ab initio Calculations in Heterogeneous and Homogeneous Catalysis
I. Methanol to Gasoline with ZSM-5
II. Carbonyl Ligand Effects on Metal-Metal Bonds

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Abstract

This thesis is composed of two studies in catalysis. The first is an exploration, using computational techniques, of the mechanism for the first carbon-carbon bond formation in the Methanol to Gasoline (MTG) reaction. The second is a study of the factors important to the understanding of ligand effects on metal-metal bonds, and in particular, to metal clusters.

Three possibilities were considered as ways to activate a carbon in the MTG process prior to formation of C2 or higher hydrocarbons. These were a free radical mechanism, a surface ylide mechanism, and a possible defect site which might lead to steric crowding of CH_2 groups.

Although the free radical mechanism was found to be thermodynamically within the parameters of the MTG process, it contained a high transition state. Consideration of the molecules available prior to hydrocarbon build-up and their specific electronic structure, led to the view that the available carbon atoms (methanol, dimethyl ether, etc.) were unlikely to be activated by a free radical intermediate.

The surface-stabilized ylide which has been proposed as an intermediate by many was studied to determine if in fact the ylide was stabilized. The total energy of the ylide was compared to that of the naked site on the zeolite and free methylene. Free methylene ranged, depending on the geometry of the ylide, between 50 and 80 kcal more stable. These numbers are qualitatively correct, but more electron correlation would have to be incorporated in the calculation to get an accurate value for the destabilization.

Starting from a defect site, two CH_2 groups were each attached to two oxygen atoms. It was thought that two CH_2 groups would take up considerably more space than either the original Al atom or the four hydrogens. Molecular

Mechanics calculations showed the zeolite to be sufficiently flexible to prevent crowding of the CH_2's.

The second study involved determining the effects of colinear carbonyl ligands on osmium-osmium bonds. Calculations at the Dissociation Consistent CI level showed that the ligands were weakening the metal-metal π-bonds through back-donation.

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INTRODUCTION

Computational Chemistry and Catalysis

INTRODUCTION: Computational Chemistry and Catalysis

The main focus of these studies is catalysis. There are two topics in catalysis that we have studied: the first is Mobil's Methanol to Gasoline (MTG) process and the second is the nature of ligand effects on metal-metal bonds. The underlying purpose for both of these studies is to develop a greater understanding of how the orbitals of reactive catalytic molecules allow or cause that reactivity. This understanding, in turn, will lead to a greater ability to manipulate catalysts to better suit our needs.

The first three chapters deal with a problem in heterogeneous catalysis. The zeolite involved in the MTG process, ZSM-5, possesses channels, through which the reactants and (at least some) products can move. The internal surfaces of these channels are the loci of catalytic activity in the zeolite. In addition, the shape of the channels helps guide the chemistry.

Although the MTG process has been optimized, empirically, for the production of gasoline, ZSM-5's ability to create new carbon-carbon bonds can be exploited--in combination with other catalysts--to make different new hydrocarbon or oxygenated products. The question of how the first carbon-carbon bond is formed is key to design new industrial processes using the MTG ability to create carbon-carbon bonds to make other chemicals. As this would be likely to involve a second catalyst, it would be quite difficult to make both the carbon-carbon bond formation and the new chemistry efficient and selective if the two catalysts interfere with each other. Therefore, in order to make these new processes possible, we need to understand how the first carbon-carbon bond is formed in MTG. The first chapter is a necessary prelude to the discussion of our calculations and results in the second. The first carbon-carbon bond formation in the MTG process has been disputed for twenty years,

and there has been tremendous progress in deciphering various aspects of that chemistry. However, there has yet to be a proposed mechanism which either fits all of the available experimental data, or does not contain some element which would seem atypical in the zeolite environment. This chapter discusses, in detail, these results from the literature, in an attempt to weed out older data which has been superseded and highlight those results which are most likely to shed light on the nature of the carbon-carbon bond formation mechanism.

Our goal is not just to understand the literature, but to use computational chemistry to help decipher which of the proposed mechanisms is likely to be involved. In the second chapter, the results of a series of studies of various possible mechanisms is discussed. These mechanisms were chosen to be illustrative of some possibilities and problems associated with each. Our study explores the reactive site and mechanism for a complicated heterogeneous catalyst. We need to keep in mind that the catalytic cycle demands low barriers and shallow wells, and we need to make sure that as far as is possible, within the current knowledge of the system, we do not contradict experimental and industrial evidence concerning possible mechanisms and reactive sites.

The third chapter deals primarily with individual transition metal complexes and structures, rather than with a surface like the interior of the zeolite channels. There are two aspects to the catalytic activity of transition metal clusters: the ligand effects directly on the reactants, and the ligands effects - indirectly- on the metal-metal bonds. The triosmium cluster, $H_2Os_3(CO)_{10}$, which acts as a catalyst in olefin isomerization, has an unusual bonding structure, and the chemistry of the cluster is centered at that Os_2H_2 site. This chapter discusses the results of calculations designed to look at the possiblity of metal-metal bonding at this site, and to develop the principles of

ligand effects on metal-metal bonds for Os-Os bonds, in particular. If we can develop an understanding of which ligand properties effect the M-M bonds of metals with various electron configurations, we can design cluster catalysts with built-in reactivity in the form of purposely strong or weak metal-metal bonds. The results of this study should be applicable both to other metals and other ligands.

A catalytic cycle is sustained when there are no high barriers or deep wells at any of the reaction steps. When there is a question about or a choice of one or more of these steps, quantum mechanics provides a useful tool for determining the thermodynamics of the reactions--something that is often quite difficult to measure in the reaction chamber. Likewise, if in the course of a catalytic reaction the "catalyst" breaks apart to form, in situ, the actual catalyst, it can be quite time-consuming to determine what the actual catalytic species is, and hence the mechanism of reaction. Quantum mechanics can also provide data to help determine that species, by determination of the weakest bond or bonds--the points where the starting material is most likely to break apart.

One of the most frustrating aspects of heterogeneous catalysis, particularly when surfaces are involved, is the difficulty in determining at which site the interesting reaction is occurring and what, exactly, that reaction is. Molecular Mechanics calculations can be useful in determining properties of proposed reaction sites. In particular, these types of calculations can be used to determine how much space is available in a given area of the surface and how reagents and products can diffuse through or over that channel or surface.

Day-to-day use of *ab initio* and molecular mechanics calculations in the chemical industry is on the rise, but much needs to be done to understand how to implement these calculations in studying complex catalytic systems. These tools can be quite powerful, when selected and employed properly, in gaining the information needed to enhance understanding and, from that understanding, find expanded uses for catalysts.

Chapter I

Introduction to Zeolites, ZSM-5 and the Methanol to Gasoline Process

Chapter I:

Introduction to Zeolites, ZSM-5 and the Methanol to Gasoline Process

In the early seventies, a research group at Mobil Oil Co. discovered that when methanol was added to the zeolite ZSM-5 in a reactor, gasoline range hydrocarbons were formed.[1] This process was patented[2], and in 1983 a plant was built in New Zealand to manufacture gasoline using this process[3].

The gasoline from that plant can be used directly in an automobile, due to the empirical optimization of Methanol-to-Gasoline (MTG) to give the best possible fraction of gasoline range hydrocarbons.[4] This optimization involves a variety of modifications, including addition of other compounds and changes in reaction pressure. Despite this empirical optimization there are aspects of the process upon which researchers do not agree. The most important of these is the mechanism by which the first carbon-carbon bond is formed.

There are several common ways to form carbon-carbon bonds. These methods involve molecules which are in some way activated for that bond formation. One example is conjugated molecules such as those that contain carbonyl groups, olefins, and aromatic compounds. With these conjugated molecules C-C bond formation can occur either with standard substitution reactions or as free radical chain reactions. Other ways to activate molecules for this type of reaction are as follows: a) to have a good leaving group such as a halogen atom, or b) to reductively couple the C's via either a transition metal complex intermediate or photolysis.

In the ZSM-5/MTG system (barring impurities), at the time of the <u>first</u> carbon-carbon bond formation, there are no conjugated molecules, no halogens, no transition metals, and no photochemistry. Yet, gasoline does form and so the methanol must be activated.

This challenge has generated numerous studies over the last twenty years. Due to the complexity of MTG it is necessary, in any comprehensive discussion of the mechanism for C-C bond formation, to give a considerable amount of background information on the zeolite itself. In addition, it is also imperative that all that is relevant concerning MTG be detailed as part of this background discussion. This chapter will serve these two purposes. The first part of this chapter will include discussions of general properties of ZSM-5 and those aspects of ZSM-5 and MTG chemistry, which are crucial to understanding the possible mechanisms, that do not pertain to any specific mechanism. The second part will discuss, in detail, the various mechanisms that have been proposed and the pros and cons of each.

Background

This first section is not meant to be a comprehensive review of zeolite chemistry, as that can be found elsewhere[5,6,7,8] but to provide the basic background information for zeolites, ZSM-5, and Mobil's methanol to gasoline process.

Structural Features

Without defect sites, caused by dealumination or any other process, ZSM-5 has the structure shown in figure 1[9]. Each atom with tetrahedral coordination, either Al or Si (T atom), is surrounded by 4 oxygen atoms. The O-T-O is the usual tetrahedral 109 degrees while the T-O-T angle averages around 150 degrees. The T-O bond distance averages about 1.59 A.

ZSM-5 has a 2-dimensional channel structure. The straight channel (figure 2), with free diameter 5.4x5.6 A, runs perpendicular to the sinusoidal channel (figure 3) with free diameter 5.1x5.4 A[9]. They intersect at the bend in the sinusoidal channel.

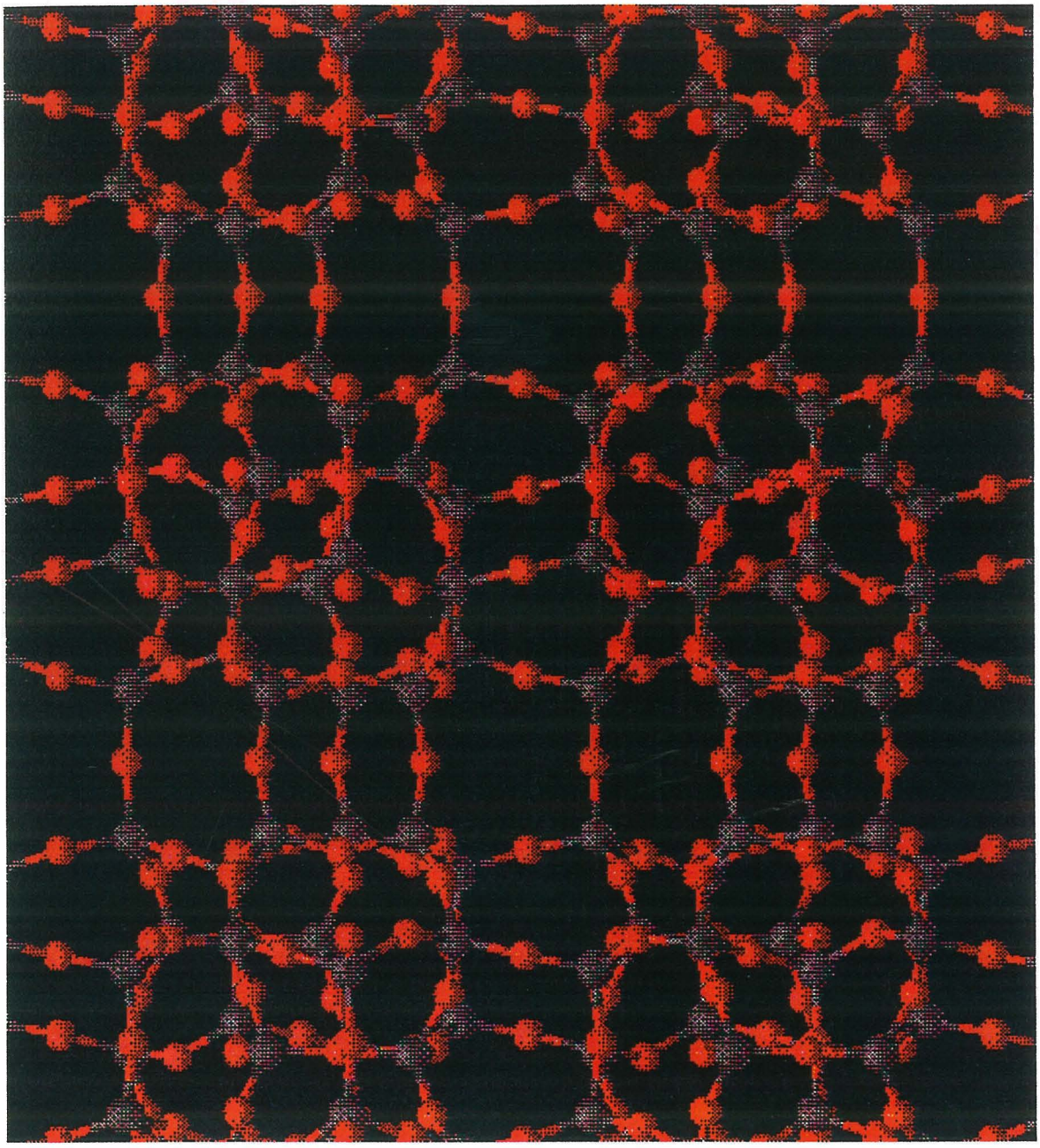


Figure 1

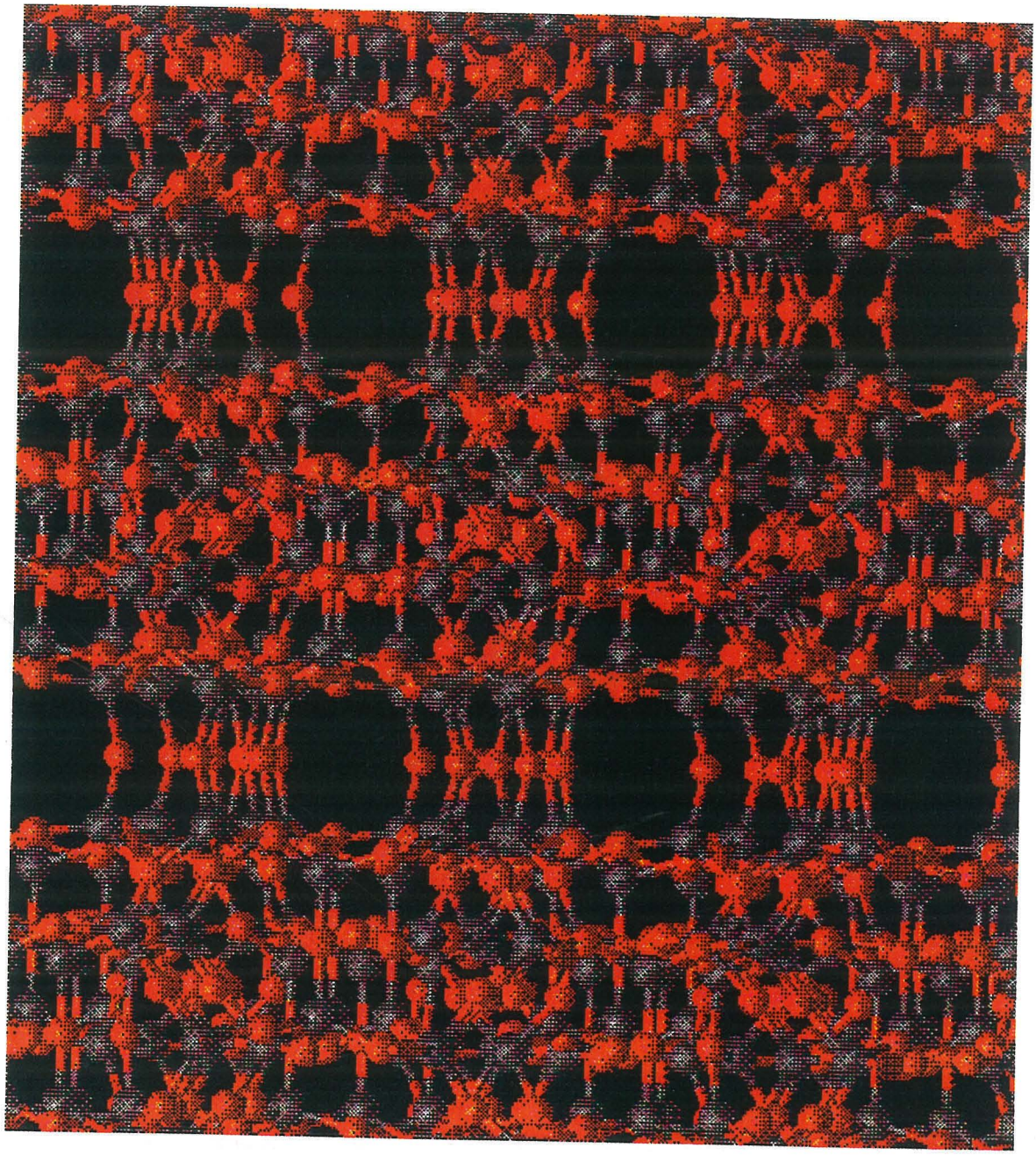


Figure 2

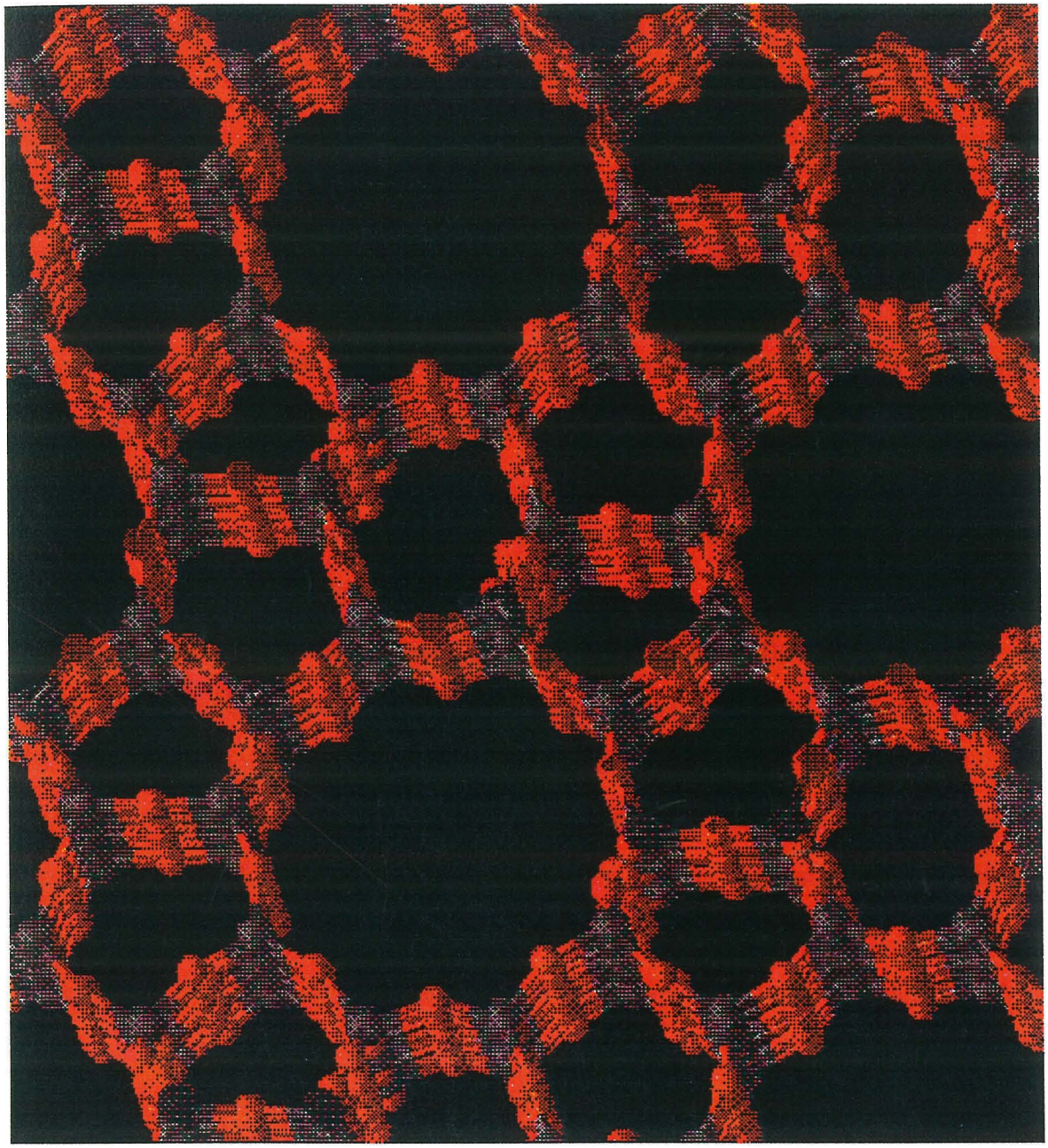


Figure 3

The structures in figures 1-3 are actually that of silicalite, the all Si member of the ZSM-5 family. As such it does not contain the standard reaction sites contained in reactive ZSM-5 because it does not have the Al atoms which allow those sites to be reactive. Because Al has one electron fewer than Si, it must have a negative charge to be tetrahedrally coordinated as it is in the ZSM-5 framework. That, in turn, requires the presence of a counterion. When this counterion is H+, the site becomes a Bronsted acid site, shown in figure 4. In addition to the Bronsted sites, there are also Lewis acid sites associated with Al atoms (shown in figure 5) which may play an important role in MTG chemistry. There is some evidence to suggest that the Lewis sites are not stable with respect to the framework structure and that the Lewis sites detected by spectroscopy are extra-framework sites[6], Nevertheless, this does not preclude their activity in MTG chemistry.

Dealumination is known to cause at least one defect site. IR investigations during dealumination process have revealed a broad peak at ~3500 cm-1[10], indicative of an OH stretch under hydrogen-bonded conditions, which some believe to be the vacated site. There is also a peak at 3720-3740 cm-1[11] many believe to be the vibrational band for this vacated site, while others attribute it to non-hydrogen bonded, isolated terminal hydroxyls[10]. Whichever assignment is correct, the site is proposed to have the structure in figure 6 and has been termed a "hydroxyl nest.[11]" An investigation of the extra-framework aluminum produced during the dealumination process shows a variety of aluminum complexes, some of which no doubt come from post-dealumination reaction, with no simple way of discerning the direct dealumination species. Without that direct relationship, it is difficult to accept the hydroxyl nest depicted above as the only possible site created by dealumination. Dealumination does decrease the total number of Bronsted acid sites.

Bronsted Site

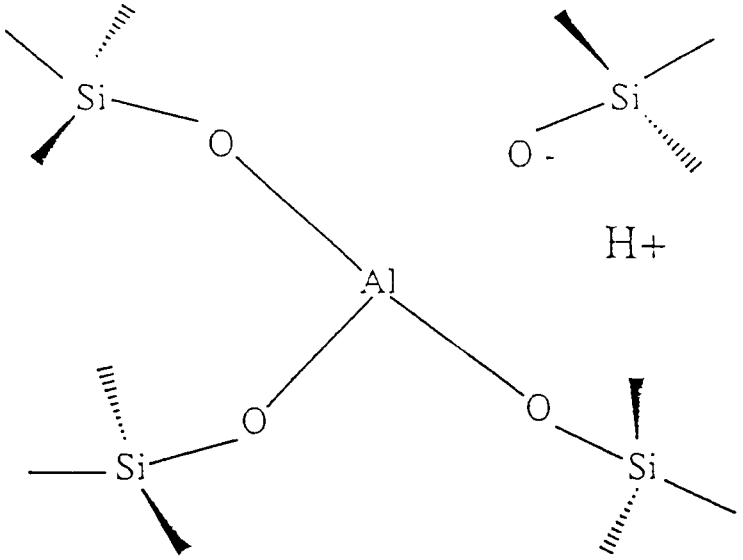


Figure 4

Lewis Acid Site

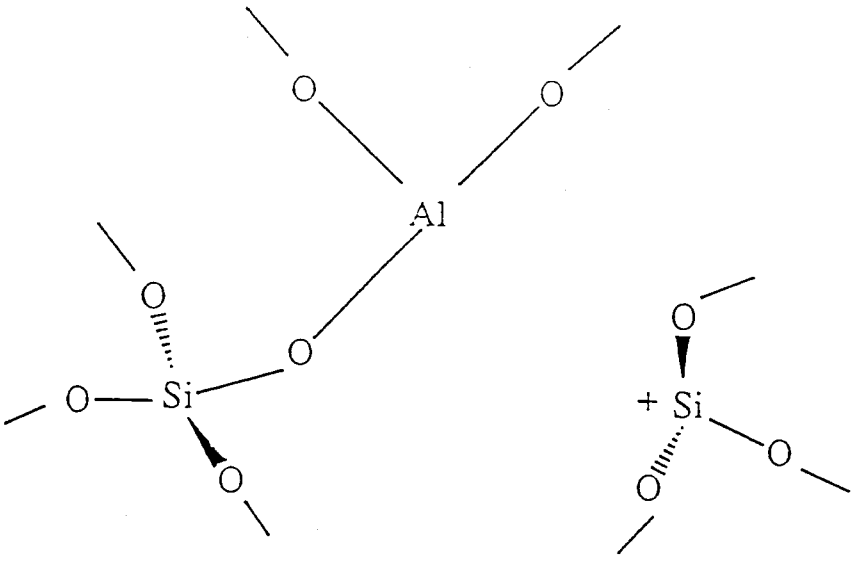


Figure 5

Hydroxyl Nest

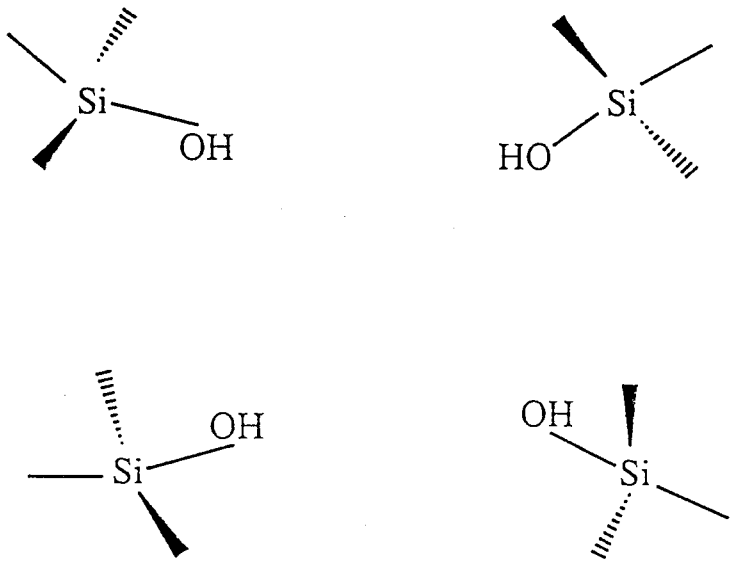


Figure 6

Other possible defect sites are likely, as free radicals have been detected in zeolite samples by ESR before any reactants have been added[12]. It is probable that there are radical defect sites in the zeolite, although no structure for such a site has been proposed.

