SUMMARY

This project was started on Sept. 5, 1991 and was titled "The Mechanism of Hydrogen Incorporation in Coal Liquefaction". The purpose of the research was to determine the detailed molecular mechanism for the introduction of hydrogen into coal when it is heated in an atmosphere of $H_2$ in the absence of catalysts and to use this information as a baseline for the study of catalyzed processes. The plan was to study the reaction of model compounds with $D_2$ in a glass-lined reactor of our design and, by determining the distribution of D atoms in the reaction products, to deduce the reaction mechanism(s). As of the date of this report (Nov. 1995), we have, we believe conclusively, demonstrated the mechanism of the thermal process. We have studied several gas-phase reactions and, recently, have extended these to surface-immobilized models. The data are consistent in their support of the proposed sequence. Within the past year, we have begun to look at catalyzed hydrothermolysis and, while the work is at an early stage, we can draw a few significant conclusions, presented below. Most of the work has been published, at least in preprint form and two important papers are currently in preparation. Work is continuing despite our recent lack of success in securing continued funding for the project.
The Glass Reactor

The design of our reaction vessel is shown in Figure 1. Substrates are introduced through the constricted opening evident in the left-hand drawing. The constriction is then sealed and the glass vessel is placed under a cold pressure of 800 psi inside the steel apparatus on the right side of Figure 1. The entire assembly is then placed in a fluidized sand bath at the desired reaction temperature. In experiments requiring activated silica, the thermal activation is carried out by packing fumed silica in the tube, placing the tube in a cylindrical furnace and passing argon through from the capillary end at the desired activation temperature.

Figure 1

Glass Reactor Before and After Sealing

Metal Housing for Glass Reactor
The Diphenylethane (DPE) System

Our first choice of a model was diphenylethane, DPE. This compound has been used in many previous model studies. It is aromatic and contains a representative, radical-forming scissile bond. DPE was subjected to thermolysis under D₂ pressure and a careful analysis of deuterium distribution in the reaction products was carried out. Several specifically labeled compounds were also synthesized and thermolyzed to provide additional clarification. The results of these studies have been published¹ and copies of the relevant publications are included with this report. The important mechanistic steps are reproduced below in equations 1 - 14.

\[
\text{PhCH}_2\text{CH}_2\text{Ph } \rightarrow \text{ 2 PhCH}_2^* \quad (1)
\]

\[
\text{PhCH}_2^* + \text{D}_2 \rightarrow \text{PhCH}_2\text{D} + \text{D}^* \quad (2)
\]

\[
\text{PhCH}_2^* + \text{DPE } \rightarrow \text{PhCH}_3 + \text{PhCH}_2\text{CHPh}\quad \text{DPE}^* \quad (3)
\]

\[
\text{DPE}^* + \text{D}_2 \rightarrow \text{PhCH}_2\text{CHDPH} + \text{D}^* \quad \text{DPE-d}_1 \quad (4)
\]

\[
\text{DPE}^* + \text{DPE-d}_1 \leftrightarrow \text{DPE} + \text{DPE-d}_1^* \quad (5)
\]

\[
2 \text{DPE}^* \rightarrow \text{PhCH}_2\text{CH(Ph)CH(Ph)CH}_2\text{Ph} \quad \text{TPB} \quad (6)
\]
Important conclusions from this initial work were:

1. Deuterium incorporation results supported previous suggestions by Vernon\(^2\) and others\(^3\) that H atoms are involved in the formation of "hydrocracking" products, benzene and ethylbenzene.
(2) It was also evident that D atoms attacked other positions on the aromatic rings present, giving H atoms which could, themselves be involved in hydrocracking reactions. For the most part, the D atom reactions were unselective in these systems.

(3) The likely mechanism for the initial production of D atoms was shown to be the reaction of 1,2-diphenylethyl radicals with D₂, eq 4. Support for this conclusion was provided by the separate study of the thermolysis of 1,2,3,4-tetraphenylbutane (reverse of eq 6).

(4) 2-Phenylethyl radicals, formed by eq 12, proved less selective in their reactions and, therefore, more D was incorporated into ethylbenzene than observed in other species of radical origin such as toluene.

