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CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
QUARTERLY REPORT: January 1 to March 31, 1982

Heinz Heinemann

April 1982

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QUARTERLY REPORT
January 1 to March 31, 1982

Chemistry and Morphology of Coal Liquefaction

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II Technical Program for Fiscal 1982

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

Analytical methods will be developed to better define product distribution in each carbon number product (n/i ratio, paraffin/olefin ratio) and to test the Schultz-Flory theorem for each hydrocarbon type. This will also permit distinction between primary and secondary products. The extent of olefin saturation and hydrogenolysis will be investigated. 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 - J. W. Evans

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 gases. Plans are to start with oriented graphite then later use coal char and finally coal. Gaseous atmospheres would be water vapour, hydrogen or mixtures of the two. 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.

Task 3 - Catalysed Low Temperature Hydrogenation of Coal - G. A. Somorjai

Exploration of the mechanism of alkali catalyzed reactions of carbon and steam will include attempts to detect CH_x and COH intermediates by electron spectroscopy and exploration of the possibility of alkali 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 ($\text{C-H}_2\text{O}$) reaction. The combination of transition metals and alkali-metal compounds as catalysts should be explored in order to aid the formation of hydrocarbon molecules larger than CH_4 .

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

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.

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 will be begun.

Work will continue concerned with delineating mechanism and scope of transition metal mediated hydrogen shifts of organic π -ligands.

Task 5 - Chemistry of Coal Solubilization and Liquefaction - R. G. Bergman,
T. Vermeullen and R. H. Fish

Plans for FY 1982 are to move into the area of metal-catalyzed transfer hydrogenation. We intend 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.

Further work will be done on the important selective hydrogenation of N-containing rings in polynuclear aromatic hydrocarbons with homogeneous catalysts, discovered in 1981. In particular, the question of catalyst recovery, e.g., by heterogenizing the metallo-organic complex will be investigated.

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

Short term plans are a series of experiments similar 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. The 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 residua and coal derived liquids, their solubility in hydrocarbon solvents is limited. Steady-state experiments rather than semi-batch will be used. Also, to make the desulfurization global activity measurements easier, we plan to add dibenzothiophene as the sulfur component.

III Highlights

1. All tasks of this project were active in the second quarter of fiscal 1982 and four publications based on this work have been submitted to refereed journals.
2. Studies in the environmental cell of an electronmicroscope dramatically demonstrate the catalytic nature of the reaction of steam and graphite in the presence of alkali at relatively low temperatures, supplementing and reinforcing previous findings by surface science tools. Reaction proceeds on the alkali-carbon interface.
3. While no higher hydrocarbons than CH_4 have yet been produced from steam and carbon, mechanistic considerations for such a production are encouraging.
4. Impregnation of graphite with calcium oxide followed by reaction with water gave quite different results than impregnation with potassium hydroxide. While little, if any methane was produced in the presence of CaO , the graphitic carbon was converted at about 500°C to a very reactive "carbide" type carbon, which readily produced methane when reacted with hydrogen. Indications are that this conversion of unreactive to reactive carbon underlies all catalysed steam-carbon reactions.
5. Hydrogenation of a series of aromatic model compounds containing nitrogen in one of the rings, using "Wilkinson's catalyst" at mild conditions (250 psig 150°C) results in 100% selectivity at high conversion to hydrogenation of the nitrogen containing ring only. Catalytic cracking of the products should remove nitrogen as ammonia and result in saving more than 60% of the hydrogen currently required to remove nitrogen. The reaction is more specific to nitrogen than to sulfur. Work is underway to use an immobilized heterogeneous catalyst.
6. Kinetics of the formation of various hydrocarbons in a Fischer-Tropsch slurry reactor have been determined. It was found that production of light gases (particularly CH_4) can be suppressed by using high CO partial pressures.
7. Studies of adding small olefins to the Fischer-Tropsch synthesis showed that these olefins do not enter very efficiently into the chain growth process and may even undergo hydrogenolysis.
8. Hydrogen in the presence of platinum has been found to significantly suppress polymer formation in the aluminum chloride catalyzed cracking of saturated and benzenoid hydrocarbons.

Kinetic studies and labeling experiments have allowed an initial delineation of the mechanism of a remarkable cobalt mediated vinyl-hydrogen activation process.

IV Progress of Studies

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

The chromatographic system used to analyze the products of Fischer-Tropsch synthesis has been optimized so that a complete on-line analysis can be carried out of virtually all products. A 1/8-in by 9 ft. column packed with Chromsorb 106 is used to separate CO, CO₂, C₁ through C₅ hydrocarbons, as well as acetaldehyde and acetone; C₄ through C₃₀ hydrocarbons and oxygenates are separated on a 50 m glass capillary column coated with OV101. The retention times of major products have been identified by GC/MS.

A series of experiments have been carried out using the slurry reactor, to establish the effects of H₂ and CO partial pressures on the reaction kinetics and product selectivities. These studies were conducted at 242°C, and with space velocities high enough to maintain differential conversions of CO. The kinetics of forming α -olefins and normal paraffins, the principal synthesis products, are roughly first order in H₂, independent of the carbon number. The rates of forming C₅₊ products are zero order in CO partial pressure. An inverse CO dependence is observed for C₁ through C₄ hydrocarbons, which is most pronounced for methane. For a H₂ partial pressure of 10 atm, the rate of methane formation decreases by a factor of about two as the CO partial pressure is increased from 2 to 10 atm. The significance of this observation is that the production of light gases can be suppressed by using high CO partial pressures. Further exploration of this effect will be undertaken to establish whether the relative production of C₁ to C₄ hydrocarbons can be further affected by temperature and H₂/CO ratio.

The influence of CO conversion on the distribution of synthesis products formed over a precipitated iron catalyst were investigated using the fixed reactor system. These experiments were carried out at a pressure of 5 atm and a temperature of 305°C, using an H₂/CO ratio of 2. The CO conversion was increased from 1 to 10% by decreasing the gas flow rate from 120 to 20 cm³/min/g cat. The distributions of α -olefins and normal paraffins were represented on plots of $\log (R_C / R_{C_1})$ versus n, where R_{C_i} is the rate of formation of a product containing n carbon atoms. For each of the flow rates examined, the distribution of olefins and paraffins could be described by two straight lines. The magnitude of the slope of the line passing through the C₁ through C₇ products is larger than the magnitude of the slope passing through the C₈ through C₁₂ products. This type of product distribution was found consistently, and the slope of each branch was independent of CO conversion. Based on these observations, it is concluded that the catalysts contains two types of sites characterized by different α values. The origin of the two types of sites is very likely the maldistribution of the potassium promoter over the surface of the catalyst.

