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CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION ANNUAL REPORT, OCTOBER 1, 1980 TO SEPT. 20, 1981.

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Author
Heinemann, H.

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CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
ANNUAL REPORT
OCTOBER 1, 1980 TO SEPTEMBER 20, 1981

Heinz Heinemann

September 1981

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ANNUAL REPORT
October 1, 1980 to September 20, 1981

Chemistry and Morphology of Coal Liquefaction
Contract 4006/4048

Principal Investigator: Heinz Heinemann
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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II. Introduction

This report covers the second year of operation of this program. While much of the first year had been devoted to setting up equipment and testing it, all tasks of the program were fully operative in FY 1981.

Interesting experimental results forced reconsideration of some of the proposed technical program and modifications of it. The success of this basic research project is perhaps best shown by the fact that the work during 1981 has resulted in nine publications in the scientific literature plus four others submitted to journals but not yet published.

A number of significant findings are listed in the "Highlights" section.
III Technical Program for Fiscal 1981

TASK 1 - Selective Synthesis of Gasoline Range Components from Synthesis Gas – A. T. Bell

Investigation of the possibility to obtain non-Schulz-Flory product distribution during Fischer-Tropsch synthesis of hydrocarbons.

TASK 2 - Electron Microscope Studies of Coal During Hydrogenation – J. W. Evans

Reaction of single crystal graphite with predetermined gas mixtures in the environmental cell of a 650 Kv electron microscope. Morphological changes of the graphite at different temperatures and pressures will be observed while chemical products will be identified in a mass spectrometer attached to the cell. Reactions will be studied in the presence and absence of catalysts and will be extended to coals of high crystalline character.

TASK 3 - Catalyzed Low Temperature Hydrogenation of Coal – G. A. Somorjai

Transition metal catalysts will be deposited on a coal surface. Hydrogenation or steam-carbon reaction will be carried out on these samples at low temperatures (150-400°C). Catalyst-coal surface changes will be observed at various stages of reactions by means of a low pressure-high pressure apparatus, permitting the analysis of the surface structure and surface composition of reactants and catalysts. Surface science techniques such as Auger and photo electron spectroscopy will be applied.

TASK 4 - Selective Hydrogenation, Hydrogenolysis and Alkylation of Coal and Coal Liquids by Organo Metallic Systems – K. P. C. Vollhardt

Study of novel transition metal catalysts, capable of cleavage of carbon-carbon and carbon-heteroatom bonds with concomitant reduction. Application of findings to selective coal depolymerization, hydrogenation and liquefaction under mild conditions.

TASK 5 - Chemistry of Coal Solubilization and Liquefaction – R. G. Bergman

This study will concentrate on the hydrogen transfer from donor molecules such as tetralin to condensed aromatic coal-like molecules. Both thermal and catalytic mechanisms will be investigated with the ultimate objective of a catalytic donor mechanism at lower temperatures than are used in current practice.

TASK 6 - Coal Conversion Catalysts–Deactivation Studies – A. V. Levy and E. E. Petersen

Cobalt-molybdena-alumina catalysts will be aged by metal deposition under controlled conditions and a mechanism for scale formation on spent catalysts will be defined. Porosity and diffusion measurements will determine whether the scales form a diffusion barrier.
IV Highlights

1) The carbon number distribution of $C_2-C_{12}$ hydrocarbons produced via Fischer-Tropsch synthesis over an iron catalyst shows virtually no change as the conversion of CO is varied from 4 to 33, and only a small change in the olefin to paraffin ratio is detected. What is significant, though, is that the proportion of methane relative to $C_2+$ hydrocarbons decreases with increasing conversion. Similar effects were observed using both fixed-bed and slurry reactors.

2) Anatase has for the first time been identified by electron diffraction in the electron microscope as a titanium mineral in a bituminous Kentucky coal. Since anatase had previously been found as a deposit on catalysts used for hydrogenative coal liquids and since it has not been found in coal ash, a question arises about the mechanism of its migration during coal liquefaction.

3) The reaction of graphite with water has been investigated using alkali or alkali hydroxide or carbonate catalysts. Methane and $CO_2$ were produced steadily at the surprisingly low temperature of 500°K using potassium on graphite. Lithium was the most active of the alkali catalysts.

4) Work on the laser-powered homogeneous decomposition of tetralin was completed, a compound which has frequently been used in model studies of hydrogen transfer processes occurring during coal liquefaction. Our results show that the primary homogeneous mode of decomposition involves carbon-carbon bond cleavage resulting in ethylene loss, rather than hydrogen loss as had been claimed earlier by other workers. We believe the hydrogen-loss pathway is primarily surface catalyzed. This work demonstrated the utility of the laser technique for insuring that one is examining truly homogeneous, rather than surface-catalysed, processes.

5) In work related to the laser studies mentioned in 4), we generated vibrationally excited tetralin by creating it in chemical reactions of varying exothermicity ("chemical activation"). These studies reinforced our conclusion that the major homogeneous decomposition pathway in tetralin involve loss of ethylene rather than $H_2$.

6) Work on the generation and study of benzene-1,4-diyl diradicals ("1,4-dehydrobenzenes") was completed and published. In this work we uncovered one of the few examples of chemically induced dynamic nuclear polarization (CIDNP) arising from diradicals at high temperature, demonstrated conclusively that these diradicals exist as true intermediates in the reactions of 1,2-diethynylethylenes; and obtained evidence that the diradicals react in the singlet state.

7) A perusal of various first, second and third row transition metal carbonyl compounds, as homogeneous catalyst under water gas shift (WGS) conditions (CO, $H_2O$, base) with polynuclear aromatic hydrocarbons (PNA) reveals that only manganese and iron can effect reductions of these potential coal models to their partially reduced analogs in low yields (~10-30 percent). Dimanganese decacarbonyl (Mn$_2$(CO)$_{12}$) and various phosphine substituted analogs react with PNA compounds, under synthesis gas (CO, $H_2$ 1:1) conditions, to provide good yields of partially reduced PNA analogs (30-80 percent).
8) Polynuclear heteroaromatic hydrocarbon compounds (PNHA, nitrogen as the heteroatom) are more reactive in homogeneous hydrogenation reactions under either WGS or syn gas conditions than their carbon analogs, i.e., acridine is more reactive than anthracene.

