphine (^{t}TAPM).

In mild conditions (benzene, 20 C, inert atmosphere, $t_r \leqslant$ 0.5h) cyclohexane was oxidized to cyclohexanol and cyclohexanone mixture with ratio 1.2-1.5/1, the total yield reaching 80-90% on hydroperoxide used. (In these conditions the oxidation of n-hexane leads to the 2- and 3-hexanols and 2- and 3-hexanones mixture with ratio 2/1). Turnovers of the catalysts are 26, 1200, 3550 and 4600 for ^{t}PcCo, ^{t}TAPCo, ^{t}TAPFe and ^{t}PcFe, respectively (ferrous complexes were used in the form of μ-oxodimers).

The kinetics of cyclohexane oxidation and the accompanying cumene hydroperoxide decomposition have been investigated and the mechanisms of both reactions are discussed. The influence of axial ligands such as pyridine, quinoline was studied with the purpose of clarifying the methods of catalysts stabilization. The nature of active species and their role in the formation of oxidation products have been suggested.

The discovered relationships were used in the development of novel convenient method of the juglone synthesis by catalytic oxidation of 1,5-dihydroxynaphtalene with peracetic acid (10-15%). The yield of juglone reached 80-85% on substrate when t_r=0.5h and turnover of catalyst 100-200.

POLYMER-BOUND IRON(III) PORPHYRINS AS OXIDATION CATALYSTS IN AQUEOUS SOLUTION

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It has been suggested that oxidative destruction of metalloporphyrins is caused by two catalyst molecules, one having been activated by the oxidant, reacting with each other in a face-to-face manner.[1] If this is correct, then site-isolating the catalyst on a polymeric support should hinder these interactions and increase its stability.

The aim of this work has been to investigate how binding 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrinatoiron(III), [Fe(III)T4MPyP] to poly(styrene-4-sulphonate) influences its reactivity and stability in aqueous solution, with tertiary-butyl hydroperoxide as the oxidising agent. This system is compared with the reactions of the porphyrin in the absence of polymer. Reactions catalysed by the polymer-bound porphyrin are slower than those of unbound Fe(III)T4MPyP. This observation is consistent with our findings on the nature of the Fe(III)T4MPyP species bound to the polymer, where the porphyrin has been found to exist as cofacial aggregates. In contrast, at the same concentration in free solution, Fe(III)T4MPyP is known to be monomeric.[2] Differences between the polymer-bound and unbound porphyrin catalytic systems are discussed.

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P-11, MON

COBALT PHTHALOCYANINE CATALYSIS IN AUTOXIDATION OF 2-AMINOPHENOL BY DIOXYGEN

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The kinetics and mechanism of the O_2-oxidation of 2-aminophenol (H_2AP) to 2-aminophenoxazine-3-one under ambient conditions, catalyzed by the recently synthesized tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-dodecachlorophthalocyaninato(cobalt(II), (R_4PcCo) have been studied by ESR and UV/VIS spectroscopic methods. The rate of 2-aminophenoxazine-3-one formation is first order in [R_4PcCo] and obeys a Michaelis-Menten type kinetics with respect to [H_2AP]. The suggested mechanism involves a rate-determining inner-sphere electron transfer from coordinated H_2AP to coordinated O_2 in the superoxo complex:

$$Co + H_2AP \underset{}{\overset{K_1}{\rightleftharpoons}} Co(H_2AP)$$

$$Co(H_2AP) + O_2 \overset{K_2}{\rightleftharpoons} (H_2AP)CoO_2$$

$$(H_2AP)CoO_2 \xrightarrow{slow} HAP^{\cdot} + Co + HO_2^{\cdot}$$

THE ROLE OF COBALT ALKYLPEROXO COMPLEXES IN THE CATALYTIC OXIDATION OF PARAFFINS.

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The bis(acetylacetonato)cobalt - cumylhydroperoxide - cyclohexane system has been studied. The special technique of simultaneous ^{1}H and ^{59}Co NMR spectra registration was employed and found to be useful method in the catalyst state monitoring during reaction process.

The following results were obtained. The presence of pyridine derivatives in benzene solution stabilizes alkylperoxo complexes $Co(acac)_2(OOR)B$, where R is cumyl, B is 3-Br-Py, Py or 4-$((CH_3)_2NH)$-Py. In the absence of this substances cobalt alkylperoxo complexes are not found in sufficient amounts and three isomeric hydroxo derivatives $[Co(acac)_2OH]_2$ are observed as predominant species. The comparison of this two systems reactivity (with and without pyridine derivatives) gives valuable data for elucidating of the alkylperoxo complexes role in the hydroxylation of paraffins.

Our results suggest that the process of interest has homolytic mechanism and the role of cobalt catalyst is just to generate, reacting with ROOH, free RO$^{\cdot}$ (ROO$^{\cdot}$) radicals which directly attacks alkane. And the cobalt alkylperoxo derivatives formation is not the catalytic cycle step but side reaction.

DIOXYGEN ACTIVATION AND CATALYTIC ALKANE OXIDATION USING IRON COMPLEXES SUPPORTED ON SILICA.

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Methane monooxygenase, the enzyme oxidizing methane to produce methanol in the first step, is known to contain binuclear complex of non-heme iron. To mimic the enzyme iron (III) was immobilized on the surface of silica modified by imidazole groups. The reductive O_2 activation at this surface species by zinc powder in the presence of methylviologen as an electron transfer agent and acetic acid as an effector in acetonitrile has been studied. The system catalyzes the oxidation of alkanes by O_2 to alcohols and ketones or aldehydes. The oxidation of methane, ethane, n-hexane, cis-1,2-dimethylcyclohexane and dimethylsulfoxide have been studied. At appropriate conditions the catalytic methane oxidation to methanol was observed at room temperature.

The mechanism of dioxygen activation in the present system will be discussed.

P-14, MON

DETERMINATION OF THE COMPOSITION OF COBALT CATALYSTS DURING OXIDATION OF p-XYLENE

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When oxidation of p-xylene by molecular oxygen proceeds in an aqueuos sytem, cobalt catalysts are active only in the presence of p-toluic acid or phase-transfer catalysts[1]. The formation of complexes between $CoBr_2$ and p-toluic acid was studied potentiometrically in water and p-xylene at different pH. At room temperatures a significant amount of cobaltous toluate is formed only at higher pH. An increase of pH from 4 to 8 decreases the rate of oxygen consumption observed after the initial period. The solubility of cobaltous toluate in p-xylene is negligible, but the solubility of cobaltic toluate is high.

In order to determine the content of toluate ligands bound to the cobalt catalyst during oxidation of p-xylene , a method based on the combination of chelatometry and gas-liquid chromatography was developed. Nitrilotriacetic acid dissolved in pyridine reacts with cobalt catalysts and totally liberates aromatic acids acting as ligands. The liberated aromatic acids were esterified and analyzed as methylesters by gas-liquid chromatography. This method was used for the determination of the composition of cobalt catalysts separated from the reaction mixture of p-xylene oxidation . It was found that the content of p-toluate ligands in the catalysts is influenced mainly by the initial concentration of p-toluic acid in the reaction mixture formed from p-xylene and water and by the conversion of p-xylene. Composition of the catalyst from the industrial DMT process was analyzed too.

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P-15, MON

ALKYLCARBONATE SYNTHESIS BY NEW CATALYTIC SYSTEM

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A new synthetic method of alkylcarbonate using new catalytic reaction system was studied. Cu-Zeolites X and Y were tested as the catalysts for the oxidative carbonylation reaction which is from methanol, carbon monoxide and oxygen. The catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Auger electron spectroscopy.

Ion-exchanged zeolites X and Y in $CuCl_2.2H_2O$ of 0.5M solution showed the activity for the dimethylcarbonate synthesis. In the reaction, dimethylcarbonate(DMC) is produced as major reaction product and carbon dioxide is formed by oxidation of carbon monoxide. A CuNaX catalyst exhibits the highest activity and it shows the selectivity of 60% to 75%. In CuNaX, the faujasite structure was destroyed during catalyst preparation, but the amorphous silica-alumina could performed a role of support.

The yield of DMC depends on reaction time, reaction temperature, reaction pressure but is slightly changed by increase of methanol. The activity of catalyst is affected by water content, and Cu^{++} cation existed in zeolite cage strongly interacts Al in zeolite. The active component in the Cu-Zeolites catalysts seemed to be Cu_2OCl_2.

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SELECTIVE OXIDATION OF SOME TERPENE HYDROCARBONS

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Selective oxidation of four Terpenes, Limonene, α-Terpinol, Terpinolacetate and 3-Carene, were carried out by Gif-oxidation systems.

The main products are ketones as expeceted. Some ketones from substrates having asymmetric center show no optical activities. To verify whether it goes through radical reaction or not, we tried some experiments and the results lead to radical intermediates are not involved.

Therefore, we propose a symmetrical π-allyl complex mechanism instead of the known Iron-Carbene mechanism.[1]

To simplify the reaction system some trials attempted.

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P-17, MON

THE SELECTIVE ALKANE OXIDATION BY H_2O_2 IN PYRIDINE, CATALYSED BY COPPER AND IRON SALTS.