Experiments were also conducted to test whether the feedback of olefins could be used to alter the product distribution. For these runs, the fixed bed reactor was operated at 305°C and 5 atm, using a H₂/CO of 2 in the feed gas. To simulate olefin feedback, 5% of ethylene, propylene, or cis-2-butene was added to the synthesis gas feed. It should be noted that the concentration of added olefin is much greater than that present due to synthesis alone.

Careful analysis of the products shows that the addition of ethylene causes a 60% increase in the production of propylene and no more than a 10% increase in the production of butenes. The balance of the products are unaffected by ethylene addition. The addition of propylene causes a 15% increase in the formation of butenes and a slight increase in the formation of ethylene, but has no other effect. The only effects of cis-2-butene addition are a 40% increase in propylene formation and a slight increase in ethylene formation. From these results, it is concluded that small olefins do not enter into the chain growth process very efficiently, and in fact may undergo hydrogenolysis to produce lower molecular weight products.

Task 2 - Electron Microscope Studies - J. W. Evans and D. J. Coates

In conjunction with work performed under Task 3, in-situ carbon-gas reaction experiments have been carried out in the environmental cell of a high voltage transmission electron microscope. The catalytic reaction of carbon and steam is under investigation and results of experiments using potassium hydroxide as a catalyst are reported. Thin film specimens were cleaved from a block of highly oriented pyrolytic graphite, supported on copper grids, dipped in a 0.38M solution of KOH and allowed to dry. Specimens were then placed in the environmental cell of the HVTEM. Water vapour, in an argon carrier gas, was introduced into the environmental cell at 500 Torr total pressure. The graphite specimen was observed periodically as it was heated. At room temperature the KOH was present mainly as a film covering the surface of the carbon, with occasional discrete particles present. No difference in the morphology was noticed until the temperature had risen to about 500°C when the film coalesced, giving a dispersion of particles 0.1-1.0µm in diameter on the carbon surface. Particles at the edges of the graphite crystals then started moving toward the centre of the crystals leaving channels behind them.

Figure 1 shows the same region at 500°C after a) 22 min., b) 26 min., and c) 33 min. exposure to the argon-water vapour mixture. Figure 1 a) shows a number of channels emanating from the edges of two adjacent graphite crystals, with particles of the catalyst material at the head of each channel. With further exposure to the water vapour (Figures 1b and 1c) the length of the channels increase, as the carbon in contact with the catalyst particles is gasified. This can be clearly seen by the channels arrowed. Another feature observed at longer exposure times is the fact that KOH particles lying on the surface of the graphite crystals also eventually cause catalytic gasification. Thus, in Figure 1 a) the surface of the carbon is covered by a dispersion of particles showing distinct outlines. At a later stage (Figure 1b) the particles have a diffuse outline and later still (Figure 1c.) holes or pits are evident in the graphite surface at the sites of the particles. The catalytic material is present within the pits and in some cases catalytic channeling by these particles away from the original pits is evident.

Similar work has been carried out using NaOH as a catalyst. Channeling of the graphite was evident at 600°C, again with catalyst particles at the heads of the channels. Since work in Task 3 had shown methane production reaching a steady state at 225-300°C electron microscope observations will be undertaken at this temperature.

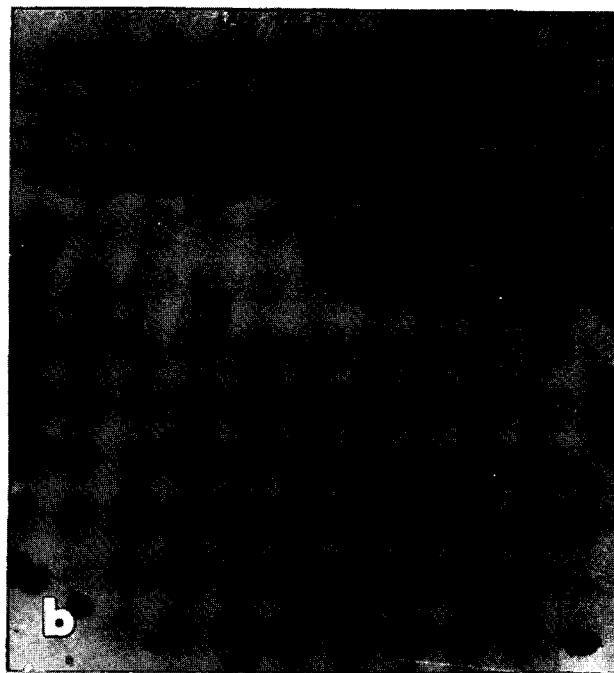
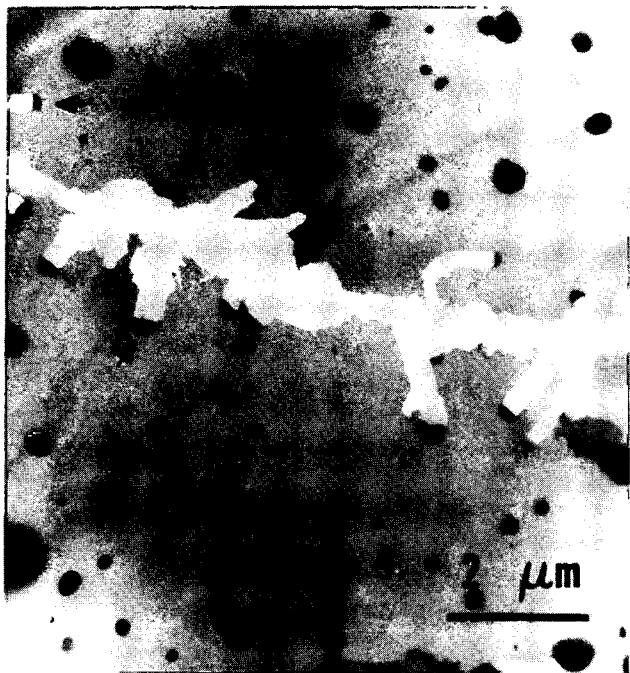


Figure 1

XBB823-2027

Task 3 - Catalysed Low Temperature Hydrogenation of Coal - G. A. Somorjai with
A. L. Cabrera

Further insight into the low temperature (225-300°C) reaction of graphite with steam in the presence of alkali metal and its mechanism has reinforced the belief that it should be possible to produce higher hydrocarbons than CH₄, even though this has not yet been accomplished.