9) The ruthenium cluster compound, Ru\textsubscript{3}(CO)\textsubscript{12}, is an extremely good catalyst (H\textsubscript{2} only) for the homogeneous hydrogenation of both PNA and PNHA compounds.

10) The regiochemistry in the Ru catalyzed hydrogenation reveals high specificity for nitrogen heterocyclic rings.

11) The purported Fischer-Tropsch alkylation of benzene with W(CO)\textsubscript{6}-AlCl\textsubscript{3} has been shown to be the result of Lewis acid catalyzed cracking of benzene.

12) Evidence has been accumulated which shows that retrocyclization of component alkynes occurs in \(n^5\)-cyclopentadienyl-\(n^4\)-cyclobutadiene cobalt complexes.

13) A novel transition metal mediated activation of vinyl-hydrogen bonds has been uncovered.

14) High performance reverse phase liquid chromatography has been shown to be a valuable tool in the separation of air sensitive organometallic compounds.
V Accomplishments and Plans for FY 1982

Task 1: Selective Synthesis of Gasoline Range Components from Synthesis Gas.
   Task Manager: A. T. Bell

A) Accomplishments:

The goal of these studies is to determine whether it is possible to obtain non-Schulz-Flory product distributions during the Fischer-Tropsch synthesis of hydrocarbons. Two approaches are being explored. The first involves the recycle of olefin products to interfere with the normal chain growth. The second approach is to use small pore zeolite supports or cocatalysts to either limit the extent of chain growth or to reform the nascent products. These techniques for modifying the product distribution are being investigated using both a fixed-bed and a well-stirred slurry reactor. Products from these reactors are analyzed directly by gas chromatography, without the use of collecting traps, to avoid product fractionation.

Experiments conducted during the past year have focused on determining the effects of reaction conditions on product distribution prior to the imposition of measures designed to modify the product distribution. All of this work has been conducted with a precipitated iron catalyst, promoted with copper and potassium.

Investigation with the fixed bed reactor were conducted at 10 atm and 300°C, using a 2:1 H₂/CO ratio in the feed gas. For syn-gas flow rates of 120 to 10 cm³/gm/min, the CO conversion increased from 4 to 33. The distribution of C₂ through C₁₂ products was unaltered over this range of conversions, but the formation of methane relative to other products was suppressed as the conversion increases. This effect was unexpected and at present no completely satisfactory explanation is available. In parallel with these effects, it was found that the olefin to paraffin ratio of the products decreased only slightly with increasing conversion. The change was most noticeable for products containing two and three carbon numbers but was virtually undetectable for products containing four or more carbon atoms. Representation of the olefin distribution on a Storch/Anderson-Schultz/Flory (SA-SF) plot shows that the data are in perfect agreement with a SA-SF distribution. The data for C₉+ paraffins follow the expected SA-SF distribution, the data for C₂ through C₈ paraffins fall below the line, and the point for methane lies well above the C₁ point on the line. This pattern is similar to that seen previously for synthesis over Ru. The effects of reaction conditions on the distribution of paraffins must be explored further before an explanation for the observed deviations from the SA-SF distribution can be given.

Preliminary results have been obtained using the slurry reactor. Working with a synthetic ammonia catalyst, it has been observed that at 10 atm and 300°C variations in the stirring speed from 800 to 1450 rpm have no effect on either the product distribution or the olefin to paraffin ratio. These results indicate the absence of mass-transfer effects under the chosen reaction conditions. Variations in the syn-gas feed rate produced effects virtually identical to those observed with the fixed bed reactor.
B) Plans for FY 1982

Experiments will be conducted in which increasing concentrations of ethylene, propylene, or butylene are added to the syn-gas feed. Analysis of the reaction products will reveal the extent to which the olefinic additive enters into chain growth and whether or not a deviation from a normal SA-SF distribution can be achieved. An important part of these studies will be to determine the extent of olefin saturation and hydrogenolysis, competitive processes which would interfere with the intended use of the olefin. The relative reactivity of different low molecular weight olefins will also be established through these experiments.

In a second series of experiments, tests will be conducted with iron catalysts prepared on either ZSM-5 type zeolites or carbon molecular sieves. The emphasis of this work will be on determining the effect of the support structure and composition on the distribution of products obtained. The degree to which the formation of high molecular weight products can be curtailed by this means will be examined as a function of support pore size and composition, as well as reaction conditions.
Task 2: Electron Microscope Studies of Coal During Hydrogenation.  
Task Manager: J. W. Evans

A) Accomplishments

During this twelve-month period we have continued to use the transmission electron microscope, the scanning transmission electron microscope and optical microscopy to identify mineral matter in coal samples. A particular achievement has been concerned with the derivation of anatase which has been identified by other workers as a deactivating deposit on cobalt-molybdenum hydrodesulfurization catalysts used in coal liquefaction. Two hypotheses had been advanced to explain the origin of the anatase on the catalyst. One was that the titanium oxide originated from organically bonded titanium in the coal which in some way formed anatase during coal liquefaction. The second hypothesis was that the anatase was present in the coal as inorganic matter and found its way to the catalyst surface by merely physical processes. The second hypothesis was weakened by the fact that anatase had not been identified in coal.

We have now been able to identify anatase in a Kentucky bituminous coal by electron diffraction. (See Figure 1.) Deposits on catalyst particles used in liquefaction of the same coal also were found to contain anatase by electron diffraction. Furthermore, the particle size and morphology of the titanium containing mineral in the catalyst-deposit and the coal were similar. The implication is that the second hypothesis advanced above may be true and that catalyst life might be extended if physical techniques can be developed to remove the anatase particles from the coal prior to liquefaction. A full account of this work is contained in report LBL 13244.

Another achievement this year has arisen from an examination of the oriented graphite being used in Task 3 of this project to study the catalysis of gasification by alkali metal compounds. Examination of the graphite before and after partial gasification in the presence of potassium hydroxide suggests that gasification takes place within pits on the graphite surface. The pits contain particles presumed to be potassium compounds, and if this is the case, the dispersion of the catalyst particles on the graphite surface will have a significant influence on catalysis.