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Alkanes were found to be efficiently oxidised by H_2O_2 in the presence of copper and iron salts (perchlorates or carboxylates) in pyridine + $HClO_4$ or pyridine + acetic acid solvents to give selectively ketones. The usual alkane conversion approached 20-30%, the product yield on consumed H_2O_2 was about 10-20%. Free alkyl radicals or alcohol were proved not to be the primary products of sec- C-H bond oxidation to ketone. The competitive oxidation of cycloalkanes (C_5, C_6, C_7, C_8, C_{12}), linear and branched alkanes were examined to make the conclusion that the selectivity of the oxidation both with iron or copper catalyst was very weakly dependent on the nature of the catalyst used. The exception was the oxidation of the cyclohexadienes, the mixture of benzene and phenol was formed in copper system and benzene was the only product in iron one.

The examined systems were concluded to have "Gif-type" selectivity[1] and HO· radicals were not reactive species. The alternative mechanisms are discussed.

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The catalytic oxidation of naphthalenes to naphthoquinones

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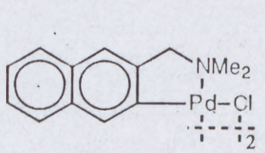
The oxidation of aromats to quinones has always suffered from several problems with respect to the selectivity. In, for example the oxidation of 2-methyl-naphthalene to 2-methyl-1,4-naphthoquinone, an important intermediate in the industrial synthesis of vitamine K, with CrO_3 in a strongly acidic medium, at least 4 by-products are formed, while the total yield of 2-methyl-1,4-naphthoquinone seldomly exceeds 60%. To gain more insight in the oxidation reactions of naphthalene we investigated the oxidation of metallated derivatives of our model system 2-(dimethylamino)-naphthalene, which is known to be cyclopalladated on position 1[1].
Our first discovery was that palladation took place on position 3 instead of position 1, to give compound **1**. Removal of the chlorine, followed by oxidation with *tert*-butylhydroperoxide in the presence of $OV(acac)_2$ yielded the naphthoquinone derivative **2** in a 55% yield.



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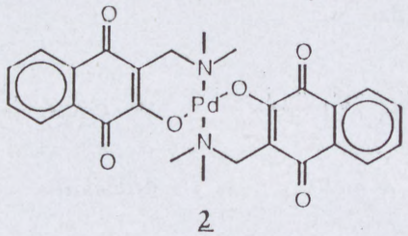

2

We were able to unravel the reaction mechanism by independant synthesis of possible intermediates. One of these intermediates could be oxidized to the naphthoquinone derivative **2** with $Pd(CH_3CN)_4(BF_4)_2$ acting as a catalyst.

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P-19, MON

OXIDATION OF A METHYL TO A FORMYL GROUP IN 2,3-DIHYDRO-2,2,4-TRIMETHYL-1H-1,5-BENZODIAZEPINE BY O_2 IN THE PRESENCE OF METAL SALTS AND COMPLEXES

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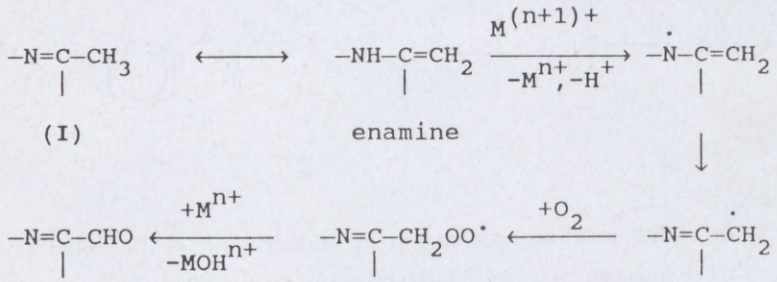
Metal salts such as manganese(II) chloride, manganese(III) acetate, copper(II) perchlorate and cobalt(II) and manganese(III) porphyrines have been found to promote the oxidation of 2,3-dihydro-2,2,4-trimethyl-1H-1,5-benzodiazepine, I by dioxygen at ambient temperature. The oxidation products have been analyzed by HPLC. Tetra(4-chlorophenyl)porphyrinato-cobalt(II) catalyzes the selective formation of 4-formyl-2,3-dihydro-2,2-dimethyl-1H-1,5-benzodiazepine, II from I. In other cases II undergoes further oxidation via C-C cleavage. A radical chain mechanism involving tautomerization of I to an enamine has been suggested:



(I) enamine (II)

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P-20, MON

HETEROAROMATIC RADICAL CATIONS AND THEIR REACTIONS WITH HYDROCARBONS

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Electrochemical oxidation of heteroaromatic N-oxides (substituted pyridines and diazines) was studied by cyclic voltammetry (CVA) in MeCN. The radical cations (LO^+) were proved to be the primary intermediate. Their redox potential (E_o) and reactivity depend on the substituents and the number of nitrogen in the heteroaromatic ring. The most stable radical cations are produced from the following compounds: I - 4-MeO-pyridine-N-oxide (1.40; 10^{-2}); II - quinoxaline-di-N-oxide (1.62; 0.1) and III - phenazine-di-N-oxide (1.38; 10), in brackets the values of E_o (V, SCE) and lifetime (s), respectively.

The reactivities of alkanes, substituted toluenes and alcohols towards II and III radical cations were studied by CVA. The following trend of reactivity were observed: i-PrOH > toluene > cyclohexane >> benzene. In some cases the surprising accelarating effect of dioxygen was discovered in the reaction of LO^+ with hydrocarbons. Under the preparative electrolysis the LO^+ induced the oxidation of cyclohexane to appropriate ketone and alcohol, the III being deoxygenated to phenazine-mono-N-oxide. The oxygen transfer from LO^+ to hydrocarbon was concluded the probable way in the functionalazation of C-H bonds. The presence of bases was found to be of importance for the reaction. The oxidation of i-PrOH to acetone induced by III radical cations was suggested to proceed via hydrogen atom abstraction. Some prelimanary results are published in[1,2].

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HYDROPEROXIDES IN LIQUID PHASE HYDROCARBONS OXIDATION

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Hydroperoxides are less sensitive to oxidation by dioxygen than products of their decomposition as ketones and alcohols which often are final products of industrial processes, example being cyclohexane oxidation.
Prospective method would be continuous oxidation of hydrocarbons to possibly high stationary concentration of hydroperoxides followed by selective decomposition of these peroxides to desired products. This would decrease raw material consumption figures in industrial processes.
Possibilities of such a way of carrying out oxidation process are discussed on the basis of own research results as well as on literature data.
It has been particularly shown that in cyclohexane oxidation over 50% of cyclohexane can be transformed into cyclohexyl hydroperoxide which can be either decomposed to cyclohexanone and cyclohexanol or used for epoxidation of propylene.

EPR and Optical Studies on Non-heme Iron, Substrate and Dioxygen Ternary Complexes in the Catechol Dioxygenase Model Reaction Systems

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Catechol dioxygenase model systems which consist of FeNTA[1] or Fe(salen)Cl[2], several catechols, and molecular oxygen have been investigated by simultaneous EPR and optical measurements.

In FeNTA system, all the chelated catecholate complexes show the EPR spectrum whose rhombicity parameter E/D is ca. 0.20. Only about DBC complex (DBC:3,5-di-tert-butylcatecholate), minor species (E/D=0.13; g=8.3, 5.4) could be observed (Figure I). Considering the fact that DBC complex reacts faster than the other catecholate complexes, this minor species due to the monodentate catecholate complex is the key intermediate in the catalytic cycle. Overall the reaction no semiquinone radical could be seen.

On the other hand, Fe(salen)DBC shows the signals of the chelated complex and semiquinone radical generated from the Fe(III) ⟶ DBC electron transfer (Figure II). Since the signal of semiquinone radical is observed in the sample prepared anaerobically, ferrous iron plays an important role in the reaction.

Figure I

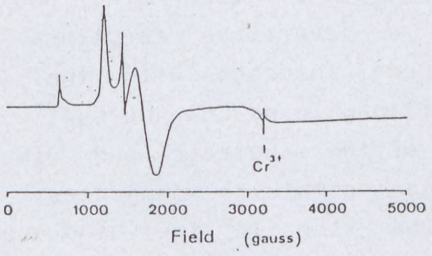
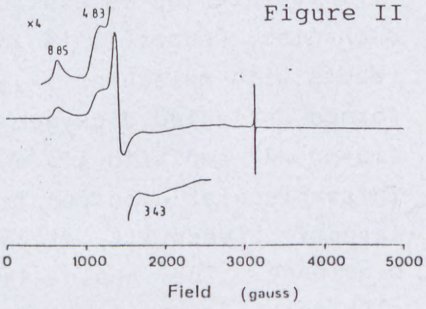


Figure II



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COPPER(II) CATALYZED AUTOXIDATION OF CATECHOL IN AQUEOUS SOLUTION

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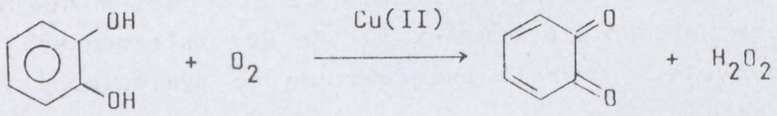
The aim of the present work was to clarify the kinetics and reaction mechanism of the copper(II) catalyzed oxidation of catechol by molecular oxygen in slightly acidic solution. The reaction may be a good model for the action of some oxygenase metalloenzymes e.g. tyrosinase.

The reaction was followed by oxygen-sensitive electrode and spectrophotometric methods.