Synthesis

The synthesis of ZSM-5 has been detailed in many places so only those aspects of the synthesis relevant to ZSM-5-MTG will be discussed here. The zeolite has two types of sites inherent in its structure, the Bronsted and Lewis sites described above. However, since this is a catalytic process, defect sites or impurities which may be introduced during the synthesis and preparation of the catalyst must be considered in searching for a mechanism and associated active site for the first carbon-carbon bond formation. The general procedure involves crystallization of the zeolite from a slurry of aluminate and silicate.

Zeolites are, by definition, metastable aluminosilicates. It is for this reason that the method of synthesis and careful control of all the synthesis variables is crucial to crystallizing the desired structure. The conditions and variables which dictate that ZSM-5 will form are presence or absence of template, Si:Al ratio, type of template, and amount of hydroxide with presence and nature of the template and Si/Al ratio being most important. When initially formed, the zeolite is a salt, either with an organic or inorganic template and/or Na+ as the counterion. As with many molecular sieves, changing these parameters even over a relatively small range will change which zeolite is formed and/or the material properties of the crystallizing zeolite. In order to remove the template, or other impurities in the channels, the zeolite is calcined at about 500-600 degrees Celsius. In order to create the reactive acidic structure of the zeolite, H-ZSM-5, the Na+ ion must be exchanged with H+. This can be carried out by washing with a protic acid such

as HCl[5]. Crystallization, calcining, and H+ exchange for Na+ may all be important in the creation of defect sites in the zeolite.

Dealumination

Dealumination may do more than just remove Bronsted sites. Dealumination can be done purposefully, as a separate process for particular reasons, but it also occurs as part of the synthesis and preparation of ZSM-5. Aggressive steaming (Water is abundant in the zeolite channels after synthesis.[5]) will remove Al from the tetrahedral sites[13]. This extraframework Al is proposed to form octahedrally coordinated Al species, as shown by ^{29}Si and ^{27}Al NMR[6]. Many extra-framework Al species can be found, but it is not known which are formed as a direct result of dealumination[14]. A loss of reactivity is seen after dealumination under these conditions occurs[13].

However, after mild steaming at partial pressures of water vapor of about 100 Torr, there is an increase in activity. It has been proposed that this is due to the formation of extraframework Al species in such a way as to enhance the acidity of near-by intact Bronsted sites[13]. However, there is no evidence as yet of such a species or how the enhancement might take place. Zeolites can also be dealuminated without steam by using chemicals such as, monovalent fluorides, other inorganic halides and oxyhalides[13].

Other Catalysis

ZSM-5 is used in many catalytic reactions other than MTG. It is a good cracking catalyst; it is used in xylene isomerization, ethylbenzene production, and several others such as dewaxing processes[7]. In these cases the reactivity is thought to be based on either the Bronsted acid sites or Lewis acid sites of the zeolite. None of these processes requires forming carbon-carbon bonds in the absence of C2 or higher hydrocarbons.

MTG and ZSM-5: Non-Mechanism Specific Properties

There are properties of the ZSM-5/MTG process which are crucial to understanding the mechanism for carbon-carbon bond formation which are intrinsic to the zeolite chemistry and not based on the chemistry of any one of the proposed mechanisms.

Any discussion of MTG must include, at the beginning, the description of the general path of reaction which occurs in three phases:

1) formation of dimethyl ether from methanol
2) formation of the first carbon-carbon bond

and

3) buildup of the hydrocarbons to gasoline range.

It is generally agreed that the third stage is catalyzed by the Bronsted acid sites of the zeolite.[15]

There are two distinct kinetic phases for the carbon-carbon bond processes (STAGE 2 and 3, above) for ZSM-5/MTG. In the first phase, the conversion of methanol is slower, and the primary reaction products are ethylene and methane.[16] In the second phase, there is a rapid jump in the rate of methanol conversion which suggests that this phase is autocatalytic.[17,18] No methane is formed during the second phase, implying that the two phases have distinctive reaction mechanisms for forming carbon-carbon bonds. This has shed light on the problem that many proposed mechanisms were thought to be infeasible because of obvious methane producing side reactions. Even though the total percentage of CH_4 produced is small, in the first kinetic phase that percentage is much larger. Chen et al.[17] have proposed that the autocatalytic phase carbon-carbon bonds are formed by the reaction of methanol with ethylene and higher hydrocarbons.

Knowledge of the reactivity of other molecular sieves with regard to the MTG process could be crucial to elucidating the mechanism of first carbon-carbon bond formation. ZSM-5 effects the formation of gasoline range hydrocarbons from methanol in two distinct ways. First, as a surface catalyst forming carbon-carbon bonds, and second as a shape-selective catalyst allowing only hydrocarbons of a certain size (and shape) range or smaller to escape from its channels and be recovered as product. Methanol will form hydrocarbons in other zeolites, but due to the size and shape of the channels, the largest fraction will not be gasoline range hydrocarbons[15]. However, this does suggest that the mechanism by which the first carbon-carbon bond is formed is not specific to ZSM-5.

The zeolite that we have been discussing is really H-ZSM-5. Each framework Al atom in ZSM-5 has a negative charge, so there must be a counterion. Generally, the counterion for the catalytically active zeolite is H+, forming the Bronsted acid sites. The Na salt of the conjugate base of HZSM-5 will form ethylene and propene, but not higher hydrocarbons[19]. This strongly implies the need for the Bronsted sites in the build-up of the hydrocarbons, but the converse conclusion is less clear for the first carbon-carbon bond formation due to the possibility of protic impurities.

Silicalite is the member of the ZSM-5 family of molecular sieves which contains no aluminum. The only published account of silicalite performing an MTG process involved supporting the sieve on a silica based honeycomb structure[20]. There is NMR data which shows that silicalite does, in fact contain some Al in framework sites[6].

If it could be shown that silicalite is rigorously without Al and that it could catalyze methanol conversion to hydrocarbons, then we would have to conclude that Al sites (Bronsted, Lewis, or extraframework) were not necessary in the MTG

process. Whether or not silicalite and ZSM-5 are the same thing and can do the same chemistry has been disputed both in laboratories and in courthouses, and given the lack of published data, the ability of silicalite to perform MTG will not be considered further here.

Much of the rest of the interpretation of data from ZSM-5/MTG research is subject to dispute. The next section will discuss some of the more important mechanisms that have been proposed for the first carbon-carbon formation phase of MTG.

Proposed Mechanisms for ZSM-5/MTG

Since ZSM-5 was first found to catalyze the conversion of methanol to gasoline, a variety of mechanisms have been proposed to explain the first carbon-carbon bond formation. These include free carbene, carbocation, oxonium ylide and surface ylide, free-radical radical recombination, free radical to surface ylide, and superacid (pentavalent carbon). There are essentially three classifications for these mechanisms, illustrated in Table I.

Table I

Classes of Proposed Mechanisms

Mechanism Type	Example
CH_2 intermediate	Free carbene, oxonium ylide, surface carbene or ylide
carbocation	superacid, standard carbocation chemistry
free radical mechanisms	radical recombination, radical chain reaction, free radical formation of CH_2

The first includes all mechanisms which involve generation of a CH_2- species of one sort or another. This includes the free methylene or carbene mechanisms, the oxonium-ylide mechanisms, surface carbene, and the surface stabilized ylide mechanisms. The second class of mechanisms involves carbenium ion chemistry and includes proposed mechanisms which contain pentavalent carbons (superacid) as well as more standard carbocation reactions. The third class are free radical reactions.

Essentially, each of these mechanisms is proposed in an attempt to find a way to activate the methanol carbon. Ones which propose formation of a CH_2 group as a reactive intermediate or which allow two C· to bond are examples of the proposed activation schemes.

In this chapter we will take each of these mechanisms or a representative sample and discuss the experimental results which pertain to that mechanism, either pro or con. It is important to stress that to this date no mechanism has received enough experimental support to be deemed unequivocally "the mechanism." However, it should also be noted that there are few experiments currently available which can pinpoint a site and show which chemistry is occurring at that site. A lack of experimental evidence, for any of the mechanisms, can not out of hand be considered a definite "minus" for that particular mechanism. Theoretical results from the literature will be reviewed in the discussion sections for the relevant mechanisms.

In order to properly discuss the mechanisms which we have considered and/or explored using computational means, it is necessary to review the literature data, both experimental and theoretical, that pertains to the various mechanisms. There have been several excellent reviews of methanol conversion

including most of the proposed mechanisms.[15,21] This section is intended to emphasize the controversial nature of the experimental data and to illustrate why we chose to explore the free radical and surface carbene mechanisms. Just as important, the theoretical results in the literature relevant to each mechanism will be reviewed in the appropriate sections.

As was mentioned in the previous section, there are two phases to carbon-carbon bond formation; an initial slower phase and an autocatalytic phase. It has been shown that these two phases are likely to have different carbon-carbon bond formation mechanisms, and that the mechanism for the autocatalytic phase involves reactions with Cn hydrocarbons, where n=2 or greater. Since we are interested in how that first C2 is formed, the real meat of the problem lies in the first, slow phase of hydrocarbon production.

The underlying questions which need to be answered for all of the mechanisms are as follows:

1) Is there a kinetically and thermodynamically way to form the reactive intermediate?

2) Is that reactive intermediate stable with respect to decomposition products, e.g., surface stabilized ylide with respect to free methylene?

3) Is there a thermodynamically and kinetically feasible way to form a C-C bond with that intermediate?

4) Is there any direct experimental or theoretical evidence supporting that moiety as the reactive intermediate to the first carbon-carbon bond formation?

These considerations can be summed up as follows: Is there a kinetically and thermodynamically feasible way to activate a carbon in the absence of C2 or higher hydrocarbons, transition metals, halogens, or photochemistry?

There is one mechanism that does not really fall under any of the above categories. It was proposed recently and may have more to do with a non-ZSM-5 based MTG process as compared with the other mechanisms that have been proposed. However, there is not enough evidence to completely preclude the possibility that such a mechanism might have importance in ZSM-5/MTG and so it will be discussed here.

Jackson and Bertsch used the observation that the Pearson reaction wherein methanol over polyphosphoric acid at 200 degrees Celsius (much lower temperature than MTG with ZSM-5) forms CO as an initial product, to develop a mechanism shown in figure 7 for the catalysis of the first carbon-carbon bond formation for that process using CO as the catalyst and calculated the thermodynamics of each step of that mechanism using the Gaussian programs[22]. Subsequent experiments by another group did not show a change in the activity of the Mobil MTG process with changes in the partial pressure of CO, so it is unlikely that the Mobil MTG process is catalyzed by CO[23]. There is one study which shows that CO is the product of the MTG process[24,25]. Other studies focusing closely on the early stages of catalysis find that methane and ethylene are the predominant first products. The mechanism for the Pearson reaction is beyond the purpose of this discussion.

The first class of mechanisms all have in common the formation of a CH_2, in different ways (Free radical formation of CH_2 will be discussed with the other free radical mechanisms.). There is some experimental evidence for the presence and possible role of CH_2 species in the carbon-carbon bond formation, but it is by no means definitive (*vide infra*).

The proposed mechanisms *en masse* include four possible CH_2 moieties: free carbene, surface bound oxonium methylide, and free oxonium-ylide.

Carbon Monoxide
Ethene + CO
Propene + CC
New C-C Bond forms here
X, Y = H, CH3, Si(OR)3, Al(OR)3, P(O)(OR)2

Figure 7

Oxonium Ylide (free and surface-bound)

Oxonium ylide mechanisms are attractive in that a C1 species is invoked that may provide carbon that is activated enough to bond to another carbon while not being so reactive that its lifetime is too short to accomplish that chemistry. van den Berg and coworkers first proposed an intermolecular C-C bond formation from an oxonium ylide species in 1980[26]. They invoked a intramolecular Steven's rearrangement to allow for the carbon-carbon bond formation (figure 8). The Steven's rearrangement has since been considered unlikely given the results of a deuterium labeling study which favor an intermolecular mechanism[27,28]. However, Olah[29], Chang[30] and Hutchings[19] (separately) have proposed different oxonium ylide mechanisms. In Olah's mechanisms, pictured in figure 9, the trimethyl oxonium ion is involved in forming the carbon-carbon bond intermolecularly. Chang and Hutchings both propose in methylating a surface ylide to create the carbon-carbon bond. The thermodynamic question mark for the surface ylide mechanisms involve the stability of the surface species with respect to decomposition products and the favorability of formation of that methoxylide. A key question for both intermolecular formation of the carbon-carbon bond and trimethyloxonium methylation of a surface methoxylide is the availability of a base strong enough to remove a methyl proton from the zeolite surface or from the trimethyloxonium ion.

HZSM-5 is an acid, with its reactive sites being Bronsted and Lewis acids. Neither of those types of sites is likely to be such a weak acid, however, that its conjugate base would be strong enough to remove a proton from a methoxy group. There is some theoretical evidence[31] that the electrostatic field in the zeolite is sufficiently strong to stretch the C-H bond. This may provide a way for that deprotonation, but there is still the problem of competition for basic sites by more protic hydrogens which would be equally affected by the electrostatic field.

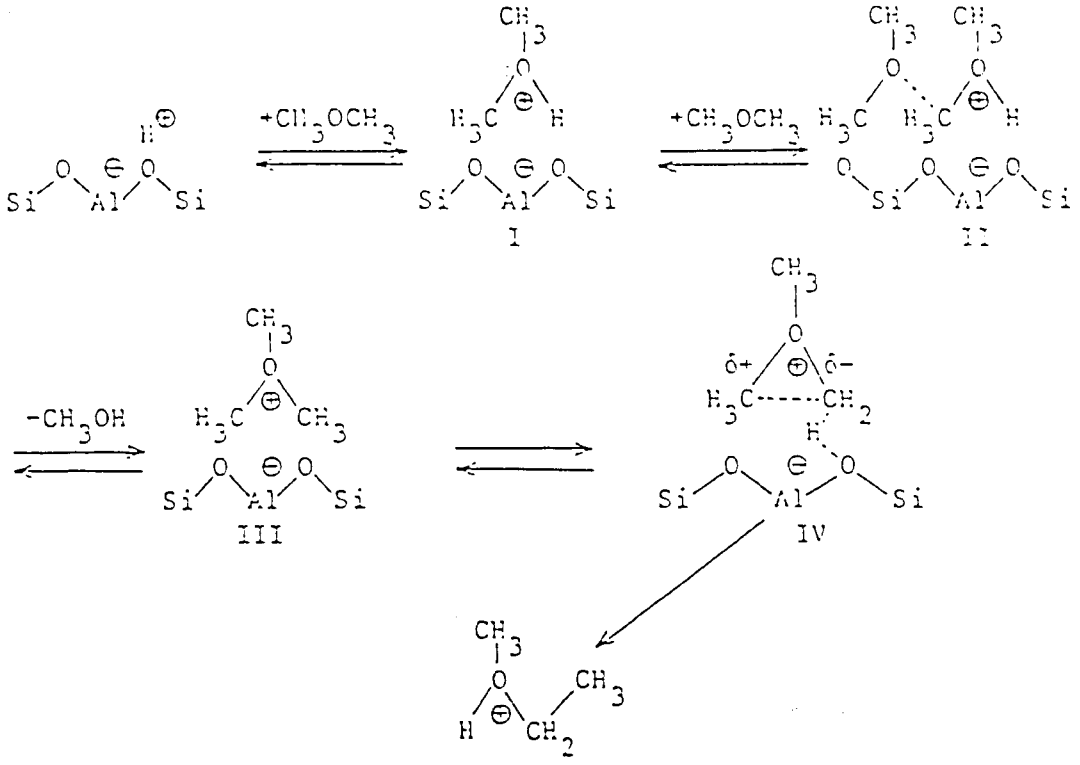


Figure 8

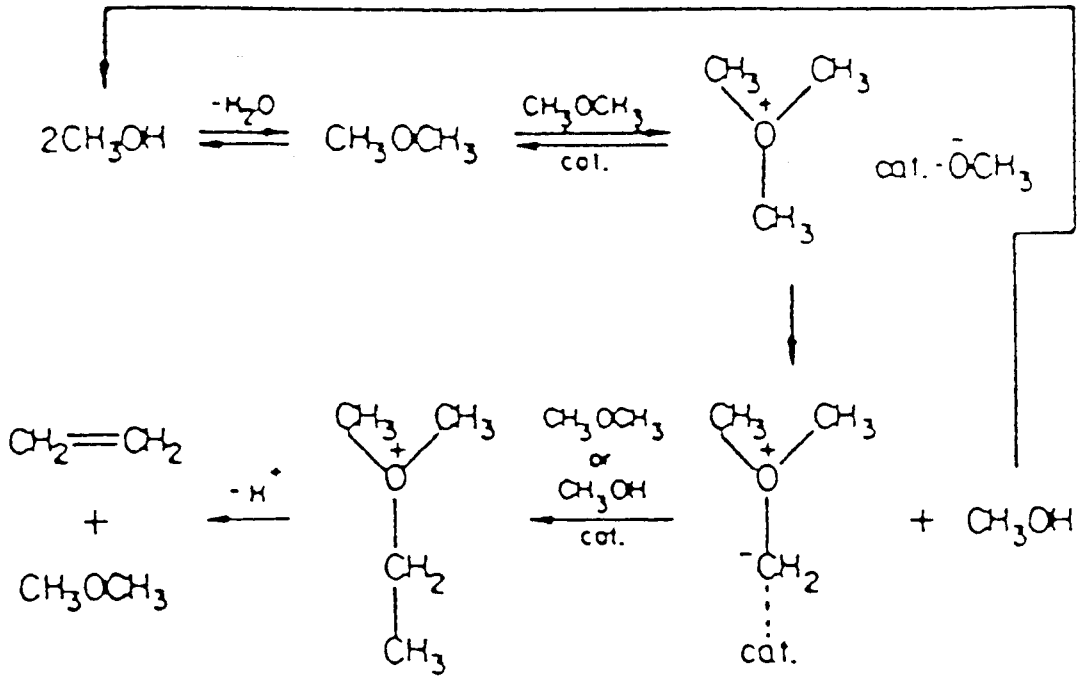


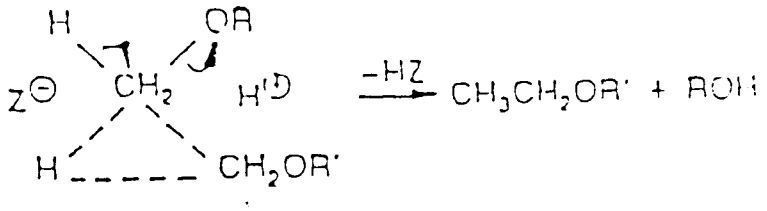
Figure 9

There is a relation here between the superacid proposals, the evidence that mild steaming promotes activity and by inference, at least, acidity and the need for a strong base to remove such a proton. If there could be enhanced acidity in this system, then there may also be factors as yet unrecognized which enhance the basicity of the conjugate bases of the Bronsted and Lewis acid and extra-framework Al sites in the zeolite, either through decreasing the acidity of these acid sites or through direct interaction with the conjugate bases. With that said, the zeolite is a strongly acidic system. Even if a moderately strong base were in evidence, it is more likely that it would remove a more weakly held proton than that of a methyl group, even with that methyl group attached to an electron-withdrawing oxygen atom. The question of the missing base remains in dispute in this field.

Free Carbene

The second category of proposed mechanisms involves carbene species as the reactive intermediates. There is some indirect experimental evidence for free carbene as the reactive intermediate. An experiment was done to see if the iso/normal butane ratio changed when the reaction mixture was changed from just methanol to a propane and methanol mixture. For methanol alone the i/n ratio was 3.8. This was lowered to 1.1 for the propane-methanol mixture. The propane, normally inert under these conditions, was a receptor for the reactive intermediate. When ^{13}C labeled methanol was used, singly labeled butane was found in larger quantities than would be required from random distribution. This was considered to be more indicative of carbene insertion than a carbocation mechanism because the carbene would not be selective for a tertiary carbon as would a carbocation[32]. Chang and Silvestri earlier proposed the formation of

MeOEt by the concerted mechanism of carbene generation with sp3 insertion into the C-H bond of dimethyl ether to form methyl ethyl ether (figure 10)[1].



Later proposals by Lee and Wu invoked framework stabilization of the carbene. Their experiment, using CH_2N_2 as the methylene source, showed increased hydrocarbon formation from acidic surfaces such as ZSM-5, but also showed reactivity from "inert" materials[33].

All of these proposals share the same problem as the oxonium ylide chemistry, namely how do you form the CH_2 in the absence of a base strong enough to remove the proton from a methyl group. However, as mentioned above, there are properties of this system which might enhance or decrease acidity or basicity. There is a thermodynamic question as well: is the carbene stabilized by the zeolite (not as a surface methoxylide as that is discussed above)? One calculation, done by W. Drenth[34] in 1983, shows that the carbene is stabilized on the surface. This calculation invoked models (figure 11) which at the time were needed to accommodate the size of the calculation. In addition, as pictured, they do not represent a framework site in the zeolite. Nonetheless, it is not inconcievable that such an arrangement of portions of other molecules might exist near the acid sites in the zeolite. In light of the results presented in the next chapter, it would be interesting to rethink this calculation in terms of where the

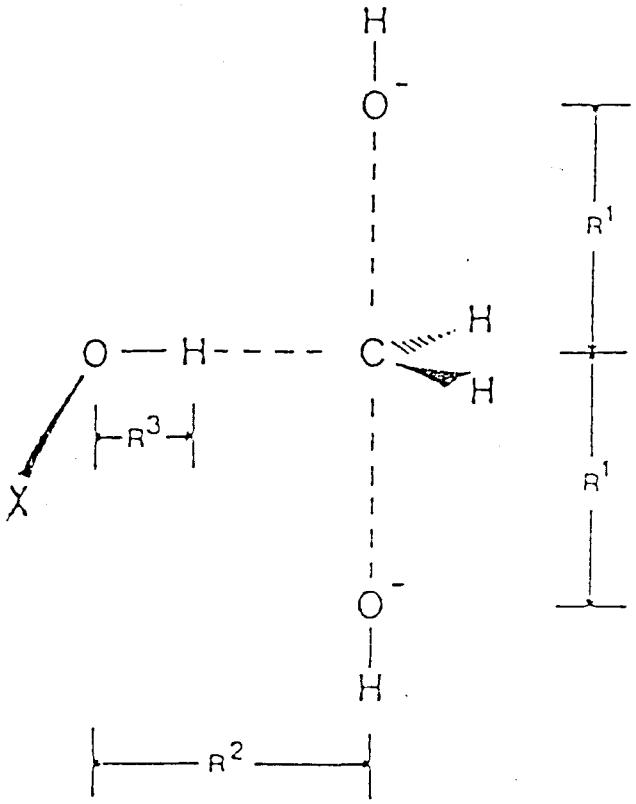


Figure 11

carbene might lie within the zeolite and which molecules, particularly extra-framework Al complexes, might be surrounding it. Such a calculation would be more feasible now with more powerful programs and faster computers as well.

Carbocation Mechanisms

There are two major carbenium ion mechanisms. The first, proposed by Kaeding and Butter in 1980[35] and Nagy[36], involves formation of an incipient methyl carbonium ion followed by attack on this ion by a deprotonated methyl ether molecule (figure 12). This mechanism illustrates the difficulty with such an acidic system, namely that in a system where it is facile to produce a CH_3^+, it is quite difficult to produce the CH_2 moiety needed to form a carbon-carbon bond with that ion. As with the carbene and oxonium ion mechanisms, however, the possibility of local conditions giving rise to enhanced basicity cannot be ruled out.

The second carbenium ion chemistry invokes, as shown in figure 13, a pentavalent carbon in order to form the carbon-carbon bond[37,38]. There is precedent for this chemistry in superacid systems such as Nafion-H and heteropolyacids, which do convert methanol to gasoline[37]. There is no direct proof, however, that ZSM-5 can reproduce the level of acidity needed to stabilize the pentavalent carbon and allow the reaction to proceed. There is the inferred evidence of the enhanced acidity from the observed enhanced activity resulting from mild steaming. However, no quantitative acidity increase has been measured. In addition, dimethyl ether is converted to trimethyloxonium ion in superacid systems[39].

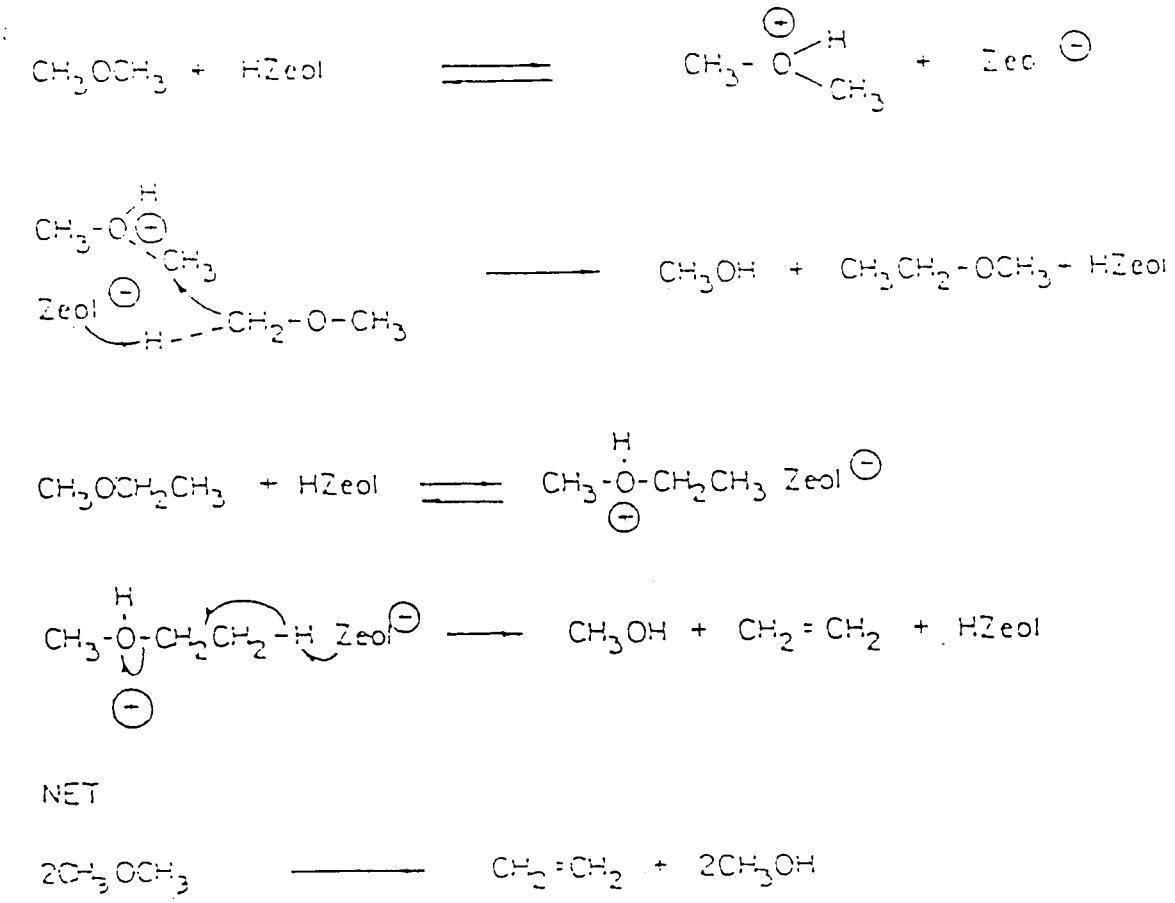


Figure 12

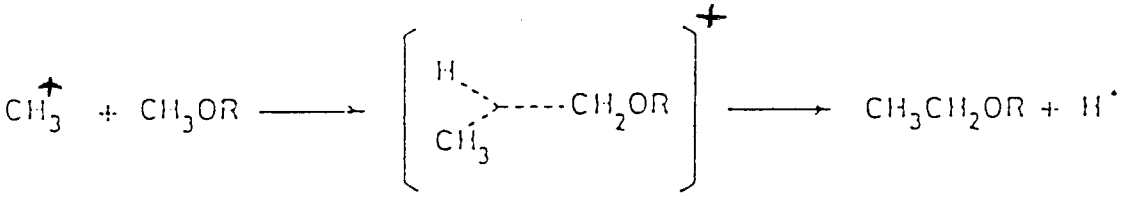


Figure 13

Free Radical Mechanisms

The final group of mechanisms involves free radical species as the reactive intermediates. Clarke et al. first detected free radicals during MTG via a combined spin-trapping and ESR experiment in 1986.[40] Since then various researchers have looked at the possibility of free radical involvement in the first carbon-carbon bond formation in MTG.