B) Plan for FY 1982

The major research activity in 1982 will be the use of the environmental cell in the Hitachi 650kV transmission electron microscope to observe reactions between carbonaceous materials (with and without catalysts present) and gasifying environments. Plans are to start with oriented graphite then later use coal char and finally coal. Gasifying atmospheres would be water vapour, hydrogen or mixtures of the two. Gaseous reaction products will be identified by analysis of the gas leaving the cell using the mass spectrometer. This will also permit a semi-quantitative measurement of reaction rate by simultaneously measuring the flow rate of gaseous reactant into the cell.

Some additional investigations of coal microstructure may be carried out as time permits.
Transmission electron micrograph of titanium containing particle in low temperature ashed coal with focused probe microdiffraction pattern identifying mineral as anatase.
Task 3: Catalysed Low Temperature Hydrogenation of Coal.
Task Manager: G. A. Somorjai

A) Accomplishments:

The major item of discussion concerns the reaction of carbon with steam in the presence of alkali and alkali compounds. Three reactions can take place. They are: 1) \(2 \text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2\); 2) \(\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2\), and 3) \(2 \text{H}_2\text{O} + 3\text{C} \rightarrow \text{CH}_4 + 2 \text{CO}\). In addition the water-gas shift reaction \(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\) can take place under the right conditions. In general equation 2 is favored by high temperatures in the range of 900 to 1,000°K. Reaction 1 is thermally neutral and can proceed at relatively low temperatures if catalysis assists kinetics. We have studied reaction 1 at temperatures in the range of 300 to 700°K and at pressures near 1 atmosphere using potassium, potassium compounds, and sodium, lithium and cesium and their compounds as catalysts. In the presence of water vapor, using graphite covered with potassium, methane is produced at the surprisingly low temperature of 500°K and this catalyzed methanation reaction continues for many hours without poisoning.

In our original experiments, an ultra high vacuum system as shown in Figure 1 was used. A pyrolitic graphite sample with a surface of about 1 cm\(^2\) was mounted on the manipulator of this system which gives a vacuum of about 10\(^{-9}\) torr. The sample surface is then accessible to surface composition analysis by Auger electron spectroscopy using a cylindrical mirror analyzer, ion sputter cleaning, and mass spectrometry. The system is also equipped with a high pressure cell which isolates the sample and allows us to perform chemical reaction studies at high pressures up to about 50 atmospheres. Product distribution obtained at high pressures can be monitored by a gas chromatograph with thermal conductivity detector.

The graphite samples are heated by resistant AC current and the sample temperature is monitored by a chromel allumel thermocouple in direct contact with the sample. In a number of cases, a monolayer of potassium was deposited on the graphite using a potassium zeolite gun at the background pressure of 1 x 10\(^{-9}\) torr. The sample was then exposed to a mixture of 30 torr of water vapor obtained from distilled water and 1 atmosphere of helium and heated to the desired temperature in this gas mixture. It should be noted that the only source of hydrogen and oxygen in the system was the water vapor since the high density graphite sample was free of hydrogen and of oxygen. The cleanliness of the graphite surface and the potassium surface concentration were monitored by Auger electron spectroscopy before and after the high pressure experiments.
Fig. 1
In the absence of the potassium catalyst, in other words in a blank experiment, no chemical reaction between graphite and water vapor is detected. In the presence of potassium, the production of methane can be readily observed. The concentrations of methane, CO₂ and CO produced during the reaction, were monitored as a function of time in the temperature range of 475 to 600°K. We were able to detect hydrogen among the reaction products, but due to the similarity of its thermal conductivity to that of the carrier gas, namely helium, it was difficult to quantitatively follow its concentration change. Figure 2 shows the build up of methane concentration for two temperatures, namely 475 and 523°K. From this figure and similar data obtained at other temperatures an activation energy for the production of methane of $10^3 + 3$ kilo calories per mole is estimated. Turnover frequency for the methane formation is calculated as $10^{-3}$/Sec. at 523°K assuming that all the graphite surface atoms are active.

The concentrations of CO₂ and CO which accumulated in the reaction chamber were about 10 to 30 times higher respectively than the methane concentration. In order to determine what other sources for formation of these reaction products were present in the high pressure chamber, several blank experiments were performed. A gold foil with and without potassium was substituted for the high density graphite sample in the chamber and the experiments were repeated using the same conditions as before. No methane could be detected under these circumstances. However, production of CO₂ and CO could be observed at rates which were not too different from those detected in the presence of graphite. It appears that the walls of the stainless steel reaction chamber must provide a source of carbon for CO₂ formation in the presence of water vapor. In order to obtain carbon mass balances for the graphite water reaction that produces methane, the CO₂ and CO produced by the blank studies must be subtracted from the total amount of CO₂ and CO detected under reaction conditions. The build-up of CO and CO₂ concentrations as a function of time obtained with the gold foil and with the graphite samples for two temperatures are displayed in the next two figures. In the case of carbon monoxide production, Fig. 3, the concentration appears to be independent of temperature and after subtracting the amount that was produced in the blank experiment, there is no carbon monoxide left within experimental error. However, the carbon dioxide concentration (Fig. 4) does depend on temperature and after subtraction of the amount produced in the blank experiments, some carbon dioxide still remains (as seen in Fig. 4) in a concentration which is stoichiometrically equivalent to the methane concentration produced at the same temperature.

It was found that the highest conversion to methane occurs at 523°K. At temperatures higher than that, the potassium surface concentration diminishes and the surface is covered with an increasing concentration of carbon monoxide as detected by Auger electron spectroscopy. At the same time the production of methane stops. However, when the CO is removed by argon ion bombardment or by thermal desorption, the production of methane starts up again. The production of methane is readily reproducible using a variety of graphite samples and different amounts of potassium. One can, for instance, dip graphite into potassium hydroxide solution to rule out the possibility that metallic potassium present on the surface would play a role in the formation of methane. In this case, the production of methane was in steady state for the length of the experiment (>24 hrs).
Fig. 3
Fig. 4
The effect of temperature on the reaction of potassium hydroxide impregnated graphite with water is shown in Fig. 5. There is always a rapid burst of methane in the first few minutes of operation before a steady state operation is obtained. In order to learn about the structure of the active graphite and the state of dispersion of KOH on the surface, samples of graphite coated with KOH were inspected by scanning electron microscopy before and after being exposed to reaction conditions. Initially, the KOH crystallites covered the surface of the graphite fairly uniformly forming a web-like network as seen in Figure 6A. After it is exposed to reaction conditions, KOH agglomerates forming crystallites of a few microns in diameter scattered all over the graphite surface as indicated in Figure 6B. Thus the KOH graphite contact area is markedly reduced. One can also notice in Figure 6B roughened patches that were absent before the water graphite reaction. These patches are perhaps the locations where graphite was chemically attacked and produced methane. The reduction in the contact surface is likely to be responsible for the reduced methane rate of production after an initial period and for the fact that steady state production is lower than an initial reaction rate. Long term reactions of up to 40 hours were carried out in a quartz reactor in which graphite powder impregnated with potassium hydroxide was exposed to helium saturated with water at 522°K. After a period of 1 minute, methane was readily detected.

