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Palladium(II) Catalysis

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PALLADIUM(II) CATALYSIS

PART ONE: KINETICS ON A [3,3] ALLYLIC ESTER REARRANGEMENT

PART TWO: A SUPPORTED CATALYST FOR OXIDATIONS

by

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To my parents

two exceptional people

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Jim (Mooney) and all the other Mooneys...special friends.

and, Bunny, fellow space being...for cheesecake.

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PREFACE

I shall therefore call it the catalytic power of substances and the decomposition by means of this power ***catalysis****, just as we use the word analysis to denote the separation of the component parts of bodies by means of ordinary chemical forces. Catalytic power actually means that substances are able to awake affinities which are asleep at this temperature by their mere presence and not by their own affinity.*

J. J. Berzelius (1836)

Palladium in the Catalysis of Organic Reactions.

Many organic reactions are catalyzed by transition metals. Palladium catalyzes a bewildering array of them. Representative classes of reactions are double bond isomerizations, molecular rearrangements, substitutions and eliminations at allylic carbons, couplings of aryl, alkenyl, allyl and alkyl derivatives, carbonylations and decarbonylations, cyclopropanations, hydrogen transfer and related reactions, and most importantly oxidations. Palladium catalyzes the oxidations of alkenes, alkynes, benzylic carbons, carbonyl compounds and alcohols.

The most common oxidation states of palladium encountered in these reactions are 0 and II. Less easily seen are the I and IV oxidation states. It is the +2 and 0 oxidation states that enjoy center stage in organometallic chemistry, especially that involved in catalysis. Pd(II) is known both for its σ and π bonded compounds with carbon moieties.

The Orientations of this Work.

It is not possible to place sufficient stress on the importance of understanding mechanism. The delineation of pathways, the determination of equilibria, the determination of kinetic expression and product analysis are all part of this picture. The studies of stereochemistry and the detection, either direct or indirect, of intermediates, is essential to the basic understanding of the often complicated pathways involved in catalyzed reactions. Mechanism helps to understand, extrapolate and apply. On the other hand, a fundamental goal of catalysis is practical application.

This thesis is aimed toward both of the mentioned aspects of catalytic work. It is divided into two parts, both of which involve palladium catalysis. The first part, which involves kinetic studies towards the determination of a much quoted intermediate, is in the study of a catalyzed [3,3] sigmatropic rearrangement. The aim is towards the understanding of mechanism. The second part of this thesis is application oriented. It aims at the development of a catalytic oxidation system for practical applications.

Each part will be introduced, subsequently, in terms of the reactions themselves, the specific aims and the approach that will be taken to achieve those ends. Each part is self contained.

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PART ONE

KINETICS ON A [3,3] ALLYLIC ESTER REARRANGEMENT

PART ONE: CHAPTER I

BACKGROUND, NATURE AND SCOPE OF THIS WORK

I.1. Historical Background.

Woodward and Hoffmann[1] defined "a sigmatropic change of order [i,j] the migration of a σ bond flanked by one or more π electron systems, to a new position whose termini are i - 1 and j - 1 atoms removed from the original bonded loci, in an uncatalyzed intramolecular process." The Cope and Claisen rearrangements are sigmatropic rearrangements of order [3,3].

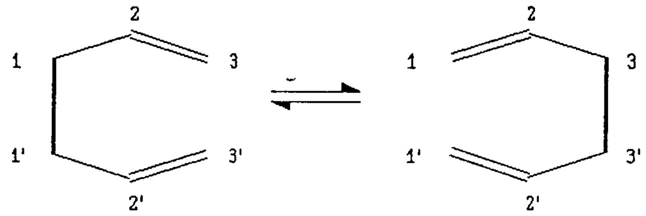


Figure I.1. [3,3] sigmatropic rearrangement with heavy line depicting the 1,1' and apparently migrated 3,3' bond

Historically, it was Ludwig Claisen who first published his observation of the rearrangement in the paper, "Über Umlagerung von Phenol - allyl - äthern in C - allyl - phenole".[2] But, to quote the words of Frederick Ziegler in a recent comprehensive review[3] on the thermal aliphatic Claisen rearrangement, "Ironically, the majority of the text of the paper and all the experimental details dealt with the substance of the title while the first paragraph mentioned in almost parenthetical fashion, the rearrangement of the O - allylation product of acetoacetic ester to its C - allylated isomer upon distillation in the presence of ammonium chloride." The aliphatic reaction is, perhaps, the one that has been more widely studied, both synthetically and mechanistically, than its aromatic counterpart. In keeping with the discussion of the above paragraph, the aliphatic reaction is simply a [3,3] sigmatropic rearrangement. The prototypical reaction is the transformation of allyl vinyl ether into 4-pentenal.

Several excellent reviews tracing the history, developement and scope of the rearrangement have appeared.[4] The stereochemistry of the reaction has been also the subject of intense scrutiny.[5]

Outside of Claisen's laboratory, the investigation of the rearrangement of ethyl β-cinnamyloxycrotonoate[6] was perhaps the first investigation of such a transformation using ammonium chloride. Claisen himself had demonstrated the allyl "migration" in the aromatic species.[7] In 1937, Lauer and Kilburn[8] described the rearangement of some β-allyloxycrotonic esters. The paper dealt with the rearrangement of ethyl β-cinnamyloxycrotonate and the rearrangement was carried out in the presence of ammonium chloride. The rearrangement was accomplished in four hours at 110 °C, reaffirming, as the authors stated, the observation of Claisen. The only product they obtained was the "transposed" ([3,3]) product. On the other hand, Hurd and Pollack[9] working with vinyl allyl ethers found that these rearranged smoothly on heating at temperatures of 175 °C - 255 °C, but gave both the transposed and the "non-transposed" products, [3,3] and [1,3] respectively. The [3,3] product was obtained in a yield of 40% - 50%. Some of the notable rearrangements were using vinyl allyl ether, α-methyl vinyl allyl ether and α-phenyl vinyl allyl ether. The authors make mention of the fact that the transposition of allyl vinyl ether is like the aromatic Claisen rearrangement. The use of the ammonium chloride in the rearrangement step was discontinued. It had been shown to give only a small but significant, increase in the rate.

Cope and Hardy[10] were synthesizing dialkylvinyl alkylcyanoacetic esters and found that they did not have any purification problems except in the case of ethyl (1-methylpropenyl)-allylcyanoacetate, which changed into a stable higher boiling substance on distillation. They speculated that the most probable way in which the rearrangement could occur would involve the shift of the allyl group from the alpha to the gamma position, accompanied by a shift of the double bond from the β,γ position to the α,β position to give the [3,3] product. The rearrangement occured in four hours at 150 °C - 160 °C or in 20 minutes at 260 °C. *This is the first case in which an an allyl group had been observed to undergo a thermally induced* α,γ *shift in an all carbon system.* Cope drew analogy to the Claisen rearrangement of allyl enol,[8, 11] phenol[11, 12] and vinyl ethers[9, 10, 13] under similar conditions. Just as in the cases cited, the isomerization probably depended on the presence of the allyl group and by analogy, Cope commented that a cyclic mechanism was probable. He speculated that if indeed this was the case, the isomerization was "intramolecular and the allyl group was turned around in the shift."

I.2. Why Catalyzed Sigmatropics?

The [3,3] rearrangement is synthetically very useful[14] and the understanding of the reaction grew with time. The reaction has strong geometrical constraints that help to provide highly stereospecific products demonstrated by mechanistic and theoretical studies. Unfortunately the high temperature requirement (generally approximately 200 °C)[15] restricts the reaction to the early part of synthetic sequences. Many studies have been carried out to ameliorate this unfortunately high temperature demand.

Efforts to accelerate the reactions have taken two paths. In the first approach, accelerations were accomplished by placing a positive charge,[16] a negative charge[17] or a zwitter ion[18] on the system. The second approach involves the use of catalysts. Catalysis can be traced back to the initial use of ammonium chloride by Claisen in his 1912 paper. One much later study showed that the apparently heterogeneous process caused a small increase in the rearrangement rate of a vinyl ether.[19] The catalyst apparently functions as a proton donor under the reaction conditions.

A very comprehensive review of the catalysis of the rearrangements has been given by Lutz.[20] The earliest attempts to homogeneously catalyze these reactions involved the use of protic (H_2SO_4)[21] or Lewis acids like BF_3,[22] BCl_3,[23] alumina,[24] and numerous other species like zinc(II) chloride, tin(II) chloride and silver(I) chloride.[25] Although rate accelerations were observed, the yields were poor and side products were a serious problem, apparently because carbocationic intermediates were formed, as witnessed by the loss of stereocontrol and the diversity of products.

One of the more impressive rate accelerations resulted from the famous Ireland method.[26] Ireland and Mueller found that the enolates of allyl esters were rapidly transformed to the corresponding acids at room temperatures. Similar rate enhancements were observed in the anionic oxy-Cope rearrangement.[27] The two approaches mentioned above are restricted to these specific types of reaction systems and the need for a more general type of catalyst for any Cope or Claisen reaction was obvious. The use of transition metal catalysts has emerged as another approach to successful catalysis.

I.2.1. Transition Metal Catalysis.

Most of the use of transition metal catalysts was oriented towards obtaining (a) new, more effective types of metal catalysts, and (b) application of known catalysts to newer substrates.[28] A representative, though not complete list, of metal catalysts, includes Ni(0), Pd(0), Ag(I), Ni(II), Pd(II), Pt(II), and Fe(0) compounds.[29] The range of rearrangements has been large and covers allyl carboxylate (C-O → C-O),[30] O-allyl thiocarboxylate (C-O → C-S),[31] allyl imidate (C-O → C-N),[32] O-allyl phosphorothionate (C-O → C-S),[33] allyl thioimidate (C-S → C-N),[34] and allyl vinyl ether (C-O → C-C).[35]

In the all carbon Cope rearrangement, the first report was by Jonassen *et.al.*[36] He described the preparation of the crystalline palladium(II) chloride complexes of 1,2-divinylcyclohexane and 1,5-cyclo-octadiene using stoichiometric amounts of [$PdCl_2PhCN_2$] with *cis, trans*-1,5-cyclodecadiene and *cis*-1,2-divinylcyclobutane respectively.[37] **(Figure I.2.)** A similar product was obtained from the reaction of Ni complexes with *cis*-1,2-divinylcyclobutane. Catalysis of the equilibration of allylic esters was first reported by Overman and Campbell in 1976.[38] Overman also has the distinction of being the first to report the catalytic Cope rearrangement of certain acyclic dienes under mild conditions.[39] Rate accelerations of the order 10^{10} were observed.

These metal catalyzed reactions can be classified into two groups according to the kinds of products formed.[40] The first group of catalysts gives the same product as the thermal product or the [3,3] product (type 1) while the second group gives two products, the [3,3] and the [1,3] product or the anti-Claisen product (type 2). The type 2 reactions are catalyzed by the zero-valent complexes [$Pd(PPh_3)_4$] and [$Pt(PPh_3)_4$].[32a, 41] The complexes of Hg(II), Pd(II) and Pt(II) gave only the [3,3] product. Of these the palladium(II) complexes were found to be the most effective.

I.2.2. Catalysis by Pd(II).

Our focus naturally shifts to the mechanism of the Pd(II) reaction, both from the point of view of the synthetic utility and our own previous interest in this reaction. Heimbach and Molin[42] noticed that there existed a certain permissible substitution pattern which prevented complex formation in the reactions of cyclodecadienes with Pd(II). Thus, if they were substituted with mono or dimethyl groups at either positions 1-, 2-, 3-, 4-, or 6- complex formation did not occur (see **Figure I.2**). This is easily understandable in terms of difficulty in forming Pd(II) complexes with tertiary carbon atoms.[43]

I.3. Mechanistic Background to the Pd(II) Catalyzed Reaction.

In studying Pd(II) allylic oxidations using palladium(II) acetate Winstein *et.al.*[44] suggested that allylic isomerization probably occurred in the case of allylic esters via an

$$CH_2{=}CH-X \text{ (or) } CH_2{=}CHCH_2-X + Y^- \rightleftharpoons CH_2{=}CH-Y \text{ (or) } CH_2{=}CHCH_2-Y + X^-$$

$$X \text{ (or) } Y = OOCR,\ Cl,\ OR,\ NR_2 \qquad \text{(I.1)}$$

oxypalladation - deoxypalladation route. Henry, who investigated the mechanism of the palladium(II) catalyzed isomerizations, was studying the exchanges of vinylic and allylic species in acetic acid at the time.

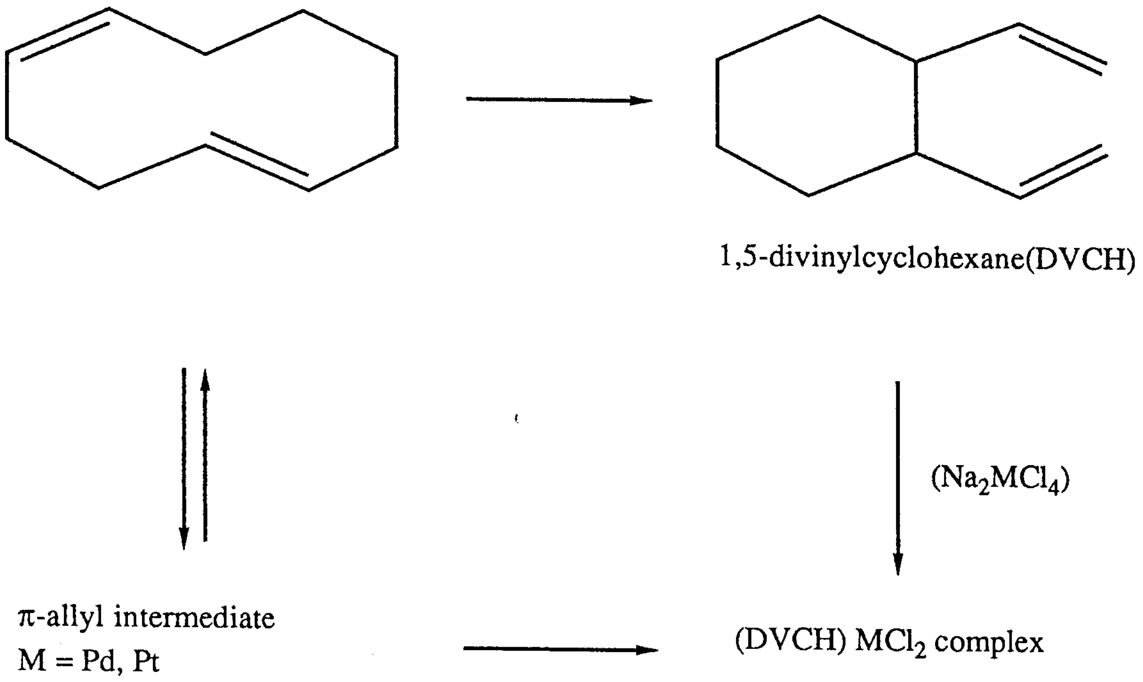


Figure I.2. ***Cis, Trans*** - 1,5-Cyclodecadiene with Pd(II) and Pt(II).

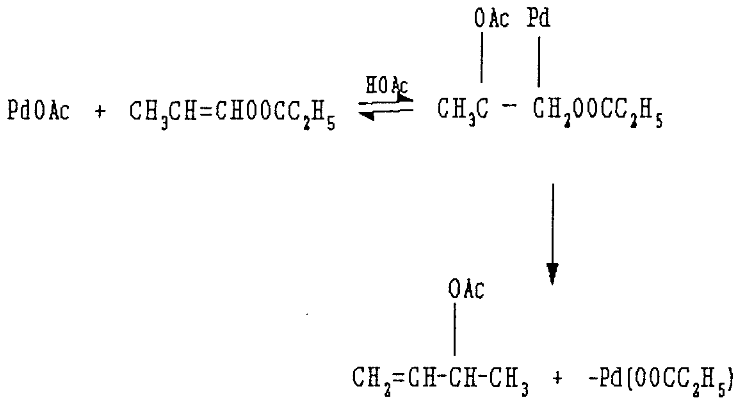
In studying palladium catalytic pathways, Henry was investigating both oxidative and non-oxidative reactions. Among the non-oxidative reactions were those of the general type shown in equation **I.1.**

The reactions are convenient to study because they are non-oxidative in nature. Thus, they do not precipitate palladium metal and their rates are in a convenient range for measurement at 25 °C.

Henry found that vinylic (equation **I.2**) and allylic ester (equations **I.3** and **I.4**) exchange complemented each other.

$$\mathbf{CH_2 = CHOOCR + HOAc \rightleftarrows CH_2 = CHOAc + HOOCR} \qquad \textbf{(I.2)}$$

Allylic ester exchange does not give any information on the stereochemistry of the addition unless optically active allylic esters are used. However, exchange of unsymmetrical esters readily distinguishes between S_N2, π-allyl and acetoxypalladation routes. The acetoxypalladation route would predict that exchange occurs only with isomerization of one allylic isomer into another. For instance, crotyl propionate would exchange to give 2-buten-



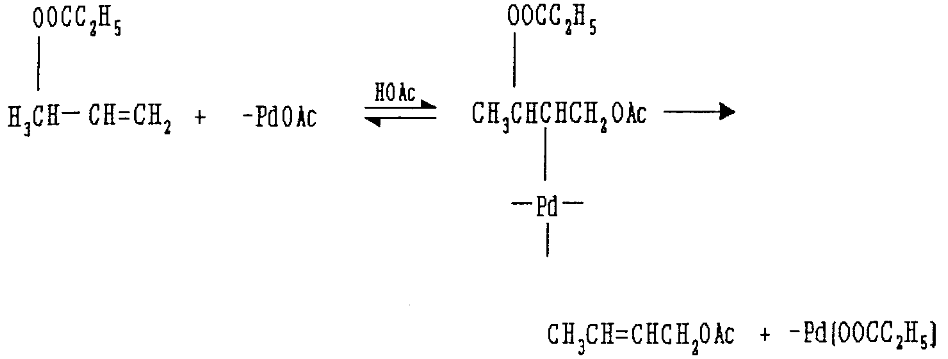
$$PdOAc + CH_3CH{=}CHOOCC_2H_5 \xleftarrow{HOAc} CH_3\overset{\overset{OAc}{|}}{C} - \overset{\overset{Pd}{|}}{C}H_2OOCC_2H_5$$

$$\downarrow$$

$$CH_2{=}CH-\overset{\overset{OAc}{|}}{CH}-CH_3 + -Pd(OOCC_2H_5)$$

(I.3)

2-yl acetate (see equation **I.3.**), while 3-buten-2-yl propionate would give crotyl acetate. (see equation **I.4.**). The S_N2 and π-allyl routes would predict different product distributions from acetoxypalladation.[45]



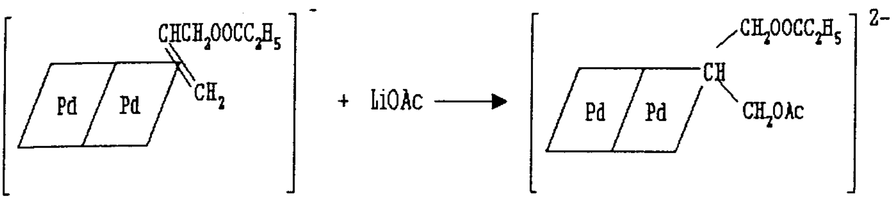
(I.4)

The kinetics of the exchange were first studied using allyl propionate as the organic substrate.[46] The rate expression for the exchange is analogous to that found for vinyl ester exchange.

$$\textbf{Rate} = \frac{[\mathrm{Li_2Pd_2Cl_6}][\text{allyl propionate}]}{[\mathrm{LiCl}]} \times (k_2' + k_2''[\mathrm{LiOAc}]) \qquad \textbf{(I.5)}$$

The first step would be π-complex formation, followed by attack of acetate to give the acetoxypalladation adduct as shown in equation **I.6**. Reversal of this step, but with elimination of $OOCC_2H_5$ instead of OAc would complete the exchange.

A complication noticed at this stage was the inhibition of the rate by the allyl

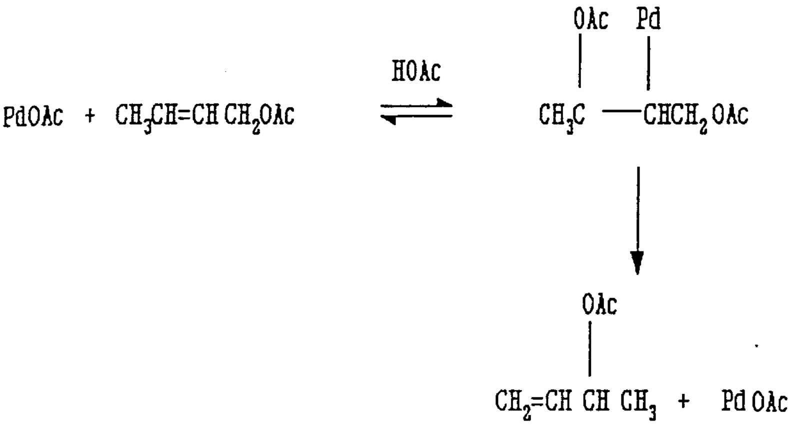


[I.6]

propionate itself. The analogous phenomenon was not seen in the vinyl ester exchange. In addition the product allyl acetate was about as effective an inhibitor as allyl propionate itself. The cause for this inhibition was shown be the unreactive monomeric π-complex. Since the kinetics require a dimeric π-complex and none was detected it probably indicated that the dimeric catalyst was many times more reactive than the monomeric π-complex. The formation of the unreactive monomeric π-complex is as shown below:

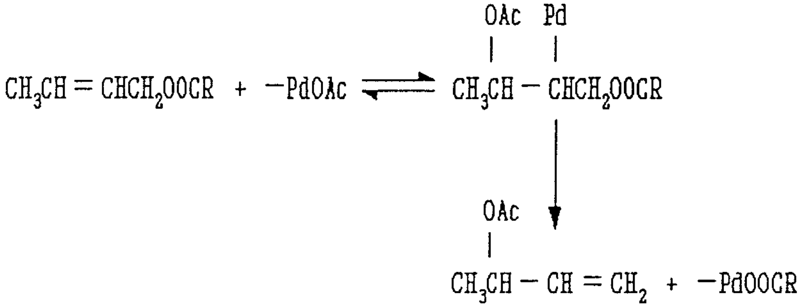
$$\mathbf{Li_2Pd_2Cl_6 + 2\ allyl\ ester \ \overset{K}{\rightleftarrows}\ 2\ LiPdCl_3(allyl\ ester)} \qquad \mathbf{(I.7)}$$

A value of 0.25 M^{-1} was obtained for K from the kinetics and this was confirmed spectrally. The exchange of the unsymmetrical esters, crotyl propionate and 3-buten-2-yl propionate was studied next.[47] Two pathways were found to be present indicating two separate reactions. One was the expected exchange reaction with the rate expression analogous to that for the exchange with allyl propionate as give in equation **I.5**. This reaction is isomerization with exchange. It proceeded by the addition of the Pd(II) and acetate across the double bond (acetoxypalladation) immediately after π-complex formation. This is followed by the elimination of Pd(II) and propionate. When crotyl acetate is the starting material the scheme



$$PdOAc + CH_3CH{=}CHCH_2OAc \underset{}{\overset{HOAc}{\rightleftharpoons}} CH_3\overset{OAc}{C}-\overset{Pd}{C}HCH_2OAc \longrightarrow CH_2{=}CH\overset{OAc}{C}HCH_3 + PdOAc \qquad (I.8)$$

in equation **I.8.** is operative.



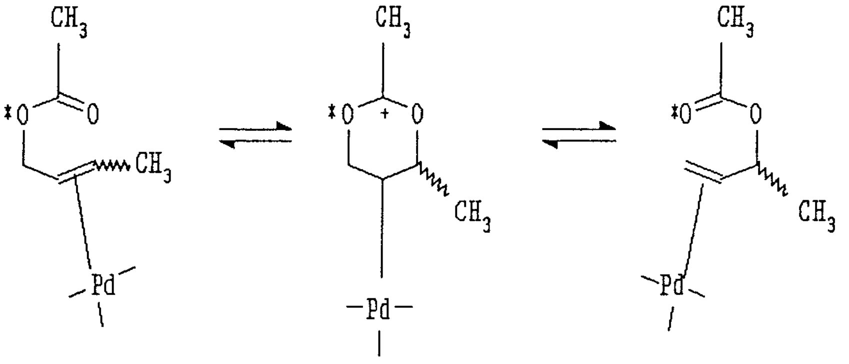
$$CH_3CH = CHCH_2OOCR + -PdOAc \rightleftharpoons CH_3\overset{OAc}{C}H - \overset{Pd}{C}HCH_2OOCR \longrightarrow CH_3\overset{OAc}{C}H - CH = CH_2 + -PdOOCR \qquad (I.9)$$

This mechanism can be tested by isomerizing esters of other acids in acetic acid with excess acetate. If the mechanism shown above is operative then exchange should occur when and only when there is isomerization. For example when the starting material is another crotyl ester, the scheme in equation **I.9.** should occur.

The second reaction, isomerization without exchange has the following rate expression:

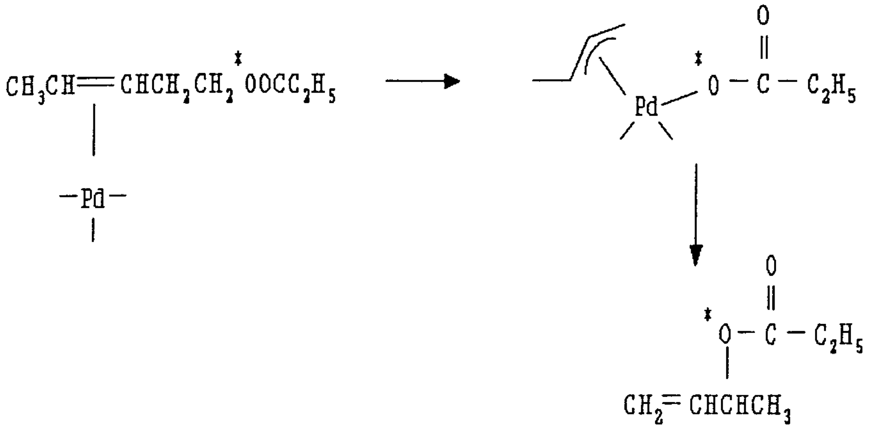
$$\text{Rate} = \frac{[Li_2Pd_2Cl_6][\text{allylic ester}]}{[LiCl]} \times \frac{k'}{(1 + k''[LiOAc])} \qquad \text{(I.10)}$$

During isomerization it was found that an ${}^{18}O$ label was found to transfer from the ester oxygen to the carbonyl oxygen. Another very important piece of information was the fact that when the same reaction was carried out using trifluoroacetate esters in place of propionate esters the rate of isomerization without exchange was decreased by a factor of 500. Based on those two pieces of evidence and other details from the work, Henry proposed an internal oxypalladation[48] as explained in equation **I.11.**



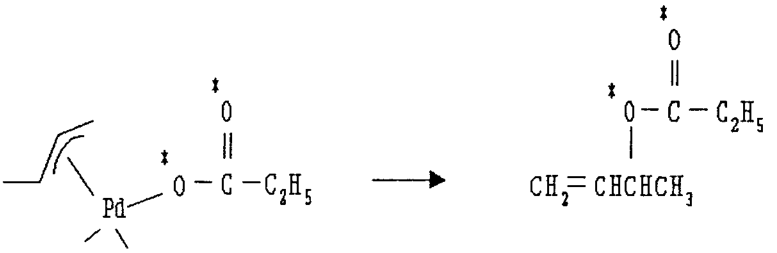
(I.11)

The isomerization without exchange, which had no analogy in Pd(II) catalyzed reactions, is formally similar to the 1,3-deuterium shift in Pd(II) catalyzed isomerization of olefins. The possibility of π-allylic intermediates is ruled out by the ${}^{18}O$ experiments. If ester ${}^{18}O$ labelled crotyl propionate is isomerized via a π-allyl Pd(II) acatete formed by breaking the C-O ester bond, as shown below, then two limiting possibilities exist for the ${}^{18}O$ distribution. First, if there is no ${}^{18}O$ scrambling in the π-allyl intermediate, the principle of microscopic reversibility requires all the ${}^{18}O$ to remain in the ester oxygen. On the other hand, if there is complete scrambling, the ${}^{18}O$ will be divided equally between the ester and the carbonyl oxygen. (see equations **I.12.** and **I.13**).



(I.12)

Neither limiting case nor degree between the extremes is consistent with the results obtained. This is where the reaction displays novelty. The first step is the same as for the exchange reaction, π complex formation. However, rather than attack by external acetate, the



(I.13])

next step would be internal attack by the carbonyl oxygen. This explains the isomerization to give the [3,3] product with complete ^{18}O transfer. The slowing down of the reaction by a CF_3 group occurs because the positively charged intermediate is destabilized by this electron withdrawing species. In this particular reaction the LiOAc inhibition arises because of the capture of the proposed 1,3 acetoxonium ion by the LiOAc.[49] Henry proposed this mechanism based on all the experimental evidence.[50]

Palladium metal activates the olefin for nucleophilic attack. It is an interesting historical aside that although reports of analogous hydroxythallations[51] and hydroxymercurations[52] existed, oxy-metallations with palladium giving rise to unstable bridged intermediates were unknown.

Among the many cited reports of the catalytic capabilities of the various metal complexes in [3,3] isomerizations, Hg(II) and Pd(II) species share the unique distinction of catalyzing a wide variety of sigmatropic rearrangements and with extreme specificity. The reactions occur under mild conditions and they show a remarkable number of similarities in forming C-N, C-S, C-C and C-O bonds. There is ample evidence, of course, to preclude mechanisms involving allylic cation or π-allylic intermediates. There are no competing [1,3] shifts in the Pd(II) catalyzed reactions which occur with clean suprafacial stereochemistry.

Jacobsen and Overman studied (3*R*, 5*E*)-2,3-dimethyl-3-phenyl-1,5-heptadiene and showed that the rearrangement catalyzed by *bis*(benzonitrile)dichloropalladium(II) occured with complete 1,4 transfer of chirality. The transformation occurs with chair topology similar to that established for the thermal rearrangement by the classic experiment of Doering and Roth,[53] and the related experiment of Hill and Gilman.[54]

Although most workers cited it as the correct intermediate, there was, however no evidence for the cyclic carbocationic intermediate that arose from the internal oxypalladation. Subsequently Overman used this cyclic intermediate to explain Hg(II) catalyzed allyl carbamate,[38b] allyl imidate,[22b] and the palladium induced Cope rearrangements.[32b]

In the all carbon Cope rearrangement, Overman and Jacobsen[55] did chirality transfer experiments and unambiguously ruled out mechanisms involving suprafacial formation and then fragmentation of a metallocyclopentane (palladabicyclo[2.2.1]heptane) intermediate. They argued against mechanisms involving oxidative addition of the allylic fragments.

In a very definitive and elegant piece of stereochemical work Bosnich and Schenk[56] catalyzed the rearrangement of allylic imidates to allylic amides. In this [3,3] process, they were studying the catalysis by various metal species like Pd(0), Pd(II), Rh(I), and Ir(I). They found different mechanisms in operation for different species. The most versatile species was the Pd(II) species. The stereochemistry of the Pd(II) catalyzed rearrangement of the allylic imidate to the allylic amide was clearly established.

The thermal reaction gave the optically pure (*E*) allylic amide. The catalytic reaction gave 78:22 ratio of E:Z isomers with corresponding optical purity. An explanation of the course of the reaction[57] is based on the fact that the chosen olefin has two energetically distinct diastereotopic faces to which the metal can bind. A chair six membered ring was postulated with palladium in an equitorial position and the stereochemistry of the product is based on the discrimation of the two diasterotopic binding faces of the olefin (see **Figure I.3**).

Overman and Renaldo did the only substituent effects work in the Pd(II) catalyzed all carbon Cope rearrangement. They used the hexadiene system and found no definite correlation in their investigation.[58]

I.4. Purpose of this Work.

Pd(II) has been established to be the most versatile species in the catalysis of the [3,3] sigmatropic rearrangements. Researchers have found many uses for Pd(II) catalyzed

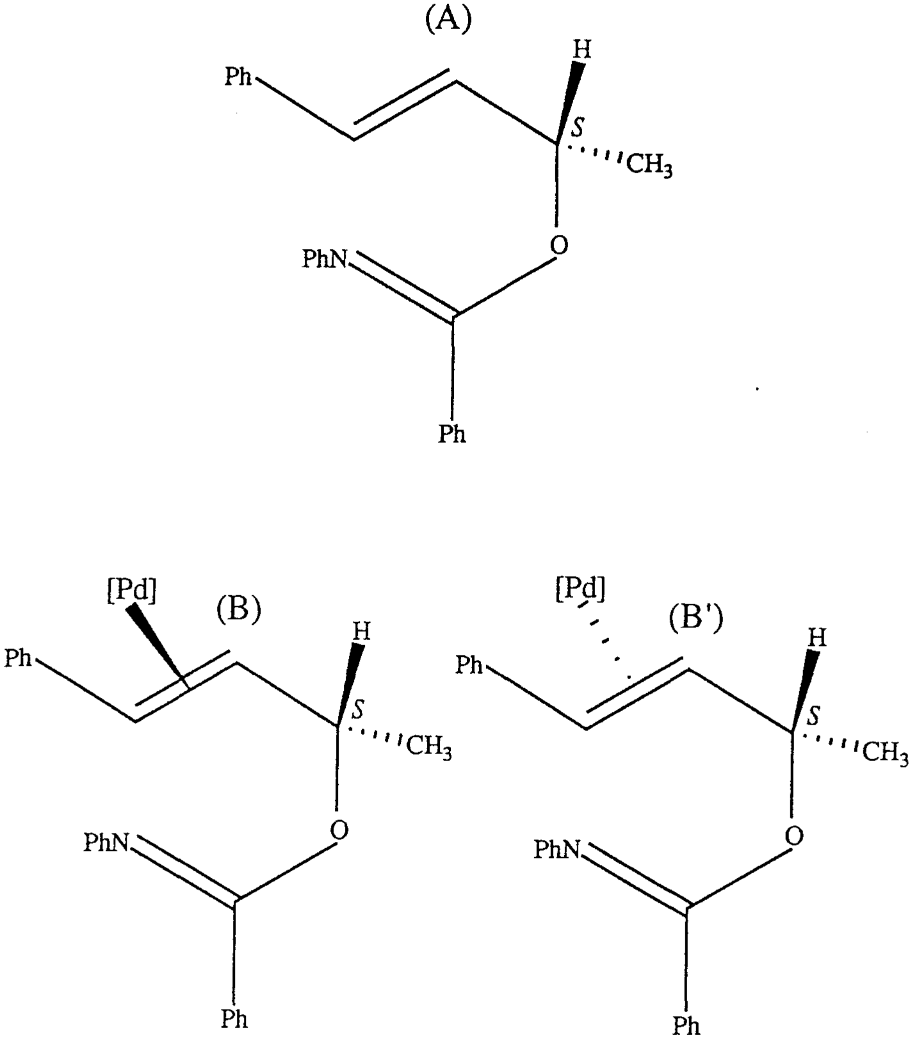


Figure I.3. (A) Optically Active Allyl Imidate from Bosnich and Schenck.; (B) and (B') Show the [Pd] Species Binding to the Two Diastereomeric Faces of the Olefin, thus Determining the Chirality of the Product.

reaction[14, 59] Yet other than the initial studies from Henry and the individual stereochemical studies of Bosnich (allylic imidate) and Overman (Cope), many mechanistic questions still remain unanswered. This work will attempt to answer some of the unanswered questions.

I.4.1 Electronic Effects in Palladium(II) Catalyzed Reactions.

As opposed to Tl(III) and Hg(II), many palladium(II) reactions with organic species are relatively non-polar and the rates of reaction are governed largely by steric factors. Certain palladium(II) reactions suggest intermediates formed by the electrophilic attack on olefins and aromatic species. These include aromatic coupling,[60] aromatic substitution,[61] olefin cis - trans and allylic isomerization[48] and olefin coupling. However in the case of the aromatic reaction the amount of meta isomers formed were so high that some workers doubted the reactions proceeded through an aryl palladium(II) species formed by an aromatic palladation reaction. Stock, in a significant study, showed that the aromatic palladation, although non-selective, adheres to the selectivity relationship.[62] The ability of palladium(II) to undergo these reactions with transition states that are charge starved or carbocationic in nature, depends on the Pd(II) species. Thus $Li_2Pd_2Cl_6$, the species present in acetic acid containing chloride, will cause olefin isomerization but not the other reactions. It would be possible, therefore, to prepare several known palladium(II) cationic species like $[Pd(CH_3CN)_4](BF_4)_2$, $[Pd(PPh_3)_2(CH_3CN)_2](BF_4)_2$, $[Pd(PPh_3)_3(CH_3CN)](BF_4)_2$, $[Pd(\eta^5\text{-}C_5H_5)(PR_3)(R'CN)]^+$. These cationic species are certainly more electrophilic than neutral or negatively charged species used normally in Pd(II) catalysis. These species do in fact catalyze some reactions more effectively than the more common acetate and chloride containing catalysts. This is certainly due in large measure to their positive charge but also may result from the fact they have labile ligands in the co-ordination sphere of the Pd(II). The transition states of these species must contain considerable carbonium ion character. In fact new reactions related to this carbonium ion character, like olefin oligomerization[63] and polymerization[64] have been observed.

There has been no systematic effort to quantitatively measure the degree of carbonium ion in the transition states for the various Pd(II) species whether anionic, neutral or cationic for any of the reactions with polar transition states. Mechanistic studies require (a) the equilibria in question be clearly delineated; (b) the rate expression be established for the reaction in question, and if possible without the interference of side reactions; (c) the possible detection of intermediate(s); and (d) the establishment of stereochemistry under the reaction conditions.

The approach is to prepare esters of an allylic alcohol species to serve as probe molecule for a [3,3] rearrangement. In keeping with earlier work, allylic esters would be chosen because (a) they would be a logical continuation of the earlier work, and (b) a number of substituted benzoic acids are freely available to prepare benzoate esters. The use of an aromatic ring is useful in the study of electronic effects, and as long as the ortho position is avoided, steric interference is avoided. In addition, the two oxygens could provide stabilization for a positively charged intermediate. The predominant task would then be kinetic. Quantitative evaluation of the degree of carbocationic nature, if such exists in the intermediate, would come about in studying the electronic effects of the reaction.

I.5. The Approach.