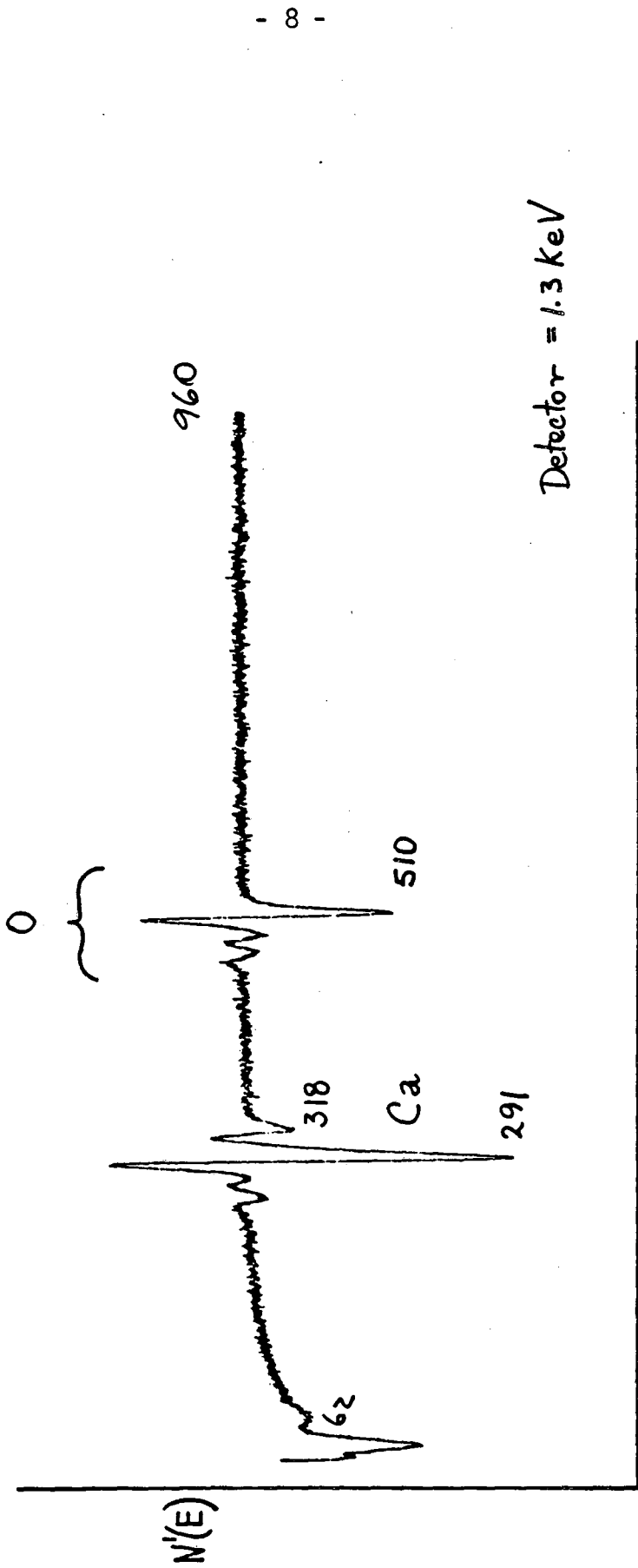
The electron microscope work described in Task 2 is a unique demonstration of the catalytic nature of the reaction and shows in sequence how reaction between carbon and water proceeds on the alkali-carbon interface.

Additional work in the high vacuum chamber was carried out by observing graphite specimen containing KOH and CaO before and after reaction with water by means of Auger electron spectroscopy and by ESCA.

Calcium oxide was deposited on the graphite by impregnation with calcium nitrate and decomposition of the nitrate at 200°C. Fig. 2 shows an AES spectrum of the graphite surface. No nitrogen was detected, assuring complete decomposition of the nitrate. The sample prepared in this way was exposed to 20 torr of H₂O and 1 atm of He and heated at increasing temperatures. No products of any kind were detected between 200°C and 500°C. But after heating the sample at 500°C in water vapor for about two hours, ESCA revealed the presence of a carbidic type of carbon that was not present before this treatment. Carbidic carbon is an "active carbon" that can be easily reduced with hydrogen to methane. The sample was exposed to 1 atm of H₂ and heated at 500°C. Methane was readily detectable and CH₄ production lasted for about 15 hours. Once the CH₄ production stopped the sample was again inspected with ESCA and it was found that the carbidic carbon was completely removed. In Fig 3 the ESCA spectra of the different steps previously described are displayed. This should be compared with Fig 4, showing a clean graphite spectrum. The carbon peak labeled C_{1s} is graphitic carbon, the peak labeled C⁺ corresponds to the carbidic type. Since water seems to promote the formation of the carbidic carbon and hydrogen reduces it to methane, additional experiments were carried out using mixtures of 20 torr of H₂O and 20 torr of H₂. Under this condition some methane was produced and this data is displayed in Fig 5. In this same figure we have plotted the production of methane from the sample containing CaO treated at 500°C and the production of methane from a KOH-graphite sample at 295°C. It is clear that a major difference between CaO and KOH impregnated graphite samples is that very little, if any, methane was produced from carbon and water alone on the CaO containing samples even at 500°C, while methane was produced at a steady rate already at 225°C with the KOH impregnated sample.

It is further interesting to note that samples of graphite treated with KOH showed no activity when they were exposed to 1 atm of pure hydrogen in the absence of water. This suggests that the mechanisms for CH₄ production from samples coated with KOH and samples coated with CaO are different.

