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Molecular Catalytic Hydrogenation of Aromatic Hydrocarbons and the Hydrotreating of Coal Liquids

Final Report

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Molecular Catalytic Hydrogenation of Aromatic Hydrocarbons and the Hydrotreating of Coal Liquids

Abstract

This report presents the results of research on the development of new catalytic pathways for the hydrogenation of multiring aromatic hydrocarbons and the hydrotreating of coal liquids at The University of Chicago under DOE Contract No. DE-AC22-91PC91056. The work, which is described in three parts, is primarily concerned with the research on the development of new catalytic systems for the hydrogenation of aromatic hydrocarbons and for the improvement of the quality of coal liquids by the addition of dihydrogen. Part A discusses the activation of dihydrogen by very basic molecular reagents to form adducts that can facilitate the reduction of multiring aromatic hydrocarbons. Part B examines the hydrotreating of coal liquids catalyzed by the same base-activated dihydrogen complexes. Part C concerns studies of molecular organometallic catalysts for the hydrogenation of monocyclic aromatic hydrocarbons under very mild conditions.

The results presented in Part A show that strong organic bases are able to catalyze the hydrogenation of multiring aromatic hydrocarbons such as naphthalene and anthracene. The research suggests that dihydrogen is activated by the strong base to form an intermediate complex that then transfers an activated hydrogen in the complex to the unsaturated substrate.

liquid. The multiring aromatic hydrocarbons in the coal liquid were hydrogenated to give saturated molecules that contained only one aromatic ring. Of the several organic bases investigated, potassium bis(trimethylsilyl)amide was found to be the most effective catalyst. Temperature and hydrogen pressure all affect the hydrotreating. In general, 200°C and 1000 psig of hydrogen was needed to ensure that the hydrotreating

proceeded completely. The results of this investigation strongly suggest that there are broad opportunities for practical applications of the basic catalysts by using simple alkali metal amides in commercial equipment.

After scoping experiments with a variety of molecular metallic reagents, the research, which is discussed in Part C, was focused on the studies of a molecular organometallic catalyst, chloro(1,5-hexadiene)-rhodium(I)dimer ($[1,5\text{-}HDRhCl]_2$ as a catalyst precursor. The hydrogenation of monocyclic aromatic compounds such as 1,2,3,4-tetrahydronaphthalene occurred readily under very mild conditions (room temperature and 1 atm of dihydrogen) in a biphasic system with an organic solvent as the hydrophobic phase and an aqueous buffer solution as hydrophilic phase. Although high concentrations of surfactant molecules negatively effected the catalytic activity in this system, it was established that low concentrations of a surfactant created an emulsion that stabilized the catalyst at a significant high level of activity. Surfactant molecules such as cetyltrimethylammonium bromide (CTAB) and tetrabutylammonium hydrogen sulfate (THS) were especially effective. An active and stable catalyst system was discovered for the useful hydrogenation of monocyclic aromatic compounds under mild conditions. Moreover, the system has practical consequences because the metal can be easily separated from the products and recycled. The effectiveness of the catalyst was established by its use for the hydrogenation of the mixture of tetralin and a coal liquid derived from liquefaction. It was found that about 80-85% of tetralin in the mixture was hydrogenated to decalin in the presence of coal liquids, implying that the catalyst system can be operated smoothly under extremely mild conditions in the presence of typical catalyst poisons in coal liquids.

Molecular Catalytic Hydrogenation of Aromatic Hydrocarbons and the Hydrotreating of Coal Liquids

Part A

Base-activated Reduction of Aromatic Compounds with Dihydrogen

Introduction

Coal liquefaction and the upgrading of the coal liquids are being considered as a future alternatives of petroleum to produce synthetic liquid fuels due to the declining crude oil reserves and the high dependence on the foreign oil supplies (Anderson and Tillman, 1979; Whitehurst and Mitchell, 1980). Since the late 1970s, coal liquefaction processes have been developed into integrated two-stage processes, in which coal is hydroliquefied in the first stage and the coal liquids are upgraded in the second stage (Schindler, 1989; Newworth, 1984; Comolli et al., 1993). Upgrading of the coal liquids is an important aspect of this approach and may determine whether such liquefaction can be economically feasible. Coal liquids are largely unacceptable as refinery feedstocks because of their high concentrations of aromatic compounds and high heteroatom and metals content. Successful upgrading process will have to achieve significant reductions in the content of the aromatic components. However, the hydrogenation of coal liquids with multiring, aromatic hydrocarbons with gaseous dihydrogen is a difficult process from the technological point of view due to the stable structures of the aromatic compounds and the poor dynamic yields at low pressure and low temperature (Stanislaus and Cooper, 1994). The catalysts commonly used for coal liquid hydrotreating are mixtures of nickel and molybdenum oxides supported on alumina. They deactivate rapidly by active site suppression and often also exhibit undesirable pore choking (Dadyburjor and Raje, 1994). Hence, other pathways to upgrade the coal liquids need to be explored to provide basic information to underpin future technology.

Despite the importance of the reduction of polycyclic, aromatic compounds in the upgrading of coal liquids and in the oil refining industry, the subject has not received much attention (Stanislaus and Cooper, 1994). Compared with the extensive literature on hydrodesulfurization (Dautzenberg and de Deken, 1984; Jacobson et al., 1987; Speight, 1981), hydrodenitrogenation (Ho, 1988; Perot, 1991; Katzer and Sivasubramanian, 1979; Ledoux, 1985) and hydrometallation (Quann et al., 1988; Mitchell, 1990; Toulhoat et al., 1990), the number of publications on the chemistry of aromatic hydrogenation is relatively small. Except for the commercial catalysts such as sulfide supported nickel- and cobalt-molybdenum. mixtures and supported noble metals, only a few of studies regarding the chemistry of the reduction of multiring aromatic compounds have been published in the past two decades.

1. Hydrogenation Catalyzed by Supported Catalysts

Two types of supported catalysts are commonly used for aromatic hydrogenation in industry. One type is the sulfided Ni-Mo, Ni-W, or Co-Mo on $A1_2O_3$ catalysts that are generally used for the hydrorefining of feedstocks that contain appreciable concentrations of sulfur and nitrogen. Another is the supported noble metal catalysts, which have been used for materials that are essentially free of sulfur and nitrogen. Within the series of Co- or Ni-promoted group VI metal (Mo or W) sulfides supported on γ-Al_2O_3, the ranking Ni-W > Ni-Mo > Co-Mo > Co-W has been found (Frank and Le Page, 1981) for the hydrogenation, and Ni-W and Ni-MO/Al_2O_3 catalysts are widely used to reduce sulfur, nitrogen, and aromatic compound levels in coal liquefaction by hydrotreating (Comolli, et al, 1993). Catalysts containing noble metals on Y-zeolites have been reported to be more sulfur tolerant than those on other supports (Gallezot and Bergeret, 1987; Jacobs, 1986). Such catalysts have increasingly been used in recent years for hydrogenation of aromatic compounds in light and middle distillates (Suchanek, 1990; Peries, et al., 1991).

The hydrogenation of aromatic compounds is reversible, and at typical hydrotreating conditions, complete conversion is not possible owing to equilibrium limitations. The hydrogenation of an aromatic species, A, is given by:

$$A + nH_2 == AH \qquad \text{(eq. 1)}$$

where AH is the hydrogenated product. It can be shown (Gully and Balard, 1963) that the equilibrium concentration of the aromatics species can be approximated by eq. 2

$$\frac{YA}{Y_A + Y_{AH}} \quad \frac{}{1 + K_\alpha X (P_{H2})^n} \qquad \text{(eq. 2)}$$

where Y_A and Y_{AH} are the mole fractions of the aromatic and naphthalene species, respectively; K_α is the equilibrium constant, and P_{H2} the partial pressure of hydrogen. In the derivation of this equation it is assumed that liquid activity coefficients and fugacities for A and AH are equal. and that the hydrogen activity coefficient and the ratio of fugacity to total pressure at hydrotreating, conditions are both unity.

It was clear that high pressures favor low equilibrium concentrations of aromatic compounds (high conversions). This is particularly suited for reactions where the number of moles of hydrogen, n, required for complete saturation is high. Aromatic hydrogenation reactions are highly exothermic. with heats of reaction typically in the range 63-71 kJ/mole of H_2) (Reid et al., 1977; Jaffe, 1974). K_α decreases with increased temperature, and therefore the equilibrium aromatic concentration increases as the temperature is increased.

The hydrogenation of multiring aromatic substances proceeds via successive steps, each of which is reversible. The equilibrium constant is generally higher for the hydrogenation of the first ring (Lepage, 1987), but since more moles of hydrogen are involved in the final ring hydrogenation (3 moles compared with 1 or 2 moles for hydrogenation of the first ring in phenanthrene), hydrogenation of the first ring is usually less favorable from a thermodynamic view than hydrogenation of the final ring under typical hydrotreating conditions (Gully and Balard, 1963).

Figure 1 shows the equilibrium constants for hydrogenation of phenanthrene (Zoller, 1989) and Figure 2 shows the equilibrium concentrations for first- and last-ring hydrogenation of phenanthrene and naphthalene as a function of hydrogen pressure (Gully and Balard, 1963). These data have been used to calculate the equilibrium concentrations of the reagents and products for the saturation of phenanthrene and naphthalene as a function of temperature at three levels of hydrogen pressure. The equilibrium aromatic concentration for the first-ring hydrogenation is higher than that for final-ring, hydrogenation at temperature below 375°C (648K) at 3 MPa, and at temperature up to 435°C (708 K) at 10 MPa. These curves also demonstrate the strong effect of hydrogen pressure on the equilibrium aromatic concentration: At 350°C (623K), the equilibrium concentration for the reaction naphthalene to tetralin decreases from 11.4% at 3 MPa to 1.2% at 10 MPa, while the equilibrium concentration decreases from 21.5% at 3 MPa to 4.5% at 10 MPa for the conversion of phenanthrene to tetrahydrophenanthrene.

Kinetics of hydrogenation of aromatic hydrocarbons containing two or more rings are more complicated. Most kinetic studies of aromatic compounds with several rings that ate reported in the literature deal mainly with the reaction pathways and reactivities rather than quantitative kinetic models that include adsorption mechanism of reactants, intermediates and products (Girgis and Gates, 1991). Spare and Gates (1981) proposed reaction pathways for hydrogenation of naphthalene, biphenyl, and 2-phenyl naphthalene over a sulfided Co-Mo/γ-Al_2O_3 catalyst at 325°C and 75 atmospheres. The reactions are approximately first-order in the aromatic reactants. The rate constants for various forward and reverse reactions are shown in the network. The rate data for the benzene hydrogenation are also included in the network for the purpose of comparison. The rate data for various reactions in the network show that the rate of hydrogenation of naphthalene to tetralin is about 21 times faster than that of benzene hydrogenation as reported by others (Weiser and Landa, 1973). The presence of alkyl substituents in benzene or naphthalene has no significant effect. The expected enhancement in reactivity resulting from the electron-donating influence of the aryl substituents is probably compensated for by increased steric hindrance of adsorption.

Patzer et al.(1979) studied the hydrogenation kinetics of 1-methyl naphthalene over a series of commercial coal liquefaction catalysts in the temperature range 343°C to 482°C and found the reaction to obey first-order kinetics. These authors also noticed that the ratio of concentrations of tetralin to naphthalene in the product remained constant at about 0.49 $\pm$ 0.03, being unaffected by changes in catalyst composition, feed flow rate, and reaction temperature in the range 316-399°C. They attributed these results to an equilibrium limitation and proposed reaction networks for the processes. Their interpretation of an equilibration of the products was disputed by Spare and Gates (1981) in view of the lack of dependence on the ratio of tetralin to naphthalene on temperature. They pointed out that in the experiments reported by Patzer et al. (1979), the residence time (defined as reciprocal of hourly space velocity, LHSV-1) was typically varied over only a small range (0.3-0.6). Estimation of relative concentration profiles from kinetic parameters showed that both naphthalene and tetralin concentrations are almost linearly dependent on the residence time (LHSV-1) in this range as displayed in Figure 3, and consequently the naphthalene-to-tetralin ratio is almost constant, giving the incorrect impression of an equilibrium distribution.

Hydrogenation reaction pathways for condensed polynuclear aromatic hydrocarbons such as fluorene, fluoranthrene. and phenanthrene over sulfided Ni-W/Al_2O_3 catalysts are summarized in Figure 4. The results show that hydrogenation of these polynuclear aromatic compounds occurs ring by ring in a series fashion. The hydrogenation reactions were essentially first-order in the aromatic hydrocarbon. No kinetic rate equations were proposed for the above reactions.

With polycondensed ring aromatic hydrocarbons, the first-ring hydrogenation has been observed to be most favored kinetically. The rates of hydrogenation of subsequent rings tend to become lower, and the hydrogenation of the last ring proceeds with considerable difficulty compared with the initial hydrogenation steps. The relative rate constants for the hydrogenation of the first ring of several condensed di- and triaromatics such as naphthalene, anthracene and phenanthrene over different sulfided catalysts are presented in Table 1.

The ranges of the reported resonance energies of various aromatic compounds are also included in the Table. The results indicate that the resonance energy per six member ring varies significantly. The results show, for example, that the resonance energy per ring in naphthalene is considerably lower than that of benzene, and that the molecules with three rings have even lower values. The lower aromatic character of the rings in the naphthalene and anthracene molecules are experimentally shown by their ability to undergo addition reactions across the 1,4 positions in naphthalene and the 9,10 positions in anthracene. Careful investigations of the elementary ionic halogenation reactions of naphthalene and anthracene indicate that addition products are often formed. The middle ring of anthracene is so reactive that that phase of its chemistry is often described as that of an alkene. The 9,10 double bond of phenanthrene has similar chemistry. In multiring aromatic compounds, the ring with the lowest aromaticity is hydrogenated first. The rate data presented in Table 1 indicate the following order of reactivity for one-ring hydrogenation

Anthracene > naphthalene > phenanthrene> benzene

The results for benzene, naphthalene and anthracene are in accord with this simple analysis, but the one measurement for phenanthrene is not in the expected order.

In a more insightful analysis of the problem, Neurock and coworkers (1989) found a good correction between the rate constants for hydrogenation of a series of polycyclic aromatic hydrocarbons and the π-electron density at the initial reaction position. The value of π was determined at each potential site of hydrogenation, and the one with the largest value of π was considered

$$\log k = A + B\ (\pi)$$

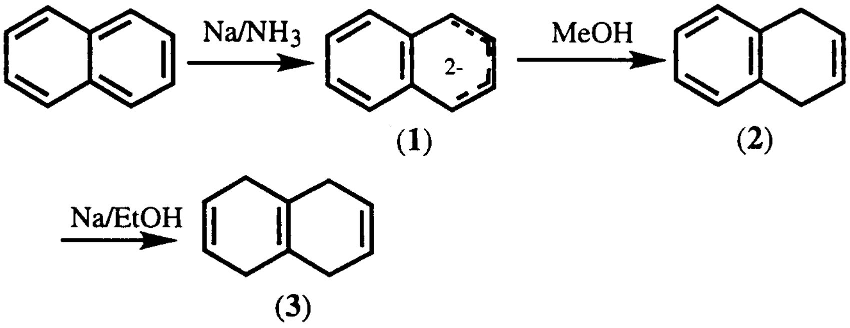
to be the kinetically significant site. The correction is shown in Figure 5.

where A is -155.66 ± 34.12 and B is 151.23 ± 33.88. A possible explanation of the good correction between π and the reaction rate constant is that there is a Coulombic attraction between the carbon site on the aromatic ring and the attacking reagent. Thus, the site with the highest π value is the kinetically favored. This correlation is compatible with a broad array of data for the substitution reactions of aromatic molecules.

2. Reduction with Group I and II Metals in Amines

Multiring, aromatic compounds can be reduced to their dihydro or monohydro derivatives by dissolving alkali metals in amines. The most commonly used procedure is that established by Wooster and Godfrey (1937; 1939) and extensively developed by Birch and Smith (1950; 1958). Typically, the Birch reduction is performed with a solution of the substrate in a mixture of liquid ammonia with an alcohol (usually ethanol or *tert*-butyl alcohol) and an inert cosolvent such as diethyl ether, tetrahydrofuran with lithium, sodium or potassium. In Benkeser reduction, low molecular weight amines are utilized in place of ammonia, and this procedure then leads to more extensive reduction.

Metals of Groups I and II dissolve readily in liquid ammonia. The resulting solutions of the solvated electrons are powerful reducing agents that may be used to perform highly, selective reactions. Naphthalene reacts with sodium in liquid ammonia to form a red complex which is quenched by methanol to form the 1,2- and 1,4-dihydro derivatives (Huckel and Bretscheider, 1939). Treatment of naphthalene with an excess of sodium in ethanol, ether, and ammonia affords 1,4,5,8-tetrahydro-naphthalene (3)

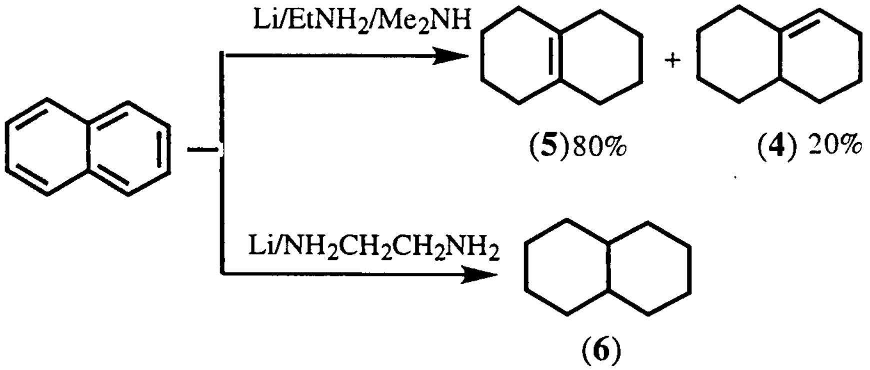


(eq. 3)

in good yields (Birch, 1951; Huckel and Schlee, 1955). When the reaction is carried out with a deficiency of metal, though, less reduction occurs affording 1,4-

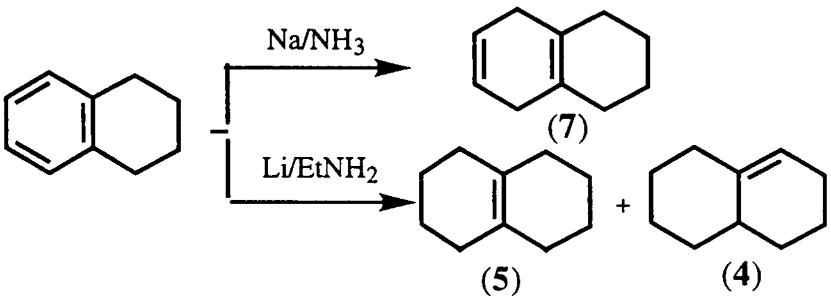
dihydronaphthalene (**2**). Incidentally, ether is used in these systems to increase the solubility of the hydrocarbon in the ammonical media. 1-Naphthyl derivatives are reduced in the unsubstituted ring, but there is a marked steric effect, and this preference is reversed in the case of 2-*tert*-butylnaphthalene.

Solutions of Groups I metals in the lower molecular weight amines are more potent reductants than those in liquid ammonia, and as a general rule, the substrates are more extensively reduced than by the Birch method. Naphthalene, for example, is reduced by a solution of lithium in ethylamine to a 1:1 mixture of $\Delta^{1(9)}$- (**4**) and Δ^{9}-octalins (**5**). If ethylenediamine is employed as the medium, the completely saturated decahydronaphthalene (**6**) is formed, while the proportion of Δ^{9}-octalins may be increased to 80% by utilizing a (1:1) mixture of ethylamine with dimethylamine (Kaiser and Benkeser, 1970). The formation of the more-substituted alkene appears to be a general result for such primary and secondary amine mixtures and has been used to good advantage in the reduction of both toluene and cumene to their 3,4,5,6-tetrahydro derivatives, respectively, in about 80% yield.



(eq. 4)

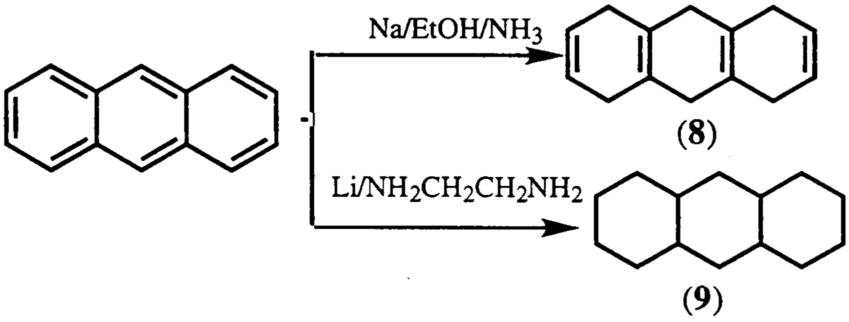
Reduction of tetralin by the Birch and Benkeser methods is similar to that of naphthalene. Thus, treatment of tetralin with sodium/methanol ammonia gives 1,2,3,4,5,8-hexahydronaphthalene (**7**) (Huckel and Worffel, 1956), while the use of, lithium in ethylamine gives a mixture of $\Delta^{9(10)}$ (**5**) and $\Delta^{1(9)}$-octalins (**4**) (Benkeser and Robinson, 1955) (eq. 5)



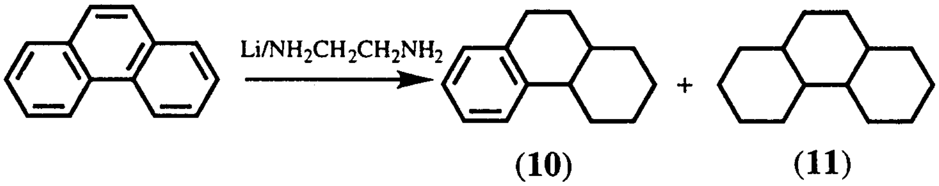
(eq. 5)

Anthracene was reduced by sodium in ethanol and ammonia to 1,4,5,8,9,10-hexahydroanthracene (**8**) (Birch and Fitton, 1963) and the treatment of anthracene with excess lithium in low molecular weight amines gives the fully hydrogenated perhydroanthracene (**9**) (Melikadze et al., 1959). With lithium in ethylenediamine an unspecified mixture of dodecahydro- and tetradecahydroanthracene was obtained (Reggel et al., 1957).

Similarly, phenanthrene was reduced to a mixture of *cis*- and *trans*-1,2,3,4,9,10,11,12-octahydrophenanthrene (**10**) by sodium in ethanol and ammonia in good yield (Majer, 1961). More extensive reduction of the phenanthrene ring was achieved by using lithium in low molecular weight amines.



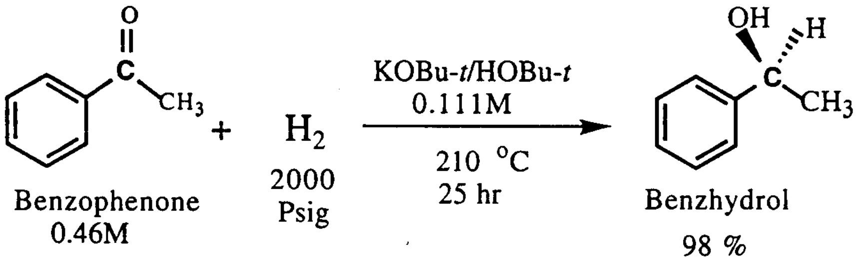
(eq. 6)



(eq. 7)

This reaction gives isomeric perhydrophenanthrene (**11**) (Melikadze et al., 1959), and the reaction with lithium in ethylenediamine affords decahydro- and dodecahydrophenanthrene (Brooks et al., 1964; Reggel et al., 1957).

Benkeser and his coworkers (1982) discovered that calcium metal dissolved in a mixture of methylamine and ethylenediamine was capable of reducing simple aromatic hydrocarbons to cycloalkenes. Naphthalene was reduced to a mixture of $\Delta^{9(10)}$ - and $\Delta^{1(9)}$-octalins (77/23) in 92% and tetralin was reduced to a mixture of $\Delta^{9(10)}$ - and $\Delta^{1(9)}$-octalins (80/20) in 92% yield. It was interesting to note that anthracene was converted into 1,2,3,4,5,6,7,8,9,10-decahydroanthracene in 85% yield. In virtually all of the calcium reduction reactions where a solvent mixture of methylamine and ethylenediamine was used, the metal was almost entirely consumed even when present in large excess. Calcium is converted into calcium alkylamide, a grayish precipitate that forms during the course of such reductions. It was established that this metal amide did not reduce ρ-xylene to the corresponding dimethylcyclohexene.

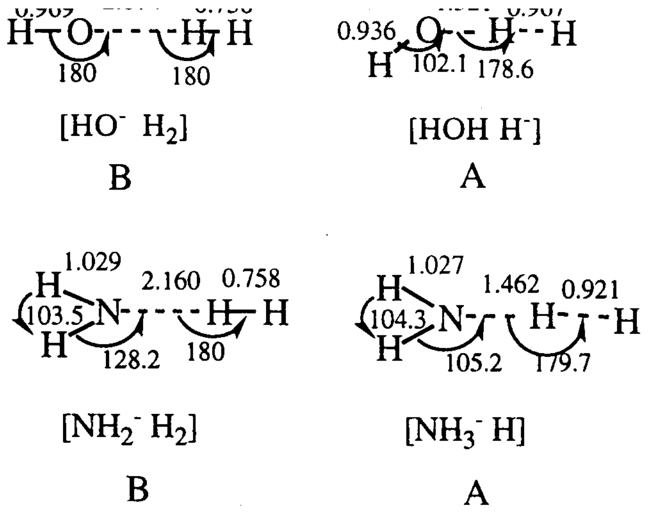


(eq. 8)

3. New Research Objectives

It has been known for a long time that simple basic molecules such as potassium tert-butoxide catalyze the hydrogenation of benzophenone at 130-200°C under approximately 1500 psig of H_2 (Walling and Bolyky, 1961; 1964).

Rathke and Klingler and their coworkers (1989; 1991; 1992) have studied and reviewed the role of simple bases on the reduction of carbon monoxide. In even earlier work, it was established that hydroxide ion and amide ion catalyzed the exchange of deuterium with water and ammonia, respectively (Dayton and Wilmarth, 1950). The energy barrier for the exchange of deuterium with potassium amide in liquid ammonia is about 5 kcal. mol^{-1}, and that for the exchange of deuterium in aqueous potassium hydroxide is approximately 25 kcal. mol^{-1}. Several lines of evidence including the kinetic isotope effects imply that the dihydrogen molecule forms an adduct with hydroxide ion and that hydrogen exchange occurs within this adduct rather than through free hydride anion. The proposed intermediates, the ions H_3O^- and $ND_2H_2^-$, have been detected as long-lived species in ion cyclotron resonance experiments as shown in Figure 6 (Klingeld et al., 1983; Ingemann et al., 1982). The nature of the bonding within these species has been investigated by extended basis set molecular orbital calculations (Cremer and Koraka, 1986; Chalasinski et al., 1987). The theoretical work suggests that H_3O^- and NH_4^- are most stable in the form of hydride-like adducts, A, with theoretical binding energies of 26 and 15 kcal. mol^{-1}, for water and ammonia respectively. The ions rearrange via internal motions to anion-dihydrogen complexes, B, which are estimated to be 2 to 15 kcal.mol^{-1} less stable than the hydride form A. The hydrogen-hydrogen bond in dihydrogen is greatly weakened in these substances due to the interaction with the basic anions, and we postulated that the intermediates, which are certain to be reactive, may have an adequate lifetime in solution to react with unsaturated hydrocarbons.



$[HO^- \ H_2]$ B

$[HOH \ H^-]$ A

$[NH_2^- \ H_2]$ B

$[NH_3^- \ H]$ A

Theoretical molecular structure of H_3O^- and NH_3^-

Consequently, we investigated the chemistry of these activated hydrogen molecules for the hydrogenation of the multiring aromatic hydrocarbons commonly present in coal liquids and fossil materials. We also explored the role of the strong inorganic and organic bases on the activation of the dihydrogen molecule for the transfer of a hydrogen to aromatic compounds. Naphthalene was chosen as a representative compound because naphthalene derivatives are abundant in coal liquids and because the naphthalene derivatives are more difficult to reduce than the other aromatic compounds.

Experimental Section

The reagents used in this work including lithium diisopropylamide (LDA), lithium diethylamide, lithium dicyclohexylamide, lithium dimethylamide, lithium bis(trimethylsilyl)amide, lithium *tert*-butoxide, sodium *tert*-butoxide, potassium *tert*-butoxide, naphthalene (99+%), anthracene (99%), phenanthrene (98%) were all purchased from Aldrich Chemical Company. The alkali metal amides ($NaNR_2$, $LiNR_2$, and KNR_2, R= methyl, ethyl, isopropyl, cyclohexyl, ...) are called as organoamides in this report to distinguish them from the alkali metal amides ($NaNH_2$, $LiNH_2$, and KNH_2). All the air-sensitive and moisture-sensitive chemicals were handled in a glove box filled with nitrogen or argon. The solvents that were used for the reactions were carefully purified before use. For instance, hexane was purified by refluxing commercial anhydrous hexane over sodium hydride. It was then distilled in nitrogen before use.

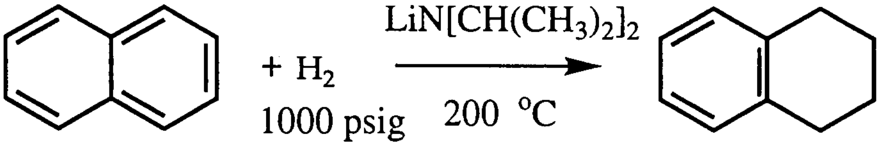
The hydrogenation reactions of the multiring aromatic compounds were performed in a Model 4576 HP/HT T316 autoclave system manufactured by Parr Instrument Company. The temperature was controlled by a Model 4842 temperature controller. In typical experiment, naphthalene (6.4 g, 0.05 mol) and freshly distilled hexane (37.6 mL were charged in the autoclave and a suspension of lithium diisopropylamide (13.4 mL, 0.0125 mol) in hexane was added to the autoclave under nitrogen. The sealed autoclave was purged with nitrogen and then with hydrogen several times to replace the air with hydrogen. The reaction system then was stirred at 200°C for 18 hrs. The product mixture was hydrolyzed by the dropwise addition to 1N aqueous NH_4Cl. The aqueous solution was extracted with methylene chloride three times. The combined organic phase was washed with 1N HCl and water (three times) and dried over $MgSO_4$. The solvent was removed by rotary evaporation and 6.2 g of tetralin was obtained.

The products were identified by gas chromatographic analysis on a Perkin-Elmer Sigma 3B instrument using a 11.83 m x 0.32 cm column packed with 10% OV-101. The GC conditions for the analysis of the products of the hydrogenation of naphthalene were injector temperature: 300°C; detector temperature: 300°C; initial column temperature: 120°C; final column temperature: 200°C; ramp rate: 5°C/min; initial time: 1 minute, final time: 1 minute. For some reactions, the products were also analyzed by GC-MS using a Hewlett-Packard 5970 series mass detector (70 eV) connected to a 5890 gas chromatograph (OV-101 capillary column, 15 m x 0.25 mm, 100-180°C, 5°C/min). ^1H NMR and ^2H NMR were obtained on Varian XL 400 -MHz spectrometer.

Results and Discussion

1. Dihydrogen Activated by Strong Bases for Naphthalene Hydrogenation

As described above, this work was based on the concept that the hydrogen molecule can be activated by strongly basic reagents to form an adduct that can affect the hydrogenation of unsaturated organic compounds. Our current research was designed to investigate whether basic reagents ranging from hydroxide to amide ions could accomplish the addition of hydrogen to multiring aromatic compounds. Therefore, various strong bases were tested as catalysts for the hydrogenation of naphthalene (eq. 9).



(eq. 9)

Representative results, such as the data shown in Table 2, indicate that alkali metal hydroxides (sodium hydroxide, potassium hydroxide and lithium hydroxide) and alkali metal *tert*-butoxides (sodium *tert*-butoxide, potassium *tert*-butoxide and lithium *tert*-butoxide) did not accomplish the hydrogenation of naphthalene at 200°C and 1000 psig of hydrogen using hexane or *tert*-butanol as solvent. However, we confirmed that potassium *tert*-butoxide did lead to the reduction of benzophenone to benzhydrol (Walling and Bolyky, 1961 and 1964). Sodium amide ($NaNH_2$) or lithium amide ($LiNH_2$) catalyzed the same reaction in very low yields (1.0% for $NaNH_2$ and 7.0% for $LiNH_2$) at 200°C and 1000 psig of hydrogen. The conversion of naphthalene was increased to 44% by increasing the [$LiNH_2$]/[substrate] ratio to 0.5 and the reaction temperature to 300°C. Work with the lithium organoamides such as lithium diisopropylamide and lithium dicyclohexylamide gave very encouraging results. These substances were found to exhibit very active catalytic properties for the hydrogenation of naphthalene to tetralin in more than 95% yield under 1000 psig of hydrogen at 200°C. The reaction was very clean with no traces of any byproducts.

Table 3 shows the results for a series of lithium organoamides as catalysts for the hydrogenation of naphthalene to tetralin. The important dependence of the catalytic activity of the lithium organoamides on the ligands in the molecules is displayed in these results. For instance, lithium diisopropylamide catalyzes the hydrogenation of naphthalene at 100% conversion, but lithium diethylamide and dimethylamide only give 3-7% conversion. These results indicate that the lithium organoamides with the larger aliphatic substituents such as lithium diisopropylamide and dicyclohexylamide exhibit higher activities than those with smaller substituents such as lithium diethylamide, lithium dimethylamide as well as lithium bis(trimethylsilyl)amide. These observations may be related to the different solubility of the bases in the solvent (hexane) employed in the system, because the lithium organoamides with large aliphatic substituents (more hydrophobic) are more soluble in hexane. This explanation is based in part on conversions with Professor David Collum.