Hunter and Hutchings and Chang et al.[41,42] have both found a decrease in activity of the catalyst when the known free radical reaction poison, NO, is added to the reaction mixture. Chang suggested that this result was ambiguous because the NO could react to form an ammonium ion which could poison the catalyst regardless of whether or not the carbon-carbon bond formation was free-radical. Hunter and Hutchings have proposed a different reaction, the Barton reaction (figure 14), which would also poison the catalyst. This different proposal is based on the observation that the kinetic parameters for deactivation by NO do not match the parameters for deactivation by NH_3. Either way, there is not enough evidence to show that the decrease in reactivity is due wholly or in part to either a poisoning reaction, or to the trapping of a free radical reactive intermediate to carbon-carbon bond formation.

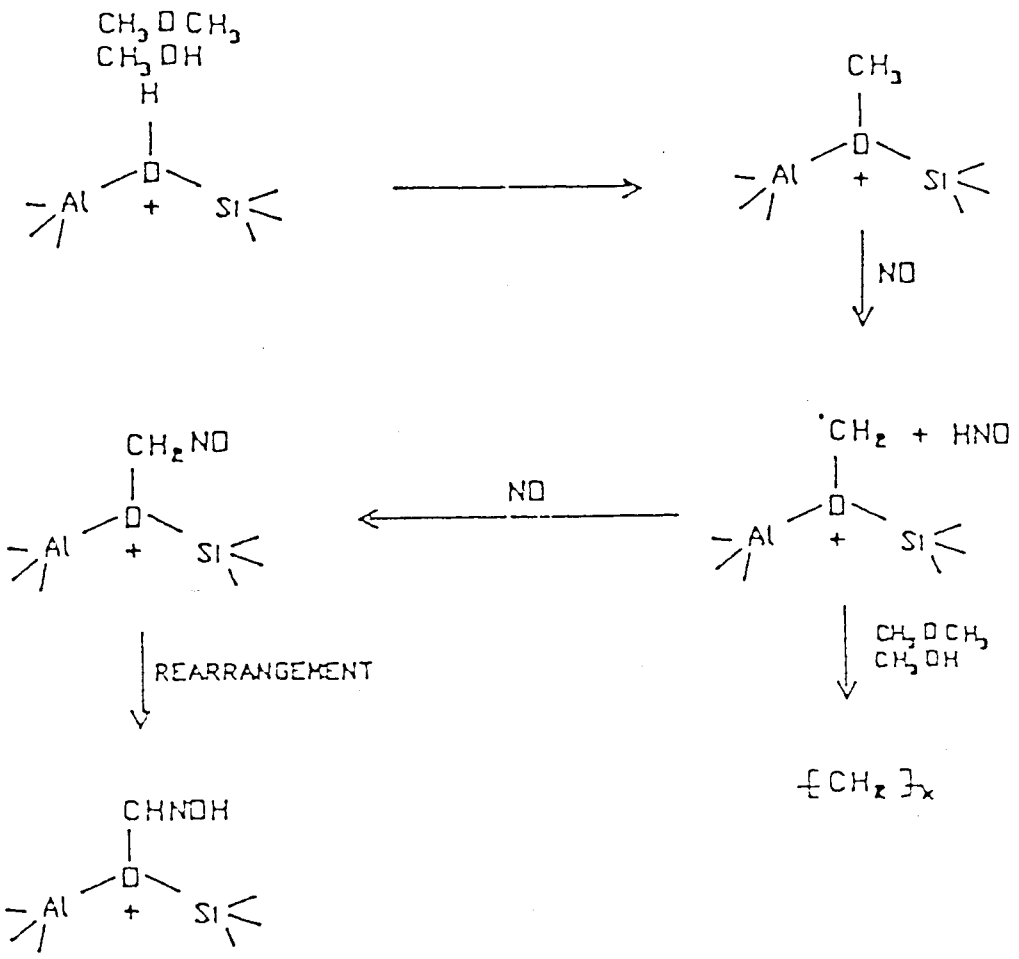

CH3OCH3
CH3OH
H
Al
O
+
Si
CH3
NO
CH2 + HNO
CH2NO
REARRANGEMENT
CHNOH
CH3OCH3
CH3OH
(CH2)x

Figure 14

The first free radical mechanism (below) was proposed by Zatorski and Krzyzanowski long before Clarke's experiment. [43]

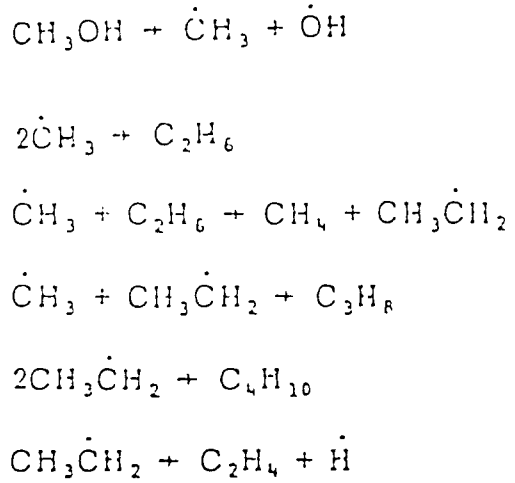


Figure 15

It is unclear how or why the methanol would split to $CH_3\cdot$ and $OH\cdot$

Clarke et al.[40] proposed a mechanism involving radical hydrogen abstraction from two molecules of dimethyl ether and then radical recombination of those two molecules to form the diether species shown in the mechanism below:

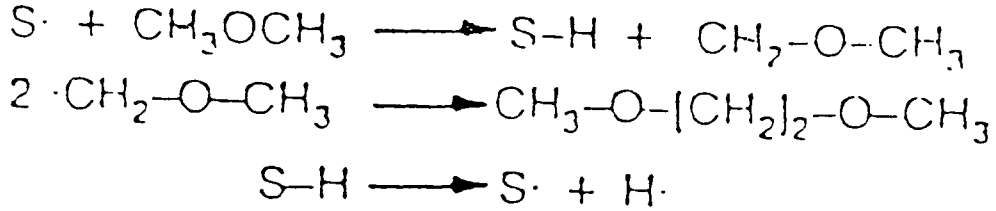


Figure 16

This diether has not, to this date, been detected at any time during the MTG process.

The other possible pathway for the ·CH2OCH3 is:

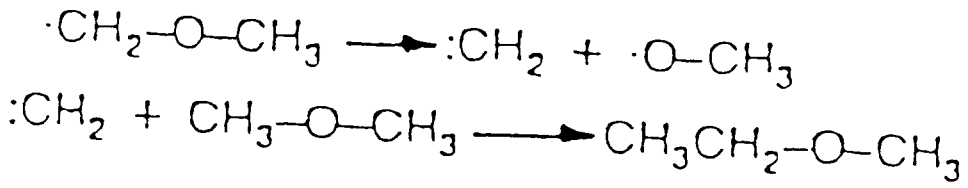


Figure 17

No mention is made of how the :CH_2 would be stabilized.

Chang, et. al. have proposed the free radical mechanism in figure 18 for the carbon-carbon bond formation[42]. This mechanism is attractive in that it does not involve radical recombination, or, as in the CH_2 mechanisms, the presence of a very strong base. However, it does require a radical inversion at a carbon atom. Even though such an inversion may be thermodynamically feasible, it would involve a very high activation energy. The most common exceptions to this are inversions where transition metals are involved to facilitate. The metals have empty orbitals which can overlap both the bond that is breaking and the bond that is forming, thereby lowering the energy of the transition state[44]. Without such a metal, the first bond must break completely before the new bond can form. The original patent for the MTG process does mention, without being specific, the inclusion of transition metals[2] and in nature, at least, it is rare to find a zeolite which does not contain iron impurities[8]. An experiment which

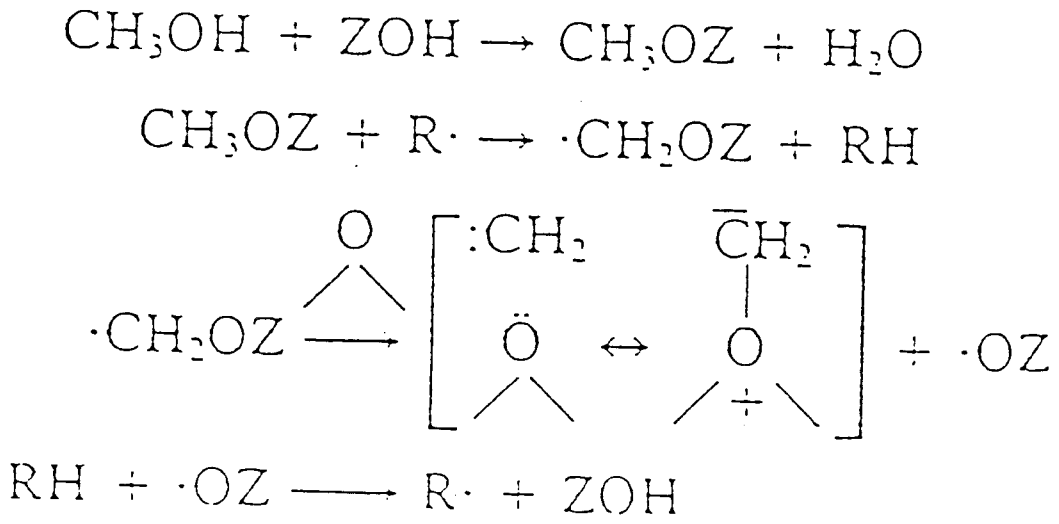

CH3OH + ZOH → CH3OZ + H2O
CH3OZ + R· → ·CH2OZ + RH
·CH2OZ
:CH2
CH2
+ ·OZ
RH + ·OZ → R· + ZOH

Figure 18

rigorously excluded transition metals and measured catalytic activity would contribute understanding to this aspect of free radical chemistry and MTG. Currently, there has been no publication of such an experiment.

Conclusion

None of the mechanisms proposed thus far is clearly without flaws. However, these perceived flaws may be due to an, as yet, incomplete understanding of the ZSM-5/MTG system. It is therefore important to explore those aspects of the mechanisms which may be viable in order to further our understanding of the entire system.

To this end, we have extensively studied possible free radical mechanisms for this carbon-carbon bond formation. Given the difficulties involved with forming a CH_2 species in the likely absence of a strong base, it is only reasonable to explore all aspects of free radical chemistry, which does not require such a base and which might produce a carbon-carbon bond in this system.

Ignoring, for the time being, the missing base problem, we have also studied the concept of a surface stabilized ylide to see if this species is, in fact, stable. Mechanisms which involve surface stabilized ylides in resonance with surface carbenes are currently well-favored in the literature, and the basis for these mechanisms is that stability, providing a C1 moiety which is long-lived enough to do the required chemistry. Much of the experimental evidence favors a CH_2 reactive intermediate of some sort.

There also is sufficient experimental evidence to warrent further investigation of the chemistry of the extra-framework aluminum complexes. It may well be that activation of the methanol in order to form the first C-C bond requires the presence of one or some of these compounds.

We have not, as yet, studied aspects of the ZSM-5 system which may enhance acidity or basicity. This does not imply that they are not important, as presence of such agents may not only enhance the chemistry, but how we view many of the catalytic processes of zeolites.

The following chapter describes in detail our understanding of the free-radical mechanisms and the question of stability of the ylide. Results of calculations are given which provide thermodynamic data for the various mechanisms, as well as results from a molecular mechanics study relevant to the flexibility of the zeolite. These calculations should provide additional information concerning the ability of the zeolite framework to activate methanol in order to form the first carbon-carbon bond.

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Chapter II

Methanol to Gasoline: Study of Possible Mechanisms

Chapter II: Methanol to Gasoline: Study of Possible Mechanisms

Introduction

As discussed in the previous chapter, there are two main types of mechanisms which show promise. The first, an ylide stabilized by the zeolite surface as a surface carbene, has the support of experimental evidence which favors a reactive "CH_2" as the intermediate. The second, a free radical mechanism of some description, is attractive because it would not require a strong base to make a carbon-carbon bond.

Our goal in studying the ZSM-5/MTG carbon-carbon bond formation is to determine the feasibility, in terms of thermodynamics, of various proposed mechanisms. Aside from the arguments presented in the last chapter (pro or con), if a mechanism is not thermodynamically feasible, it will not be able to achieve the catalysis observed in MTG. Contributions to understanding this process have and will come only from examining aspects of each mechanism with the proper tools. In this case, the quantum chemistry is ideally suited to determining the thermodynamics of these reactions, whereas it would be virtually impossible to design an experiment to obtain the same information.

In one case we have also chosen to do molecular mechanics studies, so that we can understand the structure of the active site for that mechanisms. Actually visualizing a site for the mechanisms we have chosen to study was a crucial first step in understanding the chemistry. These sites are rarely defined in the literature well enough to take directly and use in a model. For each mechanism where this was required, we developed a picture of the active site from the known chemistry of the zeolite under MTG conditions.

Another purpose of this study is to determine whether or not the framework, or portions thereof, is solely responsible for the first carbon-carbon bond formation. The trend in the literature, as seen in the previous chapter, has

Hydroxyl Nest

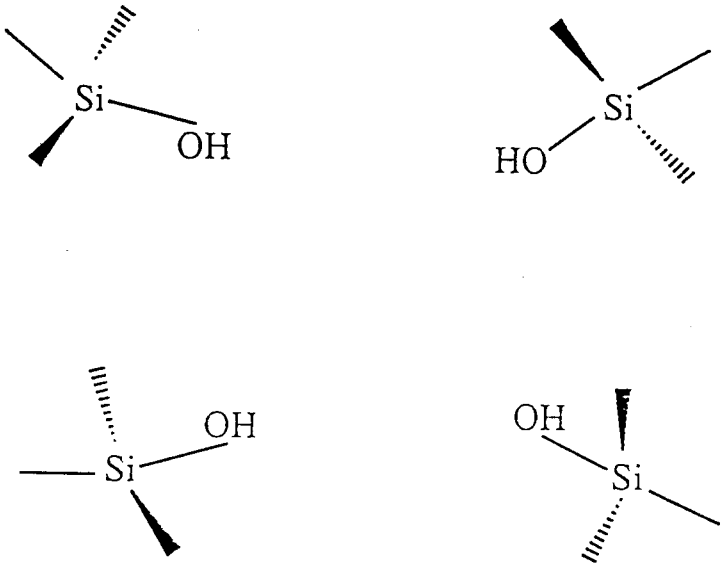
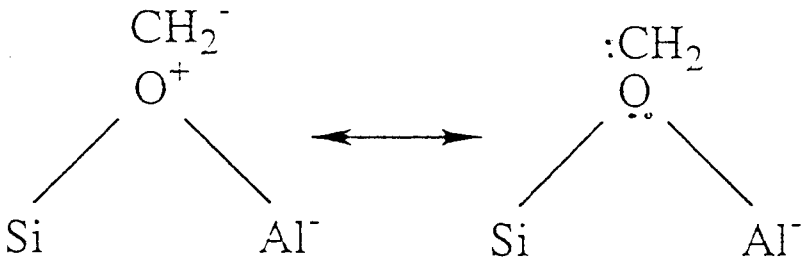


Figure 1

been proposed mechanisms in which part of the zeolite framework is considered to be the active site. The only exception to this are those mechanisms which include trimethyl oxonium ions, based on the ylide mechanism proposed by van den Berg[1]. In these mechanisms, the most likely role for the trimethyloxonium ion is as a methylating agent[2,3], or as in the case of Olah's mechanism[4], the ion itself activates the carbon. To that end, the mechanisms presented in this chapter will have that one point in common: they all involve some portion of the zeolite framework, either as a defect site such as the hydroxyl nest (figure 1) or as a part of the regular structure, as the reaction site for the mechanism, with the reactive intermediate attached to that site. It may be that the task of activating the methanol C requires more than the framework of ZSM-5 (Chap. 1, figure 1).

The mechanisms to be presented are a free radical mechanism and a surface-bound ylide mechanism. The ylide mechanism study includes a look at the stability of the standard surface bound ylide proposed in the literature, pictured below.



The surface ylide mechanisms in the literature, as well as some views of free carbene mechanisms, are based on the assumption that the surface of the zeolite framework stabilizes that moiety[5]. In addition, although there has been no mechanism invoking such a site, a molecular mechanics study was done to

determine if there could be a CH_2 moiety stabilized due to steric constraints. The free radical mechanism is loosely based on that published by Chang et al. (figure 2)[6] and involves the site shown below termed an oxy-Al radical site. This site was chosen because it could bring the second molecule of methanol close to the reactive site by mean of the coordination of the hydroxyl oxygen to the nearby Al atom.

From the information presented in the previous chapter ,it is clear that there are complexities in the ZSM-5/MTG process that could not be modeled solely using computational techniques. In order to gain information about this system, we have chosen to look at the thermodynamics of these two types of mechanisms as they are at least somewhat favored in the literature. This does not mean that our thermodynamics coupled with the known experimental data will make "the mechanism" clear. For each case, there are strong arguments (outlined in the preceding chapter), both for and against, and the contrary arguments cannot be ignored. Instead, our results point out aspects of those mechanisms which require further study and help delineate the direction those studies should take.

I. Methods and Calculational Details

Although there are aspects to the methods we used which differ for each mechanism, there is much in common. Those points which are particular to each proposed mechanism will be discussed within the section of the respective mechanism.

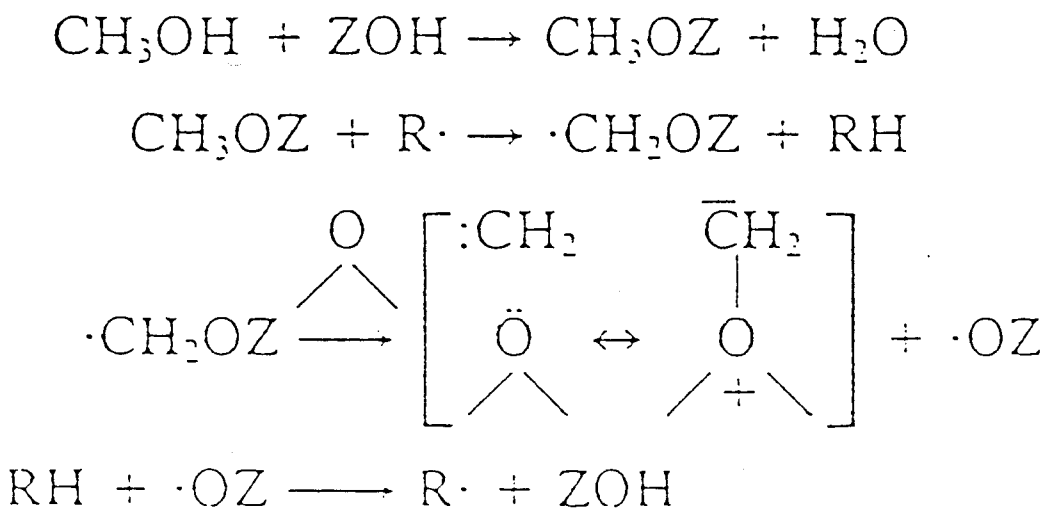
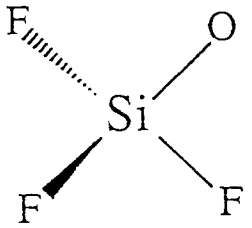

CH3OH + ZOH → CH3OZ + H2O
CH3OZ + R· → ·CH2OZ + RH
·CH2OZ
:CH2
CH2
+ ·OZ
RH + ·OZ → R· + ZOH

Figure 2

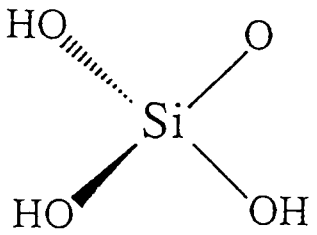
1. Model

The most important choice for a computational project is which molecule to use as a model that is appropriate to the system and chemistry under examination. The ideal choice would be to make no substitution and to compute properties of the system as it exists in the real world. For many systems, this choice is not suitable for quantum mechanics calculations. For example, ZSM-5 contains 288 atoms in the unit cell. It is simply not currently possible to calculate the wavefunction for this cell, at a level necessary to determine bond strengths accurately, or even to do so for all but a very small fraction of the cell. We must choose a model molecule that well-represents the chemistry of the framework atoms, the nature of the active site and, if possible, some of the surrounding atoms in the framework.

The following model



was chosen to represent a Si atom in a tetrahedral site of the zeolite framework. While this molecule,



would make a more accurate representation of that framework site, the calculations needed to get accurate bond energies for the thermodynamics would be prohibitively large for this model. We did have a choice as to whether to use F atoms or H atoms in the tetrahedral positions around the Si. The model with F atoms shown above was chosen because it more accurately represents the electronegativity of the oxygen atoms which, along with Si and Al, make up the zeolite.

2. Basis Sets

Once a model is chosen, basis sets for each atom in the model are needed. Both accuracy and size of the calculation need to be taken into consideration in choosing the basis sets. A series of calculations was done on known molecules to determine the best basis sets for these atoms. The goal was to improve the basis set until little or no change in the bond energy was calculated, and the bond energy calculated was, within reasonable error (1-4 kcal) of the experimentally determined bond energy.

Silicon:

There are several choices for Si, the first being whether or not to use an effective potential for the core electrons of the Si atom. In this case, size

constraints require use of such an effective potential to model these core electrons. The potential and accompanying double zeta basis set which were used were developed by Rappe, Smedley and Goddard[7]. Good agreement with experimental bond energies were obtained for test molecules containing Si using this basis and potential along with two sets of d polarization functions (Table 1),

Oxygen and Carbon:

For both oxygen and carbon, the standard Dunning/Huzinaga[8] double zeta basis set were used along with a set of d polarization functions.

Fluorine:

A standard Dunning/Huzinaga[8] double zeta basis set was used. D polarization functions were not used due to size considerations.

Hydrogen:

The Dunning/Huzinaga[8] double zeta basis set, with scaled exponent, was chosen. For cases where an H atom is part of the bond being broken, a p polarization function is added.

3. Methods of Calculation

Most of these calculations were done at the GVBCI*Singles method. This calculation allows simultaneous correlation of the electrons in the bond and in all of the bonds adjacent to the one of interest. It was found that, particularly when an O atom was involved, the correlation of the adjacent single bonds was necessary to determine an accurate bond energy. In addition, this method includes singles excitations which allow the orbitals to change shape when the bond is broken.

A preferred calculation would have been the Correlation Consistent CI developed in the Goddard Group[9], but again we were constrained by the size of the calculation and the lack of symmetry in many of the molecules of interest.

In several cases optimum geometries needed to be calculated. These calculations were performed with A. K. Rappe's gradient program and with Erik Bierwagen's[10] upgrade to that program.

This method and the basis sets were tested on several molecules for which bond dissociation energies have been determined experimentally. The results of the calculations compared with the experimental values are shown in Table I. The calculated bond energies compare favorably with experiment.

Table I

Comparison of Bond Energies from Experiment and Calculation on Selected Molecules

Molecule	Calculated Bond Energies in kcal	Experimental Bond Energies in kcal[10]
CH_3O-H	101.3	104
CH_3-OH	88.58	92
CH_3O-CH_3	81.8	83
SiF_3-F	160	164
HO-H	112.7	119

Note that the bond energy for H_2O is 6 kcal too low. This is likely to be due to the large effects the oxygen lone pairs have on the water molecule. With this level of calculation, and with only the O-H bonds correlated, the O-H bonds of water are not adequately described.

4. Geometry

Wherever possible, geometries were taken from experiment. One aspect of the model F_3SiO is that it is a small molecule meant to represent a portion of a semi-rigid framework. For that reason, all of our bond energies calculated do not allow relaxation of the F_3Si-O portion of the molecule. However, the results of a geometry optimization calculation for SiF_3O (figures 3 and 4) show that the relaxed geometry is very close to the crystal structure T-O distance of 1.59 Å[11] and the tetrahedral angles used in the bond energy calculations.

SiF_3O optimized geometry - bond distances

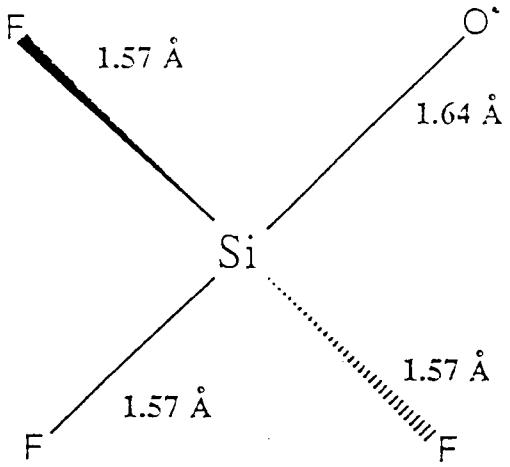


Figure 3

SiF_3O optimized geometry - angles

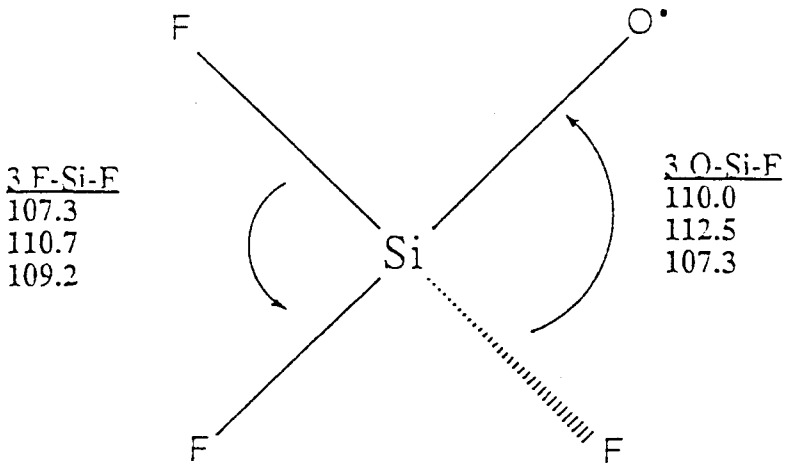


Figure 4

II. Free Radical Mechanism

One of the attractions of a free radical mechanism for formation of the first carbon-carbon bond is that a strong base is not required to form a $CH_2\cdot$ as would be required for removing H from a methyl or methoxy group. There are two possible types of radical mechanisms, a straightforward radical chain mechanism and a radical recombination mechanism. A recombination mechanism would require the chemical bonding of two radicals to form the desired product whereas the chain mechanism forms the product as part of the chain and only involves recombination as a terminal step to the chain reaction.