Potassium carbonate on graphite gives essentially the identical pattern as does potassium hydroxide as shown in Figure 7.

Different samples of graphite coated with solutions of the hydroxides of lithium, sodium, and cesium, were studies at 522°K. All were good catalysts for the production of methane from water and graphite. The methane concentration at 522°K is plotted as a function of time in Figure 8. One can see that potassium, cesium and sodium hydroxides on graphite yielded nearly the same methane production rates in steady state but that the lithium hydroxide graphite is clearly more active. On the other hand, the initial rate of methane production follows the sequence cesium, potassium, sodium, and lithium from highest to lowest. It is, therefore, assumed that the rates of crystallization of the alkali hydroxides differ between different metals.

In summary, the production of gaseous methane and CO₂ or methane and CO from graphite occurs rapidly in the temperature range 500 to 650°K with a low activation energy in the presence of alkali compounds. As a catalyst, the alkali metal hydroxides and carbonates appear to catalyze both the reduction of carbon to methane and its oxidation to carbon monoxide or carbon dioxide. This is a process of considerable complexity that requires many sequential reaction steps. The dissociation of water to OH⁻ and H⁺ is clearly catalyzed by alkali hydroxides. This has been shown by studies of the photo-decomposition of water vapor on strontium titanate surfaces. This reaction proceeds at 300°K only in the presence of alkali hydroxides which catalyze the hydroxylation of the oxide surface. Thus, the alkali hydroxide aides what must be one of the first reaction steps, the dissociation of water on the graphite surface. The hydroxyl and hydrogen ions produced in this way then participate in multiple steps of oxidizing and reducing reactions. Hydrogen ions appear to form C-H bonds and OH ion is able to donate its oxygen to produce C-O bonds and eventually produce desorbed CO or CO₂. The presence of
Figure 6

(a) XBB 816-5635

(b) XBB 816-5635
Fig. 8

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Graph showing the reaction rate of CH\(_4\) molecules vs. time (min) for different alkali metal hydroxides and graphites.}
\end{figure}
high density oxygen-free graphite rules out the possibility that hydrogen or oxygen that appear in the final gaseous products, namely methane and CO₂, can come from sources other than the water molecules.
B) Plans for FY 1982

Further studies aimed at exploring the mechanism of this catalyzed reaction include attempts to detect CH$_x$ and COH intermediates by electron spectroscopy and exploration of the possibility of K intercalation into the graphite that may be an important reaction step needed to break the C-C bonds of the reactant efficiently. The use of alkaline earth compounds as possible catalysts will be investigated to optimize the activity of the carbon-water (C-H$_2$O) reaction. The combination of transition metals and alkali-metal compounds as catalysts should be explored in order to aid the formation of gaseous hydrocarbon molecules other than CH$_4$. 
Task 4: Selective Hydrogenation, Hydrogenolysis, and Alkylation of Coal and Coal Related Liquids by Organometallic Systems
Task Manager: K. P. C. Vollhardt

A) Accomplishments

a. The Reaction of Benzene With Aluminum Trichloride

In 1979 it was reported\(^1\) that certain transition metal carbonyls \(M_m(\text{CO})_n\) \((M = W, \text{Rh, Ru, Cr, Co})\) in the presence of \(\text{AlCl}_3\) catalyzed the so called Fischer-Tropsch alkylation of benzene. The reaction appeared of great significance since it was unprecedented and thought to be homogeneous.

We have found that alkyl benzenes are formed under the reported conditions. However, use of \(\text{D}_2\) does not give deuterated products. Similarly, application of \(^{13}\text{CO}\) does not result in (significant within the error limits of GC/MS) incorporation of the label. Moreover, neither CO or \(\text{H}_2\) nor the transition metal are necessary for formation of the observed products. Simply heating benzene and \(\text{AlCl}_3\) in a glass pressure vessel furnishes alkyl benzenes in addition to a variety of other products in rather similar proportions to those observed using literature\(^1\) conditions. Application of pressure reduces the number of products (resulting in cleaner GC traces) and their overall yield. A typical GC trace of the reaction of benzene with \(\text{AlCl}_3\) is shown in Figure 1.

In the presence of \(\text{W}(\text{CO})_6\) (even more so with added diphos) we observe significant amounts of diphenylmethane. The \(\text{W}(\text{CO})_6\)-diphos system furnishes much more isopropyl than \(\pi\)-propylbenzene. Other Lewis acids such as \(\text{FeCl}_3\) and \(\text{AlEt}_2(\text{OEt})\) were inactive, \(\text{AlEt}_2\text{Cl}\) was weakly active.

The major product of the reaction of benzene and \(\text{AlCl}_3\) (0.18M) at reflux temperature is phenylcyclolhexane. At higher \(\text{AlCl}_3\) concentration increasing amounts of alkylbenzenes (mainly toluene and ethyl benzene) are observed suggesting the possibility that phenylcyclolhexane as a primary product undergoes cracking reactions to the observed volatile products. However, at higher temperature the reaction is complicated by condensations, secondary cracking, and catalyst deactivation, most likely by \(\pi\)-complexation to higher benzenoids (Figure 2). Such complexation evidently prevents further turnover of benzene and its reaction products. Addition of more \(\text{AlCl}_3\) leads to a new spurt in benzene turnover. The hydrogen necessary for alkyl-benzene production is envisaged to arise via \(\pi\)- and polyphenyl formation, as well as Scholl-type condensation reactions.\(^2\) Further evidence for the intermediacy of phenylcyclolhexane is derived from the observation of very similar product formation to that depicted in Figure 1 on its reaction with \(\text{AlCl}_3\).

