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Quarterly Status Report

Molecular Catalytic Coal Liquid Conversion

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Abstract

In this Quarter, the research was focused continually on the two general tasks: Task 1, molecular organometallic catalysts for hydrogenation and Task 2, organic base catalysts for arene hydrogenation and the hydrotreating of the coal liquids.

With regards to Task 1, the mechanism of the hydrogenation of aromatic compounds catalyzed by $[1,5\text{-HDRhCl}]_2$ /buffer system in the presence of small amount of surfactant under biphasic condition has been investigated.

For the Task 2, potassium bis(trimethylsilyl)amide was applied for the hydrogenation of polycondensed aromatic hydrocarbons such as pyrene and anthracene. These polycondensed aromatic hydrocarbons can be hydrogenated in high yields to the corresponding monoaromatic hydrocarbons. Anthracene was hydrogenated to octahydroanthracene, a monoaromatic compound, in near 100% yield under 1000 psig of H_2 and 250 °C. Pyrene was hydrogenated to tetrahydropyrene in more than 95% yield under 1500 psig of H_2 at 250 °C.

A communications that described the very exciting use of H_3O^- for the hydrogenation of representative coal compounds was submitted to Energy and Fuels

Introduction

Research work has focused continually on the two general tasks that were described in the original proposal. The first task concerns the development of molecular organometallic homogeneous catalysts that can be eventually used in the hydrogenation of coal liquids. The second task concerns non-metallic organic bases that can activate dihydrogen for arene hydrogenation, and that can be used in the hydrotreating of coal liquids.

Results and Discussion

Task 1 Molecular Organometallic Catalytic Reactions

In last quarter, we investigated the catalyst performance and the relationship between the catalyst's turnover number and the reaction time. It was found that the turnover numbers of the catalyst increase linearly with the reaction time in an eight day operating period in which the same catalyst was used for eight cycles. Other aromatic compounds such as toluene, n-butylbenzene, tetralin, o-xylene all can be hydrogenated into the corresponding substituted cyclohexane derivatives in more than 94% yield when catalyzed by $[1,5\text{-HDRhCl}]_2$ in the presence of small amounts of surfactant molecules. The optimum catalyst system has been applied for the hydrogenation of tetralin in the presence of a coal liquid derived from the coal liquefaction. It was found that 80-85% of tetralin in the mixture was hydrogenated to decalin under the conditions of these experiments.

In this quarter, 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 the biphasic conditions has been investigated. The hydrogenation reaction was monitored by ^1H NMR. Because the sensitivity of ^1H NMR is better

than that of ^2H NMR, the reaction was carried out using deuterated substrate (toluene- d_8) and deuterated solvent (cyclohexane- d_{12}).

Experiments:

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 buffer (pH=7.4) containing 28 mg of CTAB was added to the system to start the hydrogenation. At the interval time planned, 2 ml of solution was withdrawn from the system, and the organic phase are separated and transferred into the NMR tube to perform the ^1H NMR spectrum.

The ^1H NMR spectra, which were taken at 10 min, 30 min., 1 hour, 2.5 hour, 4.5 hours and 24 hours were shown as in Figures 1, 2, 3, 4, 5, and 6, respectively.

Results:

1) Fig. 1 shows the ^1H NMR of the solution of toluene- d_8 and $[1,5\text{-HDRhCl}]_2$ in cyclohexane- d_{12} . No complex between toluene and the rhodium compound was detected in the ^1H NMR. 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 main reaction path. This result indicates that $[1,5\text{-HDRhCl}]_2$ does not form a complex with aromatic compounds at the stage of the reaction.