After some consideration, it was determined that most or all conceivable radical recombination mechanisms would not be thermodynamically feasible under the MTG conditions. This is because the recombination step would be considerably exothermic creating a very deep well in the catalytic cycle. In order to get out of the well and complete the cycle, there would have to be one or several reaction steps which involved large barriers. From the bond energies calculated in the course of our studies, it seems clear that the depth of the well would be too large to sustain the catalytic cycle.

This left exploration of possible free radical chain mechanisms. The most prominent one in the literature is that of Chang, et al.[6] (figure 2). In order to avoid involving a surface ylide (vida infra), we explored a new mechanism (figure 5). After completing the thermodynamic studies, we realized that this mechanism as well as that of Chang's contains a high kinetic barrier due to a radical inversion step at carbon. However, the study of this free radical mechanism is included here to illustrate the methods used to calculate the thermodynamics and which are applicable to other mechanisms. In addition, study of the mechanism brings up the possibility that a free radical chain mechanism may not be possible

for first carbon-carbon bond formation in the absence of conjugated bonds or higher hydrocarbons.

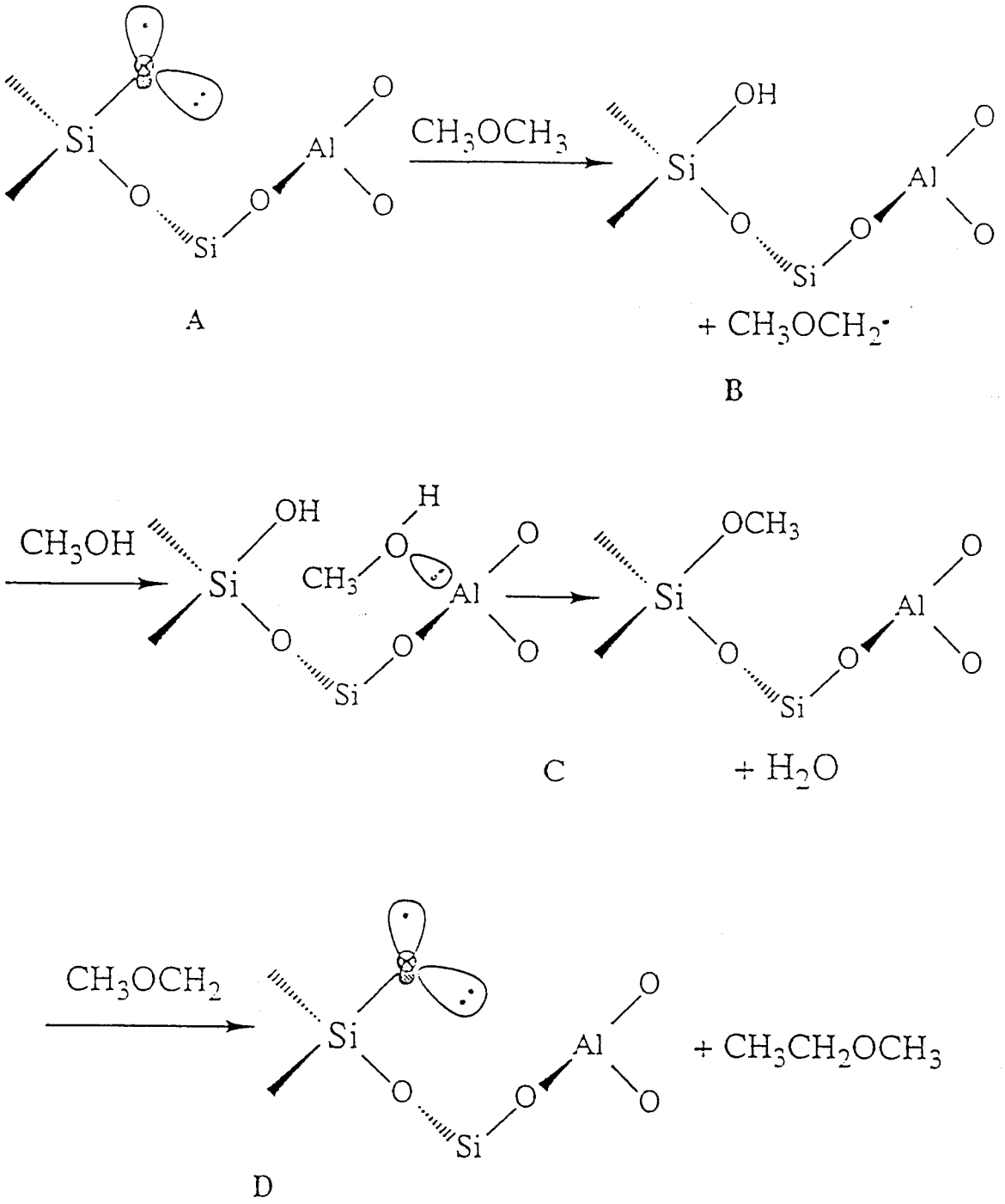
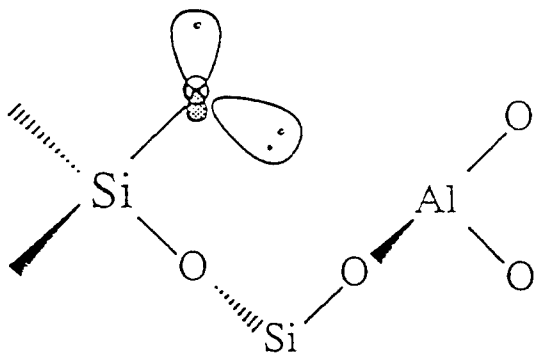


Figure 5

We have proposed a free-radical mechanism that is similar to the Chang mechanism in that it involves formation of a methoxyl group on the zeolite. The key difference between the mechanisms is that Chang's relies on the stability of the formed surface-ylide to make the C-C bond, presumably by methylation, whereas this mechanism involves a radical attack on carbon to form the C-C bond.

One other difference between this mechanism and many of the others in the literature is the nature of the C_2 product formed. Most of the mechanisms in the literature propose ethylene, $CH_2{=}CH_2$, to be the primary C_2 product formed. van den Berg's[1] oxonium ylide Steven's rearrangement mechanism is another exception, also proposing $CH_3CH_2OCH_3$ as the primary C_2 product.

This mechanism requires an oxy-Al radical defect site on the zeolite, as pictured below, for the locus of catalytic activity for the carbon-carbon bond formation.



This site is a likely defect site, in ZSM-5, and has the advantage of bringing the second molecule of methanol close to the reaction site via the coordination to the framework Al atom.

The overall equation for the formation of ethyl methyl ether in our mechanism is shown below. A description of the mechanism follows. The Si atom of this site will be referred to as " the zeolite silicon" or "the zeolite Si."

$$CH_3OCH_3 + CH_3OH \longrightarrow CH_3CH_2OCH_3 + H_2O$$

The first step starts with the dimethyl ether that is known to form from methanol during the MTG process[12]. The equation for that reaction is as follows:

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

A hydrogen atom of dimethyl ether is abstracted by the oxygen radical creating the radical $CH_3OCH_2\cdot$, and leaving a hydrogen bound to the oxygen on the zeolite Si. A molecule of methanol can associate with the Al adjacent to the OH group just formed. The methanol can dissociate to form H_2O and a methoxy group, OCH_3, on the zeolite Si. The radical formed by hydrogen abstraction, $CH_3OCH_2\cdot$, attacks the methoxy C on the zeolite Si to form ethylmethyl ether. $CH_3CH_2OCH_3$, and regenerate the initial oxy-aluminum radical site.

The mechanism for carbon-carbon bond formation as illustrated in figure 5:

A) Start. Oxy-Al radical site.

B) Addition of dimethyl ether. Abstraction of H by oxy radical.

CH_3-O-$CH_2\cdot$ leaves site. Si-O-H remains.

C) Addition of methanol. Oxygen of methanol bonds datively to Al. H_2O product is formed as methyl from methanol bonds to Si-O.

D) Radical formed in step (B) attacks methoxy carbon on zeolite Si. Ethyl methyl ether is formed. Oxy-Al radical is generated.

Geometry

The geometries used for these calculations follow the prescriptions in Section I. The bond distances and angle for each molecule calculated are shown in Tables II and III. Figures 6 and 7 show these bonds and angles for SiF_3OH and SiF_3OCH_3.

Table II

Bond Distances for Calculated Molecules

Molecule	Si-F distance, in Å	Si-O	O-H	O-C	C-H
SiF_3OCH_3	1.585	1.585	----------	1.44	1.08
SiF_3OH	1.585	1.585	0.96	----------	----------
CH_3OCH_3	----------	----------	----------	1.41	1.09
H_2O	----------	----------	0.98	----------	----------
CH_3OH	----------	----------	0.94	1.42	1.09

SiF_3OH Geometry in Calculation

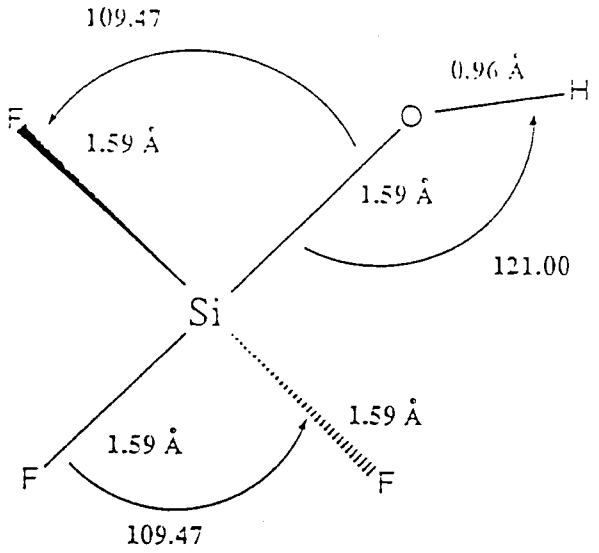


Figure 6

SiF_3OCH_3 Geometry in Calculation

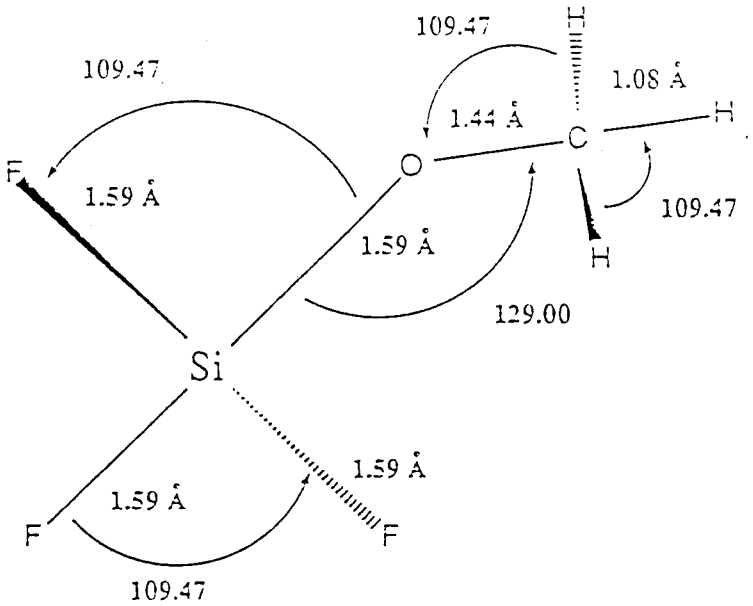


Figure 7

Table III

Angles in Calculated Molecules

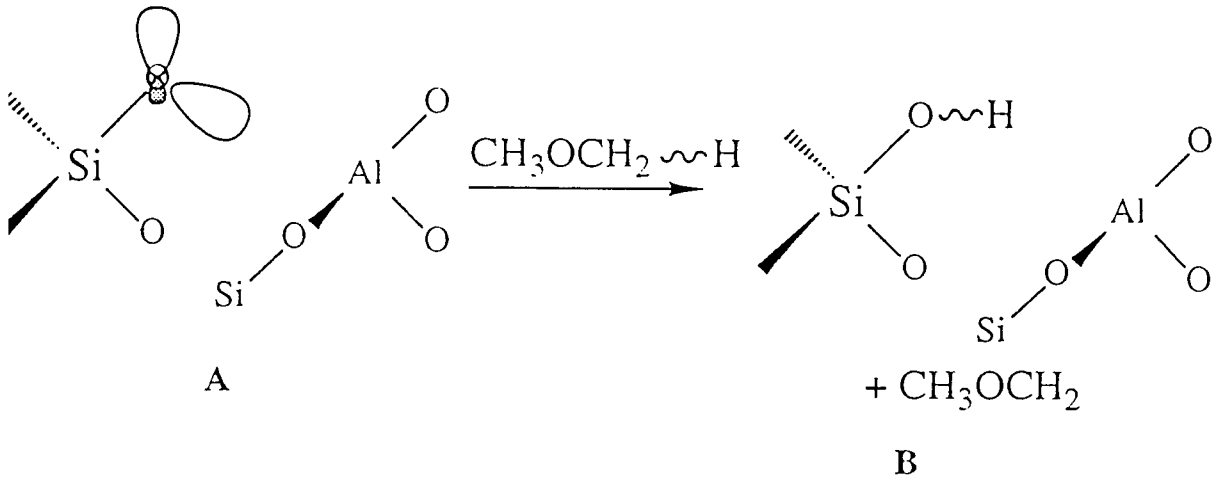
Molecule	F-Si-F	O-Si-F	H-O-Si	C-O-Si	H-O-H	H-C-O	C-O-H	C-O-C	H-C-H
SiF_3OCH_3	109.47	109.47	--------	129.00	--------	109.47	--------	--------	109.47
CH_3OH	--------	--------	--------	--------	--------	110.33	108.57	--------	108.60
H_2O	--------	--------	--------	--------	104.50	--------	--------	--------	--------
CH_3OCH_3	--------	--------	--------	--------	--------	109.47	--------	111.7	109.47
SiF_3OH	109.47	109.47	121.00	--------	--------	--------	--------	--------	--------

Due to the large numbers of degrees of freedom in the molecule, the O-C distance, Si-O-C angle, and C-H distances for SiF_3OCH_3 were determined by a sequence of single-point calculations, rather than with the geometry optimization program.

Results

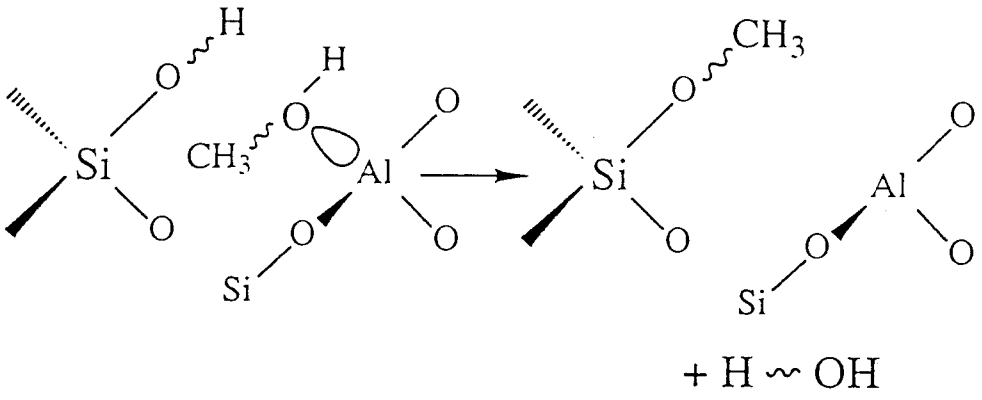
The main focus in this study is to determine ΔE's for each step of the catalytic cycle in order to evaluate the feasibility of the proposed mechanism. These ΔE's have been determined from the calculated bond energies using equation (1). Since the energies we obtain for the ΔE's are dependent on our calculated values for the bond energies, we will also present this data.

For each step, the bonds made and broken are shown in figures 8, 9 and 10. Note that only the covalent bond energies are considered. The bond energies are our calculated bond dissociation energies or, where calculated values were not obtained, experimentally determined bond dissociation energies.



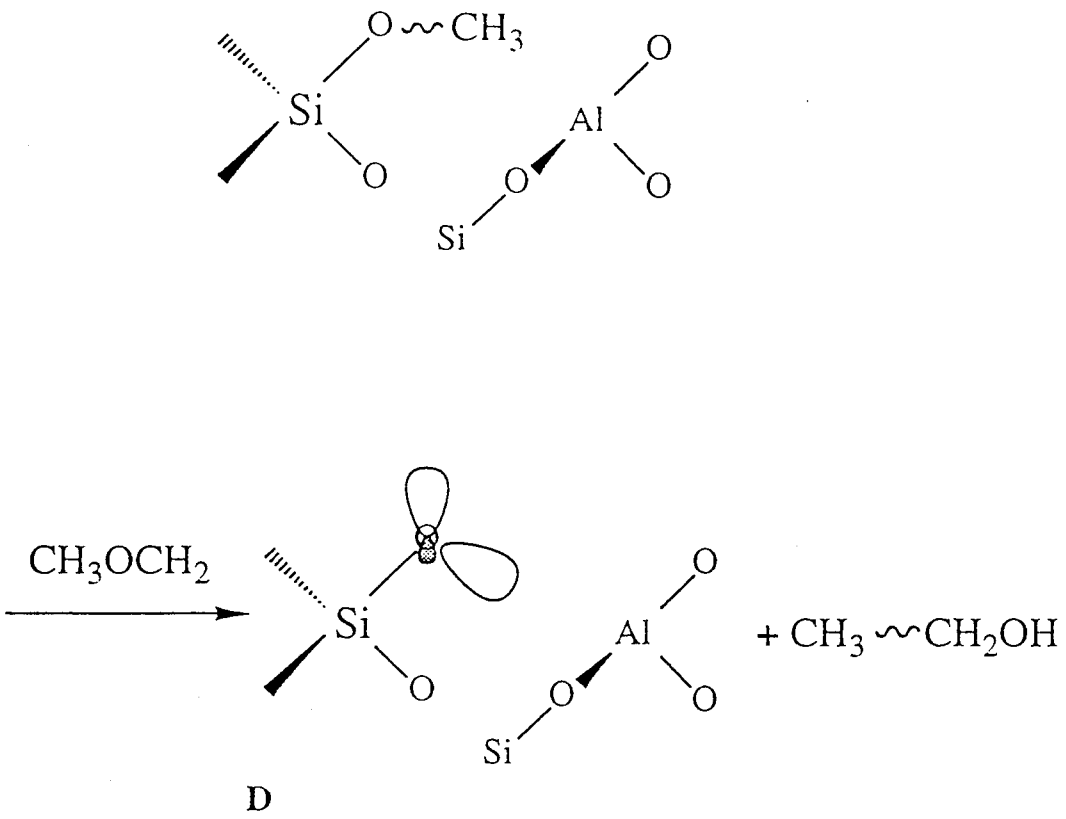
Bonds Made and Broken in Step B Shown as Squiggles

Figure 8



Bonds Made and Broken in Step C Shown as Squiggles

Figure 9



D

Bonds Made and Broken in Step D Shown as Squiggles

Figure 10

In step B of the mechanism (Figure 5) the zeolite oxygen radical abstracts an H· of dimethyl ether breaking a C-H bond of (93) kcal and forming an O-H bond of (123) kcal. The ΔE for this step is (**-30**) kcal. In step C several bonds are made and broken. The C-O bond of the methanol bound datively to the Al is broken (88.6 kcal) and O-H bond, (123 kcal), of the zeolite is broken. An H-OH bond is made to form water, (112.7 kcal), and an O-C bond, (106.7 kcal), is made as the methoxyl group from the methanol bonds to the zeolite Si. The overall ΔE of this step is (**7.8**) kcal. In step D the dimethyl ether radical previously formed attacks the methoxy carbon of the zeolite forming a C-C bond of (86.4) to make ethylmethyl ether and breaking a C-O bond of (106.7) kcal to regenerate the oxyradical site of the zeolite. The ΔE of this step is (**+20.3**) kcal. The ΔE's for these reactions are shown in figure 11. The bond energies used to obtain the ΔE's are given in Table IV. No correction has been made for the zero-point energy for any of the calculated values.

Table IV

Bond Energies for Bonds Made and Broken in the Mechanism

Molecule	Exp. Bond Dissociation Energy[10]	Calc. Bond Energy
CH_3OCH_2-H	93 kcal	
SiF_3O-CH_3	NA	106.7 kcal
SiF_3O-H	NA	123.1
CH_3OCH_2-CH_3	86.4	
H-OH	119	112.7
CH_3-OH	92.3	88.6

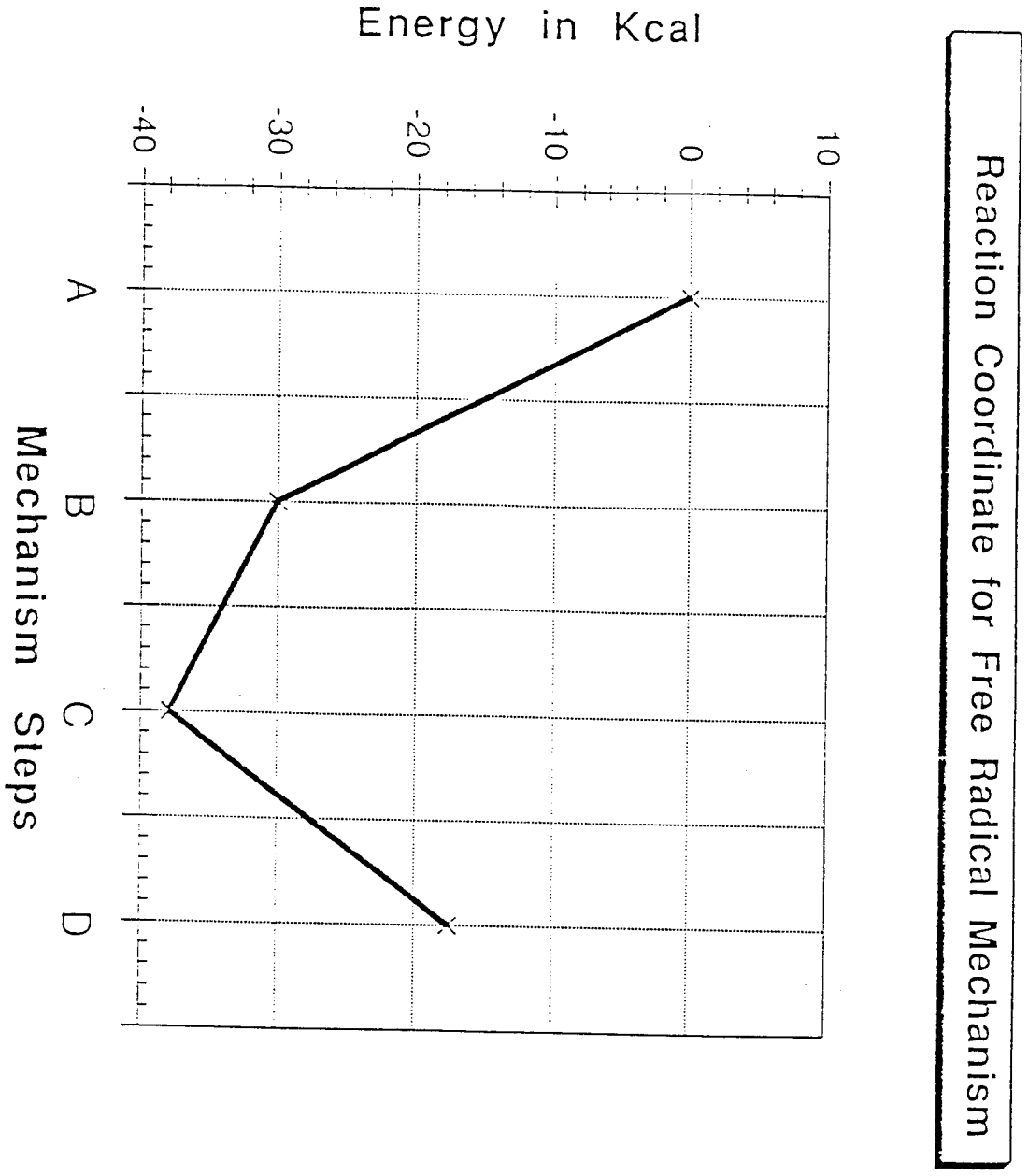

Reaction Coordinate for Free Radical Mechanism
Energy in Kcal
10
0
-10
-20
-30
-40
A
B
C
D
Mechanism Steps

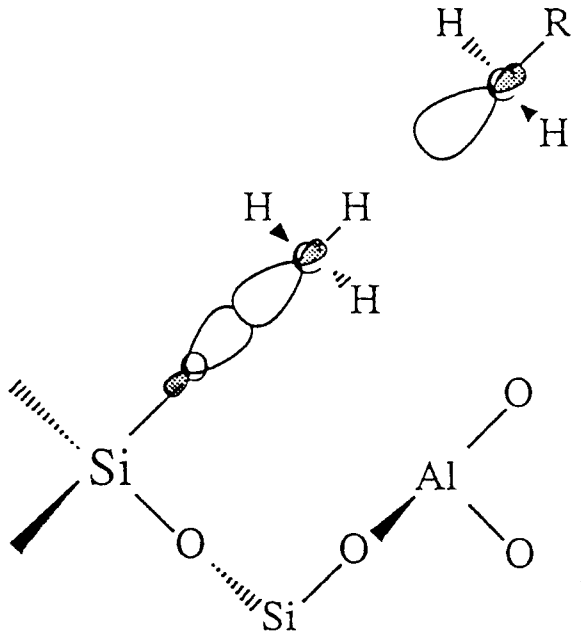
Figure 11

Discussion and Conclusion - Free Radical Mechanism

The bond energies calculated can be used, as above, to determine DE's for each step of the reaction. The results of so obtained show that for each individual step of the mechanism, the barrier or well in the reaction coordinate is small enough to be likely that a catalytic cycle could be sustained.

The reaction path pictured in figure 11 shows the overall process to be exothermic. This is consistent with experiment as it has been shown that both the methanol > dimethyl ether stage and the carbon-carbon bond formation stage are exothermic.[12] However, that second stage includes carbon-carbon bond formation on C2 and higher hydrocarbons, in addition to the formation of C2 hydrocarbons. These other reactions are also likely to exothermic and could obscure the energetics of the first carbon-carbon bond formation mechanism. Given that, it would be useful to calculate, using our methods, the bonds for which we are currently using only experimental value, CH_3OCH_2-H and CH_3OCH_2-CH_3.

The results of our calculations, given in Table IV and Figure 11, show that this mechanism for the carbon-carbon bond formation is thermodynamically feasible. However, the following orbital diagram shows that a transition state would have to involve completely breaking the C-O bond resulting in a very high energy state, not necessarily consistent with the (relatively) low temperatures for the MTG process.



