

HYDROCRACKING OF HEAVY OILS: DEVELOPMENT OF STRUCTURE/REACTIVITY CORRELATIONS FOR KINETICS

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ABSTRACT

The catalytic hydrocracking reaction pathways, kinetics and mechanisms of 1-methyl naphthalene and phenanthrene were investigated in experiments at 350 °C and 68.1 atm H₂ partial pressure (190.6 atm total pressure), using a presulfided Ni/W on USY zeolite catalyst. 1-methyl naphthalene hydrocracking led to 2-methyl naphthalene, methyl tetralins, methyl decalins, pentyl benzene and tetralin. Phenanthrene hydrocracking led to dihydro, tetrahydro and octahydro phenanthrene, butyl naphthalene, tetralin to butyl tetralin and dibutyl benzene. The rate constants for the dealkylation of butyl tetralins produced in the phenanthrene hydrocracking network conform to a linear free energy relationship (LFER), with the heat of formation of the leaving alkyl carbenium ion as the reactivity index.

INTRODUCTION

Catalytic hydrocracking is a versatile process for increasing the hydrogen to carbon ratio and decreasing the molecular weight of heavy oils. This versatility may prove extremely valuable in the search for optimal processing conditions and catalysts for production of "reformulated" gasolines. Associated reaction models will likely increase in detail as increasingly molecular output is desired. However, the complexity of hydrocracking feedstock structure and reactivity has kept traditional models somewhat global and, thus, often feedstock dependent. Therefore, the new, feedstock-sensitive, "molecular" models of hydrocracking reaction chemistry require the development of a critical mass of consistent molecular reaction pathways and kinetics as an essential data base. To this end, we report here on hydrocracking reaction pathways of 1-methyl naphthalene and phenanthrene, components among a broader set aimed at sampling the structural attributes of hydrocracking feedstocks. Special attention is devoted to the efficient organization of the resolved kinetic information into quantitative structure/reactivity correlations that will serve as a component of a broader kinetic data base.

The present work builds on the significant current understanding of the hydrocracking of paraffins (Froment, 1987) and extends to examine aromatic hydrocarbons. The aromatics' hydrocracking literature is less comprehensive. Several investigations on hydrocracking model bare ring polynuclear aromatic hydrocarbons involved Al_2O_3 or $\text{Si}/\text{Al}_2\text{O}_3$ catalysts (Qader, 1973; Shabtai et al., 1978; Lemberston and Guisnet, 1984). The effect of zeolite catalysts is examined in more recent publications (Haynes et al., 1983; Lapinas et al., 1987).

We report here on the reactions of 1-methyl naphthalene and phenanthrene. The experiments were focused on the target of discerning reaction families and characterizing them in terms of Quantitative Structure/Reactivity Correlations. We describe the work by first considering the experimental methods. The kinetics of 1-methyl naphthalene and phenanthrene hydrocracking are considered next. Finally, discernible linear free energy relationships are examined.

EXPERIMENTAL

Cyclohexane (HPLC grade, 99.99%, Aldrich) served as the solvent for the study of the reactions of the remaining compounds. Phenanthrene (98%+, Aldrich), served as the prototype three-ring aromatic moiety. Its staggered structure, makes it thermodynamically more stable than anthracene, and thus more abundant in heavy oils. 1-methyl naphthalene (98%, Aldrich) could in principle be obtained from the phenanthrene network, but its high rank in the network made parameters estimated statistically insignificant. All reactants were used as received.

The catalyst was a Mobil conditioned Zeolyst 753 Ni/W on USY zeolite, received in standard 3.0 mm pellets. Prior to all experiments, it was sulfided for two hours at 400°C by a 10% H_2S in H_2 gas stream (99%, Matheson Gas Products) at a flow rate of 30 cm^3/min . The catalyst was equilibrated by reaction with phenanthrene at 350°C and 68.1 atm H_2 for ≈ 10 hours to achieve a steady-state activity that lasted about 50 more hours on stream.

A one-liter spinning basket batch autoclave (modified from original as received from Autoclave Engineers) was the core of the reaction system. A detailed description of the system is available elsewhere (Landau, 1991). The catalyst basket was mounted on the autoclave's agitator which was equipped with baffles to ensure turbulence. Varying the stirring speed revealed the absence of diffusion limitations for a stirring rate of 10 s^{-1} or greater. Also, phenanthrene hydrocracking with powdered catalyst (50-200 mesh) in a slurry exhibited the same kinetic behavior as with the 3.175mm pellets, which suggested that internal transport limitations were not important.

Experiments were routinely performed at 350°C and 68.1 atm H_2 (190.6 atm total pressure, the balance from cyclohexane vapor pressure), with 10g of catalyst in the spinning basket arrangement. The stirring rate was 15 s^{-1} , increased by 50% for 10 min. immediately following the injection. Total pressure was regulated with continuous hydrogen makeup. Sampling was scheduled to remove no more than 5% of the total liquid volume.