The overall stoichiometry of the reaction was found to be:



The rate describing the oxidation can be expressed in the form of a rather complex rate equation:

$$-d\left[O_2\right]/dt = \left(\left[Cu^{2+}\right]\left[CuA\right]\right)^{1/2}\left(k_1\left[HA^-\right] + k_2\left[CuA\right] + k_3\left[CuA_2^{2-}\right]\right)\left[O_2\right]^{1/2}$$

This rate law is explicable in terms of a chain reaction mechanism. Copper(I) is formed in the initiation step and it reacts with molecular oxygen in a reversible reaction. The formed activated dioxygen adduct CuO_2^+ interacts with the free ligand HA^- and with its copper(II) complexes CuA and CuA_2^{2-}. The intramolecular electron transfer of the monomeric and dimeric ternary copper(II)-catechol-oxygen complexes generates the o-quinone. The chain termination step is the bimolecular elimination of the activated dioxygen adduct.

THE EFFECT OF MAGNETIC FIELD ON THE PROPAGATING CHEMICAL FRONT IN THE Co(II)–CATALYZED AUTOXIDATION OF BENZALDEHYDE

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It has recently been found and interpreted that the autoxidation of benzaldehyde in glacial acetic acid catalyzed by Co(II) acetate may take place as a front–reaction[1].

The effect of magnetic field on the propagating reaction front has been studied in one and two dimension in different geometrical arrangement. It has been found that the magnetic field has an unexpectedly profound effect on the front velocity; it may completely stop or accelerate by orders of magnitudes the front velocity.

It may be stated as a general rule that no front–propagation is possible "against" the increasing field strength, and the front–propagation follows the steepest descent in inhomogeneous magnetic field. Figure 1 and 2 show an example to demonstrate this general trend.

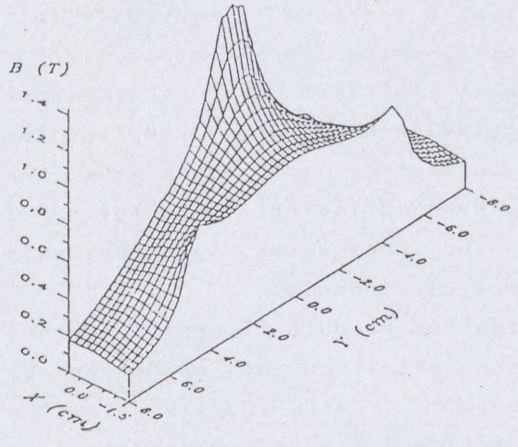

Figure 1.Magnetic field strength between conic and flat poles (see figure 2.).

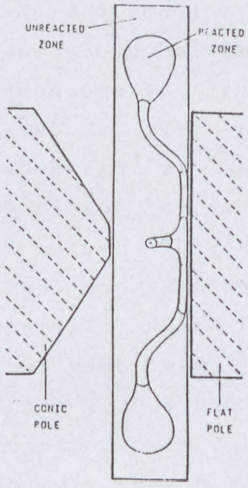

Figure 2.The development of 2 D front boundary from the centre in inhomogeneous magnetic field.

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MIMICKING GALACTOSE OXIDASE CATALYZED ALCOHOL OXIDATION WITH COPPER COMPLEXES CONTAINING BIDENTATE LIGAND

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Selective catalytic oxidation of alcohols with dioxygen to carbonyl compounds under mild conditions is of great importance in organic synthesis. Recently, some Cu(II) complexes containing tetradentate ligand catalyzed oxidation of alcohols have been studied as model system for the galactose oxidase.

We found that the catalytic activity of Cu(II) complexes containing bidentate ligand, such as picolinato, $Cu(C_5H_4NCO_2)_2$, is better than that containing tetradentate ligand Cu(Salen) for oxidation of benzyl alcohol to benzaldehyde with dioxygen in the presence of aprotic polar solvent and NaOH. Primary alcohol was oxidized more easily than secondary alcohol, but oxidation selectivity of the latter is greatly higher than that of the former.

Oxidation of cycloalkanols with dioxygen is more difficult than that of secondary alkanols. Among the bidentate ligands used in this study, the best catalyst for cyclohexanol oxidation is bis(8-hydroxylquinolinoate) copper complex. The conversion of cyclohexanol increased with increasing the strength of base added. When different structures of cycloalkanols were oxidized, the conversion was obviously affected by the steric hindrance of alcohols.

H_2O_2 was detected in oxidation product of benzyl alcohol with $Cu(C_5H_4NCO_2)_2$ catalyst, and inhibition of oxidation by H_2O_2 was also observed. Therefore, $Cu(C_5H_4NCO_2)_2$ catalytic system is a model system for active site of the galactose oxidase. Based on study of ESR and *in situ* electronic spectra of this model system and catalytic performance of Cu(I) complex containing the same ligand, an oxidation mechanism involving Cu(II)/Cu(I) catalytic cycle is proposed.

Quantative Formation of Spin-coupled Intermediate in a System Cosisting of Co(III)tetramine Complexes and Catechols.
- A Model Intermediate of Dioxygenase Reaction -

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A model system consisting of a cobalt(III)-tetramine complexes (CoTE and CoTT; Fig.1) and 3,5-di-tert-butyl catechol (DBcat) has been examined to elucidate the reaction mechanism of catechol dioxygenase. The complexes were made to react with DBcat in mixed solvent (H_2O:MeOH =1:1) at 50°C in the presence or in the absence of dioxygen. NMR showed that the reactions yielded oxidatively cleavaged products of DBcat. As the intermediate species, a cobalt(III)-semiquinone(DBsq) radical and a high-spin cobalt(II) complex were detected by ESR (Fig.2) regardless of the presence of dioxygen. These species are in equilibrium with a high-spin cobalt(II)-DBsq binary complex formed by one-electron transfer from DBcat to the mother complex. The magnetic moment of the binary complex isolated from the solution exhibited that there is an antiferromagnetic spin-coupling between the high-spin(S=3/2) cobalt(II) ion and the semiquinone radical. This one-electron transferred intermediate species plays a key role in the reaction. (Scheme I) Further product analysis of the reactions is now under way.

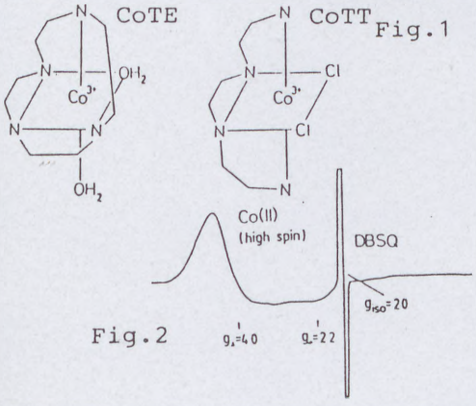
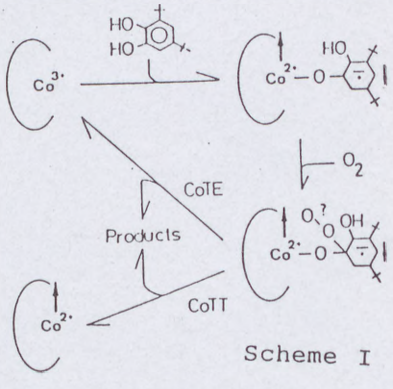


Fig.1

Fig.2



Scheme I

MONOMERIC CU(II) COMPOUNDS WITH N AND N,S-DONOR LIGANDS; DIOXYGEN CONSUMPTION AND CATALYTIC ACTIVITY.

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The metal site in Cu proteins often plays an important role in reactions with dioxygen. Low-molecular weight Cu compounds which mimic certain aspects of proteins have been made. As a test reaction, the oxidation of 2,6-dimethylphenol (DMP) to polyphenylene oxide (PPO) and diphenoquinone (DPQ) was studied by following O_2 uptake at 25°C; (1 atm. as pure O_2).[1] $Cu(BF_4)_2$ and $Cu(NO_3)_2$ complexes with the didentate N,S-donor ligand memi (5-methyl-4-ethylmercaptomethyl-imidazole) show the same reactivity and selectivity for PPO.[2] Reaction rates are $1\text{-}5\times10^{-5}$ mol $O_2.L^{-1}s^{-1}$, at [Cu(II)]=0.0035M and [DMP]=0.03-0.3M. About 50% of the phenol was converted after one hour and less than 5% DPQ was formed. These results together with the study of the dioxygen uptake and catalytic activity of other possible biomimetic systems will be presented.

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CATALYTICAL INFLUENCE OF Fe/III/ ON DIOXYGEN OXIDATION OF THIOGLYCOLIC ACID

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The influence of ferric ions on thermal and photo-initiated reactions of thioglycolic acid with molecular oxygen was studied.

Thermal reaction depends dramatically on ferric ions presence: no measurable reaction occurs with Fe^{3+} concentration less than 1×10^{-5} mol l^{-1}; above the threshold value initial reaction rate increases, for Fe^{3+} concentration 2×10^{-3} mol l^{-1} the v_o value is 3×10^{-5} mol l^{-1} s^{-1}. By thermal reaction exclusively the disulfidic product is formed; O_2 consumption stops sharply after the stoichiometric value mols of O_2 consumed : initial mols of substrate = 1 : 4 is reached.