The effect of the cations of the organoamides on their catalytic activity is shown in Table 3. The catalytic activity of the alkali metal trimethylsilylamide decreases in the order $K^+ > Na^+ > Li^+$ in toluene solution. Potassium bis(trimethylsilyl)amide, like lithium diisopropyl-amide, also exhibits very active catalytic activity for the hydrogenation of naphthalene to tetralin. Complete conversion was obtained without any byproducts with toluene as solvent under 1000 psig of hydrogen and 200°C. In comparison, the yield of tetralin decreased to 51 and 3% when sodium bis(trimethylsilyl)amide and lithium bis(trimethylsilyl)amide were used as the catalysts under the same conditions.

2. Catalytic Properties of Strong Bases for the Hydrogenation of Multiring Aromatic Hydrocarbons

The hydrogenation of naphthalene to tetralin was also influenced by the amount of the catalyst used (Figure 7). The yield of tetralin reached 100% when the mole fraction of the catalyst was more than 12.5%. The yield decreased with decreasing amounts of the catalyst employed. Figure 8 shows the dependence of the conversion on the initial hydrogen pressure. The reaction proceeds very well (80% conversion) at hydrogen pressures as low as 300 psig (20 atms). The low yield (13%) under low hydrogen pressure (150 psig) is clearly a consequence of the insufficiency of hydrogen in the reaction system. Elementary calculations show that fully hydrogenating 0.05 mole of naphthalene to tetralin in a 200 mL autoclave requires about 200 psig of hydrogen at room temperature. The experimental observations mean that the reaction can proceed at very low pressure.

Table 4 shows the effect of temperature on the reaction. A sharp dependence of the conversion on the temperature was observed. The yield of tetralin decreases from 100% at 200°C to about 0.5% at 100°C, implying that the reaction has a relatively high activation energy. Table 5 shows the influence of reaction time on the conversion. Four to five hours were needed for the reaction to proceed completely.

Lithium diisopropylamide does not dissolve in hexane at room temperature, so a suspension in hexane was used as the catalyst. It was postulated that its solubility would increase during the reaction at higher temperature. Indeed, a clear homogeneous solution was observed when the autoclave was opened at the end of the reaction, then a white solid precipitated. This white solid was collected, washed with hexane several times to remove tetralin and other impurities, dried in vacuum at room temperature for 24 hours. The elemental analysis indicated only 4.87% carbon, 3.84% hydrogen and 0.91% nitrogen. The lithium in the solid was determined by precipitation as trilithiurn phosphate (Simmons, 1953). The solid contains about 35 wt% of lithium, implying that it is probably LiOH (Li %: 28.98) or a mixture of LiOH and Li_2O (Li % in a 1:1 mixture: 37.72). This material was presumably produced by the hydrolysis of lithium diisopropylamide in moist air after the reaction system had been opened to the atmosphere.

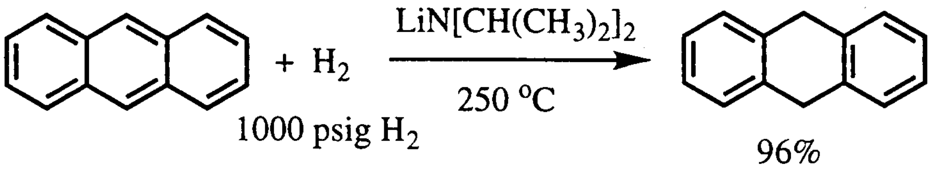
The new results described in this section indicate that some organoamides especially lithium diisopropylamide and potassium (trimethylsilyl)amide are very active catalysts for the hydrogenation of multiring aromatic hydrocarbons. Their catalytic properties are different from commercial catalysts such as Ni-Mo/Al_2O_3, Ni-W/Al_2O_3 or Co-Mo/Al_2O_3 (Prins, De Beer and Somorjai, 1989; Topsoe and Clausen, 1986; Chianelli and Daage, 1989). First, the hydrogenation of aromatic compounds catalyzed by the commercial heterogeneous catalysts is reversible. Under the typical hydrotreating conditions, complete conversion is impossible owing to the equilibrium limitations. The conversion of naphthalene to tetralin remains almost constant at about 30-40%, being unaffected by changes in catalyst composition, feed flow rate, and reaction temperature in the range from 310 to 400°C under 1000 psig of hydrogen pressure (Patzer, Farrauto and Montagna, 1979). However, the results of this study indicate that lithium diisopropylamide accomplishes the naphthalene to tetralin conversion in 100% under relatively mild conditions (200°C, 1000 psig of H_2). Second, the commercial catalyst systems obey first-order kinetics. Inasmuch as high pressure favors the high conversion of the aromatic compounds, the pressure employed is usually higher than 1500 psig and the temperature is about 300-450°C. For the organoamide catalysts, naphthalene can be converted in 100% yield at a pressure as low as 500 psig of H_2, and temperatures in the range of 200-250°C are sufficient for the reaction to proceed completely.

3. Hydrogenation of Other Multiring Aromatic Compounds Catalyzed by Strong Bases

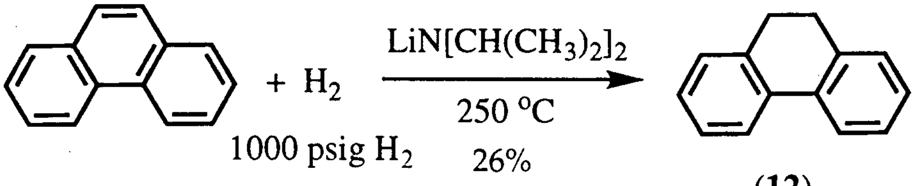
This section of the report contains considerable detail about the experimental methods that were used to investigate the reactions and to establish the structures of the products. The reaction products of the reduction of the polycyclic aromatic compounds are rarely simple and it was necessary to employ NMR and MS methods to establish the structures of the materials with confidence. These details will be omitted in later sections of this report, it is understood, however, that similar procedures were used to establish the structures of the products with other catalysts.

Other multiring aromatic compounds were also hydrogenated with the strong organic bases. When we used lithium diisopropylamide as the catalyst at the molar ratio of [base]/[substrate] of 0.25, anthracene was hydrogenated to 9,10-

dihydroanthracene in 96% yield, phenanthrene to 9,10-dihydrophenanthrene (**12**) in 26% yield and acridine to 9,10-dihydroacridine (**13**) in 77 % yield.

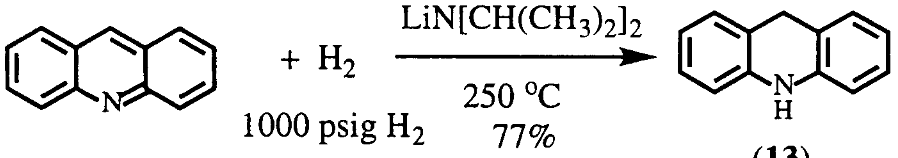


(eq. 10)



(**12**)

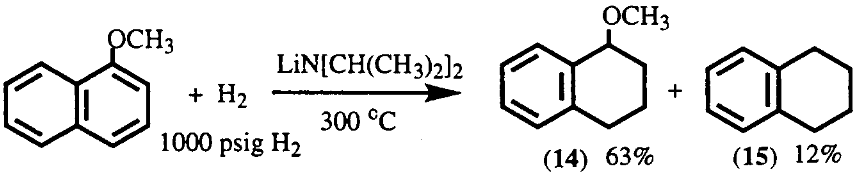
(eq. 11)



(**13**)

(eq. 12)

At 300°C, 1-methoxynaphthalene was hydrogenated in 95% yield, the main products are 1,2,3,4-tetrahydromethoxynaphthalene (**14**) and 1,2,3,4-tetrahydronaphthalene (**15**).

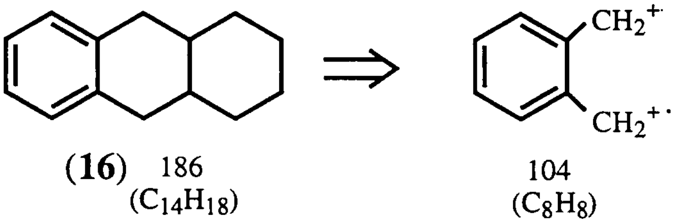


(14) 63% (15) 12%

(eq. 13)

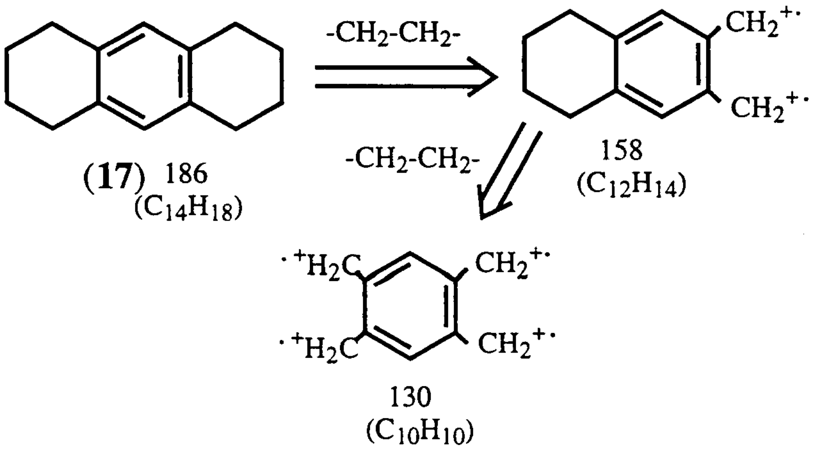
When potassium bis(trimethylsilyl)amide was used as the catalyst, the multiring aromatic compounds were hydrogenated to the corresponding monoaromatic derivatives in high yields. Anthracene, for instance, was hydrogenated under the usual conditions (250°C and 1000 psig of H_2, [base]/[substrate] = 0.36) to give a clear liquid, which crystallized to a white solid at room temperature.

The gas chromatogram of the product, Figure 9, contains three major components designated as 256, 265 and 343, respectively. The first two components constituted 14% of the material and the last one 84%. Figure 10 show the EIMS spectra of the first two components located at 256 and 265 in the GC-MS, respectively. These two components are isomers of 1,2,3,4,9,10,11,12-octahydroanthracene (**16**).



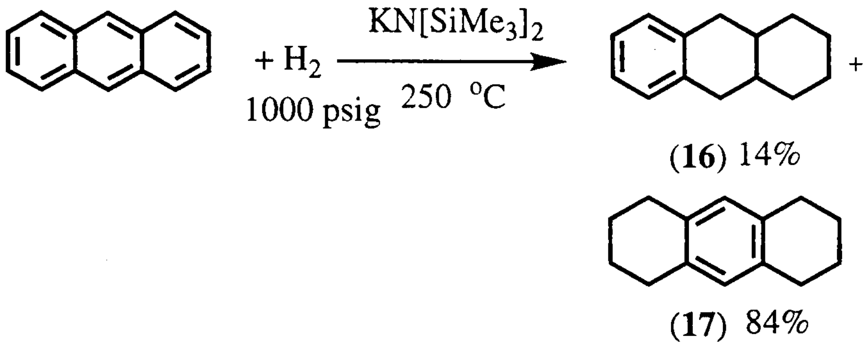
(eq. 14)

The EIMS spectra establish the molecular weight of 186 ($C_{14}H_{18}$) and the main species m/e: 104 ($C_8H_8^{+\cdot}$) as sketched in eq. 14. Figure 10c is the EIMS spectrum of the component located at 343 in the chromatogram. The main species in the EIMS spectrum are shown in eq. 15, i.e. m/e: 186 ($C_{14}H_{18}^{+\cdot}$), 158 ($C_{12}H_{14}^{+\cdot}$) and 130 ($C_{10}H_{10}^{+\cdot}$).



(eq. 15)

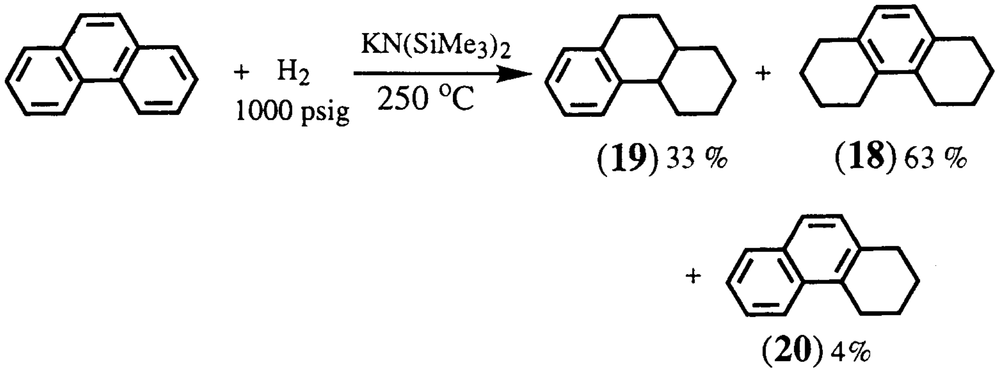
These data coupled with the ^{1}H NMR spectrum of the product (Figure 11) in which there are three absorptions located at 6.8 ppm (2H), 2.8 ppm (8H) and 1.8 ppm (8H), respectively, imply that the component is 1,2,3,4,5,6,7,8-octahydro-anthracene (**17**). Therefore, the experimental results indicate that anthracene was hydrogenated into the mixture shown in eq. 16.



(eq. 16)

The elemental analysis of the product support this interpretation: Calcd. for ($C_{14}H_{18}$): C, 90.26; H, 9.74. Found: C, 90.05; H, 9.80.

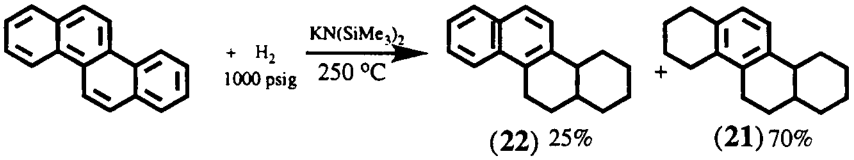
Similarly, phenanthrene was hydrogenated to a mixture of 1,2,3,4,5,6,7,8-octahydrophenanthrene (**18**) and 1,2,3,4,9,10,11,12-octahydrophenanthrene (**19**) and 1,2,3,4-tetrahydrophenanthrene (**20**) as shown in eq. 17.



(eq. 17)

The analytical results were obtained: Calcd. for ($C_{14}H_{18}$): C, 90.26; H, 9.74. Found: C, 90.04; H, 9.72. Figure 12 shows the EIMS spectra of the three products. Figure 13 is the ^{1}H NMR spectrum of the mixture of products. These results quite clearly indicate that the product is a mixture of 1,2,3,4,5,6,7,8-octahydrophenanthrene and 1,2,3,4,9,10,11,12-octahydrophenanthrene.

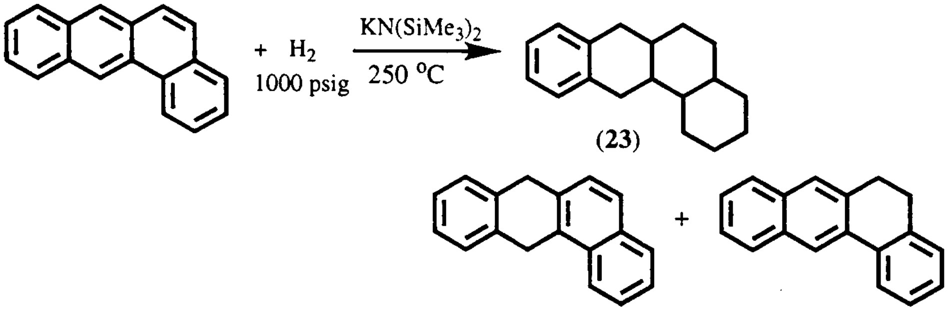
Chrysene was hydrogenated in the presence of excess potassium bis(trimethylsilyl)amide under 1000 psig of H_2 at 250 °C to give a yellow liquid. The liquid was separated by TLC to give another clear viscous liquid which was characterized by MS (Figure 14) and 1H NMR (Figure 15) as well as elemental analysis (Anal. Calcd for ($C_{18}H_{24}$): C, 89.94; H, 10.06. Found: C, 89.76; H, 10.12). The structures can be assigned with some confidence as shown in eq. 18 as the corresponding monocyclic



(eq. 18)

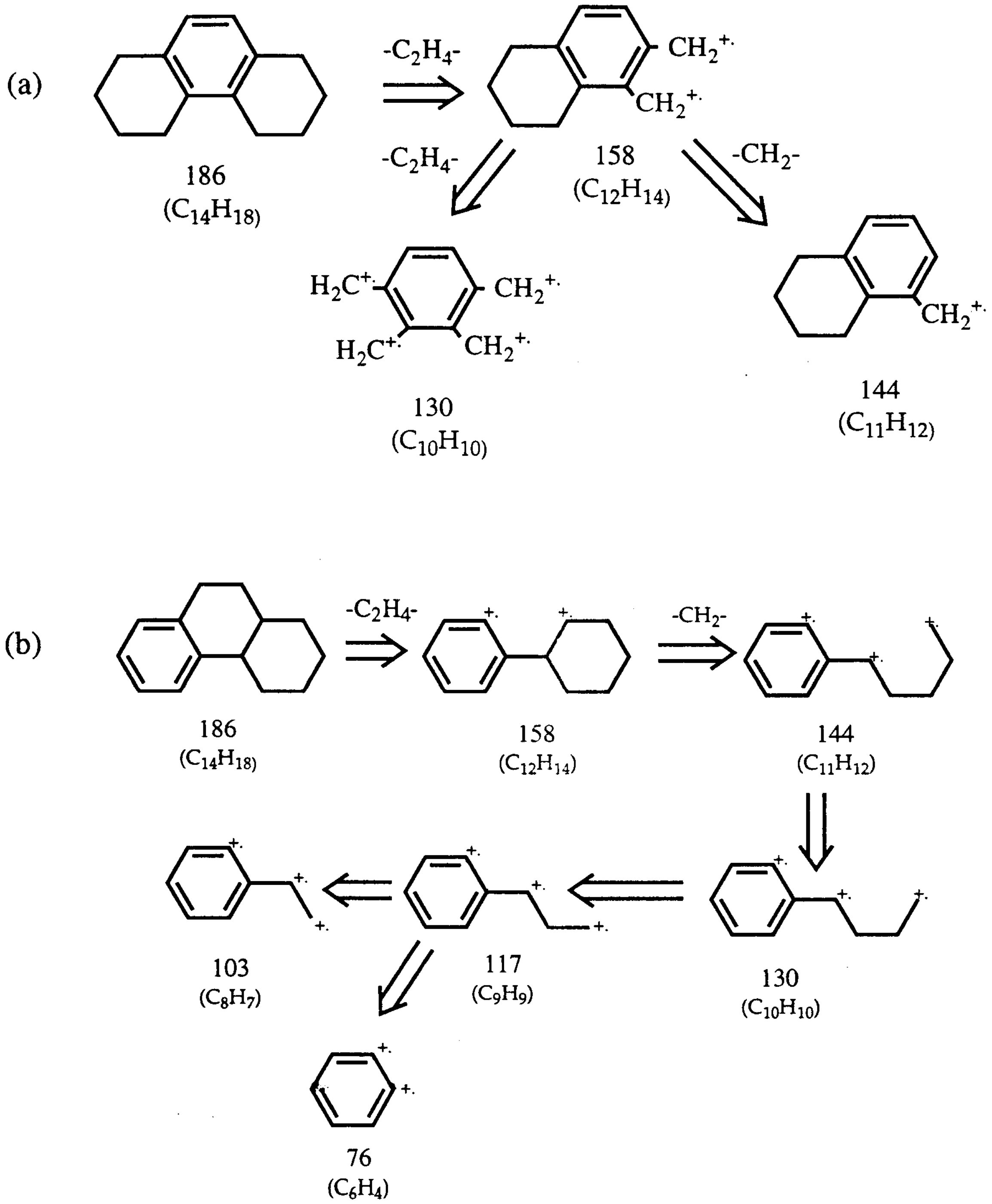
aromatic compounds 1,2,3,4,5,6,7,8,9,10,13,14-dodecahydrochrysene (**21**) and 5,6,7,8,9,10,13, 14-octahydrochrysene (**22**).

Under 1000 psig of H_2 at 250°C without stirring, 1,2-benzoanthracene was hydrogenated to monoaromatic compounds. The structure of 1,2,3,4,5,6,8,9,10,13,14-dodecahydro-1,2-benzoanthracene (**23**) was assigned on the basis of its spectroscopic properties (Figures 16 and 17) and the elemental analysis: Calcd. for ($C_{18}H_{24}$): C, 89.94; H, 10.06. Found: C, 89.76; H, 10.12. Two other dihydro derivatives (MW: 230) were also detected as shown in eq. 19. The structures of these products are based on the nuclear magnetic resonance spectra of the products.



(eq. 19)

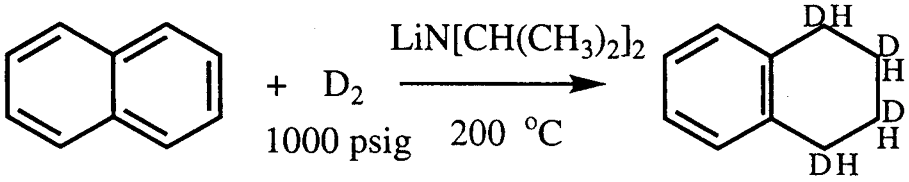
In summary, the research has established that naphthalene, anthracene, phenanthrene and chrysene are reduced with hydrogen in strongly basic solutions predominately to molecules that retain only one benzene ring. In some cases, small amounts of naphthalene derivatives are also obtained. In all cases, the conversions are very high. This is no doubt that these reduction reactions would be effective for the polycyclic aromatic hydrocarbons in coal liquids.



Scheme 3 The mass spectroscopic cracking pathway of the products obtained by hydrogenation of phenanthrene.

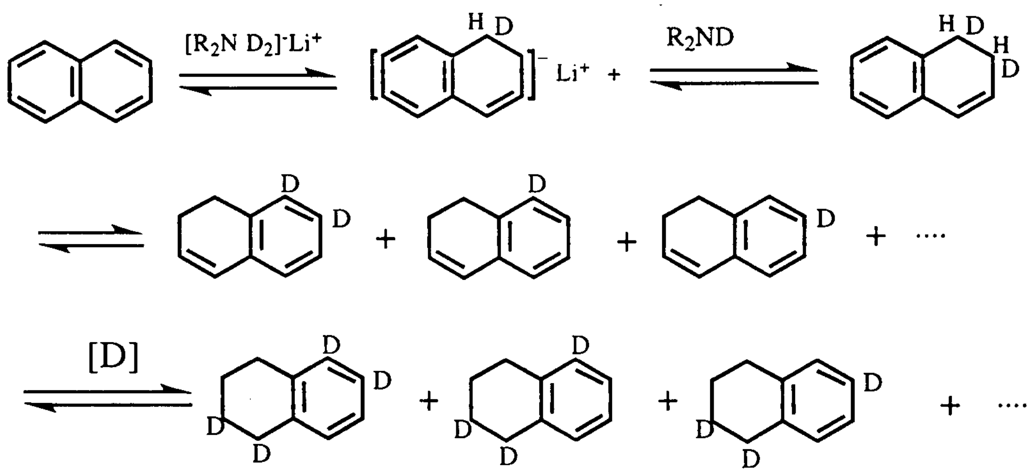
4. Deuterium Gas Experiments and Plausible Mechanistic Pathways in Hydrogenation

The substitution of deuterium gas for hydrogen gas in the catalytic hydrogenation of naphthalene (eq. 20) has provided some useful



(eq. 20)

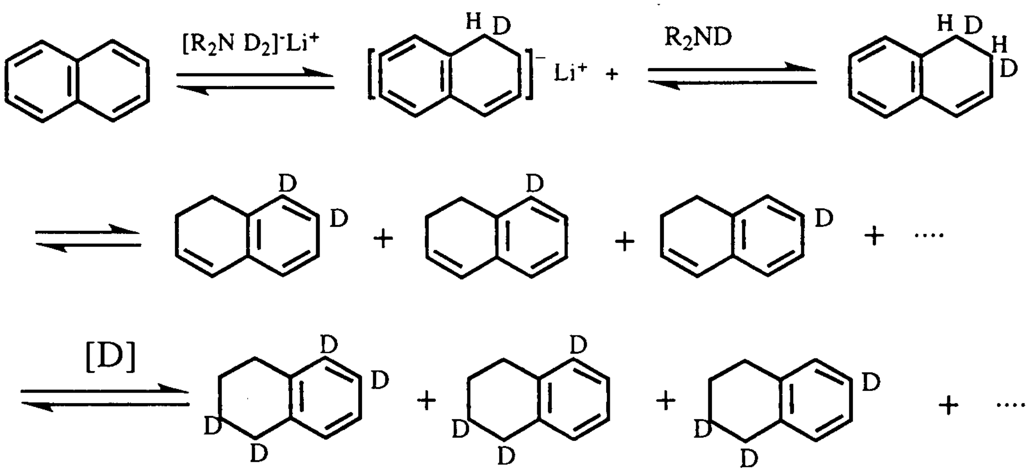
information about the reaction pathway. The ^{1}H and ^{2}H NMR spectra of the isotopically substituted tetralins that were obtained by the deuteration of naphthalene with deuterium are shown in Figure 18. The ratios of peak 1 to peak 2 to peak 3 reflect the differences in the deuteration at three different hydrogen positions, specifically the 5,6,7,8, the 1,4, and the 2,3 positions . The integration of the ^{1}H NMR and ^{2}H NMR spectra indicated that the ratio was 1:1:1. However, this ratio should be 2:1:1 (4H:2H:2H) in the 1H NMR and 0:1:1(OH:2H:2H) in the ^{2}H NMR if no deuterium-hydrogen exchange reactions occur during the reaction process. For comparison, tetralin was treated with deuterium gas under the same conditions as naphthalene (200°C, 1000 psig of D_2 pressure and 18 hrs, [LDA]/[naphthalene] = 0.25). The results show that only 8 to 10% of the protons at positions 5 and 8 and 2 to 4% at positions 1 and 4 were exchanged by deuterons, indicating that the D-H exchange does not occur significantly after the hydrogenation process has been completed. The assumption that D-H exchange occurs randomly in the naphthalene prior to the hydrogenation can not explain the product distribution because if the exchange process was random, then another product (1, 1,2,3,4,4,5,8-octadeuterotetralin) should be obtained or at least the intensity of peak 2 should be decreased in ^{1}H NMR and increased in ^{2}H NMR to a greater extent than was observed experimentally. Therefore, the isotopic exchange in the reduction of naphthalene must take place simultaneously with the reduction process. In addition, the fact that naphthalene can not be hydrogenated by Na/THF or butyllithium implies that naphthalene anions formed by the extraction of protons, especially in positions 1,4,5 or 8, is not the driving force for the hydrogenation process. The EIMS spectrum of the tetralin (Figure 19) shows that the product of naphthalene reduction with deuterium gas is an isotopic mixture of tetralin, which include tetralin-6*d* (m/e: 138), tetralin-7*d* (m/e: 139) and tetralin-8*d* (140) etc. It is inferred that the dihydrogen compounds are especially susceptible to exchange. One of the possible pathway to produce the deutero-containing tetralins is shown in Scheme 4.



Scheme 4 A possible pathway for the formation of deuterotetralins during the hydrogenation

Figure 20a shows the ^{1}H NMR of 9,10-dihydroanthracene, Figure 20b shows the spectra of the compound obtained by treating anthracene with deuterium under 1000 psig of deuterium pressure at 200°C. It can be seen that the peak (3.8 ppm) for the protons at 9,10 positions of the product disappeared almost completely when deuterium gas was used in the reduction of anthracene. The intensity of the peak at 3.8 ppm in Figure 20b was only 8% of that in Figure 20a. The ^{2}H NMR of the product shows two peaks, one at 3.8 ppm and another at 7.2 ppm, their ratio is about 7:1. These data and the results of the analysis of the products by ^{1}H NMR spectroscopy indicated that the two protons at 9,10-positions in anthracene were almost completely exchanged by deuterium during the reaction but that only 10-15% of protons in the rings was exchanged. These observations are also compatible with the concepts displayed in Scheme 4.

We did not conduct any experiments to establish the nature of the reactive base-hydrogen complex, but we infer that the hydrogen molecule was activated first by the strong base to form an intermediate $[R_2N..H ... H]\text{-}Li^+$, which then transfers one hydrogen of the in equivalent group of hydrogen atoms in the complex to the substrate. We also postulate that there are significant differences in the transition state energies for different unsaturated functional groups. Hence, the energy requirements for the reduction of the polar ketonic function investigated by Walling and the carbon monoxide molecule investigated by Rathke and his group will be less than the energy requirements for the reduction of the essentially unpolarized carbon-carbon double bonds investigated in this study. We also infer that the reduction proceeds through a polarized activated-hydrogen adduct. Generally, the non-polar substrates require more activated hydrogen molecules. Vinyl groups are also more reactive than aromatic molecules. For instance, although the vinyl group and carbonyl group (stilbene and benzophenone) can be hydrogenated by hydroxide-activated hydrogen adducts, the more stable polycondensed aromatic rings (naphthalene and anthracene) require the more reactive organoamides adducts to effect their hydrogenation. A reaction pathway that displays the proposed overall reduction process is shown in Scheme 5.



Scheme 5 A reaction pathway for the hydrogenation of naphthalene catalyzed by a strong organic base

Conclusion

Some strongly basic organoamides such as lithium diisopropylamide and potassium(trimethylsilyl)amide were found to activate the dihydrogen molecule presumably by the formation of adducts. The reagent can affect the hydrogenation of multiring aromatic hydrocarbons. In presence of lithium diisopropylamide, naphthalene was hydrogenated to 1,2,3,4-tetrahydronaphthalene in 100% yield under a relatively mild conditions (200°C, and 1000 psig of hydrogen, 5 hrs) and anthracene was converted to 9,10-dihydroanthracene in 95% under the same conditions. Potassium bis(trimethylsilyl)amide was found to be an even more active catalyst for the reaction. Polycondensed aromatic compounds with three and four resonance rings can be hydrogenated into the corresponding monoaromatic compounds in high yields. For instance, anthracene, a triaromatic substance, was completely hydrogenated into a mixture of the corresponding monoaromatic compounds, 1,2,3,4,5,6,7,8-octahydroanthracene (**17**) and 1,2,3,4,9,10,11,12-octahydroanthracene (**16**). Chrysene, a tetraaromatic substance, was hydrogenated in the presence of excess potassium bis(trimethylsilyl)amide under comparable conditions to give a liquid which was the mixture of the corresponding monoaromatic compounds, 1,2,3,4,5,6,7,8,9,10,13,14-

dodecahydro-chrysene (**21**) and 5,6,7,8,9,10,13,14-octahydrochrysene (**22**). The catalytic properties of the strong base depend on (1) its chemical structure, whether a hydroxide or amide derivative or whether an amide or a dialkyl amide, and the gegen cation, lithium, sodium or potassium, in the ionic catalyst and (2) the reaction conditions such as the temperature, hydrogen pressure, time etc. The reaction does not require high pressure, but high temperatures are necessary. Substitution of deuterium for hydrogen gas in the hydrogenation provide some evidence regarding the mechanistic pathways. The reactions are apparently successful because the dihydrogen molecule is activated by the strong base and forms a polarized intermediate, $[R_2N..H... H]\text{-}Li^+$, which then transfer the activated hydride like hydrogen to the substrate.

Part B

Hydrotreating of Coal Liquids Catalyzed by Strong Organic Bases

Introduction

Coal liquids can contain high concentration of aromatic hydrocarbons and other heteroaromatic materials. This feature reduces their value as special end-products either for direct sale or for use as refinery feedstocks. Therefore, upgrading by the addition of hydrogen for the reduction of aromatic compounds and for the removal of the heteroatoms is necessary. Many processes have been studied to produce suitable refinery feed liquids from coal liquids. The methods presently used in the treatment of heavy fractions from the distillation of petroleum include thermal cracking, hydrotreating and hydrocracking. Coal liquids require greater upgrading than petroleum and this requirement calls for a dramatic improvement in the existing technology.

Early attempts that were made to achieve the desired levels of coal dissolution and upgrading used a single reaction stage. But, the recognition that different conditions are required for optimum coal dissolution and for the upgrading of coal liquids has led to the development of several two-stage processes, in which the second catalytic reaction stage is used to upgrade and refine the initial liquid products obtained from liquefaction processes to obtain the desired materials for further processing. Major advancements resulted from the operation of a two-stage liquefaction pilot plant at Wilsonville, Alabama, which converted about 70% of an Illinois No. 6 coal to distillate on a moisture ash free basis (Weber and Stewart, 1987). The research on the on-line hydrotreating of the close-coupled catalytic two-stage liquefaction (CTSL™) process conducted by Commolli and Johanson (1993) at Hydrocarbon Research, Inc. indicated that the on-line hydrotreating was very effective in reducing the heteroatom contents of the distillate and caused significant saturation of the aromatic compounds, especially in the middle distillate range (280-325°C). The sulfur contents of the hydrotreated Separator Overhead (SOH) were between 2 and 14 ppm and the nitrogen contents were reduced to 9 ppm. with the lightest hydrotreater feeds, but were 89 and 72 ppm with the heavier hydrotreater feeds. The H/C ratio of the distillate (500-650°F) increased 0.10 from 1.54 to 1.64. However, the catalysts were deactivated gradually due to the carbonaceous and metal deposits. In addition, the rejuvenated catalyst had much lower physical strength, and a very much shortened particle length than the fresh catalyst.

In recent years, work has been done on the upgrading of the coal-derived liquids. Table 6 shows some examples of the work where different feedstocks and products are produced. In a total upgrading procedure where gasoline or other refinery products are produced, both upgrading and refining reactions would have to be carried out. Usually, upgrading involves only those treatments that would result in a crude oil that would be acceptable in a conventional oil refinery. In the most of the studies performed, molybdenum and nickel catalysts supported on alumina or zeolites were the main upgrading catalysts. As described above, potential commercial catalysts suffered from two major problems, one is the rapid deactivation of the catalytic activity due to the carbonaceous and metal deposits, another is their poor mechanical properties. When the metals (Mo or W) that are used in the catalysts are expensive their use must be compensated for by appropriate catalyst life performance. The approximate relative costs of various metals used or considered as catalytic materials are shown in Table 7. This shows the incentive for research directed toward the discovery of cheap, metal based catalysts such as iron or iron-based materials as well as the need for catalyst recovery methods for many of the materials that are being considered for use in upgrading processes.