CaO - graphite



Energy (eV) →

XBL 823-8754

Figure 2

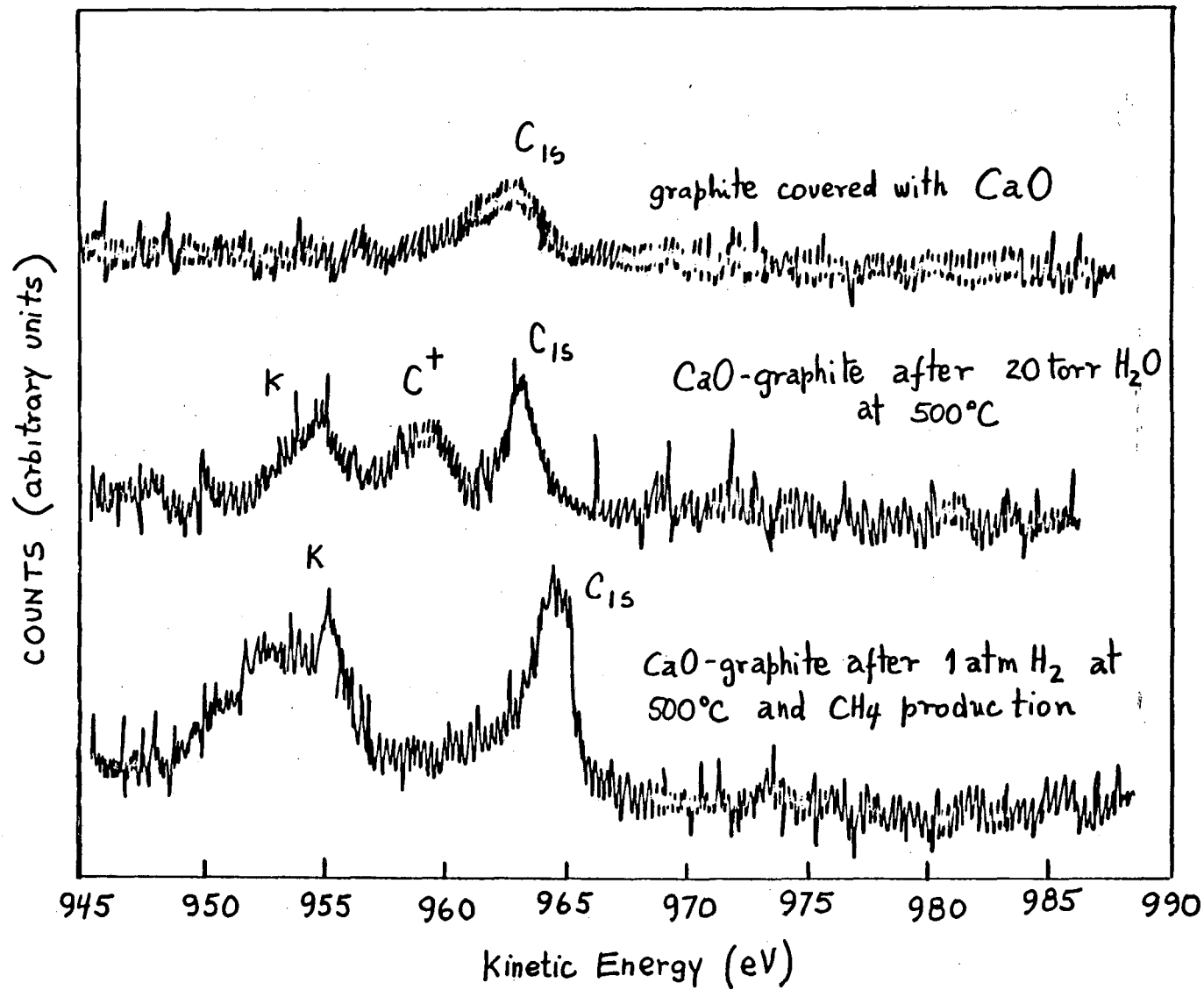
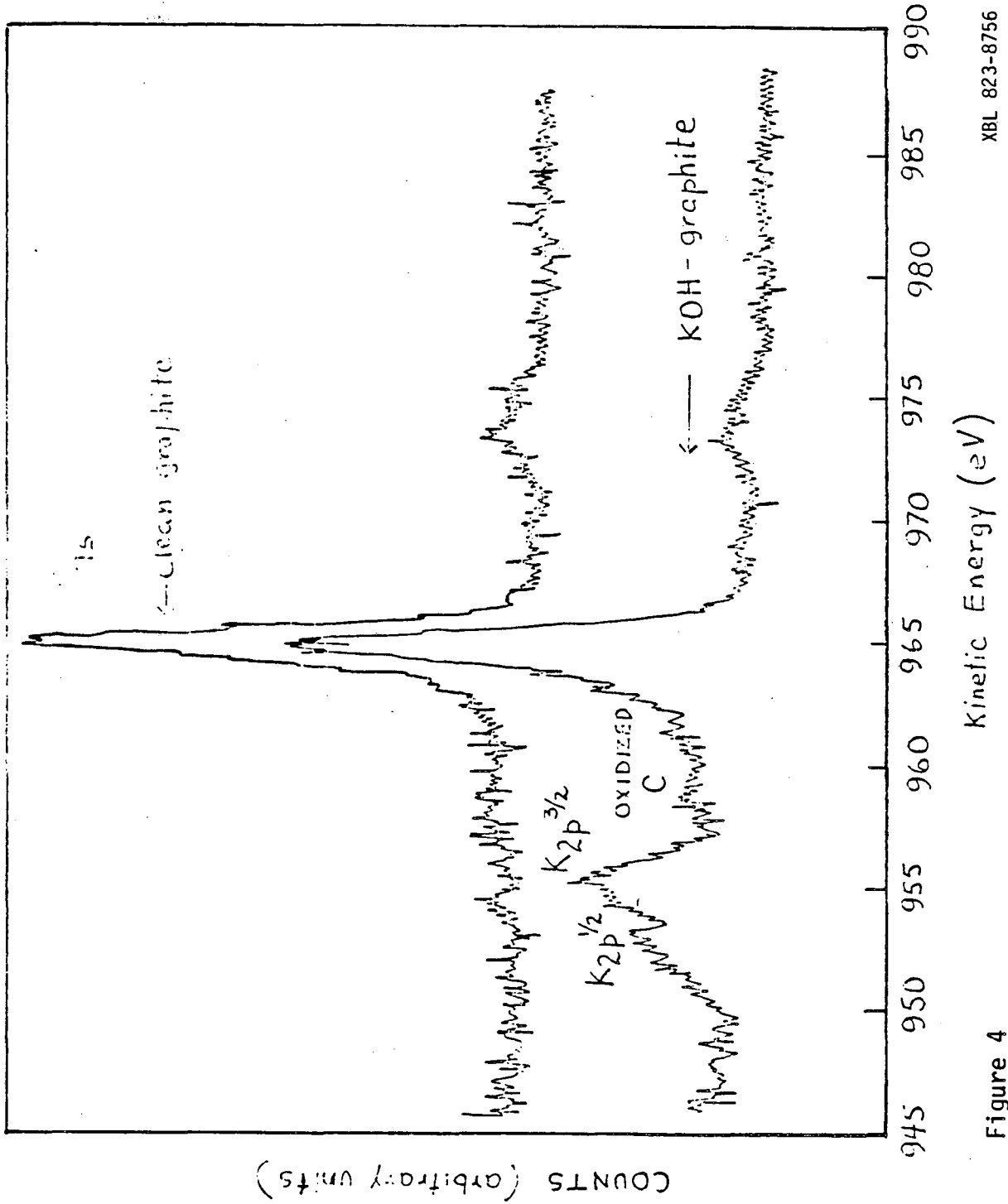