2) a) Multi peaks appeared at 2.21-2.25 ppm when the reaction started, which increased in intensity as the reaction proceeded (Fig. 2 at 30 min, Fig. 3 at 1h, Fig. 4 at 2.5 h) and then decreased (Fig. 5 at 4.5 h) and disappeared completely (Fig. 6 at 24 h) at the end of the reaction. These peaks were assigned

to the protons of methylene groups (-CH₂-) in the mixture of 1,3-cyclohexadienes (-CH₂-C=C-C=C-). The fact that no signals in the region of 2.80 - 2.90 ppm corresponding to 1,4-cyclohexadiene (-C=C-CH₂-C=C-) were observed implies that the aromatic ring was first reduced to 1,3-cyclohexadiene derivatives. b) The peaks in the region of 0.83-0.92 ppm were assigned to the methyl (CH₃-) group in the methylcyclohexane and methylcyclohexenes. Because the substrate is deuterated toluene (CD₃C₆D₅), It is clear that D-H exchange in the methyl group has taken place extensively in the process of the reaction. The multi peaks in this regions were attributed to an isomeric mixture of the intermediates, i.e. methylcyclohexane and methylcyclohexenes.

The reaction pathway:

For the homogeneous hydrogenation of benzene by RhCl₃-aliquat 336, the arene complex (or an analogous dihydride) is apparently formed during the induction period, which was shown to vary in length in accord with the substrate employed. 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 [1]. The low-field 300 MHz FT-NMR spectrum consisted of three triple triplets at -22.35 (J=7.6 Hz), -23.122 (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 (-CH₂-C=C-C=C-) and their changes with the reaction process, it was clear that cyclohexadiene derivatives were formed, which are assumed to be the intermediates. The peaks in the region of 0.83-0.92 ppm, assigned to the methyl (CH₃-) 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. Because no signals for cyclohexene derivatives in the region of 1.80-1.95 ppm for the protons of (-CH₂-C=C-) or of 5.40-5.60 ppm for the protons of (-CH=CH-) were detected during the hydrogenation of toluene, the intermediate of η^2 complexes is

suspected. However, the hydride transfer ($\eta^2 \rightarrow \eta^1$ conversion) and the reductive elimination of the product are well known features for alkene hydrogenation. Therefore, it was assumed 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 $-\text{CH}=\text{CH}-$ 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.

A reaction pathway that is consistent with these findings is shown as Fig. 7.

Task 2 Organic base-catalyzed arene hydrogenation and the coal liquid hydrogenation

Recent work has focused on the hydrogenation of coal liquids. Substitution of dideuterium for dihydrogen in the hydrotreating of coal liquid at 250 °C and 1000 psig of dideuterium yielded a product that was characterized by ^2H NMR. Two groups of deuterons located in the region of 6.5 - 8.0 ppm and 1.0 - 3.5 ppm, respectively, were observed. The former group was assigned to the deuterons on carbon atoms of aromatic rings and the latter to the deuterons linked to the aliphatic carbon atoms. In addition, naphthalene was hydrogenated completely to tetralin in the presence of the coal liquid under the same conditions, implying that the reduction of multiring aromatic compounds was not adversely influenced by the existence of the coal liquid which contains potential catalyst poisons such as sulfur, nitrogen and oxygen.

More recently, potassium bis(trimethylsilyl) amide was applied for the hydrogenation of polycondensed aromatic hydrocarbons such as pyrene and anthracene. It was found that these polycondensed aromatic hydrocarbons can be hydrogenated in high yields to the corresponding monoaromatic hydrocarbons. Anthracene ($\text{C}_{14}\text{H}_{10}$) can be hydrogenated to octahydroanthracene ($\text{C}_{14}\text{H}_{18}$), a

benzene derivative, in near 100% yield under 1000 psig of H₂ and 250 °C. Pyrene (C₁₆H₁₀), can be hydrogenated to tetrahydropyrene (C₁₆H₁₄) in more than 95% yield under 1500 psig of H₂ at 250 °C. However, it can not be reduced under the same conditions in the absence of potassium bis(trimethylsilyl)amide. Other polycondensed aromatics have also been investigated. The results will be described in the future.

A communication on this exciting topic was written and submitted to Energy and Fuels.

Plan for Next Quarter

The work will continue to focus on the two tasks. More work will be needed in the rhodium catalyst system to improve the catalyst performance and to test the application of this catalyst system for the hydrotreating of coal liquids. The investigation of hydrotreating of coal liquids catalyzed by organic bases will proceed in parallel. Work will begin on the preparation of the final report and the preparation of manuscripts for publication in Energy and Fuels and other journals.