The major alkylbenzene products are toluene and ethyl benzene. This is consistent with the fact that \(\text{AlCl}_3\) catalyzes the cleavage of diphenylalkanes to alkylbenzenes and that the higher members of the latter are fragmented to the above products. The finding that no xylenes and poly-substituted benzenes are detected is most likely due to the low turnover of the reaction. Thus, such products do appear when toluene and other alkylbenzenes react with \(\text{AlCl}_3\).
A typical GC trace of the products from the reaction of benzene and \( \text{AlCl}_3 \) \([\text{AlCl}_3] = 0.7 \text{M}, \text{N}_2 \) (1 atm), 160\(^\circ\)C, 48h). 1 = toluene, 2 = ethylbenzene, 3 = isopropylbenzene, 4 = \( n \)-propylbenzene, 5 = butylbenzenes, 6 = tetralin, 7 = phenylcyclohexane, 8 = biphenyl, 9 = diphenylmethane, 10 = 1,2-diphenylethane. 1-10 were identified by GC/MS and coinjection of authentic samples. Other minor products were (GC/MS computer library): methyl-, dimethyl-, and ethyltetralins, phenylcyclopentaene, fluorene, methyl- and ethylbiphenyl, 1,1-diphenylethane, phenylnapthalene, and phenyltetralin. The shoulder in peak 4 could not be resolved.
Figure 2. Plot of relative molar ratio of selected products versus reaction time in the AlCl₃/benzene reaction ([AlCl₃] = 0.7M, N₂ (1 atm), 160°C, 48h). n-Octane was used as internal standard. Different scales have been used for clarity. The smooth curves are drawn arbitrarily.
In order to shed further light on the mechanism of the benzene cleavage-hydrogenation process several additional labeling experiments were run. Reaction of C₆D₆ gave completely labeled products. A 1:1 mixture of C₆H₆ and C₆D₆ gave complete scrambling. An equimolar mixture of C₆H₆ and ¹³C₆J₆ (90 percent enriched) was exposed to AlCl₃ [N₂ (1 atm), 160°, 48h]. Surprisingly, ¹³C⁻¹²C exchange (ca. 5 percent) is observed in recovered "unreacted" benzene and additional scrambling in all other volatile products as analyzed by GC/MS. Despite this perturbation, the mass spectral peak patterns indicate substantially intact incorporation of alkyl chains derived from the original benzene ring. Thus, the connectivity of the initial carbon arrays is extensively preserved in the alkylbenzenes (including annulated and cycloalkylbenzenes) formed. Processes such as those described here must play a significant role in any reaction that attempts to liquify coal in the presence of Lewis acids.
Diastereomeric 1,2-bis(trimethylsilyl)-3-alkycyclobutadiene cyclopentadienyl cobalt complexes 1 and 2 (see Scheme) in which the alkyl group contains a chiral center may be synthesized, separated, and equilibrated in the gas phase at 540-650° by flash pyrolysis or in solution in refluxing pristane (301°C). The process is unimolecular as shown by crossover experiments and kinetic analysis. Isomerization occurs by inversion at the four-ring, demonstrated by the pyrolysis of complexes enantiomerically enriched at the chiral carbon center and analysis of the products by optically active NMR shift reagents. No other processes but diastereoisomerization are observed in solution. In the gas phase increasing temperatures lead to increasing decomposition of starting complexes to cobalt metal and alkynes derived by retrocyclization of the cyclobutadiene ligand, in addition to positionally isomerized complexes. Such positional isomerization proceeding through B is also the mechanism of diastereoisomerization as shown by the pyrolysis of 1-triethylsilyl-2-trimethylsilyl substituted (1d → 2d); (1e → 2e) and 13C-labeled complexes. The data strongly imply that the cyclization of alkynes to cyclobutadienes in the coordination sphere of cobalt is reversible. They do not necessitate the intermediacy of a metallacycle A, which, if present, would have to be configurationally stable (i.e., the n5-C5H5 ligand has to remain on one face of the other π-ligand). This constitutes the first demonstration of reversible alkyne formation from cyclic π-systems in the coordination sphere of metals and suggests experiments aimed at aromatic hydrocarbon activation.
c. Models for Metal Catalyzed Thermal Hydrogen Shifts

In an effort to determine the potential feasibility of a metal catalyzed (reversible) ring opening reaction of the type $3 \rightleftharpoons 4$, we have uncovered a novel rearrangement to the binuclear systems $5$ and $6$. The structures of $5$ and $6$ have been determined (see figures 3 and 4) by X-ray analysis.
The exact mechanism of these transformations is not understood. However, it is clear that the metal is capable of effecting a remarkably facile hydrogen shift from a vinyl position to another sp²-hybridized carbon (e.g., $3 \rightarrow 5$). Moreover, subsequently the metal enables the migration of a vinyl hydrogen to a metal bound carbene center (e.g., $5 \rightarrow 6$). Inasmuch as the dinuclear metal fragment might serve to mimic a metal surface, this system appears to be a good model for the heterogeneously catalyzed hydrogen migration in coal related structures.
d. Preparative Separation of Organometallic Compounds by High Performance Liquid Chromatography

Successful separations of complex mixtures of organometallic compounds by chromatography are rare. However, high performance reversed phase liquid chromatography (HPLC) of isomeric $\eta^5$-cyclopentadienyl-$\eta^4$-cyclobutadiene cobalt complexes, and of structurally analogous dinuclear molybdenum derivatives has been achieved. Although some of these compounds are moderately to strongly air-sensitive, quantitative isolation on a preparative scale is possible by using deoxygenated and argon saturated mobile phases. Among the organometallic complexes resolved are diastereomers and structural isomers; their separation demonstrated both the versatility and high resolving power of HPLC (Figs. 5-8). All separations were accomplished using 10 mm x 250 mm ULTRASPHERE ODS columns (sample Loop 1 ml). Conditions are specified in the figure captions. Initial gravity elution chromatography of the compounds shown gave inseparable mixtures.
Fig. 5. Chromatogram of 5 to 10 mg of a mixture of (I)-(III) in 1.0 ml; flow 1.3 ml/min; CH$_3$CN-H$_2$O, 9:1.