(5) We have carried out a computer modeling study using the reactions listed in eqs 1 - 14. Rate constants for the various reactions were taken, as possible, from the chemical literature or, where unavailable, adjusted to fit the data. A reasonable fit was obtained in support of the proposed model. As will be described below, eqs 14 and 4 constitute a chain sequence which would accomplish the hydrogenation of stilbene (PhCH=CHPh) under the reaction conditions. We are in the process of checking our calculations as they apply to stilbene hydrogenation and will publish all of the modeling studies when this is complete, probably next summer.

The 2,2,5,5-Tetramethyl-3,4-diphenylhexane (TMDH) System

Following the studies with DPE, we sought to confirm our analysis by study of a system wherein the initiating bond homolysis event took place at a lower temperature.
Prior studies by Rüchardt, suggested that 2,2,5,5-tetramethyl-3,4-diphenylhexane, TMDH, might work. Our results with this system confirmed our earlier conclusion that it was possible for benzylic radicals to react with D₂ to produce D atoms and thus, in theory, to initiate D-atom chains of the sort proposed for the DPE system (eqs 8 and 9 or eqs 11, 12 and 13). The thermolysis of TMDH produces neopentylbenzene and, as predicted, the yield of this product was greatly increased under D₂ pressure. This demonstrated the sequence of eqs 15 and 16 wherein homolysis of TMDH (eq 15) leads to phenylnopentyl radicals NP which react with D₂ to give D atoms.

Our initial plan anticipated using this system to generate D-atoms for studies of their reactions with various organic compounds including structures believed representative of species present in coals. Given that NP lacks hydrogen atoms in positions β to the radical center, we believed that it would be prevented from engaging in kinetic-chain-shortening processes such as the disproportionation reaction of eq 7, believed responsible for reducing hydrocracking efficiency in the reaction of DPE with H₂ or D₂. As it turned out, the chemistry of the meso-isomer of TMDH is more complex than anticipated in that the loss of tert-butyl radical is a significant side reaction and the products which follow become involved in sequences which lead to radical-removing termination steps. A detailed description of the complex chemistry of this system is given in our papers.

As we see it, the ideal system with which to generate H atoms for the study of their reactions with coal-like compounds would be one which produces organic radicals at moderate temperatures. The radicals thus produced should be sufficiently reactive to
remove D atoms from D₂ but be prevented in some way from self-destruction. We have tried a number of alternatives to TMDH which have turned out to be less effective. Our analysis suggests that in order to have a radical-producing reaction which occurs at moderate temperature, it is generally necessary that the incipient radicals be too stable to react with D₂. We believe that the effectiveness of the TMDH system is due to the fact that its proclivity for dissociation is the result of steric compression in the TMDH molecules rather than inherent stability of the radicals (NP•). Rather remarkably, it turns out that the problems with side reactions in the TMDH system are less severe for d,l-TMDH which, unfortunately, is much harder to prepare and purify than the meso-isomer. We are currently trying an alternative preparation of the d,l-compound.

1-[4-(2-Phenylethyl)benzyl]naphthalene, NMBB. Another popular coal-model compound, 1-[4-(2-phenylethyl)benzyl]naphthalene, NMBB, studied extensively by Farcasiu⁶ was selected for study and heated under pressure of D₂ both in the absence and presence of catalysts.⁷ For the most part, the uncatalyzed reactions proceeded in analogy with the sequence suggested for the DPE system. The presence of typical liquefaction catalysts promoted extensive H-D exchange of the aromatic rings, particularly that of the naphthyl moiety. This along with the appearance of substantial amounts of compounds containing saturated rings suggested the possibility that some hydrocracking in this system may be the outcome of a sequence involving prior partial ring hydrogenation. We plan to explore this possibility further using simpler compounds.
Based on the mechanism of the uncatalyzed reaction and what has been observed with catalysts, thus far, in model systems, we see several possible roles for catalysts in hydroliquefaction treatments of coal. The most obvious is a direct hydrocracking process wherein the catalyst transfers H atoms directly to the target site and the resultant adduct then cleaves either in concert with or immediately following the transfer. However, a second possibility is that, the catalyst transfers H atoms in pairs, probably stereoselectively, and the resultant partially non-aromatic, cyclic polyene undergoes inter-ring bond scission. The radicals produced could then rearomatize to give the appearance of Ar-C cracking. The presence of ring-hydrogenated materials among the products of the NMBB reactions is permissive evidence for such a scheme. Still a third possible role for hydrogenation catalysts is the lengthening of H-atom chains through removal of materials which might otherwise serve as H-atom traps. In principle, the reactions of eqs 11, 12 and 13 (with D₂) constitute a kinetic chain capable of continuously "cracking" Ar-C bonds. However, when the reaction of eq 14 intervenes by trapping the H atoms, radical chains are shortened when the termination process of eq 7 follows. In the future we plan to explore the relative importance of each of these roles with the aim of more systematic catalyst design. Further discussion will be offered in the context of the silica-catalyzed hydrogenations to be discussed later.