References:

1. Alum, J., Amber, I., *J. Org. Chem.*, **1987**, 52, 2804; Amer, I.; Amer, H.; Ascher, R.; Blum, J.; Sasson, Y.; Vollhardt, K. P. C. *J. Mol. Catal.*, **1987**, 39, 185

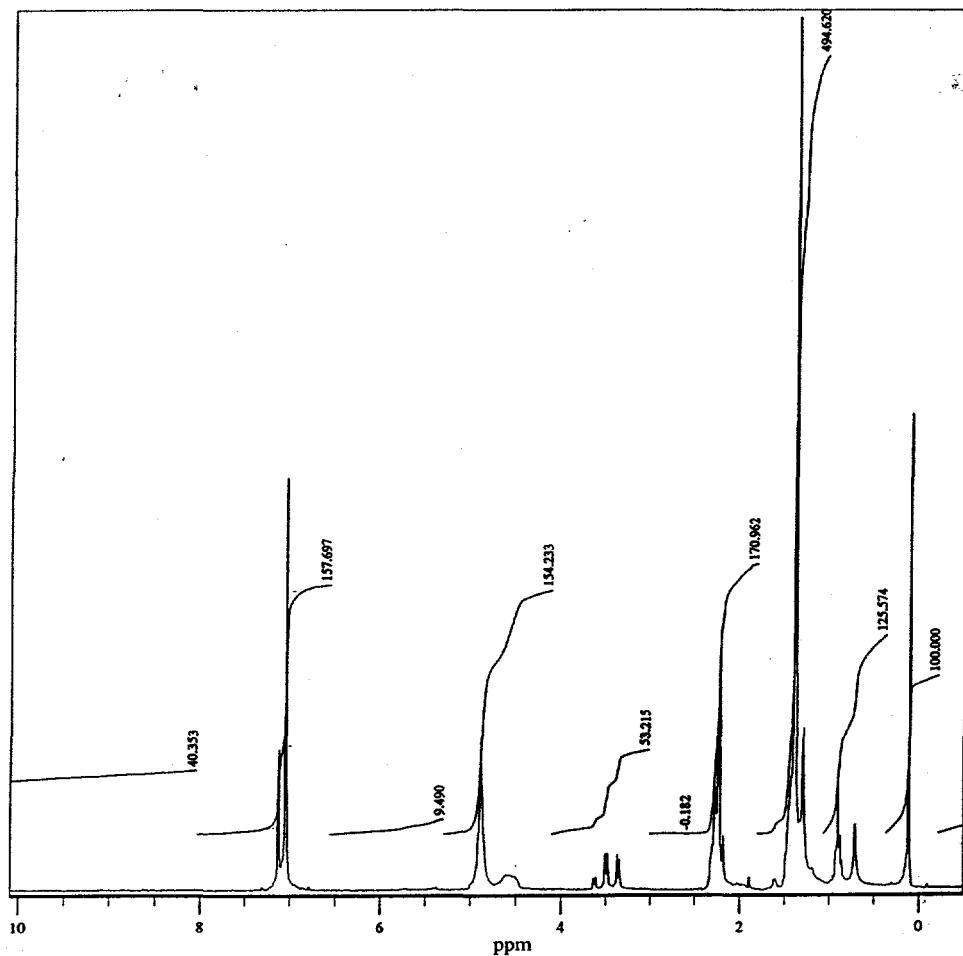


Fig. 1 ¹H NMR spectrum of the organic phase after the reaction proceeds 10 minutes