Fig. 6. Chromatogram of 5 to 10 mg of a mixture of (IV)-(VII) in addition to other compounds in 1.0 ml; flow 2.8 ml/min; CH$_3$OH-H$_2$O, 19:1.
Fig. 8. Chromatogram of 5 to 10 mg of a mixture of (I), (II), and (VIII) in 1.0 ml; flow 3 ml/min; CH$_3$OH-H$_2$O, 9:1. This separation necessitated the coupling of two preparative columns in series.

Fig. 8. Chromatogram of 5 to 10 mg of (IX)-(XIV) in 1.0 ml; flow 0.5 ml/min; CH$_3$OH-H$_2$O, 5:1.

B) Research Plans for FY 1982

The Lewis acid catalyzed cleavage and alkylation of benzene will be investigated in great detail. Scope and limitations will be explored with a variety of substrates, particularly substituted benzenes and higher condensed aromatic molecules. Heteroaromatic systems will be exposed to similar reaction conditions. The mechanism of the reaction will also be subjected to scrutiny, using kinetic and labeling techniques.

We will begin an investigation of the potential use of transition metals as catalysts and/or reagents in the cleavage of aromatic carbon-carbon bonds with the particular aim to effect hydrogenation and hydrogenolysis.

We will continue our work concerned with delineating mechanism and scope of transition metal mediated hydrogen shifts of organic $\pi$-ligands.
Task 5: Chemistry of Coal Solubilization and Liquefaction. Pyrolysis Studies.

This task was divided during the year. Part A-I was carried out with R. B. Bergman as Task Manager and Part B-1 with T. Vermeullen and R. Fish as Task Managers.

A-I) Accomplishments

(1) We have found that unsaturated compounds of general structure 1 (Scheme 1) undergo a thermal rearrangement which interchanges the vinyl and acetylenic carbons in these molecules. Studies of these reactions have revealed that "1,4-dehydrobenzene" diradicals are involved as intermediates; the products isolated may be derived from either unimolecular or bimolecular reactions of the intermediate. In this work, we have found that (Z)-4,5-di-ethynyl-4-octene (2) undergoes rearrangement to yield 2,3-di-n-propyl-1,4-dehydrobenzene (3). Solution pyrolysis of 2 in inert aromatic solvents produces three unimolecular products, (Z)-dodeca-4,5-diyn-6-ene (4), benzo­cyclooctene (5), and o-allyl-n-propylbenzene (6), in high yield. When 1,4-cyclohexadiene is added to the pyrolysis solution as a trapping agent, high yields of the reduced product o-di-n-propylbenzene (7) are obtained. The kinetics of solution pyrolysis of 2 in the presence and absence of trapping agent establish that 2,3-di-n-propyl-1,4-dehydrobenzene is a discrete intermediate on the pathway leading to products. When the reaction was run in the heated probe of an NMR spectrometer, CIDNP was observed in 6. This observation, along with kinetic and chemical trapping evidence, indicates the presence of two additional intermediates, formed from 3 by sequential intramolecular [1,5] hydrogen transfer, on the pathway to products. The observation of CIDNP, coupled with the reactivity exhibited by 3 and the other two intermediates, implicates a biradical description of these molecules. Biradical 3 has been estimated to have a lifetime of about $10^{-9}$ s at 200°C and to lie in a well of about 5 kcal per mole with respect to the lowest energy unimolecular pathway ([1,5] hydrogen transfer). Ring opening (expected to be the lowest energy processes of 1,4-dehydrobenzenes in which intramolecular hydrogen transfer is unlikely) to the isomeric diethynyl olefin 4 appears to have an activation enthalpy of about 10 kcal/mol.
Scheme 1

1. \[ \begin{align*}
&\text{CH}_3 \\
&\text{CH}_3
\end{align*} \]

2. \[ \begin{align*}
&\text{CH}_3 \\
&\text{CH}_3
\end{align*} \]

3. \[ \begin{align*}
&\text{CH}_3 \\
&\text{CH}_3
\end{align*} \]

4. \[ \begin{align*}
&\text{CH}_3 \\
&\text{CH}_3
\end{align*} \]

5. \[ \begin{align*}
&\text{CH}_2 \\
&\text{CH}_3
\end{align*} \]

6. \[ \begin{align*}
&\text{CH}_2 \\
&\text{CH}_3
\end{align*} \]

7. \[ \begin{align*}
&\text{CH}_2 \\
&\text{CH}_3
\end{align*} \]

8. \[ \begin{align*}
&\text{CH}_2 \\
&\text{CH}_3
\end{align*} \]
Two approaches have been used to investigate the spin state(s) of the 1,4-dehydrobenzene diradicals. One method relies on the "spin correlation effect" which postulates a relationship between the spin state of a caged radical pair and the ratio of cage and escape reactions (C/E) which may occur in the pair. When the 2,3-di-n-propyl-1,4-dehydrobenzene biradical (3) abstracts hydrogen from 1,4-cyclohexadiene, a radical pair is generated. If a mixture of 1,4-cyclohexadiene-d0 and -d4 is employed, it is possible, by performing a VPC-MS analysis, to determine the C/E ratio leading from the radical pair to the reduced product, o-dipropylbenzene (7). When this method was applied to the reaction of (Z)-4,5-diethynyl-4-octene (3), C/E was found to be 0.6, independent of the concentration of 1,4-cyclohexadiene (between 0.1 and 10M) in the chlorobenzene reaction solution. This result indicates the presence of the singlet state of 3 in the reaction of 2. Additional support for this analysis came from the reaction of 3,4-dimethyl-1,5-hexadiyn-3-ene in hexachloroacetone solvent in a 1H NMR probe. The single polarized signal (emission) observed is attributed to the major product of the reaction, 1,4-dichloro-2,3-dimethylbenzene, obtained by chlorine abstraction from the solvent. The interpretation of this result indicates solvent trapping of the singlet state of the intermediate 2,3-dimethyl-1,4-dehydrobenzene, consistent with the chemical trapping study. These experimental approaches indicate that at least a substantial portion of the products formed from 1,4-dehydrobenzenes at elevated temperatures arise from the singlet state of the biradical. This suggests that either the singlet is the ground state, or, if the triplet is lower in energy, the rate of intersystem crossing from the singlet must be < 10^9 s^-1 at 200°C.