Figure 3

XBL 823-8757



XBL 823-8756

Figure 4

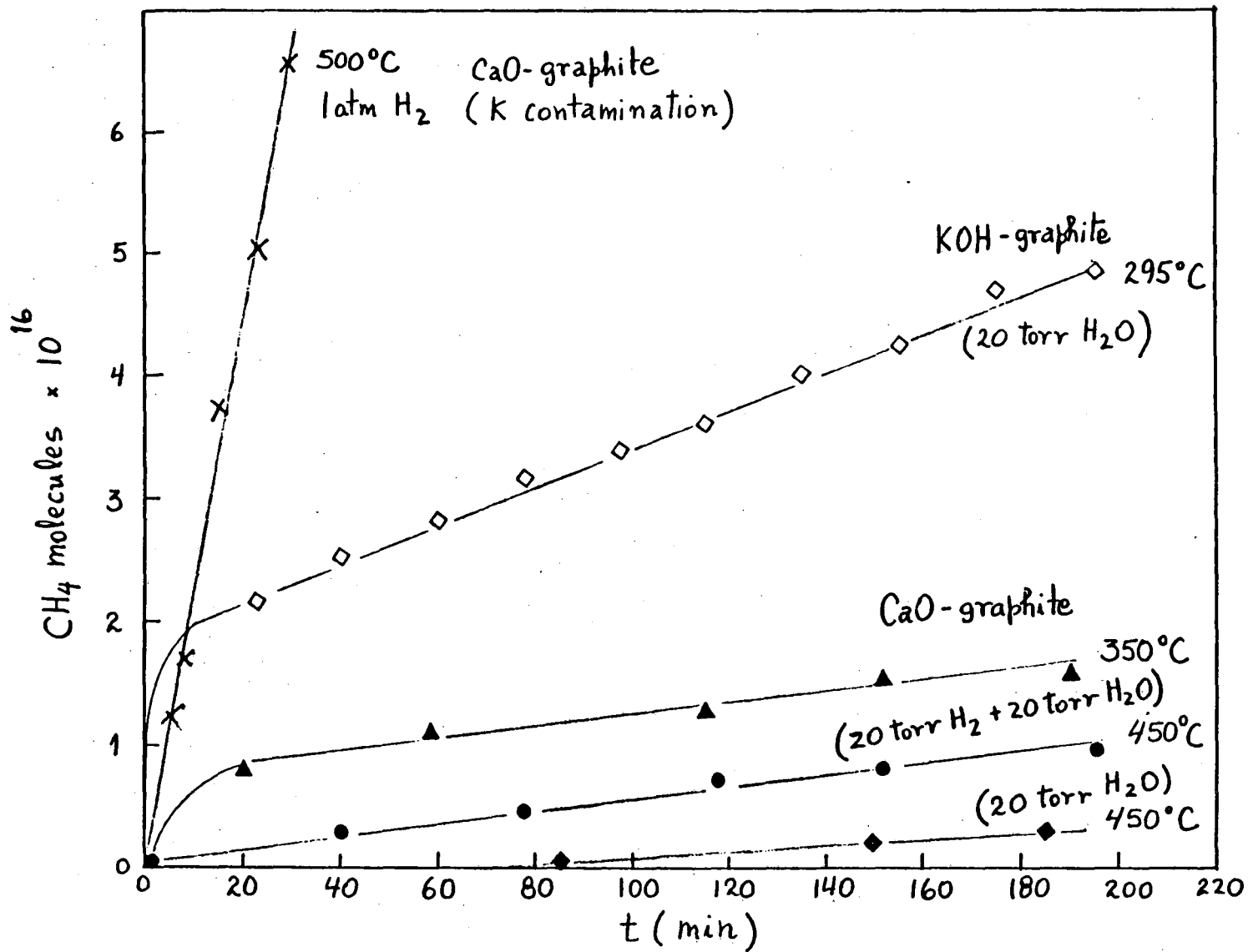


Figure 5

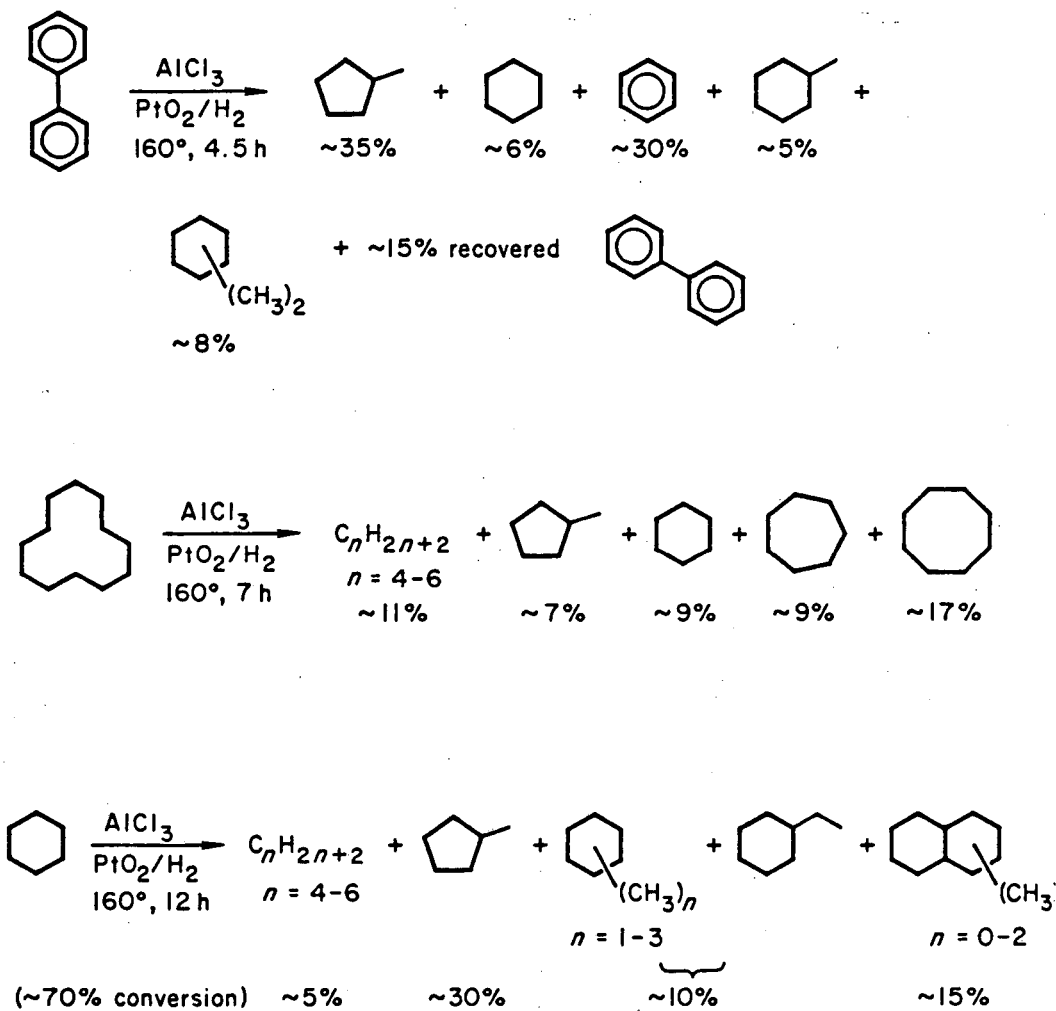
XBL 823-8755

In order to ascertain whether KOH transforms graphitic to carbidic carbon in the presence of water, samples of graphite were coated with a KOH solution and inspected by ESCA before and after being exposed to heat and water vapor. At temperatures of 300°C and heating time of the order of 15 min., no transformation of any kind were found. Nevertheless, when the samples are exposed to 500°C and kept under this condition for a period of 20 hours while being exposed to 20 torr of H₂O, a carbidic type of carbon was detected on the surface of the sample. This indicates that this carbon transformation from graphitic to carbidic type is a common step previous to the formation of methane at least at higher temperatures. At lower temperatures, it is speculated that the carbidic carbon formed from graphite might be dissolved by the alkali or alkali earth compound and can be removed by hydrogen. If the diffusion of the carbon is a slow step, then in order to build a detectable amount of this "active carbon" on the surface of the sample, high temperatures and prolonged heating times are required.