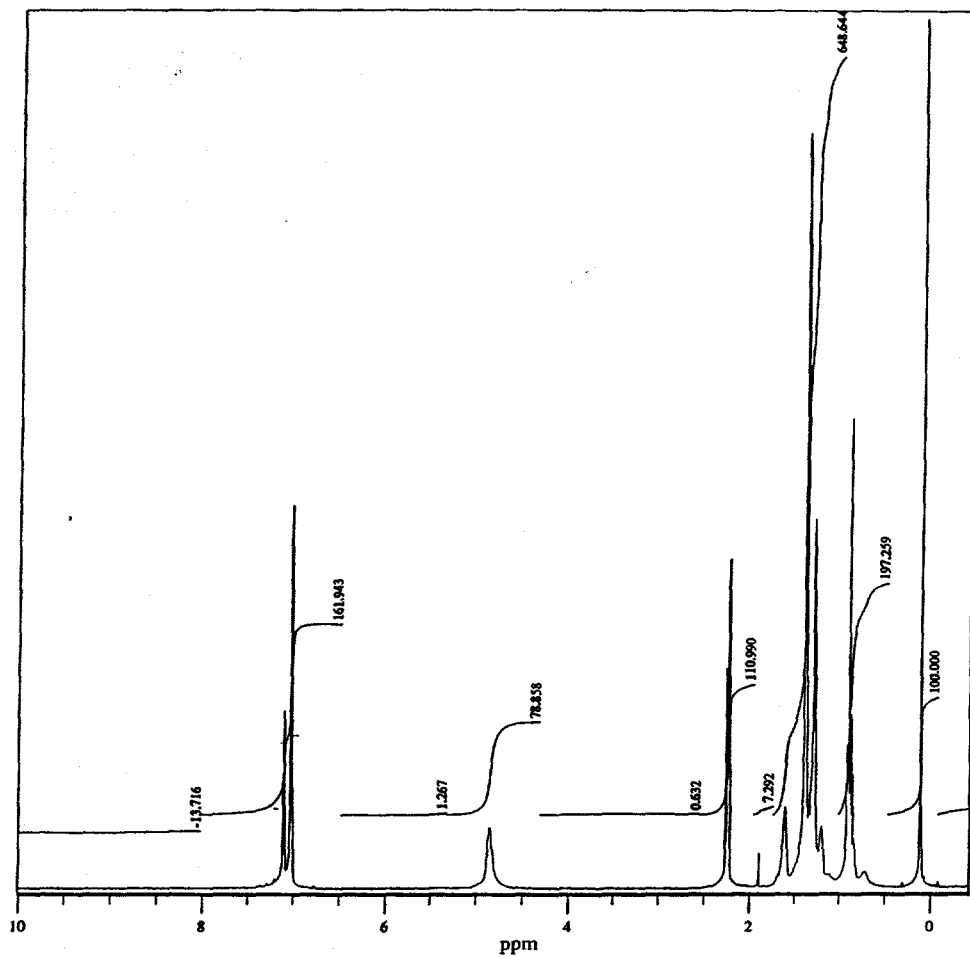


Fig. 2 ^1H NMR spectrum of the organic phase after the reaction proceeds 30 minutes