C-C coupling might occur in the zeolite as a result of transition metal impurities as some complexes have been shown to reductively couple methyl groups[13]. This certainly does not imply that this is compelling evidence for the role of impurity levels of transition states in ZSM-5/MTG chemistry, but it suggests that an experiment which rigorously excludes such impurities (if possible) would provide evidence either for or against any free radical mechanism which requires a radical inversion transition state. If one takes a closer look at Chang's free radical mechanism, it, too, requires such a radical inversion. This occurs as the CH2· is transferred to the zeolite oxygen to form the surface carbene (figure 12).

Most of the known free radical chain reactions work because after the initiation step--usually abstraction of a hydrogen atom or halogen--what remains is more reactive and can either split apart to form new reactants or create new bonds other than reabstracting an H atom. This reactivity can come from the following properties: conjugation, aromaticity, presence of a halogen atom, etc.[14]

C-O bond must break completely to form carbene

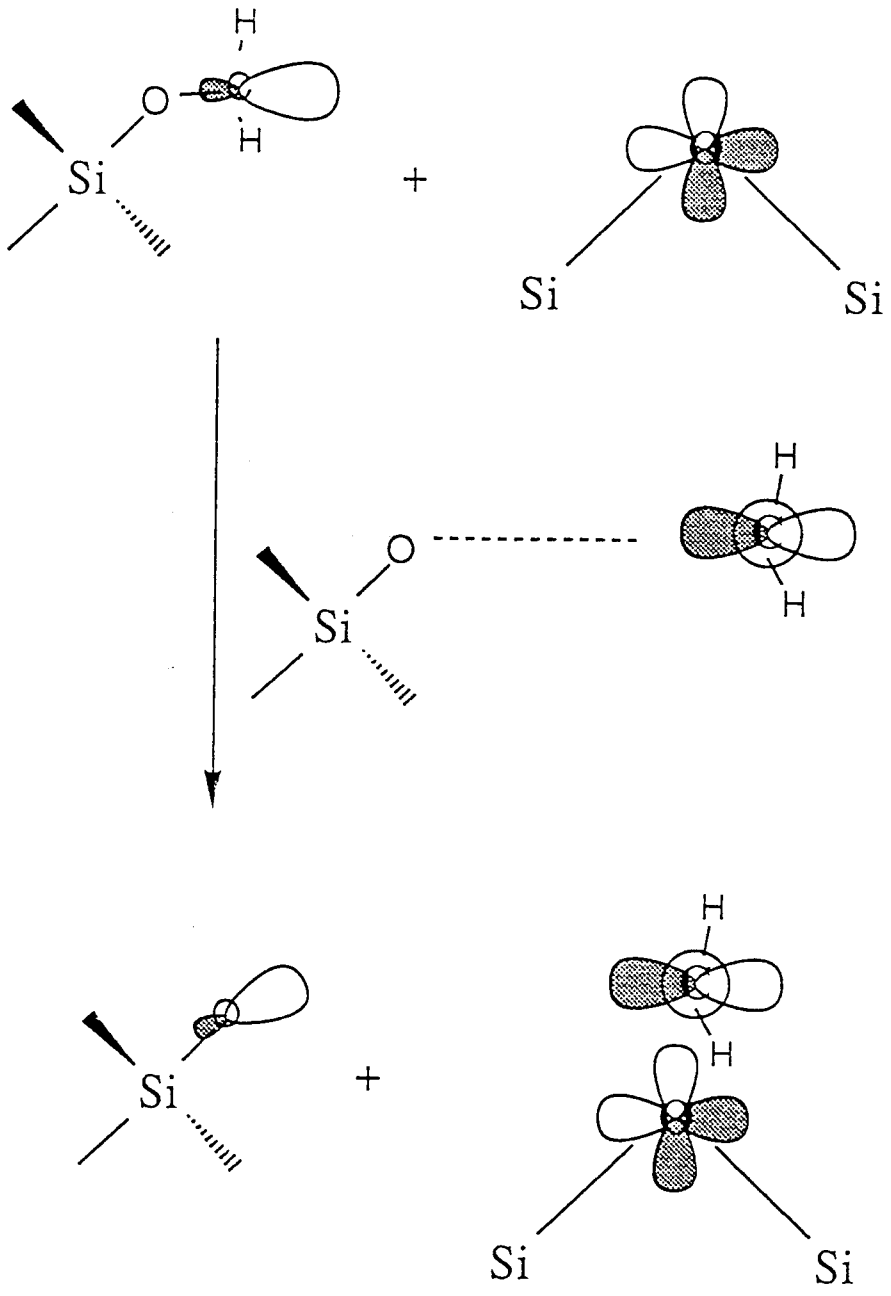
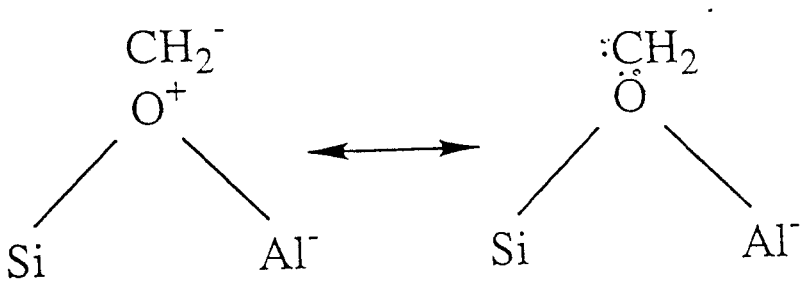


Figure 12

Since at the time of the first carbon-carbon bond formation there are no conjugated hydrocarbons, or even C2 or larger hydrocarbons (again except at the impurity level, and these would not be catalytic species), all possible free radical mechanisms must either include such a transition state or involve radical recombination. Both of these have serious flaws in terms of kinetics and thermodynamics, respectively, and are unlikely to be responsible for the catalytic cycle which forms the first carbon-carbon bond. However, we cannot preclude all possible free radical participation simply because there may be aspects of the system which we have failed to consider which may lower the transition state.

III. Ylide Mechanism

Several mechanisms have been proposed that invoke, in one way or another, the following surface bound ylide or surface carbene:[1,2,3,4]



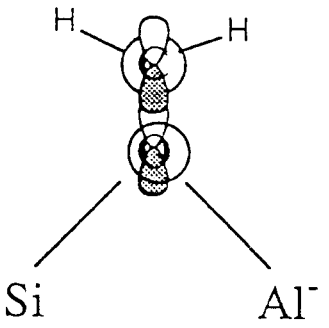
The concept behind this type of proposal is clear: ZSM-5 must be able to produce a C1 species which is both activated enough to bond with another C1 species and stable enough to stick around long enough to do the chemistry. A surface stabilized C1 would be ideal: reactive but held in place for some time by the zeolite surface. However, it seems clear from the orbital pictures in figure 13 that that stabilization may be non-existent, and that in fact, this ylide is unstable, thermodynamically, with respect to the zeolite framework and free methylene. It would be, in effect, a surface destabilized ylide.

Actually, the orbital pictures in figure 13 show two possible positions for the CH_2 atop the zeolite framework O atom. It seems clear that there will be a very high energy interaction between the O lone pair orbital and the doubly occupied orbital of the carbon if the two hydrogens are parallel to the Si-O and Al-O bonds. Likewise, the doubly occupied orbital on carbon will have a bad interaction with the T-O bonds if the hydrogens are twisted 90°. A third possibility is for the CH_2 to be entirely out of the Si-O-Al plane, pictured in figure 14. This will only work for a small subset of angles because at a certain point the carbon will be positioned too close to the Si and Al angles. In all three cases there is a cost for promoting the methylene to the $^1A1$ from the $^3B1$ ground state.[15] All three should also have a dative bonding interaction between one lone pair of O and the empty orbital on C. If that bond is strong enough, the ylide will be bound.

Calculational Details

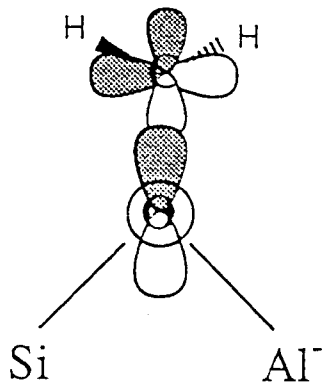
The calculation of the bond energy between the carbon and oxygen of the surface ylide was done with a different set of programs than the other calculations described in this chapter due to large size. The calculations themselves are similar to the others described herein, with the following exception. In general, we have discovered that in order to properly calculate bond energies, where an O atom is involved, we must correlate not only the bond

Orbital Diagrams for surface ylide



The C and O lone pair orbitals coming out of the plane of the page will have a high energy interaction.

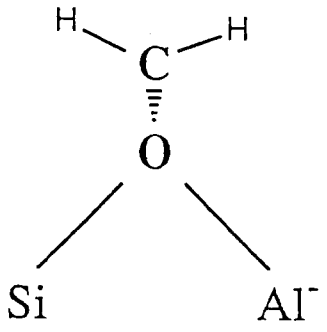
OR



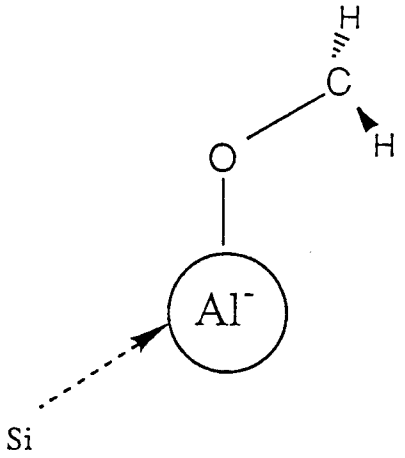
The H-C bonds will have to orthoganolize from the O lone pair coming out of the plane of the paper and the lone pair of C will have to orthoganolize to the T-O bonds.

Figure 13

Surface Ylide - CH_2 out of plane



Front view



Side view

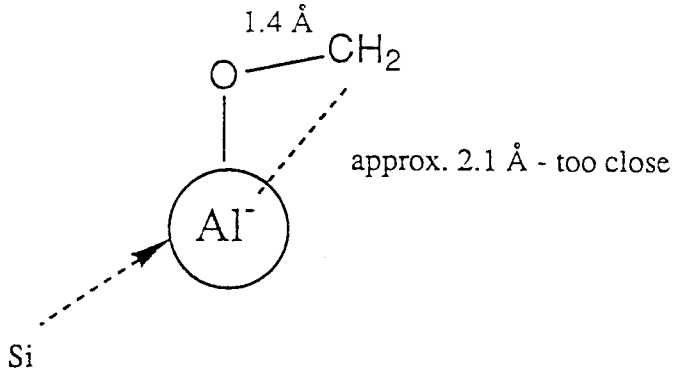


Figure 14

that we are interested in, but also the second bond of O to the other atom, e.g., in dimethyl ether, both O-C bonds had to be correlated with each other in order to get the correct bond energy. This makes sense as the hybridization of one bond will strongly effect the hybridization of the other.

In calculating the ylide, we found this correlation, with the Molecule-Sweden program suite[16], to be difficult to converge. Therefore, we have only correlated the C-O interaction, and this is essentially a GVB-PP[17] calculation. From our other studies, we know that this has an inherent error, and we expect any bond energies calculated to be inaccurate. However, a GVB-PP calculation is accurate enough to determine relative stabilities, e.g., whether or not the CH_2 is more stable bound to the zeolite oxygen as we have modeled or as free methylene. This result can be considered a screening test: if necessary, as delineated in the results section, we can go back and correlate the other two bonds to an O atom. It may even be that that correlation will be less difficult with one O interaction already correlated.

Another obvious difference between this exercise and the calculations for the other mechanisms is the presence of Al. We chose to match the Al basis set with that of Si, i.e., to have the double zeta plus 2 sets of d polarization functions for the valance electrons, and an effective potential for the core electrons.[7] We have added an additional diffuse basis function to account for the negative charge on the Al atom. This may have inadvertently unbalanced the basis set to a slight degree and contributed to the difficulties in correlating all of the bonds to oxygen.

Some mention should be made about the mechanics of this calculation. The GVB method used for the other mechanisms allows correlation of pairs of orbitals, and a subsequent CI correlating all of those pairs. For the molecule representing the surface-bound ylide, use of a Cray (more for disc space and

speed than for core memory) was required due to the size of the calculations. Therefore, the Complete Active Space Self Consistent Field (CASSCF) Molecule-Sweden Program was used to accomplish the GVB-PP calculation.[16]

Geometry

Clearly an important aspect of this calculation is the geometry of the CH_2 moiety attached to the O atom. Two geometries were chosen, reflecting the two choices in orientation of the hydrogen atoms with respect to the T-O bonds. These two structures are shown in figures 15 and 16. The Si-O-Al angle, and the Si-O, Al-O, Si-F, and Al-F were taken from the Si, Al, and O angles and distances in the zeolite crystal structure. The C-O-Si or C-O-Al angle was chosen to reflect a common angle found in organic molecules. The C-O bond distance of 1.44 A is normal for a C-O single bond.[18] It is likely that this is not exactly the optimum geometry for this molecule, but it is an educated guess based on the orbitals of the atoms involved. The relatively new pseudospectral geometry optimization program would be ideal for this calculation,[19] as it would not require the disk space for the integrals that standard programs require. This program is near implementation.

In addition to the two geometries chosen for R_e, a calculation was done, with all else being equal, with a C-O "bond" distance of 20 Å - for practical purposes, infinity. This result for this geometry is the energy, at this level of calculation, for the zeolite site plus free methylene. These molecules (not including the C-O at 20 Å case) and the bond lengths are shown in figures 15, 16, 17, and 18. The common bond angles are shown in Table V.

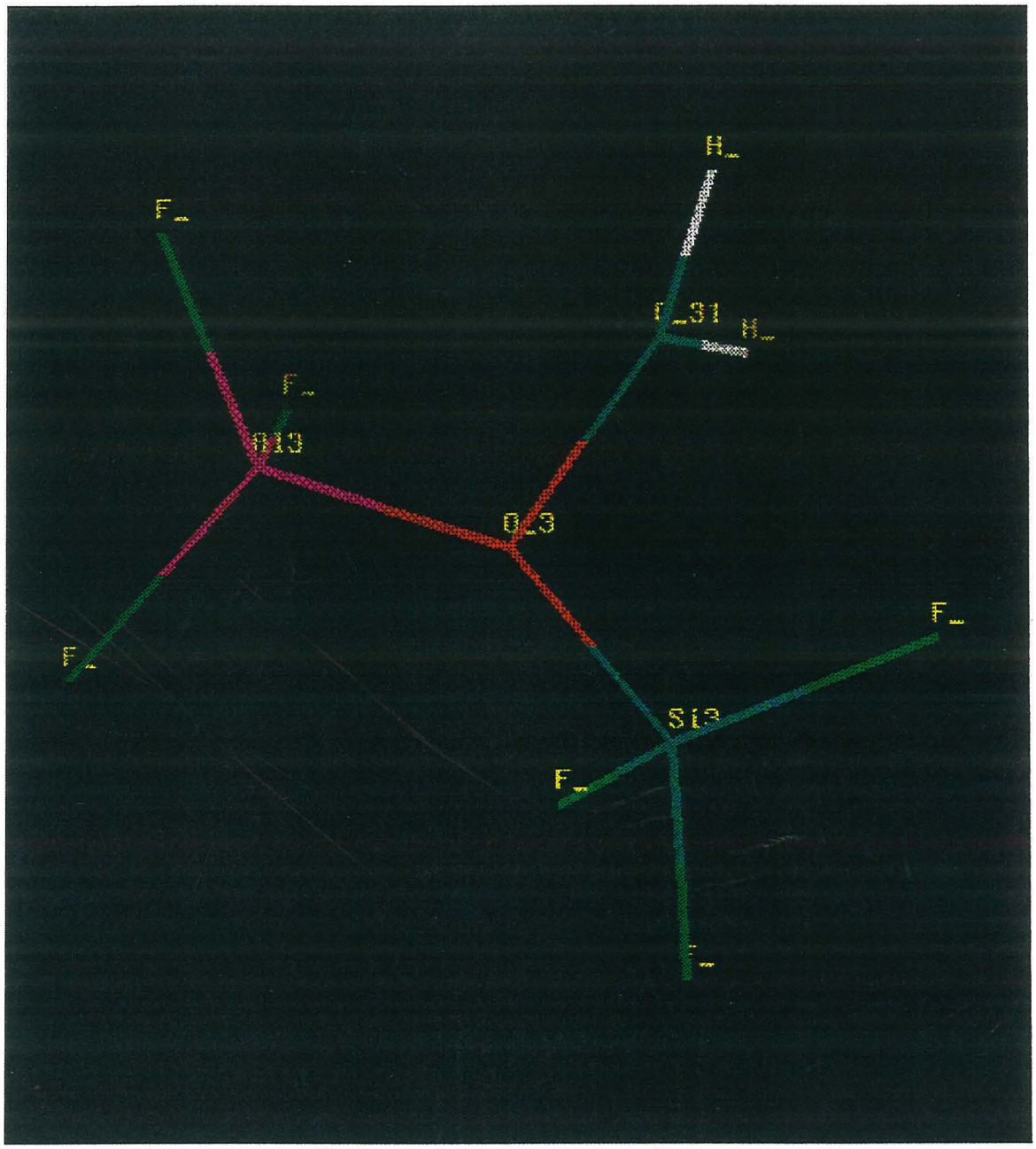


Figure 15

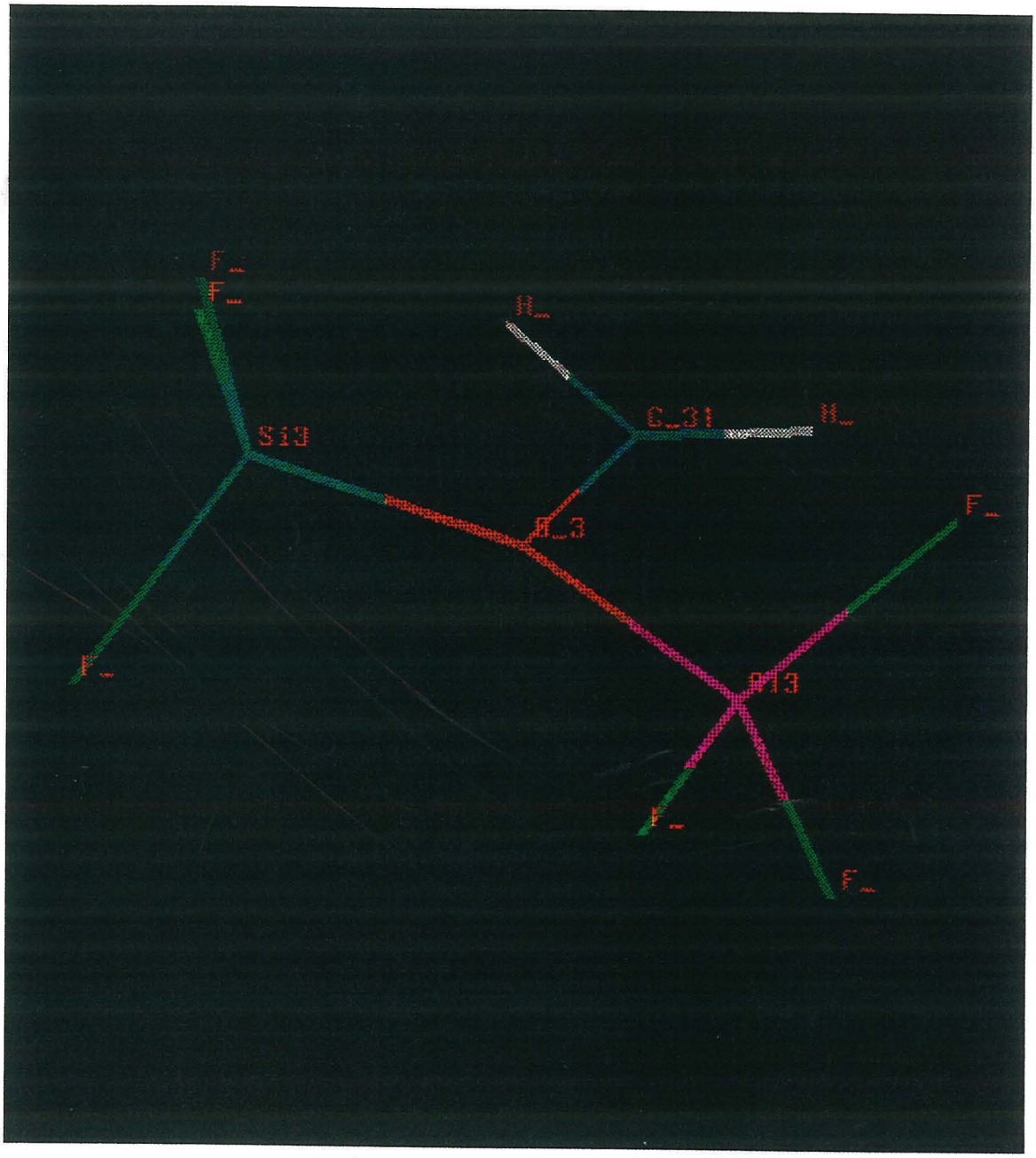


Figure 16

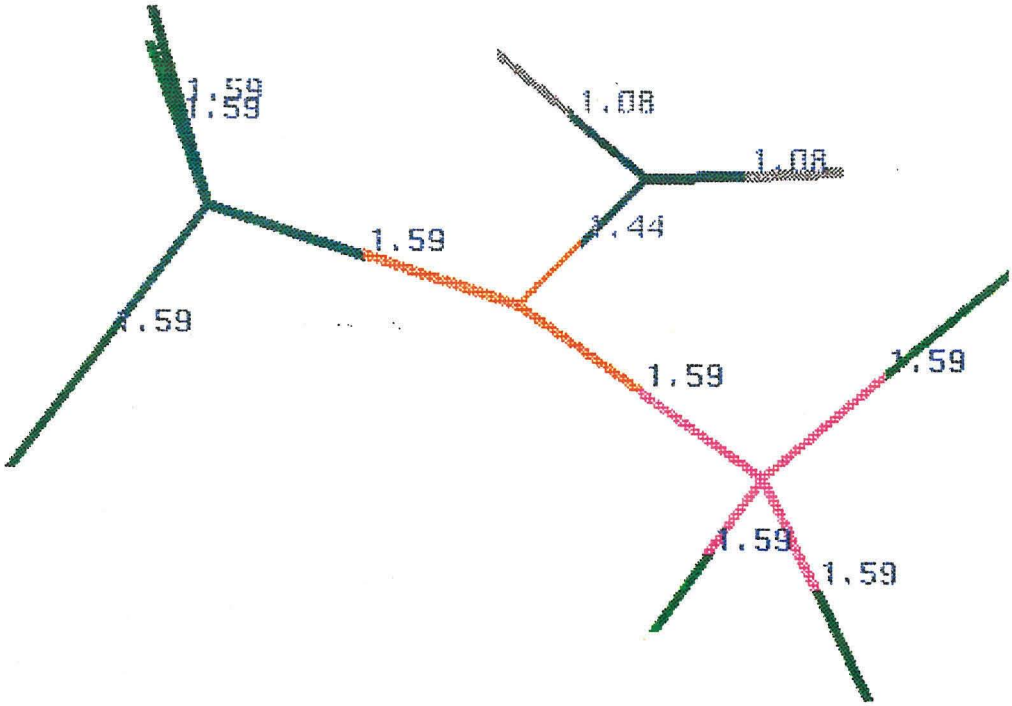


Figure 17

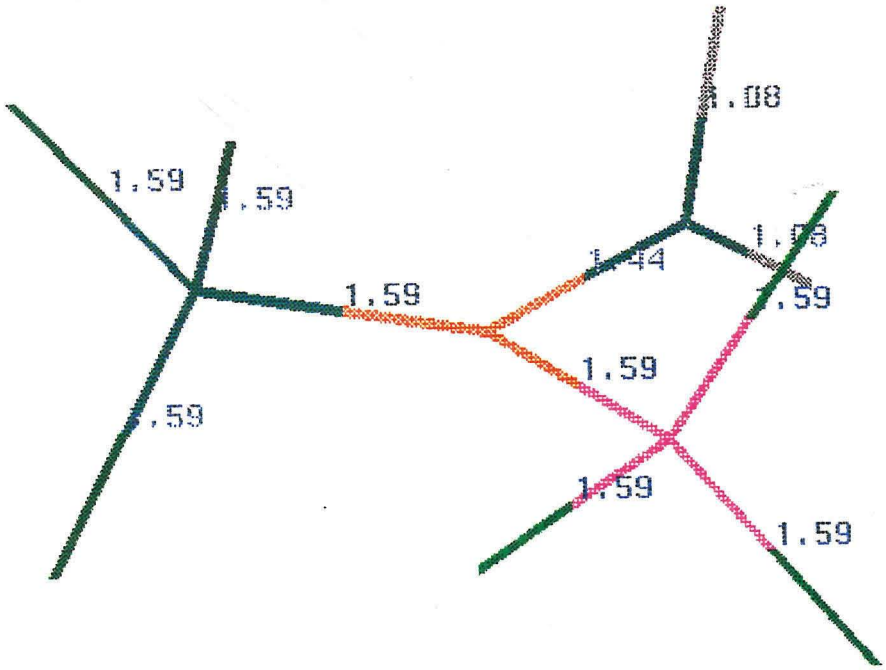


Figure 18

Table V

Geometry of Calculated Surface-Ylide: Angles

Structure	Angle (Degrees)
F-T-F	109.47
F-T-O	109.47
Al-O-Si	150.00
H-C-H	110.00

Results

The total energies from the GVB-PP calculations at the three calculated geometries are given Table VI, along with the difference between the energy at Re and at infinity for the first two cases.

Table VI

Calculated Total Energies for Surface Ylide

Geometry	Total Energy, in hartrees	Difference in Energy from R_{inf}, in kcal/mol
Parallel H's	-716.71492844	80.00
H's at 90°	-716.75144571	57.10
Infinity	-716.8424786	----------

These results show the ylide of either orientation to be quite unstable: 80 kcal/mol and 57 kcal/mol, respectively. It should be noted that due to the unoptimized geometry and low-level of correlation, the numbers should not be

considered quantitative. However, due to the large differences in energy, it is near certain that the results are qualitatively correct. The ylide is not stabilized by the zeolite surface as modeled. The dative bond due to O lone pair donation to an empty carbonyl orbital is more than offset by the poor interactions of the lone pair orbitals and/or T-O bonds with the doubly occupied carbon orbital and the cost of promoting the CH_2 to the $^1A1$ excited state.

Conclusion - Surface Ylide

We have shown that the ylide is not stabilized by the zeolite surface structure as we have modeled. However, this does not preclude the possibility of extra-framework Al structures in the channels providing additional stability, either electronically or sterically.

IV. Sterically Constrained CH_2

In the previous section, it was shown that a surface ylide is not a stable structure, electronically. It is possible that there could be, due to a defect in the zeolite structure, a site which could cause enough steric strain to make a C1 moiety which would be just reactive enough to do the required chemistry. The obvious starting point (as the most understood defect site) was the hydroxyl nest site, pictured in figure 1, formed by dealumination[20].