Since it will be many years before any of these catalyst system will be employed, it seemed most appropriate to search an alternative strategy that is based upon alternative approaches to heterogeneous catalysis. Consequently, we explored the use of the basic reagents discussed in Section A for upgrading the crude fossil fuel liquids obtained from coal. As described in Part A of this report, the dihydrogen molecule can be effectively activated by certain strong organic bases to form an adduct which enabled the hydrogenation of multiring aromatic hydrocarbons. Many organic bases are inexpensive and are not poisoned by reactions with the sulfur-, nitrogen-, or oxygen-containing hydrocarbons that are commonly present in the coal liquids or other crude fuels. Accordingly, these organic bases have been investigated as catalysts for the hydrotreating of coal liquid in this laboratory. Here are the results regarding this research.

Experimental

Materials: The reagents used in this work including lithium diisopropylamide (LDA), potassium bis(trimethylsilyl)amide (PTA), lithium bis(trimethylsilyl)amide (LTA), sodium bis(trimethylsilyl)amide (STA) were all purchased from Aldrich Chemical Company. The coal liquid was supplied by the U. S. Department of Energy (Sample VSOH, date of sample: July, 19, 1994; Time of sample: 0200; Run 260-05-368, Elemental analysis: C, 89.53; H, 10.20; others: 0.27; H/C: 1.36). All the air-sensitive and moisture-sensitive chemicals were handled in a glove box filled with nitrogen or argon. The solvents that were used for the reactions were carefully purified before use. For instance, hexane was purified by refluxing commercial anhydrous hexane over sodium hydride and the distilled in nitrogen before use.

Procedure for the hydrotreating of coal liquid: The hydrotreating of the coal liquid was performed in a Model 4576 HP/HT T316 autoclave system manufactured by Parr Instrument Company. The temperature was controlled by a Model 4842 temperature controller. In a typical experiment, coal liquid (10.0 g) in hexane (10.0 g) and PTA (2.0 g) in toluene (0.5M) were charged in the autoclave under nitrogen. The sealed autoclave was purged with nitrogen several times to replace the air, then charged with dihydrogen to 1000 psig. The reactor was stirred at 200°C for 18 hrs. After cooling to room temperature, the autoclave was opened and the product mixture was hydrolyzed by the dropwise addition of 1N aqueous NH_4Cl. The aqueous solution was extracted with hexane three times. The combined organic phase was washed with IN HCl, then water (three times) and dried over $MgSO_4$. The solvent was removed by vacuum evaporation and 9.2 g of clean, yellowish liquid was obtained.

The products were studied by ^{1}H NMR and ^{2}H NMR on a GE Omega 500-MHz spectrometer and UV-Visible spectra were recorded by using Perkin Elmer Lambda 6 instruments. Elemental analysis was performed by Atlantic Microlab, Inc.

The method for calculating the conversion of the aromatic constituents into saturated hydrocarbon. The UV-Visible spectrum of the coal liquid shows two absorptions located at 321 and 338 nm, respectively, which are attributed to the π to π^* absorptions of the multiring aromatic compounds in the coal liquid. A plot of absorbance versus concentration is a straight line passing the origin in accord with the Lambert-Beer law: $A= \varepsilon bC$, where A is the absorbance, ε is the molar absorption coefficient, and b is the sample path length, C is the concentration of the aromatic constituents. Therefore, the conversion of the multiring aromatic compound could be calculated by the following formula:

$$Y(\%) =(C_o-C_i)/C_o \times 100 = (A_o-A_i)/A_o \times 100$$

where Y is the conversion that needs to be determined, C_i and C_o are the concentrations of the multiring aromatic compound in the coal liquid after and before the hydrotreating, respectively, A_i is the intensity of the hydrotreated coal liquid and A_o is the intensity of the original coal liquid.

Results and Discussion

Potassium diisopropylamide and potassium bis(trimethylsilyl) amide were proven to be active catalysts for the hydrogenation of multiring aromatic compounds at more than 200°C and 1000 psig of hydrogen pressure. Under these conditions, naphthalene can be hydrogenated to tetralin in more than 99% yield and anthracene can be converted into a mixture of 1,2,3,4,5,6,7,8-octahydroanthracene (**17**) and 1,2,3,4,9,10,11,12-octahydroanthracene (**16**) in 98% yield. These catalysts have been applied for hydrotreating of the coal liquid sample (VSOH) supplied by the U. S. Department of Energy. Figure 21a shows the UV-Visible spectra of the original VSOH and Figure 2lb shows the hydrotreated VSOH obtained by using PTA under 1000 psig of H_2 at 200°C. The two peaks of the coal liquid located at 321 and 338 nm, respectively, that are attributed to the π to π* absorptions of multiring aromatic hydrocarbons in the coal liquid, decrease in intensity after the coal liquid is hydrotreated. The conversion obtained in the hydrotreating reaction can be calculated from the decrease in intensity of the absorptions as described in the Experimental Section. Table 8 shows the results of hydrotreating of coal liquid VSOH catalyzed by lithium diisopropylamide (LDA) and potassium bis(trimethylsilyl)amide (PTA). For LDA as the catalyst, conversions as high as 82% at 338 nm and 97% at 321 nm, respectively, were achieved when the ratio of [coal liquid]/[catalyst] (g/g) is 10:4. However, the conversions decreased with increasing the [coal liquid]/[catalyst] ratios, only 17% at 338 nm and 22% at 321 nm of conversions were obtained if [coal liquid]/[catalyst] ratio is 10:1. For PTA, the conversion reached 100% when [coal liquid]/[catalyst] (g/g) was 10:2. This means that the multiring aromatic hydrocarbons in the coal liquid characterized by the UV spectra were reduced completely. In general, the hydrotreated coal liquid has a higher hydrogen content as demonstrated by the higher WC ratios for the products. For instance, the coal liquid hydrotreated by PTA at [VSOH]/[catalyst] (g/g) of 10/4 and 200°C under 1000 psig of H_2 contains 86.27% C, 11.05% H. Thus, the H/C ratio is 1.53, an increase of 0.15 units compared to the value of 1.38 of VSOH.

Figure 22a shows the ^{1}H NMR spectrum of the untreated VSOH liquid and Figure 22b shows the 1H NMR spectra of the hydrotreated coal liquids provided by the PTA catalyst at [VSOH]/[catalyst] ratio of 10:2 and 200°C under 1000 psig of H_2. The peaks at 8.0- 8.3 ppm, which are assigned to the protons in the multiring aromatic rings, disappear and new resonances in the region of 6.5-7.9 ppm, which are assigned to the protons in the single isolated aromatic rings, are observed. Also, we observed some new resonances in the region of 2.0-3.5 ppm that are attributed to the protons in the aliphatic hydrocarbons. These results confirmed that multiring aromatic hydrocarbons in the coal liquid were hydrogenated into aliphatic materials under the conditions employed. The elemental analysis for the product indicates that the carbon content (88.17) decreases as the hydrogen content (10.74) increases by 0.42 compared to the untreated coal liquid.

We found that PTA is a more active catalyst for the hydrotreating of the coal liquid than LDA, the same conclusion was reached in the study of the hydrogenation of multiring aromatic compounds in Part A. This fact can be seen from the conversion of aromatic substances during the hydrotreating and from the H/C ratios of the hydrotreated coal liquid. For instance, the conversion with PTA as the catalyst reaches 100% when the [coal liquid]/[catalyst] (g/g) ratio is 10:2, while it is only 60-80% with LDA as the catalyst with the same [coal liquid]/[catalyst] ratio and even higher temperature (300°C). In addition, the H/C ratio of the product at [coal liquid]/[catalyst] of 10:4 reaches 1.53 for PTA as catalyst at 200°C compared to 1.43 for LDA at 300°C. Further evidence was obtained from the ^{1}H NMR spectra of the hydrotreated coal liquids produced by the two different catalysts (Figure 23). The hydrotreating of the coal liquid by PTA produced a new liquid with an abundance of protons in the region of 7.2-7.4 ppm in ^{1}H NMR spectrum and almost all of the protons in the region of 8.0-8.2 ppm disappeared. However, the product obtained by the hydrotreating catalyzed by LDA gave a product that still contained some protons in the region of 8.0-8.2 ppm, indicating that the multiring aromatic hydrocarbons were not reduced completely.

The effect of temperature on the hydrotreating of the coal liquid with the PTA catalyst is shown in Table 9. The conversion reaches 100% when the temperature is higher than 200°C, and the H/C ratios continually increase to 1.53 at 300°C. The fact that the continual increase in H/C ratios after the conversion reaches 100% at 200°C demonstrated that the hydrotreating of the coal liquid contains products not only from the hydrogenation of the multiring aromatic hydrocarbons that were characterized by the UV absorptions at 321 and 338 nm, but also that some other substances, possibly heterocyclic aromatic compounds, are reduced. The former compounds are relatively easy to hydrogenate at temperature lower than 200°C and 1000 psig of hydrogen pressure while the latter reactions may need higher temperatures to proceed effectively.

The hydrotreating of coal liquids was also influenced by the hydrogen pressure employed (Table 10). The WC ratios increased with the increasing the hydrogen pressure. It can be seen that 1000 psig of hydrogen was needed to hydrotreat the coal liquid in 100% conversion and reach a H/C ratio of 1.49. It should also be noted that control experiments were performed with these systems. Specifically, no apparent hydrotreating could be detected in the absence of hydrogen. For instance, the increase of H/C ratio was not observed if the coal liquid was treated at 250°C in the presence of all the reagents except hydrogen.

Besides PTA, other alkali metals bis(trimethylsilyl)amides, lithium bis(trimethylsilyl)amide (LTA) and sodium bis(trimethylsilyl)-amide (STA) were also investigated as catalysts for the VSOH hydrotreating. The results in Table 11 show that the potassium amide derivatives is more active than the lithium or sodium amides. Under the same conditions, PTA gave a product with higher H/C ratio than LTA or STA.

In another series of experiments, we showed that naphthalene was hydrogenated completely in the presence of coal liquid under the same conditions. This result implied that the reduction of multiring aromatic compounds was not inhibited by the coal liquid which contains some traditional catalyst poisons such as sulfur, nitrogen and oxygen. Thus, the reduction of the naphthalene and the other multiring aromatic hydrocarbons in the coal liquids can be catalyzed by strong organic bases.

Substitution of dideuterium for dihydrogen in the hydrotreating of the coal liquid at 250°C and 1000 psig yielded a product which was characterized by ^{2}H NMR as shown in Figure 24. Two groups of deuterium resonances were observed in the region of 6.5-8.0 ppm and 1.0-3.5 ppm, respectively. The former was assigned to the deuterium bonded to the carbon atoms of aromatic rings and the latter to the deuterium linked with the aliphatic carbon atoms. There are two sources for these heavy nuclei, one is from the reduction of the aromatic compounds and another is from the D-H exchange. As we concluded in the previous section of this report, in which naphthalene was reduced with PTA and dideuterium. instead of dihydrogen, the D-H exchange occurs simultaneously with the reduction of the aromatic compounds. The deuterium in the region of 6.5-8.0 ppm may be from the D-H exchange during the reduction process and the deuterium in the 1.0-3.5 ppm from either the reduction of aromatic compounds or the D-H exchange during the reduction process.

Conclusion

Strong organic bases are active catalysts for the hydrotreating of coal liquids with elemental hydrogen. The hydrogen to carbon ratios increased compared to the original coal liquid and the naphthalene and other multiring aromatic hydrocarbons in the coal liquid were reduced to give saturated monoaromatic compounds. Of the several organic bases investigated, potassium bis(trimethylsilyl)amide was found to be the most effective catalyst. Temperature and hydrogen pressure all affect the hydrotreating. The reaction clearly proceeds in stages with the more undesirable polycyclic aromatic compounds reduced under the least severe conditions.

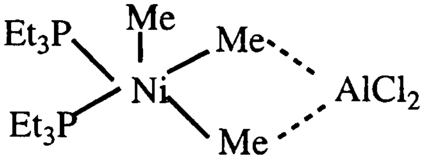
Part C

Molecular Organometallic Catalysts for Hydrogenation of Aromatic Compounds

Introduction

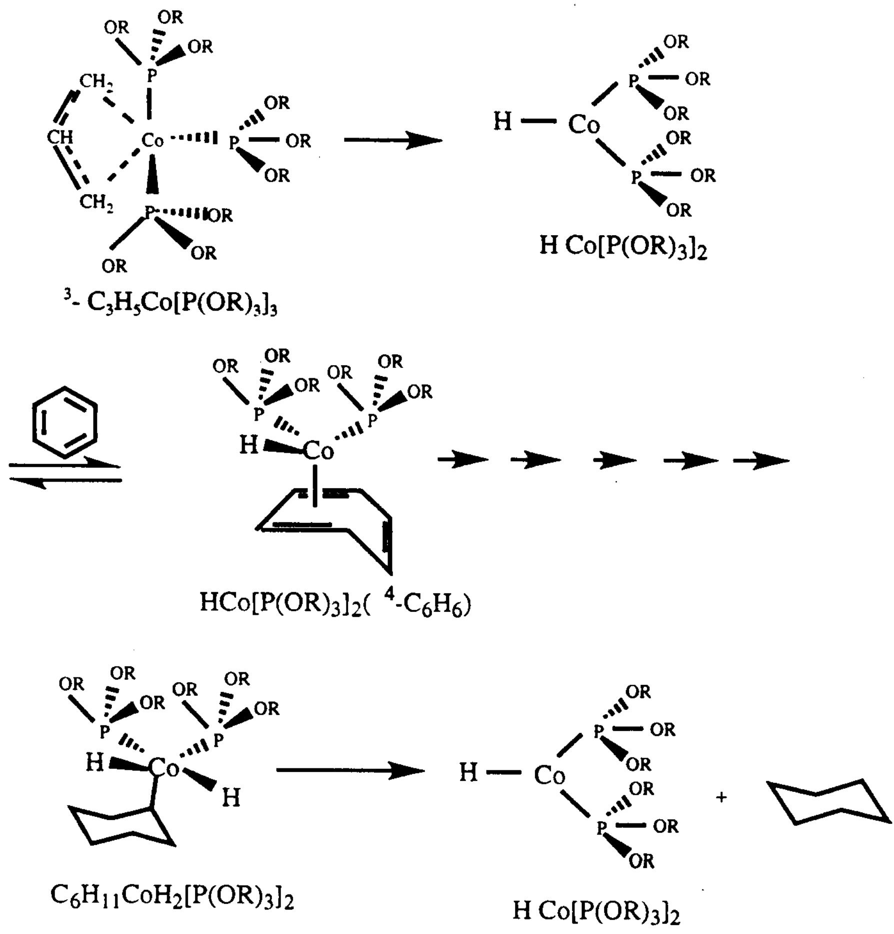
The third part of the research, which was also described in the original proposal, concerns the development of molecular organometallic catalysts for the hydrogenation of aromatic compounds that are found in petroleum and coal liquids. Research on coal has been focused almost exclusively on traditional heterogeneous catalysts and we have explored a different approach that exploits some newer elements of hydrogenation chemistry based upon organometallic chemistry. In brief, two types of molecular organometallic catalysts have been investigated for the hydrogenation of aromatic compounds under mild conditions in recent years. One approach exploits homogeneous organometallic catalysts and the other approach uses colloidal transition metal catalysts in biphasic or phase transfer systems.

The hydrogenation of aromatic compounds by homogeneous catalysts was first reported at mid century (Wender et al., 1950). However, due to the extraordinarily effectiveness of heterogeneous catalysts for these kinds of reactions, the homogeneous catalysts have not received much attention until recently when two major developments were made in the industrial hydrogenation of benzene, one is the IFP (Institute Francais du Petrole) Ni-Al catalyst (structure 21) generated from $NiCl_2(PEt_3)_2$ and $Al_2Me_3Cl_3$ for the hydrogenation of benzene to cyclohexane (Chauvin et al., 1980) and the other is a ruthenium catalyst for the hydrogenation of benzene to cyclohexene (Nagahara and



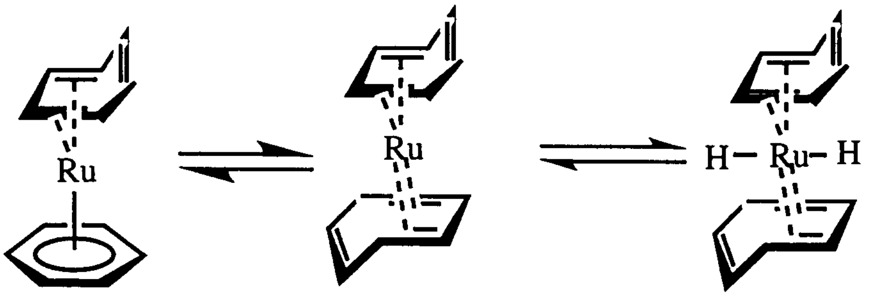
(21)

Konishi, 1988). Several papers regarding the catalysis of the hydrogenation of multiring aromatic compounds by homogeneous organometallic catalysts have also published (Stuhl et al. 1978; Blum et al., 1987; Fish et al., 1985). Muetterties and coworkers (1979) discovered that simple organocobalt compounds of general formula, η^3-$C_3H_5Co[P(OR)_3]_3$ (R= CH_3, C_2H_5, C_3H_7), readily hydrogenated aromatic hydrocarbons in a steroselective manner at ambient temperature and a low pressure of dihydrogen. Unfortunately, the lifetimes of these catalysts are very short (Muetterties et al., 1979). The mechanism of hydrogenation proposed by Bleeke and Muetterties (1981) for arenes is shown in eq. 22. The first step apparently is the loss of the allyl ligand with the formation of propane to give a 14 electron complex, $HCo[P(OR)_3]_2$ which can then form a η^4-benzene complex, $HCo[P(OR)_3]_2(\eta^4\text{-}C_6H_6)$. Then, by a series of hydrogen atom additions to one face of the coordinated arene followed by oxidative addition of dihydrogen to cobalt, a postulated sequence of η^4-η^3-η^3-η^4 - η^3- η^3- η^2 - η^1 hydrogenated arene complexes can be envisioned. The last complex, $C_6H_{11}CoH_2[P(OR)_3]_2$, reacts to provide *cis*- cyclohexane and $HCo[P(OR)_3]_2$, which then starts the catalytic cycle again. The reaction has a pronounced steric requirement with the following order of arene reactivity: benzene > toluene > xylene > mesitylene > 1,2,4,5-tetramethylbenzene > 1,2,3-trimethylbenzene > hexamethylbenzene. The electronic effect is also pronounced with electron-withdrawing substituents such as fluoro, cyano, and nitro groups, on an arene ring causing the system to be unreactive.



(eq. 22)

Among the many factors that are important for arene hydrogenation to proceed is η^4 coordination, which distorts the aromatic compound from its normal planar structure and lowers the aromatic resonance stabilization energy and provides a driving force for arene ring hydrogenation. The formation of η^4 as well as η^2 arene complexes may well be critical for any successful hydrogenation catalyst. Bis(hexamethylbenzene)ruthenium(0), for instance, with one arene ring in a η^4 coordination and the other η^6 is a long lived catalyst for arene ring hydrogenation (Bennett et al., 1979, 1980). A physical mechanism (eq. 23) consistent with the established permutational character of the exchange involves a bis(η^4-arene) ruthenium. The latter, a 16-electron complex, may react with hydrogen in what could be the first



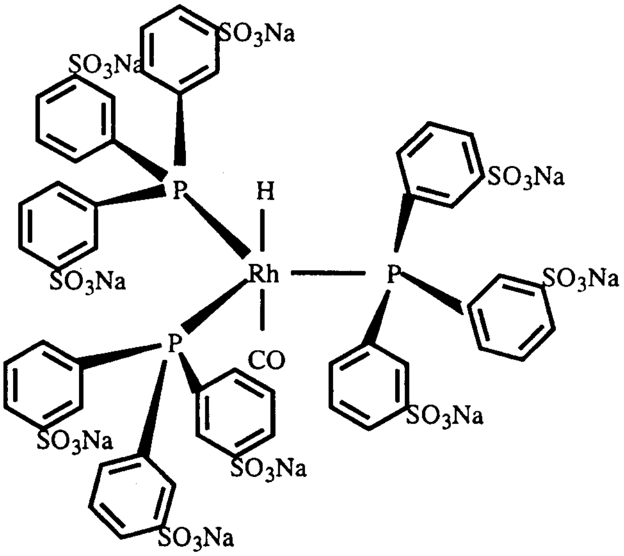
(eq. 23)

step in the catalytic sequence. Arene exchange to allow introduction of a reducible arene into the coordination sphere was presumed to be a subsequent step and probably rate determining. It is thought that the η^4 coordination 16 electron situation is important in that molecules with this configuration can oxidatively add dihydrogen. Maitlis and coworkers (1978) found that the catalyst precursor with the formula $[Cp^*RhCl_2]_2$ (Cp* =pentamethylcyclopentadienyl) was also efficient for arene hydrogenation in the presence of a basic cocatalyst such as triethyl amine. The base is thought to be required to neutralize the hydrogen chloride produced in the heterolytic, cleavage of the dihydrogen molecule, a necessary step in the formation of the active catalyst. Fish and coworkers (1984, 1985, 1986) discovered that $(Ph_3P)_3RhCl$ (tris(triphenylphosphine)rhodium(I) chloride) and $(Ph_3P)_3RuCl_2$ (tris(triphenylphosphine)ruthenium(II) chloride) were excellent homogeneous catalyst precursors for the hydrogenation of polynuclear heteroaromatic nitrogen compounds. They investigated the structure activity relationships with the nitrogen containing compounds and found the order to be as follows: phenanthridine >> acridine >> quinoline > 5,6-benzoquinoline >> 7,8-benzoquinoline. It was also discovered that pyridine derivatives totally quenched the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. Interestingly, compounds such as pyrrole, carbazole, thiophene and ρ-cresol enhanced the initial rate of the rhodium catalyzed hydrogenation of quinoline by a modest factor of 1.5 to 2.5.

Biphasic and phase transfer catalysis technologies have attracted much attention in recent years due to their successful applications for hydroformulation and related processes (Lubineau et al., 1994; Wiebus and Cornils, 1994, 1995). The basic principles of biphasic homogeneous catalysis were recently reviewed (Kalck and Monteil, 1992), and the general feature of the method were discussed at a NATO Advanced Research Workshop in 1994 (NATO, 1994). At this workshop, the state-of-the-art aqueous biphasic catalyst systems were highlighted (Haggin, 1994).

One example is the Ruhrchemie/Rhone-Poulenc (RCH/RP) process, in which water-soluble rhodium complexes (eq. 24)

$$HRh(CO)_4 + 3\ P(m\text{-}C_6H_4SO_3Na)_3 \rightarrow HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3 \quad \text{(eq. 24)}$$



$HRh(CO)[P(m\text{-}C_6H_4\text{-}SO_3Na)_3]_3$

with sulfonated triphenylphosphine ligands catalyze the hydroformulation of propene (Cornils and Falbe, 1984; Bach and Wiebus, 1984). The reactants and the products remain in the organic phase and the catalyst remains in the aqueous phase, the mobile aqueous phase can easily be separated from the organic phase. The RCH/RP operation uses this technology to produce 3.0 x 10^5 tons/year of *n*-butanol, a very inexpensive chemical that is made with an expensive catalyst. The advantages in using aqueous biphasic techniques include (1) the reduced complexity in the preparation of the catalyst, (2) the higher catalytic activity and selectivity, (3) the mild reaction conditions under which the reaction proceeds smoothly and (4) the elimination of the difficult separation problems that are associated with homogeneous catalysts after the completion of the reaction. This problem can be overcome easily by separating the organic phase with the product from the aqueous phase with the catalyst. Other successful applications of biphasic homogeneous catalyst systems have been Shell's SHOP process (Shell Higher Olefins Process) (Moulijin, et al., 1993) (biphasic, but not aqueous) and processes by Rhone-Poulenc (Rhone Poulenc Ind. Patent; Mercier and Chabardes, 1994), and Kuraray (Tokitoh and Yoshimura, 1989) for manufacturing higher olefins, vitamin precursors, telomers, and fine chemicals. These reactions include oligomerization, metatheses, telomerizations and carbonylations. The aqueous phase in the system plays an important role both in improving the activity and selectivity of the catalyst (Joo, Csiba and Benyei, 1993).

Biphasic and phase transfer techniques have been exploited for the hydrogenation of aromatic compounds at room temperature and one atmosphere of dihydrogen with colloidal rhodium or ruthenium catalysts. The solvated ion pair $[(C_8H_{l7})_3NCH_3]+[RhCl_4]^-$ generated from rhodium chloride and tricaprylylmethylammonium chloride (Aliquat 336) in an aqueous-organic biphasic medium was reported to catalyze the hydrogenation of aromatic compounds at 30°C and one atmosphere of dihydrogen (Blum et al., 1983; 1987; 1987). It was found that the presence of water was essential, a dried dichloroethane solution of the- ion pair $[(C_8H_{17})_3NCH_3]+[RhCl_4]^-$ was completely inactive. The electronic nature of the substrate effects the duration of the induction period and the reaction rate is quite sensitive to steric effects. Nassar and coworkers (1994) discovered that the hydrogenation of disubstituted aromatic rings can be achieved under mild reaction conditions in a biphasic system in the presence of rhodium chloride and phase transfer agents such as trioctylamine. The catalytic system was optimized for the 2-methylanisole reduction by the adjustment of the amine/rhodium ratio, which was high enough to stabilize very small colloidal rhodium particles and low enough to avoid deactivation. The optical amine/rhodium ratio was found in the region of 2.6-3.5. Even though the cost of rhodium and ruthenium (used at 5% molar) are high, Fache and coworkers (1995) studied colloidal ruthenium catalysts for the hydrogenation of substituted aromatic compounds. They discovered that different substituted aromatic substances such as methyl 2-methylbenzoate and 2-methylanisole can be hydrogenated to the corresponding cyclohexane derivatives in more than 70% yields using colloidal ruthenium catalysts stabilized by trioctylamine at 50 atm of dihydrogen and at room temperature in a methanol-water system. It was found that replacing the solvent methylene chloride-water (50-50) by methanol-water (50-50) increased the reaction rate by a factor of 12. The optimized methanol-water ratio turned out to be 70-30. Water is the best solvent for ruthenium chloride and, without water, the reduction become slower. Apler and his associates (1983) reported in a short communication that $[1,5\text{-HDRhCl}]_2$ is an active catalyst precursor for the hydrogenation of aromatic hydrocarbons and heterocyclic compounds. Toluene and butylbenzene can be hydrogenated to the corresponding cyclohexanes in high yields. However, no information was provided concerning the scope and limitations of the method or the stability of these catalysts.

Prior work has unambiguously established that aromatic compounds could be hydrogenated by the colloidal rhodium or ruthenium catalysts in the biphase or phase transfer systems under very mild conditions. Virtually all of the published papers have emphasized the methods for catalyst preparation and their chemical activities and selectivities. But, to our knowledge, no systematic studies regarding the influence of the reaction parameters and catalyst compositions on the overall performance of the catalysts in potentially practical applications have been carried out. We have, accordingly, conducted research on the colloidal rhodium catalysts under biphasic and phase transfer catalysis conditions for the hydrogenation of selected monocyclic aromatic compounds that are representative of the substances found in petroleum and coal liquids, and attempted to determine the important reaction parameters that would allow these very desirable reduction reactions to be carried out effectively under very mild conditions and would allow the catalyst to be easily separated from the reaction system and recovered and recycled. Obviously, this research has the potential to find new pathway for the upgrading of coal liquids and petroleum distillates.

Experimental

Material: Tetralin (99%, Aldrich) was distilled and stored under nitrogen. Water was distilled twice under nitrogen before use. Buffer (pH = 7.4) was prepared by dissolving the hydrion buffer powder (Aldrich) in water (500 mL) without using the color key buffer preservative. $[1,5\text{-HDRhCl}]_2$ (98%, Aldrich), tetrabutylammonium hydrogen sulfate (THS, 97%, Aldrich) and cetyltrimethylammonium bromide (CTAB, Aldrich) were used as received. Even though the reagents were eventually used in aqueous systems, all the air-sensitive and moisture-sensitive chemicals were handled in a glove box filled with nitrogen or argon for the most effective preparations of the catalyst precursor. The solvents that were used for the reactions were carefully purified before use. For instance, hexane was purified by refluxing commercial anhydrous hexane over sodium hydride and then distilling in nitrogen before use.

Hydrogenation: The following general procedure was used for the hydrogenation of aromatic compounds: An oven-dried 250-mL round flask was equipped with a mechanic stirrer guided by a vacuum-withstanding Teflon stiffer bearing, a gas inlet linked to a pressure cylinder and an outlet connected to a mineral oil bubbler. Tetralin (25 mmol) was added to a mechanical stiffed solution of $[1,5\text{-HDRhCl}]_2$ (0.125 mmol, 55 mg) in hexane (30 mL) protected by dihydrogen or dideuterium at atmospheric pressure. Then a buffer solution (10 mL) containing surfactant ([surfactant]/[Rh] = 0.5 to 2) was added. An emulsion, which became black after a few of minutes, was formed immediately. The reaction was allowed to proceed for 20 hrs at room temperature. The layers were separated. The aqueous phase was washed with hexane several times and the combined organic phase was washed with water and dried. The products were concentrated with a rotary evaporator, and then vacuum dried for 2 hours. They were identified by gas chromatographic analysis on a Perkin-Elmer Sigma 3B instrument with a 11.83 in x 0.32 cm column packed with 10% OV-101 with the following conditions: Injector temperature: 300°C; Detector temperature: 300°C; Initial column temperature: 120°C; Final column temperature: 200°C; Ramp rate: 5°C/min; initial time: 1 minute, final time: 1 minute. For some reactions, the products were also analyzed by GC-MS using a Hewlett-Packard 5970 series mass detector (70 eV) connected to a 5890 gas chromatography (OV-101 capillary column, 15 m x 0.25 mm, 100-180°C, 5°C/min). ^{1}H NMR and ^{2}H NMR were obtained on a Varian XL 500-MHz spectrometer.

Procedure for rate studies and product analysis: Tetralin (25 mmol, 3.4 mL) was added to a mechanical stirred solution of $[1,5\text{-HDRhCl}]_2$ (0.125 mmol, 55 mg) in hexane (30 mL) protected by dihydrogen at atmospheric pressure. Then a buffer solution (10 mL) containing surfactant (92 mg) was added. At appropriate intervals of time, 0.5 mL of the reaction mixture were withdrawn and the organic phase was separated. The aqueous phase was washed with hexane and the combined organic phase was concentrated and aliquots were analyzed by GC and GC-MS to monitor the product distributions.

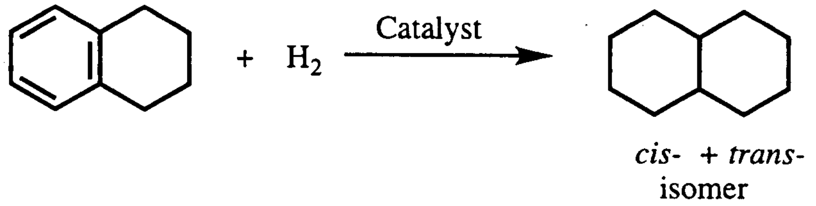
Procedure for determination of the catalytic stability and turnover numbers: The experiment was performed in the same apparatus. Tetralin (25 mmol, 3.4 mL) was added to a mechanical stirred solution of $[1,5\text{-HDRhCl}]_2$ (0.125 mmol, 55 mg) in hexane (30 mL) protected by dihydrogen at atmospheric pressure. Then a buffer solution (10 mL) containing surfactant (182 mg) was added. The conversion of tetralin was monitored by GC. When the reaction reached 80-85% of conversion, the stirrer was stopped and the organic phase was withdrawn. Another 3.4 mL, of tetralin in hexane (30 mL) was added to the system, then the reaction was started again. In this way, the catalyst was reused many times and the turnover number of the catalyst was defined as the accumulated moles of tetralin converted per mole of rhodium.

Results and Discussion

1. Catalytic Properties of [1,5-HDRhCl] for Tetralin Hydrogenation in a Biphasic System

It has been reported that $[1,5\text{-HDRhCl}]_2$ is an active catalyst precursor for the hydrogenation of aromatic hydrocarbons and heterocyclic compounds (Alper et al., 1983). The reaction is an authentic phase-transfer process as shown by the successful reduction of phenylacetone to cyclohexylacetone. In the absence of the quaternary ammonium salt the yield was much lower than that in the presence of THS as a phase transfer agent. However, no details regarding the reaction conditions or the stability of the catalyst were given. We observed in preliminary experiments that the catalyst system was active as an aromatic hydrogenation catalyst. Consequently, it was investigated systematically for the reduction of tetralin to decalin.

Table 12 shows the influence of phase transfer agents on the hydrogenation of tetralin to decalin with a [substrate] to [catalyst] ratio of 200:1. Tetralin was converted to decalin in 92% yield in the absence of any surfactant molecule, but high concentrations of surfactant molecules, for example, when the [THS]/[Rh] mole ratio = 8, reduced the conversion of tetralin to decalin to 30%. Similar results were obtained using CTAB as the phase transfer agent and other surfactants such as tricaprylylmethylammonium chloride and Tween 20 exhibited even more negative effects on the reaction. It is noteworthy that $[1,5\text{-HDRhCl}]_2$ did not catalyze the reaction in hexane, implying that water has a critical role on the properties of the Rh catalyst.



(eq. 25)

The influence of buffer solution on the hydrogenation in the biphasic system is shown in Table 13. Both the pH values and the composition of the buffer have a dramatic effect on the conversion of the substrate. The buffers with the same compositions, but different pH values (No. 1, 2, 3) and those with same pH value, but different compositions (No. 1, 4, 5, 6) all provide different yields of products. The highest yield (92%) was obtained by using the hydrion buffer with pH=7.4. Curiously, even pure water yields a low conversion of the substrate.

Figure 25 shows the effect of the volume ratio of aqueous phase to organic phase in biphasic system on the hydrogenation without any surfactant. The conversion of tetralin increases to 80% as the volume of the buffer phase increases until the [aqueous phase]/[organic phase] ratio is greater than 0.15, it then shows no further significant change.