UV irradiation results in reaction of thioglycolic acid with molecular oxygen even without Fe^{3+} added; the excitation wavelengths belong to the range 290 - 330 nm. Photoinitiated oxidation does not end with disulfide formation, higher oxidation products are formed from disulfide in a consecutive reaction. The reaction rate of photoinitiated disulfide oxidation does depend neither on Fe/III/ nor on substrate concentrations.

Photocatalytic cycle has been found to operate in photo-oxidative transformation of thioglycolic acid, traces of metal ions being the precursor of the active catalyst.

Quantum yield of the reaction thioglycolic acid + O_2 /without Fe^{3+} ions added/ is 1,05.

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COBALT SCHIFF BASE COMPLEX CATALYZED DEHYDROGENATION OF AMINES WITH TBHP

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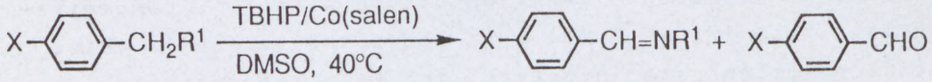
Dehydrogenation of secondary amines to imines with stoichiometric oxidizing agents is well documented. Co(salen), a representative cobalt schiff base complex, has been demonstrated to be an excellent catalysts for dehydrogenation of sec-amines to imines with O_2 in ethanol at 60°C.[1]

We now fined that sec-amines unsusceptible to the O_2/Co(salen) system undergo dehydrogenation upon using t-BuOOH(TBHP) as an oxidant in the presence of Co(salen).

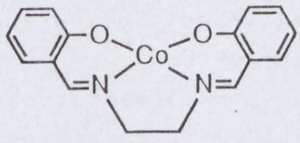


1 2 3

X, Y= H, OCH_3, CH_3, Cl, NO_2 PhCH(CH_3)NHPh PhC(CH_3)=NPh

R^1= t-Bu, 4-Y-C_6H_4 4 5

To a solution of Co(salen) (0.8 mmol) and TBHP (4.8 mmol) in DMSO (20 ml) was added N-benzylaniline (1, X=H, R^1=Ph) (4 mmol). The solution was warmed at 40°C for 8h (conv. 91%). ^{1}HNMR analysis showed that the reaction mixture is composed of N-benzylideneaniline (2; X=H, R^1=Ph) (94%) and benzaldehyde (3; X-H) (6%). Similar oxidations of N-t-butylbenzylamine (1; X=H, R^1=t-Bu) and N-(1-phenylethyl)-aniline (4) (conv; 92% and 37%) gave 2 (X=H, R^1=t-Bu) (91%) and 5 (98%), respectively. These amines are normally unsusceptible to the O_2/Co(salen) system. The reactivity of substituted N-benzylanilines (1; R^1=4-Y-C_6H_4) depended strongly on the nature of the substituent Y, but independent of X. An electron donating group accelerated the reaction rate, whereas an electron withdrowing group retereded it. The substituent effect arises stronger on aniline ring than on the benzyl moiety in 1. The Hammet plot using 1 (X= H, R^1= 4-Y-C_6H_4) vs σ_p+ gave a straight line with a ρ value of -1.1. The results suggest that dehydrogenation reaction proceeds via electron transfer from the amino group to the Co(III) species, but not hydrogen abstractoion from the benzyl group.



Co(salen)

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CATALYTIC OXIDATION OF D-MANNITOL TO CHIRAL GLYCEROL DERIVATIVES

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Chiral glycerol derivatives are versatile intermediates with broad synthetic utility[1,2]. They can be used for the preparation of the pure enantiomers of a wide variety of biologically active compounds and especially for the synthesis of β-adrenergic blocking agents.

These chiral C_3-building blocks are obtained from sugar derivatives (chiral pool) or by asymmetric synthesis (enzymatic or non-enzymatic). Most of the known procedures are based on the glycol cleavage of, for example, D-mannitol derivatives[3] and employ expensive lead tetra-acetate or sodium periodate. It would be economically more attractive to combine the obvious advantages of raw materials from the chiral pool (availability, low cost, natural chirality) with the use of a cheap oxidizing agent comprising O_2, H_2O_2, etc. and a metal catalyst.

The oxidation of D-mannitol derivatives to chiral glycerol derivatives such as 2,3-O-isopropylidene-D-glyceric acid using various metal-catalysts in combination with cheap oxidizing agents, will be reported.

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DIOXYGEN CARRYOVER AND ACTIVATION BY COBALT(II) AND MANGANESE(II) COMPLEXES

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The transition metal complexes capable of binding and activating of O_2 are simple models of natural oxygen carriers and metalloferments[1-3].

The reversible oxygenation of cobalt(II)–2,2'-dipyridyl complex in ethanol and manganese(II)-tri-n-propylphosphine in toluene has been investigated.

The kinetic parameters have been determined and the mechanism for the Co(II)-dipy and Mn(II)-n-Pr_3P catalyzed autoxidation reaction of hydroquinone and acrolein has been proposed. The effect of the solvent on the rate of reactions was stablished. The effective rate constants and activation parameters of the reactions of oxygenated catalysts with the substrates have been calculated.

It has been determined that the intermediate oxygenated cobalt and manganese complexes is the active form of catalysts in the reactions. It has been proposed that the rate-controlling step of this oxidation process is the formation of an "oxygenated complex – substrate" intermediate.

The perspective of the utilization of these cobalt(II) and manganese(II) complexes as dioxygen carriers in composite membranes has been estimated.

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P-32, MON

SYNTHESIS AND CATALYTIC PROPERTIES OF IRON TRIPHENYLPHOSPHINE OXIDE COMPLEXES

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Iron triphenylphosphine oxide complexes of the composition $FeX_3(OPPh_3)_2$ (X=Cl) Br or NCS) and $Fe(OPPh_3)_4(Z)_2$ ($Z=ClO_4$ or I_3) were prepared by autocatalytic oxidation of tripheylphosphine (PPh_3) by dioxygen to triphenylphosphine oxide ($OPPh_3$) in the presence of some iron salts and the corresponding anions X or Z. These complexes also may prepared by direct reaction of $OPPh_3$ with FeX_3 (X=Cl, Br or NCS)[1] or FeZ_2 ($Z=ClO_4$[2] or I_3).

Complexes $FeX_3(OPPh_3)_2$ and $Fe(OPPh_3)_4(I_3)_2$ act as homogeneous catalysts of PPh_3 oxidation by dioxygen in acetonitrile at about 323 K[3,4]. The oxidation rate depends on the properties of the anions coordinated in the mentioned complexes and on their structure. This rate increases in the order: Cl<NCS<Br<I. It is probably connected with oxidizability of the anions. In these catalytic systems reversible processes Fe(III) $\rightleftharpoons$ Fe(II) (for X=Cl, Br or NCS) or $I_3^- \rightleftharpoons 3I^-$ were observed.

On the contrary to complexes $FeX_3(OPPh_3)_2$ and $Fe(OPPh_3)_4(I_3)_2$, perchlorate complex $Fe(OPPh_3)_4(ClO_4)_2$ is not catalyst of PPh_3 oxidation. During the autocatalytic oxidation of PPh_3 by O_2 in the presence of $Fe(ClO_4)_3$ the irreversible reduction of Fe(III) to Fe(II) takes place and the stable complex $Fe(OPPh_3)_4(ClO_4)_2$ is formed[5].

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P-33, WED

A THEORETICAL STUDY OF THE MECHANISM FOR THE FORMATION OF MALEIC ANHYDRIDE ON A VANADYL PYROPHOSPHATE SURFACE.

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Contribution from the Department of Chemistry, University of Århus, 8000 Århus C, Denmark and the Department of Chemistry, Cornell University, Ithaca, 14853 N. Y., USA.

An analysis of the oxidation of 1,3-butadiene to maleic anhydride by molecular oxygen catalyzed by a vanadyl pyrophosphate surface is given. The surface is known to contain pairs of edge-sharing vanadium-oxygen octahedra. Each pair has two vanadyl groups, one pointing towards the bulk (Lewis acid site) and the other being free for interaction. From extended Hückel calculations on various modelsystems it is suggested that 1,3-butadiene becomes activated through a [2+4]-like cycloaddition reaction with the oxygen atom of the vanadyl group. This leads to an adsorbed 2,5-dihydrofuran species.

Molecular oxygen is found to adsorb on the Lewis acidic vanadium atom of the surface. The two possible adsorption geometries, η^1-superoxo and η^2-peroxo, are compared. It is suggested that the oxygen transfer reaction involves an initial hydrogen abstraction from the 2-position of the 2,5-dihydrofuran species, giving a surface bound hydroperoxide. A hydroxy radical is subsequently transferred back to the radical-like 2,5-dihydrofuran species, yielding a 2-hydroxy derivative. An asymmetric lactone is obtained after removal of one molecule of water from the surface. The 5-position is suggested to become oxidized in a similar way.