The main idea is that four hydrogen atoms may take up more space than the single Al atom. If in fact that is so, two CH_2 groups in the same space would be very constrained. This leads to the following two questions: 1) Does removal of the single Al atom from a tetrahedral site and the replacement of that Al with four H atoms cause steric problems, and 2) If there were two CH_2 groups, one each bound to opposite sets of two oxygen sites (as shown in figure 19), would they be sterically constrained and therefore more likely to be reactive?

Double CH_2 Site

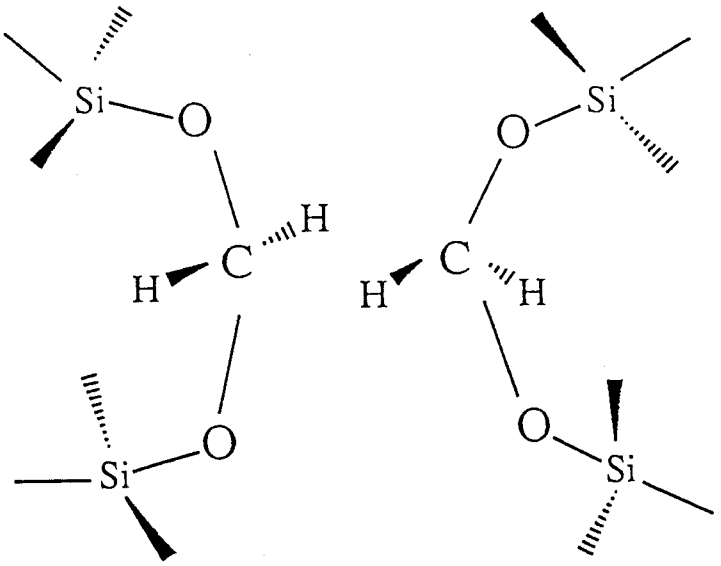


Figure 19

Methods

The POLYGRAF program was used for all molecular mechanics calculations.[21] A generic force field (genff), developed by A. K. Rappe and W. A. Goddard, optimized to give the correct crystal structure for ZSM-5 (silicalite) was used. The standard hydrogen and carbon (H_ and C_3) parameters from genff were used in calculating the defect sites. Charges on the atoms were determined using the charge equlibration method and the program developed by Naoki Karasawa, A. K. Rappe, and Bill Goddard.[22]

Each structure was minimized, followed by a few dynamics steps at 300 K, followed by minimization, to help insure that the structures were not trapped in local wells. All minimizations and dynamics steps were done with periodic boundary conditions.

Results and Conclusion - Steric Constraint

Question 1:

An "Al" atom (Actually, a Si atom since we were using the all Si structure; however, since we were interested in its absence, the removal of any T atom would serve the purpose.) was removed from a tetrahedral site and replaced by the four hydrogen atoms needed to form the hydroxyl nest defect site. The final minimized structure is shown in figure 20. From the nonbonded distances (figure 21) taken from this structure, it seems likely that there is little or no steric hindrance to movement of the atoms of the hydroxyl nest. The atoms have plenty of room to move. In addition to having enough space, the bonds themselves are of reasonable distances. Figure 22 shows the Si-O and O-H bond distances. Although the O-H bond is somewhat short, the Si-O bond is somewhat long and, taken together, there is no indication that there is a steric constraint. Table VII shows the Si-Si nonbonded distances for those Si atoms directly attached to the hydroxyl nest oxygen atoms, as well as for Si atoms not connected to that site. These distances are quite similar and suggest that there is little or no strain caused by the hydroxyl nest.

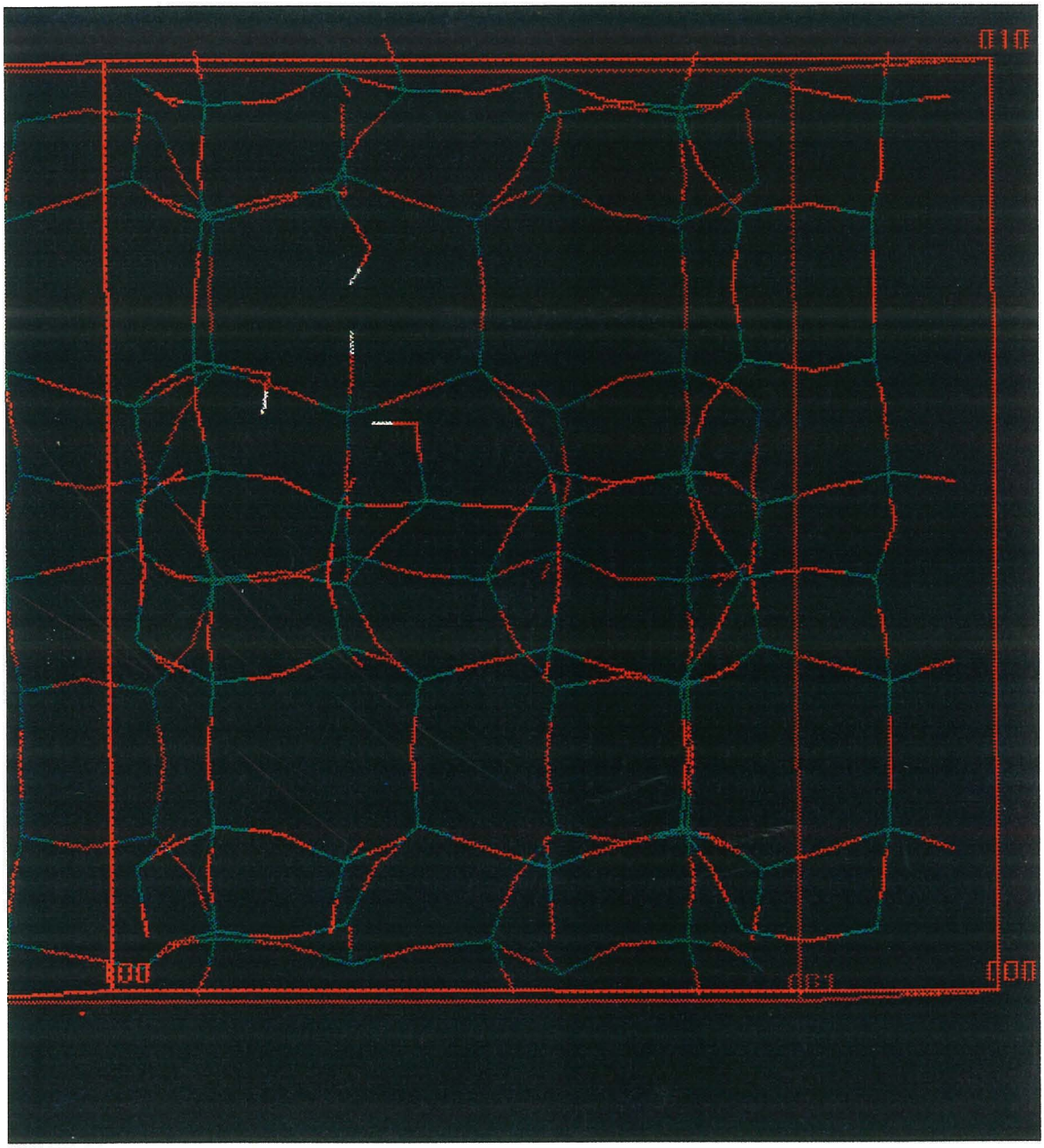


Figure 20

Bond Distances for Hydroxyl Nest

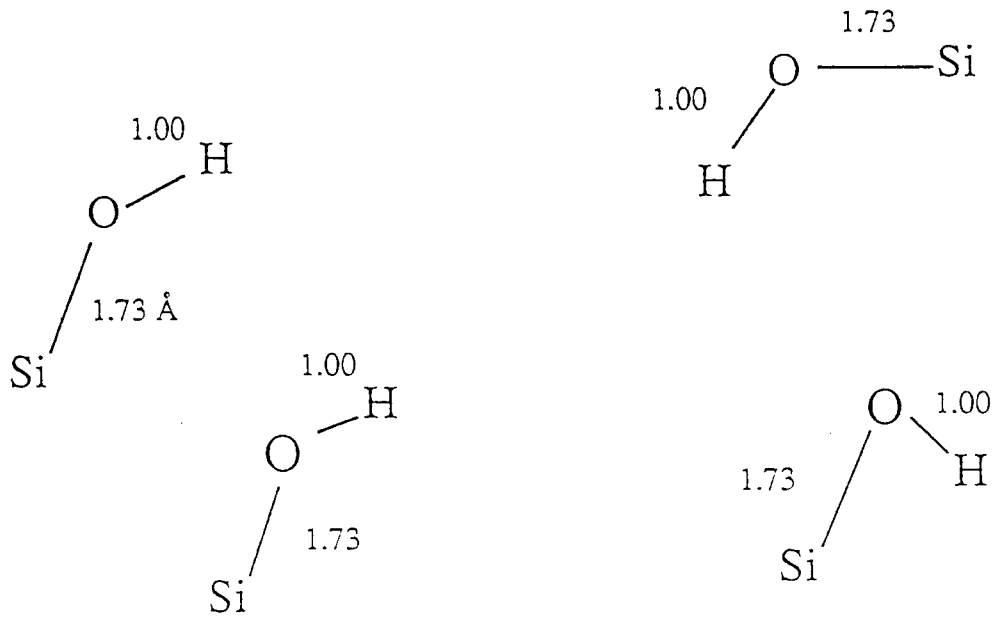
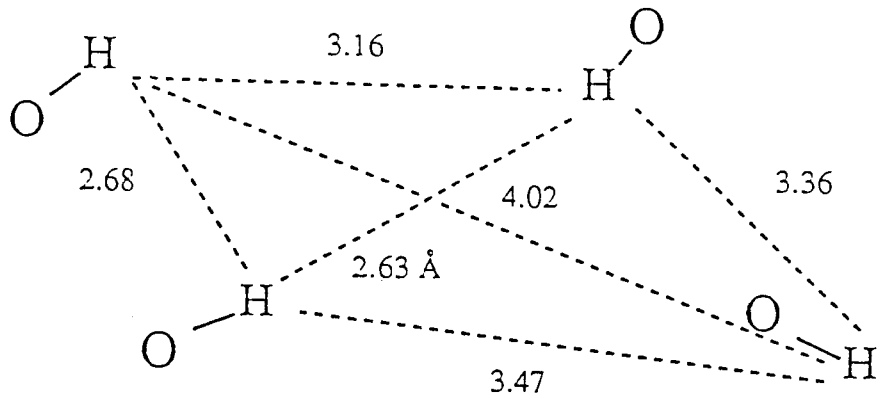
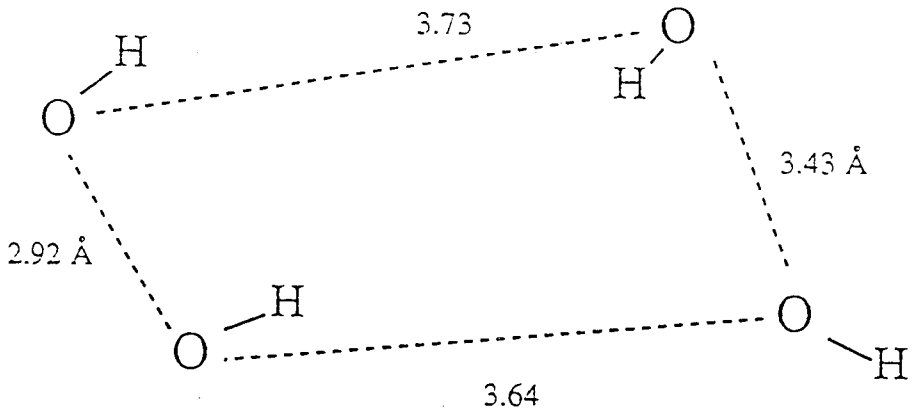


Figure 21

Non-bonded Distances for Hydroxyl Nest



H-H



O-O

Figure 22

Table VII

Si-Si Non-Bonded Distances

Non-Bond Endpoints	Distance in Å
Si-Si Hydroxyl Nest Site	3.08
"	3.05
"	3.08
"	3.00
"	3.16
"	3.16
"	3.07
"	3.08
Si-Si away from hydroxyl nest	3.07
"	3.13
"	3.11
"	3.10
"	2.97
"	3.00
"	2.98
"	2.99

In summary, there is plenty of room for the hydrogens of the hydroxylnest within the zeolite framework.

Question 2:

Starting from the hydroxyl nest structure in figure 20 the hydrogen atoms were removed and two CH_2 groups were added to each set of two oxygen atoms, in an acetal-like structure. The final minimized structure is shown in figure 23 and the nonbonded distances in Figure 24. Again, the zeolite showed enough

flexibility that there was apparently no hindrance to movement of the CH_2 groups into opposite channels and out of each other's way. The bond distances, shown in Figure 25, are also reasonable. The Si-C non-bonded distances (nearest neighbor Si to the C) are about .3Å shorter than the Si-Si non-bonded distances (Table VIII). This is reasonable given that the covalent radius for Si is 1.11 Å, .34 Å longer than that of C. Note that the Si-Si non-bonded distances are in the same range as those for the hydroxyl nest structure.

Table VIII

Si-C and Selected Si-Si Non-Bonded Distances in the Double CH_2 Site

Non-Bonded Endpoints	Distance in Å
Si-C	2.67
"	2.65
"	2.56
"	2.55
Si-Si	3.12
"	3.02
"	3.12
"	2.96

In order to ensure that this flexibility was not specific to this position in the zeolite, ten other positions (tetrahedral sites) were chosen. The same calculation was done for each of these sites, and the nonbonded distances which resulted are shown in Table IX. It appears from these results, fortuitously, that the non-bonded distances for the site above are somewhat longer than for these ten. H-H non-bonded distances should not be smaller than 2.4 Å and six of these sites

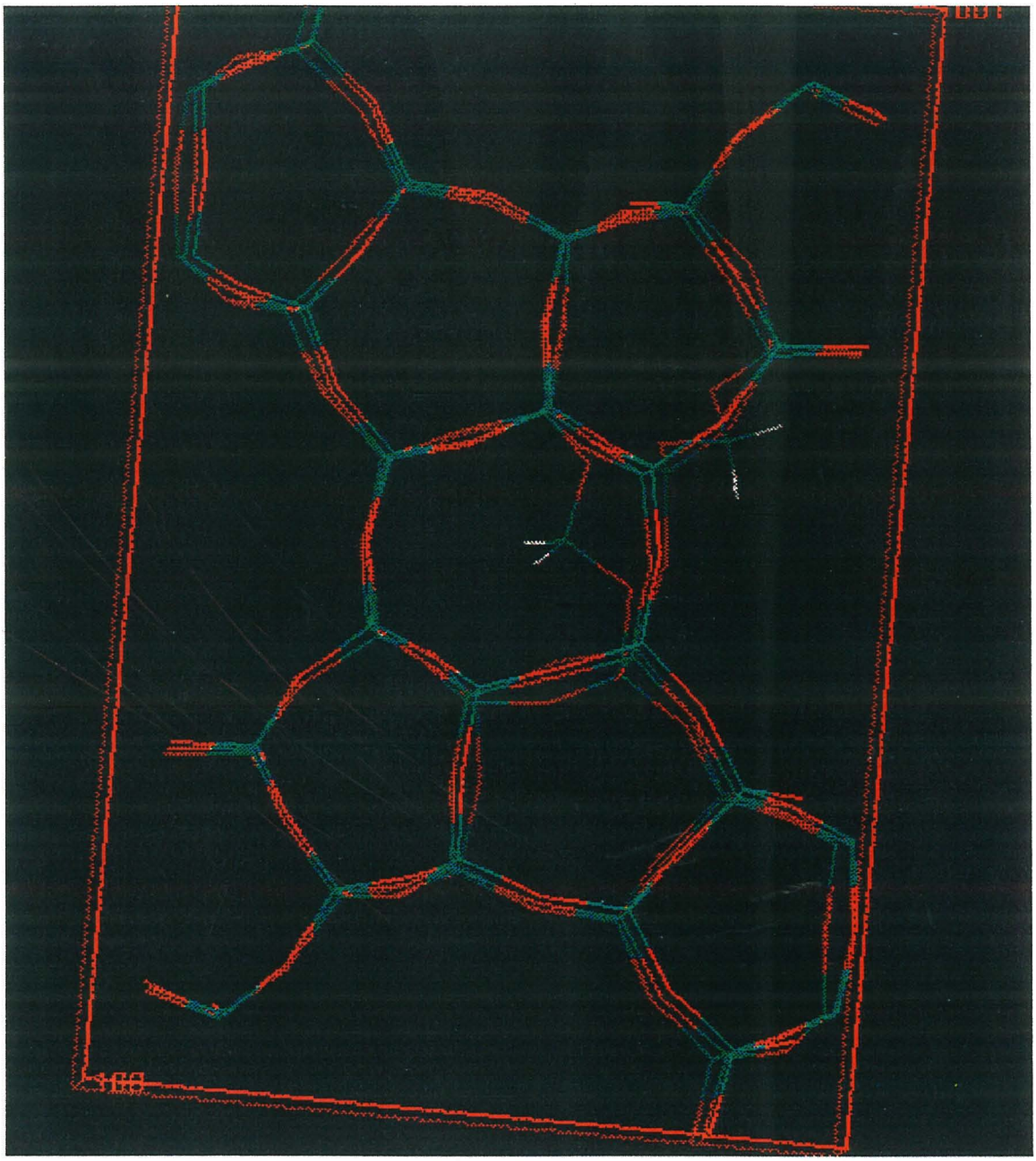
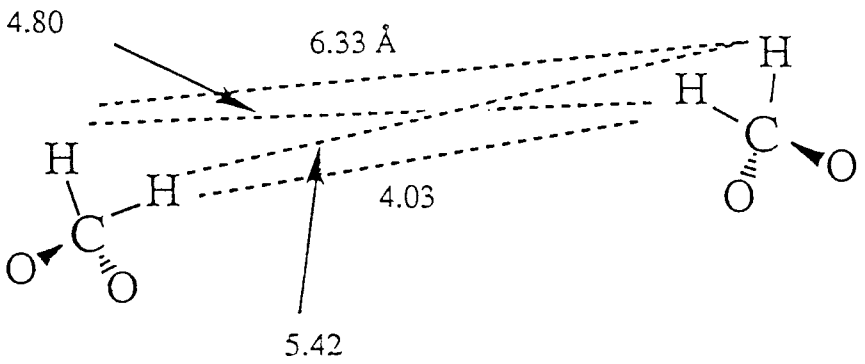


Figure 23

Non-Bonded Distances - Double CH_2 Site



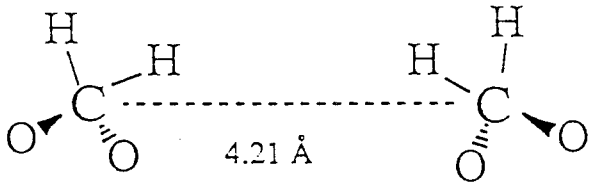


Figure 24

Bond Distances for Double CH_2 Site

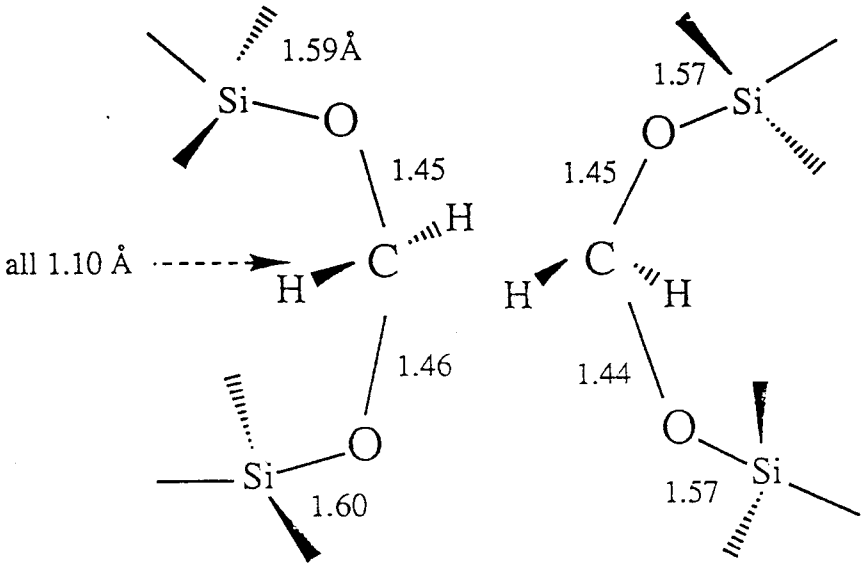


Figure 25

show one such interaction near or below that distance. One point to consider is that there is considerable zero-point angular momentum for H atoms which causes a relatively large error in the position of the H atoms in this calculation. [23] However, even considering that these distances are accurate, this one bad interaction could only provide 10 kcal or less of strain energy--too little to affect the C-O or C-H bonds.

Table IX

Non-Bond Distances for Ten Double CH_2 Sites

Site	C-C	H-H	H-H	H-H	H-H
1	3.70	4.45	3.34	4.57	5.89
2	3.91	3.72	4.90	4.60	6.01
3	3.60	**2.32**	3.66	3.96	5.21
4	3.65	**2.45**	3.97	3.64	5.09
5	3.17	**2.19**	3.45	3.50	4.90
6	3.44	3.18	3.06	3.91	4.37
7	3.65	**2.60**	4.03	3.95	5.56
8	3.95	3.87	3.64	5.50	5.05
9	3.36	**2.47**	3.72	3.73	5.21
10	3.31	**2.42**	3.52	3.64	5.01

Conclusions

The hydroxyl nest site is created when one Al atom is replaced by four H atoms. This study has demonstrated that this exchange causes little or no steric constraint on those four hydrogens or the O atoms they are attached to. The H atoms do not get in each other's way. Replacement of the four H atoms with two

CH_2 groups creates a defect site with much bulkier substituents and yet the zeolite is flexible enough that these CH2 groups can also move out of each other's way--one into one channel and the second into the other channel. However, there is a possibility that there is one constrained H-H non-bonded interaction. Given that the two CH_2 groups fit into the space once occupied by a single Al atom, it is unlikely that, within the framework, there is another defect site which could be more crowded and which would be able to produce a C1 via steric constraint with the appropriate reactivity.

The conclusions and ramifications of the results presented in this chapter will be discussed in Chapter 4.

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Chapter III

Conclusions from MTG Study

Chapter III: Conclusions from MTG Study

In the previous two chapters, a tremendous amount of information was presented, in order to give an overall view of the MTG process, the controversial nature of the mechanism for the carbon-carbon bond formation, a representative sampling of those mechanisms, and thermodynamic studies via *ab initio* calculations for the most likely types of mechanisms. In this chapter, a summary of the results of our computational studies will be provided within the context of the wide range of the background information. In this way, what is known concerning this mechanism can be shown, along with directions for future work to help ascertain what is occurring inside the ZSM-5 channels that creates carbon-carbon bonds. This conclusion chapter will be divided into three parts: free radical reactions, ylide reactions, and steric constraints.

Free Radical Reactions

The free radical reaction based on the oxy-Al site which we have proposed is clearly not the mechanism by which the first carbon-carbon bond is formed. The thermodynamics of each step are OK, but the radical inversion on the C clearly has a very high transition state.

However, our calculations only show that this one mechanism is not involved. There have been several other proposed in the literature. To date, however, these have received little support. Two of these mechanisms have steps which are likely to be energetically unfavorable: Zatorski et al.,[1] with the separation of CH3OH into CH3· and ·OH, and Chang's[2] with a high transition state in the process of removing the CH2· from one zeolite O atom to the other as a surface carbene. The third, proposed by Clarke et al.,[3] involves radical recombination to form a diether or the formation of free CH_2 from the radical CH_3OCH_2·. In fact, this last proposal may be a likely candidate. The

experimental evidence discussed in chapter one tends to support a CH_2 reactive intermediate, and free radicals are found in the system. A crucial problem is the ability of the zeolite to stabilize that carbene, however it is formed. As this problem applies directly to the results of our studies on the "surface-stabilized ylide," it will be discussed in full in the next section.

Ylide reactions

Our calculations have shown that CH_2 is more stable as free methylene than sitting on the zeolite framework O atom as a surface ylide or carbene. This would suggest that any of the proposed mechanisms in the literature which rely on such a "stabilized" carbene are simply not correct. However, we have not looked at the whole picture. Our model may accurately reflect that one small part of the framework to which the C may bond, but there is also nearby framework and extra-framework portions of the zeolite to consider as well. Drenth's[4] calculation showing the stability of a "free" carbene in an arrangement of molecules (figure 11, Ch. 1), while it does not accurately model a known site, might be an appropriate starting point for thinking about how and which extra-framework Al complexes could play a role in carbene stabilization.

There is an oxonium ylide mechanism for which there is some experimental support and which involves intermolecular formation of the first carbon-carbon bond without relying on a surface bound ylide. This mechanism (figure 9, Ch. 1),[5] like many others, does require a strong base in order to remove a proton from a methoxy group--in this case from one of the methyl groups on trimethyl oxonium ion. A Hunter and Hutchings experiment showed that this is unlikely.[6]

In combination, our results and the information in the literature lead to the conclusion that a CH_2 intermediate is more likely than a free radical intermediate,

but that there is no obvious way of forming that CH_2 given the zeolite framework. There is, however, sufficient evidence that extra-framework Al complexes may play a role in MTG chemistry, and that stabilization of a carbene or ylide by such molecules and the framework may be possible.

Sterically Constrained CH_2's

Our molecular mechanics calculations have shown that in the space once occupied by a single Al atom, two CH_2 groups can fit with little steric hindrance from each other or from the zeolite framework. This result would suggest that there are no such constrained carbons within the zeolite, but the result only applies to that one type of site. There may be other areas of the zeolite such as defect sites in the framework or extra-framework Al sites which are just as or even more sterically strained than the one proposed.

Conclusions and Further Work

Although our calculations did not reveal a mechanism which met the experimental conditions and had the appropriate energetics, our results along with a careful study of the literature has revealed several important aspects of ZSM-5 chemistry which are currently unexplored.

The most important of these is the nature of the extra-framework Al species. A number of possible complexes have been suggested,[7] but knowing which complexes are involved may not provide enough information to determine the role of these complexes. If these molecules are not part of the framework, then it follows that they are in and possibly moving through the channels.

In order to properly assess their role in the MTG chemistry, we need to know how each kind of Al complex moves through the channels, or fits into the channel depending on the size of the complex. In addition, as it is possible that

more than one type of extra-framework Al complex is present, it would be necessary to learn how a conglomeration of such molecules moves through and react, mechanically, together (and with the framework !) in the channels.

Molecular simulations calculations - molecular mechanics and dynamics would be ideally suited to this proposed study. The molecular dynamics would be especially useful in studying the diffusion of Al complexes through the zeolite channels. At the start of the project a single small complex could be studied, gradually adding more molecules that would be expected might be present.

There are several defined goals for this type of calculation. Drenth[4] has shown that a carbene might be stabilized in the zeolite by a particular arrangement of molecules with particular properties, not all of which are necessarily portions of the framework. In the diffusion studies, arrangements similar to that in the Drenth calculation would be searched for.