Surface Immobilized Models (Si-O-Ar linked).

The elegant experiments of Poutsma, Buchanan, Britt and their coworkers\(^8\) employing coal-model compounds connected to silica via aromatic-ether linkages
suggested the possibility of examining the reaction of such models with D₂. Accordingly, in collaboration with Britt and Buchanan we have attached 1-(4'-hydroxyphenyl)-2-phenylethane to fumed silica (SiODPE) and studied its behavior on heating with D₂ using the techniques described for gas-phase models. This represented our first attempt to model the more realistic hydroliquefaction situation in which the target molecules are present in a condensed phase. We were partially successful in this effort although a complete comparison of the two situations was complicated by equilibration of gas-phase and surface-attached phenols and by an unanticipated, silica-promoted, phenolic-ring-selective H-D exchange reaction.

A comparison of the thermolysis of SiODPE under N₂ and D₂ showed that the presence of D₂ pressure did not alter the tendency for retrogressive free-radical rearrangement and cyclization processes to occur under conditions of restricted mass transport. Hydrothermolysis (D₂) of SiODPE did produce expected higher yields of hydrocracking products and lower yields of stilbene than did thermolysis (vacuum or N₂). However, the relative yields of hydrocracked products are comparable to those observed for free HODPE under the same conditions. Thermolytically generated radicals react with D₂ to form D atoms which react with both gas-phase and surface-attached compounds. Importantly, we were able to show that D-atom induced D-H aromatic exchange occurs to a greater extent for gas phase than for surface-attached species. Thus, while it seems likely that a key role for dispersed catalysts in coal liquefaction is improving H₂ access to the coal network either directly or through the production of H-donor compounds, it is not clear that H-donor compounds, thus produced, will necessarily
increase the availability of H atoms or the amount of H-atom caused hydrocracking within the condensed phase during hydroliquefaction.

Experiments were reported which showed that phenolic compounds can serve as H-atom donors under hydroliquefaction conditions. The phenoxy radicals thus produced can react with D₂ to give DOAr which, under the conditions of our experiments experience silica-promoted D-atom transfer to ring positions in the phenols. This latter process complicated analysis in that phenolic components of reaction mixtures accumulate D atoms by two competing mechanisms.

**Surface Immobilized Models (Si-O Ca⁺⁺·O₂C-Ar linked).**

With the goal of finding a method of more firmly binding coal model compounds to a solid matrix, we explored the approach of linking the organic compound to the surface through ion-pairing to a Ca⁺⁺ ion. Attachment of long-chain aliphatic carboxylic acids to silica through Mg⁺⁺ or Ca⁺⁺ ions is a patented method for silica flotation which we thought might be adapted to our purposes. Aqueous Ca(OH)₂ was mixed with sufficient fumed silica (Cab-O-Sil M5 Cabot Corporation) to provide a coverage of 0.35 to 0.50 mmoles/g. The base-treated silica was then stirred with an acetonitrile solution of the appropriate carboxylic acid and filtered. The resultant solid was stirred with additional acetonitrile and filtered. The acetonitrile washing was repeated and the coated silica dried in an oven at 110 °C. Evaporation of the combined acetonitrile washings showed that most of the acid was transferred from the acetonitrile solution to the base-treated silica. Scanning electron microscopic studies on the DPECO₂-coated
material indicated that within the 200 Å resolution of the equipment used, calcium was evenly distributed on the surface.

Materials prepared in this way were subjected to the type of hydroliquefaction conditions described above for ether-linked compounds. Preliminary results showed some similarities to ether-linked materials and some striking differences. In general, the acids immobilized in this way are non volatile, because no acids appear among the reaction products which can be removed under vacuum after the reaction and very little can be removed from the surface under vacuum at reaction temperatures. However, there is some crossover between silica samples coated with different acid salts when heated under vacuum at thermolysis temperatures, indicating that it is possible for small amounts of free carboxylic acids to exist in equilibrium with the bound ion pairs.