The organic solvents also affect the reaction process (Table 14). Methylene chloride, chloroform, dimethyl ethylene glycol and alcohols provide unsatisfactory results, but aliphatic hydrocarbons such as hexane are good solvents for this reaction. However, large aliphatic hydrocarbons such as n-decane provide decreased conversions, this result may be related to the higher viscosity of these hydrocarbons, which reduce the mobility of the active catalyst in the two phase system.

Table 15 shows the results of different rhodium compounds as potentially active reagents in the catalyst system for hydrogenation of tetralin. Like $[1,5\text{-HDRhCl}]_2$, $[1,5\text{-CORhCl}]_2$ (chloro(1,5-cyclooctadiene)rhodium(I) dimer) is also an active catalyst precursor in the biphasic system. However, rhodium chloride hydride and rhodium acetylacetonate do not form active catalysts under the same conditions.

2. Improvement of Catalyst Stability in the Presence of a Surfactant Molecule

Although the catalyst exhibited higher activity for the hydrogenation of tetralin in the absence of any surfactants, it was not stable. Our results indicated that the catalytic performance was influenced by many factors such as the solvent, the concentration of the substrate, and the buffer. Even more important, the rhodium catalyst was easily aggregated on the wall of the reactor. This material was rapidly deactivated and could not be reused. The highest turnover numbers achieved under the optimal conditions ([substrate]/[catalyst]= 200:1, [aqueous phase]/[organic phase]=0.3) was only 200. In order to improve the stability of the catalyst while keeping its high activity, we investigated surfactant molecules in detail in reaction systems that might form an emulsion and stabilize the catalyst.

As mentioned above, the addition of high surfactant concentrations actually reduced the catalytic activity. However, small amounts of some surfactants had the dual effect, that is, the yield of the products remained high, while the stability of the catalyst improved. Figure 26 shows the dependence of decalin yields on the [CTAB]/[Rh] molar ratios. It can be seen that the catalytic activity remains high until the [CTAB]/[Rh] reaches 2. In this case, we postulate that an emulsion forms to encapsulate the rhodium metal and to ensure its catalytic activity. Various surfactant molecules were investigated for this purpose. It was found that THS and sodium dodecylsulfate exhibit behavior similar to CTAB. However, Aliquat 336 and Tween 20 reduced the catalytic activity even when [surfactant]/[Rh] was less than 1.

In the presence of CTAB ([CTAB]/[Rh]= 2.0), the stability of the catalyst was improved greatly. The relationship between the turnover numbers of the catalyst (the moles of hydrogenated substrate per mole of Rh catalyst) and the reaction time is shown in Figure 27. After 8 days and 8 cycles, no decrease in the catalytic activity was observed. The turnover numbers of the catalyst increased linearly with the reaction time in this period and reached about 1350. Hence, an active, stable catalyst system was found for the hydrogenation of aromatic compounds under mild conditions. In addition, the catalyst can be easily separated from the system and the noble metal (rhodium) can be collected and reused.

The conversion-reaction time profiles for the hydrogenation of tetralin to decalin is shown in Figure 28. The hydrogenation reactions proceed to completion in about 20 hours. A nearly linear relation was observed for the dependence of conversion on reaction time.

The temperature and pressure dependence were evaluated briefly. Figure 29 shows the relationship between the reaction rate and the hydrogen pressure. A linear relationship was observed under the experimental conditions. For instance, the reaction rate, 4.6 mole $h^{-1}\cdot Rh^{-1}$ under 1 atm. H_2, increased to 8.9 under 2.0 atm. H_2 and to 11.3 under 2.7 atm. H_2, respectively. It is clear that the higher hydrogen pressures accelerate the reaction significantly. For the most part, we employed hydrogen at atmosphere pressure, but these results establish that an increase in the pressure to between 2 and 3 atmospheres significantly accelerates the reaction. It may be advantageous to exploit this observation for practical applications of the catalytic reaction system in subsequent investigations.

The results regarding with the influence of the temperature on the reaction rate are shown in Figure 30. The hydrogenation rate, 4.6 mole $h^{-1}\cdot Rh^{-1}$ at 25°C, increases to 9.3 at 37°C and 9.6 at 44°C, respectively. The rate appeared to decrease at 53°C and we did not investigate higher reaction temperatures. The results infer, however, that the hydrogenation of tetralin has an optimal temperature region of 35-45°C. However, there are other mechanical explanations for the decrease in rate at 53°C and this point deserves additional study for future practical applications.

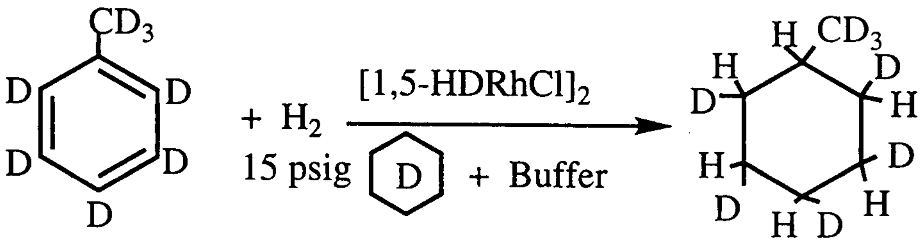
Table 16 shows the hydrogenation of other aromatic compounds catalyzed by $[1,5\text{-HDRhCl}]_2$ in the presence of surfactant molecules. Substituted benzenes such as toluene, butylbenzene, tetralin, o-xylene all can be hydrogenated into the corresponding substituted cyclohexane derivatives in very high yields. Aromatic compounds such as naphthalene also can be reduced to the mixtures of *cis*- and *trans*-decalin with a *cis*- to *trans*-isomer ratio of 6.7. It was found that tetralin is an intermediate in the hydrogenation process, but no tetralin was detected by GC at the end of the reaction. *m*-Dimethoxybenzene was hydrogenated to the *m*-dimethoxycyclohexane in 98% yield, in which the product was a mixture of *cis*- and *trans*-isomers with the *cis/trans* isomer ratio of about 1.0. This result implies that the catalyst system was effective for the reduction of electron rich aromatic rings and inert to the oxygen-containing substances in the reaction system.

3. Hydrogen-Deuterium Exchange and the Reaction Pathway

Deuterium labeling experiments indicated that substantial H-D exchange occurs both in the aromatic and aliphatic rings. The reaction of tetralin with D_2 gas under typical conditions gave a product which was characterized by gas chromatography-mass spectrometer and ^{1}H and ^{2}H nuclear magnetic resonance, as a mixture of decalins with high deuterium content. A typical product distribution is shown in Figure 31. For the trans-isomer, the peaks of m/z 144 that correspond to $C_{10}H_{12}D_6^{+\cdot}$ (144, 20%) are only accompanied by peaks of higher masses of $C_{10}H_{11}D_7^{+\cdot(}$145, 35%), $C_{10}H_{10}D_8^{+\cdot}$ (146, 55%), $C_{12}H_9D_9^{+\cdot}$(147, 75%), $C_{12}H_8D_{10}^{+\cdot}$ (148, 95%), $C_{12}H_7D_{11}^{+\cdot}$ (149, 100%), $C_{12}H_6D_{12}^{+\cdot}$(I50,75%), $C_{12}H_5D_{13}^{+\cdot}$(151, 30%), $C_{12}H_4D_{14}^{+\cdot}$ (152, 10%) and for the *cis*-isomer also by some small signals (deuterium-deficient cation radicals) of $C_{12}H_{13}D_5^{+\cdot}$, $C_{12}H_{14}D_4^{+\cdot}$, and $C_{12}H_{15}D_3^{+\cdot}$. These results indicate that deuterium is incorporated into both saturated rings during the reaction. For comparison, the treatment of pure *cis*-decalin with D_2 in the presence of the catalyst under the same conditions did not result in D-H exchange, indicating that the deuterium is incorporated only in the catalytic reaction process. H-D exchange was reported to occur in toluene reductions with the $RhCl_3$-Aliquat 336 ion pair (Blum et al., 1987). Both deuterium-deficient products and deuterium- rich products were formed in this experiment. The deuterium-deficient products were assumed to result in part from the reaction of the arenes with either H_2 or HD generated during D_2-induced H-D exchange and in part from the water effect (Blum et al., 1987). The product of toluene deutration catalyzed by $[1,5\text{-HDRhCl}]_2$/buffer catalyst shows a similar product distribution in the parent ion region of the mass spectrum. As mentioned above, the mixture of decalins obtained from the tetralin deutration catalyzed by $[1,5\text{-HDRhCl}]_2$/buffer catalyst contains only traces of deuterium-deficient isomers and many molecules with excess deuterium, demonstrating that the formation of deuterium-deficient products may be mainly attributed to reactions HD or H_2 and water effect, and to statistical factors.

The pathway for the hydrogenation of aromatic compounds catalyzed by $[1,5\text{-HDRhCl}]_2$ in the presence of a small amount of a surfactant molecule under biphasic conditions has been investigated. The hydrogenation reaction was monitored by ^1H NMR. Because the sensitivity of ^1H NMR is greater than that of ^2H NMR, the reaction was carried out using deuterated substrate (toluene-d_8) and deuterated solvent (cyclohexane-d_{12}).

Experiments were performed as follows: $[1,5\text{-HDRhCl}]_2$ (28 mg, 0.065 mmole) was dissolved in 10 mL of deuterated cyclohexane (C_6D_{12}) under a flow of dihydrogen. To this solution, toluene-d_8 (C_7D_8, 1.1 mL, 0.01 mole, [substrate]/[catalyst] = 160) was added with magnetic stirring. Then 3.0 mL of a buffer (pH=7.4) containing 28 mg of CTAB was added to the system to start the hydrogenation. At successive intervals, 2 mL aliquots of the solution were withdrawn from the system, and the organic phase was separated and transferred into an NMR tube to obtain the ^{1}H NMR spectrum.



(eq. 26)

The ^{1}H NMR spectra, which were taken at 10 min, 30 min., 1 hour, 2.5 hour, 4.5 hours and 24 hours are shown as in Figures 32, 33, 34, 35, 36, and 37, respectively.

Figure 32 shows the ^{1}H NMR of the solution of toluene-d8 and [1,5-HDRhCl]$_2$ in cyclohexane-d_{12}. It can be seen that no detectable quantity of a complex between toluene and the rhodium compound was formed. After this solution was stirred for 2 hours under dihydrogen, no organorhodium compound was isolated or detected. Some of the reduced rhodium compounds were produced, but these compounds are not on the predominant reaction pathway. This result suggests that [1,5-HDRhCl]$_2$ does not form a stable complex with aromatic compounds at this stage of the reaction. Many new peaks appeared at 2.21-2.25 ppm when the reaction was started. These resonances increased in intensity as the reaction proceeded (Figure 33 at 30 min, Figure 34 at 1h, Figure 35 at 2.5 h) and then decreased in intensity (Figure 36 at 4.5 h) and disappeared completely (Figure 37 at 24 h)at the end of the reaction. These peaks were assigned to the protons of methylene groups (-CH$_2$-) in the mixture of 1,3-cyclohexadienes (-CH$_2$-C=C-C=C-). The fact that no signal was observed in the region of 2.80-2.90 ppm corresponding to 1,4-cyclohexadiene (-C=C-CH$_2$-C=C-) implies that the aromatic ring was first reduced to 1,3-cyclohexadiene derivatives. The peaks in the region of 0.83-0.92 ppm were assigned to the methyl (CH$_3$-) group in the methylcyclohexane and methylcyclohexenes. Because the substrate is deuterated toluene ($CD_3C_6D_5$), it is clear that D-H exchange in the methyl group has taken place extensively in the process of the reaction. There are many methyl resonances, hence the product may be a mixture of methylcyclohexane and isomeric methylcyclohexenes.

It was reported that the homogenous hydrogenation of benzene by $RhCl_3$-Aliquat 336, proceeds through an arene complex, or an analogous dihydride, after the induction period, which varies in length in accord with the substrate employed (Blum et al., 1983, 1987). The formation of several metal hydride intermediates during the process has been proven by conducting the hydrogenation of naphthalene in a Wilmad's pressure valve NMR tube (Alum and Amber, 1987). The low-field 300 MHz NMR spectrum consisted of three triplets at -22.35 (J=7.6 Hz), -23.12 (J=9.1 Hz) and -24.29 (J=7.6 Hz) ppm and of one unresolved multiple at -22.78 ppm. From the signals at 2.22-2.26 ppm ($-CH_2-C=C-C=C-$) and their changes with the course of reaction (Figure 33 to Figure 37), it was clear that intermediate cyclohexadiene formed. The peaks in the region of 0.83-0.92 ppm, assigned to the methyl (CH_3-) group in the methylcyclohexane or the methylcyclohexenes, also change as the reaction proceeds, indicating that these are several intermediates in the mixture, not a single species. However, there are no signals for cyclohexene derivatives at 1.80-1.95 ppm for the protons of ($-CH_2-C=C-$) or at 5.40-5.60 ppm for the protons of (-CH=CH-) in the reaction products during the hydrogenation of toluene. The intermediacy of η^2 complexes is suspected. However, the hydride transfer (η^2 - η^1 conversion) and the reductive elimination of the product are well known features for alkene hydrogenation. Therefore, it was concluded that this stage of the reaction was very fast and no cyclohexene compound was dissociated from the η^2 complex. In addition, during the entire reaction interval, no signals for the protons of -CH=CH-were detected, implying that the D-H exchange occurs primarily in the period of the catalytic reduction. It should be noted that D-H exchange in the side chain methyl group is more pronounced than that in the ring.

These results lend support to the reaction pathways that were originally proposed for the homogeneous hydrogenation of aromatic compounds by Muetterties and his associates (1981).

4. Hydrogenation of a Mixture of Coal Liquid and Tetralin

As described above, $[1,5\text{-HDRhCl}]_2$ provides an effective biphasic catalyst system for the hydrogenation of aromatic compounds. In order to test the catalyst's tolerance to the common catalyst's poisons, we applied it for the hydrogenation of mixtures of coal liquids and tetralin. The coal liquid that was supplied by DOE for the test is 05SP19 (Date of sample: 7/19/1994; Time of sample: 1200; Run period of sample: 260-05-378). Table 17 shows the results for several coal liquid 05SP19/tetralin mixtures. From 78 to 95% of the tetralin can be hydrogenated into decalin when the ratio of rhodium to coal liquid is more than 0.025. For instance, 80-85% of tetralin (3000 mg) was converted to decalin when the amount of 05SP19 in the mixture was 1000 mg with 25 mg of rhodium. Figure 38 displays the ^{1}H NMR spectra of a mixture of coal liquid 05SP19/tetralin (12.5 wt%) before (a) and after being hydrogenated (b). Many new absorptions are located between 1.0-2.0 ppm and can be assigned to decalin. The spectral data indicate that tetralin conversion was about 80-85%. These experiments were successfully repeated three times. These results imply that the catalyst system at ambient temperature and 1 atmosphere pressure can be operated smoothly in the presence. of modest concentrations of coal liquids. However, high concentration of coal liquids hampered the reaction. For example, increasing the amount of coal liquid to rhodium to 80 inhibited the reduction of tetralin to decalin.

Conclusion

$[1,5\text{-HDRhCl}]_2$ is an active catalytic precursor for the hydrogenation of aromatic compounds under mild conditions (room temperature and 1 atm of dihydrogen) in a biphasic reaction system with an organic solution as the hydrophobic phase and an aqueous buffer solution as the hydrophilic phase. Although high concentrations of surfactant molecules negatively affect the catalytic activity, low concentrations create an emulsion that stabilizes the catalyst while keeping the activity high. Surfactant molecules such as CTAB or THS were especially effective. Thus, an active and stable catalyst system was found for the hydrogenation of monocyclic aromatic compounds under mild conditions, in which the metal can be easily separated and recycled.

Experiments with dideuterium indicate that D-H substantial exchange occurs both in the aromatic ring and in saturated ring during the hydrogenation process. Our results are comparable with the reaction scheme that was originally presented by Muetterties and Bleeke (1979). The reaction system is effective for the hydrogenation of tetralin to decalin in the presence of modest amounts of coal liquids.

Summary

The research plan that was described in the original proposal of September, 1991 was followed closely. New basic catalysts for the hydrogenation of multiring aromatic hydrocarbons to monoaromatic compounds and rhodium catalysts for the conversion of monocyclic aromatic compounds to fully saturated aliphatic substances have been examined. Both catalysts are effective in the presence of coal liquids.

It was discovered that certain strong organic bases are very active catalysts for the hydrogenation of polycondensed aromatic hydrocarbons to monoaromatic substances and for the hydrotreating of coal liquids under 1000 psig of hydrogen at 200-250°C. Under the typical experimental conditions, for instance, naphthalene can be converted completely into 1,2,3,4-tetrahydronaphthalene and phenanthrene to the isomer mixture of monoaromatic derivatives in 96% yield. The results of the investigation imply that dihydrogen was activated by the strong base to form an intermediate which then transfers a reactive hydrogen to the unsaturated substrate. The strong bases can withstand severe reaction conditions and the harsh chemicals that are present in coal liquids.

The strong base catalysts can catalyze the reduction of coal liquids to give a clean upgraded products with an increased hydrogen content as shown by an increased H/C ratio relative to the original coal liquid. The multiring aromatic hydrocarbons in the coal liquid were hydrogenated to give many saturated monoaromatic compounds. Among the set of organic bases investigated, potassium bis(trimethylsilyl)amide was found to be the most effective catalyst.

Chloro(1,5-hexadiene)rhodium(I) dimer was shown to be an active catalyst precursor for the hydrogenation of monoaromatic substances to fully saturated aliphatic hydrocarbons at room temperature and one atmosphere pressure in a biphasic system. The catalyst stability and efficiency can be improved greatly by adjusting the concentration of the surfactant molecule in the system. In this catalyst system, the noble metal can be easily separated and recycled.

In summary, we have developed two types of active catalysts for the hydrogenation of multiring aromatic compounds to monoaromatic compounds and of monoaromatic compounds to saturated aliphatic substances. The coal liquids can be hydrotreated by the catalysts to give upgraded products with much lower aromatic content and much higher hydrogen content. These results were very encouraging for future commercial applications.

References

The references are presented in alphabetical order

Anderson and Tillman, 1979. *Synthetic Fuels from Coal*, John Wiley& Sons.

Apler and Januszklewicz , 1983. *Organometallics*, **2**, 1055.

Bach and Wiebus, 1984. *Preprints Int. Symp. high-pressure Chem. Eng.* , Erlangen, 129.

Bennett, Huang and Turney, 1979. *J. Chem. Soc., Chem. Commun.*, 312.

Bennett, 1980. Chemtech , 444.

Bleeke and Muetterties, 1981. *J. Am. Chem. Soc.*, **103**, 556.

Blum, Amer, Zoran and Sasson, 1983. *Tetrahedron Lett.* **24**, 4139.

Blum et al., 1987. *J. Org. Chem.*, **52**, 2804.

Benkeser et al., 1985. *U.S. Pat. 4,533,760; 1985; U.S. Pat. 4,533, 752.*

Benkeser et al., 1982. *J. Org. Chem.*, **24** , 2796.

Brooks et al., 1964. *Aust. J. Chem.*, **17**, 55.

Birth and Fitton, 1963. *J. Chem. Soc.*, 2209.

Benkeser and Robinson, 1955. *J. Am. Chem. Soc.*, **77**, 3230.

Birth, 1951. *J. Chem. Soc.*, 1945.

Birth and Smith, 1950. *Q. Rev. Chem. Soc.*, **4**, 69; 1958. **7**, 17.

Chauvin et al., 1980. *Hydrocarbon Proc.*, 1 10.

Chianelli and Daage, 1989. *Stud. Surf. Catal.*, **50**, 1.

Cornils and Falbe, 1984. *Proceedings 4th Int. Symp. on Homogeneous Catalysis*, Leningrad, 487.

Commolli et al., 1993. *Close-coupled Catalytic Two Stage Liquefaction Process Bench Studies, Fossil Final Report, DOE/PC/88818-T5 (DE94007959)*, p. 228-248, 263-280.

Chalasinski, Kendall and Simons, 1987. *J. Chem. Phys.*, **87**, 2965.

Cremer and Koraka, 1986. *J. Phys. Chem.*, **90**, 33.

Dadyburjor and Raje, 1994. *J. Catal.*, **145**, 16.

Dautzenberg and de Deken, 1984. *Catal. Rev.-Sci. Eng.*, **26**, 421.

Dayton and Wilmarth, 1950. *J. Chem. Phys.*, **18**, 759.

Edwards et al., 1986. Fuel, **65**, 202.

Fish, Tan and Thormodsen, 1985. *Organometallics*, **4**, 1743.

Fish, Tan and Thormodsen, 1984. *J. Org. Chem.*, **49**, 4500.

Fish and Kim, 1986. *Organometallics*, **5**, 2193.

Fache, Lehuede and Lemaire, 1995. *Tetrahedron Lett.*, **36**, 885.

Frank and Le Page, 1981. *Proc. 7th Intern. Congr. Catal.* (Seiyama and Tanable, eds.), Elsevier, Amsterdam, 1981, p. 791.

Gallezot and Bergeret, 1987. In *Catalyst Deactivation* (Peterson and Bell, eds.), Dekker, New York, p. 263.

Girgis and Gates, 1991. *Ind. Eng. Chem. Res.*, **30**, 2021.

Gully and Balard, 1963. *In Advances in Petroleum Chemistry and Refining*, Vol. 7 (McKetta, ed.), Interscience Publishers, London, p. 241.

Haggin, 1994. *Chem. Eng. News*, **72**(10), 28.

Ho, 1988. *Catal. Rev.,-Sci. Eng.*, **30**, 117.

Huckel and Schlee, 1955. *Chem. Ber.* **88**, 346.

Huckel and Bretschneider, 1939. *Justus Liebigs Ann. Chem.*, **540**, 157.

Huckel and Worffel, 1956. *Chem. Ber.*, **89**, 2098.

Ingemann, Klingeld and Nibbering, 1982. *J. Chem. Soc., Chem. Commun.*, 1009.

Jaffe, 1974. *Kinetics of heat release in petroleum hydrogenation, In. Eng. Chem. Proc. Des. Dev.*, **13**, 34.

Jacobson, Cooper, and Hannerup, 1987. *12th World Petroleum Congress*, Houston, **4**, 97.

Jacobs, 1986. *In Metal Clusters in Catalysis*, Elsevier, Amsterdam, Vol. 29, p. 357.

Kaiser and Benkeser, 1970. *Org. Synth.*, **50**, 88.

Kalck and Monteil, 1992. *Adv. Organomet. Chem.*, **34**, 219.

Klingler, Krause and Rathke, 1989. *Catal. Letter.* **3**, 347

Klingler, Krause and Rathke, 1991. *Prog. Inorg. Chem.*.

Klingler, Krause and Rathke, 1992. *Adv. Chem. Ser.*, **230**, 337.

Klingeld, Ingemann, Jalonen and Nibbering, 1983. J. Am. Chem. Soc., **105**, 2474.

Katzer and Sivasubramanian, 1979. *Catal. Rev., Sci. Eng.*, **20**, 155.

Krichko et al., 1990. Fuel, **69**, 344.

Lubineau, Auge and Queneau, 1994. *Synthesis*, **741**.

Ledoux, 1985. In *Catalysis, Specialist Periodical Reports*, The Royal Society of Chemistry, London, **7**, 125.

Lepage, 1987. *Applied Heterogeneous Catalysis*, Tevhnip, Paris, 1987.

Maitlis et al., 1978. *Acc. Chem. Res.*, **11**, 301 and references cited there.

Moulijin, Van leeuwen and Van Santen, 1993. *Catalysis*, Elsevier: Amsterdam, 45.

Muetterties and Bleeke, 1979. *Acc. Chem. Res.*, **12**, 324.

Majer, 1961. *Bull. Acad. Polon. Sci., Ser., Sci. Chim.*, 9, 773.

Melikadze et al., 1959. *Akad. Nauk. Gruzin S.S.R.*, 23, 657.

Mitchell, 1990. *Catal. Today*, 439.

Martinez et al., 1988. Fuel, **67**, 34.

Mochida et al., 1986. Fuel, **65**, 1090; **65**, 633.

Nagahara and Konishi, 1988. *U.S. patent 4,734, 536.*

NATO Advanced Research Workshop "Aqueous Organometallic Chemistry and Catalysis," Debrecen, Hungary, Aug. 29-Sept. 1, 1994.

Nassar et al., 1994. *J. Mol. Catal.*, **87**, 107.

Newworth, 1984. *Tech. Fuel Process,*. **8**, 231.

Neurock, Libanati and Klein, 1989. *AIChE Symp. Ser.* **273**, 85, 7.

Perrot, 1991. *Catal. Today*, **10**, 447.

Perrot et al., 1988. Fuel. Proc. Technol., **20**, 223.

Patzer, et al., 1979. *Ind. Eng. Chem. Process Des Dev.*, 18, 625.

Peries, et al., 1991. *Preprint on the NPRA 89th Annual Meeting*, San Antonio, TX, March 17-19, 1991.

Prins, De Beer and Somorjai, 1989. *Catal. Rev.,-Sci. Eng.*, **31**, 1.

Quann, Huang and Wei, 1988. *Adv. Chem. Eng.*, **14**, 95.

Reggel et al., 1957. *J. Org. Chem.*, **22**, 891.

Reid, Pruasnitz and Sherwood, 1977. *The Properties of Gases and Liquids*, McGraw-Hill, New York.

Stuhl et al., 1978. *J. Am. Chem. Soc.*, **100**, 2405.

Schindler, 1989. *Coal Liquefaction-A Research Needs Assessment*, Vol. 2, DOE/ER-0400, U.S. Department of Energy, Washington, D.C.

Shimada, et al., 1990. *Application of Zeolite-based Catalyst to Hydrocracking of Coal -derived Liquids*, National Chem. Lab. for Industry, Tsukuba, Ibaraki 305 (JAPAN), Fuel. Proc. Technol., **25**, 153-165.

Simmons, 1953. *Ann. Chem.* **25**(9), 1386.

Stanislaus and Cooper, 1994. *Catal. Rev.-Sci. Eng.*, **36**(1), 75.

Speight, 1981. *The Desulfurization of Heavy Oils and Residua*, Dekker, New York.

Spare and Gates, 1981. *Ind. Eng. chem. Process Des. Dev.*, **20**, 68.

Suchanek, 1990. *Oil Gas J.*, May 7, 1990, p. 109.

Tokitoh and Yoshimura, 1989. *U.S. Pat. 4,808,756, 1989.*

Toulhoat, Szymanski and Plumail, 1990. *Catal. Today*, **7**, 531.

Topsoe and Clausen, 1986. *Appl. Catal.*, **25**, 273.

Wender, Levine and Orchin, 1950. *J. Am. Chem. Soc.*, **72**, 4375.

Wiebus and Cornils, 1994. *Chem. Technol.*, **66**, 916.

Wiebus and Cornils 1995. *CHEMTECH*, **1**, 33.

Weber and Stewart, 1987. *EPRI J.*, **12**(1), 40.

Walling and Bolyky, 1961. *J. Am. Chem. Soc.*, **83**, 2968.

1964. *J. Am. Chem. Soc.*, **86**, 3750.

Whitehurst, Mitchell, and Farcasiu, 1980. *Coal liquefaction*, Academic Press, New York.

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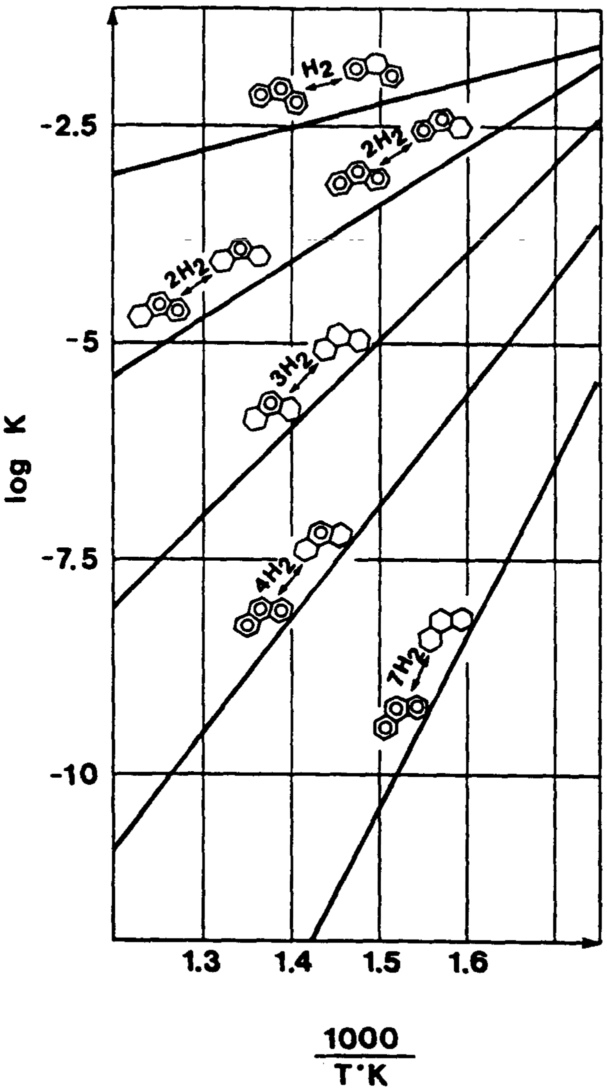


Fig. 1 Equilibrium constants for hydrogenation of phenanthrene

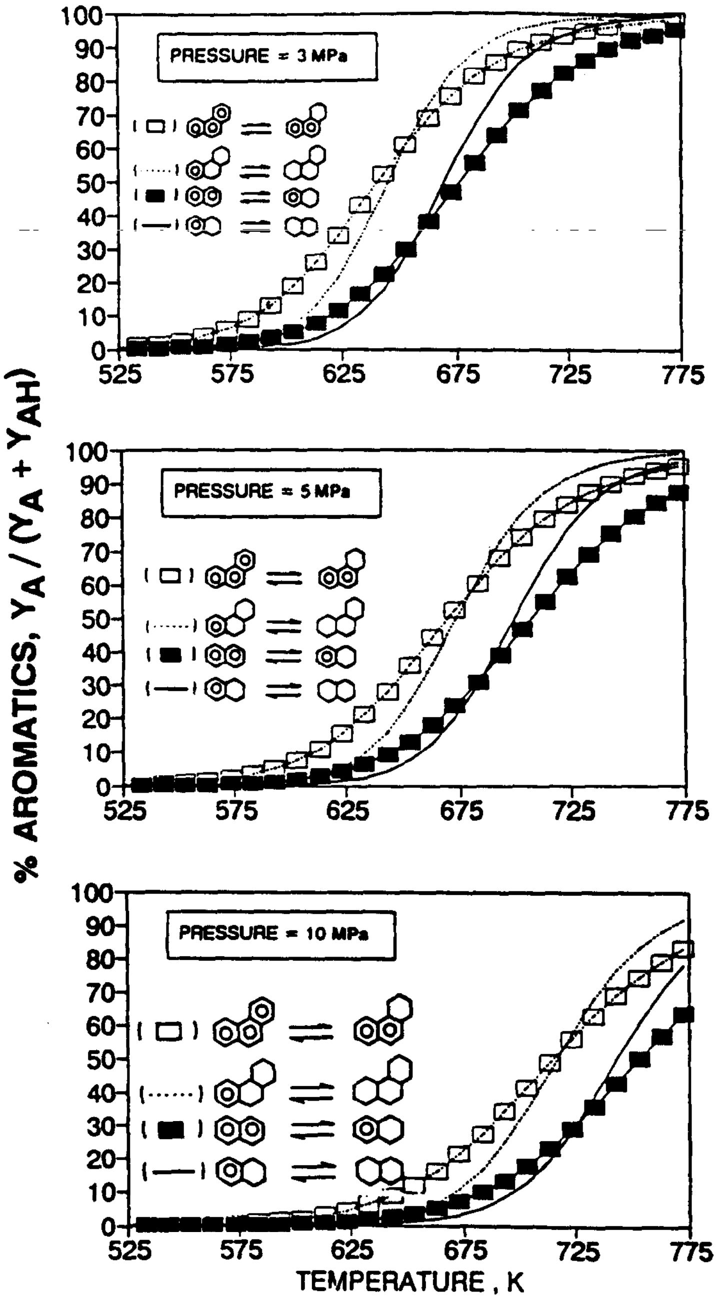


Fig. 2 Equilibrium concentrations for first- and last-ring hydrogenation of phenanthrene and naphthalene as function of hydrogen pressure

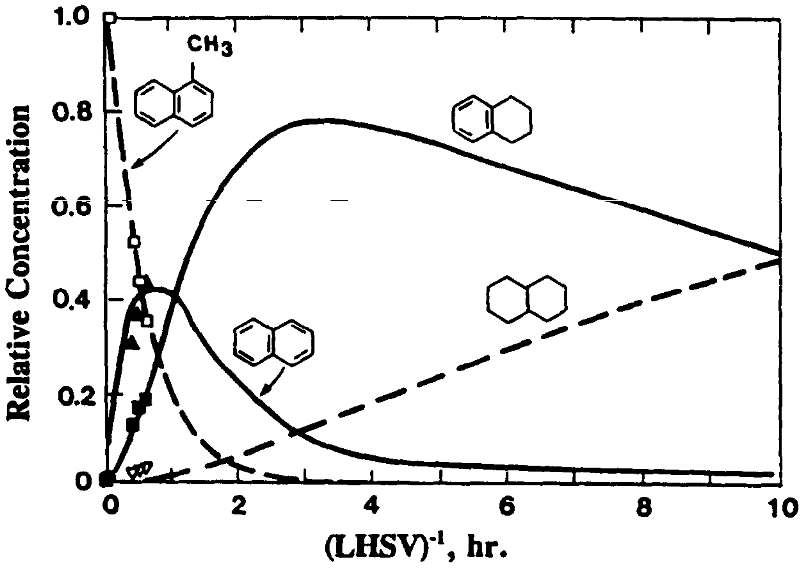
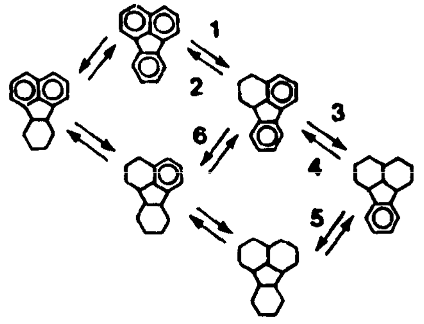
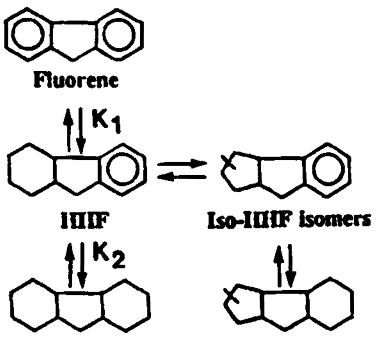