The evaluation of the electronic effects would form the major part of the kinetic studies on the allylic isomerization. Preliminary work on allylic alcohols and allylic esters provided insight which indicated that the problem should be approached in the following manner: Choose an organic probe molecule that would meet certain specifications. The benzoate ester of 2-methyl-3-buten-2-ol was chosen because: (a) it has the facility to be modified to study electronic effects and as long the ortho position is avoided, steric factors are minimized; (b) the aromatic ring and the two oxygens could help stabilize any kind of charge being formed in the transition state; (c) the substrate and any rearrangement product would possess unique NMR signals that could be used to unambiguously study kinetics; (d) the increased vinyl substitution would slow down the reaction to such an extent that the sampling of the reaction mixture would be a very convenient kinetic procedure; (e) the center carbon of the allyl moiety is left unsubstituted to favor the palladium - carbon sigma bond by oxypalladation; and (f) since the substituent groups are sufficiently separated from the double bond to which the Pd(II) will complex, their effect on the π - complex formation constants should not be too great.

Solvents and reaction conditions would be chosen appropriately. The plan is to begin mechanistic studies in acetic acid. The catalytic species would be $Li_2Pd_2Cl_6$, the predominant Pd(II) species in glacial acetic acid in the presence of excess chloride and the sequence of work would incorporate the following.

(a) The complications of the isomerization with exchange can almost certainly be avoided if the excess acetate were avoided. Of course, the absence of this complication must be demonstrated.

(b) Establish the occurence of the isomerization under convenient reaction conditions. Here convenient is defined as a set of conditions under which kinetic studies are possible, and with little or no side reactions. In addition it must be such that the region must be conducive to studying electronic effects with the various substituted benzoate species.

(c) Determine the rate expression under those conditions, and with the help of this rate expression, the product analysis and other pertinent information propose the best possible mechanism consistent with this information.

(d) Finally, extend the kinetic studies to the species with the electron donating and electron releasing groups and try to determine if the electronic effects could be quantified. Studies of such nature in palladium catalyzed reactions are few.[65] The chances of a Hammett type relationship are envisaged as the means for such correlation. In other words, if the reaction proceeded through a transition state that was positively charged then the quantification of the degree of carbonium ion would be the logical pursuit.

PART ONE: CHAPTER II

EXPERIMENTAL

II.1 General Methods.

II.1.1. Instruments.

All ^{1}H NMR spectra were recorded on a 60 MHz Varian EM 360 spectrometer or a 300 MHz Varian VXR 300 spectrometer. ^{13}C and ^{31}P NMR spectra were obtained on a Varian VXR 300 spectrometer at 75.46 MHz and 121.44 MHz respectively. The parameters given refer to $CDCl_3$ solutions unless specified otherwise. Chemical shifts for ^{1}H and ^{13}C are relative to $(CH_3)_4Si$. Where complex signals were obtained, the spectral parameters are given as chemical shift (multiplicity$_A$..., J_A, J_B...Hz, relative intensity). ^{31}P chemical shifts are relative to 85% H_3PO_4 at 0.0 ppm. IR spectra were obtained on a Perkin Elmer 1310 Infrared spectrometer. Melting points were recorded on a Laboratory Devices Mel-Temp apparatus using a calibrated thermometer. Sample weighings were performed on a Sartorius Model 2842 analytical balance and are accurate to ± 0.05 mg. Studies at constant temperature were carried out in a water bath maintained at 25° ± 0.2° C using a Messgeräte - Werk Lauda model B-1 thermostat.

II.1.2. Chemicals.

All chemicals were from Aldrich Chemical Company, unless otherwise specified, and were used as received. Solvents were reagent grade. Dichloromethane, petroleum ether and acetonitrile (Chempure brand, GC grade, Curtin Matheson Scientific Inc.) were dried over calcium hydride (CaH_2) and distilled and stored under Argon. Diethyl ether was dried using sodium and benzophenone and distilled and stored under Argon. Purified solvents were usually stored over 4 Å molecular sieves (Davison Chemical). Solvents were deoxygenated only if necessary and by standard inert gas purge - vacuum degas techniques.[66] In case a solvent or other chemical was subjected to other more stringent purification procedures, such will be mentioned in the text following.

II.2. Synthetic Procedures.

Glassware was usually oven dried overnight at 120° C and cooled under inert gas.

II.2.1. 2-(2'-Methyl-3')-butenyl Benzoate.

This procedure is a modification of the method of Triebs and Hintermeier.[67] The apparatus consisted of a three necked 100 mL round bottom flask fitted with a condensor. The side arms were used for inert gas inlet and outlet. 4.30 g (0.050 mol) of 2-methyl-3-buten-2-ol and 35 mL of pyridine (redistilled under nitrogen before use) were stirred at room temperature. An equivalent amount of benzoyl chloride was added via an addition funnel over a period of 3 - 5 minutes. Reaction solutions were initially predominantly yellow, turning to a darker shade over the day long reaction period. The solution was heated between 80° C and 100° C and the reaction was run under positive inert gas pressure.

After the reaction was stoppped, the mixture was cooled, diluted with 30 mL of CH_2Cl_2 and 30 mL water. The organic layer was washed repeatedly with 10% hydrochloric acid (HCl) to remove excess pyridine. The washes were carried out until the solution was acidic to litmus paper. The organic layer was washed with 2 x 25 mL of saturated sodium bicarbonate ($NaHCO_3$) and finally with 25 mL water. The CH_2Cl_2 layer was dried with anhydrous magnesium sulfate ($MgSO_4$) and the solvent was air evaporated after gravity filtration to remove the $MgSO_4$ to yield the crude product. Purification was carried out chromatographically using a neutral alumina (Aluminum oxide, neutral, activated, Brockmann I, standard grade, ~ 150 mesh, 58 Å CAMAG 507-C-1, surface area 155 m^2g^{-1}) column. The elutant used was petroleum ether. Product is a colourless oil (80 %)

^{1}H NMR: δ1.68 (s, 6H); 5.10 (d, J = 10.7 Hz, 1H); 5.25 (d, J = 17.6 Hz, 1H); 6.22 (dd, J = 17.5, 10.7 Hz, 1H); 7.38 - 8.07 (m, 5H).

^{13}C NMR: δ26.45; 81.12; 112.69; 128.09; 129.34; 131.48; 132.44; 142.46; 165.20.

IR(neat): C-O-C (1278 cm^{-1}); -C=O (1715 cm^{-1})

II.2.2. 2-(2'-Methyl-3')-butenyl *p*-Nitrobenzoate.

This compound was made by a procedure analogous to that of **II.2.1.** Product obtained is a cream colored solid. M.P.: 112 - 114 °C (82%)

^{1}H NMR: δ1.69 (s, 6H); 5.10 (d, J = 10.7 Hz, 1H); 5.23 (d, J = 17.5 Hz, 1H); 6.19 (dd, J = 17.5, 10.8 Hz, 1H), 8.16 (d, J = 7.0 Hz, 2H); 8.28 (d, J = 7.0 Hz, 2H).

^{13}C NMR: δ26.14; 82.78; 113.57; 123.38; 130.54; 137.04; 141.77; 145.20; 163.36.

IR($CDCl_3$): C-O-C (1274 cm^{-1}); -C=O (1703 cm^{-1}).

II.2.3. 2-(2'-Methyl-3')-butenyl *p*-Chlorobenzoate.

This compound was made by a procedure analogous to **II.2.1.** Product is a colorless oil. (76.3 %)

^{1}H NMR: δ1.65 (s, 6H); 5.10 (d, J = 10.8 Hz, 1H); 5.23 (d, J = 17.5 Hz, 1H); 6.19 (dd, J = 17.6, 10.8 Hz, 1H)

^{13}C NMR: δ26.47; 81.79; 112.93; 128.44; 130.06; 130.78; 138.88; 142.28; 164.33.

IR(neat): C-O-C (1285 cm^{-1}); -C=O (1730 cm-^{1}).

II.2.4. 2-(2'-Methyl-3')-butenyl *p*-Methylbenzoate.

This compound was made as in **II.2.1.** Reaction time was a 1 h longer.

^{1}H NMR: δ1.69 (s, 6H); 2.40 (s, 3H); 5.10 (d, J = 10.8 Hz, 1H); 5.23 (d, J = 17.5 Hz, 1H); 6.21 (dd, J = 17.5, 10.8 Hz, 1H); 7.22 (d, J = 7.0 Hz, 2H); 7.92 (d, J = 7.0 Hz, 2H).

^{13}C NMR: δ21.49; 26.59; 80.97; 112.58; 128.85; 128.96; 129.06; 142.74; 143.07; 165.39.

IR(neat): C-O-C (1284 cm^{-1}); -C=O (1728 cm^{-1})

II.2.5. 2-(2'-Methyl-3')-butenyl *p*-Methoxybenzoate.

This compound was made as in **II.2.1.** The reaction time was 6 h longer and the yield is significantly lower. (36.7%).

^{1}H NMR: δ1.68 (s, 6H), 3.86 (s, 3H); 5.10 (d, J = 10.8 Hz, 1H); 5.23 (d, J = 17.6 Hz, 1H); 6.21 (dd, J = 2.1, 1H); 6.91 (d, 7.0 Hz); 7.98

(d, 7.0 Hz, 2H).

^{13}C NMR: δ26.69; 55.28; 80.81; 112.52; 113.46; 124.00; 131.80; 142.92; 163.14; 165.10.

IR(neat): -O-CH_3 (1254 cm^{-1}); C-O-C (1284 cm^{-1}); -C=O (1708 cm^{-1}).

II.2.6. 2-(2'-Methyl-3')-butenyl *p*-Ethoxybenzoate.

This compound was made as in **II.2.1.** Reaction time was 9 h longer (64 %).

^{1}H NMR: δ1.41 (t, J = 14.1 Hz, 3H); 1.62 (s, 6H); 4.05 (q, J = 14.2 Hz, 2H); 5.10 (d, J = 10.8 Hz, 1H); 5.23 (d, J = 17.5 Hz, 1H); 6.17 (dd, J = 17.5, 10.8 Hz, 1H); 6.86 (d, J = 7.0 Hz, 2H); 7.92 (d, J = 7.0 Hz, 2H).

^{13}C NMR: δ14.65; 26.64; 63.60; 80.79; 112.53; 113.86; 123.83; 131.41; 142.83; 162.47; 165.20.

IR(neat): -O-CH_2CH_3 (1248 cm^{-1}); C-O-C (1280 cm^{-1}); -C=O (1700 cm^{-1}).

II.3. Synthesis of Catalysts.

II.3.1. Lithium Di-μ-chloro*bis*[dichloropalladate(II)].

This catalyst was made by a procedure from the literature.[68] The glacial acetic acid (HOAc) (Fisher, reagent grade) was dried in a nitrogen atmosphere by using freshly prepared boron triacetyl.[69] Distillation was carrried out in an all glass apparatus (Kontes K 547600) and the acetic acid was stored under Argon.

1.700 g (0.0100 mol) of palladium chloride (Aesar) and 0.7598 g (0.0179 mol) of lithium chloride (LiCl) were taken in a dry Erlenmeyer flask. About 75 mL of dry glacial acetic acid was added, the flask stoppered and the solution stirred for 10 h at 60 °C. The flask was cooled, the solution filtered and the dark red - brown filtrate made up to the mark in a 100 mL volumetric flask. The molar content of the palladium in the stock catalyst solution was determined by gravimetry.[70]

II.3.2. Tetraacetonitrilepalladium(II) Tetrafluoroborate.

This compound was made by a modification of the method of Schramm and Wayland.[71] 1.00 g (9.40 x 10-3 mol) of palladium sponge (Aesar) and 2.20 g (0.0188 mol) of nitrosyl tetrafluoroborate were stirred in 50 mL of degassed (to remove oxygen) CH_3CN under vacuum. The reaction was carried out in a three necked 250 mL round bottom flask that had been thoroughly purged with Argon. NO generated in the course of the reaction was vented periodically. The reaction gradually became a very pale canary yellow color. After stirring for 15 h., the mixture was filtered under an Argon atmosphere to yield a yellow filtrate from which an air sensitive pale yellow compound was obtained by the addition of anhydrous, degassed diethyl ether by cannulation. Subsequent syntheses revealed that the same compound could be precipitated out of solution using hexane or petroleum ether or dichloromethane. In later preparations petroleum ether was the preferred solvent after vacuum concentrating the reaction solution. The compound was dried under vacuum. (3.28 g - 4.08 g, 75.8% - 98%).

^1H NMR(CD_3NO_2):	δ2.65 (s)
IR(nujol):	BF_4^- (1000-1100, 760 cm^{-1}); -CN (2335 cm^{-1})

II.3.3. Diacetonitrile*bis*(triphenylphosphine)palladium(II) Tetrafluoroborate.

This compound was prepared by a modification of the method of Sen and Lai.[72] 0.25 g (5.63 x 10^{-3} mol) of tetraacetenitrilopalladium(II) tetraflouroborate was carefully weighed and taken in a 100 mL single necked round bottom flask under inert conditions in a glove bag. To this was added 0.295 g (1.144 x 10^{-3} mol, two equivalents relative to **II.3.1**) of triphenyl phosphine (recrystallized from absolute ethanol) and 35 mL of CH_2Cl_2. The bright yellow solution was stirred for 4.0 h (this reaction time is probably not needed). Following concentration of the solution on a vacuum pump, a beautiful, bright, yellow solid was obtained on addition of 40 mL of petroleum ether. The compound was washed with diethyl ether and dried under vacuum. (0.37 - 0.41 g, 74% - 80%) The compound is mildly air sensitive and repeated exposure to the air or light causes a darkening to orange, orange - red and finally through to black. The literature does not mention this fact.

^{1}H NMR:	δ1.85 (s, 6H); 7.2 - 7.4 (m, 30 H)
^{31}P NMR {^{1}H}:	δ32.1 (s)
IR(nujol):	BF_4^- (1000 - 1100 cm^{-1}); -CN (2335 cm^{-1})

II.3.4. Monoacetonitrile*tris*(triphenylphosphine)palladium(II) Tetrafluoroborate

This compound was made in a reaction analogous to **II.3.2.**[64a] 0.11 g (7.63 x 10^{-3} mol) of **II.3.1** and 0.60 g (2.29 x 10^{-3} mol) of triphenylphosphine. The reaction was run in degassed CH_2Cl_2. The solution was concentrated under vacuum after stirring for 6.0 h, and the precipitate obtained on cannulation of petroleum ether into the solution was vacuum dried after precipitation. The compound tended to decompose after a long period of exposure. The compound is a light yellow color. (0.47 g, 96 %)

^{31}P NMR{^1H} ($CDCl_3$): δ27.6 (d, J_{PP} = 11.7 Hz, 2P); 34.5 (t, J_{PP} = 11.7 Hz, 1P).

IR(nujol): BF_4^- (1000 - 1100 cm^{-1}); -CN (2335 cm^{-1})

II.3.5. *Bis*(benzonitrile)dichloropalladium(II).

This compound was made by the method of Doyle, Slade and Jonassen.[73] It was recrystallized from hot benzene by first doing a hot filtration and then by the addition of pentane to precipitate the compound. It was washed with pentane and dried *in vacuo*. The compound was stored under Argon.

II.4. Studies Using $Li_2Pd_2Cl_6$.

The primary focus of the mechanistic studies was in terms of kinetics. Kinetic studies were carried out at 25 °C in a thermostatically controlled water bath. Evaluation of data was via analysis after ^1H NMR experiments. Using $Li_2Pd_2Cl_6$, the experiments were performed in glacial HOAc.

II.4.1. Procedures in Anhydrous HOAc.

Stock solutions of $Li_2Pd_2Cl_6$ and LiCl were prepared in the dried glacial acetic acid. (see **II.3.1**). Solutions were thermostated for at least 1 h before runs were begun.

In a typical kinetic run, calculated amounts of $Li_2Pd_2Cl_6$ and LiCl were pipetted, using glass pipettes into an argon flushed, dry 10 mL volumetric flask. Glacial HOAc was added to make the volume almost 10 mL. The allylic ester substrate, **II.2.1.**, was added by mass, the solution quickly made up to the 10 mL mark, the flask stoppered, shaken and placed in the water bath. Timing was begun simultaneously.

At specific times, 1.0 mL aliquots were withdrawn using a pipette and transferred into a waiting 125 mL seperatory funnel containing 2 - 3 mL of CH_2Cl_2 and 2 - 3 mL of brine in order to quench the reaction by extracting the organic species. After shaking, the layers were separated. The aqueous layer was re-extracted with 2 - 3 mL of CH_2Cl_2. The combined organic layers were washed with 2 x 5 mL portions of saturated $NaHCO_3$, to remove the excess HOAc. A final water wash (10 mL) was followed by drying with $MgSO_4$ (anhydrous). The solvent was air evaporated in a fume hood at room temperature. The residue thus obtained was saved for analysis.

The product analysis, evaluation of extent of reaction, yield and subsequent determination of k_{obs} were based on the ^1H NMR of this residue. The reactions were usually monitored for at least three half lives (93.8 %). Kinetic runs were always run in duplicate.

II.4.2. Rate Expression.

In order to establish dependencies of the various species involved, two stages of experimental work were required. In the first stage, controls were run, in order to determine which of the species caused a variation in the rates of reaction. In the second stage the concentrations of the species that were established to be in the rate expression in stage one were varied to determine kinetic order. $[Li_2Pd_2Cl_6]$ was varied between 2.05 x 10^{-3} M and 21.3 x 10^{-3} M (see **Table III.2.**) while maintaining $[LiCl]_{(in)}$ and [**II.2.1**] at 0.0504 M and 0.100 M respectively. The order in LiCl was determined with $[LiCl]_{(in)}$ varied from 0.030 M to 0.202 M. (see **Table III.2.**). The $[Li_2Pd_2Cl_6]$ and [**II.2.1**] were held at 0.004 M and 0.100 M respectively. Each run obeyed first order kinetics and that established order in [**II.2.1**]. A separate experiment was done in which the concentration of **II.2.1** was halved and a resultant halving of the rate confirmed assumption of first order dependence. The experimental method in all these experiments was exactly as described in **II.4.1** above.

II.4.3. Energy of Activation.

Only **II.2.3.** was used for these studies. With [**II.2.3.**] at 0.100 M, [$Li_2Pd_2Cl_6$] = 12.3 x 10^{-3} M and [LiCl] = 0.050 M, the temperature effect on the rate was evaluated. Temperatures were varied from 298.2 K to 323.2 K. The method of study was the evaluation of k_{obs} values from the ^{1}H NMR of the various samples isolated at different time intervals as described in **II.4.1**.

II.4.4. Electronic Effects.

All six ester substrate species (**II.2.1.** through **II.2.6.**) were used for these studies. Rate constants were determined by experiments as described in **II.4.1.** Usually between eight and eleven data points were obtained. Kinetics were always duplicated.

II.5. Studies Using Tetraacetonitrilepalladium(II) Tetrafluoroborate.

The additions of this catalyst were made in a glove bag because of the air sensitive nature of this species.

II.5.1. Purification of CH_3NO_2.

The purification of nitromethane was performed by a modified procedure.[74] After three passes through an alumina column (30 cm in length) the nitromethane was further dried using phosphorus pentoxide (P_2O_5) under nitrogen and then 500 mL was fractionally distilled from

21.0 g of P_2O_5 using a 15 cm glass fractionating column. A middle 250 mL portion was collected and redistilled fractionally from P_2O_5. The nitromethane thus obtained, after degassing, was stored over molecular sieves and under Argon.

II.5.2. In Nitromethane Solvent.

To a degassed 10 mL volumetric flask was added 0.0218 g (4.91 x 10^{-5} mol) of $[Pd(CH_3CN)_4](BF_4)_2$, **(II.3.2)**, so that concentration would be 4.9 x 10^{-3} M in 10 mL. Almost 10 mL of CH_3NO_2 was added to the flask and the solution was thermostated for more than 1 h. To this flask was added 0.1902 g (1.0 x 10^{-3} mol) of the unsubstituted benzoate ester substrate **(II.2.1.)**. The solution was made up to the 10 mL mark, stoppered and shaken. Timing was begun simultaneously.

II.5.2.1. Isolation of Product Via Column Chromatography.

A column 5.0 cm in height and 1.0 cm in diameter was made using Florisil (J. T. Baker Chemical Company, 100 - 200 mesh, M-3697). The column was packed using petroleum ether. At particular time intervals, 1.0 mL aliquots were withdrawn via syringe, taken in a 5 mL round bottom flask and the solvent was quickly vacuum evaporated. (less than 2 minutes) The yellowish residue was loaded on the column after adding 2 mL of petroleum ether. The flask was rinsed with 2 x 2 mL of petroleum ether. All the rinses were combined and loaded on the column. The solvent collected from the column was evaporated in air and the residue analyzed by ^1H NMR.

II.5.2.2. Isolation of Product by Chelation of Palladium.

A 1.0 mL aliquot of the reaction mixture described in **II.2.6.** was taken in a beaker and acidified to ~pH 1. To this was added 10 mL of dimethyl glyoxime stock solution, made as described in **II.3.1.** The solution was covered and set aside and over a period of 1.0 h the formation of golden yellow fine needle like crystals was observed. The solution is filtered, the filtrate neutralized with saturated $NaHCO_3$ and finally washed with water and dried with $MgSO_4$ (anhydrous). The removal of the solvent afforded the product(s) to be analyzed.

II.5.3. In Acetic Acid Solvent.

Attempts were made to study the reaction of **II.3.2.** with the unsubstituted ester substrate **II.2.1.** in HOAc. On the addition of 10 mL of dry glacial HOAc at room temperature to 0.0218 g (mol) of **II.3.2.**, a yellowish green solution was obtained. To this was added 0.1902 g (1.0×10^{-3} mol) of **II.2.1.** The solution was stirred at room temperature for 10 h. The reaction was worked up by extracting the ester using hexane and brine. The hexane layer was washed with 2 x 20 mL of saturated $NaHCO_3$, 10 mL water, dried ($MgSO_4$) and finally analyzed by ^1H NMR after evaporating the solvent.

II.6. Studies Using $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$.

This catalyst was weighed out under inert conditions in a glove bag only because it was noticed that prolonged exposure decomposed the catalyst.

II.6.1. In Nitromethane Solvent.

These experiments were performed as in **II.5.2.** The product isolation corresponded to the method in **II.5.2.1.**, that is, via the florisil column.

II.6.2. In Acetic Acid Solvent.

This experiment was done as in **II.5.3.** A similar yellow - green color to that in **II.5.4.** was noticed. Isolation was by extraction.

II.6.3. In Dichloromethane Solvent.

Initial experiments were carried out in a 25 mL round bottom flask at room temperature. 0.3035 g (3.42×10^{-3} mol) of $Pd(CH_3CN)_2(PPh_3)_2^{2+}$ was taken in the degassed round bottom flask. To it was added 10 mL of CH_2Cl_2. The catalyst dissolved almost immediately to give a light yellow solution. To this solution 0.1902 g (1.0×10^{-3} mol) of the unsubstituted ester, **II.2.1.** was added and the product isolated by the florisil column procedure. The solvent was removed on a vacuum pump. Analysis of product was by ^1H NMR.

Subsequently it was found that the isolation could be performed in a simpler manner. The reaction was run in a 10 mL volumetric flask with a septum cap, at 25 °C. In a typical experiment 0.0444 g (5.00×10^{-5} mol) of catalyst (**II.3.3.**) and 0.1902 g (1.00×10^{-3} mol) of allylic ester (**II.2.1**) were added and the solution made to the 10 mL mark. Then 1.0 mL aliquots were withdrawn at regular intervals either by pipette or syringe. The aliquot was added to ca. 10 mL of petroleum ether in a 50 mL beaker. Immediate formation of a voluminous yellow precipitate was noticed. The solution was swirled, filtered via standard glass funnel and the filtrate collected. Evaporation of the solvent afforded the product(s) that were analyzed by ^1H NMR.

II.6.4. Electronic Effects in Dichloromethane.

The other five allylic ester substrates (**II.2.2.** through **II.2.6.**) were studied in a similar manner in order to obtain k_{obs} values individually.

II.7. Studies Using $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$.

This species was also weighed out under inert atmosphere conditions in a glove bag. Studies in nitromethane were performed as in **II.5.2.** 0.1108 g (1.00×10^{-4} mol) of Pd $(CH_3CN)(PPh_3)_3^{2+}$ was used with 0.1902 g (1.00×10^{-3} mol) of the allylic ester substrate. Only starting materials were recovered at 25° C.

Experiment were performed in dichloromethane as in **II.6.3.** The product was isolated after precipitating out the palladium species using hexanes.

II.8. Studies Using *Bis*(benzonitrile)dichloropalladium(II).

The catalyst was usually recrystallized before use. The kinetic studies were carried out as usual at 25 °C. The catalyst was usually added last to prevent the precipitation of the palladium species, probably because of dimerization.

II.8.1 In Acetic Acid Solvent.

A 0.1902 g (1.0×10^{-3} mol) sample of **II.2.1** was thermostated in a dry 10 mL volumetric flask with almost 10 mL of distilled, degassed dichloromethane. To this was added 0.0192 g (5.0×10^{-3} mol) of **II.3.5.**

In a precisely similar manner, the other esters, with the electron releasing and donating substrates were evaluated. Reactions were standardly followed past at least three half lives.

II.8.2. In Dichloromethane Solvent.

Attempts were made to study the electronic effects using the same catalyst, **II.3.5.** in CH_2Cl_2. Using 0.1902 g (1.0 x 10^{-3} mol) of substrate, **II.2.1.** and 0.0192 g (5.0 x 10 $^{-5}$ mol) of catalyst but the reaction was complete by the time the first sample was taken.

II.8.3. In Deuteriated Chloroform Solvent.

Using the same conditions as above, an attempt was made to monitor this reaction directly on the Varian VXR 300 NMR. The reaction was run on a 1.0 mL scale. Into a 1.0 mL volumetric flask 0.0190 g (1.0 x 10^{-4} mol) of substrate **II.2.1.** was weighed. The volume was made up to the mark using $CDCl_3$. This mixture was taken in a 5 mm NMR tube and the ^1H spectrum obtained at 25° C using the standard Varian ^1H pulse sequence using only two transients.[75] 0.00190 g (5.00 x 10^{-6} mol) of the catalyst was added, the tube shaken and the spectrum obtained. The entire process took 3.0 min and it was noticed that in this time the reaction was complete. Keeping the same concentration of substrate, attempts to reduce the amount of catalyst to 6.3 x 10^{-4} g (1.6 x 10^{-6} mol). This attempt showed that the reaction was almost complete in less than 3.0 min. Smaller quantities were not tried because weighing out minute amounts of catalyst was inaccurate.

PART ONE: CHAPTER III

RESULTS

III.1. Synthetic Results.

All the compounds synthesized were characterized by standard spectroscopic methods (^{1}H and ^{13}C NMR and IR). The yields on most of the compounds synthesized were usually not optimized.

III.1.1. Synthesis of Allylic Ester Substrates.

Six allylic ester substrates, **II.2.1.** through **II.2.6.**, were synthesized. The esters were stable for long periods of time. They were periodically rechecked just prior to use so as to monitor any decomposition that might have occured. Yields obtained in the syntheses are collected in **Table III.1.**

III.1.2. Synthesis of Catalysts.

All the catalysts were synthesized by established literature procedures. In determining palladium content, standard gravimetric procedures involving the use of DMG were employed. Thus, if stock solutions were made, they were always analyzed for palladium content.

Table III.1. Synthesis of Allylic Ester Substrates.[a]

No	Allylic ester	Substituent (*p*)	% yield
1.	**II.2.1.**	-H	80.0
2.	**II.2.2.**	$-NO_2$	81.8
3.	**II.2.3.**	-Cl	76.3
4.	**II.2.4.**	$-CH_3$	65.0
5.	**II.2.5.**	$-OCH_3$	36.7
6.	**II.2.6.**	$-OC_2H_5$	64.0

[a] Benzoate esters of 2-methyl-3-buten-2-ol.

III.2. Mechanistic Studies Using $Li_2Pd_2Cl_6$.

The kinetic studies were carried out at 25 °C in anhydrous acetic acid and involved palladium(II) chloride in solutions containing known excess amounts of LiCl.

III.2.1. Equilibria To Be Considered.

To define the kinetics of any system completely, the mode of interaction of the species involved must be known. Spectral and molecular weight studies[76] indicated the following equilibria must be considered.

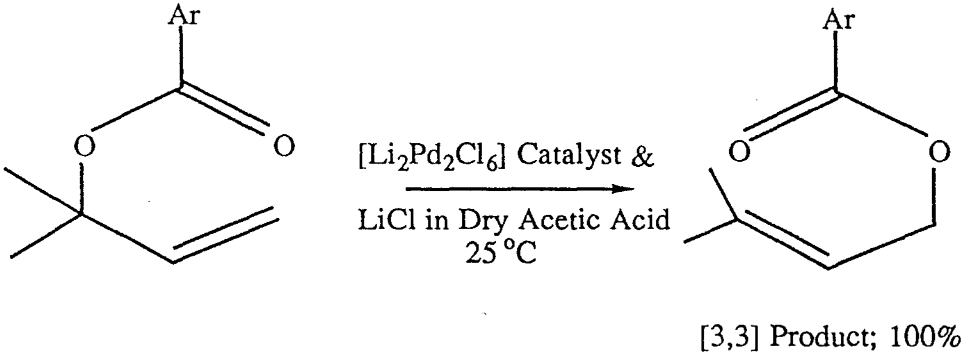
$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftarrows} 2Li_2PdCl_4 \qquad (K_1 = 0.10\ M^{-1}) \qquad (III.1)$$

$$2LiCl \overset{K_2}{\rightleftarrows} Li_2Cl_2 \qquad (K_2 = 2.6\ M^{-1}) \qquad (III.2)$$

For any set of reaction conditions, the concentrations of all the species present could be determined only after taking into account these equilibrium constants.

III.2.2. Catalyzed Product and Controls.

The major species present in solution were $Li_2Pd_2Cl_6$, LiCl, HOAc and the allylic ester, **II.2.1.** Control runs indicated that the reaction was catalyzed by the Pd(II) species. Under all conditions studied, the reaction always proceeded to completion and quantitatively gave only the [3,3] isomerized product of **II.2.1.** under all the conditions described (**Figure III.1.**). In the absence of the Pd(II) species, a test solution containing all species, afforded no measurable thermal reaction at 25 °C. This test run was monitored for a period of two



Ar = C_6H_4-X, where X = -OEt, -OMe, -Me, -H, -Cl, -NO_2.

Figure III.1. Only Product in the Catalyzed Rearrangement.

months.

In an experiment under one of the described sets of conditions (see **Table III.2.**), if the product allylic ester was used instead of the starting material no measurable reaction was detected. This confirmed the assumption of using 100% product formation for the data analysis described below.[77]

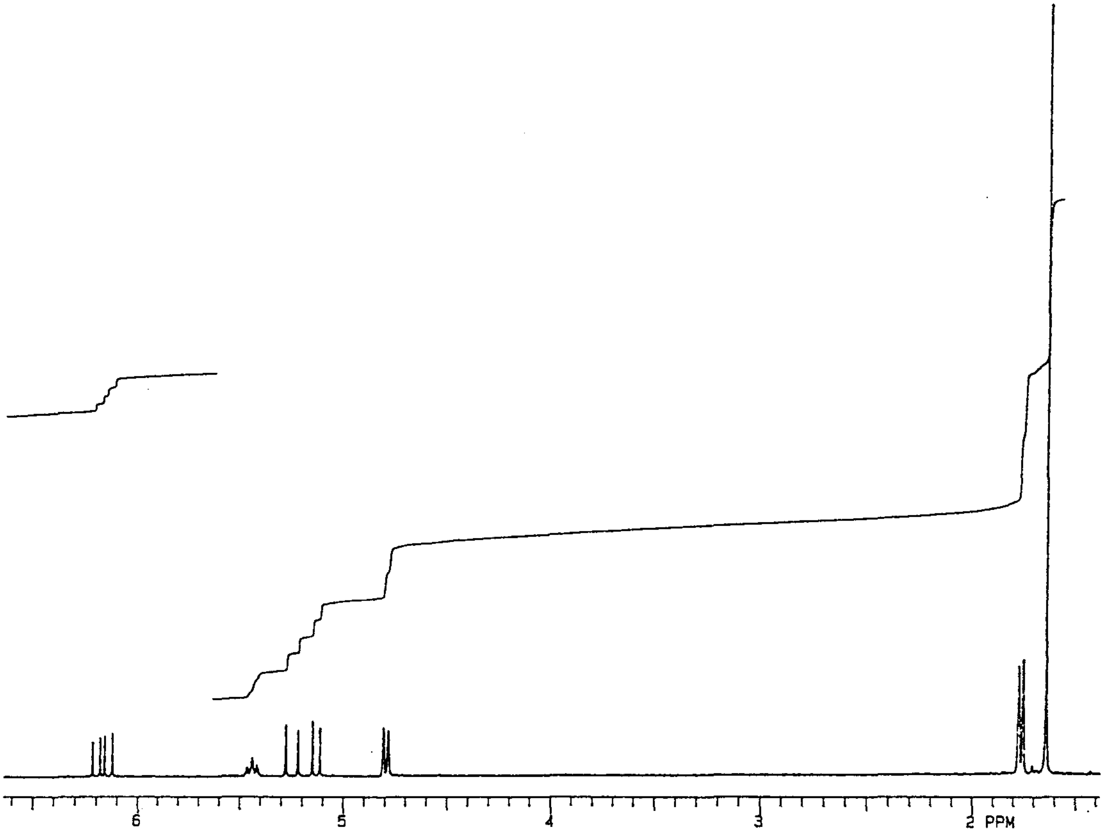
II.2.3. Method of Data Collection and Analysis.

Preliminary studies showed that the allylic ester was isomerized and the reaction proceeded to complete conversion to the [3,3] rearrangement product. Thus the relative amount of the starting allylic ester could be obtained easily as the ratio of the starting ester to the isomerized product by making use of the ^{1}H NMR integrals. All of the resonances from the starting allylic ester and the isomerized product did not overlap with any other resonance.

The methyl protons from **II.2.1.**, for example, shift downfield from a singlet at 1.68 ppm to a doublet at 1.78 ppm in the isomerized product. The signal arises further downfield because the methyl protons are now allylic in nature and it is a doublet because the methyl groups are now inequivalent (the allylic splitting is usually not resolved under the conditions of the NMR experiments) (**Figure III.2**). The positions of the protons in the isomerized product were confirmed by making the authentic product.

^{1}H NMR signals of interest appear at 1.78 ppm (d, 6H); 4.82 ppm (d, 2H) and 5.45 ppm (apparent t, further coupling, obviously due to the allylic methyls is seen, 1H: vinylic). There is some overlap in the aromatic region, but this is of little consequence for the purposes of the data analysis.

Figure III.2. Sample Spectrum Used in the Data Analysis Showing Allylic Ester (II.2.1.) and Isomerized Product.



III.2.4. Rate Expression.

In order to obtain the kinetic dependences on the various species, and thus establish a rate expression, the following experiments were performed. Each of the species present in solution, LiCl, allylic ester and Pd(II), were systematically varied while each of the other species was maintained constant. The pseudo first order rate constants in each particular species (k_{obs} values) thus obtained, were plotted versus concentration of that species to obtain order in that particular species.

III.2.4.a. Order in [Pd(II)].

By using the equilibria described earlier it can be shown that the predominant species in solution is the dimeric $Li_2Pd_2Cl_6$. Analysis of the data also shows us that the predominant species involved in the catalysis is the dimer. Order in $Li_2Pd_2Cl_6$ was obtained by maintaining $[LiCl]_{in}$ and [**II.2.1**] constant at 0.0504 M and 0.1001 M. First order k_{obs} values were obtained by plotting the natural logarithm of the relative amount of **II.2.1.** remaining versus time of sampling. The $[Li_2Pd_2Cl_6]_{in}$ was varied between 2.05 x 10^{-3} M and 21.3 x 10^{-3} M, and in each case a k_{obs} value was obtained as described above (see **Table III.2**). $[Li_2Pd_2Cl_6]_{corr}$ is the corrected concentration of the predominantly dimeric palladium(II) species after correcting for the small amount of monomer using the equilibria described in **III.2.1**. The first order rate constants were plotted against $[Li_2Pd_2Cl_6]_{corr}$ as shown in **Figure III.3**. A straight line (R^2 = 0.99) passing through the origin showed first order dependence.

The first two equilibria needed to be considered were given in equations **III.1** and **III.2**. Also, the manner in which we obtained our data depended on the fact that a given run had to be strictly first order in allylic ester. The data could only be fitted if this assumption were made. It has to be borne in mind that although a given reaction is strictly first order in allylic ester, there could be some inhibition by the allylic ester at higher concentrations due to the formation of the unreactive monomeric π complex. Formation of unreactive monomeric π complexes is shown in equations **III.3.** and **III.4.**

$$\mathrm{Li_2Pd_2Cl_6} + \text{2allylic ester} \quad \overset{K_3}{\rightleftarrows} \quad 2[\mathrm{LiPdCl_3}(\text{allylic ester})] \qquad \text{(III.3)}$$

$$\mathrm{Li_2PdCl_4} + \text{allylic ester} \quad \overset{K_4}{\rightleftarrows} \quad [\mathrm{LiPdCl_3}(\text{allylic ester})] + \mathrm{LiCl} \qquad \text{(III.4)}$$

Both equilibria shown here lead to the same monomeric π complex. The Li_2PdCl_4 shown in equation **III.3.** is the species obtained in equation **III.1.** It was found in the earlier work that assuming simultaneous equilibria for dimer and monomer with the allylic ester, there is at least a five fold excess of the monomeric π complex under certain conditions.[46] Henry attributed the low reactivity of the monomer to electrostatic effects. If the monomer species were active kinetically, then the kinetics at low [allylic ester] require that the order in $[Li_2Pd_2Cl_6]$ be one-half.

III.2.4.b. Order in Allylic Ester.