P-34, WED

SPECTROSCOPIC AND ELECTRONIC STRUCTURE STUDIES OF μ-PEROXO BINUCLEAR COPPER AND COBALT MODEL COMPLEXES

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Oxygen activation and transport is accomplished by the peroxide-bridged binuclear copper active sites contained in a variety of important proteins including the Hemocyanins and Tyrosinases. In order to understand the relationship between electronic and geometric structure and function in these sites, we present absorption and resonance Raman data for the *trans* μ-1,2 peroxo, μ-η^2:η^2 peroxo and μ-1,1 acylperoxo copper dimers which allow detailed spectral assignments. As these are the only structurally defined copper-peroxide complexes currently available, these studies have also been extended to include polarized single crystal spectroscopy on the cobalt-peroxide dimers of which there are many structurally defined examples with *cis* and *trans* μ-1,2 and μ-1,1 binding geometries. The absorption and resonance Raman data are correlated with the results of spin unrestricted, broken symmetry SCF-Xα-SW calculations in order to define in detail their electronic structure and its changes with variation of the peroxide binding geometry.

A CATALYTIC OXIDATION EMPLOYING SINGULET OXYGEN

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For the mechanism of quenching of singulet oxygen by various complexes the (partial) electron transfer is one of the possible pathways. According to our previous results [1] certain $LCo^{III}(s\text{-}BQDI)_2ClO_4$ complexes (L is organic ligand, s-BQDI is the monoanion of o-benzoquinonediimine, see [2]) prooved to be very efficient quenchers of $^1O_2^*$. In order to get some indirect support for the existence of a supposed short lived transient produced by electron transfer, the oxygen containing solution of methylene blue (sensitizer for $^1O_2^*$ production) and the appropriate complex was irradiated in the presence of large excess hydroquinone (H_2Q), an easily oxidizible substrate. HPLC analysis of the solution showed, that H_2Q was selectively oxidized to p-quinone in high yield, meanwhile in case any of the above compounds were not present or the solution was not irradiated, oxidation did not occur. So the above process can be considered as a photocatalytic oxidation, where the supposed transient is probably the oxidizing species. The mechanistic aspects of the oxidation will be discussed in detail.

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HOMOLYTIC REACTIVITY OF PEROXOVANADIUM COMPLEXES

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Vanadium peroxocomplexes, besides their heterolytic behavior in the oxidation of nucleophilic substrates, *e.g.* thioethers[1] and allylic alcohols[2], exhibit a homolytic reactivity which is revealed by the occurrence of a radical chain decomposition and by the capability of hydroxylating aromatic and aliphatic hydrocarbons[3,4]. Such a reactivity is observed only in weakly coordinating solvents[4] and it is magnified by the presence of peculiar ligands such as the picolinato anion. Both the effect of the solvent and of the ligands are not well understood. Therefore, we have initiated a mechanistic investigation of some model reactions where vanadium peroxocomplexes, bearing different ligands, display their homolytic reactivity toward a series of substrates in various solvents. The results of such an investigation will be discussed and some hypotheses on the role played by the parameters considered will be presented.

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P-37, WED

OXIDATION OF PRIMARY ALCOHOLS TO CARBOXYLIC ACIDS BY A PEROXO COMPLEX OF IRIDIUM

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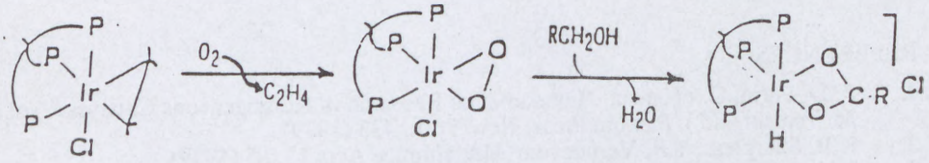
In recent years, increasing attention has been devoted to both stoichiometric and catalytic oxidation of organic substrates by transition-metal oxo and peroxo complexes. However, the oxidation of primary alcohols to carboxylic acids has no precedent for η^2-dioxygen complexes.

Herein, we report on the synthesis and characterization of the novel peroxo complex of iridium [(triphos)IrCl(η^2-O_2)] (**1**) [triphos = $MeC(CH_2PPh_2)_3$], which transforms primary alcohols into carboxylic acids and secondary alcohols into ketones.



Complex **1** is readily produced *via* displacement of ethylene by O_2 in [(triphos)IrCl(η^2-C_2H_4)]. It reacts with RCH_2OH (R = H, Me, Et, Pr, Ph) to form colorless solutions which separate white-off octahedral hydrido-carboxylate complexes [(triphos)Ir(H)(η^2-O_2CR)]Cl in excellent yield. These Ir(III) complexes are stable at room temperature in both solid state and solution, with the only exception of the formate derivative (R = H) which easily decarboxylates All of the compounds were characterized by elemental analysis and chemical-physical measurements incliding ^1H, ^{31}P, and ^{13}C NMR spectrosopy.

The reaction mechanism has been elucidated by means of cross-over experiments and reactions with deuterium-labelled reagents.It is concluded that the η^2-dioxygen ligand is protonated by the hydroxy proton from the alcohol to give η^1-hydroperoxide and η^1-alkoxide ligands. Attack by the hydroperoxide on aldehyde formed by the β-H elimination from η^1-alkoxide completes the reaction.

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OXO TRANSFER FROM AMINES N-OXIDES TO COPPER SALTS : RESULTING COPPER (III) MEDIATED OXIDATION OF ORGANIC LIGANDS .

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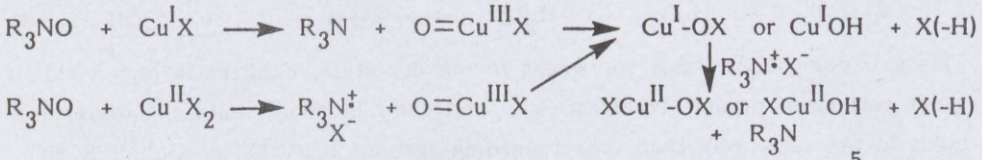
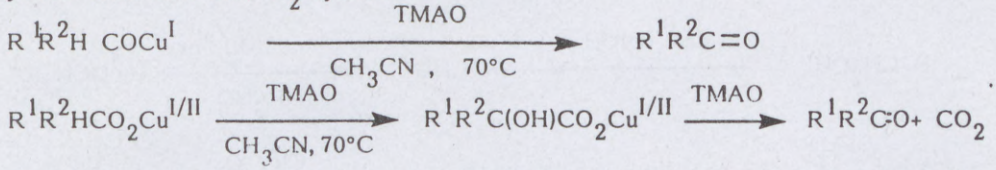
The interaction of trimethylamine N-oxide (TMAO) with Copper (I) and Copper (II) derivatives gives rise to transient Copper (III) intermediates and promotes a number of oxidations we have yet obtained through Cu^{I}/O_2 systems[1-3] or with Cu^{III} itself[4]. General mechanism is assumed to be :

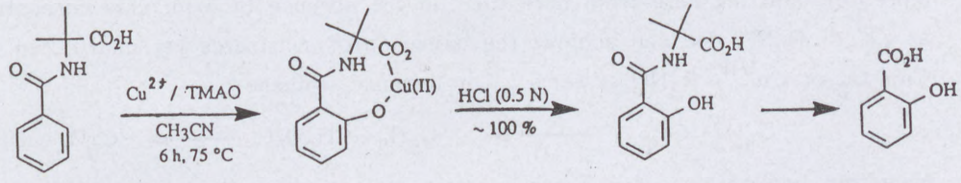


Alcohols and carboxylic acids are thus oxidized to carbonyl compounds[5], in higher yields than with Cu^{I}/O_2 systems :



α - hydroxy acids intermediates are involved in the reaction of carboxylic acids, as under oxygen[2] .

This new system allows the quantitative hydroxylation of benzoylglycine derivatives leading selectively to the corresponding salicylic compounds[6], and constitutes an original synthetic way .



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INTERACTION OF HYDROGEN PEROXIDE AND COPPER (II) : THE STABLE COPPER (III) OXIDE $\left[Cu^{III}(O)OH\right]_n$

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Cu^{++} ions react with H_2O_2 in water (pH $\simeq$ 5) to yield a brown precipitate, the analysis and first chemical properties of which demonstrate the quite simple structure of a trivalent copper oxo - hydroxide :

$$2\ Cu^{II} + H_2O_2 + H_2O \longrightarrow 2\ Cu^{III}(O)OH + 2\ H^+$$

This new compound, stable for weeks in the dry state, oxidizes in high yields a great variety of organic susbstrates, in particular alcohols, amines, carboxylic acids in the same way than the preceeding systems ($Cu^I/\ O_2$ or $Cu^{I/II}/\ R_3NO$) for which we had precisely postulated the intervention of Cu^{III}. [1-4]

$$R^1CH_2OH \xrightarrow{Cu^{III}(O)OH} R^1CHO \xleftarrow[R_3NO]{O_2\ or} Cu^IOCH_2R^1$$

$$R^1CH_2NH_2 \xrightarrow{"} R^1CH{=}NH \xleftarrow{Cu^I/\ O_2} R^1CH_2NH_2$$

$$R^1R^2CHCO_2H \xrightarrow{"} R^1R^2C{=}O \xleftarrow[R_3NO]{O_2\ or} Cu^IOCOCHR^1R^2$$

Moreover, starting here from pure Cu^{III} in the absence of oxidizable coreactants as Cu^I or R_3N , one can achieve the oxidation of substrates yet unaffected by $Cu^I/\ O_2$ or $Cu^{I/II}/\ R_3NO$ systems . For instance, toluene :

$$C_6H_5\text{-}\ CH_3 \longrightarrow C_6H_5\text{-}\ CH_2OH \longrightarrow C_6H_5\text{-}CHO$$

Numerous applications of this new reagent are under investigation .