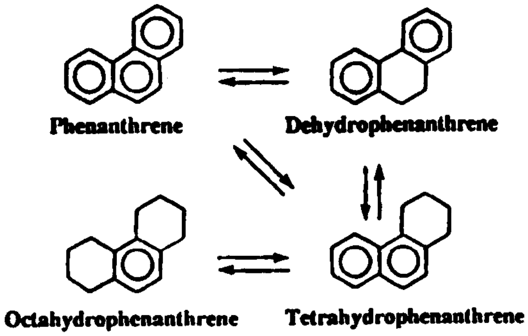
Fig. 3 Relative concentration profiles for catalytic hydrogenation of 1-methyl naphthalene at 70 atm and 316°C



(a) Fluoranthene Hydrogenation Pathways (ref. 51)



(b) Fluorene Hydrogenation Network (ref. 50)



(c) Phenanthrene Hydrogenation Network (ref. 46, 47)

Fig. 4 Hydrogenation pathways for polynuclear aromatic hydrocarbons:
(a) fluoranthrene, (b) fluorene and (c) phenanthrene

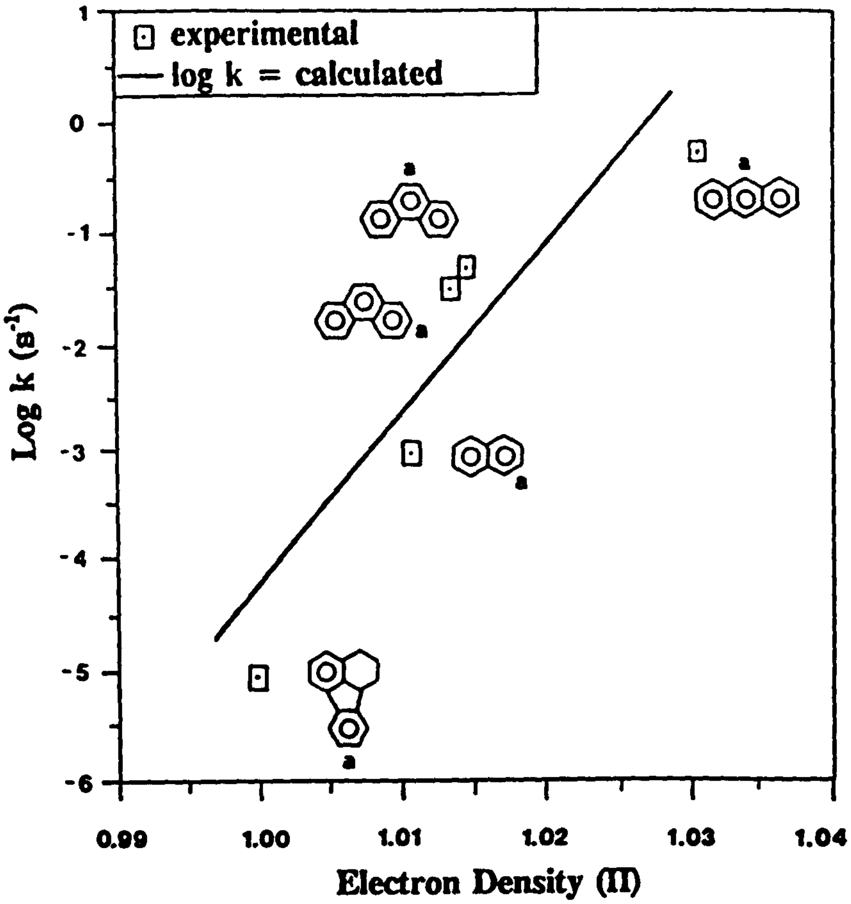
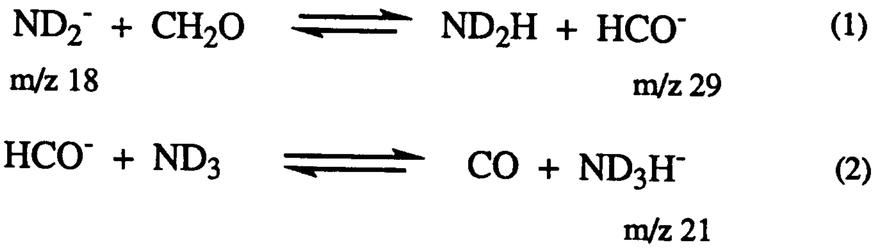


Fig. 5 Relationships between π -electron density and aromatic hydrogenation. The rate constants are for hydrogenation of the most reactive ring, marked "a"



$$\underset{m/z\ 18}{ND_2^-} + CH_2O \rightleftharpoons ND_2H + \underset{m/z\ 29}{HCO^-} \qquad (1)$$

$$HCO^- + ND_3 \rightleftharpoons CO + \underset{m/z\ 21}{ND_3H^-} \qquad (2)$$

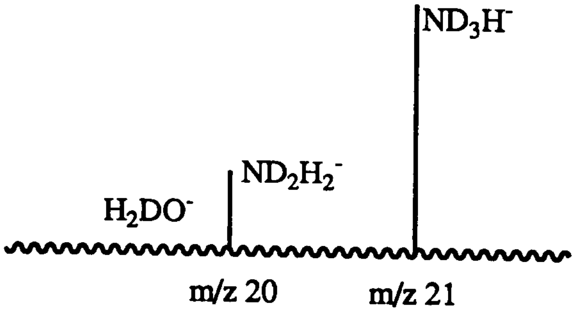


Fig. 6 Fourier transfer ion cyclotron resonance spectrum of $ND_2^-/ND_3/CH_2O$ system

Experimental conditions: $p(ND_3)$= 70 uPa, $P(CH_2O)$ = 30 uPa, magnetic field strength 1.4 T, electron energy 4.5 eV, emission current 800 nA. The spectrum is taken at a trapping time of 150 ms, 2350 transients accumulated.

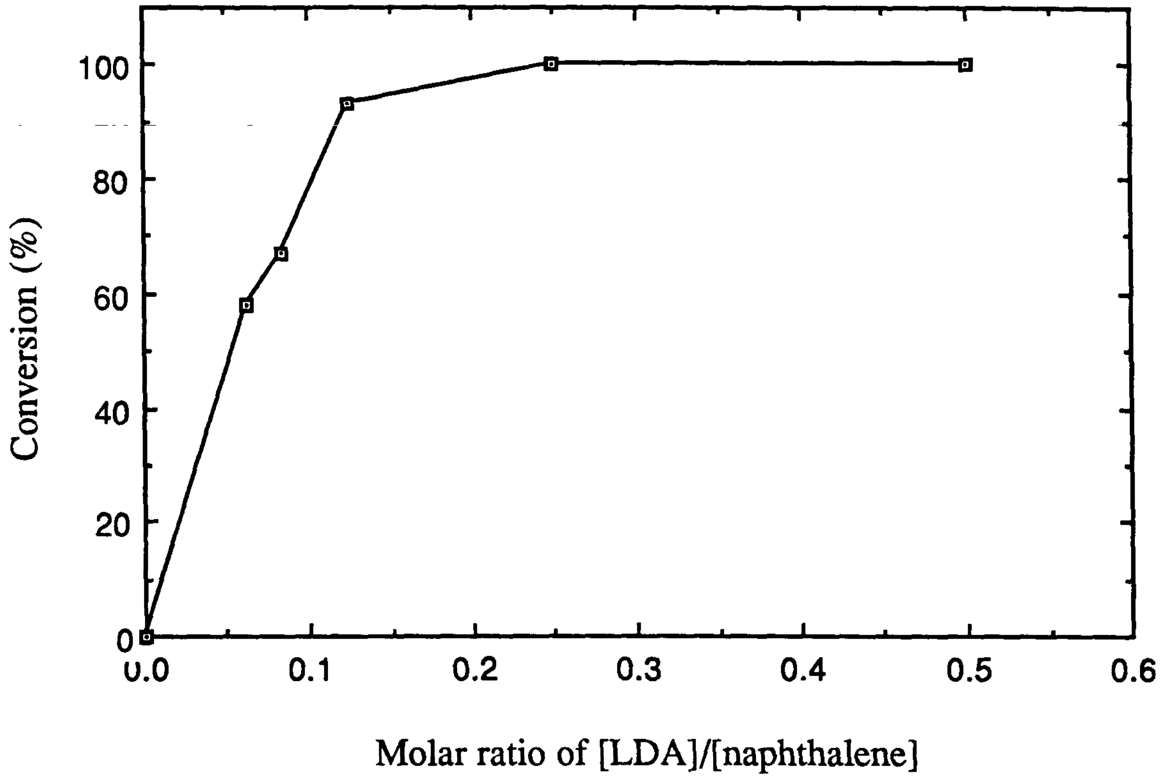


Fig. 7 Effect of the molar ratio of [LDA]/[substrate] on the conversion of naphthalene

Solvent: hexane (50 mL); Initial H_2 pressure: 1000 psig; Temperature: 200°C; Reaction time: 18 hrs

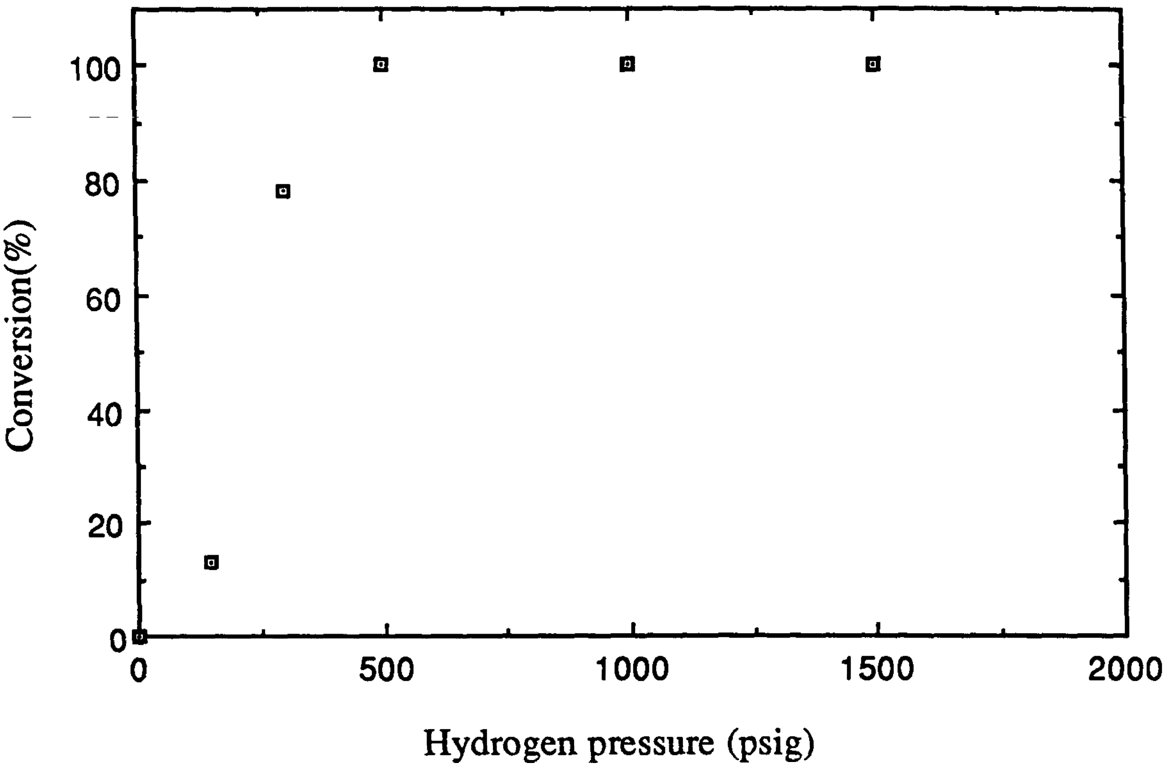


Fig. 8 Dependence of the conversion of naphthalene on the initial hydrogen pressure

Solvent: hexane (50 mL); [LDA]/[substrate] = 0.25;
Temperature: 200°C; Reaction time: 18 hrs,

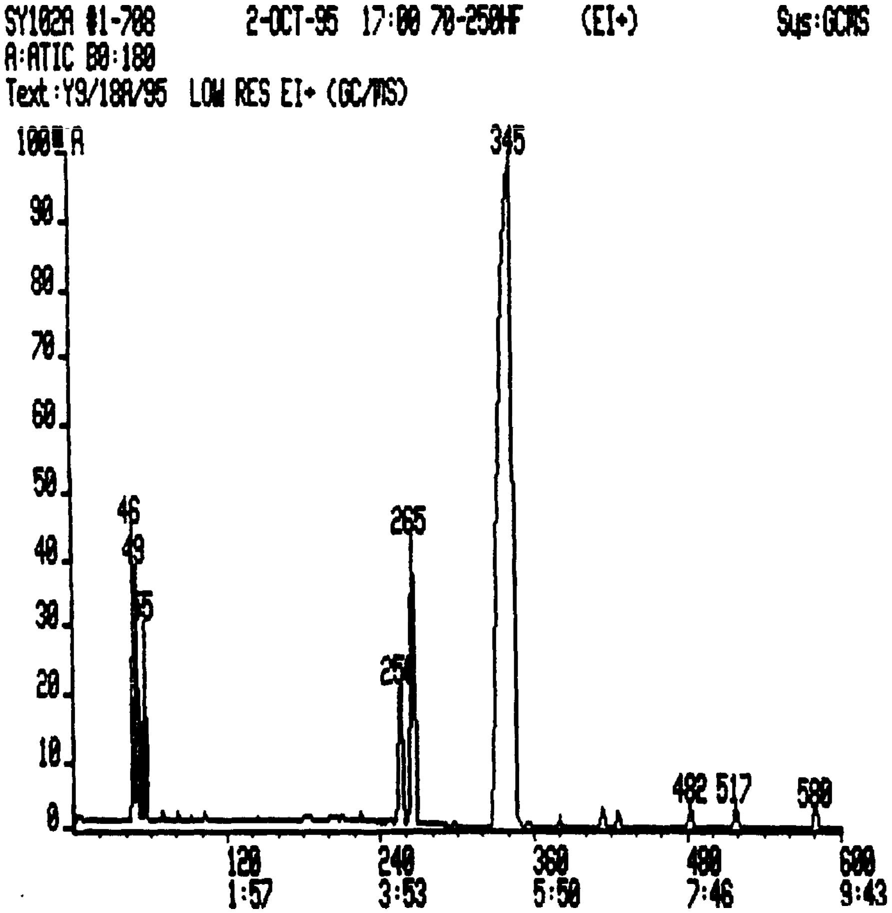


Fig. 9 GC spectrum of the products obtained by hydrogenation of anthracene

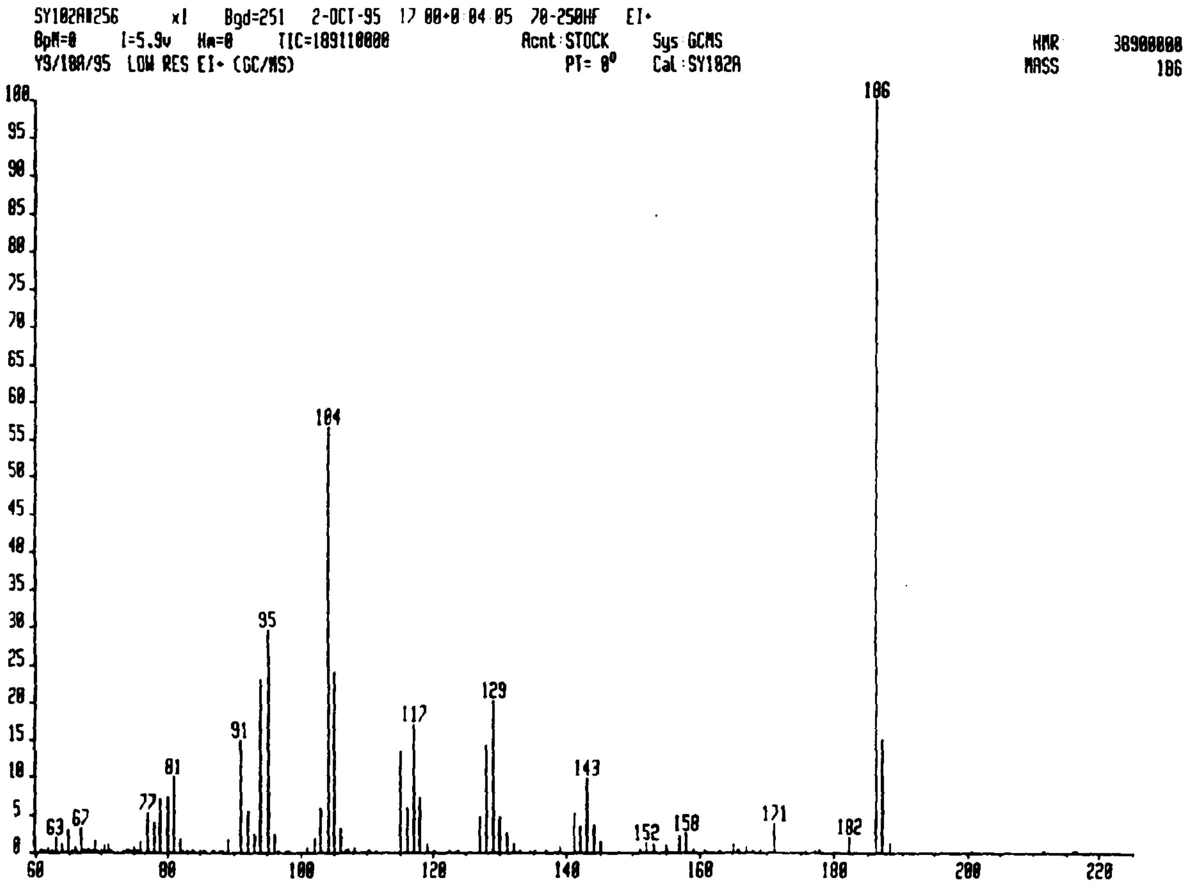


Fig. 10a EIMS spectra of the first component in the GC spectrum

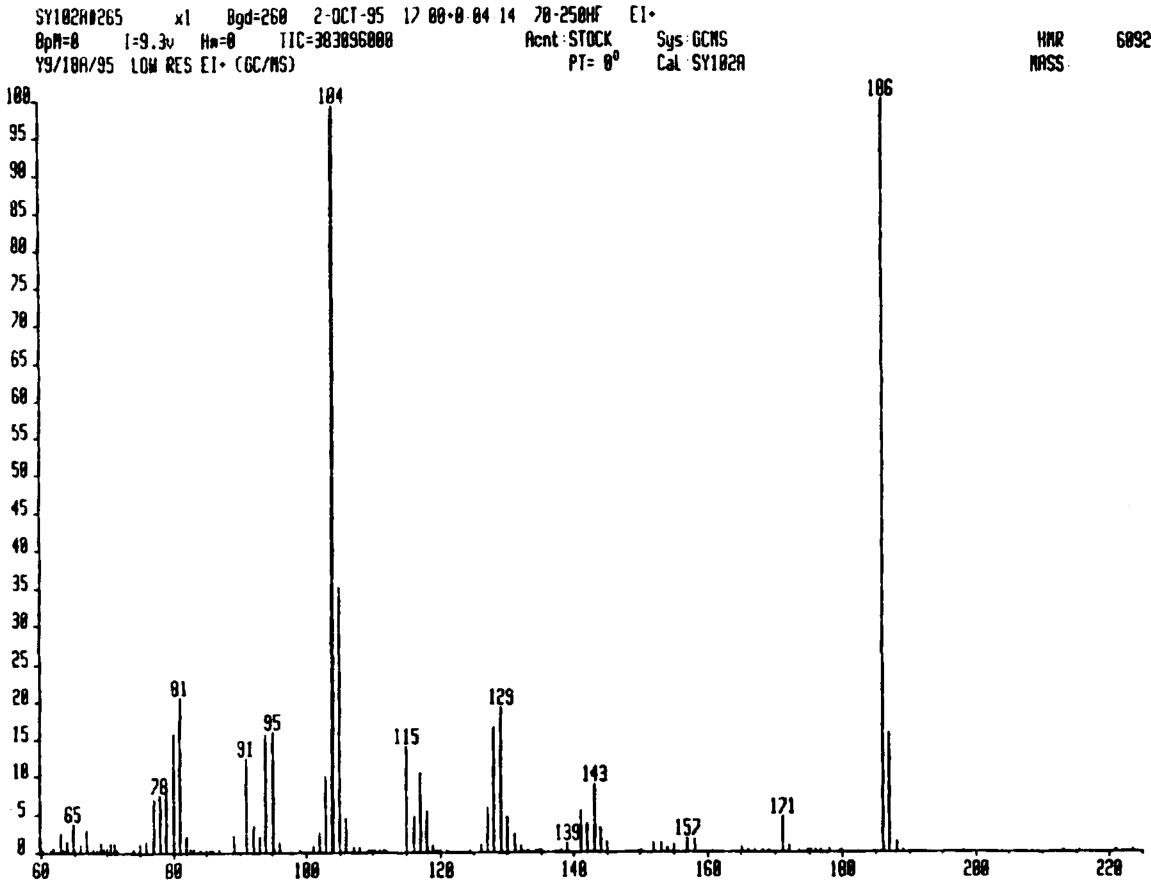


Fig. 10b EIMS spectra of the second component in the GC spectrum

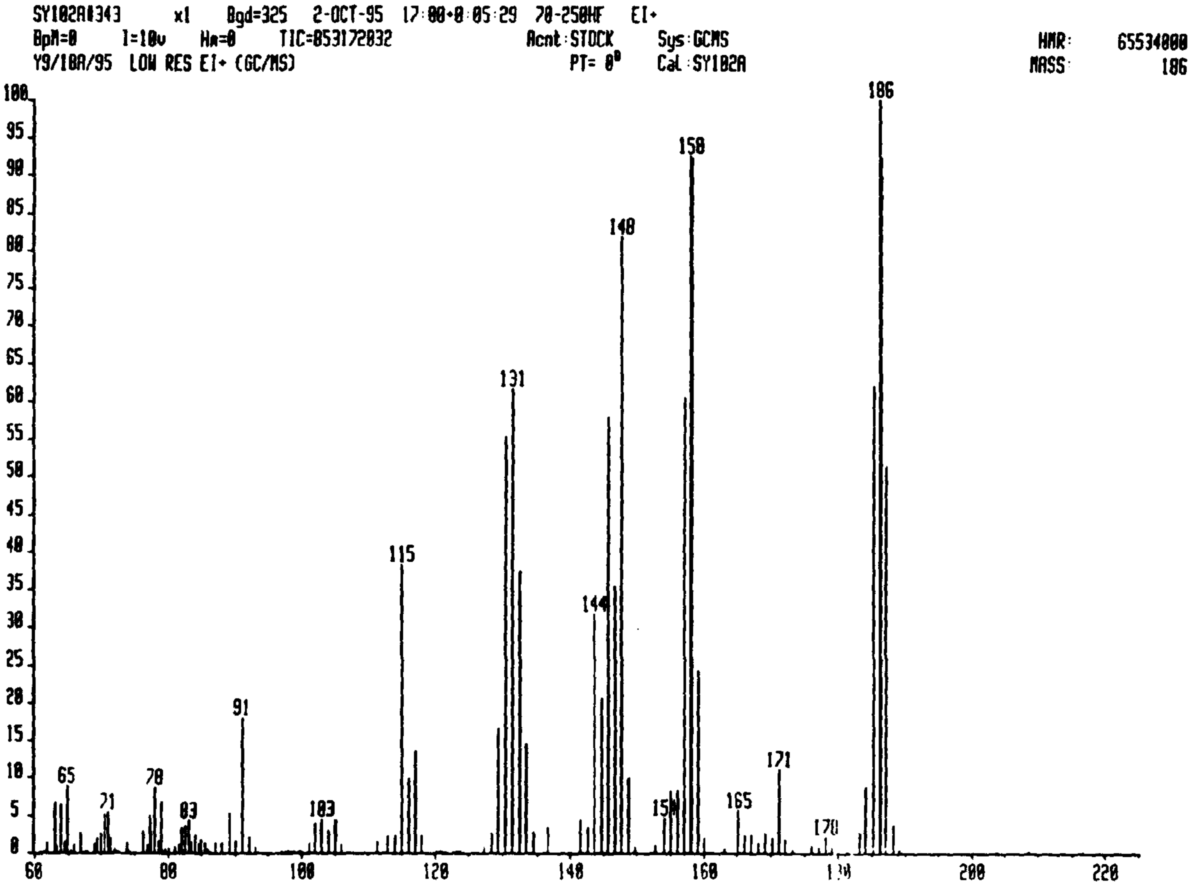


Fig. 10c EIMS spectra of the third component in the GC spectrum

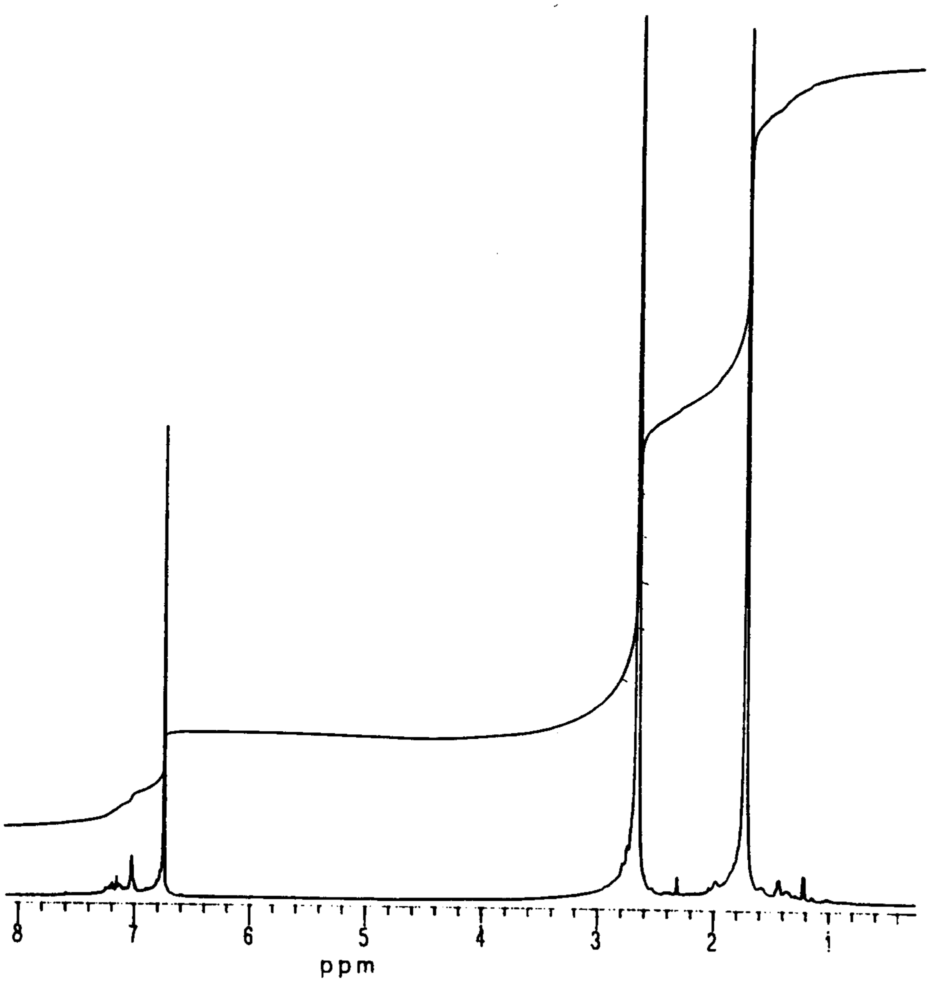


Fig. 11 ^{1}H NMR spectrum of the product obtained by hydrogenation of anthracene