All of the described experiments indicated first order dependence in the allylic ester substrate **II.2.1.**, because the kinetic plots were all first order and data could not have

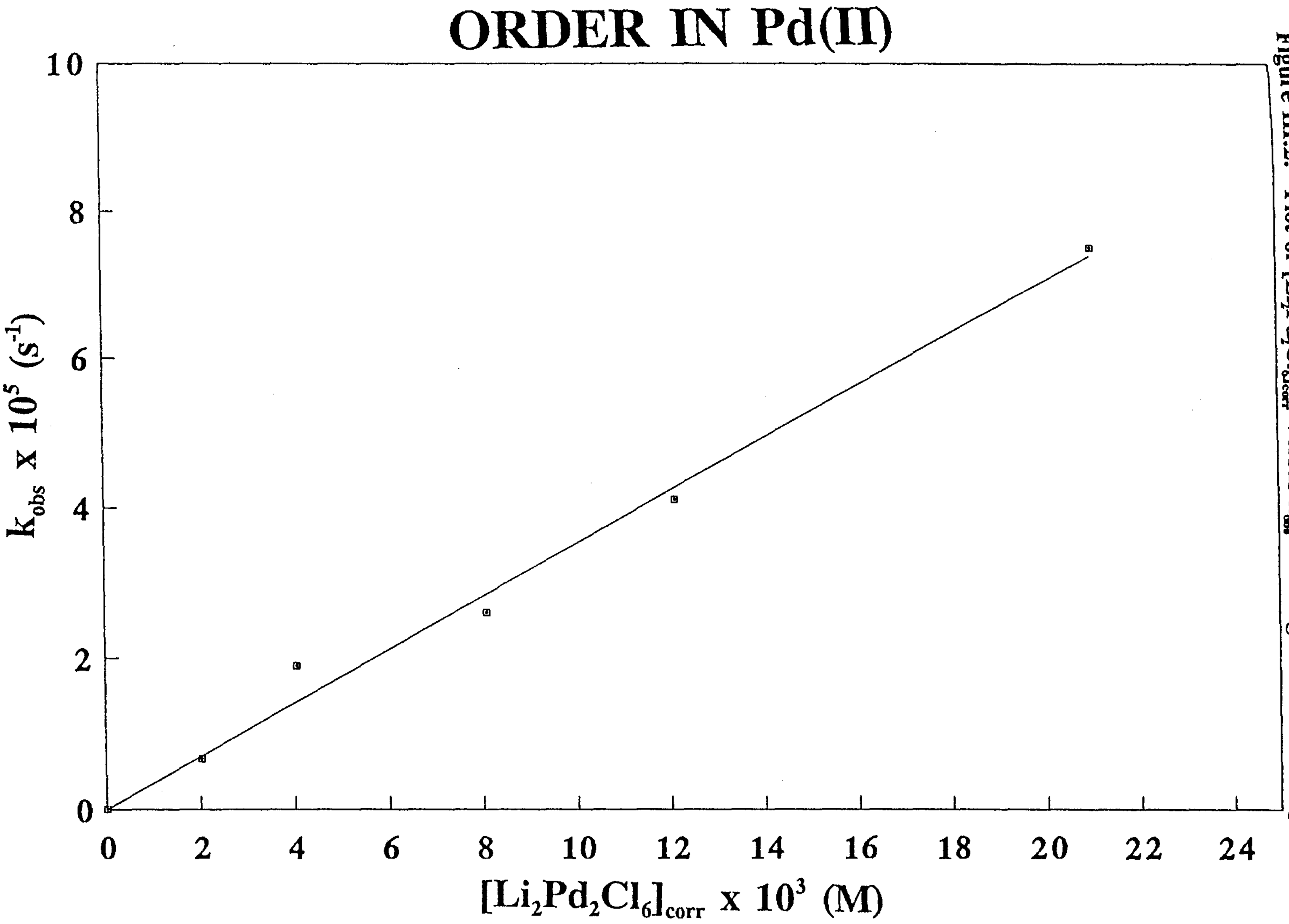


Figure III.2. Plot of [$Li_2Pd_2Cl_6$]$_{corr}$ Versus k_{obs} Showing First Order Dependence.

been treated in this manner otherwise. In addition, an experiment was run in which one-half of standardly used amount of ester was employed. The $t_{1/2}$ remained the same confirming first order reaction in [allylic ester]. Qualitatively no inhibition from the allylic ester was detected as was observed in the earlier work.[56] However this work did not explore the possibility of ester inhibition at much higher [allylic ester]. Also, there is no noticeable inhibition from the product.

III.2.4.c. Order in LiCl.

In a similar manner [LiCl] was varied with $[Li_2Pd_2Cl_6]_{in}$ and [**II.2.1**] kept constant at 0.0040 M and 0.1001 M respectively. In the range studied i.e., $[LiCl]_{in}$ varied from 0.030 M to 0.202 M. (**Table III.2.**). LiCl dimerizes to a small extent in glacial acetic acid under these conditions. $[LiCl]_{corr}$ is the corrected [LiCl] after correcting by using $K_2 = 2.6\ M^{-1}$ as described in **III.2.1**. A first order inhibition in $[LiCl]_{corr}$ was obtained as seen by the straight line ($R^2 = 0.98$) in **Figure III.4**. Thus in the range studied the rate expression is given by equation **III.5**,

$$\mathbf{Rate = k\ \frac{[Li_2Pd_2Cl_6]_{corr}\ [AE]}{[LiCl]_{corr}}} \qquad \mathbf{(III.5)}$$

The k_{obs} values from all the kinetic studies are collated along with the concentrations of the various species involved in **Table III.2**. In runs 1, 2 and 7 - 9 $[Li_2Pd_2Cl_6]$ is varied while in runs 2 - 6 [LiCl] is varied. Rate constant, k in s^{-1}, is calculated, assuming equation **III.5** is operative in the last column. The values fall within a narrow range confirming that equation **III.5** is the correct rate expression. The average value of k is $1.7 \times 10^{-3}\ s^{-1}$.

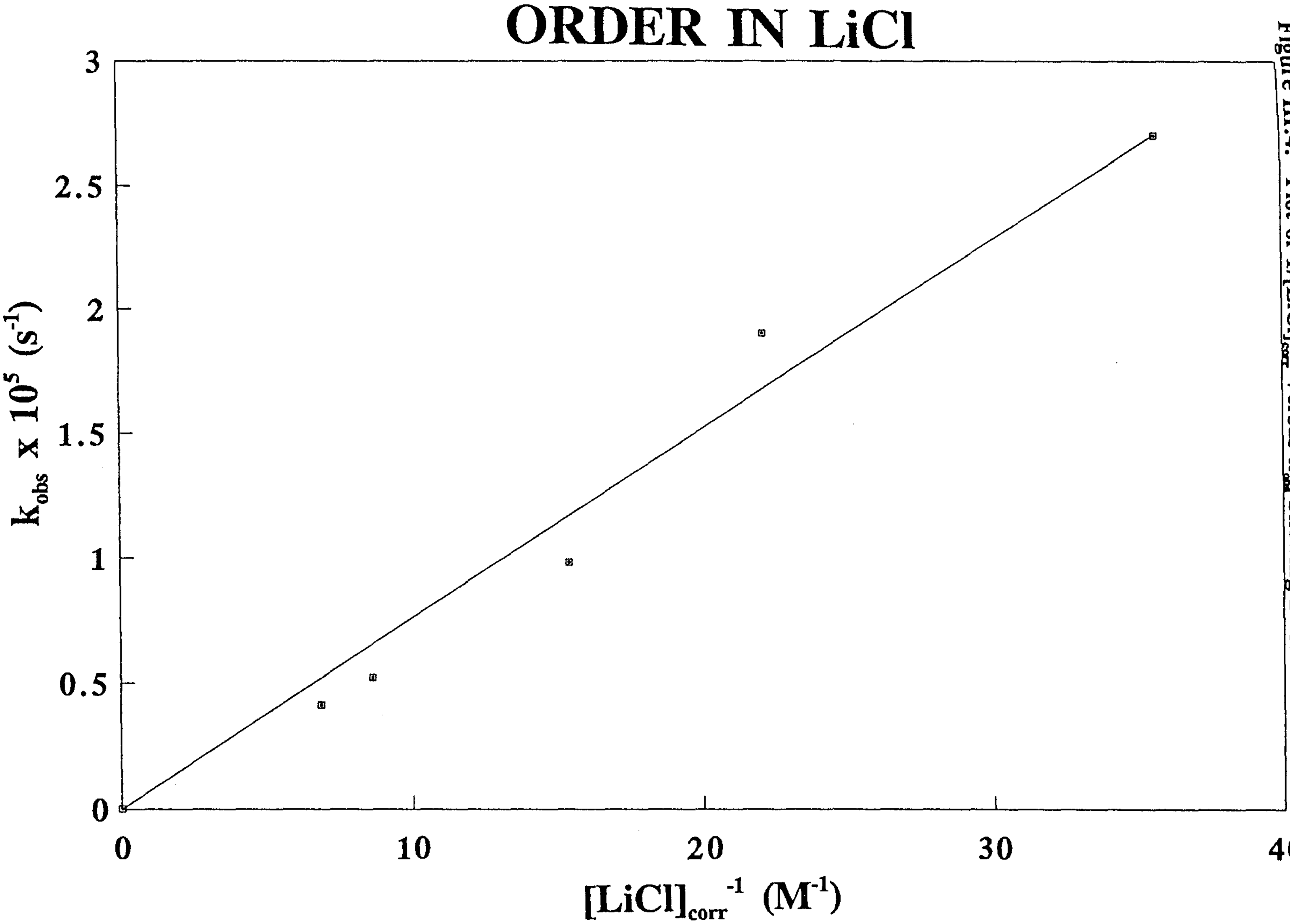


Figure III.4. Plot of $1/[LiCl]_{corr}$ Versus k_{obs} Showing First Order Inhibition

Table III.2. Rate Constants for the Isomerization of II.2.1 by $[Li_2Pd_2Cl_6]$.[a]

No.	$[Li_2Pd_2Cl_6]_{corr} \times 10^3$ M	[II.2.1] M	$1/[LiCl]_{corr}$ M^{-1}	$k_{obs} \times 10^5$ s^{-1}[b]	$k \times 10^3$ s^{-1}[c]
1.	2.02	0.100	22.1	0.67	1.5
2.	4.04	0.100	22.1	1.9	2.1
3.	4.04	0.100	35.6	2.7	1.9
4.	4.04	0.100	15.4	1.0	1.6
5.	4.04	0.100	8.60	0.52	1.5
6.	4.04	0.100	6.84	0.41	1.5
7.	8.20	0.100	22.1	2.6	1.4
8.	12.3	0.100	22.1	4.1	2.2
9.	21.3	0.100	22.1	7.5	1.6

[a] All data is the average of at least two independent runs.

[b] values obtained experimentally.

[c] calculated rate constant using equation III.5; k (average) = 1.7×10^{-3} s^{-1}.

II.2.5. Temperature Studies.

Temperature studies were carried out using only the p-chloro ester species, **II.2.3.** The first order rate constants, k_{obs}, were obtained between 25.0 °C (298.2 K) and 50.0 °C (323.2 K). The data was plotted in terms of the standard Arrhenius equation for temperature dependence, $k = A\ e^{-Ea/RT}$, where k is the rate constant at any particular temperature; A is the pre-exponential factor; E_a is the energy of activation; R is the gas constant and T is the temperature in Kelvin. In terms of the data the k values correspond to the k_{obs} values obtained at each of the temperatures studied. From the slope of **Figure III.5.**, an apparent value of E_a = 17.3 kcal. mol^{-1} and a pre-exponential factor, $A = 1.41 \times 10^8\ s^{-1}$ (log A = 8.15) were obtained.

In a plot of ln (k_{obs}/T) versus 1/T,[78] the standard thermodynamic parameters of ΔH^* and ΔS^* were determined. Apparent values of $\Delta H^* = 81.02$ kJ mol^{-1} (16.74 kcal mol^{-1}) and $\Delta S^* = -100.2$ J mol^{-1} K^{-1} (-24.10 eu) were obtained. A point to note is that in the limited temperature range of 25° (from 298.2 K - 323.2 K) studied, the rate constants changed by about a factor of 81.

III.2.6. Electronic Effects.

In order to probe the polar nature of the reaction path, the allylic ester and its congeners were subjected to an electronic effects study.

As described in **II.2.4.**, these experiments were run under one set of experimental conditions with $[Li_2Pd_2Cl_6]_{corr} = 12.3 \times 10^{-3}$ M, $[LiCl]_{corr} = 4.52 \times 10^{-2}$ M and [allylic ester] = 1.00×10^{-1} M. Under these conditions the value $k_{obs} = 4.11 \times 10^{-5}\ s^{-1}$ was obtained for the rearrangement in the case of the unsubstituted allylic ester. All six allylic ester species,

Table III.3. Temperature Dependence.[a]

No.	T, K	1/T x 10^3 K^{-1}	k_{obs} x 10^5 s^{-1}	ln (k)[b,c]	ln (k/T)
1.	298.2	3.354	2.8	-10.48	-16.19
2.	303.2	3.299	4.7	-9.97	-15.68
3.	308.2	3.245	7.7	-9.46	-15.21
4.	308.2	3.245	8.0	-9.43	-15.17
5.	313.2	3.193	13.9	-8.88	-14.63
6.	323.2	3.095	27.3	-8.21	-13.99
7.	323.2	3.095	26.8	-8.22	-14.00

[a] Using the *p*-chloro allylic ester, **II.2.3.**

[b] k here refers to the standard k_{obs} values obtained as described elsewhere in the text.

[c] ln (k) was plotted versus 1/T in a standard fashion to obtain the activation parameters.

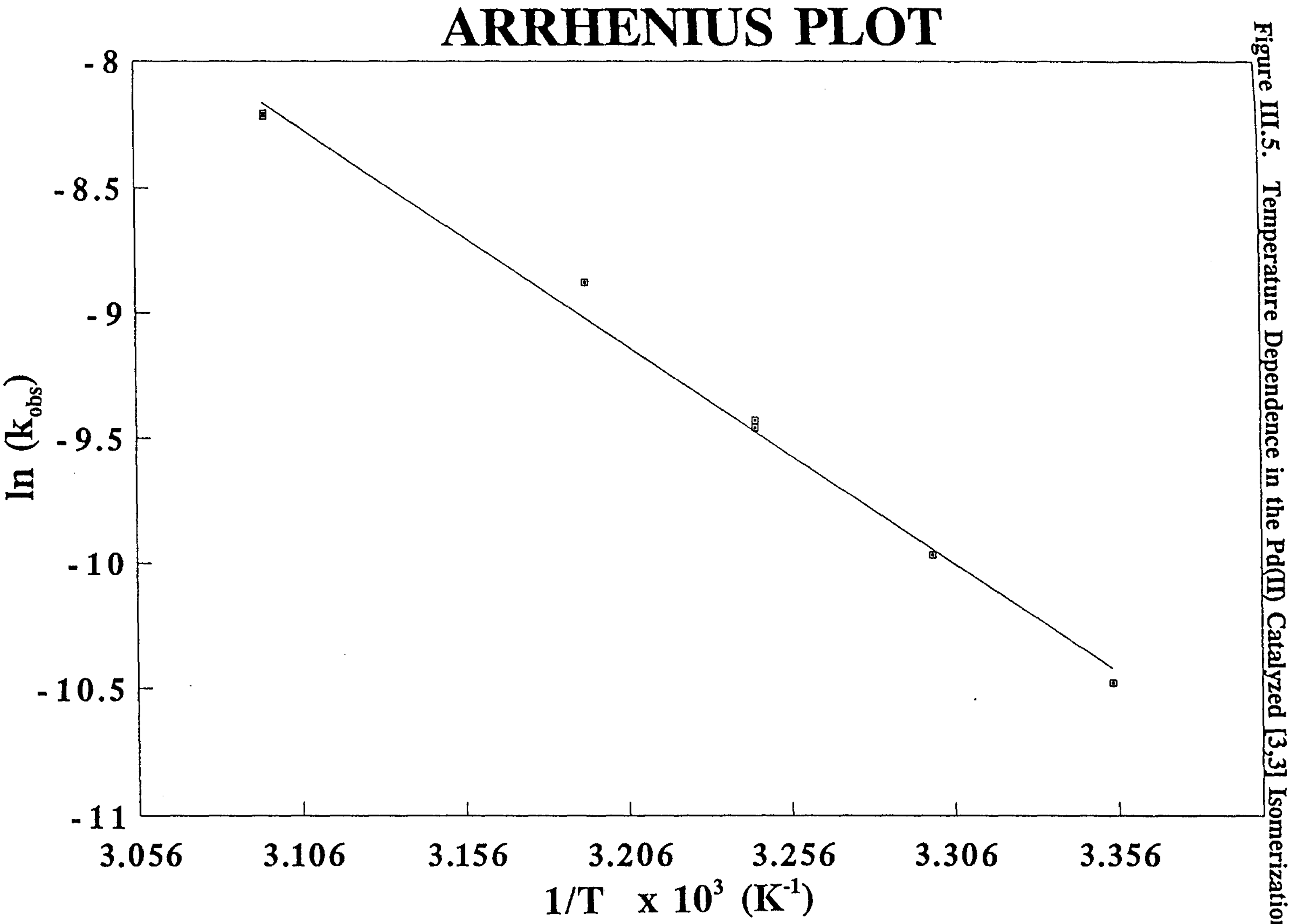


Figure III.5. Temperature Dependence in the Pd(II) Catalyzed [3,3] Isomerization.

II.2.1. - **II.2.6.** were subjected to a similar kinetic study under analgous conditions.

The quickest isomerization was obtained with the *p*-ethoxy species and the slowest with electron withdrawing *p*-nitro species. The data for this electronic effects study can be found in **Table III.4.** The difference between the quickest and the slowest species is a factor of 24.4. The data was subjected to the standard linear free energy treatement and better correlation was found with Hammett-Brown modified σ^+ than with the original Hammett σ values. In the plot with σ^+, the correlation is $R^2 = 0.96$. The slope of the plot, $\rho = -0.78$ which indicates that the transition state possesses some electron deficiency. A plot of this data can be found in **Figure III.6.**

III.3. $[Pd(CH_3CN)_4](BF_4)_2$ System.

This species dissolves primarily in two solvents, acetonitrile and nitromethane. It has some limited solubility in acetic acid. In acetic acid it was found that the ester was recovered unchanged. The solutions usually turned yellow - green on dissolving the catalyst. This is probably due to some aggregation of the Pd(II) species in solution, and with displacement of the CH_3CN.

In studies attempted in acetonitrile with the unsubstituted allylic ester, it was found that the reaction was very slow, probably because acetonitrile inhibits the reaction as it could co-ordinate to the palladium. In later studies with nitromethane, rates were improved considerably. The electronic effect studies were not pursued for three reasons. First, the rates of reaction were not fast enough to be of significant use in catalysis. Second, nitromethane is probably not easy to remove because of its relatively high boiling point. Finally, the catalyst itself shows limited stability in air.

Table III.4. [$Li_2Pd_2Cl_6$] System: Substituent Effects.[a]

No	X Group	$k_{obs} \times 10^5\ s^{-1}$	$\log(k_x/k_o)$	σ^{+b}
1.	$-NO_2$	0.811	-0.704	0.79
2.	-Cl	2.82	-0.162	0.11
3.	-H	4.11[c]	0.000	0.00
4.	$-CH_3$	6.71	0.213	-0.31
5.	$-OCH_3$	10.1	0.390	-0.78
6.	$-OC_2H_5$	19.8	0.683	-0.82

[a] Using the catalyst $Li_2Pd_2Cl_6$ in glacial acetic acid at 25° C.

[b] Hammett - Brown σ^+ values.[79]

[c] This is the k_o value.

III.4. $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ System.

The studies with this catalyst were attempted in HOAc, nitromethane and in CH_2Cl_2. In acetic acid, a similar yellow - green color was obtained on dissolving the catalyst in solution. In nitromethane, for reasons similar to those given in **III.3.** studies were not completed.

In CH_2Cl_2, a complete electronic effects study was carried out. These catalysis runs were made with 1.00 x 10^{-3} mol of ester. The amount of catalyst used was 5 mol%. This data is gathered in **Table III.5.**

The k_{obs} value obtained for the unsubstituted allylic ester is 9.4 x 10^{-5} s^{-1}. Once again the best value was obtained with the electron releasing *p*-ethoxy species. This species was only 4.8 times faster than the unsubstituted species but 18.5 times faster than the electron withdrawing, *p*-nitro congener. Correlation was better with σ^+ (R = 0.98) than with σ. Similar interpretation is made of the data with the slope, ρ = - 0.78, indicating an electron deficient transition state. A plot of the data can be found in **Figure III.6.**

III.5. $[Pd(CH_3CN)(PPh_3)_3](BF_4)_2$ System.

Studies using this species were not successful. In dichloromethane, the study revealed no reaction as only starting materials were recovered under the attempted experimental conditions. It is possible that the species is very sterically hindered with the three bulky phosphine groups.[80]

III.6. $[PdCl_2(PhCN)_2]$ System.

Electronic effects were studied using this species in glacial HOAc. The amount of

Table III.5. **$[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ System: Substituent Effects.**[a]

No	X Group	$k_{obs} \times 10^5\ s^{-1}$	$\log(k_x/k_o)$	σ^{+b}
1.	$-NO_2$	1.91	-0.691	0.79
2.	-Cl	5.43	-0.237	0.11
3.	-H	9.37[c]	0.000	0.00
4.	$-CH_3$	12.8	0.137	-0.31
5.	$-OCH_3$	23.1	0.392	-0.78
6.	$-OC_2H_5$	35.4	0.577	-0.82

[a] Using the catalyst $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ in dichloromethane at 25° C.

[b] Brown σ^+ values.

[c] This is the k_o value.

ester used was 1.00 x 10^{-3} mol and the catalyst was 5 mol%. Here too the reaction went to completion and only one product was obtained under all experiment conditions studied. The isomerization in dichloromethane also gave the [3,3] isomerized product under all conditions.

The data from this study is in **Table III.6.** The analysis of the product, the data collection and treatment were exactly as described in the studies on $Li_2Pd_2Cl_6$.

This series gave the best correlation with the σ^+ values ($R^2 = 0.99$). A similar trend was obtained in the rate constants with electron releasing groups speeding up reaction. The difference between the fastest and slowest species is 20.9. The slope of the plot ρ is -0.81. The plot can be found in **Figure III.6.**

All three catalysts showed similar trends in terms of the electronic effects. A point to note is that the values for the slopes are almost identical. Even the value of $\rho = -0.80$ for the $Pd(C_6H_5)Cl_2$ species is not significant enough to be different. Usually a difference of at least 25% is required for the difference to be of some chemical significance.[81] This indicates that in the Pd(II) catalyzed isomerization, there is a constancy of mechanism, not only across substituents, but across the type of catalytic species employed.

Table III.6. $[Pd(C_6H_5)_2Cl_2]$ System: Substituent Effects.[a]

No.	X Group	$k_{obs} \times 10^5\ s^{-1}$	$\log(k_x/k_o)$	σ^{+b}
1.	$-NO_2$	5.65	-0.951	0.79
2.	-Cl	26.6	-0.278	0.11
3.	-H	50.5[c]	0.00	0.00
4.	$-CH_3$	87.3	0.237	-0.31
5.	$-OCH_3$	110	0.340	-0.78
6.	$-OC_2H_5$	118	0.367	-0.82

[a] Using the catalyst $[Pd(C_6H_5)Cl_2]$ in glacial acetic acid at 25 °C.

[b] Brown σ^+ values.

[c] This is the k_o value.

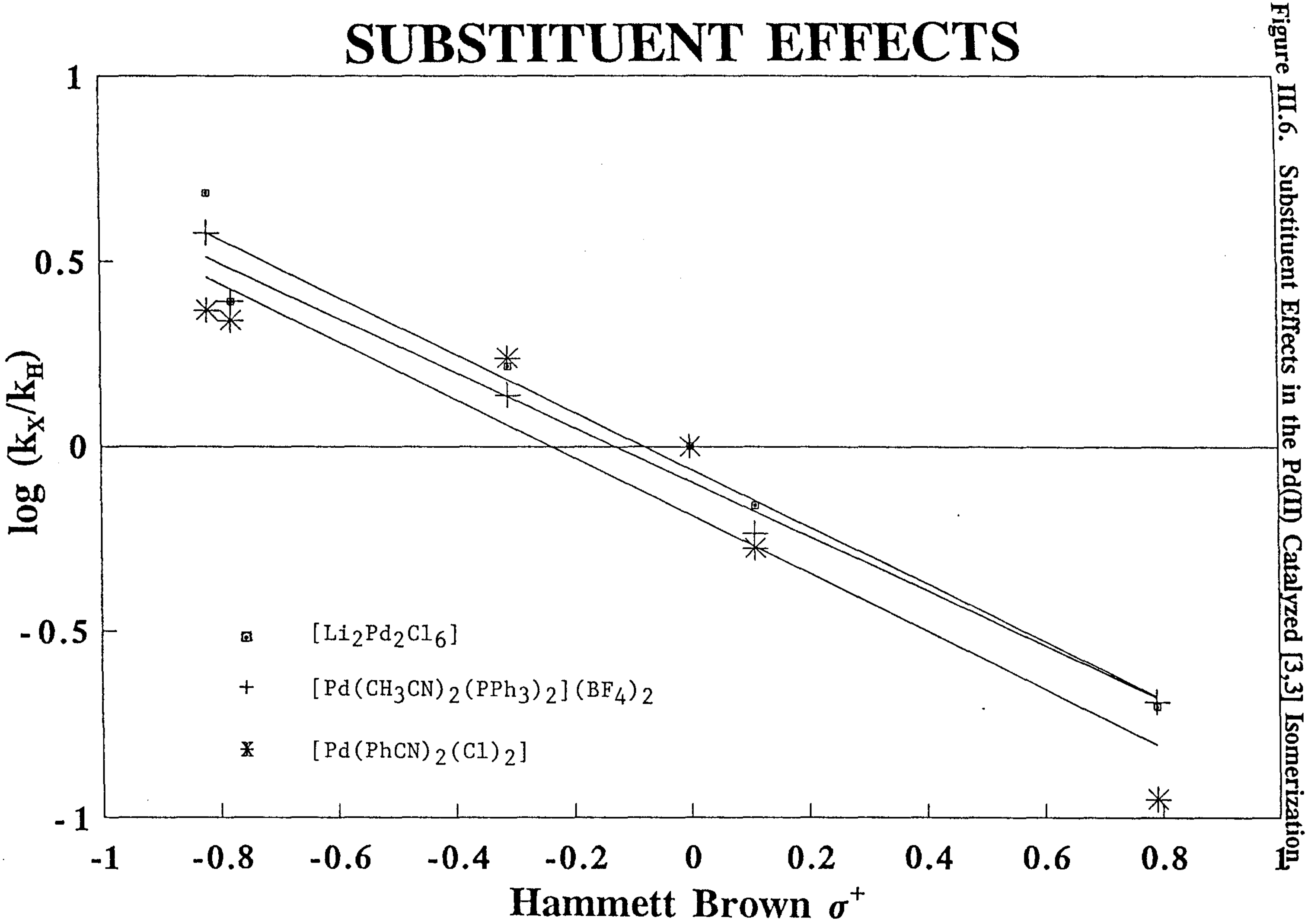


Figure III.6. Substituent Effects in the Pd(II) Catalyzed [3,3] Isomerization

PART ONE: CHAPTER IV

DISCUSSION

IV.1. Mechanism of the Pd(II) Catalyzed [3,3] Allylic Ester Isomerization.

This discussion will cover aspects of the Pd(II) catalyzed isomerization of allylic ester molecules used as mechanistic probes for electronic effects. Serving as probes are the benzoate esters of 2-methyl-3-buten-2-ol with *para* substituted electron releasing and withdrawing groups. The study centered around the $Li_2Pd_2Cl_6$ system focusing on (a) determination of the rate expression under conditions in which quantitative isomerization of the probe molecule into its [3,3] rearranged product occurs; (b) determination of the nature of the electronic effects on the intermediate in the isomerization; (c) comparison of the electronic effects of the negative dimeric chloro complex study to two other Pd(II) catalyst systems, one the neutral, $[Pd(PhCN)_2Cl_2]$, and the other the dipositive $[Pd(CH_3CN)_2(PPh_3)_2]^{2+}$ species; and (d) determination of activation parameters.

The $Li_2Pd_2Cl_6$ system is a continuation of earlier mechanistic work on the exchange and isomerization of allylic esters in acetic acid.[48] In prior studies conditions were similar to those used in this work except that LiOAc was added in the previous studies. In those studies two pathways were seen; isomerization with exchange and isomerization alone. There were different dependencies in LiOAc for each pathway. In the exchange path the rate expression was two term; one term showed first order dependence in LiOAc while the other showed no dependence. The path leading to isomerization alone, again displayed two term kinetics. In this case the dependence on LiOAc was either inverse first order or there was no inhibition.

To avoid these complications LiOAc was not added to the reaction mixtures. The range of concentrations studied in this work are: $[Pd(II)]_{in} = 2.05 \times 10^{-3}$ M - 21.3×10^{-3} M; $[LiCl]_{in} = 0.0300$ M - 0.202 M; [allylic ester] = 0.100 M in dry glacial acetic acid at 25 °C. Under these conditions the probe was isomerized *only* to its [3,3] rearranged product, the benzoate ester of 3-methyl-2-buten-1-ol, in 100% isolated yield. Thus the reaction is very clean and facile.

The first step in our reaction scheme is the formation of the dimeric π complex with the allylic ester in an equilibrium involving the loss of LiCl.

$$\mathbf{Li_2Pd_2Cl_6 + AE \overset{K_5}{\rightleftarrows} LiPd_2Cl_5(AE) + LiCl} \tag{IV.1}$$

where AE is $H_2C{=}CHC(CH_3)_2OOCC_6H_5$, the benzoate ester of 2-methyl-3-buten-2-ol.

$$\mathbf{K_5 = \frac{[LiPd_2Cl_5(AE)][LiCl]}{[Li_2Pd_2Cl_6][AE]}} \tag{IV.2}$$

This pre-equilibrium would account for the inhibition by LiCl seen in the kinetics. The lack of exchange product must result from the absence of added acetate since HOAc by itself is a poor nucleophile. In addition AE is a very sterically hindered molecule because of the presence of the bulky aromatic moiety.

Based on (1) the exclusive transfer of labelled oxygen in the oxygen labelling study in the analogous crotyl ester isomerization;[47] (2) similar studies with deuterium labels in the all carbon Cope rearrangement by Overman;[58] (3) clear [3,3] isomerizations in numerous cases when the heteroatoms are dissimilar;[82] and (4) the sterochemical studies of Overman and of Bosnich, we propose the next step to be intramolecular oxypalladation as suggested by Henry.[47]

The suggested cyclized positively charged "intermediate" was cited as the correct "intermediate" in Hg(II) carbamate rearrangements by Overman.[38] Many workers invoked the same "intermediate" to explain intramolecular isomerization mechanisms[14,20] and all the various Hg(II) and Pd(II) catalyzed [3,3] rearrangements were then designated as proceeding via analogous cyclic positively charged intermediates.

There is further evidence for cyclization in the clean sterochemistries of products in the stereochemical studies of Overman[55] and of Bosnich.[32b] It was necessary to postulate chair configurational ring formation in these studies, in order to explain the stereochemical outcome of the reactions. The $^*O$ labelling studies confirm intramolecular oxypalladation and the lack of [1,3] products rule out the formation of η^3-π-allylic intermediates.

Products from intramolecular oxypalladation have been seen in the cyclization of alkenyl phenols[83] and unsaturated alcohols.[84] It is standard to propose either a five or six membered ring in such cyclizations. In this work we propose a six membered ring because formation of a five membered ring is sterically unfavorable since that would require the σ bonding of Pd to a fully substituted carbon on oxypalladation. In all of the Pd(II) species that we used, only products from apparent six membered ring cyclization are seen. Also, this regioselectivity is largely dependent on the nature of the ligands in the Pd(II) salts. Standardly, with species like $PdCl_4^{2-}$, a six membered ring is proposed for intramolecular

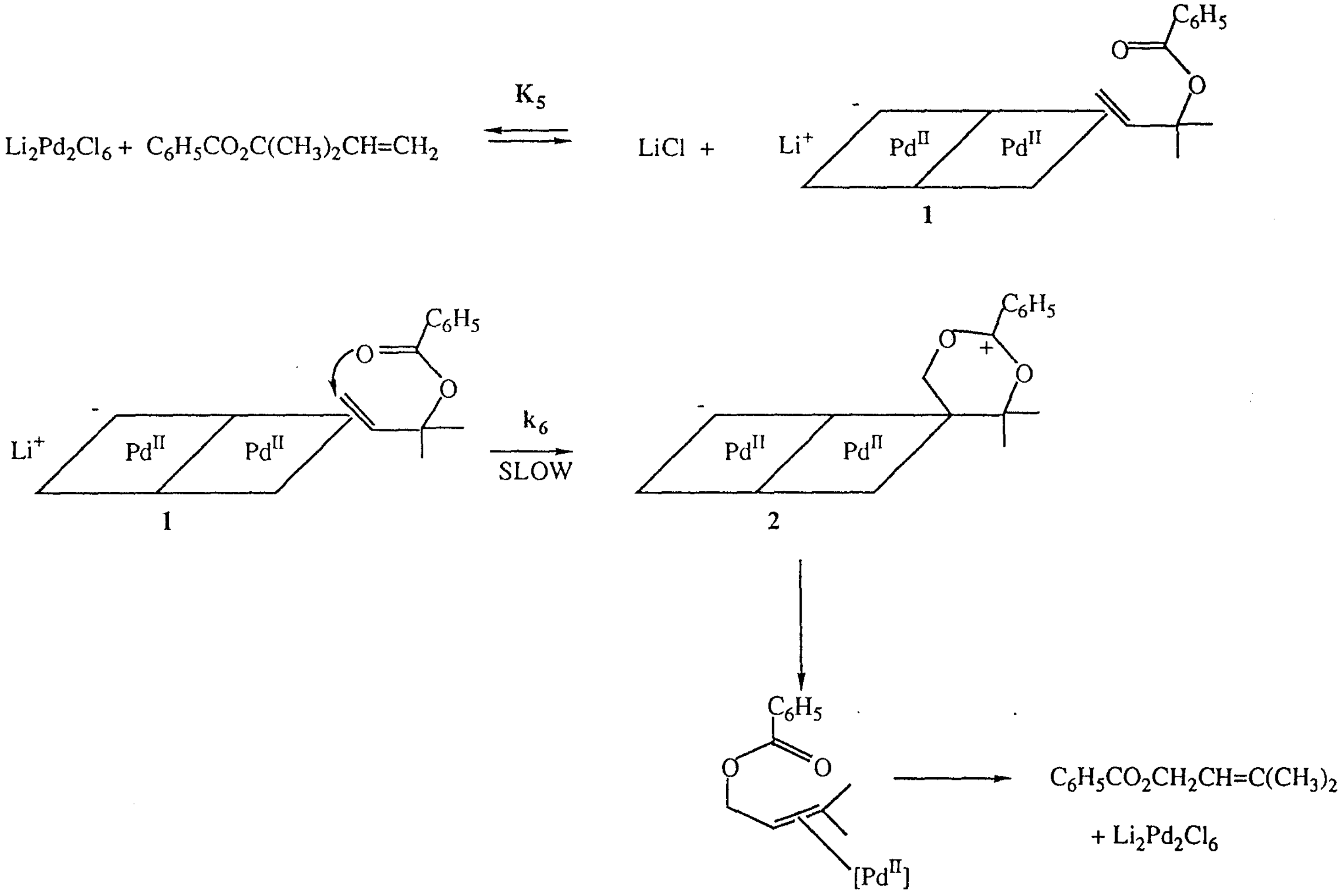


Figure IV.1. Mechanism of the [Pd(II)] Catalyzed Allylic Ester Isomerization oxypalladations.[85] Such dependence on the anionic nature of the ligands is also seen in Hg(II) promoted cyclizations of alkenyl phenols.[86] If Pd(II) acetate were used then a five membered ring could be produced assuming analogy to work from Hosokawa on the cited intramolecular cyclizations.

If internal oxypalladation occurs and a cyclic intermediate is formed as proposed then it would lead to a positive charge at the ester carbon as shown in the scheme in **Figure IV.1.** This is consistent with the results of the electronic effects with this catalyst, and with the other two Pd(II) catalysts (**Figure III.6**) of this study, and the electronic effects evidence from Overman and Renaldo in the all carbon Cope rearrangement.[58] This electronic effects study, with a negative slope provides the first[87] complete evidence for the formation of the electron deficient center. The cyclic "intermediate" is very similar to the 1,3-acetoxonium ion intermediates proposed in various solvolysis reactions.[49] In keeping with this theme, we would like to term this "intermediate" a 1,3-benzoxonium ion.

We studied the nature of this transition state by making use of the Hammett - Brown equation.[88] The only other study of electronic effects in Pd(II) [3,3] rearrangement catalysis was published recently.[58] In that study, Overman and Renaldo found no simple electronic effect relationship in the *bis*(hexanenitrile)dichloropalladium(II) catalyzed isomerization of 2-aryl-1,5-hexadienes. They were able to correlate, however, the rates of rearrangement of the dienes with electron deficient substituents, with Hammett - Brown σ^+ values and obtained a slope of 2.0 (R^2 = 0.98). They attributed the lack of correlation of the electron releasing species with "non-productive binding of the catalyst with the electron rich styrene double bond of these particular substrates".

We successfully correlated the pseudo first order rate constant that we obtained, k_{obs}, with Hammett - Brown σ^+ values and obtained a slope ρ = - 0.78, with electron releasing groups speeding up the reaction. To this we attribute the standard interpretation of a positive charge in the "intermediate" and stabilization by the species that can contribute electron density.

It is important to realize that the k_{obs} is a combination of the equilibrium constant from the initial π complexation and the rate constant for the formation of the cyclic positively charged intermediate and corresponds to k_6K_5. Hence the interpretation of the meaning of the magnitude of ρ is complicated. In order to interpret ρ the factors influencing the k_{obs} value will be considered.

Partly relevant to this work are the studies of the π complexation of olefinic species with transition metals, most notably d^8 species. A brief look at this work is needed to understand the stability of the initial step in Pd(II) reactions with olefins. An excellent review of the thermodynamics of olefinic and acetylenic complexes with transition metals is given by Hartley.[89] In terms of Pd(II) complexes, the equilibria of species with different charges have been studied. The equilibria of monoalkene complexes of Pd(II) are known and two examples are cited. The π complexation equilibrium for ethylene with $PdCl_4^{2-}$to give $[PdCl_3(C_2H_4)]^-$, has been determined in water[90] and methanol[91] solvents. The importance of the electronic effects on these equilibria has been stressed in several papers, although actual quantitative evaluations are few. For example equilibria of the cationic complexes, $[Pd(C_5H_5)(PR_3)(alkene)]^+$ with R = Ph, Et, *n*-Bu, were evaluated for electronic effects by Kurosawa, *et. al.*,[92] who were studying the configurations and relative stabilities of the complexation of olefins. An example of equilibrium studies of neutral Pd(II) species with olefins is found in the work of Partenheimer and Durham.[93] Their study covered a series of seven olefins, including cyclic olefins, acyclic olefins and styrene. The equilibria for the replacement of the olefins by pyridine from $[PdCl_2(olefin)py]$ were determined. The study found trends relating the enthapic data to catalytic phenomena, ionization potentials and the decrease in double bond stretching frequency of the olefin on co-ordination. Decreasing π contribution in the Dewar-Chatt-Duncanson sense,[94] for the series Pt(II) ~ Rh(I) > Pd(II) > Ag(I), was suggested.