Task 4 - Selective Hydrogenation, Hydrogenolysis, and Alkylation of Coal and Coal Related Liquids by Organometallic Systems - K. P. C. Vollhardt

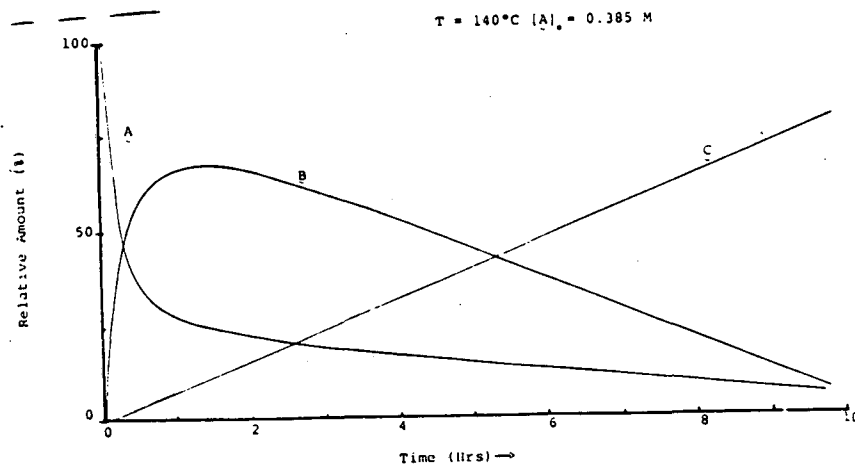
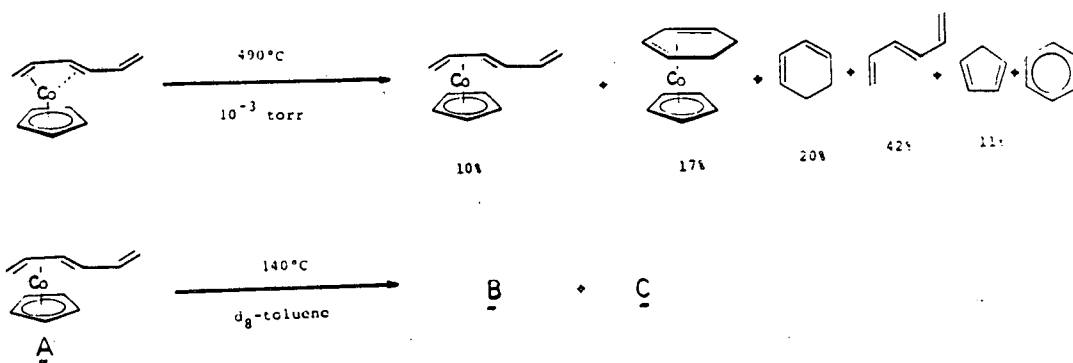
We had found earlier that the reaction of benzene and aluminum trichloride (which leads to the formation of alkylbenzenes) in the presence of hydrogen and a platinum catalyst proceeds without the formation of any significant amounts of polymeric products. This has prompted an extension of our investigations to the aluminum trichloride induced cracking of some saturated and benzenoid hydrocarbons under hydrogenation conditions as models for the hydroliquefaction of coal and/or heavy petroleum hydrocarbons. Reactions were performed in the inert solvent 1, 2,4-trichlorobenzene. Representative results are shown in Scheme 1. Our data indicate that the use of hydrogen suppresses polymerization processes. However, hydrogenolysis products are only minor components in the reaction mixtures. Interestingly, cycloalkanes undergo mainly ring contraction, whereas benzenoid hydrocarbons show accelerated benzene ring hydrogenation.