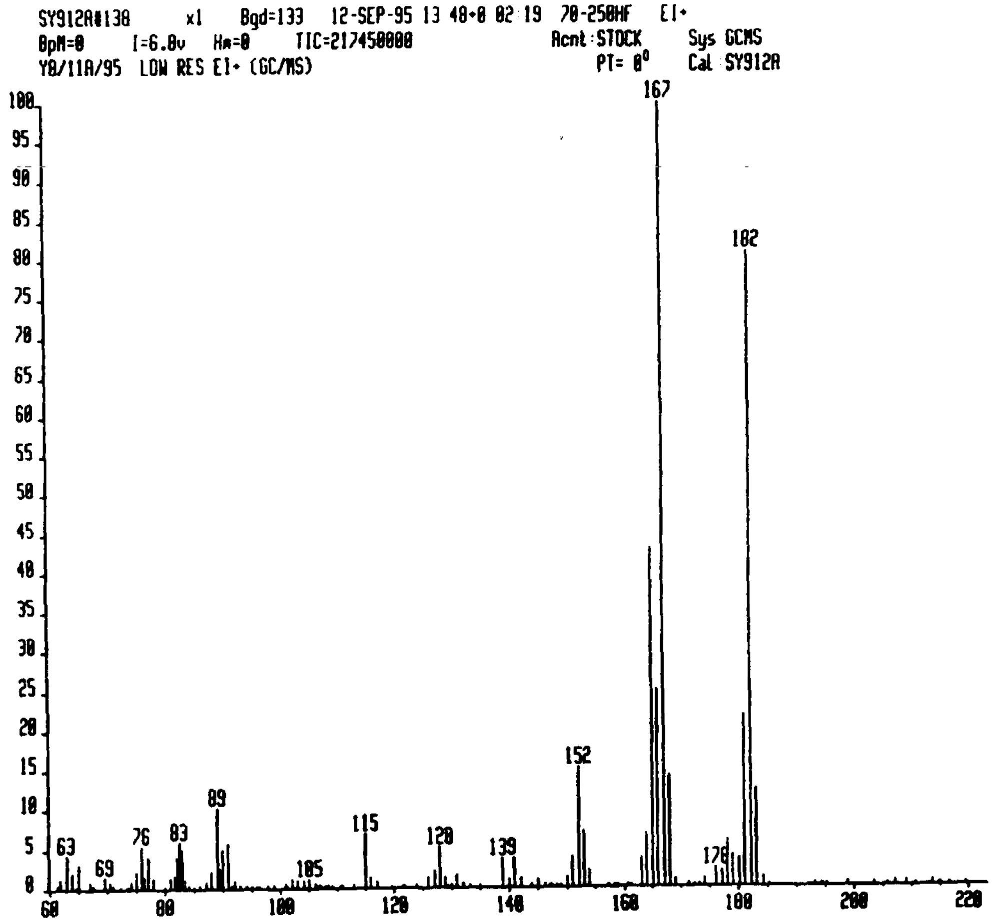


Fig. 12a EIMS spectra of compound (**20**) in the GC spectrum

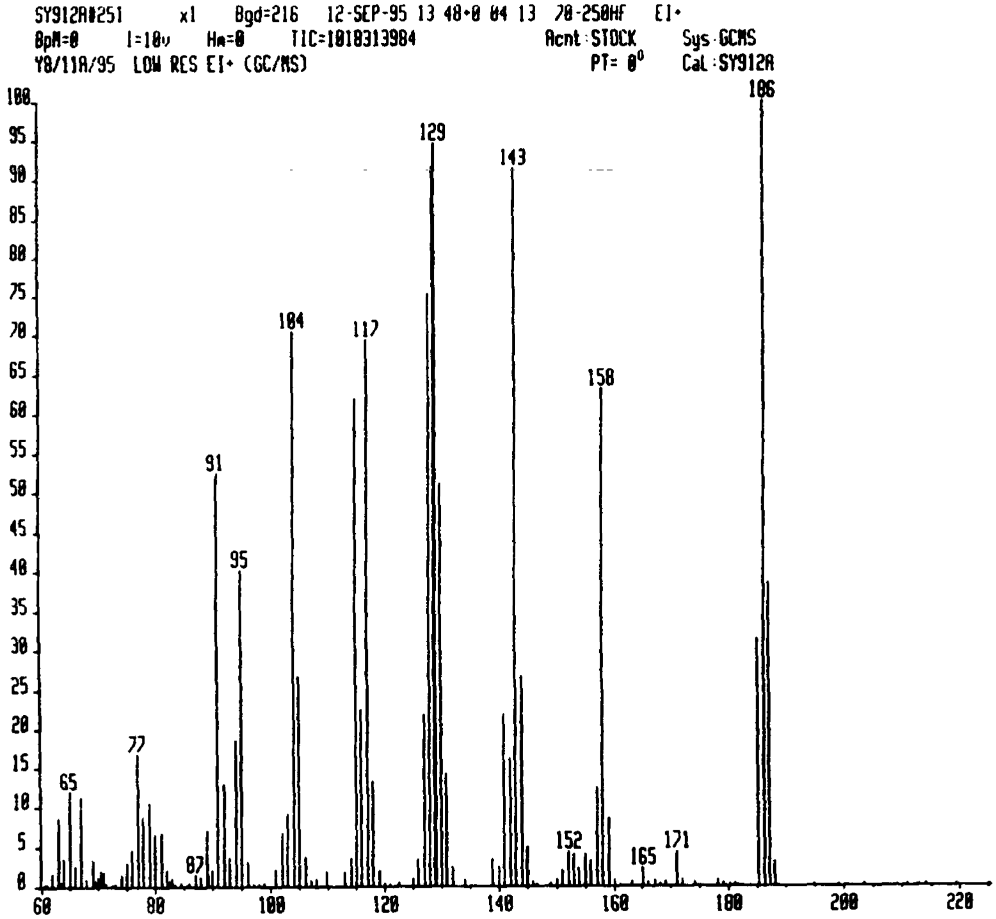


Fig. 12b EIMS spectra of compound (**19**) in the GC spectrum

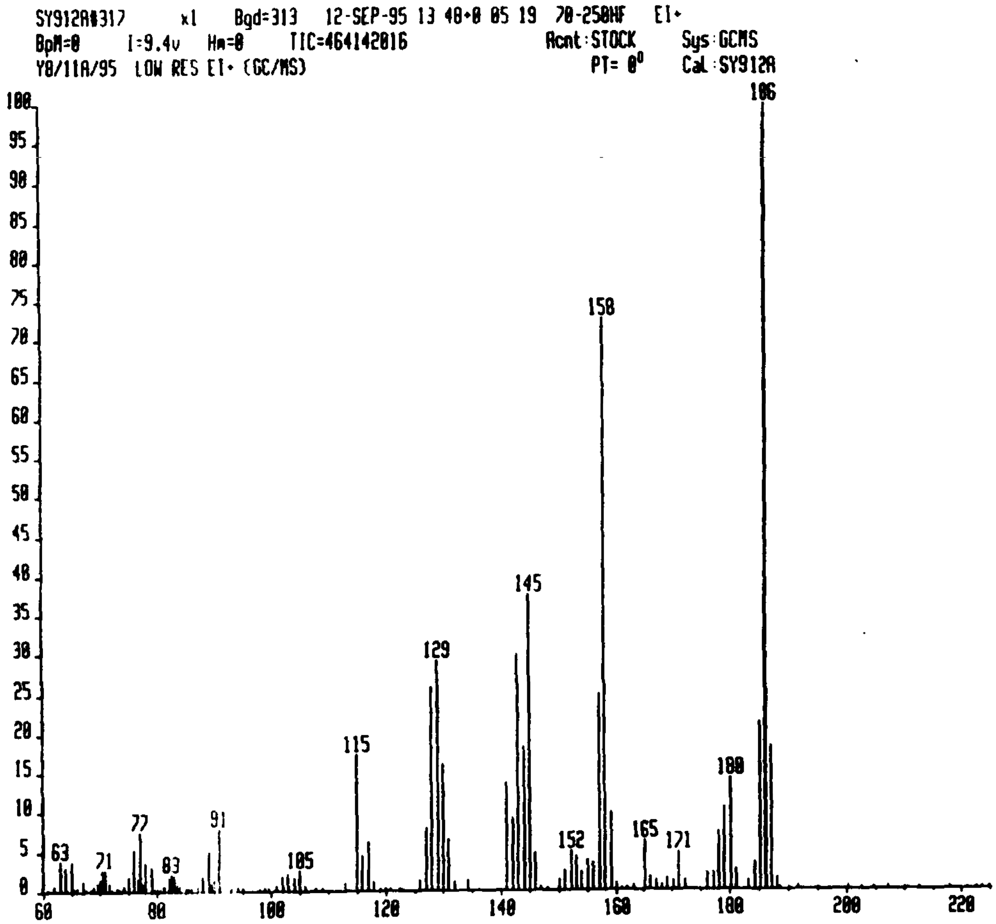


Fig. 12c EIMS spectra of compound (**18**) in the GC spectrum

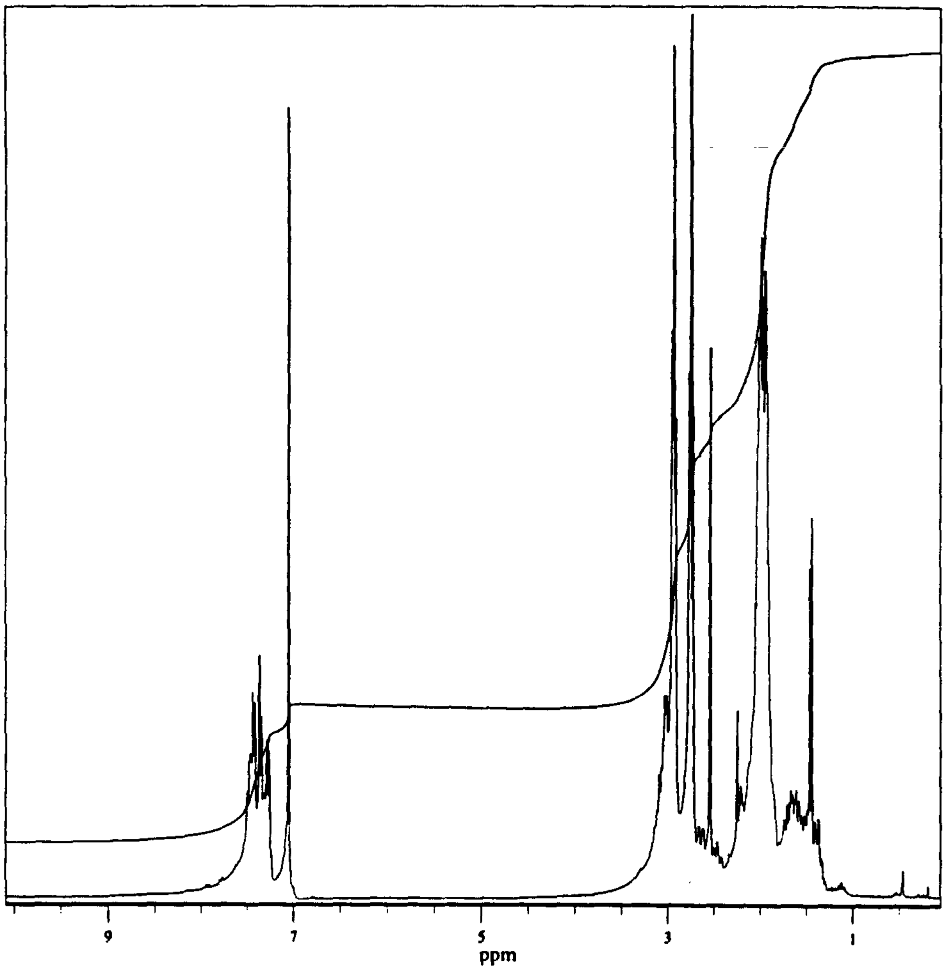


Fig. 13 ^{1}H NMR spectrum of the product obtained by hydrogenation of phenanthrene

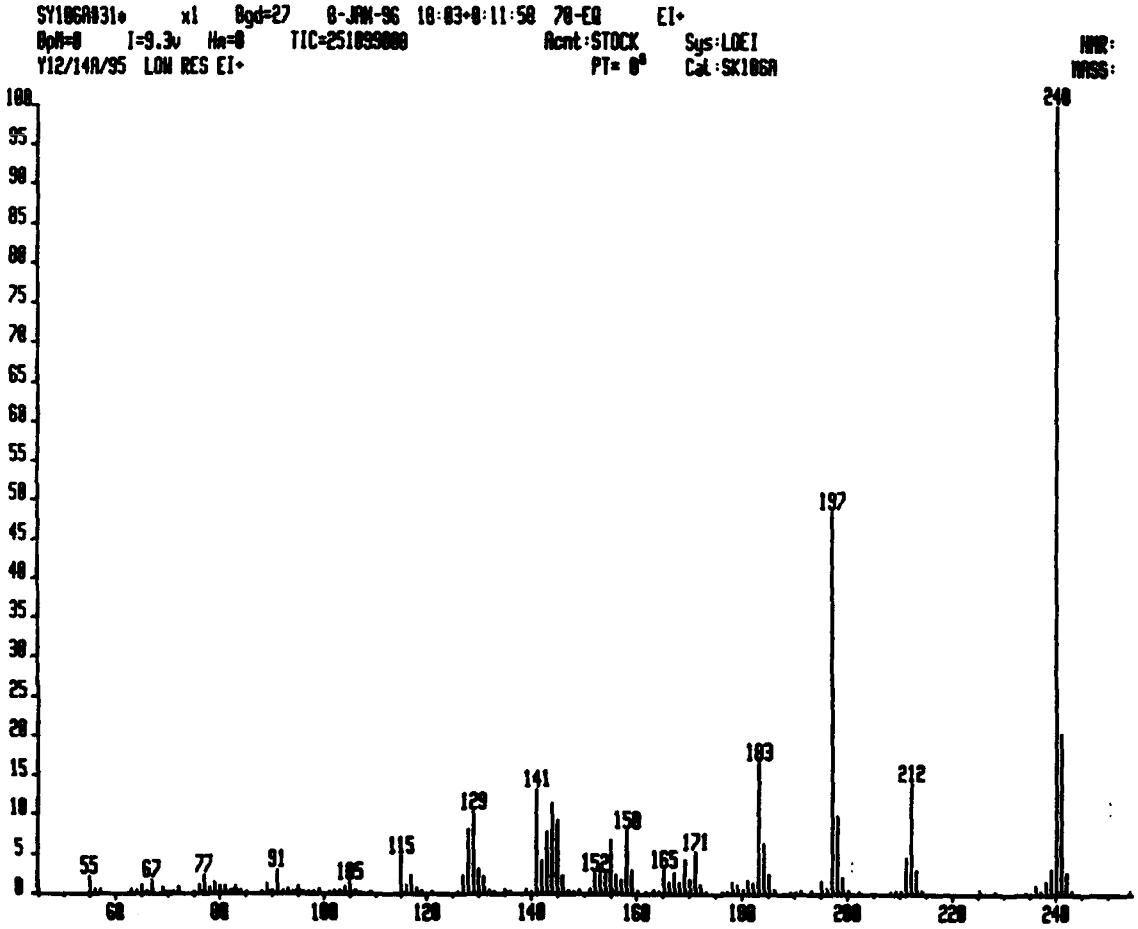


Fig. 14 EIMS spectrum of the product obtained by hydrogenation of chrysene

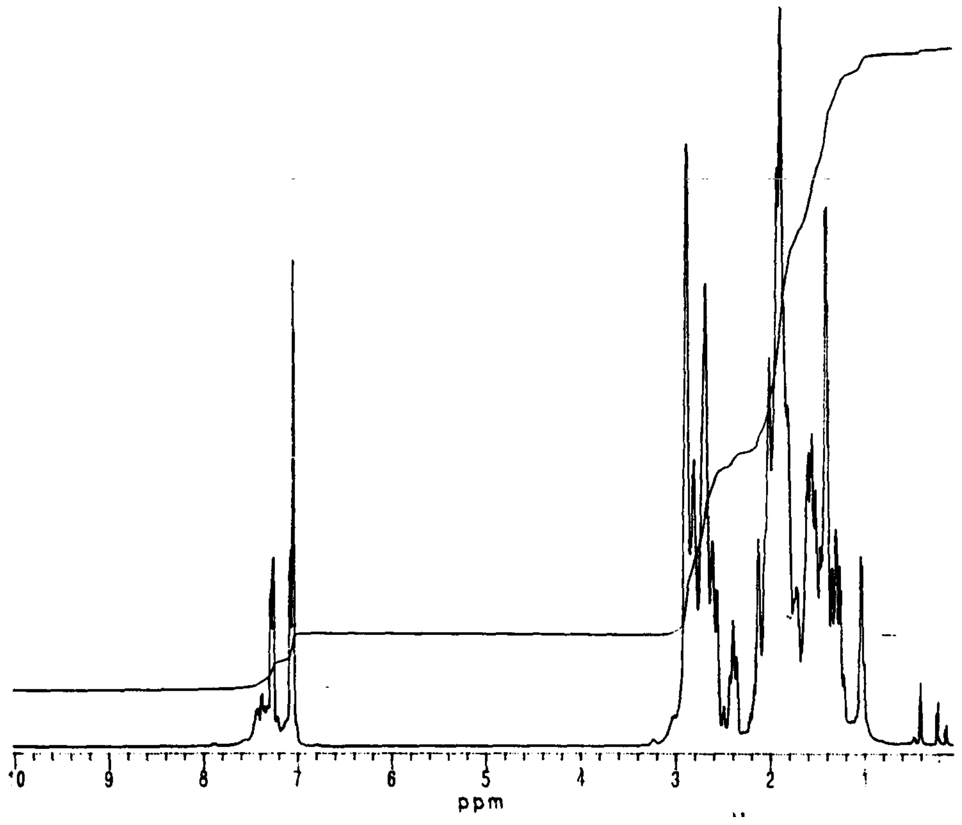


Fig. 15 ^{1}H NMR spectrum of the product obtained by hydrogenation of chrysene

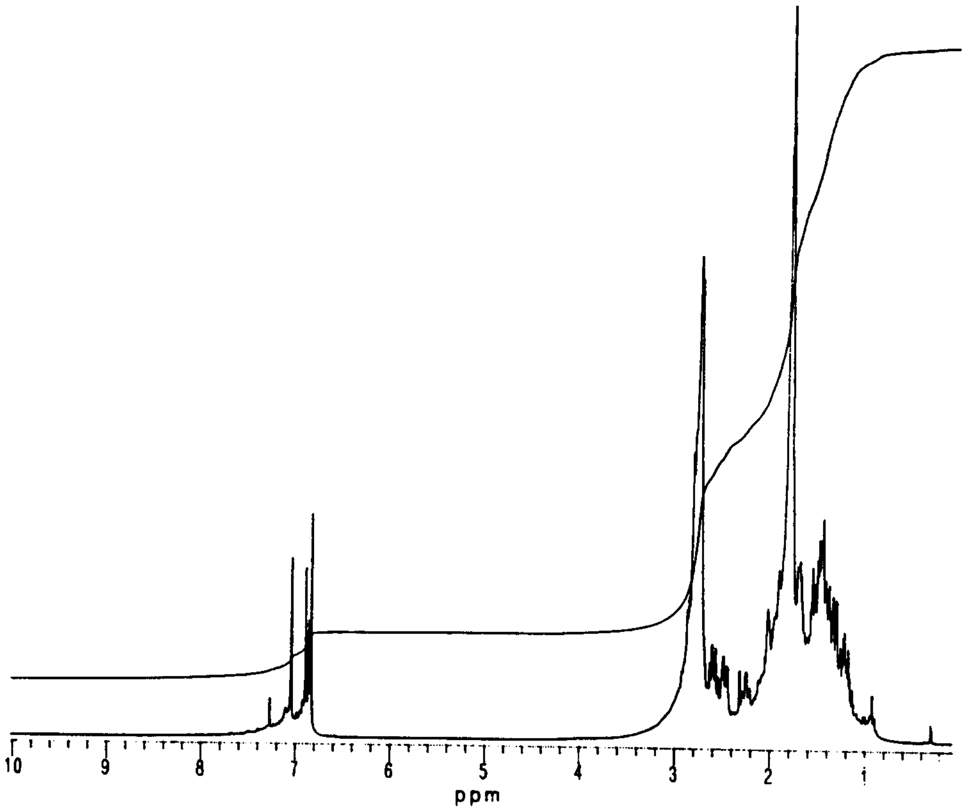


Fig. 16 ^{1}H NMR spectrum of the product obtained by hydrogenation of 1,2-benzoanthracene

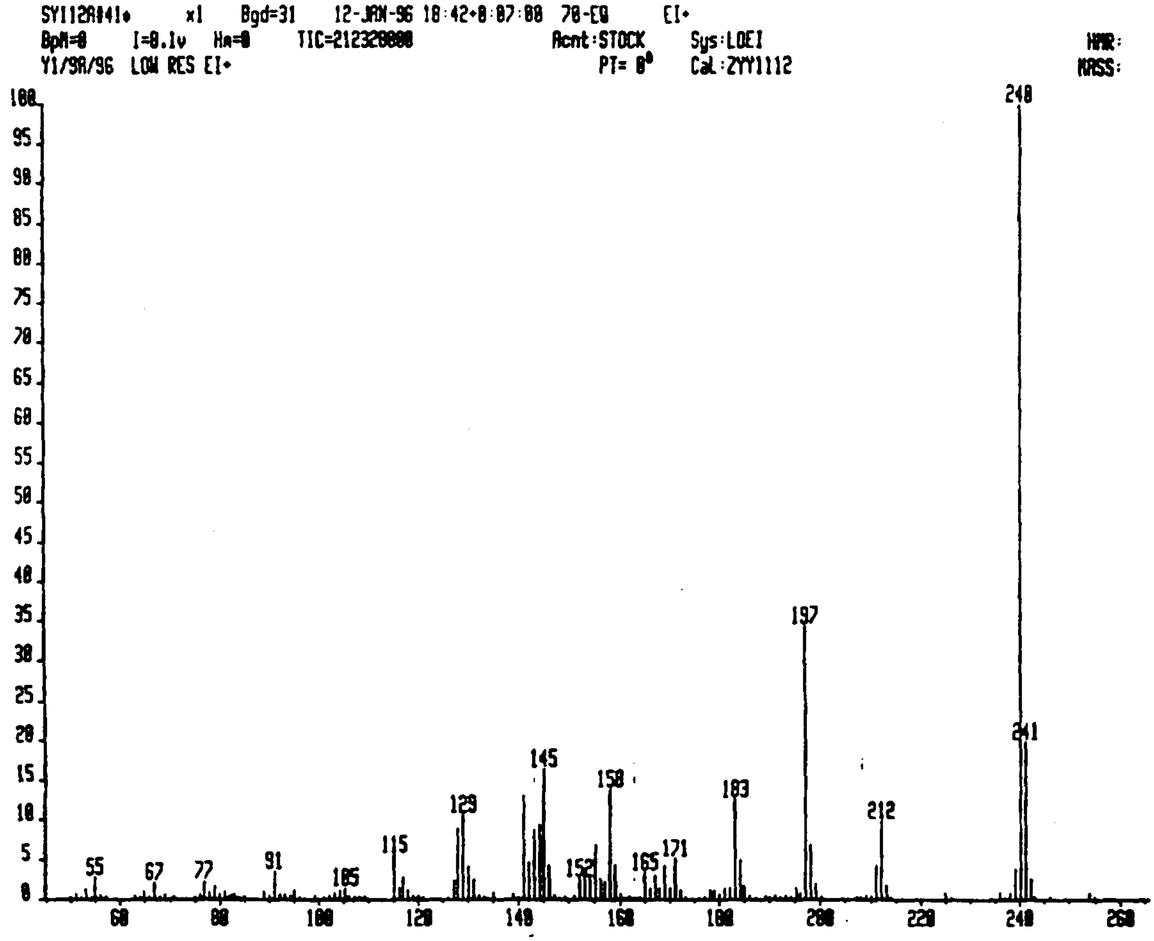


Fig. 17 EIMS spectrum of the product obtained by hydrogenation of 1,2-benzoanthracene

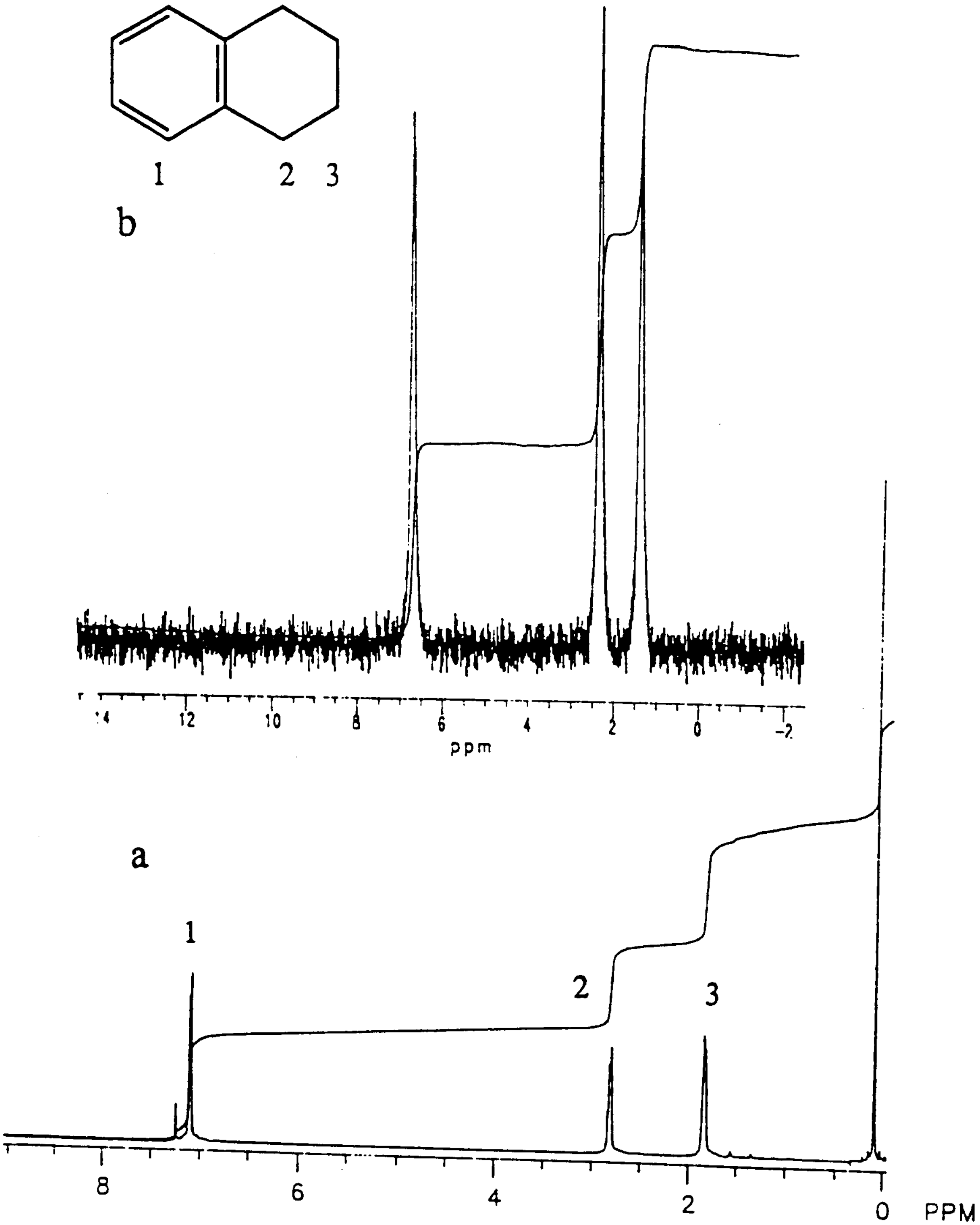


Fig. 18 ^{1}H NMR(a) and ^{2}H NMR (b) of tetralin obtained by treating naphthalene with 1000 psig of deuterium gas at 200°C

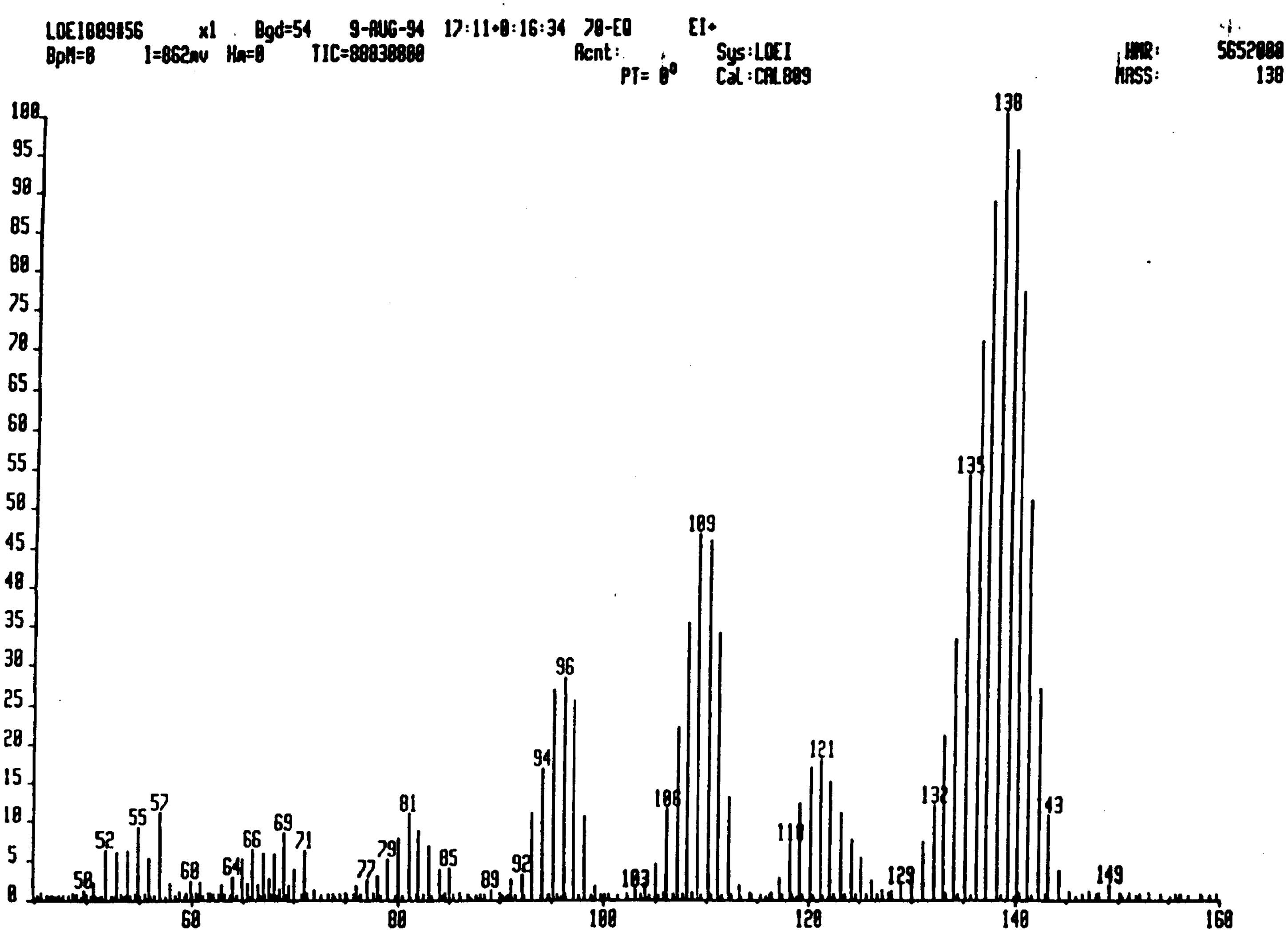


Fig. 19 Mass spectrometry of tetralin obtained by treating naphthalene with 1000 psig of deuterium gas at 200 °C

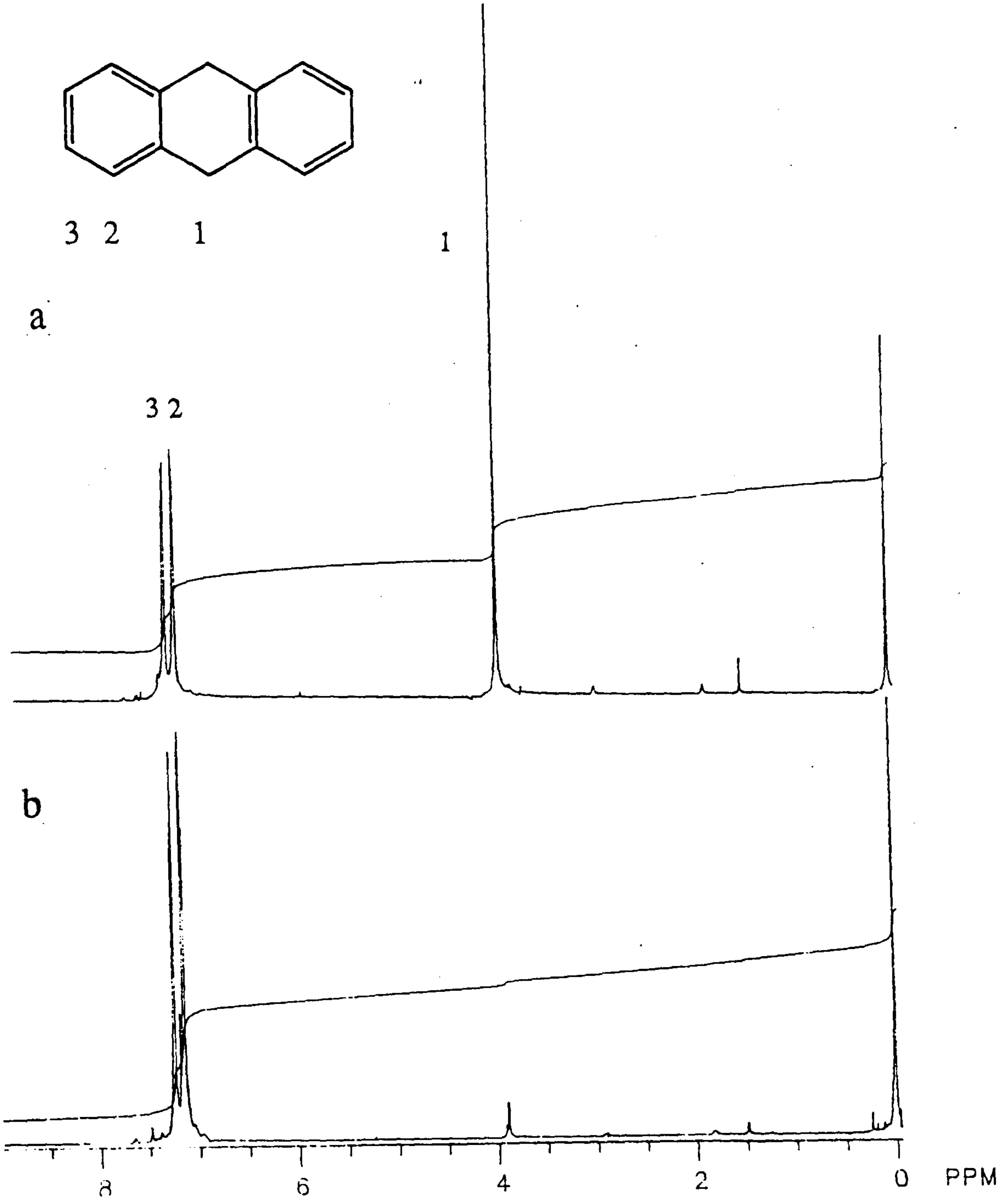


Fig. 20 ^{1}H NMR of 9,10-dihydroanthracene(a) and of the compound(b) obtained by treating anthracene with 1000 psig of deuterium at 200 °C

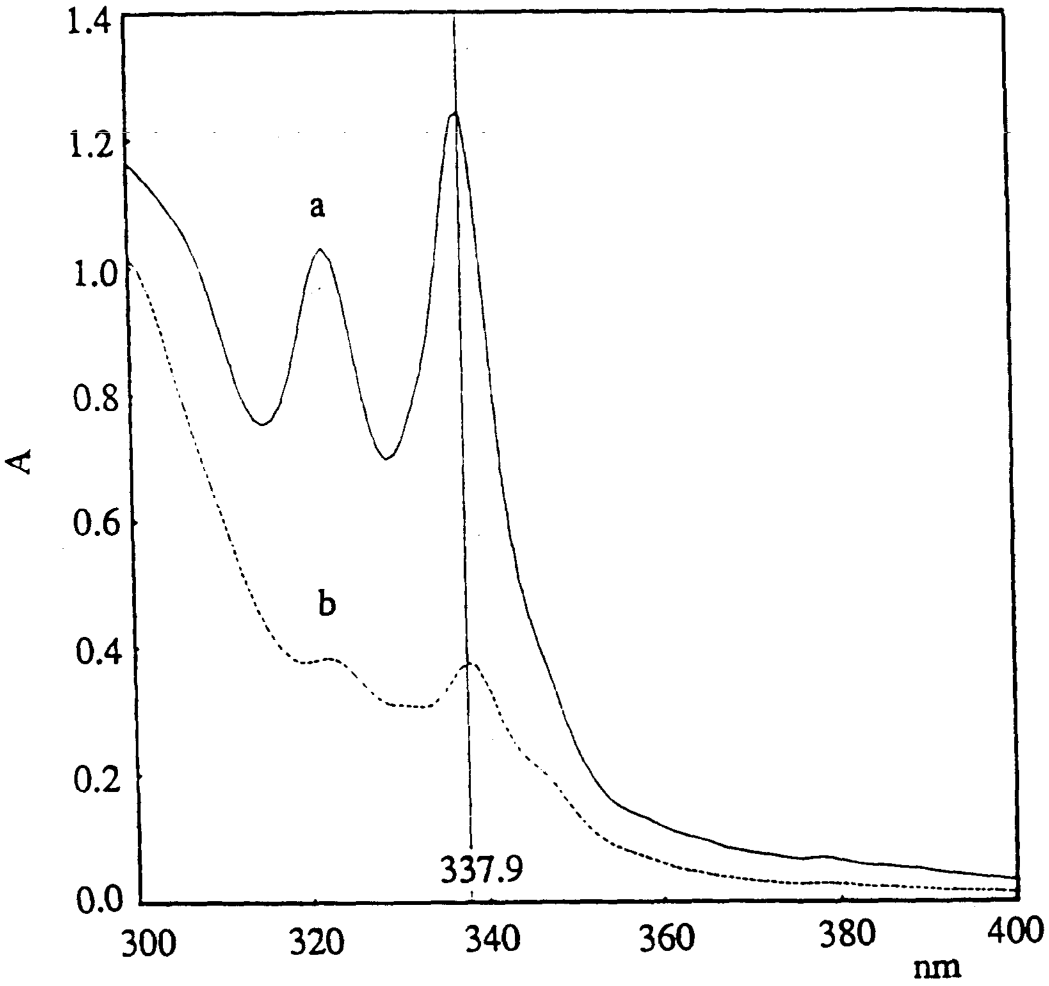


Fig. 21 UV-Visible spectra of coal liquid (a) and the hydrotreated coal liquid (b) by PTA under 1000 psig of H_2 at 200°C