Probably the first extensive electronic effects investigation was by Shupack and Orchin[95] who prepared sixty six 1-(4-substituted pyridine *N*-oxide)-3-olefin-2,3-dichloroplatinum(II) complexes where one of the olefins was a series of 3- and 4-substituted styrenes. The styrene complexes were equilibrated with 1-dodecene and the equilibrium constants for the competition were determined by UV spectrophotometry. No simple Hammett relationship was found in this work. Their results were interpreted in terms of energy level matching of the σ and π orbitals. Later Powell and other workers presented a simpler bonding idea involving predominant olefin to metal σ donation primarily on the basis of regular variation in the ^{13}C NMR[96] and X-ray structural parameters[97] with Hammett - Brown σ^+ values in $[PtCl_2py(L)]$ in which L is $CH_2{=}CHC_6H_4Y$-*p* (Y = NMe_2, OEt, OPh, Me, H, Cl, MeCO or NO_2). Powell, *et.al.*,[65(a)] also obtained very successful correlation with σ^+ in a study involving styrenes. The π complexation data of their palladium(II) species gave $\rho = -0.54$. Their interpretation of the σ character of the olefin-Pd bond being of greater importance than the π back donation was supported also by the trends in ΔH° and ΔG° values obtained.

Recently Kurosawa *et. al.*,[98] correlated substituted styrenes and several other olefins with σ^+ and substantiated Powell's interpretation. In this interesting study, they obtained excellent correlation for their log K values with Hammett - Brown σ^+ values (R = 0.996), with a slope, $\rho = -0.82$. They were studying stabilities of $[Pt(PPh_3)(methylallyl)(L)]^+$, where

L is CH_2=CHC_6H_4Y-*p* (Y = NMe_2, OMe, Me, H, Cl or NO_2). In keeping with the X-ray and the ^{13}C NMR data, the more electron releasing species gave a stronger olefin-Pt bond. Consistent with this interpretation, the most π acidic ligand they used, methyl acrylate, gave the least stable complex. In an earlier study[92] of the structures, stabilities and reactions of cationic palladium(II) complexes containing the η^5-cyclopentadienyl ligand, Kurosawa, *et. al.* found that with substituted styrenes they could correlate the ^{13}C shifts of the olefin carbons with σ^+, while the stabilities of the complexes correlated better with σ than σ^+. A possible significance of ion pair formation in determining stability trends was suggested. They attributed stronger olefin-to-metal σ donation as playing a more important role in the stability of the complexes than the back bonding from the Pd.

The ρ values from Kurosawa *et. al.* are consistent with the ρ value obtained in the complexation of styrenes with Ag^+ species in which ρ = - 0.77 was obtained.[99] By analogy with the cited equilibrium π complexation studies, it appears as though our ρ value is consistent with the ρ values obtained simply for π complexation. But, the major difference is that our site for π complexation is at least one atom removed from the site at which charge deficiency is found.[100] And, as far as the absolute value of ρ is concerned, one of the most important factors is the distance of the reaction center from the substituent.[101] Exner suggests that to a first approximation ρ decreases by a factor of one-half with every interposed atom. So it is interesting that similar ρ values are obtained although the k_{obs} is composite and the [Pd(II)] catalyst in this work is at a site slightly more removed from the position of charge formation. The ρ obtained could be expressed as

$$\rho = \rho_{eq} + \rho_2 = \rho_1 - \rho_{-1} + \rho_2 \qquad \text{(IV.3)}$$

where 1, -1 and 2 are standard notation refering to a forward first step, a reverse first step and a second step, respectively.

The standard arguments can be made about the relative magnitudes of each of the rate constants, say k_1, k_{-1} and k_2. Thus, if k_2 is greatest, the overall magnitude of ρ is determined by the first step, as in the hypothetical A → B, as shown in equation **IV.4.**

$$\mathbf{A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C} \qquad \mathbf{(IV.4)}$$

This would correspond to the formation of the π complex in our scheme. The observed rate constant is then k_1 and the observed ρ is ρ_1 of the first step. A similar argument could be made about k_{-1} being greatest; B → C is rate limiting and the observed rate constant is given by the product of k_2 and the equilibrium constant for the equilibrium A ⇄ B and the observed ρ is given by equation **IV.3**. The point is that depending on relative magnitudes of rate constants, the rate determining step need not remain the same when the substituent is changed.

Closer in nature to the equilbria involved in our study are the equilibrium studies of palladium(II) acetate with olefins in acetic acid containing sodium acetate, from Henry and Pandey.[102] In that work, no substituent effects were studied; the equilibria dealt with the formation of two π complexes, a more rapid dimeric $NaPd(OAc)_5(ol)$ equilibrium and a slower monomeric $NaPd(OAc)_3(ol)$, as shown in the equations **IV.5** and **IV.6.**

$$\mathbf{Na_2Pd_2(OAc)_6 + ol \rightleftarrows NaPd_2(OAc)_5(ol) + NaOAc} \qquad \mathbf{(IV.5)}$$

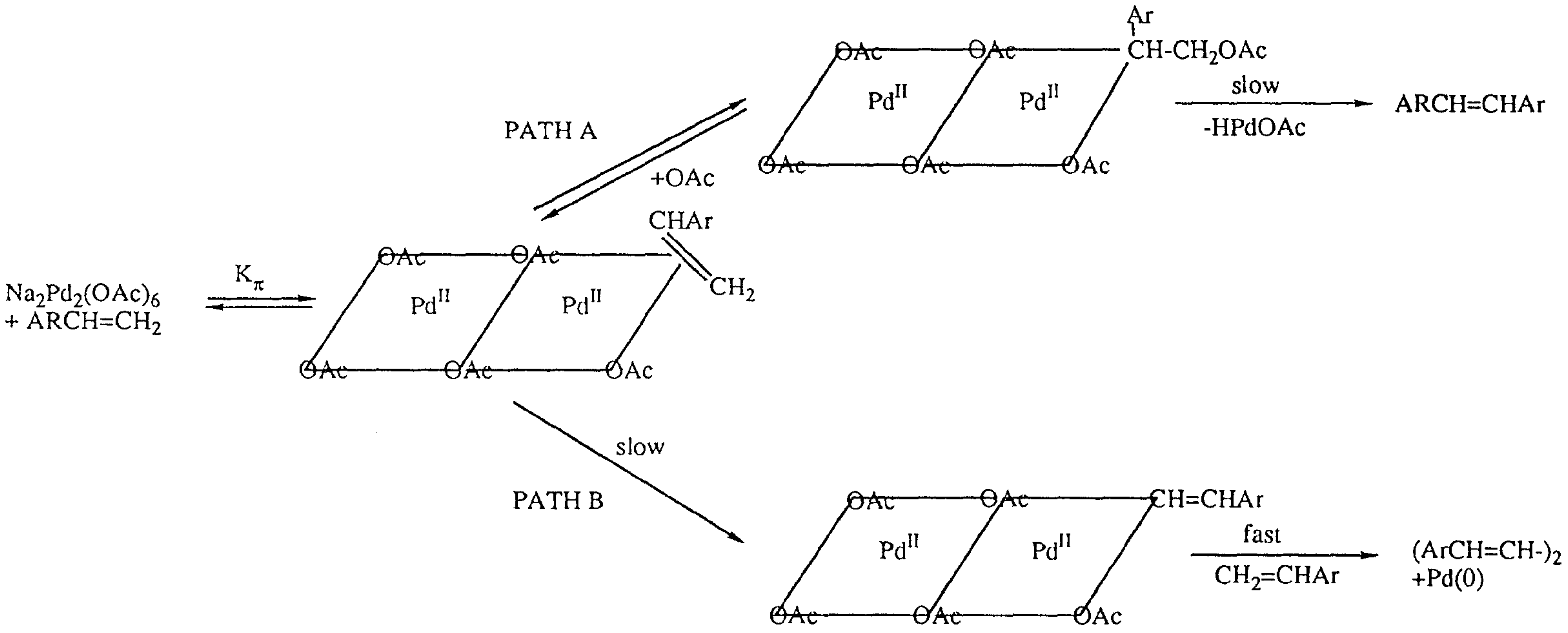


Figure IV.2. Oxidation of Styrenes with $Na_2Pd_2(OAc)_6$ from Lee and Henry.

$$\mathbf{Na_2Pd_2(OAc)_6 + 2ol \rightleftarrows 2\ NaPd(OAc)_3(ol)} \qquad \mathbf{(IV.6)}$$

These are similar to the equilibria for the interaction of allylic esters with Pd(II) in our system containing excess chloride.

It must be noted (**Figure IV.2**) that in the oxidations of styrenes, by $Na_2Pd_2(OAc)_6$ in acetic acid in the presence of sodium acetate, two paths are seen. Path B is favored by electron releasing groups indicating a polar transition state for this path. In the formation of the oxypalladation adduct as shown in path A, there is a relatively nonpolar π-σ rearrangement.[103] Two points of interest are first the equilibria of $Na_2Pd_2(OAc)_6$ with olefins, as shown in equations **IV.5** and **IV.6**, are similar to those in our system and second, the steps following π complexation obviously are affected differently in terms of electronics.

The two systems differ in three ways: first the oxypalladation in this work is intramolecular; second, the proposed site of charge deficiency in this work is directly attached to the atom serving as the nucleophile; and finally, path B in **Figure IV.2.**, the one more affected by the electronics, that is, the path leading to the coupling products, is a totally different reaction from the one we are studying.

An important aspect of the oxidation of the substituted styrenes is that while the value of the equilibrium constant for π complexation increased as the electron donating power of the aromatic substituent increased, it was almost exactly compensated by a decrease in the rate constant of the following step, so the value of the composite k remained practically constant.[104] A similar argument was made by Henry in the oxidations of olefins by $PdCl_4^{2-}$ in aqueous solution.[43]

One likely interpretation for the magnitude of ρ with any one Pd(II) species is as follows. Equilibrium π complexation is certainly faster than oxypalladation which should be the rate determining step.[105] Two limiting cases then present themselves.

In the first case, the equilibrium constants for π complexation should decrease or increase based on the nature of the *para* substituents. Therefore, equilibrium constants decrease with electron withdrawing groups. But the π complex formed in these cases should be more reactive to oxypalladation. Thus, the rate constant for oxypalladation increases. The opposite effect occurs with the electron releasing species. Equililibrium π complexation constants are higher but the more stable π complexes formed are then less susceptible to nucleophilic attack. The result, is a *dampening* on the value of the slope ρ for the composite reaction.

In the second limiting case, the effect of the electron withdrawing and releasing groups on the π complexation constants is negligible. The reason for this is the distance of the groups from the site of π complexation. The effect on ρ is thus very small, as discussed earlier. Unfortunately, to the authors knowledge, no equilibrium constant data on allylic species are available in Pd(II) chemistry. Representative equilibrium studies have been discussed, and the closest cases are the styrenes that are vinylic systems. Experimentally, it is difficult to obtain the π complexation constants because the first step cannot be isolated without drastically changing the conditions of the experiments or modifying the substrate. One possible method would be to study equilibrium π complexation of substituted benzoate esters of allyl alcohol.[106] Thus limiting interpretations of the value of ρ indicate that it is either *dampened* as discussed in the first case, or it represents *only* the formation of the positively charged intermediate of the second case. Actually, the value of ρ probably arises from a case somewhere in between; the dampening effect is present, albeit to a moderate extent.

The values obtained in this study for the slopes, $\rho = -0.78$ and $\rho = -0.81$ with the other two catalysts, the dipositive and the neutral Pd(II) species, are very similar to the slope $\rho = -0.78$ for the negative chloro catalyst. Apparently, the electronics in the reaction are affected very little by the charged nature of the Pd(II) complexes although the variously charged Pd(II) catalysts are certainly very different species. $[Pd(CH_3CN)_2(PPh_3)_2]^{2+}$, for example, is a very electrophilic species. This catalyst has been shown to catalyze rearrangements and polymerizations that are established to be very carbocationic in nature.[107] Sen claims that this kind of electrophile promotes the "slippage"[108] of the olefin thus enhancing nucleophilic attack on the co-ordinated olefin. In the hypothetical reaction shown in equation **IV.4**, that would increase k_1 and hence the ρ_1 contribution to the composite ρ described by equation **IV.3.** We are apparently not witnessing this effect.

One possible explanation, therefore, is that once again composite effects are being witnessed just as in the explanations made earlier for any individual Pd(II) species. More stable π complexes are obtained with the more electron rich [Pd(II)] catalysts. It follows that this stabilization increases the value of K_5 but there is a corresponding decrease in the value of k_6 because the stabilization makes them less reactive to nucleophilic attack. Naturally, the dipositive catalyst would have less stable π complexes. The lower π complexation would be made up by a higher value for k_6. Thus ρ values remain practically the same. Thus, just like in the oxidations of the styrenes by $Na_2Pd_2OAc_6$ and in the oxidations of olefins by $PdCl_4^{2-}$ composite effects result in the similar values for ρ. It is interesting to observe this kind of compensating effect, especially with the dipositive catalyst because such Pd(II) species have known chemistry that make them very reactive.[109]

Table IV.1. Bimolecular Rate Constants for Pd(II) Catalyzed [3,3] Rearrangements.

No	X	$[Pd(CH_3CN)_2(PPh_3)_2]^{2+a,b}$	$[PdCl_2(PhCN)_2]^{a,c}$	$[PdCl_2(C_6H_{11}N)]^{a,d}$
1.	$-NO_2$	3.82	11.3	
2.	$-CF_3$			16.5
3.	-Cl	10.9	53.2	33.8
4.	-H	18.7	101	31.5
5.	-Me	25.6	175	10.1
6.	-OMe	46.2	200	
7.	-OMe[e]			31.6
8.	-OEt	70.8	236	

[a] This is the Pd(II) catalyst used. All groups are in the para position unless mentioned otherwise. The numbers in this column are bimolecular rate constants obtained by dividing the pseudo first order rate constants by the amount of Pd(II) in the reaction mixture. All bimolecular rate constants are in M^{-1} s^{-1} and are x 10^3, and at 25 °C.

[b] From **Table III.5.** In CH_2Cl_2.

[c] From **Table III.6.** In HOAc.

[d] Excerpted from **Table III** of Overman and Renaldo.[58] In $CDCl_3$.

[e] In the meta position.

IV.2. Comparison of Rate Constants.

Collected in **Table IV.1.** are bimolecular rate constants from this work and some bimolecular rate constants excerpted from the similar study of Overman and Renaldo using *bis*(hexanenitrile)dichloropalladium(II).[58]

The Pd(II) species with the two chloride ligands and the two nitriles gives the highest values for the rates of reaction. This seems to be a feature of the lability of the nitriles in Pd(II) species with chloride ligands. The *bis*(nitrile) species are known to dissociate very easily. For example, a problem in obtaining the IR spectra of *bis*(benzonitrile)dichloroplalladium(II) has been that they always show a free nitrile stretch of equal intensity to that from the co-ordinated nitrile. In the present work, in the attempted study using this catalyst in $CDCl_3$, it was noticed that if the catalyst was added before the allylic ester, almost immediate precipitation of a red-brown solid occured. This is almost certainly some form of aggregation of the palladium which is a common feature in solvents of low dielectric constant, while using ligands such as benzonitrile. The values from the dipositive catalyst from this work are lower than the values from the neutral species by a factor of around four. The same arguments made for the ρ values apply here too. Perhaps there is a slight reduction in the positive charge because the predominant mode of bonding of the phosphines is electron donation but in aryl phosphines, there is significant π acceptor character.[110]

The fact that all the rate constants in the present work increase with electron releasing species is very significant to the proposal of positive charge formation in the reaction. This is the first time that such a result is being demonstrated. It is reasonable that the rate constants from the electron releasing species from the work of Overman decrease because of the formation of more stable non-productive π complexes with the styrene unit. It could also explain the slight difference (factor of three) between the unsubstituted species in that work from this one. The only common electron withdrawing species, the *p*-chloro species, shows all the rate constants very close to each other. Actually, the only slight variation in bimolecular rate constants from this work and from Overman supports the fairly invariant values obtained for ρ across different Pd(II) catalyst species. Also, in very different solvents all the rate constants fall within half an order of magnitude of each other as seen in **Table IV.1.**

IV.3. Note on Product Formation.

Usually, increasing steric bulk on the C=C bond decreases stability as seen in representative examples of Pd(II),[111] Pt(II),[112] and Rh(I)[113] complexes. The decomposition of the cyclic Pd(II) σ intermediate resulting from internal oxypalladation to the thermodynamically more stable trisubstituted olefin is thus favored. On account of the lack of stability in Pd(II) complexation with such an olefin and the steric hindrance offered to π complexation to the product no equilibration is seen. Thus, the reaction simply is driven to the thermodynamically more favored product.

IV.4. Activation Parameters.

By way of comparison with the thermal reaction, Hill, *et. al.*,[114] studied substituent effects on allylic esters in the gas phase. They found that the transition state possessed carbonium carboxylate character. In addition, they studied activation parameters and obtained log A values between 9.2 and 13.7, and E_a values ranging from 35.0 through 45.5. They obtained ΔS^* values that were positive and low positive ΔH^* values.

In contrast the thermodynamics of this isomerization with $Li_2Pd_2Cl_6$ in glacial HOAc was studied with the *p*-chloro substituted allylic ester and temperature effects were evaluated. An E_a = 17.3 kcal/mol was obtained. The apparent enthalpy and entropy of activation are 16.7 kJ/mol and -24.1 eu. These are very comparable to values obtained in similar homogeneous Pd(II) chemistry. For example the Wacker oxidation of ethene gave ΔH^* = 19.8 kcal/mol and ΔS^* = -8.7 eu. A better comparison is the more recent data from Zaw and Henry. They obtained 19.9 kcal/mol and -15.0 eu for the apparent enthaply and entropy of activation using a similar k_{obs} corresponding to a kK for the Pd(II) catalyzed oxidation of cyclohexenol in water.[115]

IV.5. Conclusions.

In this part, conditions were found to carry out clean quantitative isomerizations of an allylic ester into its [3,3] rearranged isomer under all conditions in which catalysis was effected. The catalysis was effected in facile manner at 25 °C in dry solvents: acetic acid, dichloromethane, chloroform, acetonitrile and nitromethane. The reaction is catalyzed by various Pd(II) species.

In terms of kinetics, the rate expression was obtained using $Li_2Pd_2Cl_6$ in acetic acid. Electronic effects were studied with three catalysts to quantitate nature of the intermediate. Negative slopes, ρ values of - 0.78, - 0.78 and - 0.81, with electron releasing groups providing stabilization for the positively charged intermediate were obtained.

An important point is that the ρ values demonstrate stabilization of a positively charged "intermediate" but do not show much variation across different Pd(II) catalysts because of composite effects. More stable π complexes are formed with electron rich [Pd(II)] species; yet nucleophilic attack on such complexes is slower. Similarly, more positively charged [Pd(II)] species form π complexes more reactive to nucleophilic attack, yet compensation in these cases occurs because of lower equilibrium constants for π complexation.

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PART TWO

A SUPPORTED CATALYST FOR OXIDATIONS

PART TWO: CHAPTER I

BACKGROUND, NATURE AND SCOPE OF THIS WORK

I.1. Why Catalyzed Oxidations ?

In the specialty chemicals industry there is currently much interest in the use of catalytic oxidation as an environmentally more acceptable alternative to employing classical stoichiometric oxidants such as permanganate and dichromate.[1] Since the majority of fine chemicals are complex, multifunctional molecules with high boiling points and limited thermal stability, processing is largely limited to the liquid phase and moderate temperatures. Although gas phase oxidations are virtually excluded, it does not mean that heterogeneous catalysis is ruled out. Chemo-, regio- and stereoselectivity are important requirements too. Processing of fine chemicals is multipurpose and batchwise. This means that not only raw material costs, but also the simplicity of the installations for these processes are important economically.[2] Thus, in liquid phase oxidations either homogeneous or heterogeneous catalysts can be employed and each have their advantages and disadvantages.

The ideal catalysts are those that combine the high activity and selectivity usually associated with homogeneous catalysts, with the ease of recovery and recycling that is characteristic of heterogeneous catalysts. Further heterogeneous catalysts are generally stable to deactivation by the oxidative destruction of the ligands surrounding the metal ion and / or the formation of unreactive μ-oxo dimers (oligomers) that characterizes many homogeneous oxidation catalysts. Hence, the need for the developement of oxidatively stable, heterogeneous catalysts that exhibit high activities and selectivities in liquid phase oxidations is currently an active research area.

I.2. Background to Supported Metal Complexes.

The first approach to a supported metal complex was to place a homogeneous catalyst on an insoluble support. This work of a supported metal catalyst was published in 1969,[3] and it involved the use of cationic metal complexes like $[Pt(NH_3)_4]^{2+}$ on sulfonated polystyrene. The idea of supporting metal complexes was probably from Merrifield who had supported enzymes for polymer synthesis and degradation on polystyrene resins.[4]

Many metallic heterogeneous catalysts on supports appear to have crystallites which are very small, containing only a few metal atoms. These atoms interact co-operatively to readily carry out reactions which cannot be achieved readily by homogeneous mononuclear catalysts. Examples on platinum surfaces include the oxidation of methanol,[5] the four electron reduction of dioxygen at fuel cell electrodes[6] and the isomerization of alkanes.[7] Fischer Tropsch chemistry is another important example of the co-operative action.[8] Such heterogeneous catalysts have a furthur advantage in that they are surface species and they would have bare co-ordination sites and thus would be more reactive than completely co-ordinated soluble catalysts.

Many homogeneous or heterogenized homogeneous catalysts require polymetallic sites. Examples include the diplatinum A-frame complex which is one of the more active catalysts for the water gas shift reaction,[9] hydroformylation by dirhodium species,[10] and the face-to-face dicobalt porphyrins, electrocatalysts for the four electron reduction of dioxygen.[11]

I.2.1. Types of Supports.

Pre-1940 references ususally refer to the support as a carrier. Reference to the supports reveals an interesting blend: blood char, bone char, chamotte, cement, kaolin and asbestos. Supports are broadly of two types: (1) organic polymers, and (2) inorganic supports.[12]

The major advantages of inorganic supports over their organic counterparts are their better mechanical and thermal stabilities coupled with reasonable heat transfer properties. The major advantages of organic polymers are: (a) They are easily functionalized, especially if they contain aromatic groups.[13] (b) They are chemically inert. The surface thus does not interfere with the catalytic group. This is sometimes a problem with metal oxide surfaces. (c) Based on the type and crosslinking in the polymer, a wide range of physical properties are possible. For example, porosity, surface area and solubilty are only three of several variable properties of commercially available polystyrene.

I.2.2. Polymer Supported Species.

After Merrifield, molecules have been attached to polymers for many purposes. These include organic and stereospecific synthesis, catalysis, separation and purification and isolation of reactive species. In addition, interest in functionalized polymers has been furthered by their analogy to multifunctional biological molecules like polypeptides and enzymes.

I.3. Advantages of Heterogenized Systems.

Obviously, the idea of supported and therefore heterogenized catalysts is not as simple as taking a successful homogeneous metal catalyst and immobilizing it on a solid support. The high selectivity of the homogeneous catalyst[14] is often difficult to achieve in a supported catalyst. Primarily, this is because systematic modification of steric and electronic factors is not easy in heterogeneous systems as opposed to similar modification in homogeneous catalysts. A major asset arises from the point of workup because of the ease of separation of the products from the supported catalyst at the end of the reaction. Some other advantages are: (a) The support provides enhanced thermal and mechanical stability (b) Moisture and oxygen sensitivity are reduced. An example is the lack of water sensitivity of polystyrene supported aluminum(III) chloride.[15] (c) The support may not be simply an inert backbone because it could induce a preferred orientation and thus promote selectivity. This is analogous to the supposition that the three dimensional structure of the enzyme plays a role in the catalytic activity of the enzyme. There is a greater than three fold increase in selectivity for the normal to the branched chain aldehyde in the hydroformylation of 1-hexene using polypropylene supported $[Rh(acac)(Ph_2P\text{-}C_6H_4CH{=}CH_2\text{-}p)CO]$[16] (acac is 2,4-pentanedione). (d) Shape selective oxidations are achieved by incorporating redox catalytic sites within a zeolite lattice framework. The first example of such a "redox zeolite" is called TS-1 and it catalyzes the shape selective oxidation of alkanes with 30 % H_2O_2.[17] The pillaring of clays with redox metal ions, as in the vanadium - pillared montmorillonite, was found to be an effective heterogeneous catalyst for the epoxidation of allylic alcohols with alkyl hydroperoxides.[18] This catalyst displays rates comparable with the homogeneous $VO(acac)_2$ catalyst. The difference, of course, is the regioselectivity: terminal allylic alcohols are not epoxidized. (e) Their chemical reactivity could be different from their homogeneous counterparts. For example, if the organic functional groups are bound covalently to the surface, their reactivity could change.

I.4. Possible Mechanisms of Operation for Polymetallic Catalysis.

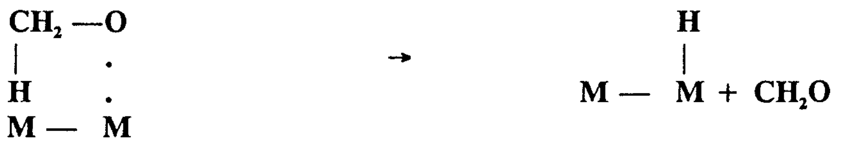
An appealing design for a catalytic site is a polymetallic environment which can allow enhanced rate effects. The purpose of having polymetallic sites is for co-operative action. There are many reasons for the co-operative action, some of which are given below.

I.4.1. Substrate Polarization.

Adsorption of the substrate by one metal center would allow the second metal to facilitate the reaction. For instance, there is little doubt that the mechanism of alcohol oxidation by group 8 metals follows the sequence shown in the equation below

$$\mathrm{RCH_2OH + MX_2 \rightleftarrows HX + RCH_2OMX \rightarrow RCHO + HMX \rightarrow HX + M(0)} \qquad \mathrm{(I.1)}$$

The first equilibrium step is alkoxide formation followed by β-hydride elimination, and finally, hydride decomposition. On a bimetallic heterogeneous catalyst the reaction would most likely involve adherence to the one metal and hydride extraction by another metal as shown in equation I.2.



$$\begin{array}{ll} \mathrm{CH_2} & \!\!\!-\mathrm{O} \\ | & \;\cdot \\ \mathrm{H} & \;\cdot \\ \mathrm{M} & \!\!\!-\;\mathrm{M} \end{array} \quad \rightarrow \quad \begin{array}{c} \qquad\mathrm{H} \\ \qquad | \\ \mathrm{M - M + CH_2O} \end{array} \qquad \mathrm{(I.2)}$$

Not only is the rate increased by the adsorption of the substrate, but the hydride asbstraction should occur more readily. This is because the carbon - hydrogen bond will be more polarized resulting in a partial negative charge on the hydrogen.

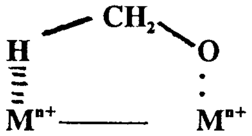
This polarization effect will be very important in the oxidations in which very high isotope effects are seen as in the k_H/k_D of 50 in the oxidation of benzyl alcohol by the Ru(IV) oxo complexes.[19] Such high isotope effects indicate that the hydride transfer is rate limiting. Hydride transfer could be greatly enhanced via polarization of the alcohol. Other oxidations by Ru(IV) oxo species such as the oxidations of tertiary aromatic hydrocarbons, apparently also involve solvent assisted hydride transfer.[20]

I.4.2. Co-operative Electron Transfer.

Oxidations in homogeneous solution by most one electron oxidants occur by two one electron steps producing a reactive free radical as an intermediate.

$$CH_3O{-}M^{n+} \rightarrow M^{(n-1)+} + CH_3O\cdot + M^{n+} \rightarrow M^{(n-1)+} + CH_2O + H^+ \qquad (I.3)$$

Bimetallic species should promote a concerted reaction allowing the oxidation to become more facile and thus enhancing the rate of the reaction. The distance between the two metals will be crucial to the success of the interaction.



$$\rightarrow H^+ + M^{(n-1)}{-}M^{(n-1)} + CH_2O \qquad (I.4)$$

I.4.3. New Concerted Reactions.

The presence of polymetallic sites can promote reactions not possible in homogeneous solution. For example, the oxidation of methanol on platinum electrodes proceeds via a strongly adsorbed intermediate which could be HCO_{ads}, COH_{ads}, or CO_{ads}.[21] More recent FTIR spectroscopic studies have identified this species to be COH_{ads} suggesting that the reaction proceeds as shown below:

$$\mathbf{CH_3OH + Pt\ (surface) \rightarrow Pt_3COH + 3H^+ + 3\ e^-} \qquad \mathbf{(I.5)}$$

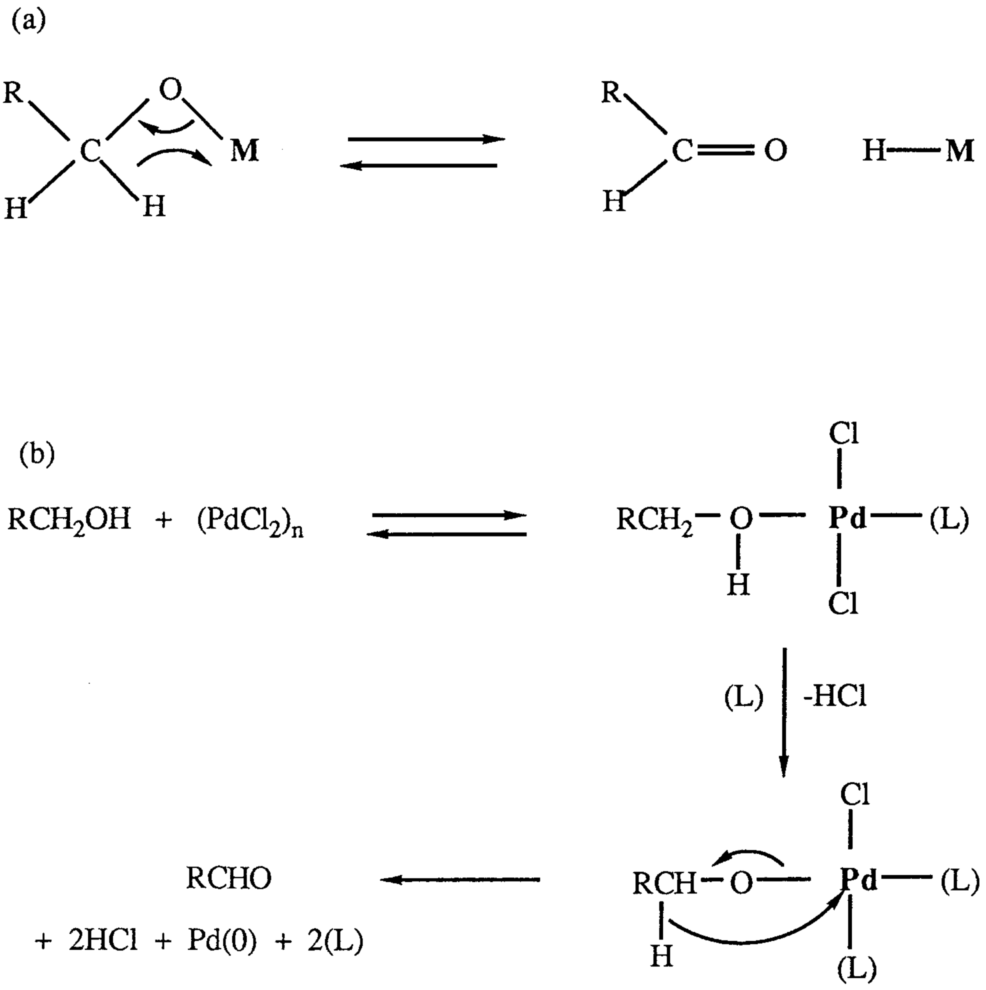
I.5. Palladium as an Oxidant

Many species are oxidized by palladium(II). A significant feature of its oxidation chemistry is the ease of reoxidation of Pd(0) to Pd(II). Thus Pd(II) can be regenerated *in situ* and thus an expensive metal has become commercially attractive.

I.5.1. Oxidation of Alcohols.

Berzelius first reported[22] in 1828 that palladium(II) was reduced upon reflux of a wet ethanolic solution of potassium palladium chloride. In 1855 Strecker oxidized cinnamyl alcohol to cinnamaldehyde using PtO and dioxygen.[23] This century one of the earliest studies was by Moiseev *et. al.*,[24] who performed studies which revealed that such ethanolic oxidations were sluggish even at reflux. Harrod and Chalk[25] noted the reduction of Pd(II) salts by anhydrous alcohols as an undesired side reaction while using the alcohols as solvents.

The first extensive study of alcohol oxidations by palladium species was by Lloyd[26] who observed that at temperatures of 70 °C - 120 °C primary and secondary alcohols were readily oxidized, and in good yield. Among the primary alcohols the only relatively stable species was methanol which gave methyl formate as the oxidation product. Lloyd



(L) = solvent etc

Figure I.1. (a) General Mechanism for the Oxidation of Alcohols by d^8 Metals. (b) Mechanism for the Oxidation of Alcohols by Pd(II).

suggested a ligand dehydrogenation involving the alcoholic hydrogen and an alpha hydrogen. Such a mechanism had been proposed before and the fact that tertiary alcohols could not be oxidized supports this hypothesis. The presence of water decreased yields of oxidized products. A general picture of alcohol oxidations is shown in **Figure I.1.**

I.5.2. Olefin Oxidations.[27]

One of the best known oxidations in palladium chemistry is the Wacker oxidation of ethene to acetaldehyde in aqueous medium. The oxidation can be summarized in the following equations

$$
\begin{array}{lcll}
PdCl_4^{2-} + C_2H_4 + H_2O & \rightleftarrows & CH_3CHO + Pd(0) + 2HCl + 2Cl^- & (I.6) \\
Pd(0) + 2CuCl_2 + Pd(0) & \rightleftarrows & PdCl_4^{2-} + 2CuCl & (I.7) \\
2CuCl + \tfrac{1}{2}O_2 + 2HCl & \rightleftarrows & 2CuCl_2 + H_2O & (I.8) \\
\hline
C_2H_4 + \tfrac{1}{2}O_2 & \rightarrow & CH_3CHO & (I.9)
\end{array}
$$

The basic reaction, the oxidation of olefins by palladium salts in aqueous solution, was discovered by Phillips but it was not until Smidt found that $CuCl_2$ could re-oxidize the Pd(0) *in situ* did the reaction become commercially important. The cuprous chloride reacts very rapidly with O_2 and hence the resulting net reaction is an air oxidation. The rate expression for the oxidation under these conditions is

$$\text{Rate} = k \frac{[PdCl_4^{2-}]\,[\text{olefin}]}{[H^+]\,[Cl^-]^2} \qquad (I.10)$$

Most palladium(II) catalyzed reactions of olefins involve addition of palladium(II) and nucleophiles to the double bond, followed by decomposition, usually oxidative, and it is difficult to interpret the kinetics unambiguously in such complicated systems.

It is firmly established that the first step in the mechanism is the π complexation equilibrium,

$$PdCl_4^{2-} + C_2H_4 \overset{K_1}{\leftrightarrows} [PdCl_3(C_2H_4)]^- + Cl^- \qquad (I.11)$$

The next equilibrium combined with that in the **equation I.12** explains the squared chloride inhibition term

$$H_2O + [PdCl_3(C_2H_4)]^- \overset{K_2}{\leftrightarrows} [PdCl_2(C_2H_4)(H_2O)] + Cl^- \qquad (I.12)$$

At this point the interpretation becomes controversial. The actual problem in the issue has been whether the oxygen nucleophile (H_2O), attacks from outside the co-ordination sphere (*trans*) or from a co-ordinated position (*cis*). In the reaction this results in a conversion of the π-bonded olefin to a palladium(II)-β-hydroxy alkyl (hydroxypalladation).

The experimental arguments in favor of one or the other mechanism are based on (1) stereochemical results since *cis* attack would give different products from *trans* attack; (2) comparison of kinetic and competitive isotope effects; (3) secondary isotope effects; and (4) demonstration of the actual rate determining step by the oxidation of deuteriated allyl alcohols which would undergo measurable isomerization if hydroxypalladation were reversible.

Stereochemistry is difficult to obtain in oxidations. Very interesting studies, mostly demonstrating *trans* stereochemistry, resorted to changes in conditions to establish this mode of attack. For example, Bäckvall demonstrated *trans* stereochemistry under conditions of high chloride concentration, in a reaction which gave chloroethanol as major product.[28]

However, a recent stereochemical and kinetic study under the Wacker conditions from Henry using the idea of 1,3 chirality transfer on a chiral allylic alcohol has demonstrated a cis mode of attack.[29]

Much useful information on homogeneous palladium oxidations has resulted from mechanistic studies on allylic alcohols.[30] On the one end of the spectrum there is information on the directing ability of oxygen in terms of initial π-complexation of the olefinic species as evidenced by the by the distributions and stereochemistries of products that are formed. On the other end of this spectrum is the information on products; for example, allylic alcohols can give hydroxy aldehydes, hydroxy ketones and allylic ketones.[30]

I.5.3. Mode of Decomposition of Palladium(II)-Hydrocarbon Adducts.

Now the mode of decomposition of Pd(II) alkyls with hydrogen β to the Pd(II) will be considered. Earlier mention had been made of the fact that in the oxidation of alcohols, the Pd(II) species is eliminated (reductively) via the transfer of a hydride to the palladium. Hydride complexes of transition metals have been known for a while.[31] Even stable Pd(II) alkyls with stabilizing groups such as phosphines have been characterized when β-hydrogens are not present. Thus methylpalladium(II) and phenylpalladium(II) can be prepared but ethylpalladium(II) decomposes easily, presumably via a β-hydrogen shift, to give ethylene and an unstable Pd(II) hydride that decomposes to Pd metal and a proton.[32]

$$C_2H_5PdL_2Cl \rightarrow C_2H_4 + HPdL_2Cl \rightarrow HCl + Pd(0) + 2L \qquad (I.13)$$

In the oxidative decompositons in the Wacker oxidation of ethylene and in the analogous oxidations of allylic alcohols Henry suggested a decomposition involving a Pd(II) β-hydrogen interaction.[33] These interpretations are consistent with data obtained in these reactions and are in keeping with extensive studies done on platinum and other late transition metal species.[34]

In a recent review,[35] Bryndza and Tam bring together evidence to show that despite general perceptions, late metal-oxygen and late metal-nitrogen bonds are *not* particularly weak but are thermodynamically quite robust. They form easily, yet they are reactive enough to demonstrate interesting reactivity. In binding to late metal centers oxygen and nitrogen σ ligands are not hard ligands relative to carbon and hydrogen; however because of increased electron affinity of the heteroatoms involved, the bonds heterolyze more easily. This kinetic lability is useful in the oxidations of oxygen or nitrogen species.