Similarly, it has been proposed that extra-framework Al complexes may be involved in enhancing the acidity of nearby Bronsted sites. These Al complexes may work by acting as electron acceptors from those Bronsted acid sites. As proposed above, these extra-framework molecules in close proximity to the Bronsted site could be searched for during the diffusion simulation.

Summary

We have learned the following things from this study:

1) There are serious energetics problems with most free radical mechanisms.

2) A CH_2 group is not stabilized by the "surface" of the zeolite at the Si-O-Al site.

3) The zeolite is flexible enough to allow two CH2 groups in the same space that was occupied by a single Al atom.

4) Extra-framework Al complexes have been relatively unstudied, and may participate in the carbon-carbon bond formation.

5) The catalyst for the first carbon-carbon bond formation is most definitely not Maxwell's Demon, even if it sometimes seems that way.

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Chapter IV

ab initio Calculations of Reactive Osmium Complexes and Clusters

Chapter IV: *ab initio* Calculations of Reactive Osmium Complexes and Clusters

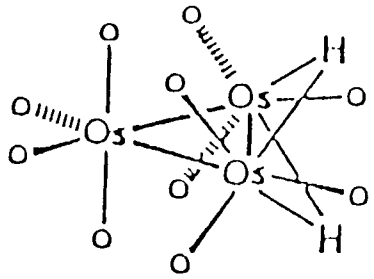
Introduction

Much of organometallic research is directed towards improving and expanding homogeneous catalysis. A lot of research has been conducted and much learned about the interaction of organic ligands with transition metals, particularly carbonyl ligands. We have investigated, using quantum mechanics, the nature of the CO ligand interaction with metal-metal bonds.

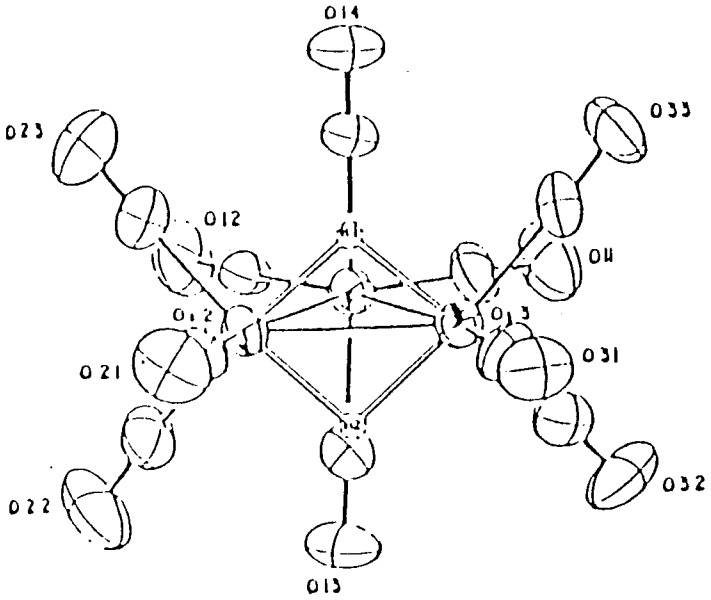
The goal of this research is to understand how the electronic structure of ligands and M-M bonds affect the chemistry of compounds which contain such bonds. By developing a systematic way of predicting ligand effects on metal-metal bond energies, we can predict the modifications necessary to improve on the catalytic activity of transition metal clusters.

$H_2Os_3(CO)_{10}$, shown in figure 1[1,2], is the starting material for many triosmium clusters and is a catalyst for isomerizing terminal olefins to internal olefins. Most of the chemistry of $H_2Os_3(CO)_{10}$[3] occurs at the site where two of the Os atoms are bridged by the two hydrogens. The bonding at this site can be viewed in the extreme ways as shown in figure 2. Structure A, to be referred to as DB for double bond, shows a double bond between the two osmium atoms, with each hydrogen bound to a single osmium atom. Structure B, which will be referred to as 4c-4el, consists of bridging hydrogens with no direct Os-Os bond. Standard MO theory describes the bonding in this region of the cluster as having a four center-four electron bond between the two osmium and two hydrogen atoms or as three center-two electron bonding as observed in B_2H_6[4,5,6]. The catalytic cycle for olefin isomerization is shown in scheme 1[7,8,9,10].

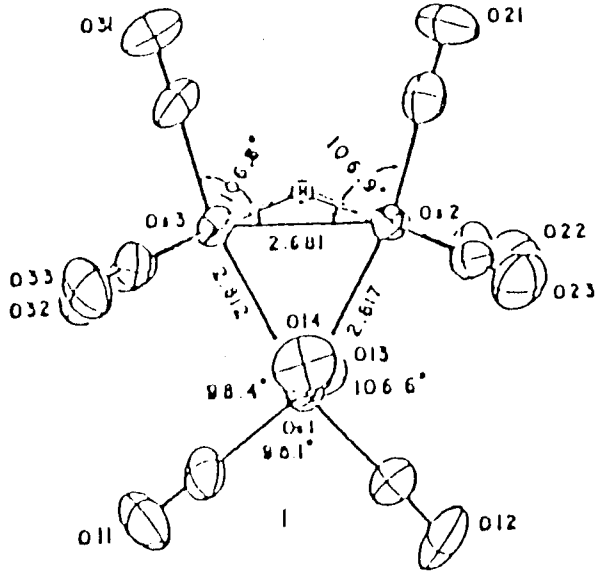
$H_2Os_3(CO)_{12}$



i.

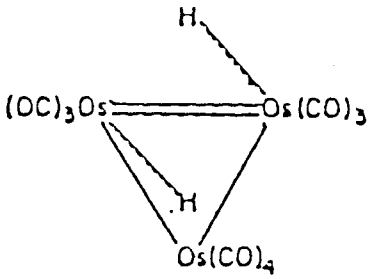


ii. ORTEP-II diagram for x-ray crystal structure.

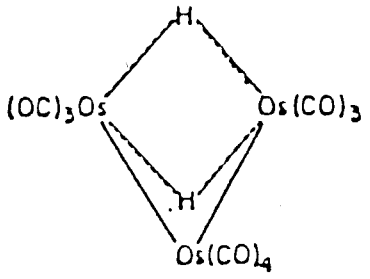


iii. ORTEP-II diagram projected onto the Os_3 plane.

Figure 1



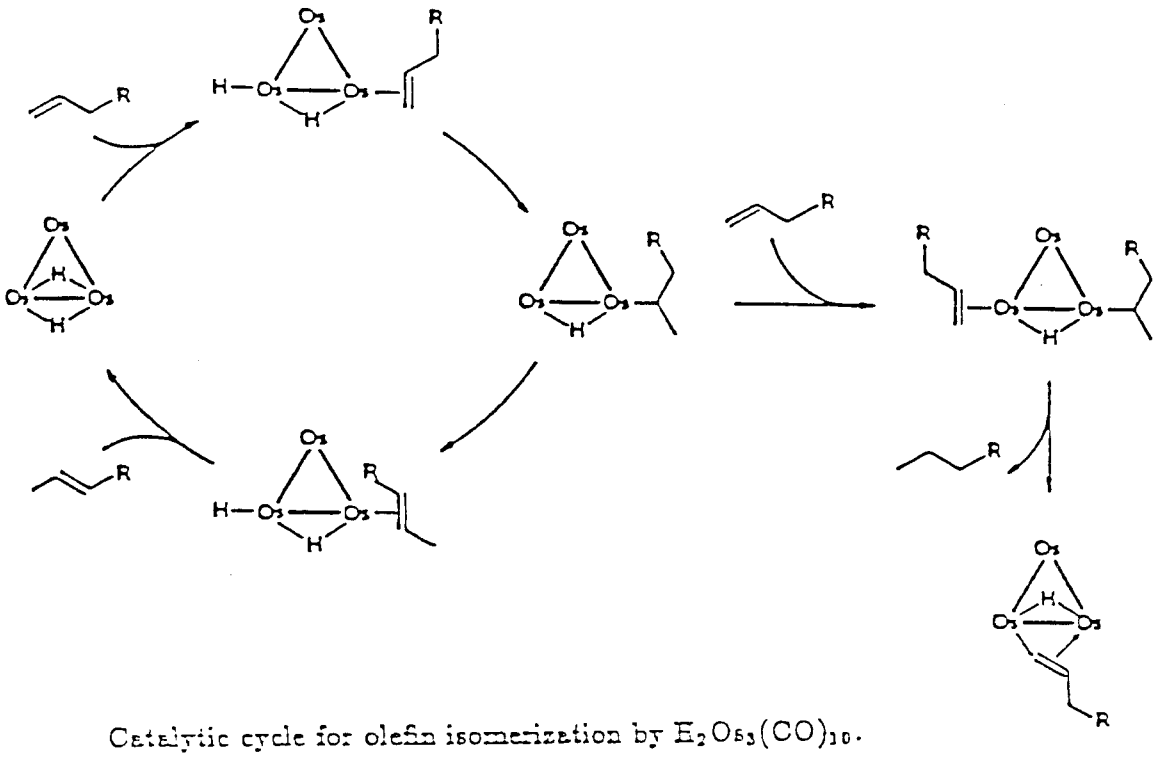
A.



B.

Figure 2

Since most of the chemistry involved occurs at the Os_2H_2 region (addition of the olefin ligand, hydrogenation, H elimination, and elimination of the olefin), we expect that this bonding in the region is fairly flexible. We also expect that the ligands of both clusters, especially the carbonyl ligands, play a large role in the metal-metal bonding.



Catalytic cycle for olefin isomerization by $H_2Os_3(CO)_{10}$.

scheme 1

To whatever extent these compounds have multiple metal-metal bonds, we expect the MO description to be inaccurate; consequently we have studied the Os_2H_2 portion of the parent cluster, $H_2Os_3(CO)_{10}$, using the GVB method. We expect this study to provide new insight into the high reactivity and bonding flexibility and that this may lead to ideas about how to design systems with even more interesting chemistry.

In studying the Os_2H_2 region it became clear that the CO ligands played a large role in the electronic structure of the cluster. Since it is well known that some transition metal cluster catalysts break apart *in situ* to form the actual catalytic species, it is important in modifying those catalyst to understand where the weak links in the cluster are as those places are like sites for metal-metal bond breaking and subsequent rupture of the cluster. If we could determine what aspects of the metal-ligand interactions most affect the metal-metal bond strengths, we could design catalysts to break apart in different ways and at different bonds.

Results and Discussion

I. $H_2Os_3(CO)_{10}$

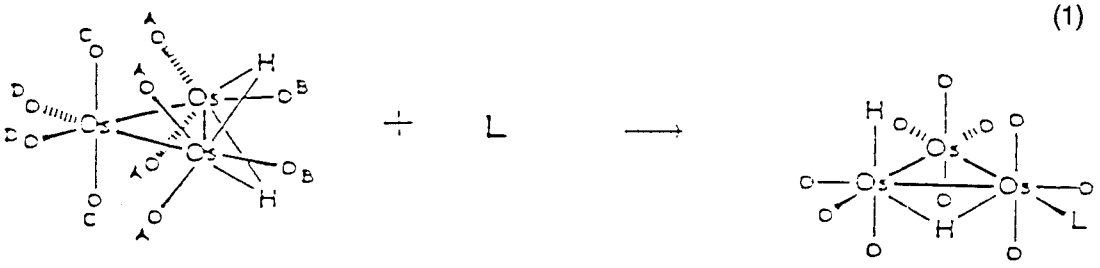
A. Experimental aspects of $H_2Os_3(CO)_{10}$ Chemistry

The crystal structure of $H_2Os_3(CO)_{10}$ shows both H atoms bridging one Os-Os bond, and both H atoms equidistant from both Os atoms. Given that osmium has eight valence electrons, there are only four electrons available for bonding in that region of the cluster. The diagrams in figure 2 show the two extreme bonding possibilities. While this is an interesting topic in the general understanding of bonding, it may also be of use synthetically. Many clusters have been synthesized from $H_2Os_3(CO)_{10}$, with most of the reactivity occurring at the Os_2H_2 region. These reactions fall into three major categories: 1) addition of nucleophiles, 2) addition of electrophiles, and 3) insertion reactions. The following examples from each of these categories demonstrate that the bonds formed in the reactions are not all standard covalent bonds and that the

orbitals involved are the same ones responsible for the unusual bonding in $H_2Os_3(CO)_{10}$. It is our goal to elucidate the electronic structure responsible for the unusual bonding modes and high reactivity and to use that information to design more reactive and more specific catalysts and stoichiometric reagents.

1. Nucleophilic addition

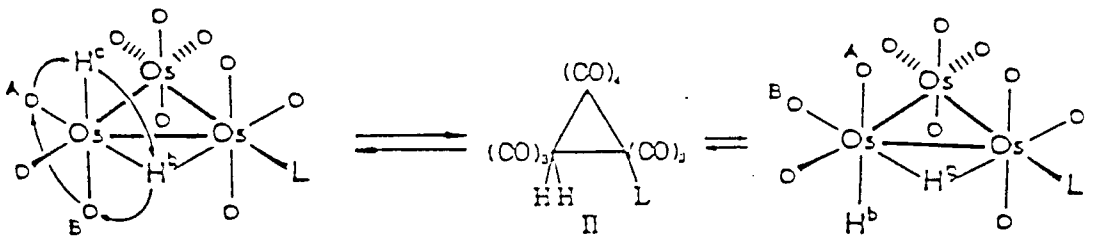
Since $H_2Os_3(CO)_{10}$ is unsaturated it is not surprising that addition of nucleophiles to the cluster is a facile reaction. Nucleophilic addition to the cluster is described by equation 1.[11,12]



(1)

The bonding in the Os_2H_2 region has changed dramatically from that found in $H_2Os_3(CO)_{10}$ and there is a new twist; the H atoms have been observed via nmr spectroscopy to exchange fairly rapidly with the mechanism shown in equation 2.

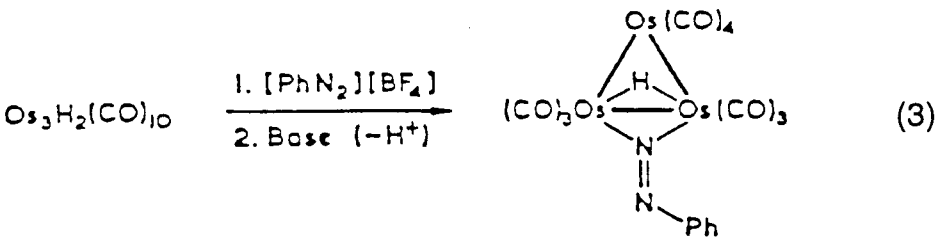
(2)



The observed ground state of this molecule is shown on the lhs of eqation 2, and it does not satisfy the 18 electron rule. The intermediate in the H exchange process does satisfy the 18 electron rule. Since the same orbitals involved in the bonding of the $H_2Os_3(CO)_{10}$ are indicated here, determining the electronic structure of the unsaturated cluster should allow us to predict the electronic effect of nucleophilic addition so that such reactions can be designed for optimum efficiency and more interesting nucleophiles can be used.

2. Electrophilic addition

In most cases where electrophiles add to $H_2Os_3(CO)_{10}$, they act as donor ligands. In one example, illustrated in equation , $[PhN_2][BF_4]$ adds to the cluster and, after deprotonation, acts as a three electron-donor, occupying the position which the second hydrogen occupied in the parent cluster[13,14].

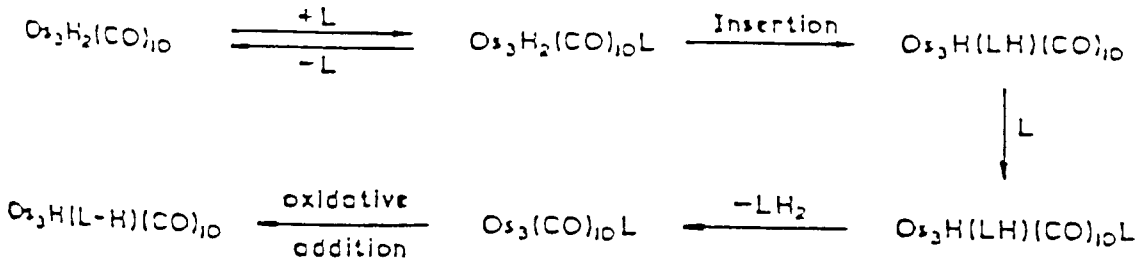


(3)

In $H_2Os_3(CO)_{10}$ there are four electrons available for bonding in this region while in the $[PhN_2]$ adduct there are five, yet both clusters have these same osmium atom orbitals available to make the different bonds.

3. Insertion reactions

In general, insertion of the ligand, L, into $H_2Os_3(CO)_{10}$ does not stop there but reacts further, displacing LH_2 and then oxidatively adding L, as shown in scheme 2.



scheme 2

In some cases, as for ketenes, isocyanates, azides, diazo compounds, isonitriles and nitriles, the simple insertion product is recovered.[15] To understand why some reactions stop at insertion and others go on requires knowledge of the electronic structure of the bonding region. Once this is determined, the clusters and reactants can be designed to stop or continue as desired.

B. Theoretical treatment of $H_2Os_3(CO)_{10}$

In order to accomplish the task of calculating the electronic structure we have studied the cluster without CO ligands to determine the state of the system while not including the full electronic effects of the CO ligands. It is reasonable to expect that the carbonyl ligands play an important part in the bonding, and we will discuss this effect later. The population of electrons on the osmium atoms assumes the presence of CO ligands; that is, no attempt is made to satisfy the 18 electron rule with the electrons present in osmium and hydrogen. Each osmium has 18 electrons--the number of electrons which would be donated by

the CO ligands in the full cluster electrons. Looking at figure 1, the electron count on Os1 is 10, and on both Os2 and Os3 it is 12.

Our objective is to calculate the electronic structure of the low-lying states of this cluster so that we may determine the bonding of the ground state. It is important to include the low-lying excited states in this study as accessible excited states with different bonding modes in the Os_2H_2 region which may account for the bonding flexibility and reactivity.

We must first consider the electronic structure of the cluster to determine the low-lying states. The unique Os atom, $Os(CO)_4$, has three σ, in-plane, orbitals and two π, out-of-plane, orbitals. Two of the s orbitals are used in bonding to the other two Os atoms. They have A1 and B2 symmetry, respectively. Since Os has eight valence electrons, the other three orbitals are doubly occupied. These orbitals have A1, A2, and B2 symmetry, respectively. The other two Os each have four σ and two π orbitals with the extra σ orbital being available because there are only three CO ligands on each of these Os atoms. Two σ orbitals are used in bonding to the unique Os; they have been accounted for in discussing that Os. One σ and one π are used in bonding to the H atoms; these are of A1 and B1 symmetry. This leaves a total of five σ and three π orbitals to accommodate the twelve electrons remaining, therefore requiring that two of these eight orbitals be empty. We expect that the empty orbitals will be anti-bonding orbitals corresponding to the bonding orbitals in the cluster, but as the bonding in the Os_2H_2 is unclear, which two of the eight orbitals is high-lying is not obvious.

One possibility is that the anti-bonding orbitals which are highest in energy correspond to the A1 and B1 orbitals used to bond the H atoms to the Os atoms. This would suggest leaving an A2 and a B2 orbital empty. This configuration of electrons will be referred to as A2B2.

Another possibility is that the high-lying antibonding orbitals correspond to the bonds between Os2 and Os3. This would suggest leaving two B2 orbitals empty. This will be referred to as B2B2.

A third possibility is that there are two empty s orbitals, each of A1 symmetry. In fourth $Os_3(CO)_{12}$ the metal orbitals which have electrons donated into them by CO ligands are the high-lying orbitals, so that without the two extra CO ligands these orbitals are available. This will be referred to as A1A1.

The fourth state tried is a perturbation of the third, with one A1 and one A2 orbital empty. This will be referred to as A1A2.

The fifth, and last, state calculated has all five available s orbitals occupied and one p, leaving two empty p orbitals. This will be referred to as A2B1.

In order to simplify the procedure, as a first step we calculated the wavefunctions of Os_3 for each of the first four states described above, allowing the orbitals which would be bonding to hydrogen to be singly occupied and triplet spin-coupled. In this case we were looking for the lowest energy structure, comparing just the four states of Os_3. Since there are no Os-H bonds present, we expect that the relative energies of the antibonding orbitals would change. Calculations were first done at the Hartree-Fock level. We then calculated the same molecules at a GVB 2/4 level, correlating two bonds for each state. Leaving the molecule at C_{2v} symmetry, one of the two correlated bonds will be an s bond between the bridged Os atoms. The other may show some p bonding between those two Os atoms.

The results for all Os_3 and H_2Os_3 calculations are given below, along with a discussion of the information gained.

Table I shows the total energies for the four states of Os_3 calculated at the Hartree-Fock and GVB levels.

Table I

Total Energies in hartrees Calculated for the States of Os_3

Level	A2B2	B2B2	A1A1	A1A2
Hartree-Fock	-270.2288	-270.3078	-270.2589	-270.2628
GVB(2/4) C_{2v}	-270.3558	-279.3545	-270.2784	-270.2839

The ground state from among these four states is different, depending on the level of the calculation. This can be understood by considering the GVB wavefunction in general. A GVB pair consists of an occupied, bonding first natural orbital and an unoccupied, antibonding second natural orbital. At C_{2v} symmetry, if the first natural orbital is of A1 symmetry, as is the case for the bonds we are considering at that level of calculation, the antibonding orbital is of B2 symmetry provided that there is an unoccupied B2 orbital available. The ground state at the GVB(2/4) level does have an extra unoccupied B2 orbital, as does the first excited states. We expect to see this same preference at the C_{2v} level for H_2Os_3. With just this data, we cannot predict any more properties of H_2Os_3, because the triplet Os_3, for all cases, has the unpaired electrons on the unique Os, rather than on the bridged atom. This does not affect the argument above because the GVB pairs involved would still require the empty B2 orbitals, even if they would display different bonding in the first natural orbitals.

The Os_3 calculations suggest that either the A1A2 or A2B2 state is the ground state of H_2Os_3. To gain more information about the ground state and bonding in the cluster, we calculated wavefunctions for H_2Os_3 at the Hartree-Fock and GVB(2/4) levels, using both C_{2v} and Cs symmetry. By using C_{2v} symmetry, we can see if there is direct bonding between the bridged Os atoms. At the lower symmetry we can compare the relative strengths of that bonding with the Os1-Os2 and Os1-Os3 metal bonds which are known to exist. The energies calculated are given in Table II.

Table II

Total Energies Calculated for H_2Os_3

Level	A2B2	B2B2	A1A1	A1A2	A2B1
Hartree-Fock	-271.3993	-271.3712	-271.2823	-271.4913	----------
GVB(2/4) C_{2V}	-271.5052	-271.4373	-271.4384	-271.4986	----------
GVB(2/4) Cs	-271.5736	-271.4890	-271.4890	-271.5736	-271.4825

At the Hartree-Fock level the A1A2 state has the lowest energy, but we cannot determine whether or not there is any metal-metal bonding between the two bridged osmium atoms because Hartree-Fock delocalizes electrons, and metal-metal bonding is better described as overlap between localized orbitals on the two metal centers. It may be that there are no localized orbitals on these centers available for such bonding, but we need to employ the GVB method in

order to ascertain the extent of metal-metal bonding. At the GVB (2/4) C_2v level, the A2B2 state is the ground state and at the GVB (2/4) Cs level, because of the lowered symmetry, the A2B2 and the A1A2 states are identical and lowest in energy. We can understand the difference in energy between the C_2v and Cs results by looking at the GVB pairs for both calculations, shown in figure 3. The upper pairs (a) are from the A2B2 state in C_2v symmetry and the lower pairs (b) are from the A1A2/A2B2 state in Cs symmetry. The GVB pairs in C_2v symmetry show a bond between the bridged osmium atoms and a delocalized bond between the unique osmium atom and the bridged osmium atoms. The Cs GVB pairs describe two very distinct bonds, one each between the unique osmium and each of the bridged osmium atoms. The energy lowering for each of these GVB pairs, shown in Table III, suggests that the Os1-Os2 and Os1-Os3 bonds are better energetically than the σ bond between the bridged osmiums. There is no evidence of a π interaction between the bridged osmiums.