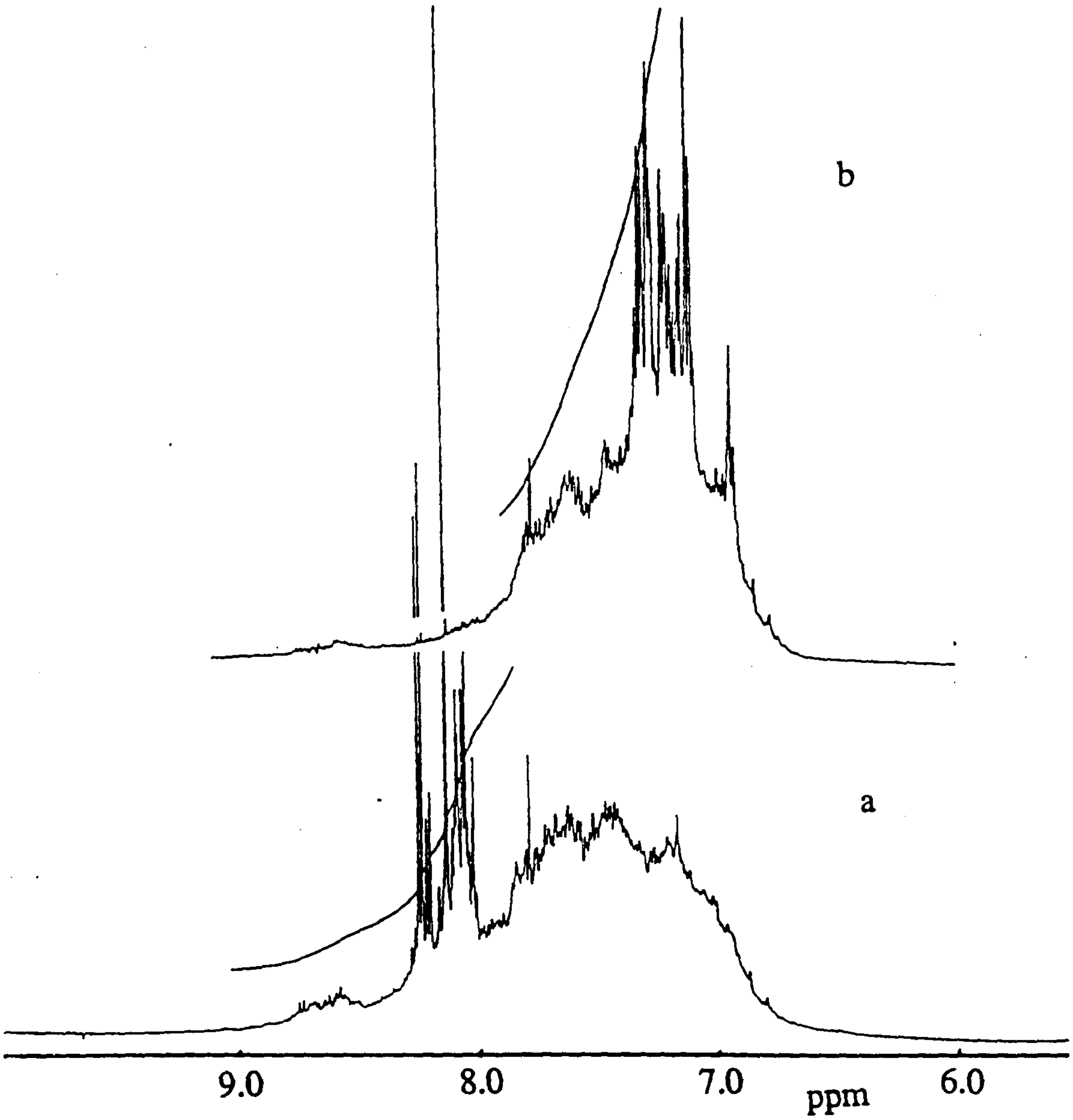


Fig. 22a ^1H NMR spectra of (a) unhydrotreated and (b) hydrotreated coal liquid (VSOH) catalyzed by PTA at 200°C under 1000 psig of H_2

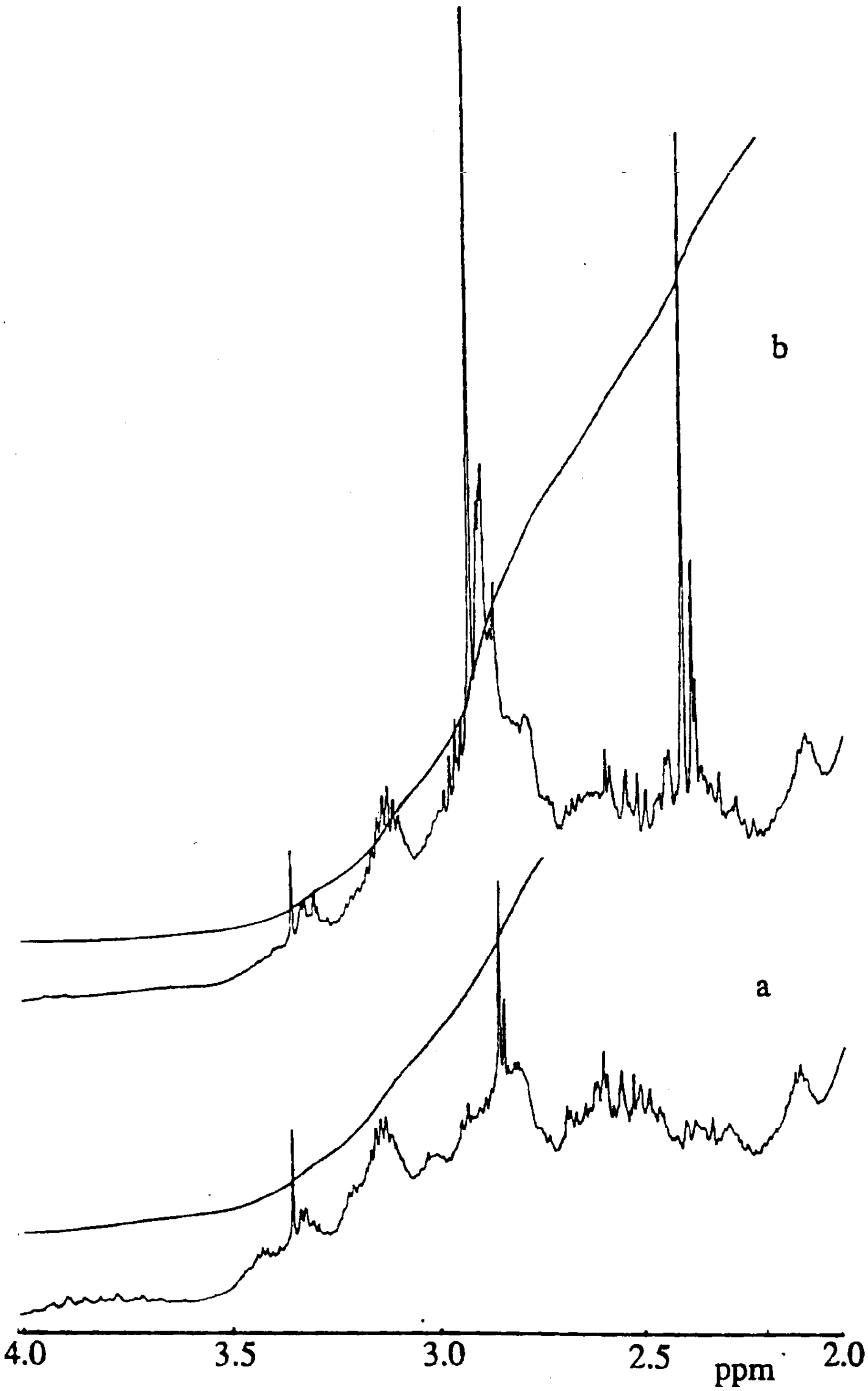


Fig. 22b ^{1}H NMR spectra of (a) unhydrotreated and (b) hydrotreated coal liquid (VSOH) catalyzed by PTA at 200°C under 1000 psig of H_2

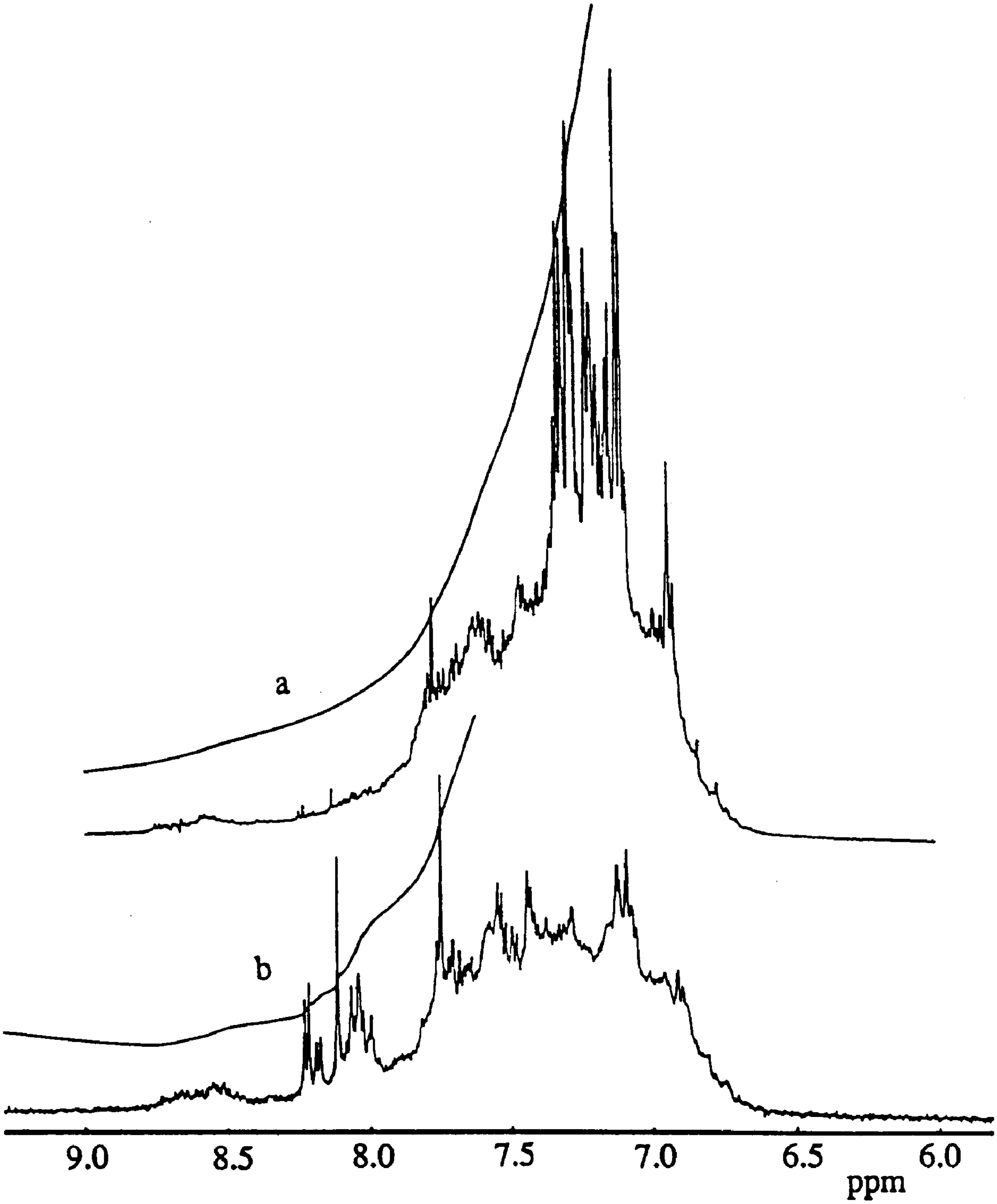


Fig. 23 ^{1}H NMR spectra of the hydrotreated coal liquids catalyzed by (a) PTA at 200°C and (b) LDA at 300°C under 1000 psig of H_2

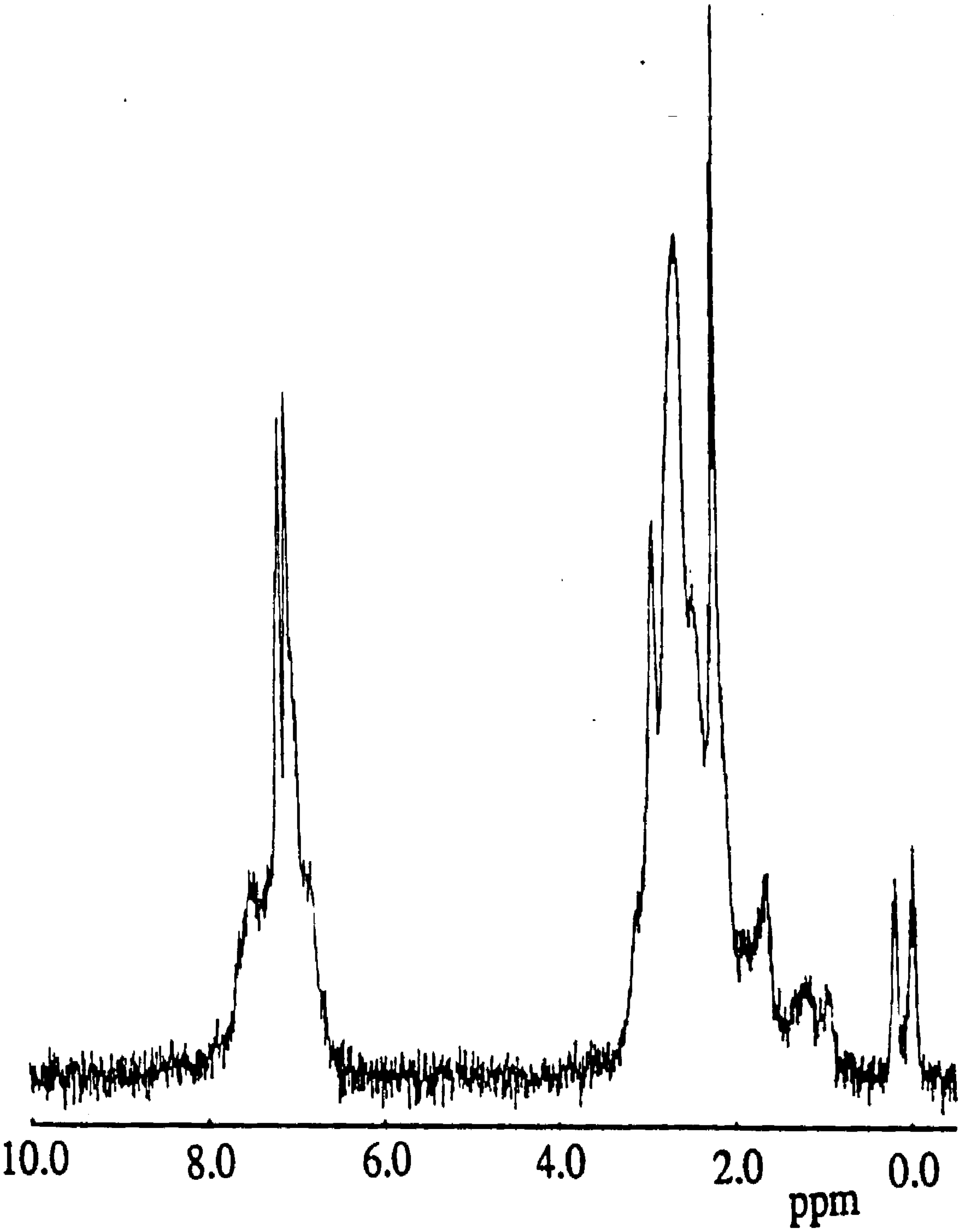


Fig. 24 ^{1}H NMR spectrum of hydrotreated coal liquid with dideuterium catalyzed by PTA under 1000 psig of D_2 at 250°C

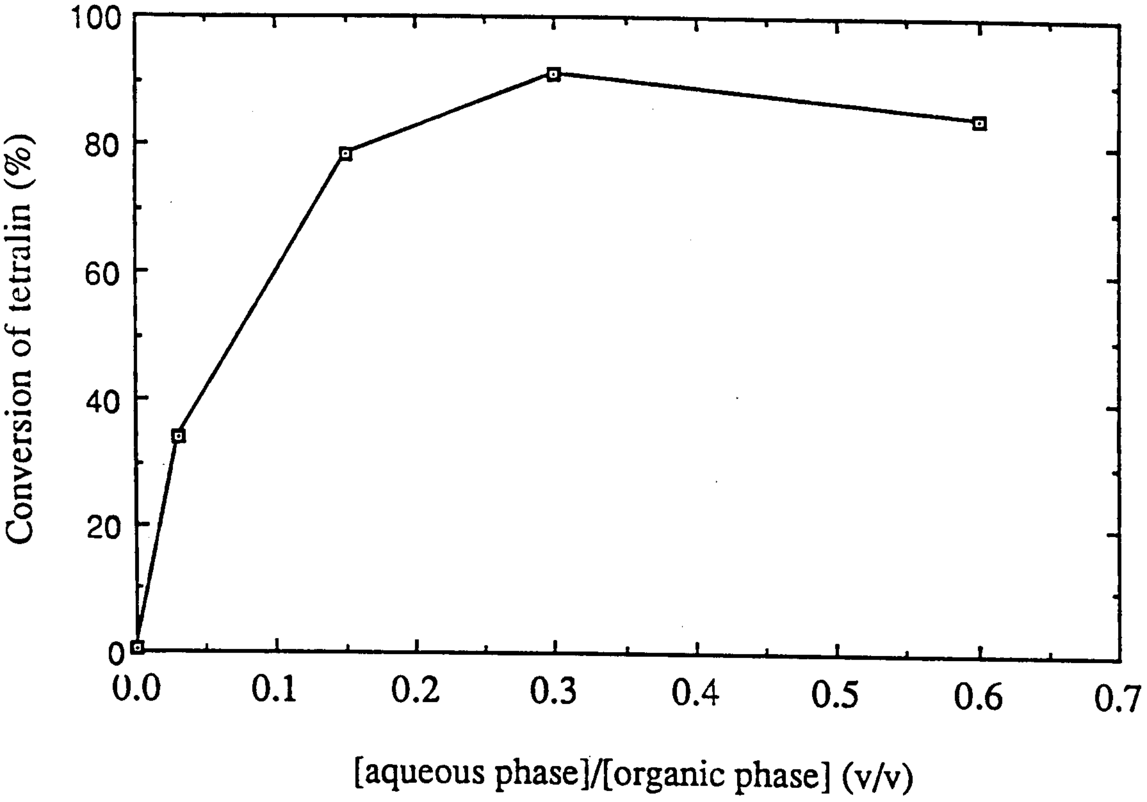


Fig. 25 Effect of the volume ratios of aqueous phase to organic phase on hydrogenation of tetralin. Reaction conditions: 25 mmol of substrate, 0.125 mmol of [1,5-HDRhCl]$_2$, 30 mL of hexane, 10 mL of buffer (hydrion, pH=7.4), temperature 25°C, 1 atm H2.

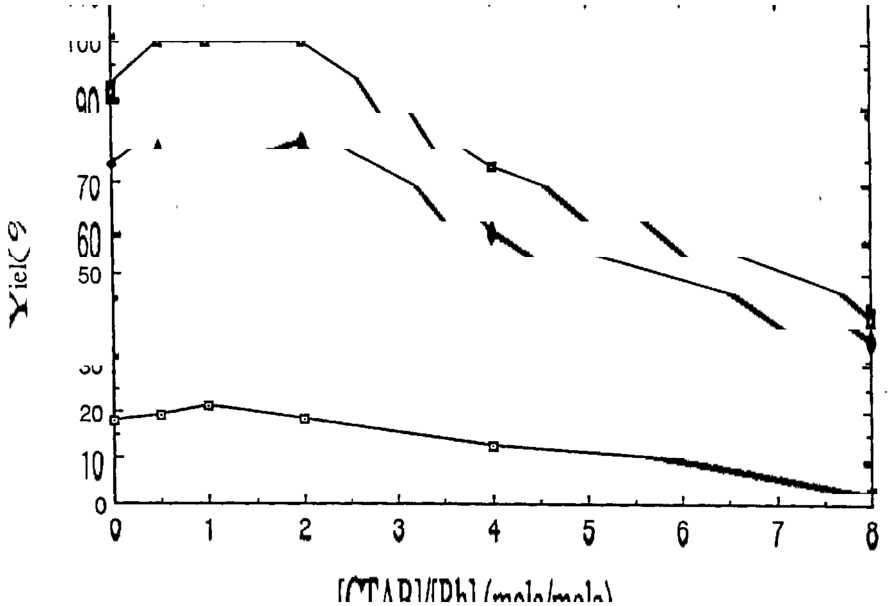


Fig. 26 Influence of the molar ratio of surfactant to rhodium on the conversion of tetralin hydrogenation. Reaction conditions: surfactant, CTAB, others as given in Fig. 25
—□—: trans-decalin, —●—: cis-decalin, —▲—: total

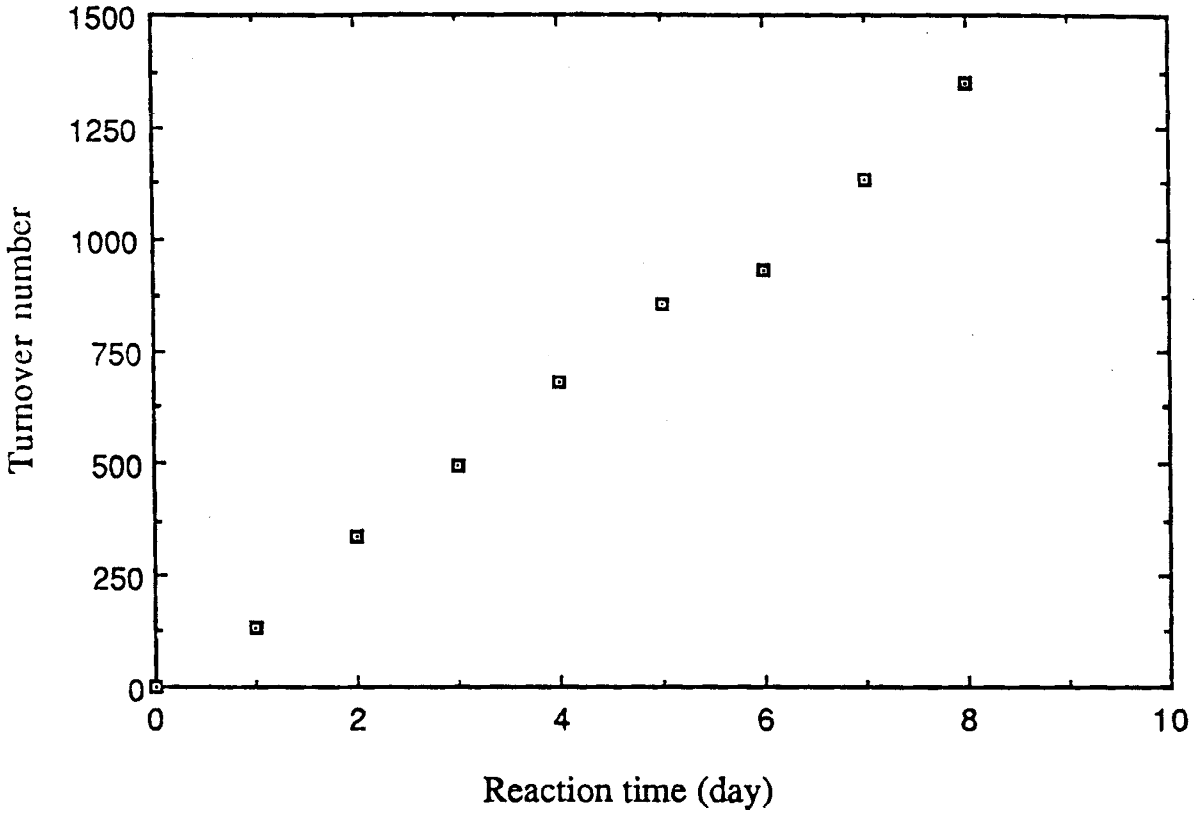


Fig. 27 Effect of reaction time on the catalytic activity of CTAB stabilized Rh catalyst.
Reaction conditions: [CTAB]/[Rh] = 2
others as given in Fig. 25

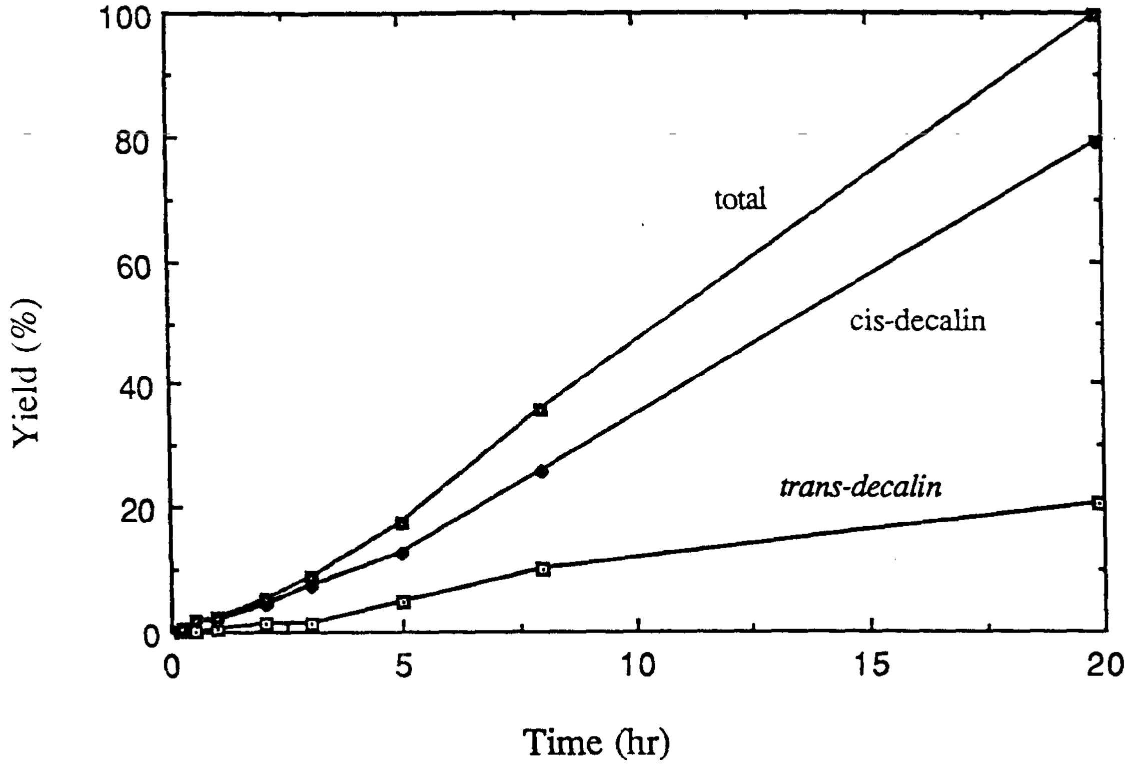


Fig. 28 Conversion - time profiles for hydrogenation of tetralin. Reaction conditions: [CTA-B]/[Rh] = 0.5, others as given in Fig. 25

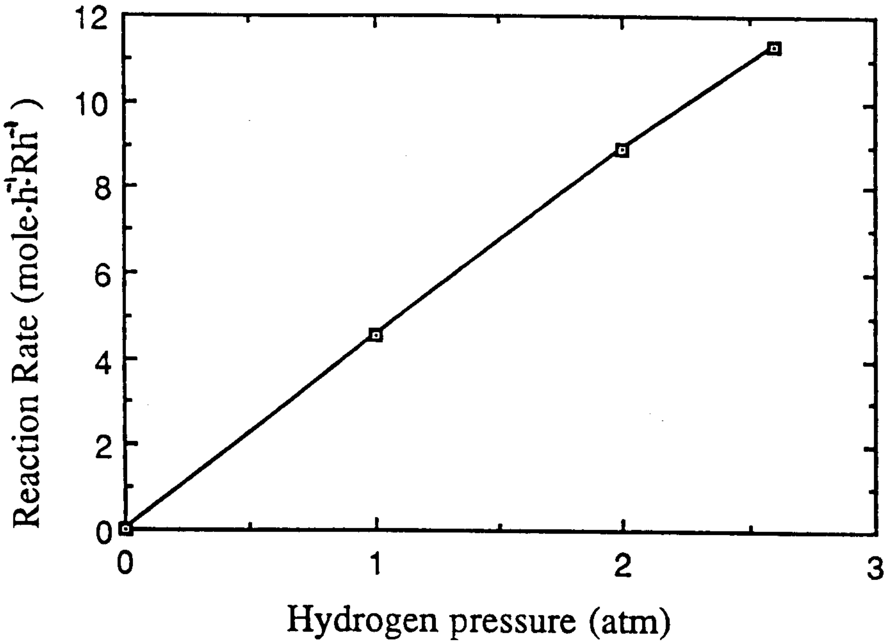


Fig. 29 Dependence on the reaction rate on the hydrogen pressure
Conditions as shown in Fig. 27

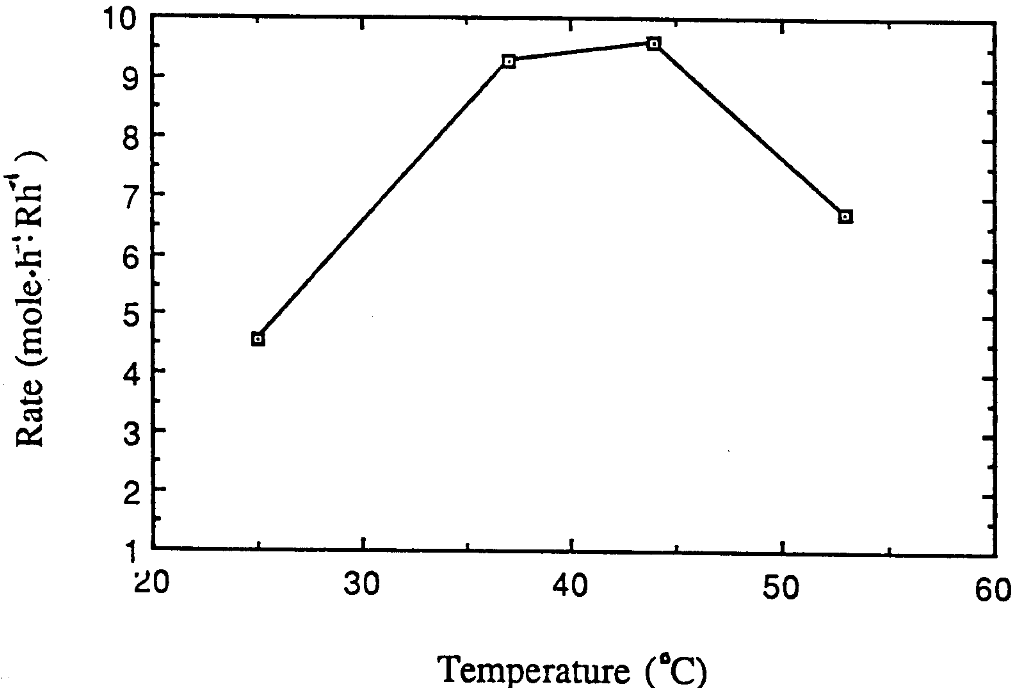


Fig. 30 The relationship between the reaction rate and reaction time
Conditions as in Fig. 27

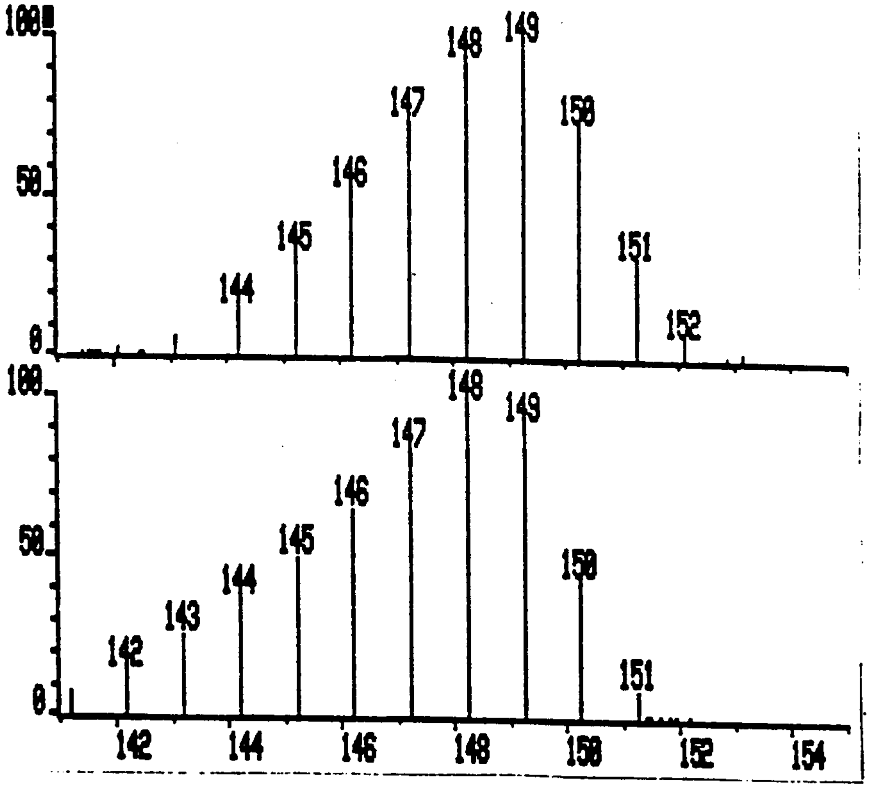


Fig. 31 Parent ion region of the EI mass spectra of decalin produced in the reaction of tetralin with D_2: upper spectrum, *trans*-decalin, lower spectrum, cis-decalin. Hydrogenation of tetralin performed under the conditions as given in Fig. 25