(2) In an effort to investigate the reactivity of highly energetic organic molecules, we have examined the laser-powered dissociation of the aromatic hydrocarbon tetralin (8), employing infrared multiphoton excitation and SiF4-sensitized infrared thermal activation. The excitation source for these experiments was a grating tuned CO2 TEA laser.

Six major products (Scheme 2) were formed upon energization by infrared multiphoton excitation and SiF4-sensitized pyrolysis. Three of these, benzocyclobutene (9), o-allyltoluene (11), and 1,2-dihydronaphthalene (13), appear to be primary dissociation products. The lowest energy reaction channel is the ethylene-loss channel resulting in benzocyclobutene. The ring cleavage channel, giving rise to o-allyltoluene, has not been previously observed. Isotope labelling studies were performed which demonstrated that the dehydrogenation reaction, which forms 1,2-dihydronaphthalene, results primarily in loss of hydrogen from C-1 and C-2 and is predominantly a non-corrected hydrogen elimination. We believe that in previous studies by other workers, where dehydrogenation was reported as the primary dissociation channel, the experiments were complicated by surface catalysis. In the laser-induced reactions, which are uncomplicated by problems due to surface catalysis, the true homogeneous decomposition takes place, and this involves primarily ethylene loss.

(3) Chemical activation of tetralin was investigated by using three different unimolecular isomerization reactions, each giving rise to 8 at different levels of internal energy. The three precursors to activated tetralin (8*, Scheme 3) were dispiro[2.0.2.4]deca-7,9-diene (15),
Scheme 2
Scheme 3

\[
\begin{align*}
\text{Et} & \quad \rightarrow & 9 \\
\text{Et} & \quad \downarrow & 16 \\
\text{Et} & \quad \downarrow & 15 \\
\text{Et} & \quad \downarrow & 8^* \\
\text{Et} & \quad \downarrow & 17 \\
\text{Et} & \quad \downarrow & 10 \\
\text{Et} & \quad \downarrow & 8 \\
\text{Et} & \quad \downarrow & 9 \\
\text{Et} & \quad \downarrow & 10 \\
\end{align*}
\]
Z-hexa-2,3-diethyl-1,5-diyne-3-ene (16), and 3,3'-tetramethylenebicyclopropenyl (17). Isomerization of 15 gave rise to no reaction from excited tetralin at the pressures studied here, even though the excess internal energy (103 kcal/mole) was approximately 33 kcal above the barrier to dissociation. Isomerization of 16 gave benzocyclobutene (9), the reaction product expected from activated 8, but no pressure dependence on the product yields was observed. The benzocyclobutene formed in this isomerization appears to be derived from an intermediate on the pathway to 8. Isomerization of 17 gave three reaction products, benzocyclobutene (9), styrene (10), and tetralin (8). Tetralin is the exclusive product at high pressures and benzocyclobutene and styrene appear at low pressures. For this reaction, activated 8 was estimated to be formed with approximately 165 kcal excess energy. The decomposition-to-stabilization ratios at different pressures could be reproduced using a step-ladder deactivation model and rate constants calculated using RRKM theory. The styrene formation in this isomerization reaction has not been conclusively identified, although labelling studies showed that it was not a product derived from the normal thermal dissociation of 8.
A-2) Plans for FY 1982

Work on the decomposition of organic materials is now largely complete. Studies of the tetralin decomposition have convinced us that many earlier investigations of the apparent thermal decomposition of this material (and presumably of other hydrocarbons at high temperatures) are predominantly or exclusively catalyzed processes, rather than simple unimolecular decompositions. Since there are many trace metals in coal, it seems likely that many hydrogen transfer processes which occur during coal pyrolysis and liquefaction are also mediated by either homogeneous or heterogeneous catalysts. From a fundamental research point of view, despite the great deal of activity that has been directed toward understanding the mechanism of homogeneous hydrogenation of organic compounds using transition metal complexes and H₂, the related process of transfer hydrogenolysis (i.e., reactions in which a second organic molecule, rather than H₂ gas, acts as the hydrogen donor) has seen very little study. Our plans for FY 1982, therefore, are to move into the area of metal-catalyzed transfer hydrogenation. We plan to begin by investigating metal complexes which serve either as hydrogenation or dehydrogenation catalysts, and determine whether they will function as transfer hydrogenation agents. If we are successful in finding workable systems, we will then investigate their mechanisms with an eye toward understanding the transfer hydrogenation in general, and improving the efficiency of the catalysts which are uncovered.
B-1) Accomplishments

Reactions of catalytic amounts of transition metal carbonyl compounds of Fe, Mn, Co, Ru, Rh, Re, Os, Cr, W and Mo, under water gas shift (WGS) conditions (CO, H₂O, base), with model coal compounds such as anthracene, phenanthrene, pyrene, acridine, quinoline, 5,6, and 7,8 benzoquinoline indicates that only Fe and Mn carbonyls react to any significant extent to produce partially hydrogenated analogs of these model coal compounds.

We have determined that carbon monoxide, in many cases, inhibits the reaction of the model coal substrate with catalytically generated transition metal carbonyl hydrides. Pertinent examples of CO inhibition that vividly make this point clear are those reactions with mononuclear and trinuclear ruthenium carbonyl compounds.

In these two cases, the use of carbon monoxide completely inhibits substrate binding to a presumed coordinatively unsaturated ruthenium carbonyl intermediate. Interestingly, dimanganese decacarbonyl catalyzed reactions are not affected by the use of carbon monoxide and establish the mechanistic differences between Mn and Ru carbonyls.

In the former example [Mn(CO)₈(PBu₃)₂], reactions were carried out under either WGS (CO, H₂O, base) or Syn Gas [CO, H₂, 1:1] conditions with 9,10-dimethyl-anthracene to provide a mixture of cis and trans-9,10-dimethyl-9,10-dihydro-anthracene compounds. This result is indicative of a free radical mechanism where both cis and trans 9,10-dimethyl-9,10-dihydroanthracene would be expected to be produced.