In our second effort we have further delineated the scope and mechanism of a remarkable dimerization process of a complexed 1,3,5-hexatriene (Scheme 2, of A). In the gas phase mainly decomposition is observed, in addition to a small amount of the originally desired ring-closed 1,3-cyclohexadiene complex. In solution the dinuclear complexes B and C are formed, the X-ray structure of which were described in a previous report. Compound A first forms B which then undergoes a unimolecular rearrangement to C. The formation of B involves a [1,6]-hydrogen shift which exhibits a strong deuterium isotope effect (Scheme 3). This has allowed us to pinpoint the regioselectivity of the subsequent hydrogen (deuterium) shift which connects B with C (Scheme 3). A probable mechanism for the entire sequence is outlined in Scheme 3. The initial [1,6]-shift occurs at temperatures as low as -20°C and thus might turn out to be one of the lowest activation energy vinyl-hydrogen activation processes known.



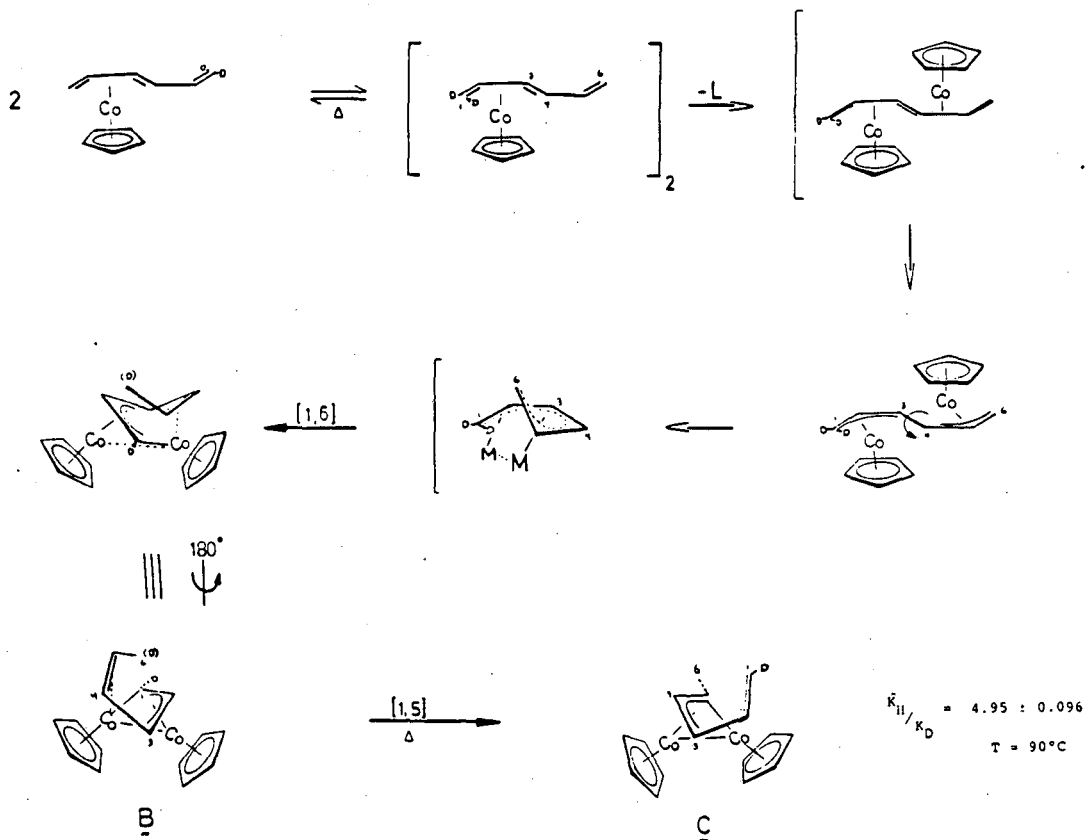
Scheme 1

Examples of the Lewis acid cracking of selected hydrocarbons in the presence of catalytic hydrogen.



~~~~~  
Scheme 2

Comparison of the gas phase and solution thermal chemistry of A. The lower graph depicts the relative amounts of A, B and C with time in the solution experiment.



Scheme 3 Mechanism of the A B C sequence. The outcome of the deuterium labeling experiment is indicated by the appropriate lettering.

Task 5 - Chemistry of Coal Solubilization - T. Vermeullen and R. H. Fish

The utilization of Wilkinson's Catalyst  $[(\phi_3p)_3RhCl]$  as a selective hydrogenation catalyst for polynuclear heterocyclic compounds of nitrogen and sulfur has been studied during this quarter. This catalyst was chosen since it has been heterogenized on polystyrene and subsequent experiments will be performed with this form of the catalyst after delineating its homogeneous catalytic hydrogenation activity.

Table 1 shows the range of nitrogen heterocyclic model coal compounds we have used with  $(\phi_3p)_3RhCl$  as catalyst. In addition, we also observed the reactivity of two sulfur heterocyclic compounds; namely, thiophene and benzothiophene, with Wilkinson's catalyst.

The results in Table 1 showing total selectivity to hydrogenation of the N containing ring are highly promising, since they provide evidence for the possible successful use of this catalyst on a polymer supported matrix. This obviously would be important for any future use of this or other catalysts in the upgrading of coal liquids.

It was also found that a facile dehydrogenation reaction was occurring when several of the substrates remained in contact with the catalyst (solution) prior to gas chromatographic analysis and at reduced pressure.

For example, if the formed dihydrophenanthridine remained in solution with  $(\phi_3p)_3RhCl$  for several hours after the initial G.C. analysis, it was dehydrogenated to phenanthridine (100%). This dehydrogenation reaction caused the erroneous per cent conversion in our G.C. analysis. Repetition of the reaction, with removal of catalyst by Florosil column chromatography, provided the 9, 10-dihydrophenanthridine in 75% yield. This dehydrogenation reaction also occurred to a smaller extent with dihydroacridine; however, it was not fast enough to cause appreciable errors in the G. C. analysis of the dihydroacridine formed.