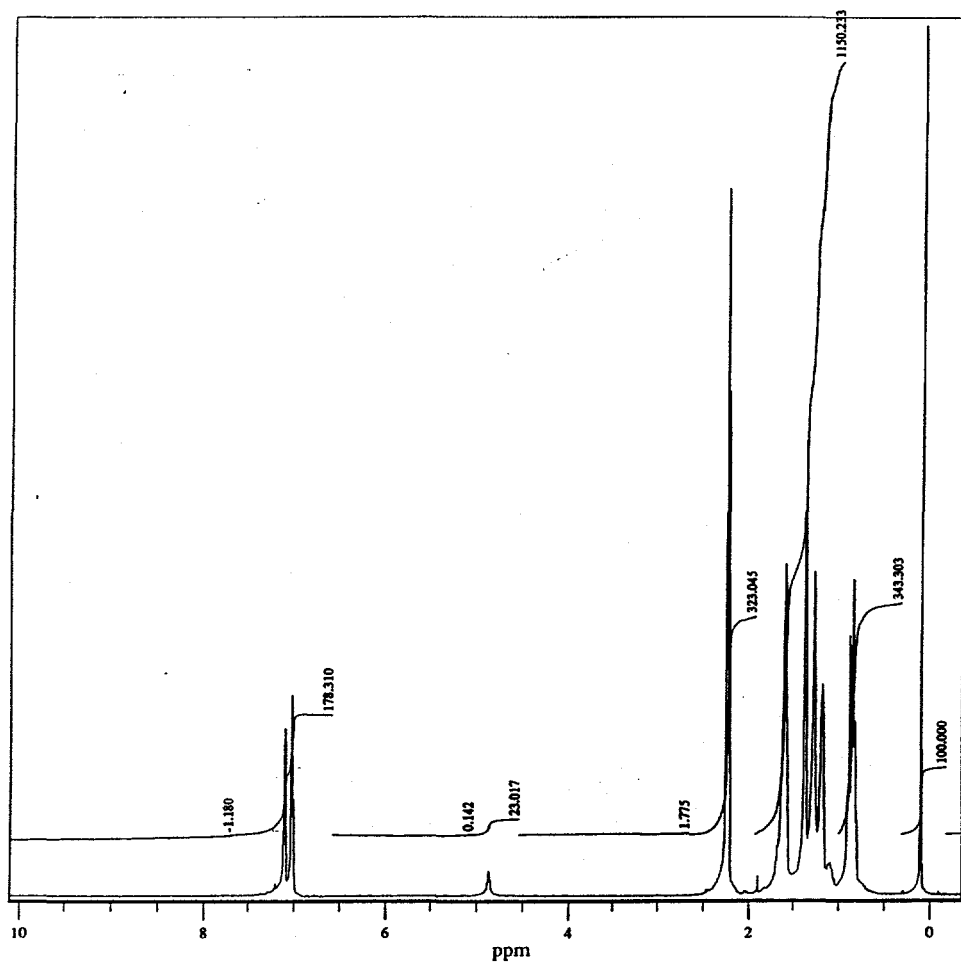


Fig. 3 ^1H NMR spectrum of the organic phase after the reaction proceeds 1 hour

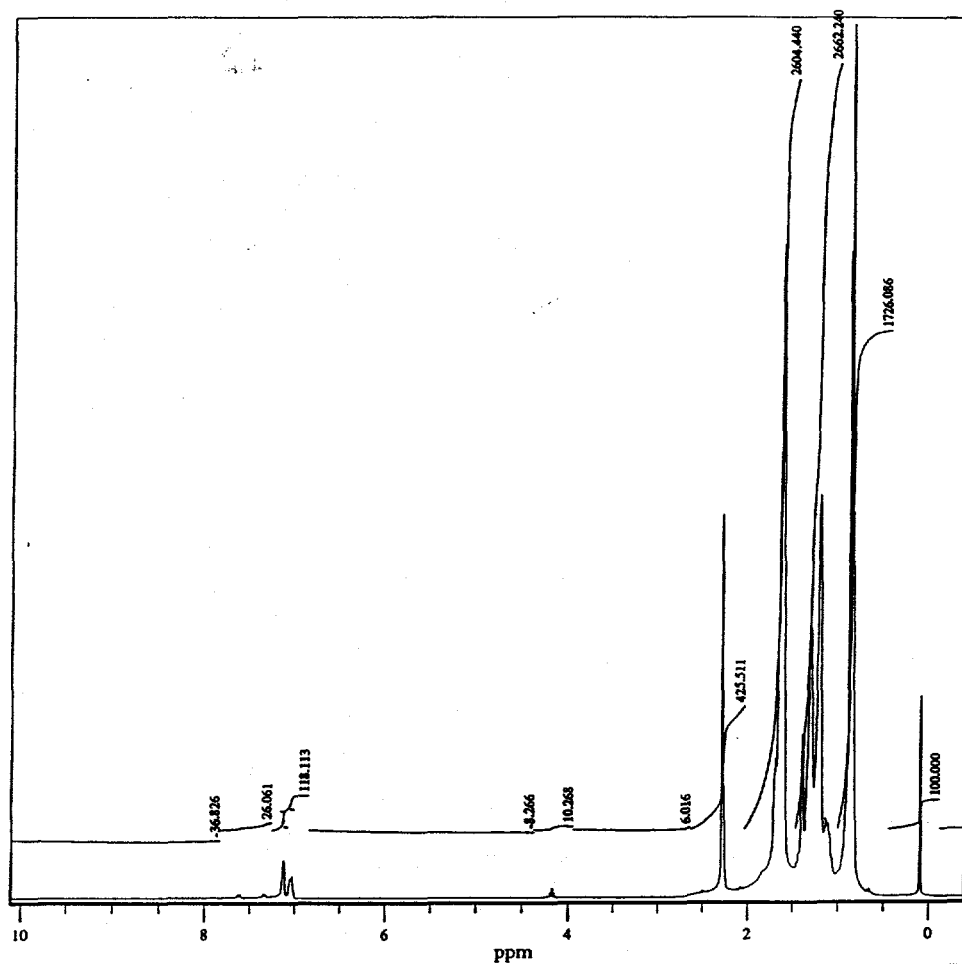