Products were identified using a Hewlett Packard 5970 Mass Selective Detector and a Hewlett Packard 5880A Gas Chromatograph, employing a fused silica capillary column and flame ionization detector. Dibenzyl ether (Aldrich, > 99.9%) was used as an external standard. Finally, the

RESULTS

Hydrocracking of 1-methyl naphthalene

Reaction of 25% wt 1-methyl naphthalene took place in cyclohexane as a solvent at 68.1 bar H₂ at 350 °C, and led to 6 identified isomeric lumps, representing 99%+ material balance closure. Kinetics are summarized in Fig. 1. There are two primary products of 1-methyl naphthalene hydrocracking, both with high selectivity : methyl tetralins (lump including 1, 2, 5, and 6-methyl tetralins) and 2-methyl naphthalene (isomerization product). The balance consists of methyl decalins, pentyl benzenes and tetralins.

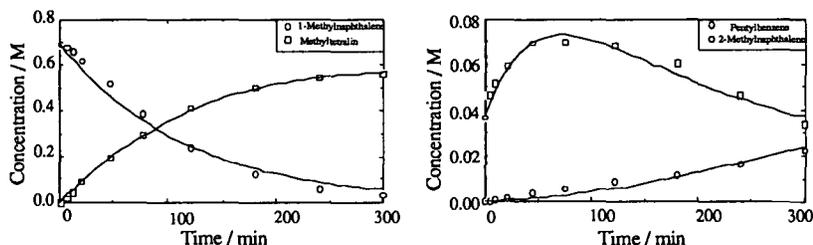


Fig. 1 : Temporal yields of some 1-methyl naphthalene hydrocracking products. Solid lines represent parameter estimation results

Delplot analysis classifies pentyl benzenes as secondary products (direct cracking of methyl tetralins), as well as methyl decalins. Tetralin appeared to be weakly primary product, which implies that their formation is the result of disproportionation reactions of methyl tetralins with the solvent, since no bare-ring naphthalene has been observed.

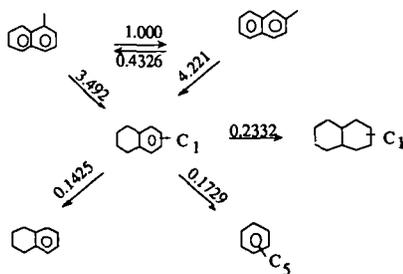


Fig. 2: Proposed network for 1-methyl naphthalene hydrocracking (normalized with $1.49 \cdot 10^{-3} \text{ l/gcat/min.}$)

Parameter estimation for the above network provided more insight into the pathways. Isomerization of 1-methyl naphthalene occurred at a slower rate than its hydrogenation, while 2-

methyl naphthalene hydrogenated at a slightly higher rate than 1-methyl naphthalene. Further reactions of methyl tetralins (hydrogenation to decalins, cracking to pentyl benzenes) occurred with rate parameters one order of magnitude lower.

Hydrocracking of Phenanthrene

Reaction of 3.4 wt% phenanthrene in cyclohexane solvent and at 68.1 atm H₂ at 350 °C led to 11 identified isomeric product lumps, representing 95%+ material balance closure. Each lump represents grouping of molecular weight isomers. For example the tetrahydro phenanthrenes lump includes molecules with cyclohexyl and methyl cyclopentyl saturated rings. *Sym*- and *asym*- octahydro phenanthrenes are in the same lump, and "butyl tetralin" refers to any tetralinic unit sheet with a side chain of four carbon atoms, regardless of its position on the unit sheet.

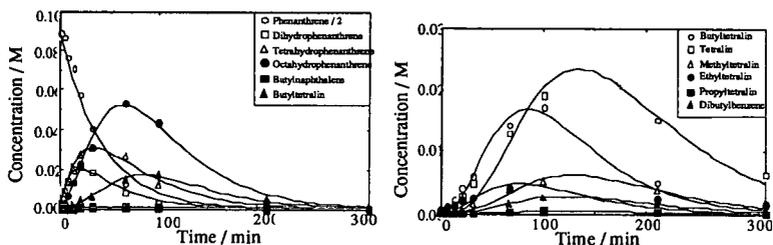


Fig. 3: Temporal yields of some phenanthrene hydrocracking products. Solid lines represent model correlations.

Reaction kinetics are summarized in Fig. 3, which shows, by the initial positive slopes, that dihydrophenanthrene (DHP) and tetrahydro phenanthrenes (THP) were the primary products, DHP forming with higher initial selectivity. Octahydro phenanthrenes (OHP) had very low initial selectivity and were interpreted as secondary products, evolving from THP. Butyl tetralins, tetralins and dibutyl benzenes were higher rank products, evolving mainly from OHP. Butyl naphthalenes, propyl- and methyl tetralins were all clearly of tertiary or higher rank.