The major volatile product from hydrothermolysis of Si-O'Ca++O_2C-DPE was DPE. This, in principle could have arisen either from recombination of reaction-produced benzyl radicals or by decarboxylation. Experiments with Si-O'Ca++O_2C-DPE-4Me, showed the main route to be decarboxylation. We suspect that the mechanism is protonation as shown in Figure 2.

Another striking difference was the appearance of 1-(4'-methylphenyl)-2-phenylethane (MeDPE). The same product is formed when the calcium salt of DPE-CO_2H is heated with D_2. The presence of excess deuterium in this product when the reaction is run under D_2 indicates that it is formed by reduction of the carboxylate group. In the reaction of Si-O'Ca++O_2C-DPE-4Me under the same conditions, 1,2-di(4'-methylphenyl)ethane is formed. DPE-CO_2H gives only a small amount of MeDPE when
heated under $D_2$ and the product does not contain excess $D$. This suggests that the route to MeDPE involving carboxylate group hydrogenation utilizes Ca$^{++}$ ions or possibly CaO as a catalyst.

Another fascinating aspect of the Si-O' Ca$^{++}$ O$_2$C-DPE system was that, like the phenol-based systems, selective hydrogen-deuterium exchange in the substituted ring was observed. With phenols, we argued that equilibration between the phenols and their keto tautomers was responsible for this phenomenon. There would seem to be no comparable possibility for aryl carboxylates. To clarify the situation we calcium carboxylate linked benzoic acid-$d_6$ to Cab-O-Sil. Heating this material even under $N_2$ gave D-H exchange in the aromatic ring and NMR studies showed that the exchange was nearly exclusively (9:1) in the position ortho to the carboxylate group. We envision this outcome as resulting from selective protonation of the carboxylate-substituted ring in the position ortho to the carboxylate group to give a zwitterionic intermediate as shown in Figure 3.

Otherwise, the Si-O' Ca$^{++}$ O$_2$C-DPE system behaves much as does Siodpe. There is evidence for preferential hydrocracking at the junction of the ethylenic bridge.
with the carboxylate-substituted aromatic ring and a strong tendency for immobilized 1,2-diphenylethyl radicals to rearrange to 2,2-diphenylethyl radicals as previously noted for ether-linked radicals. Also, the surface-attached, non-carboxylate-substituted aryl ring was partially protected from reactions with D atoms as had been found to be the case with the ether-linked substrate.

Uncatalyzed Reaction of Alkenes with D₂

In our previous study of the reaction of DPE, and other compounds with D₂ at temperatures to 450 °C and pressures of 2000 psi in isolation from metal surfaces, we were able to provide strong evidence for a mechanistic scheme wherein radicals formed by the homolysis of weak bonds, react with D₂ to give D atoms (eqs 2 and 4). These participate in short, radical-chain processes responsible for hydrocracking and exchange of H for D at unsubstituted aromatic positions. In contrast to the simple thermolysis of DPE wherein stilbene (PhCH=CHPh), STB, is formed as a major product, the reaction of DPE with D₂ produces relatively small amounts of this compound. Moreover, the mole
% of STB among the products decreases as conversion increases, indicating that initially produced STB is consumed. A likely, but unstudied mechanism would involve eqs 4 and 14 in a chain sequence which would permit the uncatalyzed hydrogenation of alkenes. Thus, it seemed important to examine the reaction of STB with $D_2$. This study has subsequently been extended to other unsaturated compounds and a preliminary account of the results has been published.$^{12}$

Several alkenes and arenes have been studied: STB, $\alpha$-methylstyrene, nonene, anthracene and phenanthrene. At the present time, only STB has been studied in detail. This appears to undergo hydrogenation following a mechanism involving short kinetic chains (eqs 4 and 14) terminated by radical disproportionation (eq 7). Kinetic modeling gives a reasonable fit to the experimental data and predicts the observed reverse concentration effect wherein the reaction is faster at lower concentrations of STB. The observed catalysis by reaction-produced DPE also is evident in computer-simulated results. We hope to publish the results of computer simulations for both this system and for the reaction of DPE with $D_2$ in the coming year.