I.6. Purpose of this Work.

Our goal is to make a practical catalyst for oxidations that are of current interest. We would like to design catalysts with the following properties:

1. The catalyst ought to be some kind of heterogenized species and can thus make use of the standard attendant advantages of heterogeneous systems like (1) ease of catalyst recovery, (2) ease of product isolation, and (3) enhanced thermal and mechanical stability.
2. The use of a polymeric setting would make coating onto an electrode easy and the system could be used for electrochemically driven oxidative degradation reactions.
3. The actual binding site for placing target metals could be triketone linkages on the polymer, although many other groups are likely to be useful for this purpose. The ligand geometry will

result in a bimetallic catalyst expected to enhance the oxidations of alcohols, hydrocarbons and aromatics like phenols and catechols via adsorption, polarization and co-operative electron effects. In particular, metal - metal distance should be close to ideal for the formation of activated O_2 peroxo species when an appropriate metal is complexed.

Many different metals could be used in such a system. Both one electron and two electron oxidants can be employed. The use of two electron oxidants in a bimetallic setting could thus give us a simultaneous four electron capability, the consequences of which would become significant for fuel cell type reactions. Thus we could choose the metal based on the criteria that would involve (a) target molecule(s) to be oxidized, (b) whether the activaton of O_2 is required, (c) whether one or two electron capability is needed, (d) value of potentials required for the oxidation in question, and (e) mode of reoxidation that would be employed.

Mixed metal systems could also be employed for achieving unique oxidations. As an example, Caselleto, *et. al.*,[36] made heterobinuclear complexes using analogous *bis*(triketones), similar to the triketone framework we are proposing to synthesize on the polymer backbone. The oxidation of substituted catechols to the corresponding quinones was accomplished using these systems.

I.7. The Approach.

I.7.1. Preparation of the Supported Bimetallic Catalytic System.

(a) Polymerization: The method involves the formation of new benzene rings by a cyclic trimerization reaction involving acetyl groups. If methyl ester groups are incorporated onto the phenyl rings, they can be modified later;

(b) Modification of the methyl ester to get triketone linkages;

(c) Coating of the prepolymer onto the heterogeneous support, and curing; and

(d) Metal ion uptake on the triketone system to get the bimetallic system.

I.7.2. Testing of the System for Catalytic Activity.

The process would involve

(a) choice of suitable substrates;

(b) the determination of a suitable reoxidant to perform the oxidations catalytically;

(c) analysis of the products;

(d) a simple and convenient means to study kinetics; and

(e) control reactions:

  (i) to show that the reactions are heterogeneously catalyzed;

  (ii) to show that catalyst leaching did not deactivate the catalyst over a period of time; and

  (iii) to demonstrate the efficacy of a bimetallic system in terms of unique capabilities attributable only to the multimetallic nature through the products obtained and in terms of enhanced rates over a like monometallic system using a diketone framework.

I.7.3. Studies of Catalyses.

It is our proposal that for a process to avoid radical intermediates, in the degradations of polyphenolics to dibasic acids, two electron oxidants are useful. This kind of reaction would be important from several points of view, especially if a clean and controlled oxidation could be demonstrated. For example, some of the studies on the oxidations of catechols show a variety of products. Clean oxidative degradation of aromatic species would be environmentally appealing and of greater practical value. It would be interesting if we could demonstrate this with a two electron oxidant and thus using the bimetallic catalyst that we are proposing, ring cleave aromatic rings.

We would like to use catechols as our models and Pd(II) mounted in bimetallic fashion in the supported polymer framework as the catalyst system. There are at least three reasons for choosing Pd(II) as our metal species for these oxidations. First of all, Pd(II) is a powerful electrophile.[37] Second, it is a good oxidant. Finally Pd(0) is easily oxidized back to Pd(II) using a variety of co-oxidants.

There are many other species we would like to try in our oxidations. We could make environmentally suitable alternatives to currently used oxidants like permanganate and dichromate. Since we do know that interactions of late metal species with heteroatoms are thermodynamically quite favorable, we will be attempting to make use of the advantages of a bimetallic system. We could, if successful, have a facile supported catalytic system.

PART TWO: CHAPTER II

EXPERIMENTAL

II.1. Synthetic Procedures for the Ligand System for the Heterogeneous Oxidations.

If special purification procedures were performed, they will be mentioned where the name of the chemical first appears. Characterization is limited to ^1H and ^{13}C NMR and IR spectroscopy, wherever possible. Sample weighings were performed on a Sartorius Model 2842 analytical balance and are accurate to ± 0.05 mg. Studies at constant temperature were carried out in a water bath maintained at 25° ± 0.2 °C using a Messgeräte - Werk Lauda model B-1 thermostat.

The heterogeneous oxidations that will be described in this chapter were performed on a very specific ligand system. The ligand system is either a β-diketone or a β,δ-triketone on a low molecular weight polyphenyl polymer. The experiments below are descriptions of the synthesis of such a system based on analogy to ferrocene[38] and mono phenyl[39] diketone and triketone model systems.

II.1.1. 4-Acetyl Methylbenzoate.

To 200 mL of methanol (Aldrich, HPLC grade) saturated with gaseous hydrochloric acid (HCl) (Aldrich) by bubbling through for 20 min, was added 5.04 g (3.07×10^{-2} mol) of 4-acetyl benzoic acid (Fluka Chemika) in a 500 mL single necked round bottom flask. The

4-acetyl benzoic acid dissolved immediately giving a yellow solution. It was refluxed for 2.25 h and then cooled to room temperature in the air after the heat source was removed. The solution was diluted by adding 150 mL CH_2Cl_2 and 170 mL of brine. The layers were separated, the aqueous layer re-extracted with 2 x 25 mL of CH_2Cl_2 and all the organic layers combined. This was washed with 3 x 150 mL of saturated $NaHCO_3$ (blue litmus paper showed no change after the second wash) and then with 125 mL of brine. The organic layer was dried (anhydrous $MgSO_4$) for 20 min and the solvent removed on a vacuum pump after filtering off the drying agent. The crude product was purified via a 125 g silica column (Mallincrodt, Silicar Silica gel, 100 - 200 mesh, type 150 Å special) using CH_2Cl_2 as the only elutant. M.P.: 94 - 96 °C; 3.56 g (65%).

II.1.2. Polymerization of 4-Acetyl Methylbenzoate with *p*-Diacetylbenzene.

This preparation was a modification of the method of Teplyakov *et. al.*[40] 3.64 g (2.04 x 10^{-2} mol) of 4-acetyl methylbenzoate and 1.40 g (8.63 x 10^{-3} mol) of *p*-diacetylbenzene (Fluka Chemika) were put in a dry 250 mL Erlenmeyer flask containing a magnetic stirrer. To this was added 100 mL of dry benzene (Aldrich, HPLC) and 11.0 g (7.4 x 10^{-2} mol) of triethyl orthoformate (TEOF) (Aldrich). The ratio of 4-acetyl benzoic acid to *p*-diacetylbenzene was 2.4 and that of the TEOF to all the acetyl groups present was 2.[41] The flask was fitted with a two holed rubber stopper. One of the holes served as inlet for the HCl gas that was bubbled into the solution with a disposable pippette. The other hole had a short piece of glass tubing that served as outlet and was connected via Tygon tubing to a drying tube and furthur into a trap containing potassium hydroxide (Fisher) solution (3.0 M). The HCl gas was bubbled slowly through the solution for 30 - 45 min. The solution was stirred at room temperature and turned an intense red within the first 15 min of passing the HCl gas into it. The reaction was stopped before the polymer molecular weight became large enough for it to precipitate out of solution.

The solution was poured into 100 mL of ethanol (Aldrich) to precipitate the polymer. The very light yellow brown precipitate was filtered and washed quickly with ethanol, copious quantities of saturated sodium carbonate solution, water and finally with ethanol. It was dried first in a stream of argon and then on a vacuum pump. This polymeric material was used for the subsequent syntheses to the diketone and the triketone by modification of the ester groups. These syntheses are described in **II.1.3.**

II.1.3. Modification of Polymers.

II.1.3.a. Triketone of II.1.2.

A dry three necked 250 mL round bottom flask that had been purged with argon was charged with 1.33 g (3.30×10^{-2} mol) of NaH (Aldrich, 60% dispersion in mineral oil). It was washed with 3 x 12 mL portions of hexanes. It was then slurried in 5 - 10 mL of THF. To this was added 1.20 g (1.20×10^{-2} mol) of 2,4-pentanedione. This resulted in very vigorous evolution of hydrogen gas for the first five minutes. The solution was gently refluxed for 2.0 h and then cooled to room temperature. The solution was stirred for an additional 1.5 h and then 0.25 g of 18-crown-6 (Aldrich) was added. The solution looked a dull orange brown. To this was added 0.70 g of **II.1.2.** in a mixture of CH_2Cl_2 and THF (total 70 mL). The solution was refluxed for 24 h and then cooled to room temperature and allowed to stand for 12 h. The THF was removed on a vacuum pump. The residue was a dark tan.

Fifty mL of CH_2Cl_2 and 50 g of ice were added to the residue that had been cooled to the temperature of ice. A mild effervescence was noticed at this stage. After the evolution of hydrogen gas ceased, 100 mL of 1 M HCl was added to the mixture which was then stirred for 30 min. There was some precipitate noticed at this stage. After removing the aqueous layer, the precipitation was completed by adding petroleum ether. The precipitate was a yellowish tan. The product was washed with $NaHCO_3$, brine and finally with water. The product was dried overnight on a vacuum pump. Yield = 0.77 g. This material was purified in the standard manner.

II.1.3.b. Diketone of II.1.2.

0.42 g (1.1 x 10^{-2} mol) of sodium hydride (NaH) (Aldrich, 60% dispersion in mineral oil) was washed with hexanes (3 x 5 mL) to remove the mineral oil, and taken in an argon purged dry 50 mL round bottom flask fitted with a condensor and argon inlet and outlet connections. Using a cannula through a septum covering the third arm of the round bottom flask was added 3 mL of THF. To the stirring slurry was added 1.01 g (1.00 x 10^{-2} mol of 3,3-dimethyl-2-butanone. The reaction was heated gently for about 0.5 h to form the anion. The formation of the anion is indicated by the presence of a yellowish color in the otherwise grey slurry. To the anion was added 0.70 g of **II.1.2.** in CH_2Cl_2. The solution was refluxed for 12 - 16 h.

At the end of the reaction the THF was removed on a vacuum pump. To the solid dark tan residue was added some CH_2Cl_2 and 1.0 M HCl. The solution was stirred for 30 min and then the layers were separated. The organic layer was washed with brine, saturated $NaHCO_3$ and finally with brine. The material was purified in standard manner. Yield 0.81g.

II.1.4. Coating of Polymers onto Support.

10.0 g of celite (Alltech Associates, Inc., Applied Science Labs)(Manville, Chromosorb W) (Chromosorb W is screened diatomaceous non acid washed celite of white color; moisture content = 0.3%, B.E.T. surface area = 1.0 - 3.5 m^2 g^{-1}, free fall density = 0.21 - 0.27 g cm^{-3}; true specific gravity = 2.30) was taken in a 250 mL round bottom flask containing a stirring bar. To it was added 0.10 g of **II.1.3.a.** dissolved in 100 mL of CH_2Cl_2 and 30 mL of benzene. The CH_2Cl_2-benzene solution was heated mildly for 15 min to ensure maximal solubility of the polymer triketone material. It was filtered to remove any undissolved solids before adding it to the celite as mentioned above. The slurry was stirred for 10 h. The solvent was rotovaped off and the polymer triketone coated on the celite support was dried on a vacuum pump.

In a similar manner to that described above, the diketone, **II.1.3.b.** was coated onto celite.

II.1.5. Curing of the Supported Materials.

The supported triketone was sprayed with *p*-toluene sulfonic acid. It was then cured by heating in a vacuum oven at 150° C - 200° C for several hours.

The supported diketone material was cured as described in a similar manner.

II.1.6. Metal Ion Uptake Using Supported Polymers.

To a degassed 500 mL two necked round bottom flask containing a stir bar was added redistilled acetonitrile (dried over calcium hydride, CaH_2). This was carried through three vacuum purge - degas cycles in order to deoxygenate the solvent. The flask was then charged with 10.0 g of the cured triketone polymer material on the celite support, **II.1.5.a**. To this was added 1.0011 g (9.90 x 10^{-3} mol) of palladium sponge (Aesar). The flask was once again purged with argon for *ca.* 5 min. 2.50 g (2.14 x 10^{-2} mol) of nitrosyl tetrafluoroborate was added to the slurried mixture. The flask was maintained under slightly positive pressure of argon. It was periodically vented to release pressure because of the formation of the nitrous oxide gas. After 2 h, the supernatant solution began to look yellow and the stirring was continued at room temperature for at least 24 h after that. The supernatant solution was cannulated out of the flask into another septum stoppered flask. The cured supported material that had, at this point, taken up some palladium was washed with 3 x 10 mL of degassed CH_3CN. Each time the CH_3CN was added the support material was stirred very thoroughly to wash it. All rinses were combined with the supernatant material cannulated out as described above.

The volume of the supernatant liquid from above was determined and then 1.0 mL of it was syringed into a beaker. It was acidified with concentrated HCl and then the palladium content was determined using the standard gravimetric method via the dimethyl glyoxime reagent.[42] The palladium metal uptake by the triketone system on the support could thus be determined by subtracting the amount of palladium in the supernatant liquid from the total palladium that had been used.

In a manner similar to that described above, the metal ion uptake on the supported diketone material was performed.

II.2. Heterogeneous Oxidations.

All of the oxidations, that will be described, were performed in methanol or in water.

The methanol (Fisher) was of reagent grade and was fractionally distilled. In later experiments the methanol was used as received, as it was found that there was no significant difference to the rates of the reactions. House distilled water was deionized via a Sybron Nanopure II (Brinkman Instruments Limited, Ontario, Canada) deionization system. Degas cycles were carried out using a vacuum pump. Purging of solvents was carried out with argon. The argon, (Airco Special Gases: Division of the BOC group) of commercial quality, was CGA grade E.

The catalyzed oxidations were all performed at 25° ± 0.2° C in a thermostatically controlled water bath.

II.2.1. Dioxygen.

The dioxygen (Airco Special Gases) was grade 5 and of commercial quality (99.5 % v/v dioxygen). It was used without further purification.

II.2.2. Stock Solution of Sodium Methoxide.

To a dry solution of methanol was added 0.0379 g (1.65×10^{-3} mol) of sodium (Aldrich, spheres in odorless mineral spirits, 3 - 8 mm) that had been washed with hexanes. After the evolution of hydrogen gas had ceased the mixture was poured into a 100 mL volumetric flask and made up to the mark.

II.2.3. Oxidation of 3,5-di*tert*butylcatechol (3,5-DTBC) in Methanol.

These oxidations were all studied on a 100 mL scale. The amount of any substrate (3,5-DTBC, for example) used was always 2.50×10^{-3} mol. The products were characterized by standard ^{1}H and ^{13}C NMR and IR spectroscopies.

II.2.3.a. Glassware and Setup.

The reactions were performed in creased two necked 500 mL flasks. The flasks were cleaned by soaking in concentrated nitric acid for 20 min, followed by rinsing with copious amounts of water, acetone, distilled acetone and finally rinsing at least twenty times with distilled deionized water.

A schematic for the setup for the oxidations is shown in **Figure II.1.**

II.2.3.b. Preparation of the solvent.

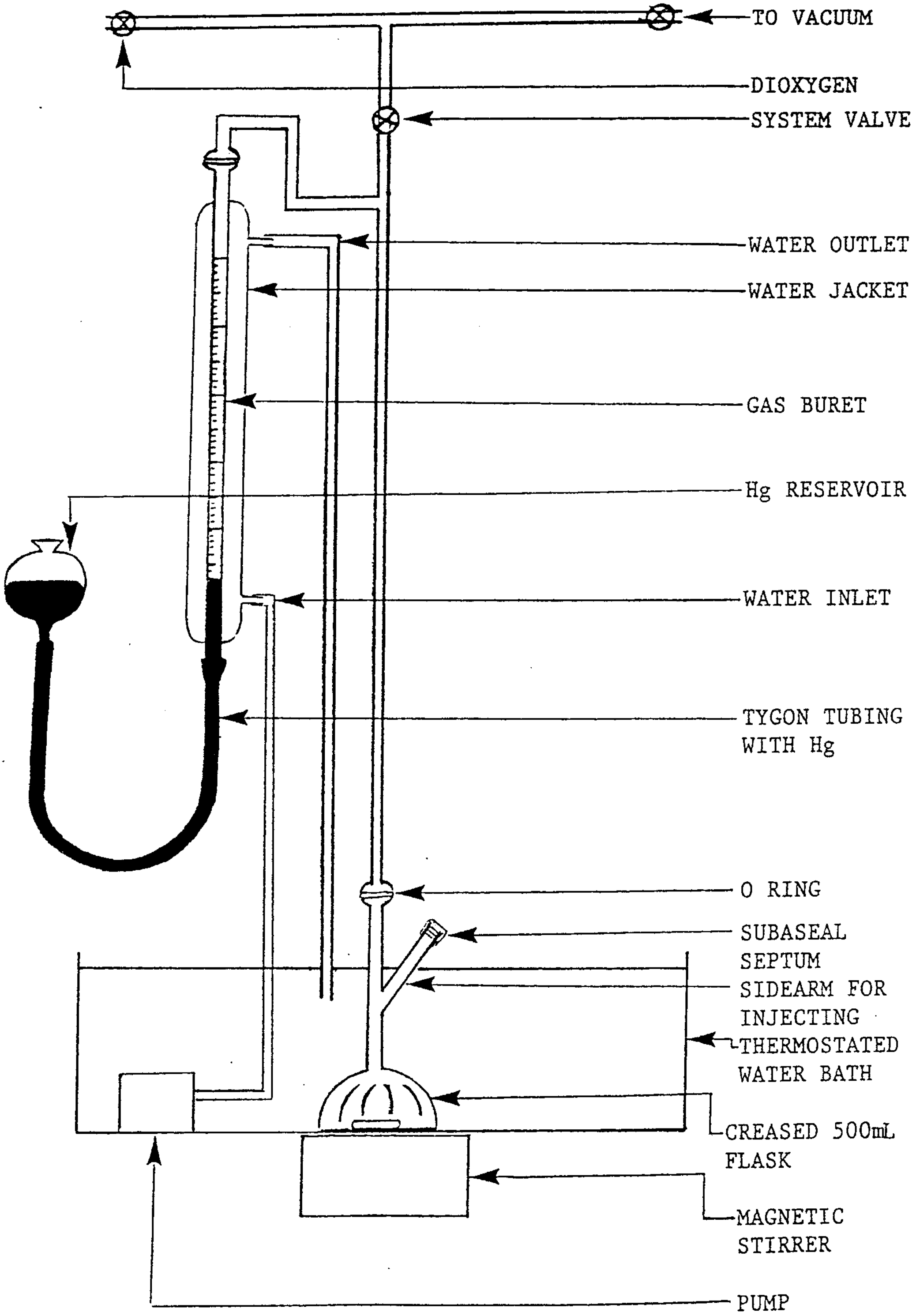
110 - 120 mL of methanol to which 5.50 g (5.18×10^{-2} mol) of TMOF had been added was subjected to extensive degassing via three argon purge and two vacuum degas cycles in a 250 mL round bottom flask. It was then taken in a 100 mL volumetric flask to obtain a precise volume. This solution was then used for the experiment to be described below.

II.2.3.c. Setting up the experiment.

A dry argon purged 500 mL two necked creased flask was charged with 0.50 g of **II.1.6.a.**, the bimolecular Pd(II) supported catalyst. About 90 mL of the above solvent was taken in the flask. The side arm of the flask was covered with a Subaseal septum (Aldrich) while the main arm was attached to a manifold that was facilitated with dual valves connected to a vacuum pump on the one side and to a supply of dioxygen on the other.

The final degassing was then carried out via the vacuum line. After the system has

Figure II.1. Schematic for the Setup for the Oxidations.



been evacuated for at least 20 min, 0.5558 g (2.50×10^{-3} mol) of 3,5-DTBC (Fluka Chemika, recrystallized from pentane) which was dissolved in the remaining 10 mL of solvent was injected directly into the reaction mixture via the septum covered side arm using a syringe fitted with a long syringe needle (Aldrich, 18 gauge stainless steel, 12 inches long, with Luer hub).

At this point the vacuum line was closed and the O_2 line opened. The Hg level was adjusted to the zero on the gas buret, stiring was begun and timing started. The time taken from the start of the injection to the manipulative procedures described including the start of timing is 15 - 25 seconds. Vigorous stirring was done to ensure that there was good mixing as the reaction involves more than one phase.

As dioxygen was consumed, a partial reduction in pressure in the system resulted in the rise in the level of the Hg in the gas buret. Readings were periodically taken by levelling the Hg in the buret with that in the reservoir to ensure that they were taken at ambient pressure in the laboratory. The reaction mixture, which was usually colorless at the start, turned to a very intense red and remained thus till about 45 mL of O_2 was consumed. It then began to decrease in intensity and gradually the red color gave way to a yellow. When about 60 - 65 mL of dioxygen had been consumed, the solution usually appeared a light straw-yellow.

II.2.3.d. Workup.

At the time it was decided to stop the reaction, the flask was removed from the manifold and the contents filtered to remove the heterogeneous catalyst. The methanol was evaporated in the air and the residue analyzed by NMR to determine the products.

II.1.3.e. Control Experiments.

The control experiments that were performed were done in similar manner to that described above in terms of setting up the experiments. In each example of a control mentioned below, the species that was *not* added to the reaction mixture is mentioned below:

(i) the bimolecular Pd(II) catalyst on the support,

(ii) 3,5-DTBC substrate, and

(iii) sodium methoxide base.

A second set of controls involved the use of the monometallic Pd(II) species made from the diketone polymer species on the support. This second type of control experiment was to determine relative rates when comparing the monometallic to the bimetallic system.

II.2.3.f. Test for Homogeneous Catalysis.

A reaction was setup as described in **II.2.3.c.** Before attaching the flask to the manifold with the vacuum - dioxygen connections, the solution was filtered and the support material was removed. The supernatant obtained was then used in an experiment monitored for dioxygen uptake. The products were analyzed at the end of the reaction. This was to check and see if there was leaching of the metal species into the solution and catalysis because of some homogeneous Pd(II) species.

II.2.3.g. Injecting more 3,5-DTBC.

After setting up a standard experiment as in **II.2.3.c.**, the reaction was allowed to run until what was determined to be approximately the half way stage, that is, *ca.* 31 mL of dioxygen had been consumed,[43] 2.50×10^{-3} mol of 3,5-DTBC in 10 mL of solvent was injected into the reaction and the kinetics monitored.

II.2.3.h. Reaction with 3,5-Di*tert*butylquinone (3,5-DTBQ).

(i) The experiment was set up as in **II.2.3.c**, except that 2.50 x 10^{-3} mol of 3,5-DTBQ was injected instead of 3,5-DTBC when starting the experiment. The reaction was monitored, as usual by the uptake of dioxygen.

(ii) A similar experiment with 3,5-DTBQ, was run with the monometallic Pd(II) species.

II.2.4. Oxidation of 3,5-DTBC Using the Supported Monometallic Species

As described in **II.2.3.**, the oxidation of 3,5-DTBC was studied using the supported monometallic Pd(II) species. The amount used was also always 0.50 g as above. Reactions were monitored by the uptake of dioxygen and the analysis of product(s) was as above. Similar control experiments were carried out too.

II.2.5. Oxidation of Catechol in Water.

Oxidations in water (specifications of the deionization apparatus and degassing procedures have been previously mentioned) were all carried out in phosphate buffered solutions at constant ionic strength. The most commonly used solution was of pH 8.0 at μ = 0.20 M.[44]

The reactions were performed in the 500 mL creased flasks as described in **II.2.3.** and the procedures for setup and experimental monitoring were also similar. The amount of **II.1.6.a.** used was always 0.50 g.

II.2.5.a. Oxidation of Catechol at pH 8.0.

Catechol (Aldrich) was oxidized using **II.1.6.a.**, the celite supported bimetallic Pd(II) species. The reaction was monitored by dioxygen uptake. The amount of catechol injected was 0.2753 g (2.50×10^{-3} mol).

II.2.5.b. pH Variations in the Oxidation of Catechol.

The oxidation of catechol was monitored at several different pH buffered solutions to determine if there was a pH dependence in the oxidation. The amount of catechol injected was always the same.

II.2.6. Oxidation of Alcohols in Water.

Alcohols (if liquids, distilled prior to use) were all oxidized in water at pH 8.0 at constant ionic strength, μ = 0.20 M. All the reactions were monitored by the uptake of dioxygen by procedures previously described in **II.2.3**. The products were either isolated by derivatization or by extraction. The characterization was by ^{1}H NMR, melting point and subsequent comparison with authentic samples using melting point as well as the spectral characteristics. All the alcohol oxidations were performed with the bimetallic as well as the monometallic Pd(II) species for purposes of comparison of rates of reaction and of products.

II.2.6.a. Oxidation of Methanol.

This experiment was performed using both 12.5×10^{-3} mol or 25.0×10^{-3} mol of methanol in separate experiments. The monitoring of the kinetics usually became slightly problematic after a short period of time because the product, methanal, being a gas, interfered with the monitoring of gas uptake. The product was identified by the injection of a large excess of a solution of 2,4-dinitrophenylhydrazine reagent.[45] The product was recrystallized twice from CH_2Cl_2 after it was filtered out of the reaction mixture.

II.2.6.b. Oxidation of Other Simple Mono-ols.

The other simple mono alcohols oxidized were ethanol (Burdick and Jackson), 2-propanol (Fisher) and 1-phenyl methanol (Fisher). The amounts of these species used was 2.50 x 10^{-3} mol. The products were isolated as 2,4-dinitrophenylhydrazone derivatives after filtering off the heterogeneous catalyst. In the case of ethanol the flask and the reagent solution were cooled in ice as the product, ethanal, is a very low boiling liquid. For the oxidation of 1-phenyl methanol, the derivatization procedure was unnecessary. The product, 1-phenyl methanal was extracted out of the aqueous layer using CH_2Cl_2 after filtering off the catalyst. The oxidation of 1-phenylmethanol-1,1-d_2 was also carried out.

II.2.6.c. Oxidations of 1,2-Diols.

The diols oxidized were 1,2-ethanediol, 1,2-propanediol, and 2,3-butanediol The amount of diol used was always 2.50 x 10^{-3} mol. The products were identified as derivatives.

II.2.6.d. Oxidation of 1,3-Diols.

The 1,3-diol oxidized was butane-1,3-diol. The kinetics were monitored in the usual manner. Products were identified via ^1H NMR.

II.2.6.e. Oxidation of α-D-Glucose.

2.50×10^{-3} mol of α-D-Glucose (Fisher, used as received) was oxidized as described above for the other alcohols.

II.2.6.f. Oxidation of Allyl Alcohol.

The oxidation of allyl alcohol (2.50×10^{-3} mol) was carried out in like manner to the descriptions above. The products were identified as derivatives.

II.2.6.g. Oxidation of a Homoallyl Alcohol.

The species chosen was 4-penten-2-ol (Aldrich) and 2.50×10^{-3} mol of it was oxidized as described for the other alcohols.

II.2.6.g. Oxidation of a Homohomoallyl alcohol.

The attempt to oxidize a homohomoallyl alcohol was made using 2.50×10^{-3} of 4-penten-2-ol. The products were extracted out of solution after filtering off the supported catalyst.

II.2.6.h. Oxidation of a Cyclic Allyl Alcohol.

The only cyclic allylic alcohol oxidized was 2-cyclohepten-1-ol. This alcohol is not commercially available and was prepared as described in **II.3.** from the cyclic allylic ketone. Under the conditions studied the oxidation proceeded so rapidly that the amounts of alcohol and Pd(II) catalyst material used were reduced to 1.25×10^{-3} mol (0.5 of the amount used in all other alcohols) and 2.5×10^{-2} g (0.05 of the support material used for the other oxidations) respectively. At the end of the reaction the catalyst was filtered off and the products were extracted out of the aqueous filtrate using CH_2Cl_2. The products were identified by ^1H NMR.

II.2.6.g. Isotope Effect Studies in Oxidation of 2-Cyclohepten-1-ol-1-*d*.

2-Cyclohepten-1-ol-1-*d* was synthesized as described in **II.3.** The alcohol was oxidized using conditions as described in **II.2.6.f.**

II.3. Preparative Procedures for Some Substrates and Reagents.

II.3.1. 1-Phenyl Methanol-1,1-d_2.

This alcohol was prepared by a modification of a literature procedure.[19] To a freshly prepared solution of 1.18 g (28.1×10^{-3} mol) of lithium aluminum deuteride (Fluka Chemika) slurried in diethyl ether (distilled from sodium and benzophenone) in a 250 mL three neck round bottom flask was added 4.5 mL (*ca.* 32×10^{-3} mol) of methyl benzoate at 0° C over a period of 15 min. The mixture was allowed to warm to room temperature and then heated at reflux for 6 h. The reaction was cooled to room temperature, neutralized with 2.0 mL of 2.0 M KOH (Fisher). The product was extracted with 2 x 50 mL of dichloromethane (CH_2Cl_2) and finally dried over anhydrous $MgSO_4$. It was purified using a 75 g silica gel column by eluting with 80% hexane / 20% ethyl acetate. The product was characterized by ^1H and ^{13}C NMR.

II.3.2. Synthesis of 2-Cyclohepten-1-ol.

This alcohol was synthesized by a modification of the method of Luche.[46] A stock 4.0 M solution of $CeCl_3.7H_2O$ was made by weighing out 14.90 g of the salt, transferring to a

100 mL volumetric flask and making up the solution using absolute methanol (Fisher, reagent grade). 3.01 g (2.70×10^{-2} mol) of 2-cyclohepten-1-one was taken in a 250 mL Erlenmeyer flask. Seventy mL of the stock 4.0 M cerium(III) solution (>0.027 mol) was added and the solution was stirred using a magnetic stirrer at room temperature for 5 minutes. To this was added 1.02 g (2.70×10^{-2} mol) of sodium borohydride ($NaBH_4$) via spatula directly to the stirred solution over a period of 4 min. The solution was mildly exothermic and it was cooled using a water bath. The evolution of H_2 gas was noticed. The solution was stirred for an additional 5-10 min and then 45 mL of a saturated solution of ammonium chloride was added to neutralize the excess $NaBH_4$. At this point the solution became clearer and appeared mildly yellow. The organic products were extracted using 3 x 30 mL of ether. The ethereal layers were combined and dried over anhydrous $MgSO_4$. The solvent was distilled off and the product was obtained. ^1H and ^{13}C NMR were used to characterize the product. Yield was 2.67 g (88%).

II.3.3. Synthesis of 2-Cyclohepten-1-ol-1-*d*.

The deuteriated species was made by the same method as above. 1.0 g (0.024 mol) of sodium borodeuteride ($NaBD_4$) was used for the reduction instead of $NaBH_4$. In order to maintain the same mole ratios 2.63 g (0.024 mol) of 2-cyclohepten-1-one and 60 mL of the 4.0 M cerium(III) solution were used. 1.60 g (62%) of the deuteriated species was obtained. It was characterized by ^1H, ^{13}C and ^2H NMR. The deuterium label was found only at carbon 1 on the ring.

II.3.4. Preparation of Stock Solutions.

II.3.4.a. 2,4-Dinitrophenylhydrazine

Into a 400 mL beaker, 3.0 g of 2,4-dinitrophenylhydrazine was taken, after being weighed out. 15 mL of concentrated sulfuric acid was added and the solution was stirred till all the solids dissolved. The color was a light yellow. A 70 mL : 20 mL mixture of 95% ethanol : de-ionized water was added carefully over 10 min. The final color of the solution was an orange-red. It was stirred, cooled and stored.

II.3.4.b. 0.2 M Li_2PdCl_4 Solution.

4.301 g (0.102 mol) of lithium chloride (LiCl) and 8.878 g (0.0501 mol) of palladous chloride (Aesar) ($PdCl_2$) were taken in a 250 mL Erlenmeyer flask. Ca. 175 mL of distilled de-ionized water was added and the flask was stoppered. The solution was stirred overnight. It was transferred to a 250 mL volumetric flask and made up so that it was 0.200 M in Li_2PdCl_4, the Pd(II) species.

II.3.4.c. 4.0 M LiCl Solution.

16.96 g (0.400 mol) of LiCl was weighed and transferred via a glass funnel to a 100 mL volumetric flask. Distilled, de-ionized water was used to make up the solution. It was noticed that the dissolution was fairly exothermic. The solution was 4.0 M in LiCl.

II.3.4.d. 2.0 M $HClO_4$ Solution.

Perchloric acid (Fisher) was standardized using sodium hydroxide which had been standardized with potassium hydrogen phthalate. The stock solution was then made by dilution.

II.4. Homogeneous Oxidation Studies of 2-Cyclohepten-1-ol.

The oxidations were carried out at room temperature. The conditions were such that [Pd(II)], [LiCl] and acid [$HClO_4$] were 0.1 M. Usually the reaction was performed in a beaker. The precise amounts of stock solutions were transferred using glass pipettes. Ionic strength was maintained at 2.0 M by using lithium perchlorate ($LiClO_4$). Quinone (recrystallized from petroleum ether) was then added to re-oxidize any zerovalent palladium formed due to the oxidation. The 2-cyclohepten-1-ol was added last. The reaction was worked up after 120 min. Powdered zinc was used to reduce the Pd(II) to Pd(0) which precipitated out of solution. After filtration, 2,4-DNP derivatives of the carbonyl products were made by adding 10 mL of the stock 2,4-dintrophenylhydrazine solution to the filtrate. The 2,4-DNPs were washed with copious amounts of water.

The products were separated by using an alumina column, made with *ca.* 12 g of neutral alumina (Brockmann, neutral, activated, 150 mesh, 58 Å, Camag 507-C-1). The initial elutant was petroleum ether; the polarity was increased by adding ethyl acetate. Six fractions were collected. The column was washed finally with CH_2Cl_2. The products were analyzed by ^1H and ^{13}C NMR. When the oxidations were carried out using the deuteriated species, ^2H NMR was used too.

II.5. Homogeneous Isomerization Studies of 2-Cyclohepten-1-ol.

II.3.3. was used for the isomerization studies. The purpose of these studies was to study the dependencies of the various species in the allylic isomerization. A series of control runs were also done in the absence of the Pd(II) species. The [Cl^-] was maintained at 1.0 M.

II.5.1. Acid Catalyzed Isomerization.

The reaction was performed in a 10 mL volumetric flask. A typical run is described here. The H^+ and Cl^- were pipetted into the volumetric flask from the stock solutions so that their final concentrations would be 0.05 M and 1.0 M respectively. $LiClO_4$ was added to make the ionic strength 2.0 M. A sample of the **II.3.3.** weighing 0.1147 g (0.101 M) was separately dissolved in *ca.* 5 mL of distilled de-ionized water. After the solutions were thermostated for an hour at 25° C, the **II.3.3.** was poured into the 10 mL flask, the volume made up and the timing started. Aliquots of 1.0 mL were withdrawn at ten different time intervals. The work up involved extracting with CH_2Cl_2 and water to which sodium chloride and sodium bicarbonate had been added. The volumes of the extracting solvents were 2-3 mL. The aqueous layer was re-extracted with 2 x 2-3 mL of CH_2Cl_2. All the CH_2Cl_2 layers were combined. The organic layer was washed with *ca.* 3 mL of water, dried ($MgSO_4$) and filtered. The alcohol species in solution were derivatized by adding 0.5 mL of phenyl isocyanate. The phenyl urethanes usually crystallized while the solvent evaporated. The species were then studied by ^2H NMR.

II.5.2. Isomerization Studies with Added Pd(II).

The procedure used was same as above. The additional species were Pd(II) and Q, the latter being added to prevent the precipitation of Pd(0). The Pd(II) study paralleled the acid catalyzed isomerization in that all the concentrations were the same as before. An additional step in the isolation involved the precipitation of Pd(0) using Zn. The filtrate obtained was extracted and the phenyl urethane derivative was made.

A few additional studies were carried out in which the extractions were performed but no derivatives were made. Both ^1H and ^2H NMR were used to characterize the products.

II.6. Heterogeneous Oxidation on a Modified Bimetallic Species.

II.6.1. Modification of Supported Bimetallic Species

To 50 mL of dry, degassed dichloromethane was added 0.1371 g (2.75×10^{-4} mol) of (+)-1,4-*bis*(diphenylphosphino)-1,4-dideoxy-2,3-*O*-isopropylidene-D-threitol ((+)-DIOP) (Aldrich). To this was added 2.50 g (0.5 equivalent of Pd(II) compared to the (+)-DIOP) of the supported bimetallic Pd(II) species. In the first 0.50 h, a color change from a grey to an off grey-yellow, was noticed in the slurried mixture that was stirred at room temperature under a slight positive Argon pressure. After 48 h, the solvent was removed using a vacuum pump. The support was then washed with 3 x 30 mL of degassed CH_2Cl_2 on a filter. It was dried initially in a stream of Argon and subsequently on a vacuum pump.

II.6.2. Oxidation of 4-Hexen-3-ol on Modified Supported Bimetallic Species.

This reaction was set up in a manner similar to that described in **II.2.** The only difference was that 0.50 g of the (+)-DIOP modified supported bimetallic species was used. The reaction was monitored by the usual gas uptake procedure and data was collected up to what was calculated to be only one-half of the total reaction based on a two electron oxidation of all the alcohol.

In a duplicate experiment, the reaction was run with twice the usual amount of alcohol substrate, that is, 5.0×10^{-3} mol. This experiment was stopped after it was *ca.* 35%

completed, based on gas uptake. The modified supported catalyst was removed by filtration and the filtrate was extracted with 5 x 15 mL of CH_2Cl_2. The CH_2Cl_2 was dried (anhydrous $MgSO_4$) and the solvent removed on a vacuum pump. The recovered materials were then separated to isolate the unreacted 4-hexen-3-ol.

II.6.3. Derivatization of Recovered 4-Hexen-3-ol.

To 5.0 g (2.135 x 10^{-2} mol) of (*R*)(+)-α-methoxy-α-trifluoromethylphenylacetic acid ((*R*)(+)-MTPA) was added 20 mL (large excess) of redistilled thionyl chloride ($SOCl_2$) (Aldrich). It was stirred under gentle heat for 5 h. The $SOCl_2$ was distilled off and the acid chloride ((*S*)(+)-MTPA chloride) was fractionally distilled. It was stored under Argon.