Fig. 5 ^1H NMR spectrum of the organic phase after the reaction proceeds 4.5 hours

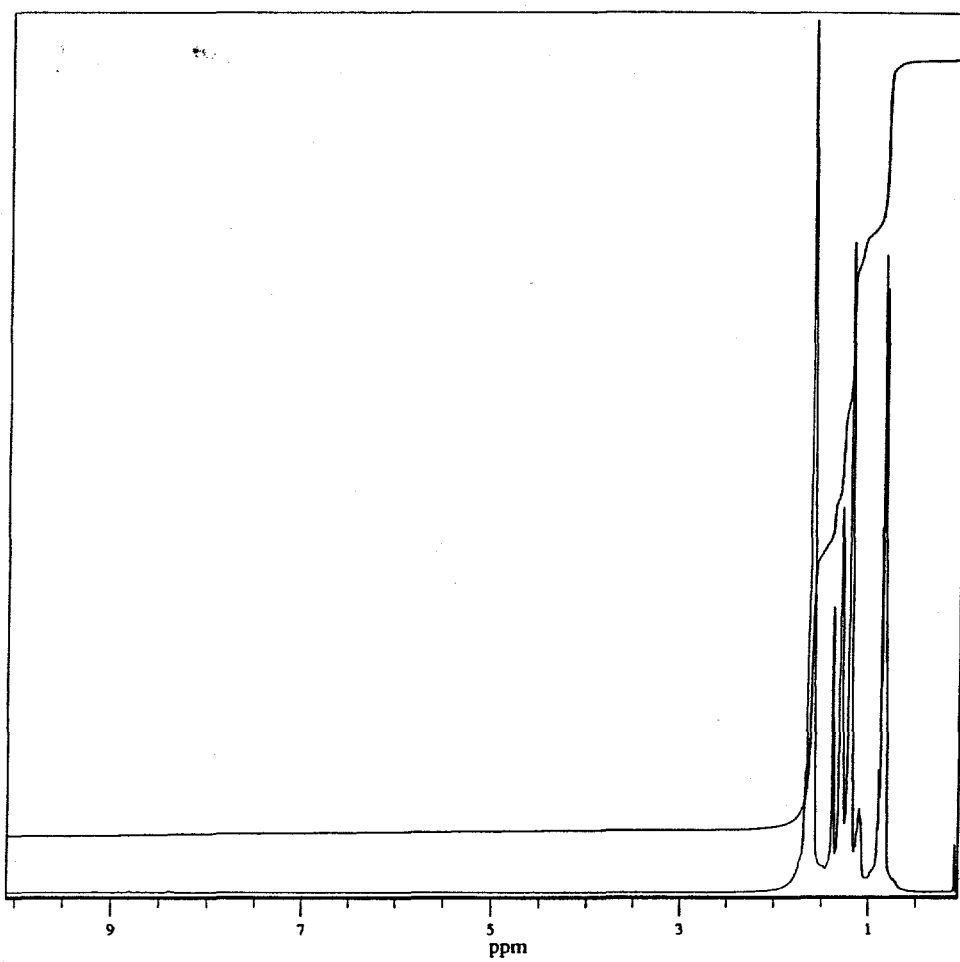


Fig. 6 ^1H NMR spectrum of the organic phase after the reaction proceeds 24 hours