As mentioned, the other choices for preliminary study have shown different behavior and have not been subjected to detailed scrutiny. The $\alpha$-methylstyrene system is complicated by the formation of high molecular weight products and the absence of a negative concentration effect suggests a different kinetic scheme. It seems likely that this reaction is initiated by a reverse radical disproportionation process involving two molecules of $\alpha$-methylstyrene. Anthracene shows no negative concentration effect and we have suggested the possibility that the hydrogenation of anthracene involves direct
[4+2]-cycloaddition. This hypothesis will require additional experimental examination before it can be accepted, however. Phenanthrene does not react under the conditions employed for hydrogenation of the other compounds listed.

Hydrogenation of Alkenes Catalyzed by Thermally-Activated Silica

As we were simultaneously working on the hydroliquefaction of coal-model compounds attached to silica and the uncatalyzed reaction between \( D_2 \) and alkene, we became aware of work by Bittner, Bockrath and Solar\(^3\) which demonstrated catalytic effects of thermally activated silica in reactions involving \( H_2 \) and \( D_2 \). Using a pulse-flow microreactor, Bittner showed that after fumed silica is heated at 330 °C for 16 h in an argon stream it catalyzes the reaction \( H_2 + D_2 \rightarrow 2 \text{HD} \) at temperatures as low as 120 °C. Moreover, this material catalyzes the hydrogenation of ethene to ethane at 150 °C and produces ethane-\( \alpha \) when \( D_2 \) is used as a flow gas. We became curious to see whether silica activated in this way would serve as a hydrogenation catalyst in a static reactor.

We have now shown that even in bulk reactions, thermally-activated silica is a viable catalyst for the hydrogenation of alkenes and even of some arenes.\(^4\) It appears likely that this is a reaction with surface-bound \( H_2 \) as we have demonstrated the stereoselectively \( \text{syn} \) nature of this process in the preferential formation of \( \text{cis-} \text{STB} \) from diphenylacetylene. We have also shown that heating silica with \( D_2 \) at temperatures above 200 °C leads to exchange of surface \( \text{OH} \) groups in what may be a related process. Although mechanistic speculation may be premature, it seems reasonable that siloxane bonds formed when silica is heated are hydrogenated open by \( H_2 \) (or \( D_2 \)) in a manner
similar to that proposed for the reaction of ZnO with H$_2$. D$_2$ reacts with Si-(O)$_2$-Si to form DO-Si-O-Si-D which could possibly be the reactive species toward unsaturated carbon compounds.

We find in some experiments that the thermally activated silica also is capable of catalyzing the hydrogenation of aromatic rings. The circumstances of this occurrence and the type of compound which is susceptible are under continuing investigation. However, it is now clear that with proper pretreatment, thermally activated silica will hydrogenate DPE to mono and dicyclohexylethane. Surprisingly this process is more facile than the hydrogenation of naphthalene and, most amazingly, the presence of a small amount of naphthalene inhibits the hydrogenation of DPE. We have now found that diphenylmethane is also subject to extensive ring hydrogenation by this catalyst. Despite the lack of precedent for this selectivity, we are considering the possibility that ring reduction requires a silica-catalyzed tautomerization of the benzyl moiety to a nonaromatic cyclic polyene which is then rapidly hydrogenated to a cycloalkyl moiety. We are tentatively suggesting that naphthalene or a product of its partial hydrogenation forms a sufficiently strong complex with the active sites which promote the isomerization that it prevents the hydrogenation of arenes. Interestingly, naphthalene has no effect on the silica-catalyzed hydrogenation of STB. However, no ring hydrogenation is observed when STB is present suggesting that STB also complexes with the isomerization-producing sites.

We have also been able to show that the silica surface undergoes H-D exchange with D$_2$ to produce a surface with SiOD groups. We are presently not sure of the
relationship of the surface deuteration to its catalysis of hydrogenation reactions, but it is interesting that some isomerization of nonene takes place without D incorporation when the surface is deuterated.

Summary

Significant discoveries regarding the mechanism of the reaction of H₂ with organic compounds, both catalyzed and uncatalyzed, have been made. We believe that the analogies between these model compound reactions and those which take place when coal is subjected to hydroliquefaction conditions are direct and add to understanding of the latter process.

References


List of Publications Resulting from Funded Research


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