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PEROXOLIGAND TRANS-INFLUENCE STRUCTURAL REVEALING IN THE VANADIUM(V) OXOPEROXOCOMPLEXES

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The vanadium(V) oxoperoxocomplexes $[VO(O_2)(bipy)_2]ClO_4$ (I), $[VO(O_2)(phen)_2]ClO_4$ (II) and $NH_4[VO(O_2)F_2(bipy)]\ 2H_2O$ (III) have been synthetized and studied by the X-ray single crystal structural analysis. In the structures of these seven-coordinated complexes the peroxoligand trans-weakening influence revealings have been found.

In the complexes I and II the influence is displaying in the lengthening of V-N bonds trans to O_2-ligand compared with those ones trans to N (224 pm against 213 pm in I and 225 pm against 214 pm in II). The common lengthening of V-N bond trans to O(oxo) due to its trans-influence is of the same extent.

Apparently, the simultaneous trans-weaking influence of "doubly bonded" oxoligand and bidentate O_2-ligand is taking place in the reaction of complex III formation and is resulting in the intraspherical rearrangement.[1] In the structure of complex III V-N bond trans to O_2-group at the equathorial plane is something longer than V-N trans to F.

On the example of complexes I-III bidentate O_2-ligand in the seven-coordinated (pseudooctahedral) vanadium(V) oxoperoxo-complexes has been shown to be an analog of "doubly bonded" oxoligand in manifesting the strong trans-influence. The $VO(O_2)$ fragment posesses characteristic for the V-VII groups d^0-metal dioxocomplexes cis-structure. The peroxoligand influence effect is accompanying by shortening of O-O and (in the smaller extent) V-O_2 bonds.

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P-41, WED

A STRUCTURE OF SOME CATALYTIC MOLYBDENUM(VI) COMPLEXES

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Oxygenated molybdenum(VI) compounds is known to be the effective catalysts for the epoxidation of olefins by hydroperoxides. With the purpose of formulating the algorithm to the catalysts selection we investigated the connection between a structure and physico-chemical properties of the β-diketonated mO(VI) complexes with different substituents.

NMR ^{95}Mo spectrums confirm the dates of X - ray-diffraction and indicate on C_2 point symmetry of Mo(VI) β-diketonates. Cis-stereochemistry of oxoligands is determined by its electron structure. The details of molecular structure are shown by the parameters of the spectrums, which depends on incoherent repulsion between donor atoms. ^{95}Mo chemical shifts of the complexes are very sensitive to the nature of chosen ligands and are equal to 3,3 ppm - for acetylacetonate, 1,5 ppm - for benzoylacetonate, - 4,0 ppm - for dipivaloylmetanate, - 15,0 ppm - for 3-trifluorineacetylcmaphorate of Mo(VI). The growth of ionicity of the chemical bond Mo - O (chelate) comes to the more screening of nuclears ^{95}Mo in the line acetylacetonate - 3-trifluorineacetylcamphorate of MoO_2. That is in agreement with increasing of electron density delocalization in a chelate circle.

Accordingly we also found a correlation with the dipole moments of studied compounds: 5,32 D - for acetylacetonate, 6,05 D - for benzolacetonate, 6,74 D - for dipivaloylmetanate, 7,74 D - for 3-trifluorineacetylcamphorate of MoO_2.

KINETIC RESOLUTION OF OXIRANES BY MOLYBDENUMOXODIPEROXO/DIOL-REAGENTS

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A new route for the preparation of unfunctionalized optically active oxiranes is the kinetic resolution by molybdenumoxodiperoxo complexes with hydroxyacid amides as bidentate ligands with the addition of chiral aliphatic diols. This method results in high enantiomeric excesses (ee > 90%) and good chemical yields[1].

In a typical experiment, the reaction was performed in 5 ml head-space-vials, which were charged with approximately 50 mg of molybdenumoxodiperoxo complex dissolved in 1 ml of 1,2-dichloroethane. After oxirane and diol had been added, ee and chemical yield were determined by complexation gas chromatography on chiral stationary phases such as Ni(II)-bis-[3-heptafluorobutanoyl-(1R)-camphorate][2].

At a stoichiometric ratio oxirane/molybdenum complex/diol of 5:1:2 or 6:1:2 an optimum relationship between ee and chemical yield is obtained[3,4]. Products of the reaction are ketones and aldehydes arising from cleavage of the oxirane ring[4]. The reaction is not stoichiometric, but partially catalytic, O_2 being believed as cause thereof[4,5].

Both enantiomers of the oxirane are readily available, because the configuration of the diol determines the configuration of the excess oxirane. With S-diols R-oxiranes are formed and vice versa[3,4,6].

Best results are obtained with $MoO(O_2)_2$ · S-PLA (S-PLA = S-piperidine-lactamide) and (2R,3R)-butandiol or (2S,3S)-butandiol respectively. Thus the kinetic resolution of trans-dimethyloxirane with $MoO(O_2)_2$ · S-PLA/(2S,3S)-butandiol results in 94,3 % ee and 71 % yield of (2R,3R)-dimethyloxirane[3]. Aromatic substituted oxiranes also give high enantiomeric excesses, but much lower chemical yields than with aliphatic substituted oxiranes. Unexpectedly, large substituents decrease the chiral recognition of the kinetic resolution[4].

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P-43, WED

EPOXIDATION OF CYCLOHEXENE CATALYSED BY PEROXOOXOMETALLATES UNDER PHASE-TRANSFER CONDITIONS

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The epoxidation of cyclohexene with hydrogen peroxide was investigated in the biphasic water-chlorobenzene system using different quaternary ammonium chlorides as phase-transfer catalyst (PTC). It was found that the yield of epoxide increased nearly linearly with increasing concentration of the molybdenum(VI) catalyst. A pH of 3-4 was found to be optimal for epoxide formation, the epoxide yield decreased with increase of the H^+ ion concentration mainly due to the H^+ ion-catalysed hydrolysis of the epoxide formed. A PTC excess inhibits the epoxidation. In the case of molybdenum(VI), arsenate ion proved to be a more active promoter than phosphate ions by a factor of 1.6 when $[Mo] \geq [PTC]$; however, the sequence of promoter activity was reversed when the PTC was applied in a 10-fold excess. Tungsten(VI) is about 3-times more active catalyst than molybdenum(VI). however, for tungsten(VI) the activity sequence was $PO_4^{3-} > AsO_4^{3-}$. The view is advanced that the enormous differences between the reactivities of the investigated oxoperoxometallate complexes and their heteropoly derivatives are connected with differences in the dissymmetry of the η^2 diperoxo ligands in these complexes, which otherwise have similar structures.

P-44, WED

NEW INSIGHTS INTO THE CATALYTIC ACTIVITY OF POLYOXOMETALATES FOR OXIDATIONS WITH HYDROGEN PEROXIDE

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Heteropolyoxometalates, more particularly those with the KEGGIN structure have been used as precursors in the catalyzed selective oxidation of organic substrates by dioxygen, alkylhydroperoxides or hydrogen peroxide.

With H_2O_2, phase transfer catalysis is suitable for lipophilic substrates at moderate temperatures and with dilute hydrogen peroxide solutions. For instance, ISHII et al[1] have studied the epoxidation of olefins in the presence of heteropolyacids (HPA) with the KEGGIN moiety $H_n[XM_{12}O_{40}]$ (M = Mo, W ; X = P, Si,...) and an onium chloride. According to these results, phosphotungstic acid, $H_3[PW_{12}O_{40}]$, x H_2O, is the most active of these HPA. Some years ago, VENTURELLO et al[2] developed a catalyst involving tungstate, WO_4^{2-}, and an "assembling anion", PO_4^{3-}, in acidic media (pH : 2-4). A catalytically efficient peroxide salt : $[(C_6H_{13})_4N]_3^{(+)}\{PO_4[WO(O_2)_2]_4\}^{3-}$, was characterized by single-crystal X-Ray diffraction analysis.

While testing these recently described systems and some novel precursors for the epoxidation of several olefinic substrates, we obtained clear evidence for a large spectrum of activities. This prompted us to perform physicochemical, mainly spectrochemical, studies (UV, IR, RAMAN, ^{31}P NMR, ...) to identify the major species in the biphasic systems.

These investigations result in a better characterization of the known catalytic systems and of those involving novel tungsten or transition-metal precursors.

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P-45, WED

CATALYTIC OXIDATIONS OF KETONES AND OF VICINAL DIOLS USING METAL-OXO COMPLEXES AND DIOXYGEN

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The oxidation of organic compounds using soluble transition metal-oxocomplexes themselves readily derived from inorganic precursors, has been extensively studied and reported. This type of oxidant is a leading contender in the development of industrially-useful catalysts for oxidations where dioxygen is the direct source of oxygenated products. In our work, we have closely studied the catalyzed oxidation of ketones and vicinal diols by O_2, comparing the simplest precursors with sophisticated complexes and with heteropolyacids $H_{3+n}[PMo_{12-n}V_nO_{40}]$. The behavior of different substrates, and effects of pH, etc., sheds further light on the mechanism of these reactions.

Oxidative cleavage of cyclic ketones[1] and of vicinal diols[2] is possible with dioxygen ; this is a valuable alternative to hydrogen peroxide or other oxidizing agents like periodic acid. Catalytic oxidation data as well as spectroscopic and electrochemical analyses relevant to the mechanism will be presented.