The reactions of either RuCl₂(CO)₂(η₃P)₂ or Ru₃(CO)₁₂ (as well as Bu₃P substituted analogs) under hydrogenation conditions [RuCl₂(CO)₂(η₃P)₂ needs base present], such as 350 psi H₂, sub/cat = 30, in THF for 2 hr, at 180°C, gives quantitative yields of partially reduced analogs of PNA and PNHA (nitrogen is the heteroatom) compounds. Coal model compounds that were used in this aspect included anthracene, phenanthrene, pyrene, acridine, 5,6 and 7,8 benzoquinoline, quinoline and pyridine.

B-2) Plans for FY 1982

Since we have been successful in studying reactions of polynuclear aromatic and heteroaromatic compounds, under homogeneous catalytic hydrogenation conditions with mononuclear, di and trinuclear transition metal carbonyls, we plan to pursue the mechanistic aspects of these important reactions and expand its use to other heteroatom polynuclear aromatic compounds of sulfur and oxygen. Additionally, the "heterogenizing" of homogeneous catalysts such as ruthenium carbonyls will be explored to ascertain if this form of the catalyst is active with model coal compounds.
Petroleum residua and coal derived liquids must be hydrotreated to remove sulfur and nitrogen compounds. These liquids also contain metals, typically vanadium, titanium, nickel and iron. Deactivation is in part, caused by the deposition of these metals on the exterior parts of the catalysts where they serve to block the access of sulfur and nitrogen compounds to the active regions of the interior. One objective of this study is to measure changes in the global rates of demetallation and desulfurization with time on stream. A second objective is to measure the amount and distribution of these metals on the catalyst with time on stream using an electron micro-probe. The latter measurements also permit determination of any migration of the active components of the catalyst under operating conditions.

A) Accomplishments

Progress towards the first objective has been made from a series of runs between 1 and 32 hours of operation at 350°C and 800psi hydrogen on a presulfided catalyst. We used a batch reactor operated in a semi-continuous manner; i.e., metal concentration was maintained at a high level by frequent injections of vanadyl naphthenate to the sour gas oil in the reactor.

We now measure metal concentrations in the liquid by atomic adsorption (Perkin Elmer 4000 AA spectrophotometer) because it is much faster, less expensive and more reliable than X-ray-fluorescence. Samples were diluted 1:10 with xylene and aspirated into an acetylene-nitrous oxide flame thus avoiding time consuming ashing and acid dissolution procedures that results in metals loss through volatization. The instrument was calibrated using NBS organometallics. Sulfur concentrations were determined by a standard microcombustion procedure.

From an analysis of the liquid metal concentrations at the beginning of the experiment and before and after each injection of metal, the global rate of demetallation can be estimated during the period between injections. Also, using a similar technique, the global rate of hydrodesulfurization is measured.

Under the mild conditions used, we have found that the global rates of demetallation and desulfurization remain approximately constant after 32 hours—the catalyst has not deactivated appreciably in that period.

A series of samples of catalyst having a history of 1 through 32 hours on-stream were prepared for, and analyzed with the electron microprobe. Profiles of vanadium within the pellets are shown in Figure 1. The figure clearly shows the highest concentration at the edge of the catalyst and a progressive accumulation with time on-stream. The rate of vanadium deposition is much slower than found for an unsulfided catalyst presented previously. This is in agreement with results of other investigators (Hung and Wei, Takatsuka, et al.). A cross-plot of these profiles as shown in Figure 2 shows the change in metal content at a given radial position as a function of time. The local rate of demetallation is given by the slope of this curve at any given time. Clearly, the local demetallation rate decreases significantly at the exterior of the catalyst.
Approximate atomic % vanadium

Distance from catalyst exterior (μm)

Figure 1  Vanadium concentration as a function of distance
Figure 2 Vanadium concentration as a function of exposure time
Unfortunately, we cannot use the same technique to obtain local values of the desulfurization rates. In order to learn more about the relationship between local desulfurization rates and demetallation rates, we are developing models of the process.

The first phase of the modeling program is nearly completed. In this phase, the various combinations of the possible kinetic rate laws for the desulfurization and demetallation reactions have been screened. The rate laws under consideration are first order in hydrogen and first or second order in the sulfur species for desulfurization; first order in \( \text{H}_2\text{S} \) and first or second order in the metal species for demetallation. The question of first or second order results from the large diversity of the sulfur or metal-bearing reactants which are present in the heavy residue or coal liquids. For individual compounds the kinetics are first order for the sulfur species and are in question for the metal species although a recent paper (Rankel) gives data which indicates first order reaction. The governing equations have been formulated and are being programmed for solution.

References


B) Research Plans for FY 1982

Our short term plans are to continue a series of similar experiments to those already carried out, but at much more stringent conditions; i.e., higher metal concentrations, higher temperatures and longer times. The objective of these studies is to deactivate the catalyst sufficiently to observe changes in the global rates of demetallation and desulfurization. These deactivated catalysts will be subjected to electron microprobe measurements, and transient diffusion measurements as well as more traditional surface area, porosimetry, and pore volume measurements to evaluate the chemical and physical factors contributing to deactivation.

All of the results to date have been obtained using vanadyl naphthenate. We envision a series of runs using vanadyl tetraphenylporphyrin to compare with the naphthenate results. We also envision a similar series using analogous titanium compounds. Although these metalloporphyrins are more representative of the metal constituents of resida and coal derived liquids, their solubility in hydrocarbon solvents is limited. The above will be run in steady-state experiments rather than semi-batch. Also, to make the desulfurization global activity measurements easier, we plan to add dibenzothiophene as the sulfur component.
One important objective of the modeling is to try to understand the maximum in the metal profiles found in industrial samples. Earlier studies (Tamm, et al.) have shown a peak in the metal content quite close to, but removed from, the particle surface. This suggests a reaction of the metal bearing species with the $H_2S$ product of the desulfurization reaction. This conclusion has been supported in Rankel's paper.

The second phase of the modeling program will be extended so that metal accumulation with time can be calculated. It is anticipated that the reduction of pore radius and the consequent reduction of metal species diffusivity will further sharpen the peak in the metal profile.

In summary our goal is to relate desulfurization catalyst deactivation to metals deposition on the catalyst. Our experimental and modeling results to date indicate the promise of the approach being used to achieve the project's objectives.
VI FY 1981 Publications

The following literature and LBL publications based on work under this program have appeared during the report year:


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