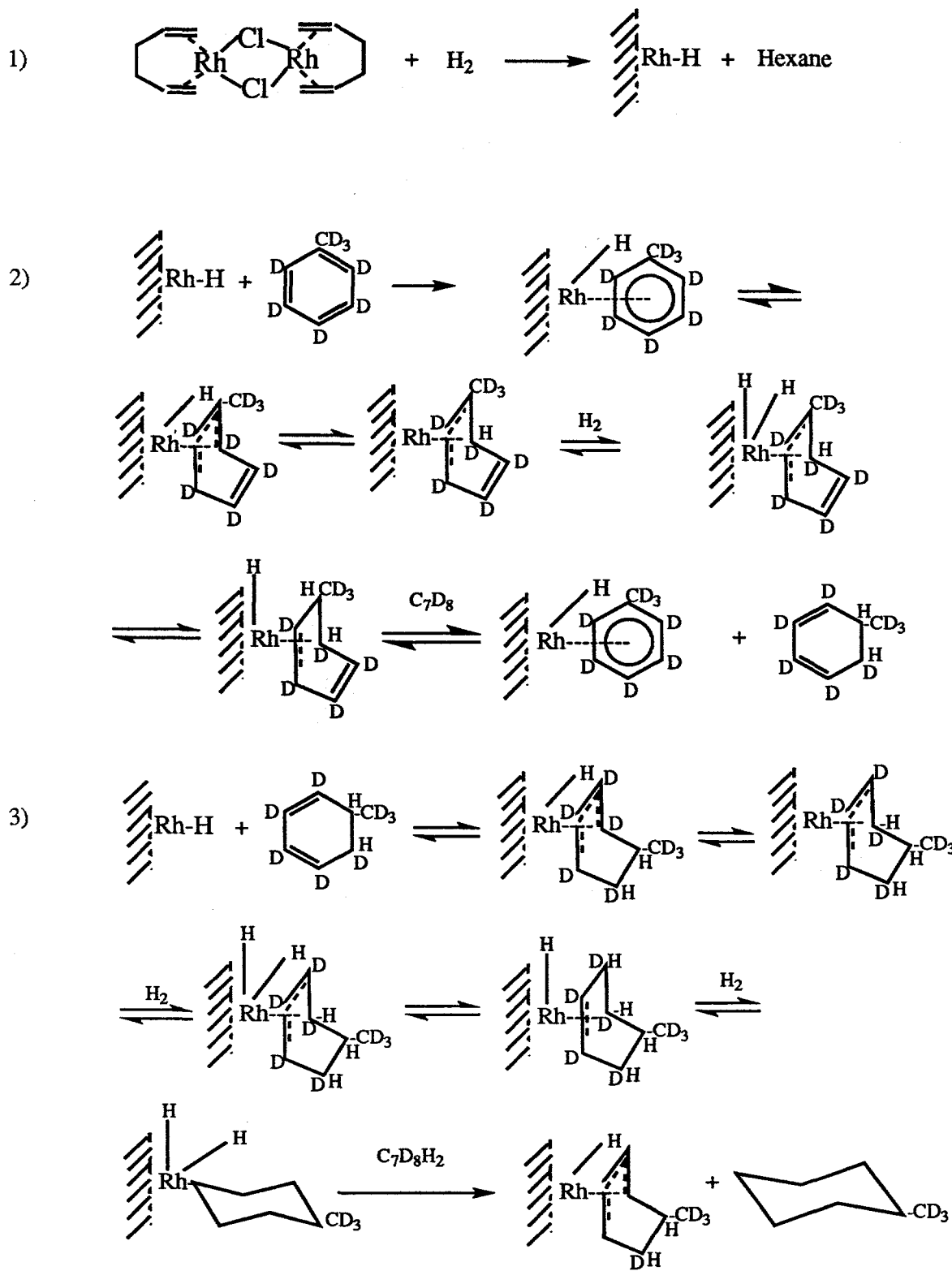


Fig. 7 The proposed mechanism for the toluene hydrogenation