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P-46, WED

OXIDATION OF ALIPHATIC AND AROMATIC AMINES BY $Mo(O)(O_2)_2L_2$ (L= H_2O, HMPA, TPPO).

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The reactions of $Mo(O)(O_2)_2L_2$ (L= water, hexamethylphosphoramide and triphenylphosphineoxide) with primary aliphatic amines, RCH_2NH_2 (R= C_6H_5, 4-Cl-C_6H_4, 2-Cl-C_6H_4, 2,4-$Cl_2C_6H_3$, 2,4-$(OMe)_2$-C_6H_3) were studied.
The original L ligands were substituted by the amines when a 1:20 ratio (complex/amine) was used in CH_3CN as solvent at room temperature.
The obtained complexes have a stoichiometry according to $Mo(O)_2(O_2)(amine)_2$ showing an oxygen atom transfer from the complex to the amine. In the mother liquor of these stoichiometric reactions, the corresponding oxidation products, RCH=NOH and $RCH=NCH_2R$ were detected.
It is interesting to note in the IR spectrum two bands in the 930-900 cm^{-1} region attributable to two oxo species, and a lower band due to the peroxo group, in accordance with the behavior showed by $Mo(O)(O_2)_2L_2$ in the epoxydation reactions [1].
Aromatic primary amines, RNH_2 (R= 4-OCH_3-C_6H_4 ,4-CH_3-C_6H_4) reacted with $Mo(O)(O_2)_2L_2$ in a more complex reaction.
Depending on the complex/amine ratio it is possible to obtain different oxidation products like nitroso, nitro, azo and azoxy derivatives.
A μ^2-nitroso complex could be intermediately involved, since the reaction of $Mo(O)(O_2)_2L_2$ with PhNHOH in CH_2Cl_2 as solvent, with a 1:5 Mo/amine ratio, gives a light green compound of probable formulation $Mo(O)_2(\mu^2$-PhNO)(PhNHOH).

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FORMATION OF ZIRCONIUM(IV) AND HAFNIUM(IV) PEROXOFLUOROCOMPLEXES IN HYDROGEN PEROXIDE SOLUTIONS BY NMR DATA

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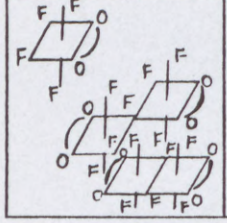
The interactions of zirconium(IV) and hafnium(IV) salts, $ZrCl_4$, $Zr(NO_3)_4 \cdot 5H_2O$, $ZrO(NO_3)_2 \cdot 2H_2O$, $MOCl_2 \cdot 8H_2O$ and $M(SO_4)_2 \cdot 4H_2O$ (M=Zr, Hf) with KF in absolute H_2O_2 have been studied by ^{19}F NMR (75,39 and 282,4 MHz). Two types of complexes are formed in the solutions: hexacoordinated zirconium and hafnium peroxofluorides with bidentate O_2^{2-} - group and more labile oxofluoro- or hydroxofluorocomplexes without peroxo- or hydroperoxoligands, the coordination number of M(IV) being probably more than 6. Complex anion $[MF_4(O_2)]^{2-}$ is predominated in the presence of free solvated fluoride ion, while the absence of F^- excess leads to formation of, besides the monomer, also $[M_2F_7(O_2)_2]^{3-}$ and small amounts of $[M_2F_6(O_2)_2]^{2-}$. Moreover, in the case of zirconium(IV) salts solutions, complicated multiple resonances in the range of -57--64 ppm and -100--115 ppm which have been likely caused by some "polymeric" species can be observed in the ^{19}F NMR spectra. The introduction of additional amounts of fluoride ion has resulted in the destruction of these complexes and formation of $[ZrF_4(O_2)]^{2-}$. In contrast to zirconium(IV) systems, in the case of Hf(IV) solutions under the same conditions the existence of such "condensed" complexes was not detected.

complex	multiplicity	δ, ppm $CFCl_3$		^2J, Hz	
		Zr	Hf	Zr	Hf
	triplet triplet	-36,0 -76,5	-62,5 -95,3	42	45
	dublet of dublets dublet of triplets triplet of quintets	-27,9 -69,6 -72,9	-56,2 -89,3 -94,0	42 49	42 54
	triplet quintet	-18,0 -75,0	-49,6 -94,0	46	50

THE SHARPLESS EPOXIDATION OF 3-METHYL-2-BUTEN-1-OL USING VARIOUS ORGANIC HYDROPEROXIDES

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The SHARPLESS epoxidation of allylic alcohols using tert-butyl hydroperoxide in the presence of $Ti(OiPr)_4$ and dialkyl tartrate is a versatile method for the preparation of homochiral epoxyalcohols[1]. 3-Methyl-2-buten-1-ol was transformed by this method into the corresponding homochiral epoxyalcohol with high enantiomeric excess (e.e.). Alkaline treatment of the obtained 3,3-dimethylglycidol provides useful homochiral intermediates as a result of PAYNE rearrangement and ring opening reaction.

The influence of the used kind of hydroperoxide on the yield and particularly on the e.e. of the generated 3,3-dimethylglycidol has been investigated. The use of the cumene- and 2-phenyl-butyl-2-hydroperoxide gives similar results as tert-butyl hydroperoxide, whereas the epoxidation with 1-phenylethyl-1-hydroperoxide proceeds with lower enantioselectivity. The use of tetralyl-1-hyroperoxide, however, results in sufficient yield but without optical induction. The effect of this variation of hydroperoxides in the SHARPLESS epoxidation is discussed.

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A STRUCTURE AND FORMS OF EXISTENCE OF CATALYTIC SYSTEMS IN REACTIONS OF EPOXIDATION AND HYDRATION

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With the purpose of modelling the structure of catalytic systems in the reactions of olefin epoxidation and hydration, we studied forms of existence of Mo(VI) compounds with mono-, di-, triethylene glycol, and propylene glycol in mixed aqueous solutions. $Mo_2O_8^{4-}$, $Mo_7O_{24}^{6-}$, $Mo_2O_8(L)_n^{4-}$, $Mo_7O_{24}(L)_n^{6-}$ (n = 1,2) was found to be the preferable forms in this conditions.

The acidity properties of molybdenyl ethyleneglycolate, propyleneglycolate and butyleneglycolate, and the full statistical analysis of hypothesis of Mo(VI) complexes in aqueous medium indicate formation of compounds with wholly substituted donor groups of ligands, i.e. the products of hydrolytical polymerization as:

$$(MoO_j)(HL) \xrightarrow{+iH^+} n(MoO_jH_i)(HL) \longrightarrow (MoO_jH_{i-m})_nL_nH_{n-k} + (k+mn)H^+ ,$$

k, m = 0, 1, 2 ... , n = 2 ... k, m.

The composition and the structure of Mo(VI) complexes with 1,2-propanediol (I), 2,3-butanediol (II), 2,3-dimethyl-2,3-butanediol (III) in nonpolar solutions (hexane, benzene, dioxane) were determined. In the solutions of Mo(VI) complexes with II and III, the equilibria are established:

$$2\,(MoO_2)(HL)_2 \rightleftharpoons (Mo_2O_3)(HL)_2(L)_2 + H_2O$$

In solutions containing complexes of MoO_2 and I, polymerization occurs by a chain mechanism without H_2O evolution and yields di-, tri- and tetranuclear compounds.

A correlation was found between H_2O, H^+ and diol concentrations, the degree of nuclearity in aqueous solutions, the type of organic solvents and the catalytic activity of molybdenum complexes in epoxidation and hydration.

COBALT SCHIFF BASE COMPLEX CATALYZED EPOXIDATION OF OLEFINS WITH NaOCl

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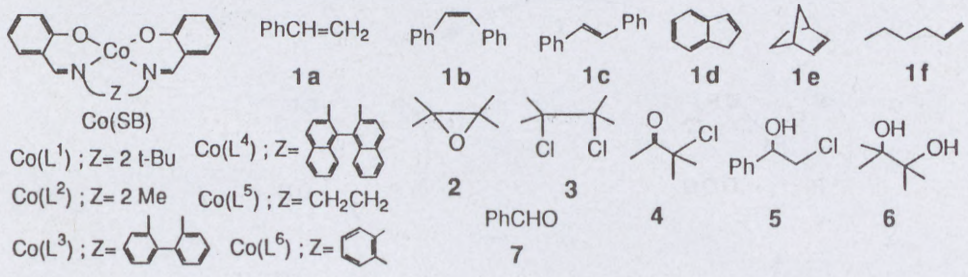
Cobalt Schiff base complexes [Co(SB)] are interesting because of their characteristic behavior as artificial oxidoreductases: dioxygenations in aprotic solvents, monooxygenations in alcohols, and dehydrogenations.[1] However, no information has been available about catalytic activity of Co(SB) for epoxidation. We report here that Co(SB) catalyze the oxidation of olefins with NaOCl mainly to give epoxides. The oxidation was examined with olefins **1a - 1f**. A solution of **1** in dichloromethane containing Co(SB) was stirred with a solution of NaOCl in a borate buffer (pH 10) at room temperature. Products **3 - 7** were isolated in addition to epoxides**2** from the resulting mixture. No reaction takes place without the catalyst. The nature and distribution of the chlorinated products depend on the



structure of **1**. On the other hand, the structure of Co(SB) does not afffect the product distribution but the reaction rate. Since both cis- and trans-stylbenes give only trans-stilbene oxide, the present oxidation should involve a radical process. Nonplanar $Co(L^1)$-$Co(L^4)$ are more effective than planar $Co(L^5)$ and $Co(L^6)$ in the present catalysis. Product and kinetic analyses of the oxidation suggest a mechanism involving rate controlling homolysis of $Co^{III}(SB)(OCl)$ under the interaction with the substrate, different from the mechanism proposed for the Mn(TPP)Cl catalyzed epoxidation.[2]