It is also of interest to note that benzothiophene, and not thiophene, was reduced in moderate yield (27%). It is conceivable that the sulfur heterocycles are less reactive than their corresponding nitrogen analogs. We plan to run experiments to provide information concerning that important point.

Finally, these experiments provided us with the data we needed to pursue a similar type of hydrogenation reactions with the heterogenized form of Wilkinson's catalyst. We are hopeful that these future experiments will lead to practical methods for future upgrading of coal liquids.

Table 1 Homogeneous Catalytic Hydrogenations  
with  $(\phi_3\text{P})_3\text{RhCl}$  as Catalyst

| Substrate          | H <sub>2</sub> (Psi) | Temp. | Time | Product (%) <sup>a</sup>                          |
|--------------------|----------------------|-------|------|---------------------------------------------------|
| Quinoline          | 240                  | 150   | 2    | 1,2,3,4-Tetrahydroquinoline (100)                 |
| Acridine           | 240                  | 150   | 2    | 9,10-dihydroacridine (76)                         |
| 5,6-Benzoquinoline | 240                  | 150   | 2    | 1,2,3,4-Tetrahydro-5,6-Benzoquinoline (71)        |
| Phenanthridine     | 240                  | 150   | 2    | 9,10-dihydrophenanthridine (25) (75) <sup>b</sup> |
| Benzothiophene     | 240                  | 150   | 2    | 2,3-dihydrobenzothiophene (27)                    |
| 7,8 benzoquinoline | 240                  | 150   | 2    | 1,2,3,4-tetrahydro-7,8-benzoquinoline (21)        |
| Thiophene          | 240                  | 150   | 2    | No product                                        |

<sup>a</sup>% conversion to product, the remaining substrate represents the % difference in product conversion

<sup>b</sup>When the catalyst was removed, as quickly as possible, and adsorbed on a Florosil column, the yield of 9,10-dihydrophenanthridine went to 75%.

Task 6 - Coal Conversion Catalysts - Deactivation Studies - A. V. Levy and  
E. E. Petersen with M. West

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During this quarter we completed an extensive set of HDM-HDS experiments at 325°C and 200 ppm vanadium. Figure 6 shows some typical results. A metal concentration profile from a randomly selected catalyst pellet is plotted for each exposure time. The amount of metal deposited and the depth of penetration are greater than for similar runs at higher temperatures. This is as we expected judging from the preliminary 325°C results of last quarter. The weight percent of vanadium at the exterior approaches the levels observed in commercial operation and is high enough that some pore mouth blocking may be expected. The furthest penetration of metal is 70 microns or about 20 percent of the diameter of a catalyst particle lobe. We are currently collecting several profiles for each exposure time and averaging them together for use in modelling.

Work proceeds on similar experiments using a more characterizable model metal compound, vanadyl tetraphenylporphyrin, dissolved in mineral oil to avoid the possible complication of excessive catalyst coking mentioned in a previous report. Recent literature establishes the presence of porphyrins in coal. Other literature indicates that a significant fraction of the titanium in coal is organically bound. We are therefore preparing to synthesize titanium or titanyl tetraphenylporphyrin for use as a model metal compound in comparison without vanadium work.

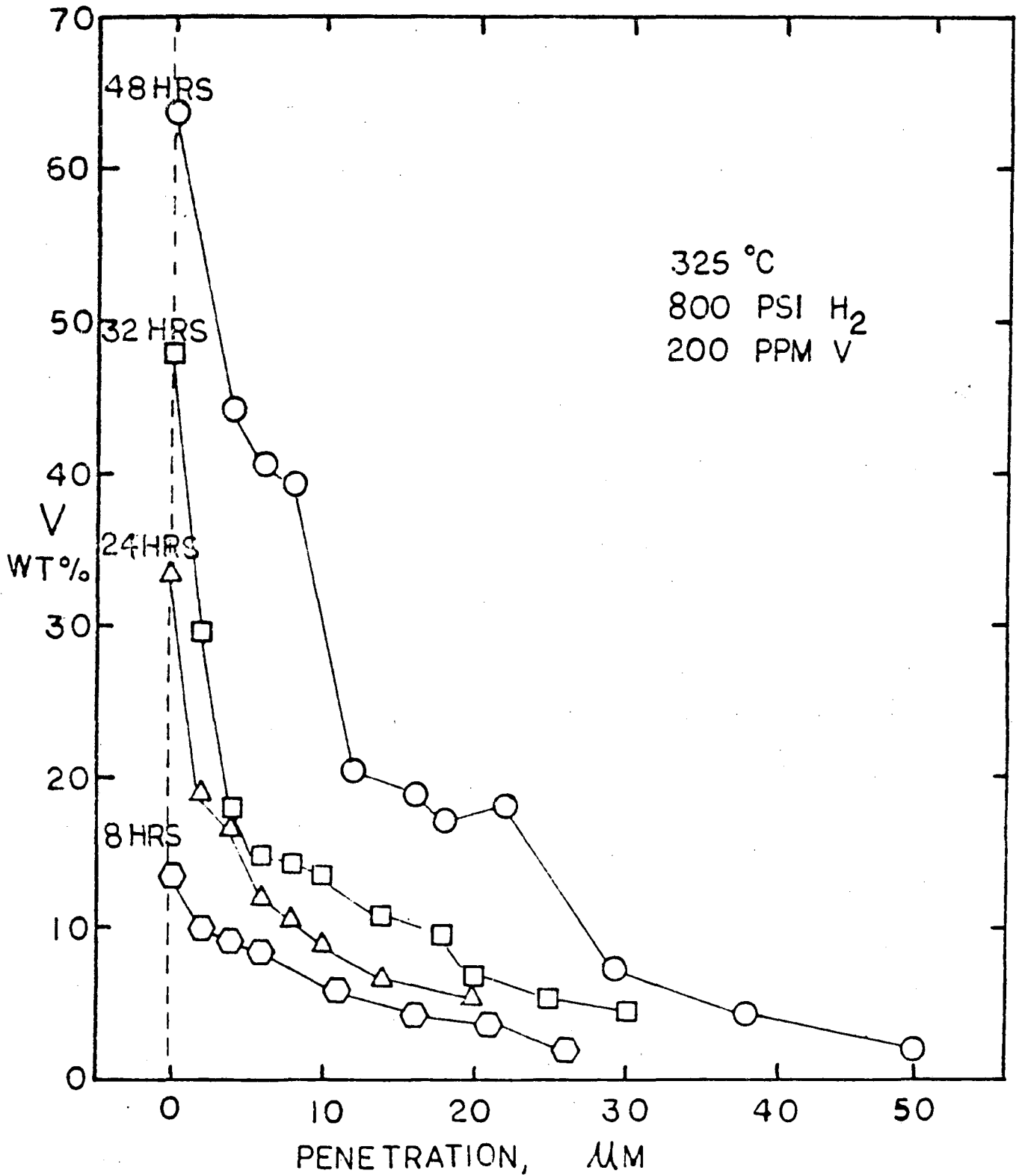


Figure 1



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