The derivatization was carried out by the standard method from Mosher *et. al.*[47] To 0.1000 g (1.00 x 10^{-3} mol) of the alcohol recovered from the latter experiment described above, was added 15 mL of pyridine (Aldrich, Sureseal) in a three neck 50 mL round bottom flask. To this was added 0.3158 g (1.25 x 10^{-3} mol) of the (*S*)(+)-MTPA chloride. The mixture was heated very gently for 24 h under Argon. After cooling down the reaction flask, the mixture was partitioned between 30 mL of water and 25 mL of CH_2Cl_2. The layers were separated, the aqueous layer rewashed with 10 mL of CH_2Cl_2 and the organic layers combined. This was washed with 10% HCl until acidic to blue litmus paper. The organic layer was washed with brine (10 mL), saturated $NaHCO_3$ (20 mL), water (15 mL) and then dried (anhydrous $MgSO_4$). The purified ester, after evaporating the solvent, was analyzed by ^{1}H NMR.

II.6.4. NMR Studies of the (*R*)(+)-MTPA Ester of the Recovered 4-Hexen-3-ol.

The analysis of the stereochemistry of the ester was carried out by the method of Yamaguchi.[48] To 0.2481 g (7.41×10^{-4} mol) of the *R*(+)-MTPA ester of 4-hexen-3-ol taken in a 2.0 mL volumetric flask was added $CDCl_3$ (MSD isotopes, distilled) to make the volume 2.0 mL. Using a pipette, 1.0 mL of this solution (3.71×10^{-1} M) was taken in a 5.0 mm NMR tube. The ^1H spectrum was obtained and the resonances identified. Then the lanthanide induced shift (LIS) of the methoxy peaks originally appearing unseparated at 3.530 ppm, of the (*R*)(+) MTPA diastereomeric esters was studied by progressive additions of *tris*[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium(III) ($Eu(fod)_3$) (Aldrich). The identification of each of the diastereomers was made by comparison with the diastereomeric *(R)*(+)-MTPA esters of a 50:50 racemic mixture of 4-hexen-3-ol.[49]

PART TWO: CHAPTER III

RESULTS

III.1. Synthetic Results for the Ligand System.

The ligand system is either a β-diketone or a β,δ-triketone on a low molecular weight polyphenyl polymer. Although each individual step is difficult to characterize while working with barely soluble species, model compounds of the β-diketone and β,δ-triketone type have been well characterized.[50] In addition, an advantage is that purification is easier to effect at each intermediate step merely by filtering and washing.[51] All ^{1}H NMR spectra were recorded on a 300 MHz Varian VXR 300 spectrometer. ^{13}C NMR spectra were obtained on a Varian VXR 300 spectrometer at 75.46 MHz. The parameters given refer to $CDCl_3$ solutions unless specified otherwise. Chemical shifts for ^{1}H and ^{13}C are relative to $(CH_3)_4Si$. Melting points were determined on a Laboratory Devices Mel-Temp apparatus using a calibrated thermometer.

III.1.1. 4-Acetyl Methylbenzoate.

This compound was characterized by standard ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR:	δ 2.63 (s, 3H); 3.93 (s, 3H); 7.99 (d, 2H, J = 8.25 Hz); 8.02 (d, 2H, J = 8.20 Hz).
^{13}C NMR:	δ 26.88; 52.46; 128.19; 129.82; 133.88; 140.21; 165.73; 197.51.

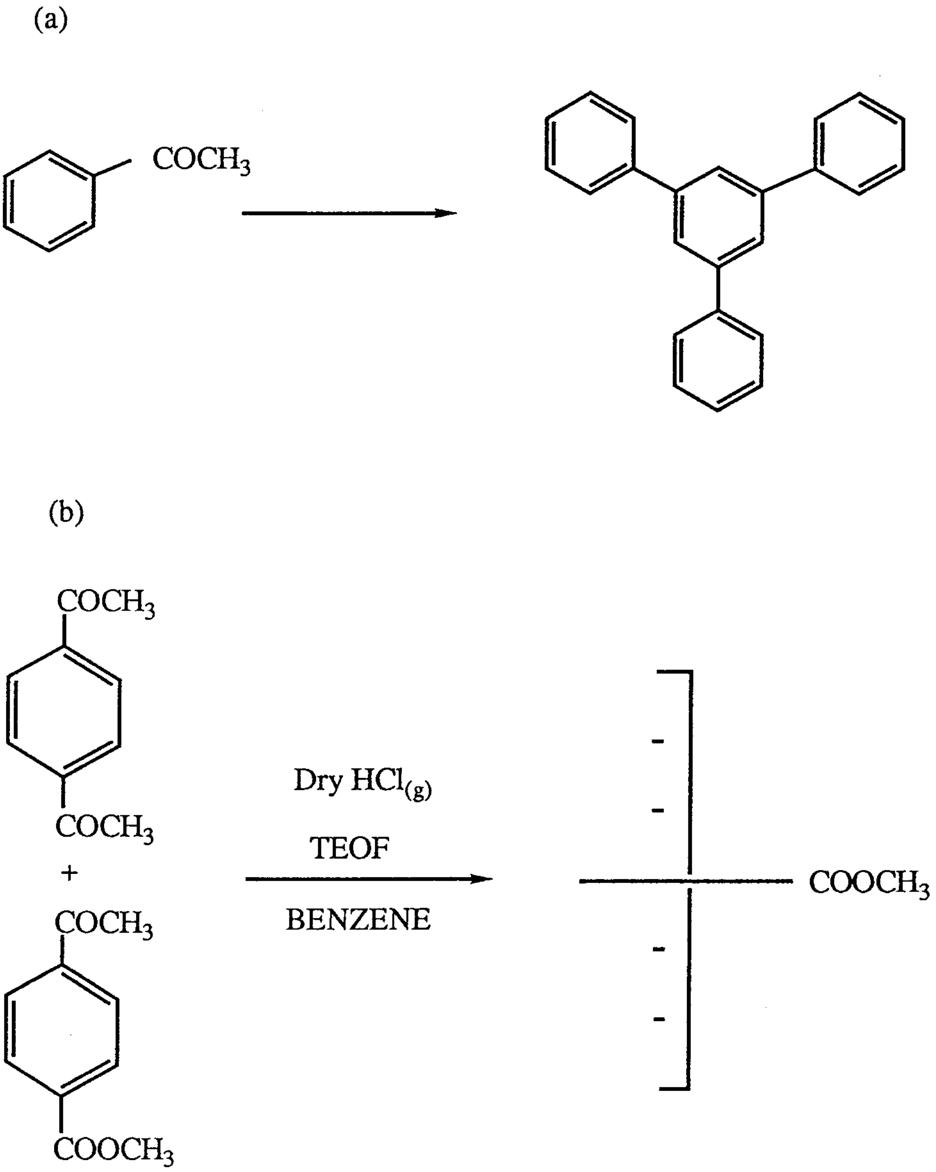


Figure III.1. (a) Cyclic Trimerization of Acetyl Benzene - the idea for the Polymers. (b) Polymerization of Diacetyl Benzene and *p*- Acetyl Methylbenzoate.

III.1.2. Polymer from 4-Acetyl Methylbenzoate and *p*-Diacetyl Benzene.

Polymers of this type have been extensively characterized,[52] by Teplyakov, *et. al.* The actual size of the polymer is irrelevant to the work being pursued. Our evidence for the formation of the "new" benzene rings in this polymerization (see **Figure III.1**) comes from the ^{1}H NMR in which a new benzene resonance is seen at around 7.35 ppm as a singlet. In addition terminal unreacted acetyl groups are seen at 2.60 ppm and terminal methyl ester group resonances at 3.93 ppm. The only other peaks in the spectrum are aromatic peaks that appear in the range from 7.5 - 8.3 ppm.

III.1.3. Modified Polymers.

III.1.3.a. Triketone of II.1.2., II.1.3.a.

Triketone of **II.1.2.** was prepared by a literature procedure that recommended the use of sodium hydride as base.[53] An outline of the synthetic pathway is shown in **Figure III.2.**

The use of an excess[54] of base (more than three equivalents) is important since the monoanion, initially produced, has an acidic proton which is capable of neutralizing the dianion of 2,4-pentanedione. It was found in model experiments that the use of 18-crown-6 improved yields dramatically.

Purification was straightforward because the 2,4-pentanedione is a liquid and can be removed by washing with copious amounts of solvent and any kind of polyketonization that occurs is not adverse to the purposes of this synthesis. The use of 2,4-pentanedione ensures triketonization. ^{1}H NMR of the triketone showed disppearence of the methyl ester resonance and appearance of new resonances at around 2.05 ppm ($-CH_3$), 2.29 ppm ($-CH_2-$) and 5.30 and 5.50 ppm ($=CH-$). All of this is consistent with the formation of the triketone from

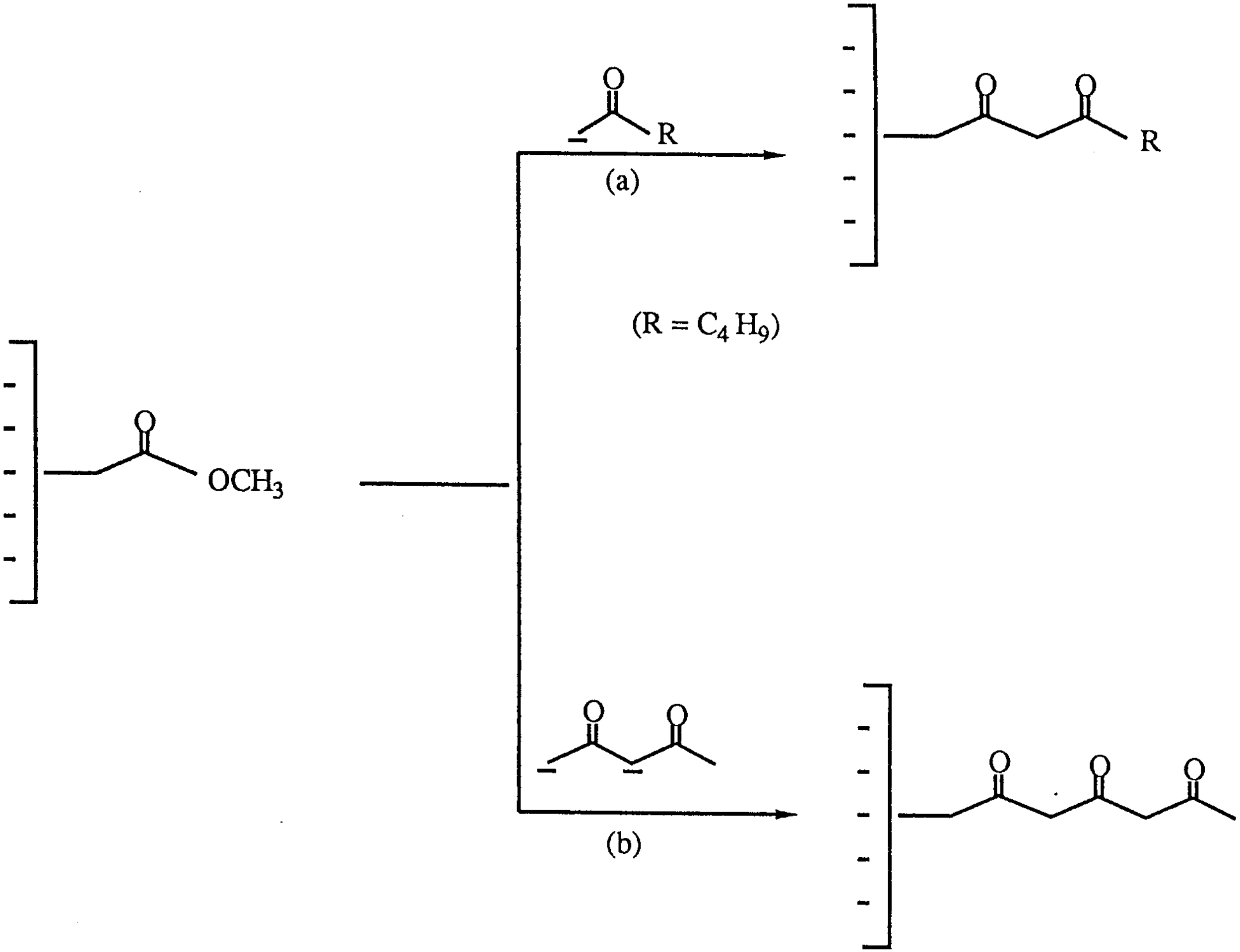


Figure III.2. Scheme Showing Conversion of Terminal Ester Group into (a) Diketone and (b) Triketone.
(The Mono- and Di- Anions Shown are Generated with Base, Usually NaH or LDA).

the model phenyl compound in which the same resonances appear at 2.01, 2.30 and 5.31 and 5.81 ppm respectively. The other peaks are in the aromatic region and fairly complex, as is expected. Close to the mentioned resonances are small resonances that one would expect of isomeric forms of the triketone system.[55]

III.1.3.b. Diketone of II.1.2., II.1.3.b.

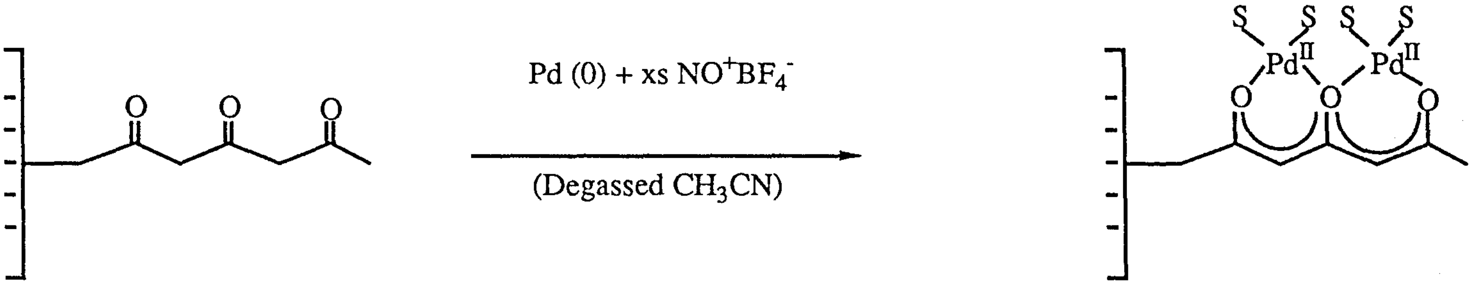
The diketone was made and characterized in similar fashion to the triketone (see **Figure III.2.**). In this case an additional advantage was the use of the $-C_4H_9$ group that could clearly be seen in the spectrum. One of the starting materials is 3,3-dimethyl-2-butanone which is a liquid and, once again, could be removed by washing with solvent. In addition the appearence of this large species as a singlet is very informative as to chemical modification. The product was characterized by ^{1}H NMR in which the methyl ester resonance disappeared and new resonances appeared at 1.10 ppm ($-C_4H_9$), 2.30 ppm ($-CH_2-$) and 5.80 ppm ($=CH-$). As before, this was compared to the diketone from ferrocene, in which very similar resonances were found.

III.1.4. Coating of Polymers on Support.

This experiment is for the purposes of putting polymer on a solid support, in this case celite. In order to ensure that this took place, the slurry was stirred for a long period of time. The absorption of the material on the material by the inorganic support is then ensured by the evaporation of the solvent.[56]

III.1.5. Curing of Supported Polymers.

The curing by prolonged heating and the use of vacuum is done for several



S = CH$_3$CN

Figure III.3. Scheme Showing Palladium(II) Incorporation onto Polymer Triketone on Support.

reasons. One of the reasons is for drying while another is to fix the adsorbed species onto the support. This is a further advantage of the polymeric system. Reagents in reactions effected by modified support species must be capable of diffusing through these gels. In the adsorbed polymer, the diffusion could occur through the porous support. Hartley claims that in supported species, the supported material is only bound on the internal surface of these pores, providing easy diffusional access.[57] Both diketone and triketone were cured in this manner.

III.1.6. Metal Ion Uptake Using Supported Polymers.

The Pd(II) was introduced in to the triketone sites by a modification of the method of Sen[58] in analogous preparations of phosphine complexes of Pd(II) and other metal species starting from the the tetraacetonitrile complex of Pd(II). The only difference is that in this method the $[Pd(CH_3CN)_4](BF_4)_2$ salt is not isolated, but rather, the $[Pd(CH_3CN)_4]^{2+}$ species is generated *in situ* , and then the triketone sites are allowed to serve as the backbone becuase of the two co-ordination sites available, as shown in **Figure III.3**. The other two (bare) sites on the Pd(II) species are occupied by labile solvent molecules.

The total amount of palladium on the polymer surface was determined by analyzing the amount of residual palladium(II) remaining in solution after the absorption. The method of analysis of the residual solution was a standard gravimetric procedure using dimethyl glyoxime. Since the amount of palladium used at the beginning of the experiment is known precisely, the difference between this initial value and the amount of palladium obtained in the gravimetric analysis gives the amount taken up by the support material. By this method it was determined that 0.50 g[59] of the supported triketone took up 1.10×10^{-4} mol of palladium.

By the same method it was determined that an equivalent amount of the monometallic system took up 6.25 x 10^{-5} mol of palladium. This shows that the difference in the amount of metal taken up is 1.76. This is indirect evidence for the fact that the bimetallic system incorporates more metal because of two available sites for the metal to be bound.

III.1.7. 1-Phenyl Methanol-1,1-*d*$_2$.

The deuteriated alcohol was characterized by ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR($CDCl_3$) :δ 1.90 (bs, 1H); 7.15 - 7.29 (m, 5H).

^{13}C NMR($CDCl_3$) :δ 64.19 (p, CD_2); 126.32; 127.44; 128.37; 140.64.

III.1.8. 2-Cyclohepten-1-ols.

The alcohol, 2-cyclohepten-1-ol, was prepared so that allylic alcohol oxidations could be performed on a cyclic system. Very few such studies have been done in Pd(II) chemistry in homogeneous solution. This would provide an opportunity to do studies of a homogeneous Wacker type oxidation and compare it with oxidation using the bimetallic supported Pd(II) species.

The Luché reduction proceeds extremely well if a slight excess of the Ce(III) solution is used. The literature recommends a 1:1:1 ratio of the allylic ketone to the sodium borohydride to the Ce(III) solution. Isolation of the product requires no special purification technique. ^{1}H NMR($CDCl_3$) shows the ring saturated ring protons between 1.40 and 2.20 ppm, the $\underline{C}$HOH at 4.30 ppm and the olefin multiplet at 5.70 ppm. The ^{13}C spectrum has olefinic carbons at 140.04 and 132.18 ppm. The alcoholic carbon appears at 74.20 ppm while the nonolefinic ring carbons are at 38.87 ppm, 30.79 ppm and 28.91 ppm.

The deuterium labelled analog was made in a similar manner to the non-deuteriated species. The ^{1}H NMR showed no peak at 4.30 ppm. The ^{13}C NMR showed a splitting of the alcoholic carbon due to the presence of the deuterium label. ^{2}H NMR ($CHCl_3$) showed one deuterium peak at 4.30 ppm,[60] confirming the presence of the deuterium label.

III.2. Heterogeneous Oxidations.

All the reactions studied were oxidations. They were studied in only two different solvent systems; the predominant solvent was water, which is of practical importance. The only experiments that were performed in methanol were the oxidations with 3,5-di*tert*butylcatechol (3,5-DTBC) as the substrate. All other oxidations, that is, of catechol and that of other alcohols were carried out in water.

III.2.1. Method of Analysis of Kinetic Data.

The reactions, as described in the experimental section, were performed on a manifold system that provided a means for measuring gas uptake. Control experiments showed that the reactions only proceeded in the presence of the catalytic Pd(II) species.[61]

In terms of collecting data, readings were taken at regular time intervals (t). Readings consisted in measuring the volume of dioxygen consumed (V_t), at time t, by the reaction.

The reactions were analyzed in terms of two electron oxidations. The rationalization and assumptions involved are the following. First, the oxidation of an alcohol to a ketone or aldehyde is a two electron oxidation. The oxidation of a catechol to a quinone is also two electron in nature. Second, the common palladium couple in oxidations is Pd(II)/Pd(0), a two electron process. Using this information, an infinity reading is calculated for the two electron oxidation (V_∞) based on the amount of substrate to be oxidized. The oxygen reoxidized the reduced form of the palladium, which was the oxidant for the organic substrate.

The amount of dioxygen taken up by the solvent[62] is between 5.0 and 5.5 mL for methanol and 1.0 - 1.5 mL for the aqueous solutions under the conditions used. The amount of O_2 taken up by the solvent was accounted for by subtracting this from the V_t readings, and the corrected readings are called $V_{t\,(corr)}$. Thus V_∞ - $V_{t(corr)}$ corresponds to the amount of starting catechol left behind.

A pseudo first order treatment in terms of the substrate that was oxidized was then made using the readings obtained and plotting the natural logarithm of (V_∞ - $V_{(corr)}$) versus the corresponding time (t).[63] Pseudo first order rate constants (k_{obs}) were then obtained from the slope. The total amount of Pd(II) on the monometallic or bimetallic Pd(II) systems was used and the k_{obs} values were divided by these concentrations to give bimolecular rate constants (in M^{-1} s^{-1}) as seen in **Table III.1. - Table III.7.** In this manner the differences in the amounts of palladium between the monometallic and bimetallic systems is accounted for, and valid comparison of the numbers can be attempted.

III.2.2. Oxidations of Catechols in Methanol.

All catechol oxidations were performed at 25 °C as described in the experimental section. Experiments were usually duplicated. The kinetic reaction mixtures were analyzed to determine products. At the end of the experiment the apparatus was disconnected from the manifold and the heterogeneous solution was filtered to remove the solid supported catalyst. The filtrate was taken in a beaker and the solvent was air evaporated to obtain product(s). The product(s) were dissolved in $CDCl_3$ and the ^1H NMR, ^{13}C NMR and IR spectra were taken for purposes of identification.

III.2.2.1. Products from the Oxidations in Methanol.

The oxidation of 3,5-di*tert*butyl catechol with the bimetallic system was very clean, giving only one major product, that is, dimethyl 2,4-di*tert*butylmuconate. The product was not subjected to any purification procedures for two reasons. First, the spectra were very clean and showed predominantly the diester product. The only other materials were 3,5-di*tert*butyl-1,2-benzoquinone and some traces of starting catechol. The second reason was that attempted purification procedures inevitably resulted in some possible lactonization to give other products. No attempt was made to try and identify these species.[64]

3,5-di*tert*butyl-1,2-benzoquinone:

^{1}H NMR($CDCl_3$) : δ 1.19 (s, 9H); 1.23 (s, 9H); 6.18 (d, J = 2.4 Hz, 1H); 6.90 (d, J = 2.4 Hz, 1H).

^{13}C NMR($CDCl_3$) : δ 27.85; 29.13; 35.44; 35.99; 122.05; 133.44; 149.90; 163.26; 180.04; 181.09.

IR($CDCl_3$) : 1650 cm^{-1} (C=O).[65]

Dimethyl 2,4-di*tert*butyl muconate :

^{1}H NMR($CDCl_3$) : δ 1.10 (s, 9H); 1.20 (s, 9H); 3.60 (s, 3H); 3.65 (s, 3H); 5.75 (d, J = 1.9 Hz, 1H); 6.25 (d, J = 2.0 Hz, 1H).[66]

^{13}C NMR($CDCl_3$) : δ 25.88; 29.37; 35.13; 39.93; 52.28; 55.16; 113.13; 132.01; 144.74; 148.79; 162.10; 163.80.

IR($CDCl_3$) : 1680 cm^{-1}.

Isolation of the reaction products was made at various time intervals to see if the reaction was proceeding in two 2 electron steps through the formation of the intermediate 3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-DTBQ) or if a direct four electron oxidation was occurring. Based on the following reasons, it was concluded that the reaction was proceeding in two 2 electron steps. The first reason is that analysis of the products at various reaction times showed initial formation of the 1,2-benzoquinone until a point. Second, after a fairly substantial amount of this had formed, only then was further reaction noticed. Observation shows that the reaction occurs in two steps. Entries 2 and 4 in **Table III.1.** indicate that the formation of the quinone in the first step is more than 12 times faster than the second, ring cleavage, step.

The corresponding monometallic system, **II.2.6.b.**, was analyzed in a similar fashion. It was observed that the only product obtained was the 3,5-di-*tert*-butyl-1,2-benzoquinone.

III.2.2.2. Kinetics for the Oxidations of Catechols in Methanol.

Kinetics for the oxidations of the 3,5-di*tert*butyl catechol were studied as described in the experimental section. The method of analysis of data is described in **III.2.1.** The conditions of the catechol ring cleavage oxidations in methanol are optimized. The reactions were carried out with 1.65 x 10^{-6} mol of added sodium methoxide to make the solution alkaline as it was found that this was necessary for us to effect ring cleavage. If more basic solution was used there is the complication of an interfering reaction that leads to faster but nonselective oxidation of the catechol. Under more basic conditions, it was found that molecular oxygen reacted direcly with the catechols, as reported by Grinstead.[67] Even under the conditions of our experiments there is a small amount of direct air oxidation of the catechol. In the case of 3,5-di*tert*butyl catechol in methanol, this air oxidation occurred to the extent of giving 28% conversion to 3,5-DTBQ in a period that is three times longer than that in which the bimetallic catalyst was able to effect ring cleavage. In terms of treating the data the reaction was attributed to a direct molecular oxygen reaction and could be treated as a parallel reaction.[68]

The rate constant for the catalytic oxidation was separated from the direct oxidation and the rate constants given in **Table III.1.** are for the catalyzed reaction alone. Entries 1 and 3 are for two separate stages in the oxidation of 3,5-DTBC with the monometallic system while entries 2 and 4 are for the bimetallic system. In the first step, that is the formation of 3,5-DTBQ, the bimetallic catalyst is more than 45 times quicker than the monometallic system.

III.2.3. Oxidations of Catechol in Water.

Catechol was oxidized in water under the conditions described in the experimental section. The pH was maintained using phosphate buffers. A complete analysis of the reaction was made at pH 8.0. The reason for using 3,5-di-*tert*-butyl catechol in methanol was because (a) 3,5-DTBC is insoluble in water, (b) catechol oxidation tends to give polymeric products in addition to muconic acid.[61,64] A comparison of the rate constants obtained for catechol in water (0.155 M^{-1} s^{-1}) and 3,5-DTBC in methanol (0.29 M^{-1} s^{-1}) can also be seen in **Table III.1.**, a difference of 1.9 in favor of the 3,5-DTBC in methanol is seen. Interestingly, the second stages have the same rate constants, within experimental error.

Table III.1. Rate Constants for the Oxidation of Catechols.[a]

No	Substrate[b]	Catalyst type[c]	k[d] (M^{-1} s^{-1})
1.	3,5-Di*tert*butyl catechol[e]	Monometallic	0.0064[f]
2.	3,5-Di*tert*butyl catechol[e]	Bimetallic	0.29[f]
3.	3,5-Di*tert*butyl-1,2-benzoquinone[e]	Monometallic	----[g]
4.	3,5-Di*tert*butyl-1,2-benzoquinone[e]	Bimetallic	0.023[h]
5.	Catechol[i]	Bimetallic	0.155[f]
6.	Quinone[i, j]	Bimetallic	0.031[h]

---

[a] Using a palladium catalyst supported on celite as described in text.

[b] Usually 2.5 x 10^{-2} M.

[c] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[d] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

[e] In methanol, with a catalytic amount of base, at 25 °C, in creased 500 mL flasks in an atmosphere of dioxygen.

[f] These rate constants are based on the first step of the oxidation, that is, the formation of the quinone.

[g] Barely any oxygen uptake was observed in several days of reaction.

[h] This is for the second step of the oxidation, that is ring cleavage. Experimentally, it is a continuation of the reaction started with the corresponding catechol. Data is treated as a separate 2e- oxidation because of the manner in which we observe the oxidation to occur.

[i] In water, in phosphate buffered solution (pH 8.0, μ = 0.20 M).

[j] Assumed based on analogy to the methanol system - no attempt has been made to isolate the quinone.

III.2.3.1. pH Study for the Oxidations of Catechol.

A short study of the pH dependence in the oxidation of catechol in water was made. The data from this study is collected in **Table III.2.** There are four points to note from this table. The first is that at pH 5.0, the reaction did not proceed past a 2 electron oxidation. The second is that the rate constants are for the first step of the oxidation, the formation of quinone. Third the reactions become faster as the solutions become more basic. The increase in rates in going from pH 5.0 to pH 8.0 or to pH 9.1 is not very large (1.6 and 2.2 times respectively). Finally, it is a little difficult to make a comparison beyond this point because the interfering reaction due to the molecular O_2 reacting directly is very serious beyond pH 9.1. Hence, although the last number is very large, it was not possible to determine the amount of interference to any degree of accuracy.

III.2.3.2. Kinetics for the Oxidations of Catechol in Water.

A complete analysis of the oxidation of catechol in water was made at pH 8.0. The reaction proceeded in two stages as described in the oxidations in methanol. In water the difference between the first and second stages was less dramatic, with a slowing down by a factor of 5.2. Data for the oxidation of catechol in water are found in **Table III.1.** and **Table III.2.** An interesting point to note is the fact that at acidic pH, there is no measurable oxygen uptake beyond the 2 electron stage, quinone formation.

III.2.4. Oxidations of Alcohols in Water.

All the oxidations of the alcohols were performed at 25 °C in water at pH 8.0 (phosphate buffered) with μ = 0.20 M. The reactions were all run at 100 mL volume.

Table III.2. Rate Constants for Catechol Oxidations as a Function of pH.[a]

No	pH[b]	k[c] (M^{-1} s^{-1})
1.	5.00	0.010
2.	8.00	0.16
3.	9.10	0.22
4.	12.0	0.55

[a] All oxidations were in water at 25 °C in phosphate buffered solutions. The pH study was done using the bimetallic Pd(II) system (see text for description of system). The substrate was always 2.50 x 10^{-2} M Catechol. The bimolecular rate constants are from the first 2e- oxidation, presumably to the Quinone.

[b] The pH values are obtained by using recipies for phosphate buffers (μ =0.20 M)

[c] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)].

The amount of substrate (alcohol) used was always 2.50 x 10^{-3} M unless otherwise mentioned. All oxidations were carried out with both the monometallic and the bimetallic systems. The amount of catalyst used was always 0.50 g, which made it 1.10 x 10^{-3} M in [Pd(II)] for the bimetallic system and 6.25 x 10^{-4} M for the monometallic system. The method of data collection and analysis was exactly as described in **III.2.1.** The data are treated as two electron oxidations. Data from the alcohol oxidations is found in **Table III.3.** - **Table III.7.**

Additional studies, like isotope effect studies, comparison of products with those obtained in a homogeneous oxidation (one case) and changes in concentrations of substrate and catalyst were done for mechanistic purposes. Usually yields, if reported, are not isolated yields, but indirectly from volume of oxygen uptake and the analysis of the NMR spectra. Usually in all of the cases analyzed carefully, the reactions went to completion, if allowed sufficient time. Sometimes because infinity time took so long to reach, the reactions were stopped short of completion.

III.2.4.1. Oxidation of Methanol.

The first alcohol that was oxidized was methanol. The oxidation of methanol was carried out at both pH 8.0 and pH 9.1. Product analysis was done only for the oxidation at the former pH. The amounts of methanol used in the oxidations were 2.50 x 10^{-3} mol, 12.5 x 10^{-3} mol and 25.0 x 10^{-3} mol.

The product, methanal, was isolated as the 2,4-dinitrophenylhydrazone (2,4-DNP) derivative (M. P.: 164 °C - 166 °C)[69] and characterized in addition by ^{1}H NMR.

Kinetic data was a little difficult to collect by the gas uptake procedure because formaldehyde is a gas at room temperature and interfered with the O_2 volume readings. Thus higher concentrations of methanol were used and data collected in the initial part of the reaction analyzed. Good pseudo first order data was obtained. The data can be found in **Table III.3.** A comparison between the monometallic and the bimetallic system shows little difference, with a rate enhancement of 1.4 for the bimetallic system. A slight enhancement of rate, from k = 0.0018 M^{-1} s^{-1} to k = 0.0023 M^{-1} s^{-1} was noticed on going to a more basic solution (pH 9.10). The data also revealed the first order dependence in the alcohol because of the constancy of the bimolecular rate constant under conditions of different initial concentrations. It indicates too that our assumption of approximating a first order in total [Pd(II)] is justified.

III.2.4.2. Oxidations of Ethanol.

The data for the oxidation of ethanol is found in **Table III.3.** Interference, similar in nature to that in the oxidation of methanol, was found in these oxidations. Difficulty in gas uptake readings, usually after about one-half of the ethanol was oxidized, was attributed to the presence of ethanal, a gas under the experimental conditions.

The only product obtained under these conditions was ethanal that was isolated as the 2,4-DNP and characterized by ^{1}H NMR. Derivative M.P.: 163 °C - 165 °C.

The difference in rates between the bimetallic and monometallic case is more striking here. The bimetallic system is 5.2 times faster in the oxidation of ethanol. Perhaps what is more remarkable is that ethanol is much faster than methanol in the bimetallic case, with ethanol oxidation being almost 11 times faster. In the monometallic system, on the other hand, the difference is only 3.7.

Table III.3. Rate Constants for the Oxidation of Primary Alcohols.[a, b]

No	Substrate[c]	Catalyst type[d]	k[e] (M^{-1} s^{-1})
1.	Methanol	Monometallic	0.0013
2.	Methanol[f]	Bimetallic	0.0018
3.	Methanol[g]	Bimetallic	0.0023
4.	Ethanol	Monometallic	0.0048
5.	Ethanol	Bimetallic	0.025

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[a] Using a palladium catalyst supported on celite as described in text.

[b] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, μ = 0.10 M) solutions at 25 °C in stirred 500 mL creased flasks in an atmosphere of dioxygen. Reactions were monitored by the uptake of dioxygen.

[c] Usually 2.5×10^{-2} M.

[d] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[e] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

[f] Methanol experiments were also run at 12.5×10^{-2} M and 25.0×10^{-2} M.

[g] At pH 9.1, all other conditions are the same.

III.2.4.2.c. Product Inhibition.

An attempted study of product inhibition was made in the oxidation of ethanol. The reaction was performed as described in the experimental section. 2.50 x 10^{-2} M of acetaldehyde was injected with an equal molar amount of ethanol at the start of the reaction. Analysis of the initial part of the kinetic data revealed no difference in rate constant, thus showing no product inhibition. It was concluded, therefore, that the acetaldehyde was interfering with the kinetic analysis simply because of high vapor pressure. This was partially confirmed because the higher the amount of acetaldehyde injected at the start, the sooner the dip in the plot in terms of the volume of dioxygen taken up with time. However initial rates remained the same, within experimental error. In addition, at very long times in the oxidation of methanol and ethanol, when higher concentrations were used, the Hg level in the buret usually indicated a gas volume increase.

III.2.4.3. Oxidations of 2-Propanol and 1-Phenylmethanol.

Both of these species were studied under the conditions of all the other oxidations. 1-Phenylmethanol-1,1-d_2 was synthesized to study the isotope efect in these oxidations.

III.2.4.3.a. Product analysis.

The product in the oxidation of 2-propanol was 2-propanone which was isolated as the 2,4-DNP. (M. P.: 124 °C - 126 °C). The product in the oxidation of benzyl alcohol was benzaldehyde, isolated directly from the reaction. In both cases ^{1}H NMR was used to characterize the product. The benzaldehyde was identified by its characteristic aldehydic peak at 9.95 ppm[70] in the ^{1}H NMR.

Table III.4. Rate Constants for the Oxidations of 2-Propanol and 1-Phenylmethanol.[a,b]

No	Substrate[c]	Catalyst type[d]	k[e] (M^{-1} s^{-1})
6.	2-Propanol	Monometallic	0.0083
7.	2-Propanol	Bimetallic	0.035
8.	1-Phenylmethanol	Monometallic	0.067
9.	1-Phenylmethanol	Bimetallic	0.14
10.	1-Phenylmethanol-1,1-d_2	Bimetallic	0.056

---

[a] Using a palladium catalyst supported on celite as described in text.

[b] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, μ = 0.20 M) solutions at 25 °C in stirred 500 mL creased flasks in an atmosphere of dioxygen. Reactions were monitored by the uptake of dioxygen.

[c] Usually 2.5 x 10^{-2} M.

[d] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[e] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

III.2.4.3.b. Kinetics.

Data from the kinetics of the oxidations of these two species are to be found in **Table III.4.** The bimetallic system shows an oxidation which is 4.2 times faster than the comparative monometallic case. The secondary alcohol is faster than both the primary alcohols methanol and ethanol. Benzyl alcohol is faster than all three species. The bimetallic system is only 2.1 times faster than the monometallic system. Benzyl alcohol is 4 times faster than 2-propanol.

III.2.4.3.c. Isotope Effect using 1-Phenylmethanol-1,1-d_2

In a similar manner the oxidation of the deuteriated species was studied. The product was 1-phenylmethanal-1-*d*. The rate constant obtained, $k = 0.056\ M^{-1}\ s^{-1}$, gives an isotope effect, $k_H/k_D = 2.5$. This is slightly higher than isotope effects obtained in comparable Pd(II) oxidations in homogeneous solution.

III.2.4.4. Oxidations of 1,2-Diols.

The 1,2-diols oxidized were ethane-1,2-diol, propane-1,2-diol and butan-2,3-diol. The alcohols having more than one hydroxy group have more than one oxidizable center and thus all of the oxidations were stopped at the two electron stage. The rate data is gathered in **Table III.5.**

The products of these oxidations were identified as the 2,4-DNP derivatives. The product of the oxidation of ethane-1,2-diol was 2-hydroxyethanal. The product of the oxidation of propane-1,2-diol was predominantly 1-hydroxy-2-propanone. The product of the oxidation of the butane-2,3-diol was 3-hydroxy-2-butanone.[71] The rate enhancements for bimetallic over monometallic were 30.2, 9.5 and 6.6 for ethane-1,2-diol, propane-1,2-diol and butane-2,3-diol. The most dramatic difference

Table III.5. Rate Constants for the Oxidations of polyols.[a, b]

No	Substrate[c]	Catalyst type[d]	k[e] (M^{-1} s^{-1})
11.	Ethane-1,2-diol	Monometallic	0.00053
12	Ethane-1,2-diol	Bimetallic	0.016
13.	Propane-1,2-diol	Monometallic	0.0021
14.	Propane-1,2-diol	Bimetallic	0.020
15.	Butane-2,3-diol	Monometallic	0.0062
16.	Butane-2,3-diol	Bimetallic	0.041
17.	Butan-1,3-diol	Monometallic	0.0032
18.	Butan-1,3-diol	Bimetallic	0.0078
19.	α-D-Glucose	Monometallic	0.0072
20.	α-D-Glucose	Bimetallic	0.077

---

[a] Using a palladium catalyst supported on celite as described in text.