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ATTEMPTED CATALYTIC EPOXIDATION OF ALKENES USING A METAL HYDROPEROXIDE: DIOXYGEN INSERTION INTO A Pt-H BOND

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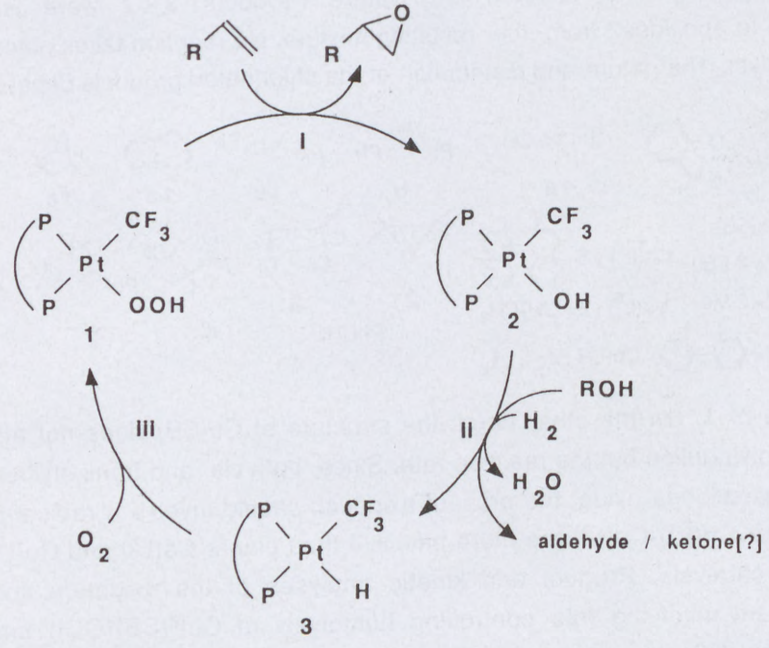
Aspects of the catalytic cycle proposed in the scheme were investigated. Step **i**, the epoxidation of an olefin by a metal hydroperoxide, has been proposed in the literature for the catalytic epoxidation of alkenes by hydrogen peroxide using **2** as the catalyst.[1] Steps **ii** and **iii** were demonstrated by the author. Step **ii** occurs smoothly at 60 °C, 75 psi H_2 in tetrahydrofuran. Step **iii** is accelerated by azonitrile free radical initiators, which supports a radical chain mechanism for the insertion of dioxygen into the Pt-H bond. Attempts to make the entire cycle catalytic have not yet succeeded.



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MOLECULAR O_2 ACTIVATION IN THE PRESENCE OF METALLIC COPPER

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Our recent work on the activation of molecular oxygen on metallic Cu[1] lead to the conclusion that organic Bronsted acids such as methanol, nitromethane and benzoic acid easily react with Cu and O_2 in the presence of a base (pyridine) according to the following scheme (X=-OMe,-OCOPh):

$$Cu + 1/2\ O_2 \rightarrow Cu{\sim}O \quad \text{(surface)}$$

$$Cu{\sim}O + HX \longrightarrow Cu\begin{matrix}OH\\ \diagdown\\ X\end{matrix}$$

$$Cu\begin{matrix}OH\\ \diagdown\\ X\end{matrix} + HX \rightarrow CuX_2 + H_2O$$

As an extension of this research, we have investigated the possibility to use metallic Cu as a catalyst for the oxidation of monohydroxilated aromatics as an alternative to the use of CuCl and $CuCl_2$. Thus, a different catalytic behaviour can be suspected starting from metallic Cu, respect to classical Cu(I) and Cu(II) salts, on the basis of either a different mechanism for oxygen activation or stabilization of different oxidation states.

While unsubstituted phenol gave 4,5-dimethoxy-1,2-benzoquinone (46%) and α-naphtol gave 2-methoxy-1,4-naphtoquinone (43%), the main product in the reaction of β-naphtol was (1,1'-binaphtalene)-2,2'-diol (41%)[2].

We here report the results obtained by reaction of 2-amino-phenol with molecular O_2 in the presence of metallic copper.When the reaction was carried out in methanol/pyridine solution the main product was 2-aminophenoxazine-3-one.

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COBALT COMPLEX WITH 2,2'-BIPYRIDYL IMMOBILIZED ON DISPERSE SILICA SURFACE IN THE REACTION OF P-HYDROQUINONE OXIDATION.

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We have shown previously[1] that cobalt complex with 2,2'-bipyridyl and supplementary base catalyzes the oxidation of p-hydroquinone by molecular oxygen in ethanol.

It has been established that immobilization of cobalt complex with 2,2'-bipyridyl on disperse silica surface - aerosil leads to receiving effective heterogeneous catalyst. The ability of immobilized complex to reversible oxygenetion which is one from the main conditions determining the catalitic activity of heterogeneous complex has been established.

The catalitic activity of the sample was determined using the O_2-uptake initial rates. Measurements were done with the volumetric Varburg apparatus. The influence of the solvent nature on the oxidation rate has been determined. The oxidation rate is decreased in the following row: methanol > ethanol > isopropanol > isobutanol. It has been determined spectrofotometrically that the oxidation product is p-benzoquinone. The investigation of kinetic dependences of p-hydroquinone oxidation in ethanol shows that the reaction kinetics is described by Michaelis-Menten equation. The Michaelis constant (k_m= 0,5 mol/l, t=20°C) of heterogeneous process is some more than that of homogeneous one (k_m = 0,095 mol/l, t=19,5°C[1]). The mechanism of process investigated is suggested.

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OXYGEN ACTIVATION ON THE OXIDE SURFACE FOR THE OXIDATIVE COUPLING OF METHANE

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CH_4 activation for the oxidative coupling of methane is fulfiled by oxygen preactivated on the oxide catalyst surface. In opinion of different researchers these active oxygen species may be both dissociated (O^{2-}, O^-, $O^\cdot$) and molecular (O_2^-, O_2^{2-}) forms. At the same time oxygen activation sites haven't been studied enough.

This report presents the data concerning the study of molecular oxygen activation on Bi-containing oxides. These data were obtained by the selection of catalytic systems with different structural properties and study of their behaviour in oxidative coupling of methane.

The structural analysis of the most effective catalysts showed that oxides with oxygen defectness are most active for C_2-hydrocarbon formation from methane. It has been shown that these oxides can activate oxygen with the formation of peroxide ions which can further disproportionate to atomic oxygen. For this oxygen activation electron donors are needed, their role can be played host or impure ions.

The catalysts which satisfy the suggested requirements have been prepared. Bi_2O_3 doping by Li or Na causes the growth of oxygen defectness and at the same time the increase of C_2-hydrocarbon formation activity in an order of a magnitude higher as compared to pure Bi_2O_3. The selectivity also increases to 72-80 %. $YBa_2Cu_3O_{7-x}$ with the high oxygen defectness is more active in C_2-formation but has lower selectivity (25 %). Essentially new catalytic systems have been suggested: 20 % at. Er/Bi_2O_3 and Bi_2GeO_5. They have a high degree of oxygen defectness and as high efficiency in C_2-hydrocarbon formation as most active catalysts. Catalytic properties of the systems studied will be discussed on the base of the suggested oxygen activation model.

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THE REACTIVITY OF THE COORDINATED HYDROPEROXO LIGAND

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Coordinated hydroperoxo groups are frequently postulated as intermediates in autooxidation reactions mediated by transition metal complexes, but few stable hydroperoxo complexes have been reported, and little is known about their reactivity. This communication reports certain features of the reactivity of the hydroperoxo complex $[Co(CN)_5(OOH)^{3-}]$ whose preparation was reported some years ago[1].

In aqueous solution the hydroperoxo complex undergoes acid catalysed aquation according to the rate law

$$\frac{d(complex)}{dt} = \frac{-k_1[Co(CN)_5(OOH)^{3-}]}{(1 + K_a/[H_3O])}$$

This rate law was observed in the pH range 3-9 and gave values for k_1 of $1.72(3)\times10^{-2}\ s^{-1}$ at 20°C and $1.53(3)\times10^{-1}s^{-1}$ at 40°C; the corresponding pK_a values were 5.27(1) and 5.25(1). The uncatalyzed aquation of the complex must be at least 10^3 times slower than the catalysed pathway.

In the pH range 7-9 the complex reacts with methionine at a rate which is faster than the aquation reaction. The observed rate of decomposition at 20°C was

$$rate = 1.92(3)\times10^{7}[Co(CN)_5(OOH)^{3-}][methionine][H_3O^+]$$

The product of the reaction is apparently a methionine S-oxide complex of cobalt which slowly aquates to give free methionine S-oxide and $[Co(CN)_6(OH_2)]^{2-}$. The hydroperoxo complex is thus effecting oxygen atom transfer to the sulphur.

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