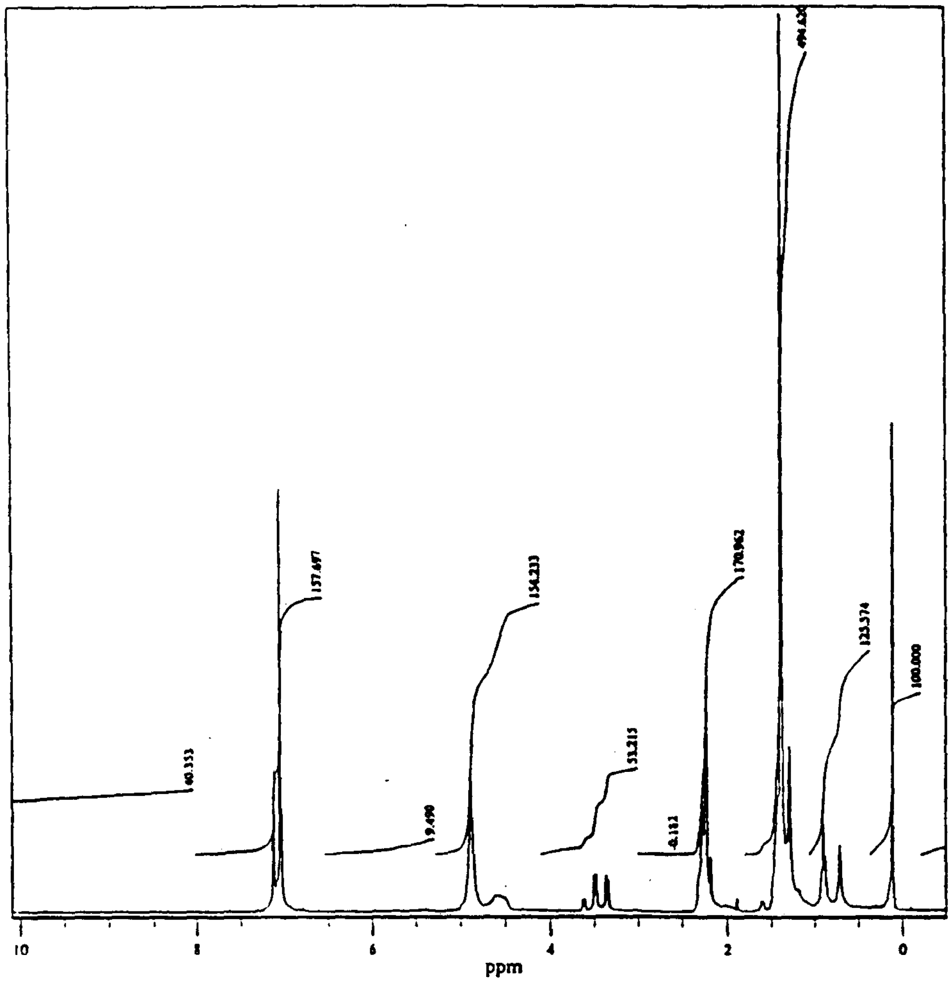


Fig. 32 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 10 minutes

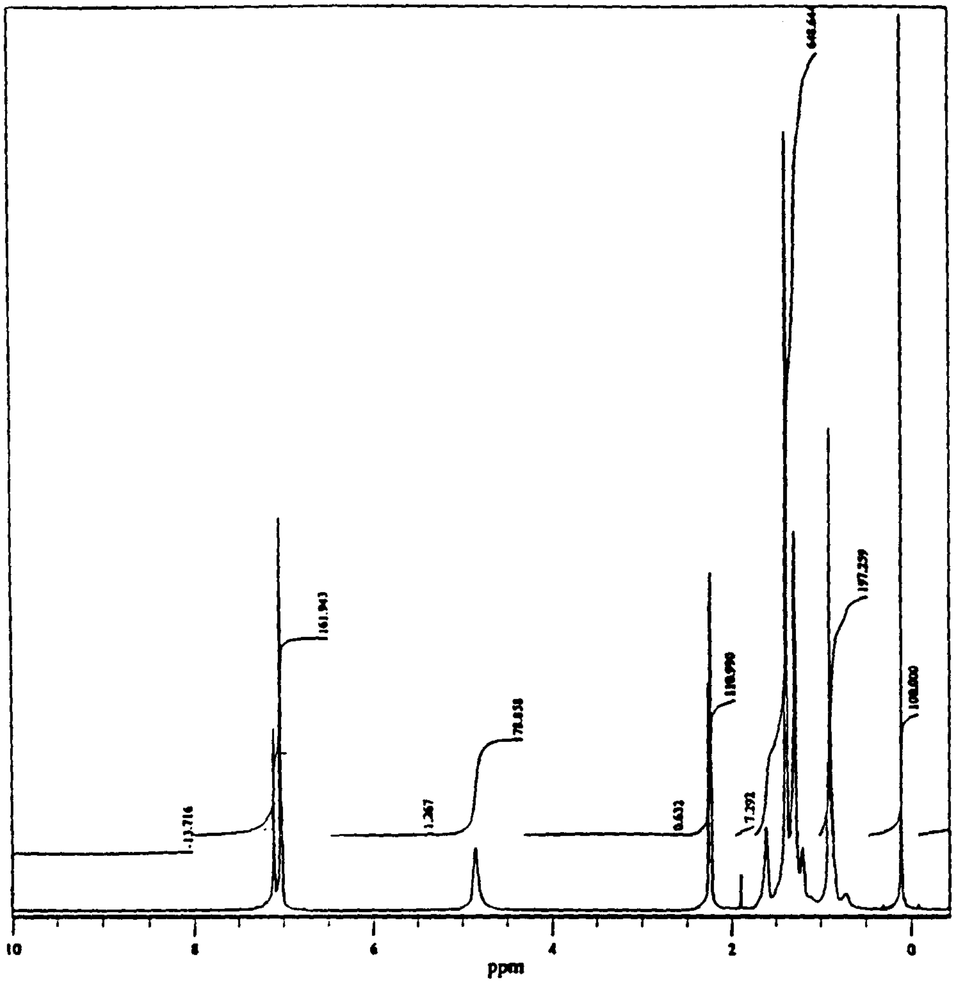


Fig. 33 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 30 minutes

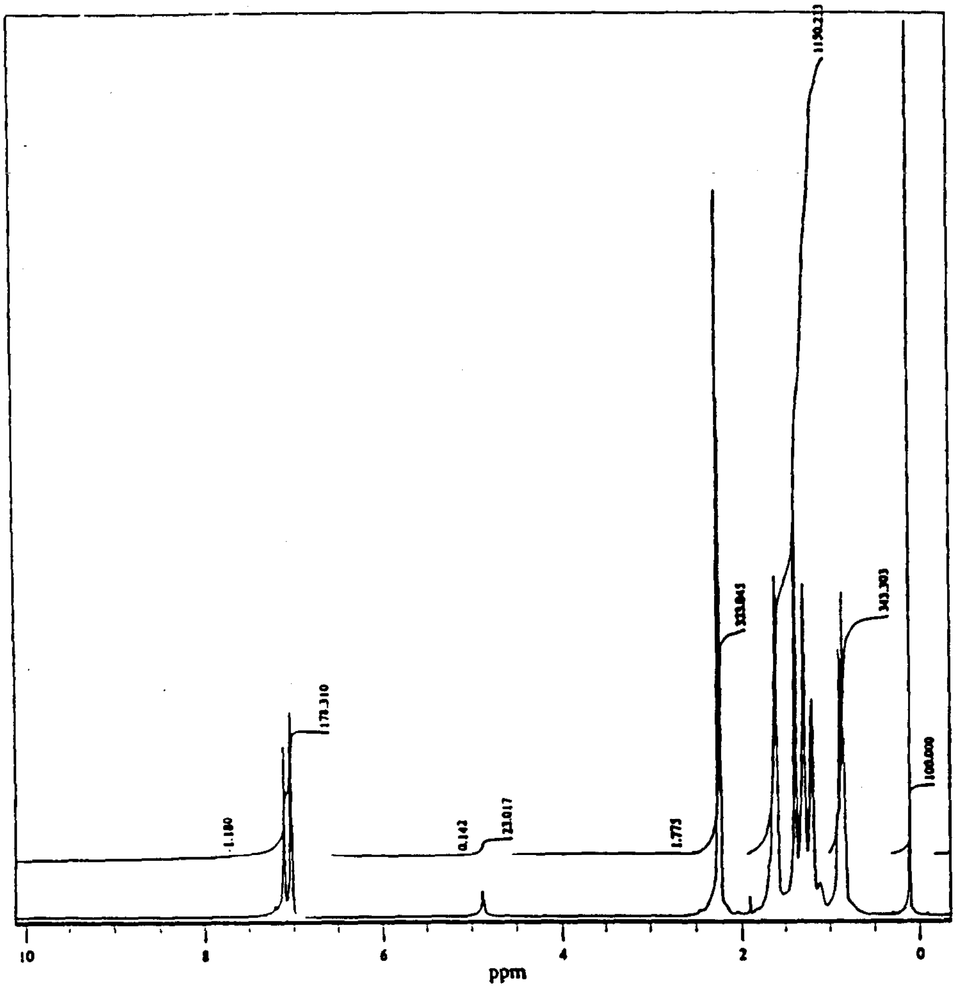


Fig. 34 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 1 hour

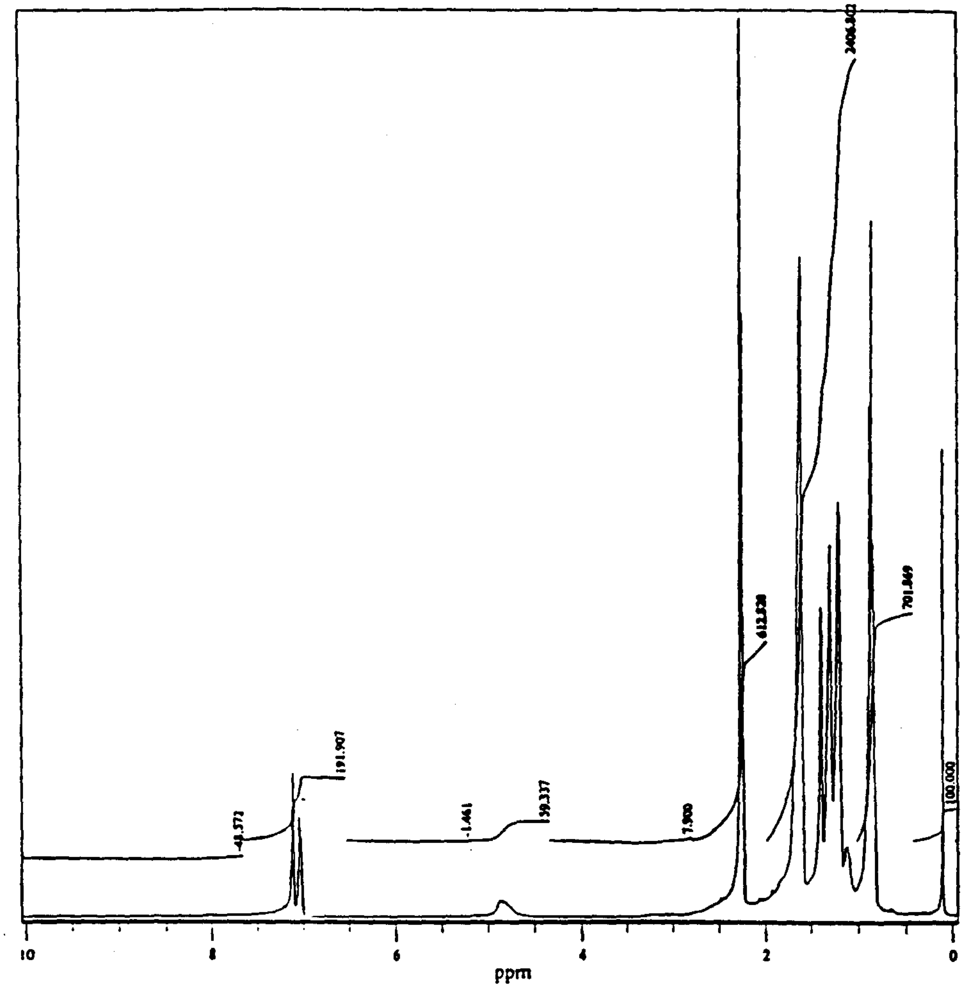


Fig. 35 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 2.5 hours

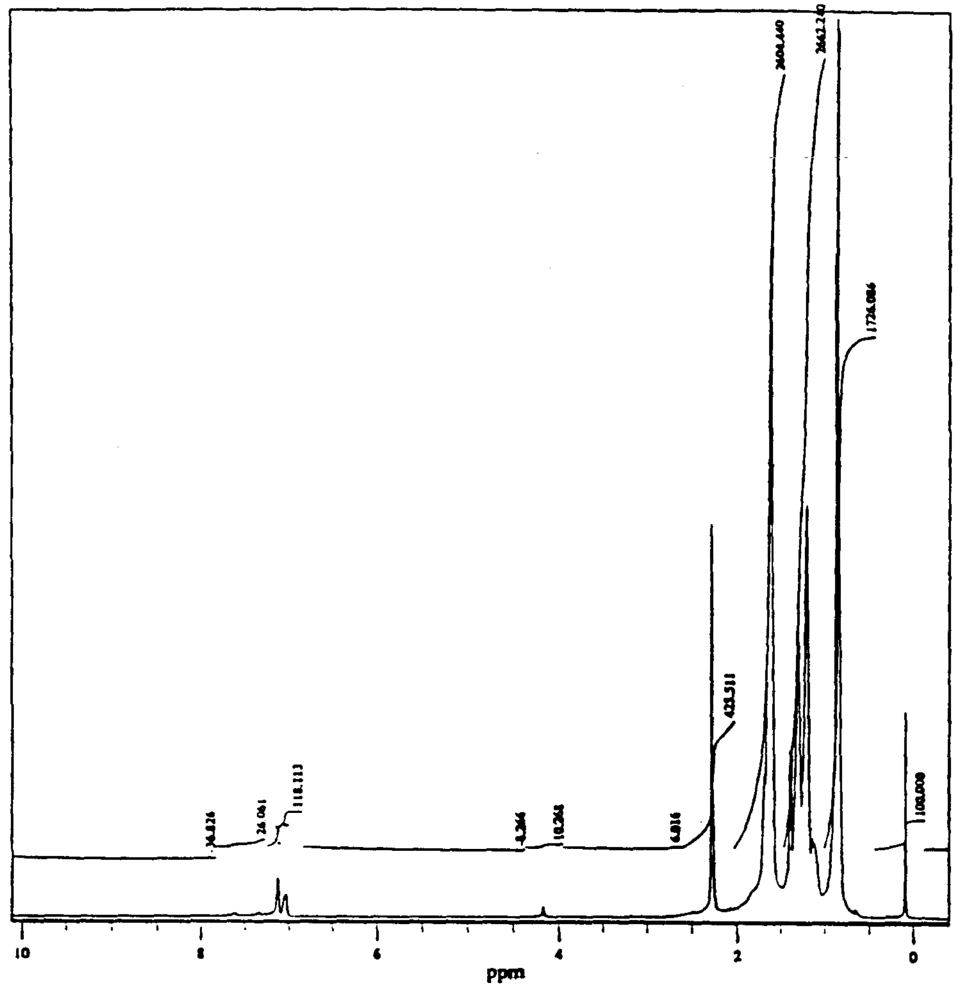


Fig. 36 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 4.5 hours

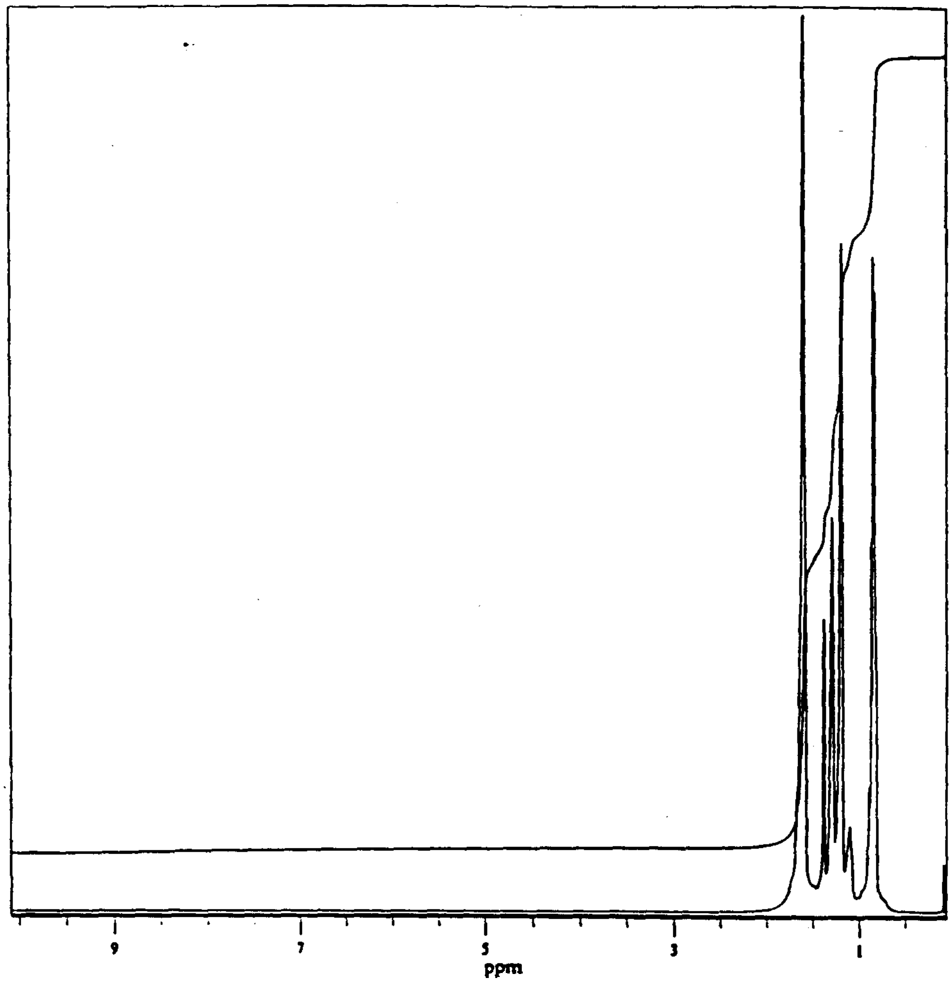


Fig. 37 ^{1}H NMR spectrum of the organic phase after the reaction proceeds 24 hours

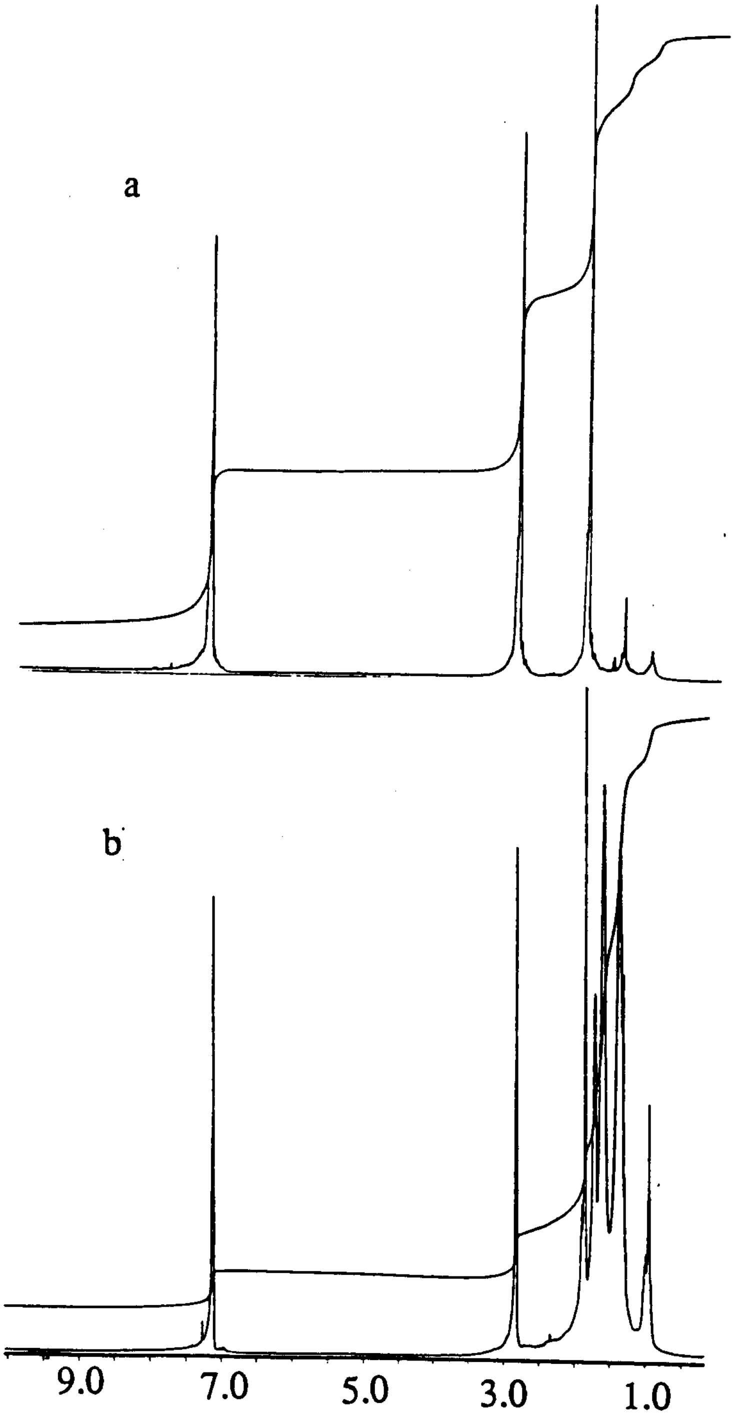


Fig. 38 ^{1}H NMR spectra of coal liquid/tetralin mixture before (a) and after being hydrogenated (b)

Table 1 Relative rate constants for hydrogenation of mono-, di, and triaromatic hydrocarbons over sulfided catalysts

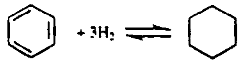
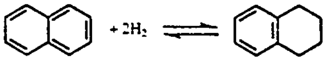
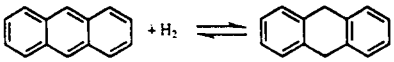
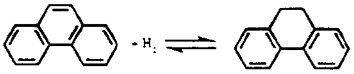
Hydrogenation Reaction	Relative Rate Constant				Total Resonance Energy, kcal/mole	Resonance Energy per Ring, kcal/mole
	Ni-Mo/ Al_2O_3	Ni-W/ Al_2O_3	Co-Mo/ Al_2O_3	WS_2		
	1	1	1	1	36-40	40
	10	18	21	23	59-75	28
	36	40	-	62	71-105	-
	4	-	-	-	85-92	-

Table 2. The organic bases used in attempts to activate hydrogen for the reduction of naphthalene

Organic Bases	[Base]/ [Substrate] (mole/mole)	Solvent	Conversion (%)
NaOH	0.50	Hexane	0
LiOH	0.50	Hexane	0
KOH	0.50	Hexane	0
t-NaOBu	0.25	Hexane	0
t-LiOBu	0.25	Hexane	0
t-KOBu	0.50	Hexane	1
t-KOBu	0.50	*t*-BuOH	0
$NaNH_2$	0.25	Hexane	1
$LiNH_2$	0.25	Hexane	7
$LiNH_2$	0.50	Hexane*	44
$LiN[CHMe_2]_2$	0.25	Hexane	100
$LiN[C_6H_{11}]_2$	0.25	Hexane	95

Conditions:
Substrate: naphthalene, Solvent: 50 mL,
Temperature: 200°C, Initial H_2 pressure: 1000 psig
Reaction time: 18 hrs,
*The temperature was 300°C in this experiment.

Table 3. Influence of the ligand on the lithium amide on its catalytic activity for the hydrogenation of naphthalene to tetralin

$LiNR_2$	$[LiNR_2]$/ [Substrate] (mole/mole)	Solvent	Conversion (%)
$LiN[CH(CH_3)_2]_2$	0.25	Hexane	100
$LiN(C_6H_{11})_2$	0.25	Hexane	95
$LiN[CH_2CH_3]_2$	0.25	Hexane	3
$LiN(CH_3)_2$	0.25	Hexane	7
$LiN[SiMe_3]_2$	0.25	Hexane	16
$LiN[SiMe_3]_2$	0.25	Toluene	3
$NaN[SiMe_3]_2$	0.25	Toluene	51
$KN[SiMe_3]_2$	0.25	Toluene	100

Conditions:
Substrate: naphthalene, Solvent: 50 mL,
Temperature: 200°C, Initial H_2 pressure: 1000 psig,
Reaction time: 18 hrs

Table 4. Effect of temperature on the conversion of naphthalene to tetralin

No	Temperature (°C)	Conversion (%)
1	200	100
2	180	55
3	150	29
4	100	0.5

Conditions:
Substrate: naphthalene, [substrate]/[catalyst]= 4: 1
Catalyst: LDA, Solvent: 50 mL hexane,
Initial H_2 pressure.- 1000 psig, Reaction time: 18 hrs

Table 5. Effect of reaction time on the conversion of naphthalene to tetralin

No	Reaction time (hrs)	Conversion (%)
1	0.5	34
2	2.0	63
3	4.0	94
4	18	100

Conditions:
Substrate: naphthalene, [LDA]/[substrate]= 0.25
Catalyst: LDA, Solvent: 50 mL hexane,
Initial H_2 pressure: 1000 psig, Temperature: 200°C

Table 6. Upgrading studies of coal liquids

Authors, Ref.	Catalysts used	Reaction Mode	Liquid products	Major reactions
Shmada, et al. (1990)	Ni/Mo on (-Zeolite	Single-stage and two-stage	Gasoline	Hydrocracking
Krichko, et al. (1990)	Ni/Mo On Alumina	Single-stage	Distillates (BP: 55-425EC)	Hydrogenation
Perrot, et al. (1988)	Cr/Mo on Active Alumina	Single-stage	Monocyclic (BTX)	Hydrocracking of bicyclic compounds
Martinez, et al. (1988)	Ni/Mo and Ni/Ti	Single-stage liquids	Upgraded	Hydrogenation heteroatom remove
Mochida, et al. (1986)	Ni/Mo on Alumina	Single-stage and two-stage	Diesel fuels	Hydrocracking HDN, HDO
Edwards, et al. (1986)	Ni/Mo	Single-stage (2nd of two)	Synthetic/ crude oil	Heteroatom remove hydrocracking and hydrogenation

Table 7. Relative costs of various metals used in catalytic upgrading of coal liquids

Iron	1	Molybdenum	65
Manganese	7	Nickel	100
Aluminum	14	Cobalt	185
Zinc	17	Tin	5,194
Copper	23	Palladium	37,000
Magnesium	30	Platinum	144,000
Tungsten	46	Rhodium	785,000

Table 8. Hydrotreating of coal liquid (VOH) catalyzed by LDA and PTA

Catalyst	[VSOH]/ [Catalyst] (g/g)	Temperature (EC)	Yield (%)	Conversion (%)		Elemental analysis		
				321nm	338 nm	C	H	H/C
	VSOH	200	95.0	0	0	89.01	10.32	1.38
LDA	10/1	300	82.4	22	17	88.71	10.51	1.41
	10/2	300	80.8	77	62	88.98	10.66	1.43
	10/4	300	78.0	97	82	89.13	10.70	1.43
PTA	10/1	200	90.6	48	33	89.06	10.48	1.40
	10/2	200	90.2	100	100	88.17	10.74	1.45
	10/4	200	92.6	100	100	86.27	11.05	1.53

Conditions:
Solvents: hexane for LDA and hexane-toluene mixture(2/3 v/v) for PTA
Reaction volume: 50 mL, Hydrogen pressure: 1000 psig at 25EC
Reaction time: 24 hrs
LDA: LiN(CHMe), PTA: KN[SiMe]

Table 9. Effect of temperature on the hydrotreating of coal liquid (VSOH) catalyzed by PTA

Temperature (EC)	Yield (%)	Conversion (%)		Elemental analysis		
		321 nm	338 nm	C	H	H/C
100	89.4	12	0.0	88.94	10.69	1.43
200	90.2	100	100	88.17	10.74	1.45
250	89.5	100	100	87.85	11.00	1.49
300	92.0	100	100	88.38	11.36	1.53

Conditions:
Solvents: hexane-toluene mixture (2/3 v/v)
Reaction volume: 50 mL, [VSOH]/[catalyst] (g/g) = 10/2
Hydrogen pressure: 1000 psig at 25EC
Reaction time: 24 hr

Table 10. Effect of hydrogen pressure on the hydrotreating of coal liquid (VSOH) catalyzed by PTA

H pressure (psig at) (EC)	Yield (%)	Conversion (%)		Elemental analysis		
		321 nm	338 nm	C	H	H/C
0				89.01	10.32	1.38
500	91.6	93	93	87.87	10.77	1.46
1000	88.5	100	100	87.85	11.00	1.49
1500	90.2	100	100	87.91	10.99	1.49

Conditions:
Solvents: hexane-toluene mixture (2/3 v/v)
Reaction volume: 50 mL, [VSOH]/[catalyst] (g/g) = 10/2
Temperature: 250EC, Reaction time: 24 hr

Figure 11. Hydrotreating of coal liquid (VSOH) catalyzed by bis(trimethylsilyl)amides with different cations

MN(SiMe)	Yield (%)	Conversion (%)		Elemental analysis		
		321 nm	338 nm	C	H	H/C
LiN(SiMe)	89.5	92	100	88.04	10.43	1.41
Na(SiMe)	91.2	97	99	88.47	10.44	1.41
K(SiMe)	90.2	100	100	87.91	10.99	1.49

Conditions:
Solvents: hexane-toluene mixture (2/3 v/v)
Reaction volume: 50 mL, [VSOH]/[catalyst] (g/g) = 10/2
Temperature: 250EC, H pressure: 1500 psig
Reaction time: 24 hr

Table 12. Effect of surfactant on hydrogenation of tetralin catalyzed by $[1,5\text{-HDRhCl}]_2$

Surfactant	[Surfactant]/[Rh] (mole/mole)	Yield of decalin, %		
		trans-	*cis*-	total
None		18	74	92
THS	0.5	12	76	88
	4.0	7	38	45
	8.0	4	26	30
CTAB	1.0	21	79	100
	4.0	13	61	74
	8.0	7	37	44
Aliquat 336	1.0	12	66	78
Tween 20	1.0	8	38	46
Sodium dodecylsulfate	1.0	17	83	100

Conditions:
Substrate: tetralin (3.3g, 25.0 mmole)
Catalyst: $[1,5\text{-HDRhCl}]_2$ (58 mg, 0.126 mmole)
[Substrate]/[Catalyst]: 200:1, Solvent: 30 mL hexane
Buffer (pH=7.4): 20 mL, [Aqueous phase]/[Organic phase](v/v): 0.60
Temperature: 25°C, H_2 pressure: 1 atm
THS: tetrabutylarnmonium hydrogen sulfate
CTAB: cetylmethylammonium bromide
Aliquat 336: tricaprylylmethylammonium chloride

Table 13. Influence of the buffer composition on the hydrogenation of tetralin catalyzed by [1,5-HDRhCl]$_2$

No	Buffer (pH, composition)	Yield (%)		
		trans-decalin	*cis*-decalin	total
1	Buffer (pH=7.4, Hydrion)	18	74	92
2	Buffer (pH=7.0, Hydrion)	9	71	80
3	Buffer (pH=8.0, Hydrion)	5	33	38
4	Buffer (pH=7.4, phosphate (0.1M))	6	29	34
5	Buffer (pH=7.4, Phosphate: 0.001M, NaCl: 0.138M KCl: 0.027M Tween 20: 0.05 %w/v)	4	36	41
6	Buffer (pH=7.4, Trizma saline: 0.05M NaCl: 0.56%)	3	25	28
7*	H_2O	6	38	44

Conditions:
Buffer (PH=7.4): 10 mL, [Aqueous phase]/[Organic phase](v/v): 0.60
The other conditions were the same as noted in Table 12.
* This experiment employed 20 mL of H_2O.

Table 14. Effect of the organic phase on the biphasic hydrogenation of tetralin catalyzed by $[1,5\text{-HDRhCL}]_2$

No	Solvent	Yield of decalin, %		
		trans-	*cis*-	total
1	Hexane	18	74	92
2	Methylene chloride	3	18	21
3	Chloroform	1	5	6
4	$CH_3O(CH_2)_2OCH_3$	3	15	18
5	2-propanol	1	4	5
6*	Octane	5	27	32
7*	Hexadecane	2	8	10

Conditions:
The conditions were the same as in Table 12.
*The [substrate]/[catalyst] = 400:1

Table 15. Comparison of the Rh compounds as the catalyst for the hydrogenation of aromatic compounds

Rh compounds	Products (%)	Total Yields (%)
$[1,5\text{-HDRhCl}]_2$	*trans*-decalin (21), *cis*-decalin (79)	100
$[1,5\text{-CORhCl}]_2$	*trans*-decalin (12), *cis*-decalin (67)*	79
$RhCl_3 \cdot H_2O$	*trans*-decalin (4), *cis*-decalin (20)	24
Rhodium acetylacetonate	No reaction	

Conditions:
Substrate: tetralin (33g, 25.0 mmole)
Rh compounds: 0.125 mmole
[Substrate]/[Catalyst]: 200:1; Solvent: 30 mL hexane
Buffer (pH=7.4): 20 mL, [Aqueous phase]/[Organic, phase](v/v): 0.60
Temperature: 25°C, H_2 pressure: 1 atm
[CTAB]/[Rh] = 1
*$[1,5\text{-CORhCl}]_2$: Chloro(1,5-cyclooctadiene)rhodium(I) dimer was used.

Table 16. The hydrogenation of aromatic compounds catalyzed by $[1,5\text{-HDRhCl}]_2$

No	Substrate	Product (%)	Total (%)
1	Tetralin	*trans*-decalin (21), *cis*-decalin (79)	100
2	Naphthalene	*trans*-decalin (13), *cis*-decalin (87)	100
3	o-xylene	1,2-dimethylcyclohexane (100)	100
5	*m*-dimethoxybenzene	*m*-dimethoxycyclohexane (98)	98
6	*n*-butylbenzene	*n*-butylcyclohexane (75)	75

Conditions:
The conditions were the same as in Table 12, except that the catalyst was stabilized by CTAB at [CTAB]/[Rh] = 2.0.

Table 17. The hydrogenation of tetralin in the presence of coal liquids

No	Coal liquid (mg)	Tetralin (mg)	Rh (mg)	Rh/ Coal liquid (w/w)	Conversion of tetralin to decalin (%)
1	67	4000	25	0.37	95
2	500	3500	25	0.05	83
3	1000	3000	25	0.025	78
4	2000	2000	25	0.0125	0

Conditions:
Catalyst: (1,5-HDRhCl$]_2$ (57 mg, 0.126 mmole)
Solvent: 50 mL hexane,
Substrate: coal liquid/tetralin mixture
Surfactant: CTAB (84 mg), Buffer (pH = 7.4): 10 mL
Hydrogen pressure: 1 atm., Temperature: 25°C,
Reaction time: 24 hrs