[b] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, μ = 0.20 M) solutions at 25 °C in stirred 500 mL creased flasks in an atmosphere of dioxygen. Reactions were monitored by the uptake of dioxygen.

[c] Usually 2.5 x 10^{-2} M.

[d] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[e] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

was mentioned with the ethane-1,2-diol. The bimetallic systems gave consistently better rates than their monometallic counterparts.

III.2.4.5. Oxidations of a 1,3-Diol.

The only 1,3-diol oxidized was butane-1,3-diol. The data for this oxidation is also in **Table III.5**. There is an increase in rate in going from the monometallic to the bimetallic system of only 2.4. The 1,3-diol is also slower than all the 1,2-diols studied. The product in this oxidation was predominantly 4-hydroxy-2-butanone.

III.2.4.6. Oxidation of α-D-Glucose.

The only polyhydroxy compound oxidized was a sugar, α-D-glucose. The data are in **Table III.5.** along with the diols. The bimolecular rate constant from initial rate data is $k = 0.077\ M^{-1}\ s^{-1}$. The reason for this high number is possibly that more reaction sites are available for the oxidation. The rate enhancement in going from the monometallic to the bimetallic system is 10.7.

III.2.4.7. Oxidations of Allyl Alcohol.

The oxidation of 2-propen-1-ol was especially important in terms of palladium chemistry because of the very detailed mechanistic work that has been done with this species in homogeneous solution with $PdCl_4^{2-}$.[30,72] The method of study was as described for all the other oxidations in water. The data for the rate constants is in **Table III.6.**

III.2.4.7.a. Product Analysis.

In the oxidation with the bimetallic catalyst two products were obtained for the oxidations of 2-propen-1-ol in water. The major product arising from direct hydride abstraction from the alcohol carbon was 2-propen-1-al (80%) and the minor product was 3-hydroxy-1-propanal arising from double bond oxidation via hydroxypalladation (20%). Derivative M.P: for 2-propen-1-al: 163 °C - 165 °C and 2-hydroxy-1-propanal: M.P.: 126 °C - 129 1,14. ^{1}H NMR data was compared with the literature.[62(a)]

With the monometallic system on the other hand, the same two products were obtained but this time 3-hydroxy-1-propanal was 75% while the 2-propen-1-al was only 25%. The difference is attributable to the idea that one metal of the bimetallic system probably forms a π-complex with the double bond while the other Pd(II) abstracts the hydride to give the alcohol oxidation. In the monometallic system this is unlikely and the only major product would then arise from hydroxypalladation.

III.2.4.7.b Kinetics.

The difference in rates is also striking. The bimetallic system is faster by a factor of 10. Both rate constants reveal far faster oxidations for the allyl alcohol over all other alcohols. The π complexation probably also increases the rates so much that there is more than an order of magnitude difference between allyl alcohol and benzyl alcohol and almost three orders of magnitude between allyl alcohol and methanol.

III.2.4.8. Oxidations of a Homoallylic alcohol.

The bimolecular rate constant obtained for oxidation of the homoallylic alcohol,

Table III.6. Rate Constants for the Oxidations of Allyl Alcohol and Congeners[a, b]

No	Substrate[c]	Catalyst type[d]	k[e] (M^{-1} s^{-1})
21.	2-Propen-1-ol	Monometallic	0.15
22.	2-Propen-1-ol	Bimetallic	1.5
26.	4-Penten-2-ol	Monometallic	
27.	4-Penten-2-ol	Bimetallic	0.0038
28.	4-Penten-1-ol	Monometallic[f]	----
29.	4-Penten-1-ol	Bimetallic[f]	----

---

[a] Using a palladium catalyst supported on celite as described in text.

[b] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, μ = 0.20 M) solutions at 25 °C in stirred 500 mL creased flasks in an atmosphere of dioxygen. Reactions were monitored by the uptake of dioxygen.

[c] Usually 2.5 x 10^{-2} M.

[d] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[e] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

[f] Insufficient data because of barely any oxygen uptake in several days of reaction.

4-penten-2-ol, with the bimetallic system was 0.0038 M^{-1} s^{-1}, almost the same as that obtained for methanol and 390 times slower than allyl alcohol itself.

III.2.4.9. Oxidations of a Homohomoallyl alcohol.

Oxidations of a homohomallylic alcohol, 4-penten-1-ol were attempted. The oxidation does not occur to any measurable extent. Data for these reactions can be seen in **Table III.6.** After leaving the reaction for several days and extracting the products out of solution with CH_2Cl_2, ^1H NMR revealed a complicated mixture, partial analysis of which revealed that bond isomerization had occured. A small amount of oxidation product was seen also. No attempt was made to separate and determine the products in quantitative fashion, as this was not the objective of the experiment. The bond isomerization is not surprising, in light of known palladium homogeneous chemistry.[73]

III.2.4.10. Oxidations of 2-Cyclohepten-1-ol.

Cyclic allylic alcohols have lower π complex stabilities than acyclic species. This could lead to, quicker rates of oxidation than with acyclic species in the case of species with π bonds becuse decomposition of the π complexed intermediate could occur quickly. The oxidations were as performed earlier except that they occurred with such rapidity, that the amounts of starting alcohol and catalyst had to be drastically reduced to be able to monitor the kinetics. The amount of alcohol used was 1.25 x 10^{-3} mol, while the amount of bimetallic catalyst used was 20 times less. The isotope effect was studied too. A k_H/k_D = 3.6 was obtained.

Table III.7. Rate Constants for the Oxidations of Allylic Alcohols.[a, b]

No	Substrate[c]	Catalyst type[d]	k^{e} (M^{-1} s^{-1})
21.	2-Propen-1-ol	Monometallic	0.15
22.	2-Propen-1-ol	Bimetallic	1.5
23.	2-Cyclohepten-1-ol	Bimetallic	6.5
24.	2-Cyclohepten-1-ol-1-*d*	Bimetallic	1.7
25.	2-Cyclohepten-1-ol	Bimetallic	35[f]

---

[a] Using a palladium catalyst supported on celite as described elsewhere in text.

[b] All reactions are oxidations in aqueous, phosphate buffered (pH 8.0, μ = 0.20 M) solutions at 25 °C in stirred 500 mL creased flasks in an atmosphere of dioxygen. Reactions were monitored by the uptake of dioxygen.

[c] Usually 2.5 x 10^{-2} M.

[d] This refers to the facility on the ligand system for either co-ordinating Pd(II) in a monometallic or bimetallic fashion at each available site.

[e] Bimolecular rate constants were calulated by assuming a homogeneous system and dividing the k_{obs} values, obtained by pseudo first order treatement, by the total [Pd(II)] in the mono- or bi- metallic case as relevant.

[f] mixed solvent system - the allylic species was injected in dichloromethane because of solubility problems in above two experiments.

III.2.4.10.a. Product Analysis.

The alcohol used in the oxidations was prepared by a Luché reduction of the corresponding allylic ketone. The two products obtained in the oxidation were 3-hydroxycyclohepten-1-ol (20%) and 2-cyclohepten-1-one (80 %). As expected from the earlier oxidation of the 2-propen-1-ol, the predominant product arises from the alcohol bond oxidation rather than olefin oxidation.

III.2.4.10.b. Kinetics.

The kinetics of the reaction were monitored in similar manner to all the other oxidations. The data are given in **Table III.7.** The reaction was 5.3 times faster than the equivalent reaction with 2-propen-1-ol. Since it was noticed that 2-cyclohepten-1-ol is not water soluble, a mixed solvent was used in that the alcohol was dissolved in CH_2Cl_2 and this allowed the alcohol better contact with the solid catalyst. It was found that the alcohol floated on the surface of the water and this did not allow it to mix freely with the supported catalyst. There was a rate enhancement noticed under mixed solvent conditions, with $k = 35\ M^{-1}\ s^{-1}$. This is more than 20 times faster than the rate constant obtained for the oxidation of allyl alcohol itself.

III.2.14.10.c. Isotope Effect.

The isotope effect for this oxidation was investigated using 2-cyclohepten-1-ol-1-*d*. The substrate was prepared as described in the section on the homogeneous oxidation of this species. The rate constant obtained was $k = 1.7\ M^{-1}\ s^{-1}$. This gives a $k_H/k_D = 3.6$. Now, since only 80% of the product is obtained by a direct abstraction of a hydride or a deuteride, the number could be only 2.9 if one assumed that there was no contibution to the isotope effect from the double bond oxidation reaction.

III.3. Homogeneous Oxidations.

Four products were obtained from the oxidation of 2-cyclohepten-1-ol in water in homogeneous solution using $PdCl_4^{2-}$. The products were 2-cycloheptenone (6%), cycloheptanone (38%), 2-hydroxycycloheptanone (25%) and 3-hydroxycycloheptanone (31%). The first and second products were identified as their 2,4-DNPs using standard ^1H and ^{13}C NMR, and by the subsequent comparison with authentic commercial samples. The hydroxy ketones were isolated via column chromatography and identified by homonuclear decoupling and COSY[74] on both the deuteriated and non-deuteriated species, in addition to the standard spectra.

The conditions for these oxidations in homogeneous solution are usually $[H^+] = 0.040$ M - 1.0 M, $[Cl^-] = 0.10$ M - 1.0 M and $[Pd(II)] = 0.0040$ M - 0.10 M. Under these conditions usually scrambling of the deuterium giving an equilibrium distribution between the allyl and the vinyl position is the predominant reaction. This reaction could be acid or Pd(II) catalyzed, if not both. Due to the fact that we were using a ^2H label at position 1 on the ring to help determine the oxidation products, it would be necessary for us to know if we did get scrambling of the label, and if we did get scrambling, to quantitate it in some manner. This information would be useful in product analysis. Under the conditions described only acid catalyzed isomerization of the deuterium label occurred.

Aliquots of the reaction mixture were quenched with bicarbonate, extracted and derivatized as isocyanates. The ^2H resonance of the derivative from 2-cyclohepten-1-ol-1-*d* appears at 5.3 ppm while that of the allylic isomer, 2-cyclohepten-1-ol-3-*d* appears at 5.8 ppm. The relative ratio of the starting isomer is obtained as a percentage of the total of the integrals of the two resonances. The natural logarithm of this value, after accounting for the equilibrium, is plotted versus time. The data is treated as that from a reaction approaching equilibrium,[75] where the equilibrium is a 50:50 mixture of the two isomers. The k_{isom} is obtained from the slope. Under the conditions of $[H^+] = 0.10$ M and $[Cl^-] = 1.0$ M we obtained a pseudo first order $k_{isom} = 7.6 \times 10^{-4}\ s^{-1}$ for acid catalyzed deuterium scrambling.

No rate data was obtained for these oxidations because of solubility problems under the chosen experimental conditions.

III.4. Heterogeneous Oxidations on the Modified Bimetallic Species.

III.4.1. 4-Hexen-3-ol Oxidation.

The data was treated by the usual method described earlier. The only difference was that V_∞ was calculated based on one-half of the total amount of alcohol. Thus it was assumed that only one of the enantiomers of the racemate reacted. The pseudo first order rate constant, $k = 6.8 \times 10^{-6}\ s^{-1}$ (R = 0.99), showed that the assumption is justified.

The recovered alcohol was subjected to the LIS study as described. A plot of the increasing differences in the positions of the diastereomeric methoxy signals subtracted from the original unseparated methoxy signal versus the molar ratio of the ($Eu(fod)_3$) to the (*R*)-MTPA ester was made. This showed that the (*R, R*) diastereomer was shifted more than the (*R, S*) diastereomer. From analysis of the integrals of the second experiment mentioned in the experimental section in these modified bimetallic oxidations, it was determined that more (*S)* 4-hexen-3-ol was present (30% ee). This indicates that one species was oxidized selectively, the *(R)* isomer of 4-hexen-3-ol. In the earlier experiment in which data was collected up to just past the oxidation of one-half of the total alcohol, the ee for the one isomer obtained was almost quantitative within experimental error.

PART TWO: CHAPTER IV

DISCUSSION

IV.1. Preparative Aspects.

This work had as its focus the design of a supported polymetallic catalyst. The plan for the supported catalyst required the placement of binucleating ligands on a polymeric surface. One factor to play a crucial role would be the geometry of the binucleating ligands with the complexed metals. In addition, the type of metal species, the substrates and the potentials required, would play important roles. The applications of such a catalyst will be discussed in terms of the oxidations studied.

IV.1.1. Polymerization.

The polymerization which used the method of Teplyakov and co-workers, is a facile process. As the polymerization involves cyclic trimerization across two monomers, there is built in cross linking which rapidly increases the molecular weight and causes the polymer to be very insoluble in all solvents after crosslinking. Thus, no polymer characterization in terms of molar mass or molar mass distribution studies by viscocity, light scattering or ultracentrifugation was attempted. The process could be followed by the appearence of the new aromatic singlet as acetyl methyl groups formed the benzene rings (**Figure III.1**).

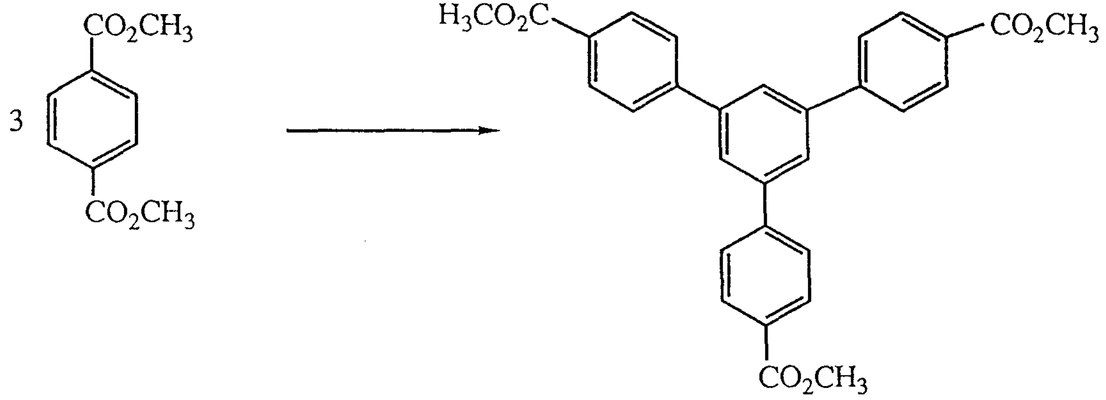


Figure IV.1. Model Reaction Showing Cyclic Trimerization of *p*-Acetyl Methylbenzoate.

IV.1.2. Inclusion of Methyl Ester Groups.

The methyl ester is incorporated for later modification to give the triketone or diketone. One of the major reasons for incorporating the acetylated aromatic ring monomer is because we found that the ester group is retained in the polymerization. To verify this, a model reaction was performed. In this reaction *p*-acetyl methylbenzoate was trimerized to obtain the trimerized product.[76]

The trimer, **Figure IV.1**, was characterized by its ^{1}H NMR and by its mass spectrum. In the ^{1}H NMR, the identification of the appropriate peaks and the ratio of 9:15 for the methyl ester : aromatic resonances and the mass spectrum parent peak at 481 confirmed this species.

IV.1.3. Di- and Tri- Ketonization.

In the related model studies involving preparations of the phenyl and ferrocenyl diketone and triketone,[77] the following were found to be of importance: (1) the use of excess base is necessary for the formation of the dianion and (2) the use of 18-crown-6 to sequester the countercation leads to dramatic increases in yield. Both procedures were incorporated into the polymer modification reaction.

IV.1.4. Coating onto the Support.

Diatomaceous earth (celite) is a naturally occurring inexpensive silicious material.[78] For example, nickel on kieselguhr is a frequently used liquid phase hydrogenation catalyst. Diatomaceous earth is also used as a filter aid, so as a support, it imparts improved filterability and ease of suspension to a heterogeneous liquid phase system. The ease of suspension usually is exploited to the extent that the liquid can be sufficiently agitated and the catalyst suspended by the oxygen, hydrogen or other gas mixture bubbling up through the slurry without supplementary mechanical agitation.[79]

Since we are using dioxygen as re-oxidant, it is important that the support possess gas diffusion capabilities; celite is best suited for this purpose.

IV.1.5. Metal Ion Incorporation.

The original synthesis of $Pd(CH_3CN)_4^{2+}$ is from Schramm and Wayland.[80] Excess $NO^+BF_4^-$ was used so that all the Pd(0) would be oxidized to Pd(II). It has been shown (Schramm and Wayland) that even the use of excess oxidizing agent does not lead to the formation of Pd(IV). The ligands are very labile and hence very reactive from a substitution point of view. The use of this species was exploited very highly by Sen who studied among other aspects olefin dimerization, oligomerization and polymerization using palladium and other metal species.[81]

The procedure employed, *in situ* formation of the Pd(II) species and co-ordination to the diketone and triketone backbone, is a modification of the methodology from Sen, who predominantly used monophosphine ligands to give stability to the unstable $Pd(CH_3CN)_4^{2+}$ species.[82] In addition to the stabilization from the oxygens of the di- or tri- ketone framework, precedence for a solid support giving stability to a relatively unstable homogeneous counterpart exists. Supporting aluminum(III) chloride on polystyrene results in insensitivity to moisture during manipulation in air.[8] The instability of rhodium(I) phosphine complexes in the presence of O_2 is well known. Analagous supported rhodium(I) complexes are resistant to oxygen degradation and can be filtered and recycled in air without the need to take special precautions.[83] Similarly, reduced oxygen sensitivity has been found with supported Pd(0) phosphine complexes.[84] So it is not surprising that the supported complex we have prepared is indefinitely stable in air, based on our qualitative observations.

Our ligand system, where the metal is co-ordinated, is of the 2,4-pentanedione type.[85] Acac complexes of many metals including palladium are well known; but these are usually *bis*(acac) complexes.[86] Mono(acac) type complexes of palladium are known, but these are usually found with other strongly co-ordinating species like olefins.[87] It may be argued that a mono(acac) complex with labile ligands may be unstable in homogeneous solution. This may well be the case. However, it has been emphasized[88] that a ligand selected for a homogeneous catalyst ought to co-ordinate fairly strongly to the metal in order to prevent ligand loss and subsequent reduction of the metal ions to the free metal. On a support, ligand dissociation is more spatially restricted so that weaker bonding ligands may be used. Thus advantages not realizable in homogeneous solution are now available.

IV.1.6. Determination of Metal Content.

The use of DMG to determine palladium metal content is a well established analytical technique. Perhaps the weak point of the method is that the final amount of Pd is determined by subtracting the amount determined as left in solution from the amount that was used at the start. The final number is very small and hence small errors in analysis can lead to significant errors in the amount of metal calculated to be on the support. Perhaps the direct determination of metal content would have been more accurate. One must bear in mind that analysis of metal content in polymeric systems is usually achieved by destruction of the substrate.[89] In order to do this, the polymeric substrate would need to be oxidized with a combination of concentrated sulfuric acid and 30% aqueous hydrogen peroxide. This would be difficult in the present case because of interference from the support . The determination of metal content becomes a similar gravimetric procedure after destruction of the polymer.

There are, however, methods available for the direct determination of metal content. Examples are X-ray florescence spectroscopy, thermal neutron activation analysis and charged particle activation analysis. All of these are non-destructive. However all suffer the major drawback of many interferences, necessitating the difficult task of preparing standards in the same matrix as the materials under test.[90]

IV.1.7. Suggestions for Characterization Methods.

Mono and bimetallic Pd(II) systems have been prepared using diketone and triketone systems on a small polymer framework, supported on celite. All the chemistry behind these preparative procedures is known, yet characterization of the resultant bimetallic and monometallic systems is limited because of the complexity of such characterization.

Some suggestions for characterization include the following. Evidence could be obtained by the use of reflectance IR.[91] It may be possible to demonstrate a bimetallic system using solid state NMR.[92] However this characterization is not a simple process. Many sophisticated methods for the characterization of surfaces are available like X-ray photoelectron spectroscopy and transmission electron microscopy.[93]

IV.2. Oxidations.

The most famous homogeneous counterpart in Pd(II) oxidations is the Wacker process for the oxidation of ethene to ethanal. The re-oxidant for Pd(0) is $CuCl_2$ which is in turn regenerated by dioxygen. Other reoxidants like benzoquinone and Fe(III) salts have been used for the re-oxidation of Pd(0). The direct use of O_2 is rarer. At higher O_2 pressures and temperatures above 80 °C, Pd(0) is reported to be directly regenerated.[94] In all of the oxidations performed at 25 °C, dioxygen (ambient pressure) was used as reoxidant. A schematic for the catalytic process is shown in **Figure IV.2.** Schwarz and Blackburn[95] used O_2, but their work was carried out at 38 °C and they commented on precipitation of Pd(0) if they did not increase oxygen pressures.

It is probable that the ease of re-oxidation under the mild conditions employed was actually because of the reoxidation of Pd(I) dimers. Some indirect evidence for this is available in the observation that the related monometallic system tended to show greater precipitation of Pd(0) over longer periods of reaction time. Also, the reactions on the monometallic system became exceedingly slow at long reaction times and deviated from first order behavior.

The reoxidation of Pd(I) by molecular oxygen under ambient conditions is not a new suggestion. Coe and Rispoli[96] showed kinetic evidence for a Pd(I) intermediate that was oxidized to Pd(II) with O_2. They were studying the kinetics and mechanism of the oxidation of Fe(II) by aquapalladium(II) and initially noticed that the precipitation of Pd(0) was delayed if dissolved O_2 was present in their reaction mixtures. The investigation revealed that the reoxidation occurred more easily in chloride free media and that even O_2 from the air could perform the reoxidation being examined. Coe and Rispoli interpreted the kinetics in terms of reoxidation of a steady state Pd(I)-O_2 intermediate. By calculations they were able to show that this was the only means to explain their data. In addition they showed that the reoxidation was not occurring because of the iron species. In our case we are also working in chloride free media. We have the additional advantage in that our solutions are blanketed in oxygen.

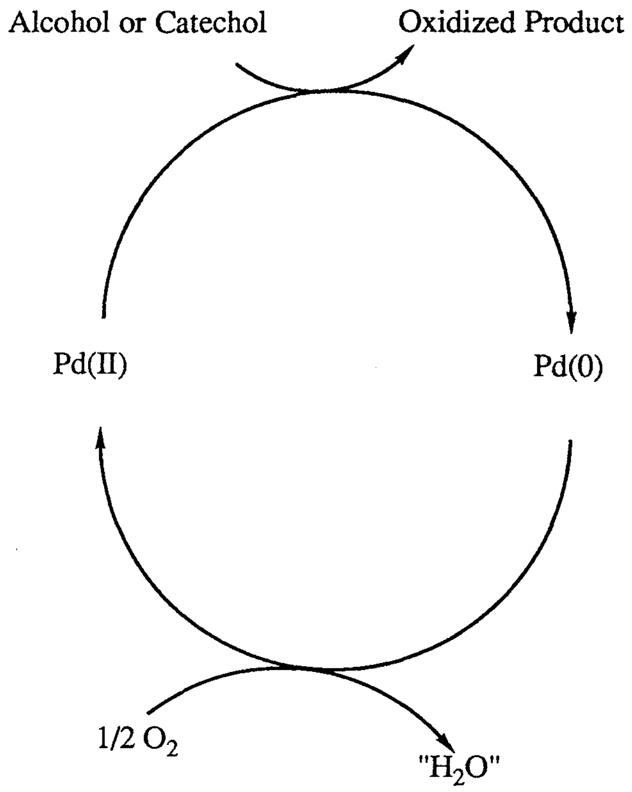


Figure IV.1. Scheme Depicting the Catalytic Process for the Oxidations Using the Pd(II) Catalysts.

IV.2.1. Oxidations of Catechols.

The supported catalyst oxidations of catechols are facile reactions occuring at 25 °C and at ambient pressure. Stringent procedures were employed in studying the oxidations of catechols in water and methanol so that unambiguous data could be obtained.

IV.2.1.1. A Note on Rate Constants.

The catechol oxidations using the bimetallic system occur in two distinct steps, each step being a two electron oxidation. Evidence for this is from monitoring the products during the course of the reaction and from the two distinct steps in the kinetic data. The product distributions determined during the course of the reaction indicated 3,5-DTBQ was the initial product and the muconic acid derivative was the final product. This result was in keeping with the color of the reaction mixture which was an intense red in the early stages when 3,5-BTBQ predominates and later appears yellow in the presence of the ring cleaved product. Also, the first step in the kinetics is much quicker than the second step (12.6 times) and has a pseudo first order rate constant $k_{obs} = 3.2 \times 10^{-4}(s^{-1})$ under the conditions of our experiments. This corresponds to a $t_{1/2} = 36$ min. The corresponding first step in the monometallic system is 45 times slower. As previously mentioned, the second step does not take place to any appreciable extent in the monometallic system.

IV.2.1.2. The Effect of pH.

In this study the pH was maintained at 8.0 for the aqueous studies. In methanol 1.65×10^{-4} M $[OMe^-]$ was employed. If there was any water present in solution, one would expect an equilibrium of the form,

$$OMe^- + H_2O \rightleftarrows MeOH + OH^- \qquad (IV.1)$$

to come into play. This would affect the mechanism of the reaction. This is highly unlikely because of the high concentration of drying agent (TMOF) that was used in these reactions when carried out in methanol.

Under the conditions of our experiments in methanol, there was a maximum of 16.4 mL of O_2 taken up in a control reaction run in the absence of the catalyst in a period that is three times longer than it takes for the bimetallic catalyst to effect ring cleavage. Observation of the solution from this blank run shows no detectable oxygen uptake for several days after this. This volume corresponds to approximately 6.7×10^{-4} mol of O_2. Subtracting out the amount of O_2 taken up standardly by the solvent, the process could be treated as a parallel reaction and the corresponding rate constant determined. The only product we detected was the corresponding quinone, 3,5-DTBQ. This reaction is attributed to a direct oxidation by dioxygen.

One of the few studies in the literature that discussed the direct oxidation with O_2 was from Grinstead.[64] His conditions were more extreme. He varied $[OH^-]$ from 0.06 M to 2.5 M. In addition, most of his studies employed heating of the solutions. Like the few other workers who mention the direct reaction with O_2, he remarks about the indiscriminate decompositions he obtained, his highest yield of quinone being only 40% under the mildest of his conditions (no NaOH and in bicarbonate buffered solution). He also performed experiments with hydrogen peroxide in basic media, and claimed optimal pH ranges of 11-12. It is our qualitative observation that the more alkaline the solution, the quicker the direct consumption of O_2, but the greater the number and nature of products. We did not investigate the direct reaction any further.

We had also observed that in aqueous acidic solution (pH 5.0) our catalyzed reactions did not consume enough O_2 to be going past the first two electron stage which involves quinone formation. For reasons discussed above, very basic conditions were avoided. The conditions chosen were a balance between having a clean, facile, catalyzed ring cleavage reaction with the least interference from the direct reaction observed with O_2 and suitable for study by gas uptake techniques.

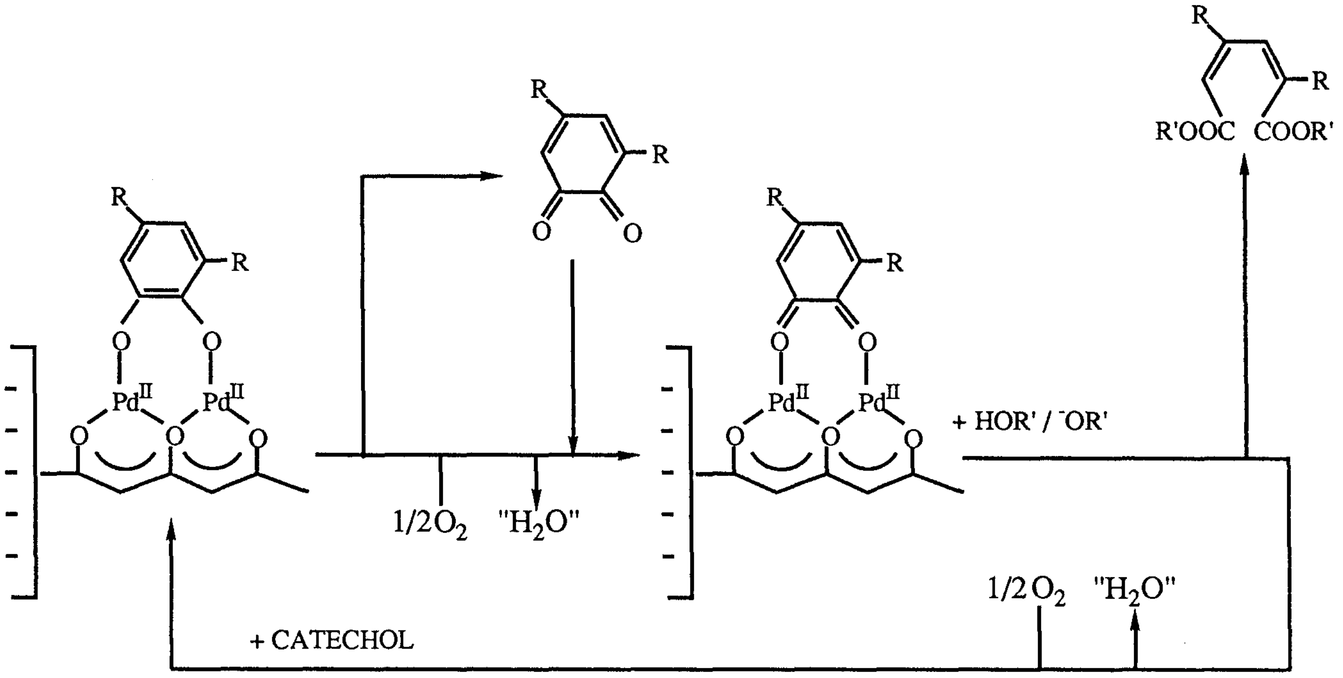
IV.2.1.3. A Note on Workup.

Many workers report lactonization of the ring cleaved product.[15] We found that as long as work up is restricted to simple filtration to remove the heterogeneous catalyst, followed by solvent evaporation, lactonization did not occur.

IV.2.1.2. Bimetallic Interaction in the Mechanism.

A scheme for the process is shown in **Figure IV.3**. A few important aspects revealed in this work are incorporated into the picture. As mentioned earlier we view the reaction as occuring in two 2 electron stages. Based on the control experiments and on known palladium chemistry, the dioxygen serves as reoxidant for some reduced form of the metal. The bimetallic interaction is proposed as necessary for the ring cleavage reaction under the conditions we employ. This is depicted in the interaction with the two adjacent oxygens in the catechol. Such bimetallic interaction has been postulated as essential in other metal oxidations of catechols too.[97]

Note that the interaction of palladium itself with catechols is known. For example,



R = H (or) C_4H_9; R' = H (or) CH_3

Figure IV.2. Proposed Scheme for the Oxidation of Catechols on the Pd(II) Bimetallic Catalyst.

Razuvaev, *et. al.*, could generate stable semiquinone species from 3,5-DTBC and palladium to obtain ESR spectra on these semiquinone species.[98] Under acidic conditions, it has been shown that 1,2-benzene diols are oxidized to 1,2-benzoquinones by Pd(II) with ease. Coe and Mentasti[99] found that acid usually reversed this reaction. They discussed their spectra in terms of the formation of a palladium(0)-quinone adduct. Quinone adducts of many metal species including palladium are known. Balch *et. al.* prepared tetrachloro-1,2-benzoquinone and 1,10-phenanthrenequinone adducts of ruthenium, iridium, palladium, platinum and rhodium. These were used for electrochemical studies in which they were able to demonstrate reversible one electron oxidation behavior.[100]

It is possible that nucleophilic type attack occurs on the co-ordinated carbonyl. The carbonyl carbon is a known electron deficient center. In the Pd(II) complex the carbonyls should be even more susceptible to such attack. The Pd(II) species would serve as a Lewis acid. The basic solution probably helps this reaction because of the presence of methoxide which is a better nucleophile than methanol. Thus esterification is a facile reaction and the high amount of drying agent probably drives the equilibrium toward ester formation.

IV.1.2.4. Role of base.

Finally, in addition to the earlier discussion on pH the slightly alkaline conditions that we employ must serve at least a dual purpose in our Pd catalyzed reaction: (a) deprotonation of the -OH of the catechols. This would make interaction with the Pd(II) system stronger; and (b) The basic conditions would also drive the reaction towards formation of the quinone as evidenced by the work of Coe and Mentasti.

IV.2.1.5. A Note on Potentials.

Grinstead used several metal ions (Co^{2+}, Mn^{3+}, Fe^{3+} and Cu^{2+}) in his study of the effect of metals on catechol oxidations.

Grinstead viewed the metal as involved in some kind of stabilization of aryl radicals, because he was using one electron oxidants. He had the best results with the metals possessing the highest potentials, namely manganese and cobalt. The view that he adopted with regard to the potentials was that complexation drastically changed potentials but that a definite trend was evident. He suggested some manner of oxygen activation as a primary role for the metal ions in keeping with earlier biochemical studies[102] that aimed at mimicing the action of certain enzymes that were believed to contain metals that played such a role. The idea was later taken up by Tsuji who studied the catechol ring cleavage with copper(II).[103] Later Rogic upset this

Table IV.1. Standard Redox Potentials of Some Metal Ions.[a]

Couple	E^0 (V)
Co^{2+}/Co^{3+}	+1.82
Mn^{2+}/Mn^{3+}	+1.51
Pd^0/Pd^{2+}	+0.915[101]
Fe^{2+}/Fe^{3+}	+0.771
Cu^{+}/Cu^{2+}	+0.153

[a] From Grinstead, R. R.; *Biochemistry*, 3 1308 (1964).

interpretation when he showed that similar copper reactions also proceeded under anaerobic conditions.

Lintvedt, *et. al.* prepared binuclear Cu(II) complexes of the *bis*(triketone) systems of the type we are using as our metal framework. They found, based on crystal structure, that the two Cu(II) atoms are 3.05 Å apart. They claimed that simply based on distance, the Cu(II) atoms were too far apart and that any direct structural metal-to-metal interaction would be very small and could be neglected.[104]

Based on electrochemical studies[105] on these Cu(II) binuclear and related mononuclear systems, Lintvedt, *et. al.*, observed information that could be of significance to this work. First, they noticed that the reduced copper species in their mononuclear system exhibited nonreversible electrochemical behaviour due to its tendancy to decompose. Second, there is an amazing stabilization of the Cu(I)-Cu(I) reduction product. They interpreted the stabilization to be due to the presence of interacting copper centers, although earlier structural characterization had not shown any evidence for this interaction. Part of the evidence for this interaction included strong antiferromagnetic coupling between the metal centers. Third, all the triketonate systems they studied showed reversible electrochemical behavior in terms of scan rates, peak current ratios and symmetries. Fourth, and perhaps most importantly, by applying the theory for multi-electron transfer cyclic voltammetry developed by Shain and co-workers,[106] they deduced that two sequential one electron transfers were occurring at the same potential.

The potential for the oxidation of catechol itself to benzoquinone, +0.699 V, is significantly higher than that possible for standard Cu(II)/Cu(I) couples.[107] Hence Rogic suggested that it is a thermodynamically uphill process for the copper system. Now this may or may not be the case in the bimetallic palladium system. Balch, *et. al.*, have shown that reversible one electron oxidation is possible in the palladium-quinone adducts that they prepared. The potential for the oxidation of $Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$ is +0.72 V. Also, by analogy with the Cu(II) systems, one might expect that the electron transfer occurs in some sequential manner from both metal centers.

Rogic[108] proposed in addition a "steric match" hypothesis that essentially suggested that the distance related geometry is important in the catechol oxidations. As mentioned earlier, in the related copper binuclear system, the Cu(II) atoms are 3.05 Å apart. Chemical and spectroscopic studies[109] on the *Neurospora* tyrosinase suggested that the "type 3" site is geometrically correct for the co-ordination of catechol axial to both coppers. This rearranges to a more side-on or equitorial position before oxidation can occur.

In this work, the absolute need for the bimetallic interaction has been demonstrated. Oxidation of the catechol to the quinone is achieved easily on the bimetallic framework. The large enhancement in rate for the bimetallic over the monometallic system in the first step, quinione formation, is proof that the bimetallic interaction is crucial to this Pd(II) oxidation. The second stage, ring cleavage, speaks for itself. Under the conditions of this work, no ring cleavage was effected with the monometallic system. The facility of the complete process and the cleaness of the ring cleavage are features of the bimetallic catalytic system. It is especially appealing to ring cleave aromatic rings of this nature because of the potential utility of such a process for degrading biomass.

IV.2.1.6. Final notes.

(1) This is the first time ring cleavage of catechols has been accomplished with a Pd(II)

system. The reaction is made catalytic by using dioxygen as a co-oxidant as in the Wacker process.

(2) This process is clean and uncomplicated both in terms of experimental procedures and products. Most, if not all of the earlier work in the literature concerning transition metal oxidations of catechols is in terms of mimicing the action of various enzyme species. Usually such work focusses on dioxygen activation.[110] This study is oriented differently. The goal was to achieve a clean uncomplicated ring cleavage process with facility.

(3) Finally, this process stresses that bimetallic catalysis is both necessary and required.

IV.2.2. Oxidations of Alcohols.

The facile oxidation of the alcohols probably involves a transfer of hydrogen from the carbon of the alcohol to the palladium. The transfer is a two electron process as is usual in palladium oxidations and this is confirmed, in part, by the kinetics which were treated as two electron processes. Very satisfactory results, in terms of the correlations, were obtained in the psuedo first order treatment.

IV.2.2.1. General.

The oxidations of primary alcohols by Pd(II) species have been known for some time.[111] Nikiforova, *et.al.*, observed that these reactions were much slower than the oxidations of olefins.[112] Several other workers have investigated these homogeneous oxidations.[113] An example is the kinetics of the oxidation of 2-propanol which was studied in the temperature range of 66 °C - 96 °C.[114]

The greater ease in oxidation under the present conditions is due probably to a chloride free media. Normally chloride shows some kind of inhibition in analogous Pd(II) catalyzed oxidations in homogeneous solution.[115] In addition palladium(II) has a higher redox potential under these conditions.[116]

IV.2.2.2. Role of the Bimetallic System.

IV.2.2.2.a. Mono alcohols.