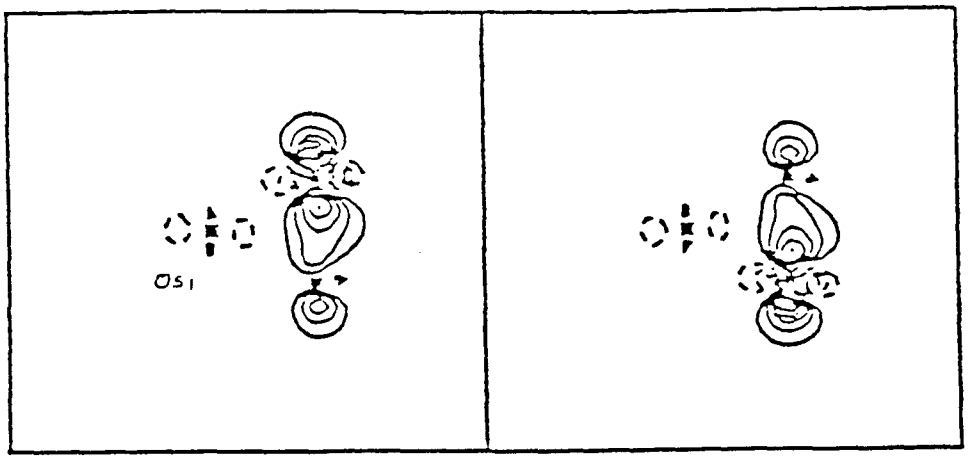
Table III

Energy Lowering of GVB Pairs Calculated for H_2Os_3

Level	GVB Pair 1	GVB Pair 2
GVB (2/4) C_2v	0.0057	0.0138
GVB (2/4) Cs	0.0579	0.0579

The information above indicates that there is a possible metal-metal σ bond between the two bridged osmium atoms, but to confirm this more data is required. Also, we still do not have a clear picture of the bonding between the bridged osmiums and the hydrogens. To get this additional information we

A2B2 state C_{2v} symmetry GVB pair 1



A2B2 state C_{2v} symmetry GVB pair 2

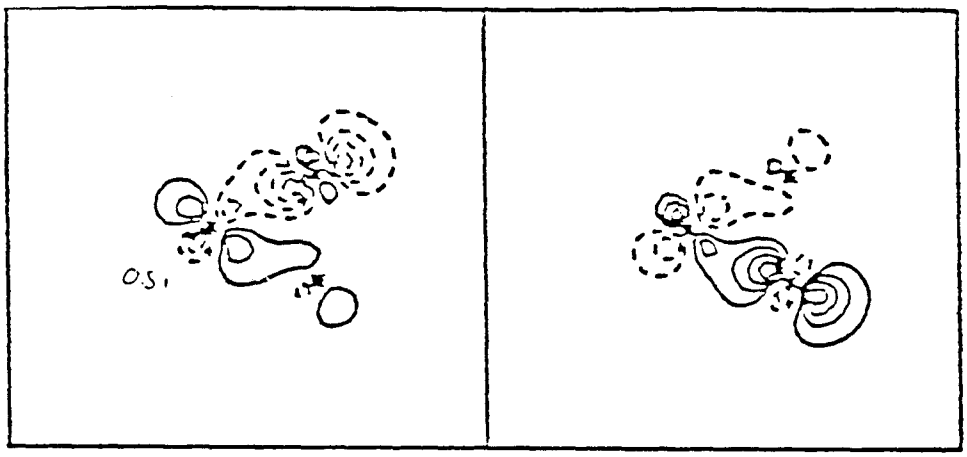
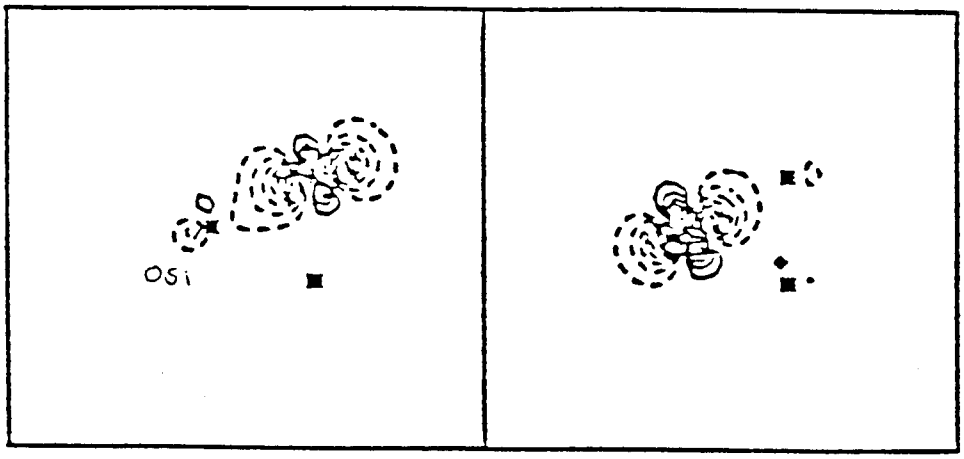


Figure 3a

A1A2/A2B2 state Cs symmetry GVB pair 1



A1A2/A2B2 state Cs symmetry GVB pair 2

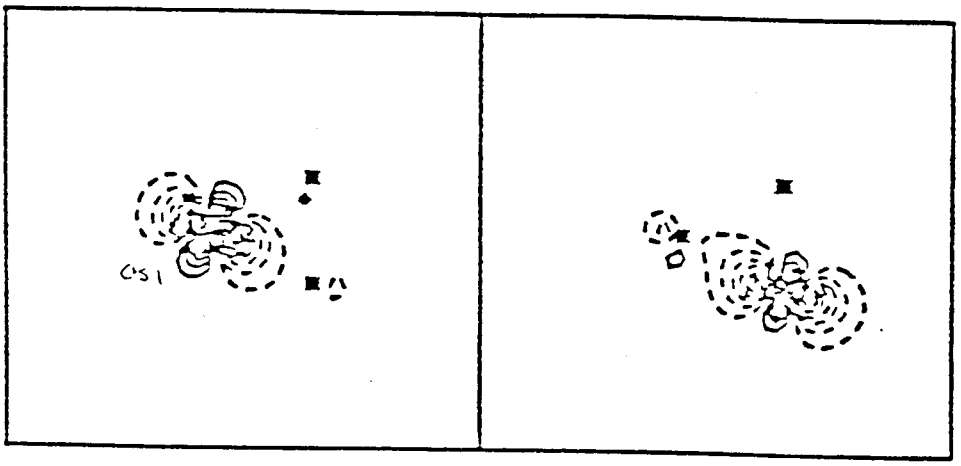


Figure 3b

need to calculate H_2Os_3 with no symmetry, in order to be able to correlate the Os-H bonding. Results of a GVB(2/4) and a GVB(4/10) calculation, both with no symmetry, are given below.

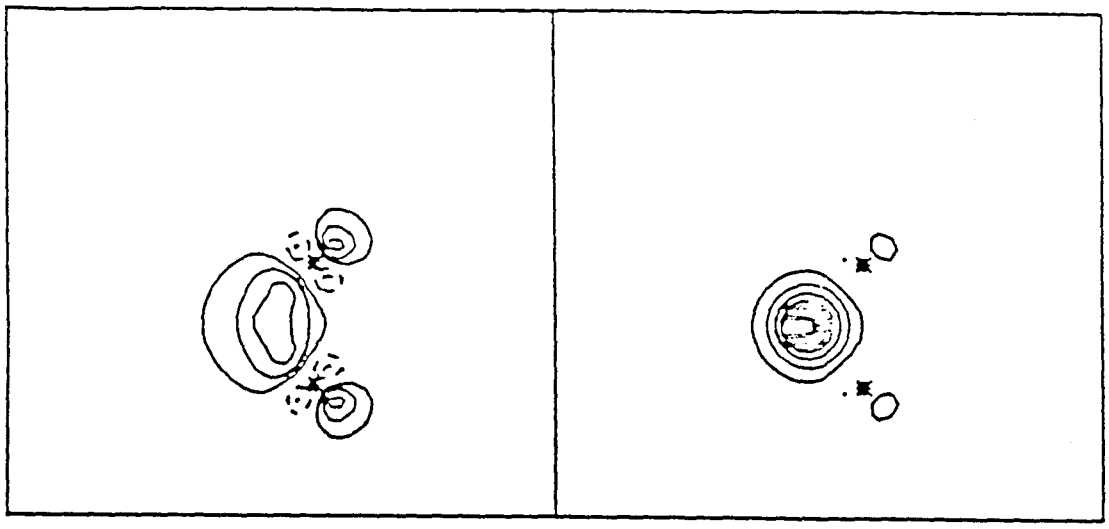
The GVB(2/4) calculation with no symmetry gives the same result as the GVB(2/4) at Cs symmetry for the A1A2/A2B2 state. The GVB(4/10) is an extension of the GVB(2/4) calculation, with two GVB(1/3) sets of orbitals which will describe the 3c2el bonding for the Os_2H_2 region. These two sets of orbitals are identical because the Os_2H_2 region is symmetric. Looking at just one set, in figure 4, we have two cross sections of the first natural orbital as paired with the second natural. The first cross section is in the plane which includes the two Os atoms and the H. This is essentially a 3c2el bonding orbital with a large amount of electron density on the H, as also shown by the Mulliken populations, in Table IV.

Table IV

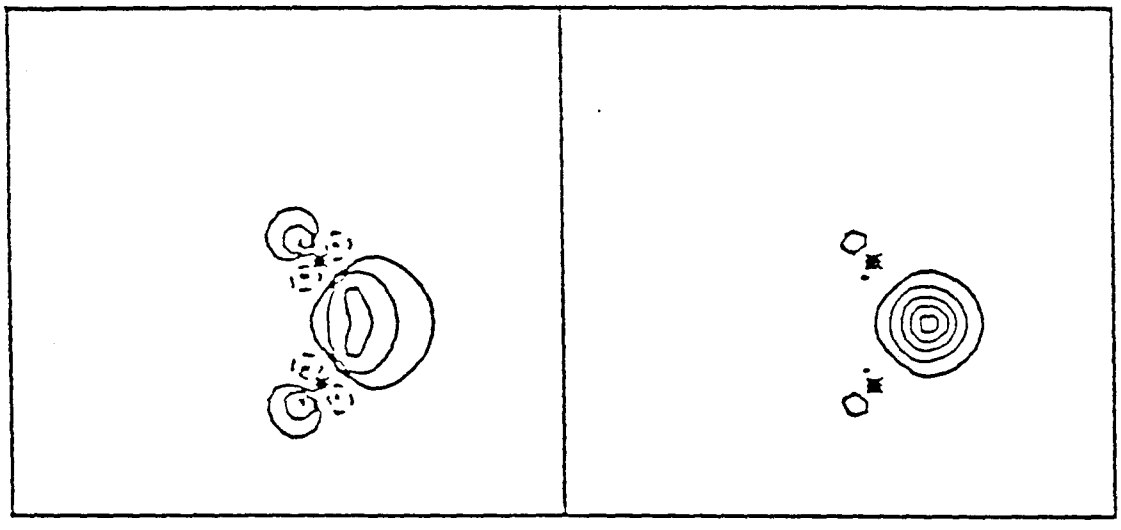
Mulliken Populations in the Atoms in the Os_2H_2 Region

Atom	Population
Os2	7.5744
Os3	7.5744
H1	1.3871
H2	1.3871

The second cross section is taken in the xy plane where z=2.475 A., passing through the two Os atoms. A 3d study of this orbital showed the entire



First and second natural orbitals through Os-H-Os plane.



First and second natural orbitals through Os-Os =2.475 Å

Figure 4

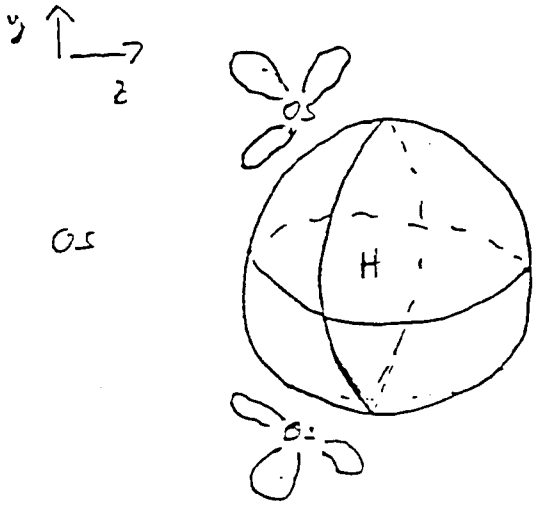
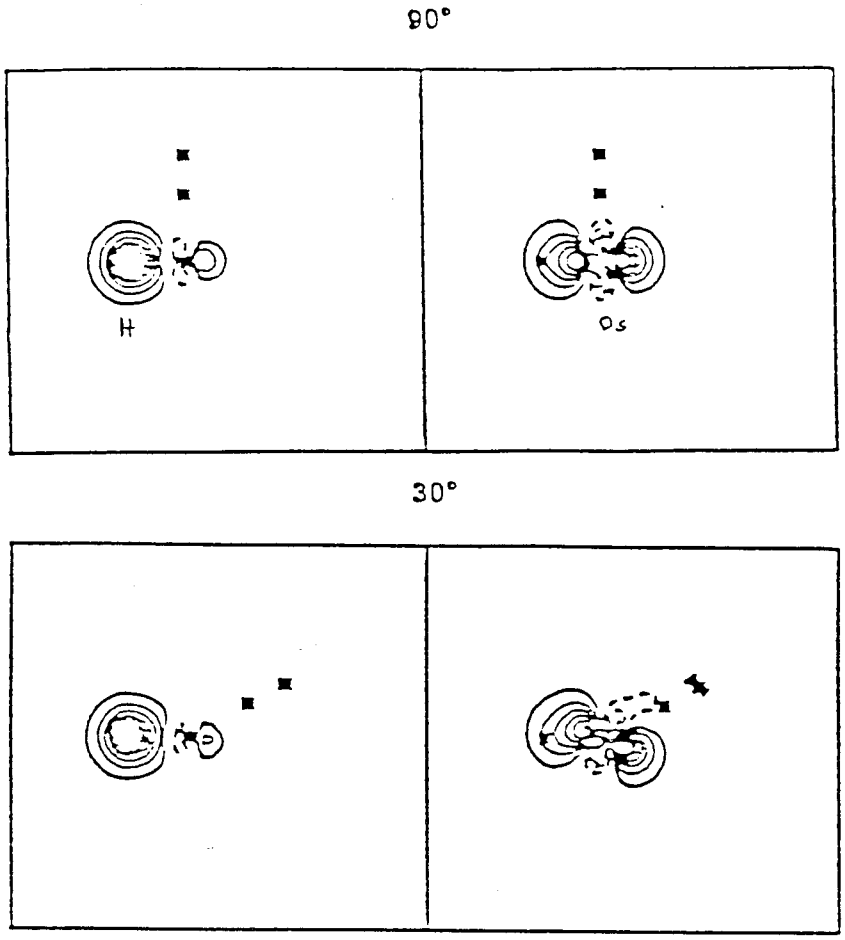


Figure 5

bonding mode, as is illustrated in figure 5. The bonding is fairly similar to that found for B_2H_6.

II. CO Effects on M-H and M-M Bonds

Since the bonding of the Os_2H_2 region is at issue, it is extremely important that we take into consideration all perturbations on the orbitals of the Os atoms. The most obvious perturbation is the effect of the CO ligands surrounding these two Os atoms. We are interested in how the energies of the bonding and antibonding orbitals affect each other, and so we must understand the effect a CO ligand has on both Os-Os and Os-H bonds. Another important issue is the effect of the CO ligands at various angles relative to the bond. The angle chosen for study, 0 degrees, 30 degrees, and 90 degrees, are the angles Os-Os-CO and H-Os-CO existing in the cluster as seen in the crystal structure. We have studied the series of complexes, Os^+-H, CO-Os^+-H q=0°, CO-Os^+-H q=30°, and CO-Os^+-H, q=90°, to determine the effect of CO ligands on Os bonding to H and to predict the effect of the CO ligands on Os-Os bonding as it relates to $H_2Os_3(CO)_{10}$. The optimum bond length for the Os-H bond, the bond dissociation energy for the Os-H and the energy lowering for the GVB pairs are given in Table V. The charge on Os and H, given as Mulliken population, are also shown in Table V. The GVB pairs for all four molecules are shown in Figure 6 (a) and (b).



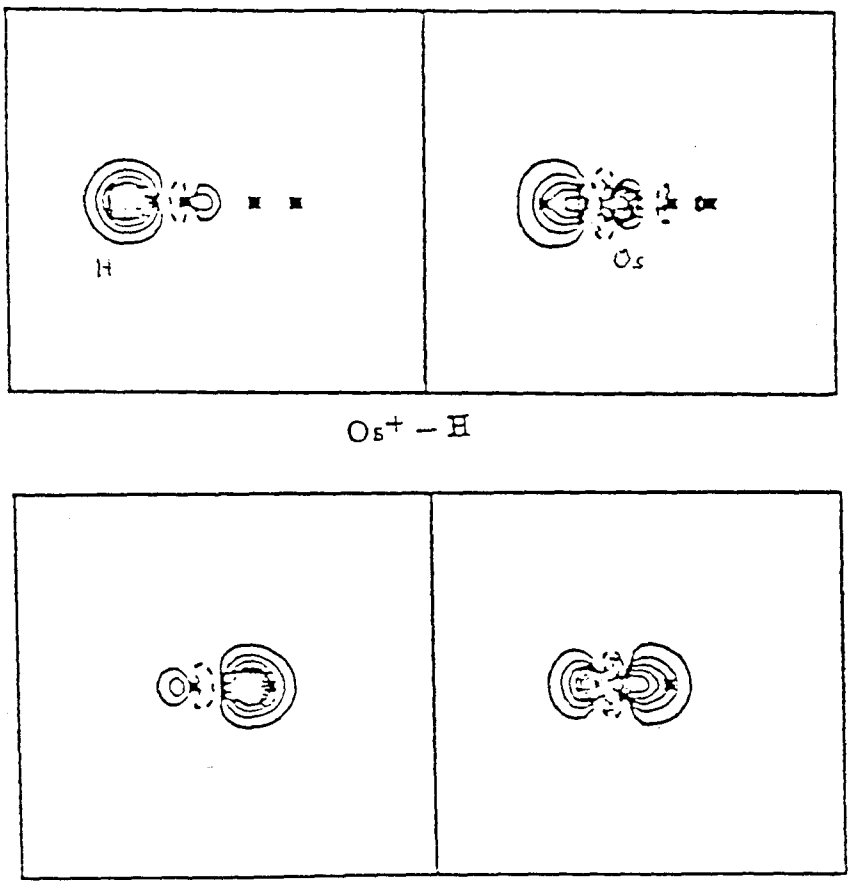
Os-H bond

GVB pairs for

$CO\text{-}Os^{+}\text{-}H$ series

Figure 6a

0°



Os-H bond

GVB pairs for

CO-Os+-H series

Figure 6b

Table V

Results for CO-Os^+-H Series

Molecule	Bond-length	Bond Energy	Energy Lowering	Mull. Pop. on Os	Mull. Pop. on H
Os^+-H	1.604 Å	54.02 kcal	0.0257 h	6.9042	1.0958
90°	1.603	56.88	0.0260	6.9650	1.0743
30°	1.722	54.63	0.0343	6.9892	1.0525
0°	1.658	19.24	0.0192	6.7770	1.1882

The largest bond energies occur for Os^+-H and when the CO ligand is orthogonal to the Os-H bond. The bond energy at 30 degrees is larger than for Os^+-H, but this is due to the lack of orbital involved in backbonding with the CO ligand on the bare metal hydride. When we stretch the bond to infinity to get a bond dissociation energy, the orbitals affected by the CO relax differently than those which don't. The energies of Os^+-H and the 90 degrees are very similar as are the GVB pairs. When the CO ligand is 30° off the Os-H bond axis, the overlap between the Os and H orbitals decreases resulting in a weaker bond than for the 90° case. Allowing the CO ligand to be collinear with the Os-H bond dramatically decreases the bond energy. The GVB pair shows less density on the Os atom as do the Mulliken populations. At this geometry the CO ligand has a filled σ orbital pointed towards the Os-H bond. The GVB pair must orthogonalize to this σ orbital, shifting electron density away from the Os towards the H. This causes less electron density between the Os and H, lowering the bond energy. The overlap is high because both natural orbitals have electron density on the H atom.

In order to fully understand the bonding in the cluster, we need to take a closer look at the CO ligand effects on the Os-Os bond. It is important to keep in mind that if we wish to use knowledge of the metal-metal bond energies to design new catalysts, we need to ascertain not only those energies and what influence the ligand has on them, but also why the CO ligands have that effect. Knowing this, we can modify the clusters in a rational way in designing new reagents.

As the base cluster Os_3 with just one CO ligand is a very large molecule for present *ab initio* methods, and since we wish to determine the direct effect of at least one CO ligand on either side of a M-M bond, we will, for the present study, restrict ourselves to calculating these properties for the dimers, Os-Os and OC-Os-Os-CO. The basis sets used will be the same as was used in the H^+-Os-CO calculations. The bond energies were calculated using the dissociation consistent CI (DCCI) developed in the Goddard Group.

The first step was to calculate the optimum geometries and bond dissociation energies for the two dimers, Os_2 and $Os_2(CO)_2$, where the CO ligands are required to be collinear with the Os-Os bond. The optimum geometries for these dimers, calculated at the GVB(1/2) level, are shown in Table VI. The π orbitals for both dimers are shown in figure 7. Some back donation is in evidence.

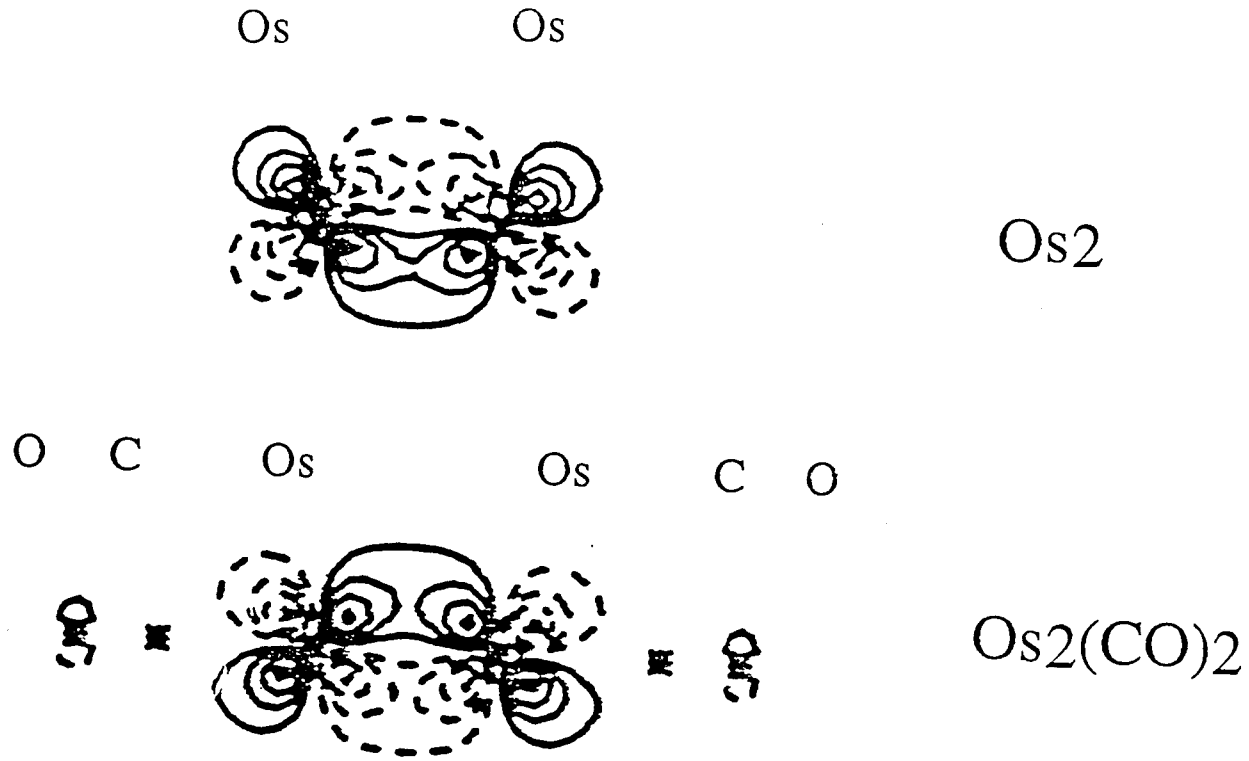


Figure 7

Table VI

Optimum Bondlengths for Os Dimers

Bond	Os_2	$Os_2(CO)_2$, fully relaxed
Os-Os	2.5 Å	2.52 Å
Os-C	----------	2.20
C-O	----------	1.13

We then calculated the Os-Os snap bond energies for the naked dimer at 2.5 Å and for the $Os_2(CO)_2$ dimer with completely relaxed geometry, Os-Os bond at 2.52 Å. Snap bond energies are obtained by not allowing the fragments to relax from the equilibrium geometries or states of the parent complex. This was done because for our model dimer, that relaxation would have produced Os d^6 fragments, whereas if these molecules were actually part of a cluster and had other ligands about them, they would remain d^8. The Os atom ground state is d6, and if we allowed the fragments, either with or without the two CO ligands, we would find that the dimers were not bound at all. These calculated snap bond energies are shown in Table VII.

Table VII

Calculated Bond Energies for Os Dimers

Molecule	Os-Os Snap Bond Energy
Os2	55.01 kcal
Os2(CO)2	24.59

As expected the CO ligands have an enormous effect on the metal-metal bond strength. In determining the cause of this effect, we considered the possiblity that it was caused by: a) a largely σ orbital effect, where the donation of 2 electrons in a σ orbital by the carbonyl ligand required orthogonalization of the Os-Os sigma bond, or b) the effect was a direct result of the π-back bonding of metal dπ electrons to the CO π^* orbital, resulting in a weakening of the metal-metal π-bond. Each Os in the dimer was held in the d^8 configuration, as it would be in the cluster, surrounded by carbonyl ligands. One would expect from this that each metal would have one singly occupied σ orbital with which to bond to the other Os. Each metal would have 3 π electrons in two π orbitals, reminiscent of O_2, and like O_2 we would expect two 3-electron π-bonds.

In order to determine which of the Os-Os bonding electrons were being most affected by the CO ligands, we needed to calculate the possible σ and π effects separately. This was accomplished by the following method. We started with the converged wavefunction of the $Os_2(CO)_2$ with the Os-C distances set at 40 Å - essentially at infinity. The wavefunction was converged at that geometry and at that point, the π orbitals of both metals were frozen. With the π orbitals frozen, the Os-C bond distances were changed to their equilibrium values, and

the wavefunction was converged. The bond energy for this molecule, with the π bonds still frozen, was calculated (Table VIII).

Table VIII

Bond Energy for Os Dimers - $Os_2(CO)_2$ π Orbitals Frozen

Molecule	Os-Os Snap Bond Energy
Os2	55.01 kcal
Os2(CO)2, π frozen	50.75

Nearly all of the influence of the CO ligands that was seen in the completely relaxed wavefunctions is missing. It seems clear that much of the effect of the carbonyl ligands is indeed caused by π-donation from the metal $d\pi$ orbitals into the CO π^* orbitals.

This is just one example of CO ligand effect on metal $d\pi$ orbitals. What does it tell us about CO ligand effects on metal bonds besides those of Os and what effect other types of ligands may have on metal-metal bonds? As described above, the Os dimer we calculated, without ligands, has two 3-electron π bonds. The CO ligands caused π back donation from these orbitals, essentially removing electron density from bonding interaction. It would seem logical that for any metal dimer with a π bonds of any description between the metals, collinear CO ligands will cause the metal-metal bond to weaken. Conversely, for a metal dimer in which all of the π orbitals on both metals were doubly occupied, it would be expected that collinear carbonyl ligands would strengthen the bond. In order to show this, calculations similar to these would have to be done with the appropriate transition metal dimers.

Other types of ligands have other bonding properties. Phosphine ligands have similar σ donation to transition metals as do carbonyl ligands, but little or no p back donation. Collinear phosphine ligands would have their strongest effect on transition metals with strong σ bonds. These properties may only apply for fairly simple ligands. Ligands such as Cp, although noted to remove σ electron character from transition metals in complexes, usually exhibit bonding with transition metals which is far more complex.

We expect that the angle dependence for the collinear effect of the carbonyl ligands will be similar to the drop-off in effect seen in the OC-Os^{+}-H case discussed above. However, this may not automatically hold true for the case where there are several carbonyl ligands around each metal center. A case in point is the triosmium cluster $Os_3(CO)_{12}$. We have shown with dimers that the osmium-osmium bond can be greatly weakened by the collinear carbonyl ligands and, as shown in figure 1, there are collinear carbonyl ligands around each of three metals in this cluster. Yet, this Os cluster is relatively stable. One possible way to explain this is to look at the formation of the derivative cluster, $H_2Os_3(CO)_{10}$. An osmium-osmium bond was lost in the formation of this new cluster, so the bond was weak enough to be reactive. The cluster holds together because of the 2c-3el bonds that have formed in place of the metal-metal bond.

III. Conclusion

Our calculations on various aspects of $H_2Os_3(CO)_{10}$ have revealed a bonding mode similar to that found in B_2H_6 as well as a weak metal-metal s interaction. In order to further resolve the electronic structure, additional correlation is needed in the Os_2H_2 region, and we need to further determine

the effects of the CO ligand on both the σ and π Os orbitals, specifically in that region. Our work with the CO-Os^{+}-H series has enabled us to pinpoint where the CO ligand has the largest effect. We have taken the study further, and determined that due to the presence of π-bonding between the two metals, the donation of electron density to the π^* orbitals of the collinear CO ligands weaken the M-M bond. This leaves unresolved the effect that multiple CO ligands might have.

IV. Calculational Details

A. Basis Set

An effective core potential which represents the innermost sixty electrons and a corresponding basis set were used for Os in all calculations.[16] The basis set is a minimum basis set for the eight outer core electrons and double zeta for the eight valence electrons. For carbon, a valence double zeta and a set of d polarization functions were used. The oxygen basis was valence double zeta.[17,18] The H basis set used throughout these calculations is double zeta in s and has a set of p polarization functions.[19]

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