The interaction from the second metal in the bimetallic system is of considerable importance to the oxidation. The fact that the bimolecular rate constants are all higher for the bimetallic system over the monometallic system, as seen in **Table III.3 - Table III.7.** substantiates this proposal. Even in the case of the smallest difference, that of the oxidation of methanol (1.3 times faster for the bimetallic), there is a consistently faster reaction with the bimetallic system.[117] The reason for the only slight increase is probably because of the small size of methanol, estimated to be *ca.* 2.0 Å from the O to a H on the carbon. On the other hand slightly better rate differences were obtained for ethanol in which a factor of 5.2 was obtained. In the case of 2-propanol and 1-phenyl methanol factors of around 4 were obtained in each case.

IV.2.2.2.b. Diols.

An argument for the bimetallic interaction can be made by using the diols in which the rate enhancements were far higher. While most of the diols give more noticable differences in rates than the standard mono alcohol, the outstanding case was that of ethane-1,2-diol in which a factor of 32 was observed. The interaction of the two alcohol groups, as in the case of the catechols provides interaction at both metal centers thus enhancing the oxidation in the bimetallic system. The availability of two oxidizable sites probably also contibutes. One cannot discount, of course, the fact that both oxygens could well interact with one metal site in the monometallic system too. Recently, for example, crystal structure has been obtained for a glyerolato-1 *O*,2 *O* complex of platinum(II) by Wild *et. al.*[118] This only serves to show that the rate inreases in going to the bimetallic system arise from factors that are in some manner unique to having the two metals next to each other in that particular manner in the system.

The oxidation of propane-1,2-diol has a rate constant similar to that of ethane-1,2-diol (20×10^{-3} M^{-1} s^{-1} as opposed to 16×10^{-3} M^{-1} s^{-1}). The related monometallic rate constant is not so drastically different as in the case of ethane-1,2-diol. This is slightly surprising. On the other hand, it could be just that the extra methyl group contributes a steric bias against the fit of the propane-1,2-diol. This restriction toward interaction in certain conformations probably hinders interaction with the bimetallic system and actually lowers the rates. Of note is the fact that one of the hydroxy groups is secondary in nature, yet 2-propanol is oxidized faster than propane-1,2-diol. The slight lowering in rate constant is probably due to a spatial restriction of the supported catalyst,[119] or simply an electronic factor because of the withdrawing nature of the hydroxy group. To contribute to this argument butane-2,3-diol has two secondary hydroxy groups and is oxidized faster than propane-1,2-diol (factor of 2), yet it is only 1.1 times faster than 2-propanol. Similar rationalization in terms of conformational restriction can be made in this case too.

Another point in favor of the steric argument is that the rate differences between the monometallic and the bimetallic systems progressively decrease as we introduce more steric interference on the substrate. The differences decrease from 30.2 to 9.5 to 6.6 from ethane-

1,2-diol to propane-1,2-diol to butane-2,3-diol.

In the oxidation of the only poly hydroxy compound (α-D-glucose) a greater increase is noticed in the rate constant ($k = 77 \times 10^{-3}\ M^{-1}\ s^{-1}$). This can be explained on the basis of more possible oxidizable positions and that the sugar is conformationally more restricted.

A brief mention must be made of butane-1,3-diol in which the rate constant is lower than in the 1,2-diols. This could be attributed to the distance effect. The bimetallic system, assuming both alcohol oxygens interact in the 1,2-diols, leading to enhanced rates, is not compatible with the 1,3 alcohol (4.2 Å) in terms of distance. There is only a small difference in going from monometallic to bimetallic in the 1,3-diol. The 1,2-diols show much larger rate differences.

The interaction from the diols is probably from both oxygens to the palladium atoms. The best known studies of interactions of species with two palladiums adjacent to each other is in the case of the "A-frame" complexes, in which stable dipalladated adducts are well characterized.[120] A look at the allylic species oxidized on our system is perhaps the most meaningful in terms of nature and evidence for the bimetallic interaction, because of the known propensity for palladium to form π bonds with olefinic species.

IV.2.2.2.c. Allyl Alcohol and Congeners.

The most noticable facet of the allylic alcohol oxidations is that the reactions are so rapid. Both allylic species used had rate constants almost three orders of magnitude faster than methanol. There is a ten fold difference between the monometallic and the bimetallic systems in the oxidation of allyl alcohol itself. In the bimetallic cases, one of the metals of the bimetallic system probably π complexes with the C=C of the allylic moiety. The other palladium could abstract the hydride very conveniently from the alcohol carbon. The fact that the major product in the bimetallic case arises from the oxidation of the alcohol as opposed to double bond oxidation, while in the monometallic case it is a minor product, as in the homogeneous oxidation, provides evidence that the bimetallic species reacts differently from the monometallic.[72(a)] In explaining the formation of acrolein in the oxidation of 2-propen-1-ol in homogeneous solution, Henry suggested the uncomplexing of the olefin to provide a vacant site necessary for the hydride abstraction from the alcohol carbon.[121] In this case there is no need for the uncomplexing of the olefin to provide a vacant site, if it is the other palladium that is responsible for abstracting the hydride in the bimetallic case.

Thus evidence for the differences due to the bimetallic system are evident. The nature of the interaction is dependent on the particular species being oxidized. The evidence, both from kinetics and from products, is especially strong in the allylic case.

IV.2.2.3. Isotope Effects.

The values obtained for the isotope effect, k_H/k_D in these oxidations are 2.5 in the case of benzyl alcohol and 3.6 in the case of 2-cyclohepten-1-ol. The isotope effect for the benzyl alcohol is itself slightly higher than that obtained for analogous Pd(II) catalyzed oxidations in homogeneous solution. As an example, Kozhevnikov, *et. al.*,[114] obtained an isotope effect of 1.8 in the oxidation of 2-propanol with $PdCl_4^{2-}$ in water. Other values obtained for olefin species in water are between 1.7 and 1.9 for ethene and 2-propen-1-ol.[122] Closest to the value of 2.5 is the value of 2.2 obtained by Henry and Zaw in the oxidation of 2-buten-1-ol.

In this study, the oxidation of benzyl alcohol almost certainly involves some manner of hydride shift as in the case of the simple non olefinic alcohols.[123] In the allylic case, the predominant product arises from oxidation of the alcohol moiety, that is, via hydride (or, deuteride) shift. Since detailed mechanistic investigations of the oxidation of 2-cyclohepten-1-ol had been performed in homogeneous solution, it was decided to oxidize this species on the supported heterogeneous system. The higher isotope effect with the allylic species is interesting and slightly unusual. The reason for the higher number, compared with the deuteriated benzylic species, probably results from the more pronounced interaction of the Pd(II) with the C=C bond, providing greater ease for hydride abstraction especially in such a bimetallic system.

In comparison, the most dramatic isotope effects for alcohol oxidations in the literature is from Roecker and Meyer[19] who obtained an isotope effect of 50 for the oxidation of benzyl alcohol by $[(bpy)_2(py)Ru(O)]^{2+}$. Even the much lower number he obtained for methanol ($k_H/k_D = 9$) is still larger than those obtained in this work. Meyer suggests that the dominant pathway for the oxidation of alcohols by polypyridyl monooxo complexes of Ru(IV) is very polar and involves the C-H bond in an intimate way.

Other literature reports on isotope effects in alcohol oxidations are not so dramatic. In the oxidation of 2-propanol by RuO_4 in aqueous acidic solution Lee and Engh[124] found isotope effects, k_H/k_D, ranging from 1.3 (high acid) to 4.6 (low acid). The differences were attributed to a change in the mechanism. In oxidations of alcohols by Ce(IV), V(V), Mn(III) and Cr(VI) a range of isotope effects from $k_H/k_D = 1.9$ for the oxidation of cyclohexanol by Ce(IV), to $k_H/k_D = 3.6$ for the oxidation of cyclohexanol by V(V), to $k_H/k_D = 7$ for the oxidation of 2-propanol by Cr(VI), are seen. In all these oxidations direct or kinetic evidence is available to suggest the formation of discrete, inner sphere metal-alcoholate complexes which decompose by homolytic or heterolytic pathways.[125] The kinetics of these pathways are usually described by relatively complex proton dependent rate laws.

In palladium chemistry, high isotope effects ($k_H/k_D = 5.0$) were seen in the aromatic metallation reaction. This was interpreted in terms of a rate determining step involving C-H bond breaking rather than a simple π-co-ordination of the arene or formation of the Wheland intermediate. The formation of the Wheland intermediate was proposed as the slow step in the aromatic metallation of arenes by Pt(IV).[126] The electrophilic mercuration of arenes is usually accompanied by similar large isotope effects.[127]

In general though, the low numbers obtained in this work reflect that the hydride shift transition state has little or no carbonium ion character. It has also been suggested by Henry that discrete Pd(II)-H species are present as intermediates in the hydride transfer.[128] It is possible that other mechanisms also come into play. For example, the homogeneous Pd(II) oxidations used to compare isotope effects were all performed in acidic solution and proton dependences were present in those rate expressions.

IV.2.2.4. Rate Constants.

Bimolecular rate constants using the supported catalyst range from 1.8×10^{-3} M^{-1} s^{-1} for methanol to 35 M^{-1} s^{-1} for 2-cyclohepten-1-ol. In general, the following trend is seen for the alcohols: primary < secondary < benzyl < < < allyl. Diols are scattered depending on the diol in question. All of this is consistent with other known palladium chemistry.[129] Rigorous rate expression studies have not been performed. The oxidations are first order in [alcohol] and first order in total [Pd(II)]. Dioxygen is used as reoxidant for the palladium. Arguments have been made earlier as to why this may be more easily possible in this system under the milder conditions employed.

It is difficult to compare the rate constants of our reactions with those obtained from other palladium oxidations because of different rate expressions. In the case of the 2-propanol though, the bimolecular rate constants from Kozhkevnikov, *et. al.*, are smaller, at least by an order of magnitude. In other saturated alcohol oxidations, Roecker and Meyer oxidized methanol with a bimolecular rate constant of 3.5×10^{-4} M^{-1} s^{-1}, a factor of 5 times slower than that obtained in this work. In the same work, his rate constants for 2-propanol and ethanol were comparable with those obtained in this work, while all of his benzylic species were faster by an order of magnitude. Many other oxidations of alcohols are available in the literature, but few report rate constants that can be used for meaningful comparison.[130]

Major olefinic type oxidations using Pd(II) species have been carried out by several workers. The rate expression for these mainly Wacker oxidations is different, and comparison is difficult because of different rate expressions.

One final comment with regard to the rate constants. In the case of 2-cyclohepten-1-ol, under the mixed solvent system there is an increase in rate constant by a factor of 5. This is not that unusual. For example in a recent ruthenium catalyzed oxidation of primary alcohols, Bäckvall, *et. al.*, obtained a rate increase of 10 in changing solvent to dichloromethane.[131]

IV.2.2.5. Products.

All of the saturated alcohol oxidations gave only one product. The primary alcohols gave aldehydes and the secondary alcohols ketones. Secondary alcohols were preferentially oxidized over primary. In the allylic cases, the bimetallic system gave preferential alcohol oxidation (*ca.* 80%) over double bond oxidation. The minor product 3-hydroxy propanal, in the case of oxidation of 2-propen-1-ol, could be explained by a hydroxypalladation type mechanism[132] followed by hydride transfer. Interestingly, the monometallic system gave predominantly double bond oxidation similar to homogeneous Pd(II) oxidation chemistry. This is true for the cyclic allylic alcohol as well.

In the homogeneous oxidations allyl alcohol gave 2-hydroxypropanal, 1-hydroxy 2-propanone, 2-propenal, propanal and propene as products. One study in basic solution[133] reported only 3-hydroxy propanal as the product. Earlier a study in acidic solution had reported acrolein as major product (75%), along with the formation of some π-allyl palladium chloride.[134] In the oxidation of 2-cyclohepten-1-ol four products were obtained: two hydroxy ketones along with the saturated and unsaturated ketones.

IV.2.2.6. Comment on Distances.

Apparently the geometry of the bimetallic system is vital to the oxidations. We do not have precise distance characterization in this system. But careful structural characterization is available in the related homogeneous triketone systems.[135] Such systems are *bis*(triketone) complexes. With Cu(II) the metal-metal distance is about 3.05 Å, for Ni(II) it is 3.17 Å and for Co(II) it is 3.27 Å. Estimates made for Co(III) peroxy complexes[136] make the two cobalts about 3.1 Å apart. It is highly likely that the two palladiums in the bimetallic settting are somewhere between 3.0 Å and 3.3 Å apart.

Some indications of the optimal distance are evident from the geometry of the species oxidized. The catechol oxygens are approximately 2.8 Å apart. We have made ALCHEMY II minimized estimates of distances in the alcohols oxidized.[137] These distances are shown in the Appendix. The best rates in the oxidations of the diols are obtained when the distance between the two oxygens is between 2.6 Å and 3.0 Å. 1,3-butandiol has the two oxygens 4.42 Å apart and this could account for the decrease in rate. The sugar (α-D glucose) apparently has three sets of oxygens that are at the optimal distances. This could explain the enhanced rate with this polyhydroxy compound which is more than three times faster than all the diols.

The role of catalyst geometry and bimetallic rate enhancement are brought out in these studies. In addition, indirect evidence about the distance between the two metals in the bimetallic system is revealed.

The allyl cases are very interesting. In some manner the distance for 2-propen-1-ol is close to optimal for the bimetallic system. The distance from the outer carbon of the C=C bond to the alcohol oxygen is 2.825 Å, while that from the inner carbon of the C=C to the alcohol oxygen is 2.445 Å. The calculated distance for a π-complex is therefore 2.630 Å. Distances from the inner carbon of the π bond to the hydrogen on the alcohol carbon is 2.130 Å and from the outer carbon it is 3.321 Å.

The oxidation of the homoallylic alcohol, 4-penten-2-ol, was carried out to investigate the distance effect. It has been a quantitative observation thus far that the bimetallic system provides enhanced rates over the monometallic counterpart. It has been a qualitative observation that the distance between the two metals in the bimetallic system makes a difference in the rates. Incompatible distances ought to slow the reaction. Thus in going to the homoallylic and the homohomoallylic species, this is apparently the case. With a closest distance of 4.92 Å in the homohomoallylic alcohol, that would be too far for any significant interaction of the oxygen with the other metal. The fact that we barely had any oxygen uptake is possible indirect confirmation of this idea.

The homoallylic alcohol is an interesting case. The measured distances (see Appendix) do not seem too far for the bimetallic catalyst, although they are certainly higher than in the case of allyl alcohol. It is therefore likely that there may be more than one factor involved. One possibility is a conformational problem as discussed in the case of the diols.

IV.3. Note on the Observed Kinetic Resolution.

In the oxidations using the (+)DIOP modified bimetallic catalyst, in effect, the observed oxidation corresponds to a fractional resolution in which one enantiomer of a racemate is selectively oxidized. The experiments are at a very preliminary stage. Thus it is difficult to make quantitative predictions on the relationships between rate constant, ee and the amount of conversion because of insufficient data.[138] It is not known if the phenomenon seen in this work is general. The cause of the enantioselectivity and the stage at which it occurs are not known. Fractional resolution to obtain one enantiomer of a racemate is not a very common phenomenon outside of resolutions by enzymes and micro-organisms.[139] There are very few processes that are known; the most famous and, probably the only effective method to date, is the Sharpless epoxidation.[140]

IV.4. Implications for Catalysis, Conclusions and Directions.

(1) This work shows evidence that a supported bimetallic catalyst can catalyze facile oxidations under mild conditions, namely 25 °C and ambient pressure. The bimetallic catalyst is superior to the monometallic catalyst. Reoxidation of the catalyst is easily accomplished with dioxygen.

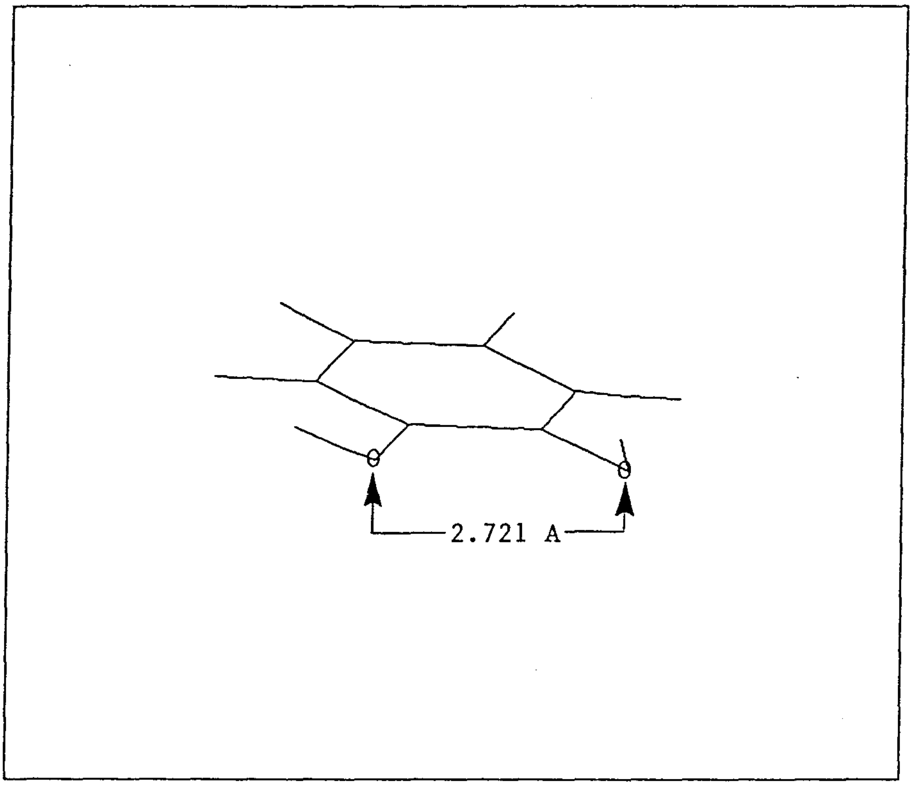
(2) Perhaps the most notable oxidation accomplished is the clean ring cleavage of catechols with this bimetallic system. A variety of alcohols were oxidized too. On the bimetallic system,

species that are bifunctional enjoy greater interaction with both metal sites especially if distances are optimum. The interactions of the bifunctional species lead to enhanced rates. There is evidence from the types of products that the bimetallic interactions are important and in one case, that of catechol, necessary.

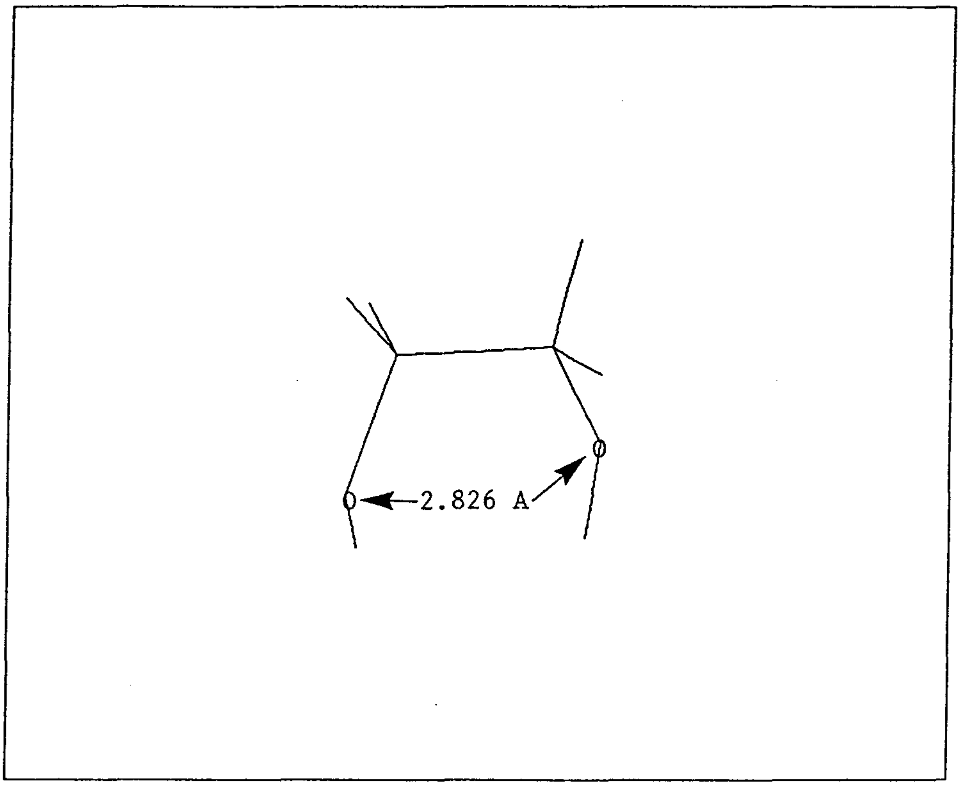
(3) There remain many studies yet to be performed to establish the nature of this catalyst and its mode of interaction. The major tasks are: (a) structural characterization of the catalyst via surface studies as mentioned earlier in this discussion; (b) increase in metal loadings by incorporating more sites for metal ions by using monomers that have more ester groups; and (c) detailed mechanistic work, both kinetic and stereochemical.

(4) In addition, many new reactions could be attempted on this system; (a) reactions from known homogeneous palladium catalytic chemistry; (b) reactions with other good oxidants like ruthenium or cobalt, via oxygen activation or otherwise; (c) reactions using frameworks other than the β,γ-triketone framework, so that different potentials are possible; and (d) asymmetric catalytic reactions, especially if the initial results from the fractional resolution can be shown to be consistently successful with other secondary allylic alcohols. The origins of the selectivity and the efficiency of the process will require to be evaluated over a large range of substrates to determine these aspects.

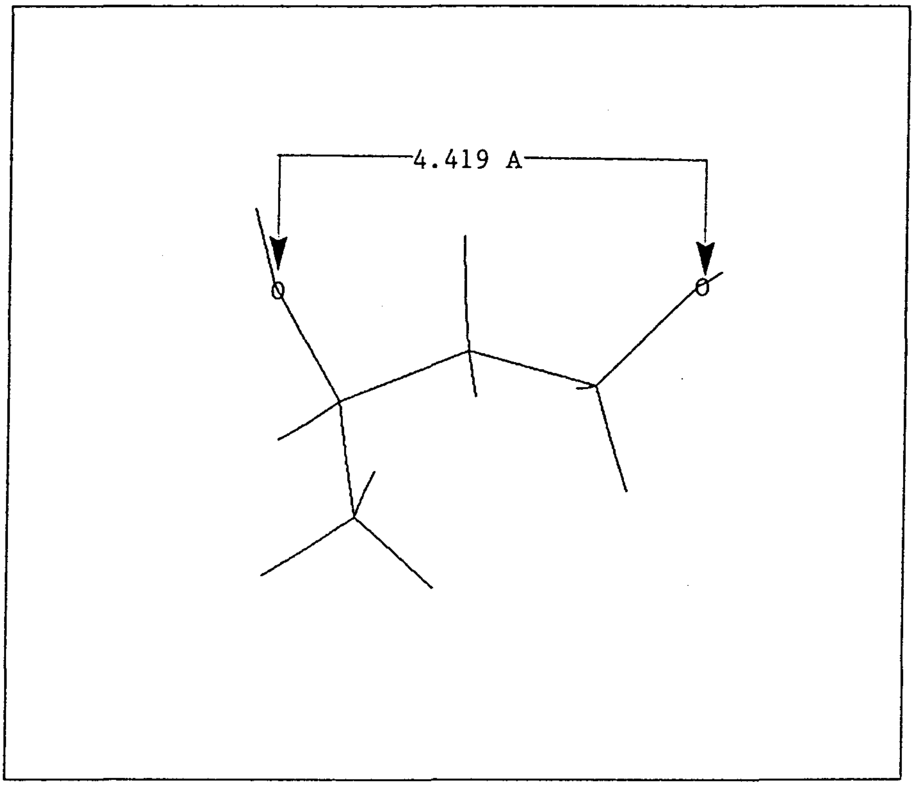
APPENDIX



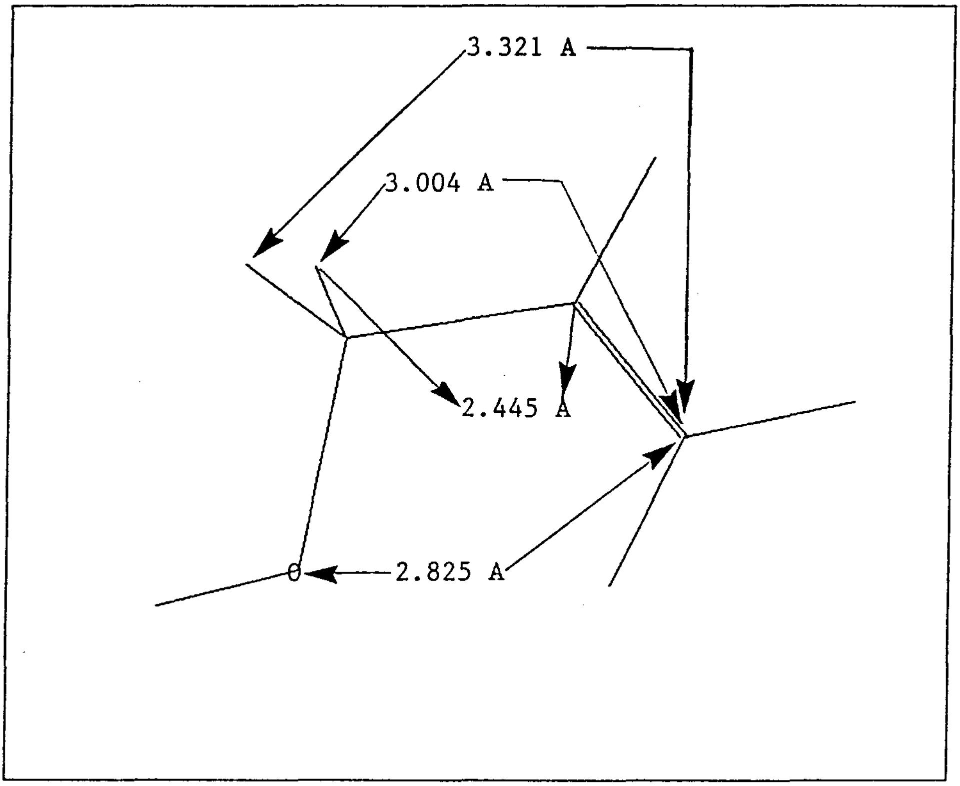
CATECHOL



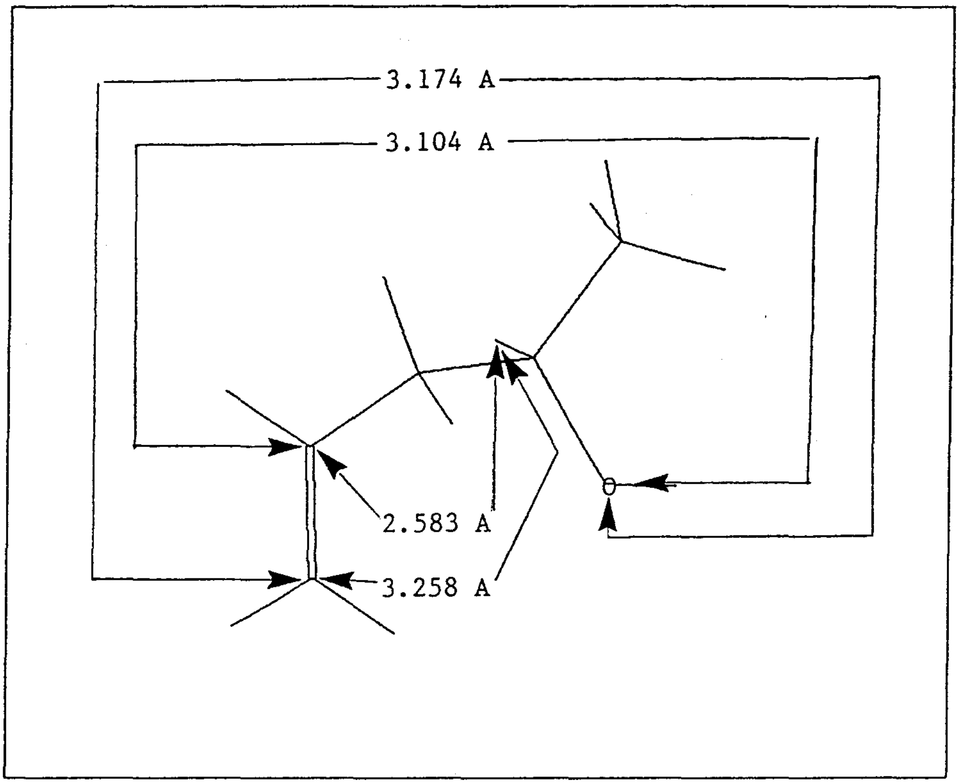
ETHAN-1,2-DIOL



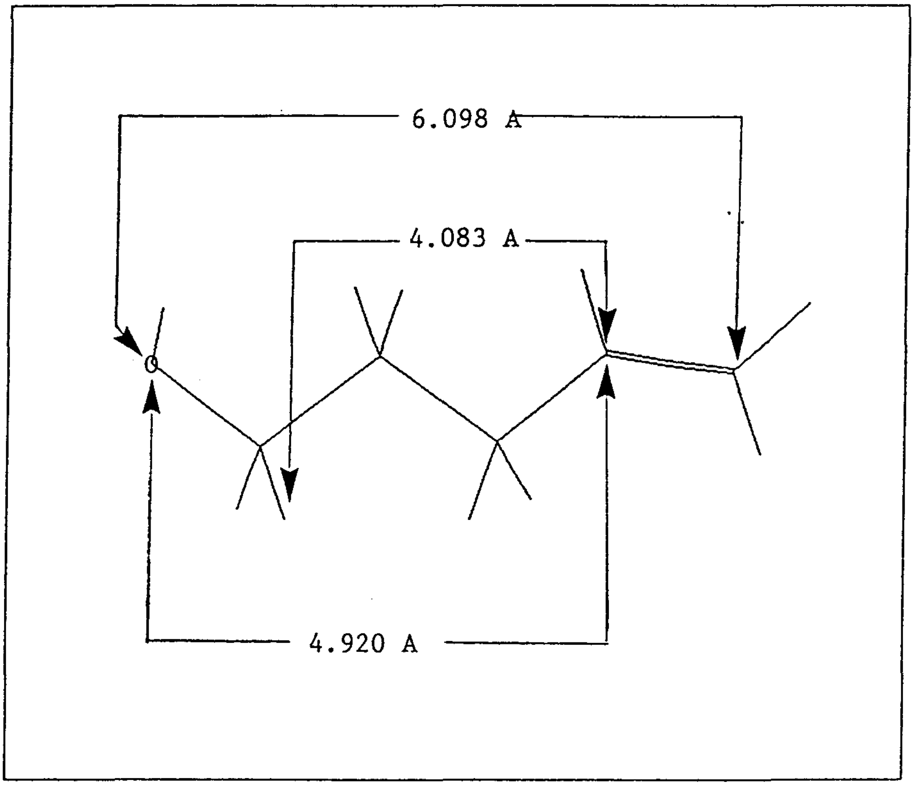
BUTANE-1,3-DIOL



ALLYL ALCOHOL



HOMOALLYL ALCOHOL



HOMOHOMOALLYL ALCOHOL

PART TWO: REFERENCES AND NOTES

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60. After locking the instrument (Varian VXR 300) on $CDCl_3$, chloroform is referenced to 7.24 ppm (internal standard tetramethyl silane at 0.00 ppm) and then the lock is disabled. ^2H NMR are then run unlocked in $CHCl_3$ solvent. The peaks are referenced to the 7.24 ppm peak.

61. This is not a totally accurate statement in the catechol oxidations. There is a small amount of oxidation of the catechols to the corresponding quinone under the reaction conditions.

62. This was determined in another set of control experiments. All species were taken in the reaction flask except for the substrate to be oxidized. The reaction was started by injecting the *ca.* 10 mL of solvent as described in the experimental section and the amount of initial uptake of dioxygen uptake by the solvent was noted.

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116. The couple Pd(II)/Pd(0) has E° = 0.91 V as mentioned earlier, while that for PdCl$_4^{2-}$ /Pd(0)(Cl$^-$) is 0.59 V.

117. The difference is larger if the solution is more alkaline.

118. Appelt, A.; Willis, A. C. and Wild, S. B.; *J. Chem. Soc., Chem. Commun.*, 938 (1988).

119. The actual reasons for greater selectivity in many supported catalysts are not known, although this is seen in experimental observation. See for example, for similar argument Pierre Laszlo in ref 56, p. 10.

120. See for example: Higgins, S. J. and Shaw, B. L.; *J. Chem. Soc. Dalton Trans.*, 457 (1988) and references therein.

121. In keeping with criteria from the work of Whitesides *et. al.*, on the decomposition of platinum alkyls. See ref 34.

122. References (a), (b) and (c) are for ethene, while (d) is for allyl alcohol: (a) Henry, P. M.; *J. Org. Chem.*, **38**, 2415 (1973). (b) Kosaki, M.; Isemura, M.; Shinoda, S. and Saito, Y.; *J. Mol. Catal.*, **2**, 351 (1977). (c) Saito, Y. and Shinoda, S.; *J. Mol. Catal.*, **9**, 461 (1980). (d) Ref 72 (a).

123. This statement does not preclude allylic alcohols. It is simply that other products are formed in the allylic cases. In this work itself, more than one product is obtained in the allylic oxidation, even though the other product is minor.

124. Lee, D. G. and Engh, M. van den; *Can. J. Chem.*, **50**, 2000 (1972).

125. (a) Ardon, M.; *J. Chem. Soc.*, 1811 (1957), (b) Littler, J. S.; *J. Chem. Soc.*, 4135 (1959), (c) Littler, J. S. and Waters, W. A.; *J. Chem. Soc.*, 4046 (1959), (d) Littler, J. S.; *J. Chem. Soc.*, 2190 (1962), (e) Westheimer, F. H. and Nicolaides, N.; *J. Am. Chem. Soc.*, **71**, 25 (1949), (f) Kaplan, L.; *J. Am. Chem. Soc.*, **77**, 5469 (1955), (g) Rocek, J. and Radkowsky, A. E.; *J. Am. Chem. Soc.*, **95**, 7123 (1973).

126. Shul'pin, G. B.; Nizova, G. V. and Nikitaev, A. T.; *J. Organomet. Chem.*, **276**, 115 (1984).

127. Lau, W. and Kochi, J. K.; *J. Am. Chem. Soc.*, **108**, 6720 (1986).

128. See also: Alyea, E. C.; Dias, S. A.; Ferguson, G. McAlees, A. J.; McCrindle, R. and Roberts, P. J.; *J. Am. Chem. Soc.*, **99**, 4985 (1977).

129. Henry claimed[72(a)] that the rate of formation of acrolein from allyl alcohol is faster at 25°C than oxidation of saturated alcohols at 96° C. He was making comparison with the oxidation of 2-propanol[114] in which it was found that 2-propanol > ethanol >> methanol.

130. Gagné, R. R. and Marks, D. N.; *Inorg. Chem.*, **23**, 65 (1984). In the reference cited, methanol, ethanol, 1-butanol, 2-butanol and cyclohexanol using ruthenium complexes of 1,3-bis(2-pyridylimino)isoindolines.

131. Bäckvall, J. -E.; Chowdhury, R. L. and Karlsson, U.; *J. Chem. Soc., Chem. Commun.*, 473 (1991).

132. Oxypalladation products are normally obtained in homogeneous oxidations with Pd(II) species in solution.

133. Ahmed, I. and Ashraf, C. M.; *Int. J. Chem. Kinet.*, **11**, 813 (1979). No yields were reported. Potassium hexacyanoferrate(III) was used as a reoxidant for the Pd(0).

134. Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Ruttinger, R. and Kojer, H.; *Angew. Chem.*, **71**, 176 (1959).

135. (a) Heeg, M. J.; Mack, J. L.; Glick, J. L. and Lintvedt, R. L.; *Inorg. Chem.*, **20**, 833 (1981). (b) Lintvedt, R. L.; Borer, L. L.; Murtha, D. P.; Kuszaj, J. M. and Glick, M. D.; *Inorg. Chem.*, **13**, 18 (1974). (c) Guthrie, J. W.; Lintvedt, R. L. and Glick, M. D.; *Inorg. Chem.*, **19**, 2949 (1980). (e) Kuszaj, J. M.; Tomlonovic, B.; Murtha, D. P.; Lintvedt, R. L. and Glick, M. D.; *Inorg. Chem.*, **12**, 1297 (1973).

136. (a) Schaefer, W. P.; *Inorg. Chem.*, **7**, 725 (1968). (b) Fronczek, F. R. and Schaefer, W. P.; *Inorg. Chimica Acta*, **9**, 143 (1974).

137. ALCHEMY II is a registered tradename for a structure modelling program from TRIPOS Associates. The program performs a conjugate-gradient minimization to put the molecule in a minimal energy conformation.

138. (a) For example, the treatment of Sharpless from the cited reference could be used. (b) Detailed mathematical treatments can be found also in Chen, C. -S.; Fujimoto, Y.; Giraudas, G. and Sih, C. J.; *J. Am. Chem. Soc.*, **104**, 7294 (1982) and Brandt, J.; Jochum, C.; Ugi, I. and Jochum, P.; *Tetrahedron*, **33**, 1353 (1976).

139. For an example of biochemical kinetic resolution see Bentley, R. in *"Molecular Asymmetry in Biology"*, Academic Press, New York , 1969.

140. (a) Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M. and Sharpless, K. B.; *J. Am. Chem. Soc.*, **103**, 6237 (1981). (b) Sharpless, K. B.; Behrens, C. H.; Katsuki, T.; Martin, V. S.; Takatani, M.; Viti, S. M.; Walker, F. J. and Woodard, S. S.; *Pure and Appl. Chem.*, **55**, 589 (1983). (c) Sharpless, K. B.; Woodard, S. S. and Finn, M. G.; *Pure and Appl. Chem.*, **55**, 1823 (1983). (d) Woodard, S. S.; Finn, M. G. and Sharpless, K. B.; *J. Am. Chem. Soc.*, **113**, 106 (1991).

VITA

The author of this dissertation, Glenn Noronha, was born in Mysore in India. He spent most of his early life in Madras where he received all his schooling and subsequently a degree in Chemistry.

In addition to Chemistry he has some training in Journalism and extensive training in German grammar and literature and has been awarded prizes for his essays in German. He is a member of Amnesty International (since 1982), the American Chemical Society (since 1986) and the Jesuit honor society Alpha Sigma Nu into which he was inducted in 1990.

In the Fall of 1986, he joined the Chemistry Department at Loyola University of Chicago in the Ph. D. program. He was a Graduate Teaching Assistant for almost that entire period. He has been awarded the Departmental teaching award on two separate occasions in 1988 and 1991. His research involved palladium catalysis and was carried out in the laboratories of Professor P.M. Henry. He has presented this research at both national and international forums.

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