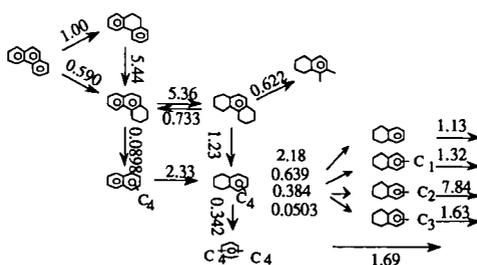


Fig. 4: Proposed network for phenanthrene hydrocracking (normalized with $1.49 \cdot 10^{-3} \text{ l/gca/min.}$)

DHP did not appear to dehydrogenate back to phenanthrene, as reported over non-acidic catalyst supports (Girgis and Gates, 1991), but rather hydrogenated further to THP. This difference was probably due to the higher H₂ partial pressure employed in this work. THP in turn underwent further hydrogenation to OHP; this was more selective than ring opening to n-butyl naphthalene. The terminal naphthenic ring in OHP was cracked to butyl tetralin, and cleavage of the butyl side chain occurred at various positions.

The optimized kinetic parameter fitting on all the network components of Fig. 4 is presented in Fig. 3, as modeled species' concentration vs. time. Clearly the fit is good. The chemical significance of the rate constants regressed is thus the remaining issue. This is considered more fully below.

LFER DEVELOPMENT

The organization and chemical significance of these kinetics data can be enhanced by the existence of linear free energy relationships (LFER). A LFER will exist for a reaction family with similar transition state sterics (essentially constant A-factor) and reactivities that differ because of differences in activation energies. This will assume the form of a linear correlation between the reactivity of a molecule, as it is expressed through its rate parameter, and its structure, as expressed by a reactivity index pertinent to each reaction. The existence of a LFER not only helps to establish the reaction mechanism, but can also concisely summarize an enormous amount of information in a handful of slopes and intercepts. The data bases constructed in this way will be general and flexible enough to draw useful correlations for process modeling.

The applicability of LFERs in heterogeneous catalysis has been hindered in part because of the uncertainty of controlling elementary steps (Dunn, 1968). Observable kinetics are generally the expression of many elementary steps acting in concert. However, Mochida and Yoneda (1967) uncovered a linear relationship between the logarithm of the observed rate constant for dealkylation of a particular alkyl benzene and the enthalpy change for hydride abstraction from the related paraffin, $\Delta H_C^+(R)$ (Olah et al., 1964). The mechanistic information in this correlation is the suggestion of a rate limiting step for the dealkylation reactions that correlates with the formation of the alkyl carbenium ion. It is also possible that several steps correlate in concert with the same reaction family index. In any case, the modeling value of this correlation is that it allows for the *a priori* prediction of other dealkylation reactions. We follow this perspective in the search for useful correlations to summarize hydrocracking kinetics data.

The butyl tetralin dealkylation reactions observed during hydrocracking of phenanthrene seemed a reasonable point to search for a relationship like that found by Mochida and Yoneda (1967). Careful scrutiny of the kinetic parameters regressed reveals a trend for the dealkylation of butyl tetralins. The dealkylation rate constants increase as the stability of the leaving alkyl carbenium ion increases. This is consistent with the energetics of the formation of the alkyl carbenium ions. This suggests that the formation of the alkyl carbenium ion could contribute to the controlling energetics of the process.

This information was tested more quantitatively using a linear free energy relationship for the butyl tetralin dealkylation reactions with the stability of the dealkylating carbenium ion as the reactivity index. Two options for the value of the reactivity index were available, reflecting the nature of the alkyl carbenium ion: the energetics of either the primary (n-alkyl) or the most stable alkyl carbenium ion could be used. The experimental data were not sufficiently precise to adjudicate.

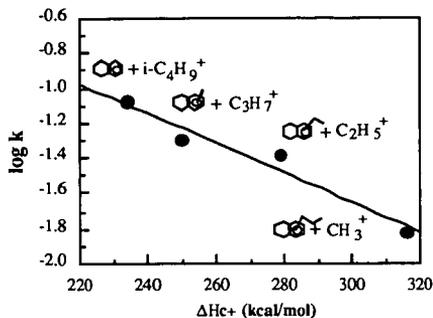


Fig. 5: LFER for the butyl tetralin dealkylation reactions. (k in min.^{-1})

CONCLUSIONS

1-methyl naphthalene hydrocracking resulted in isomerization to 2-methyl naphthalene, as well as hydrogenation to methyl tetralins. Hydrogenation of the single ring in methyl tetralin was one order of magnitude slower than hydrogenation of methyl naphthalenes, and comparable to the naphthenic ring opening reactions. Phenanthrene hydrocracking proceeded mainly through sequential hydrogenation to dihydro, tetrahydro and octahydro phenanthrene, followed by opening of the terminal naphthenic rings and dealkylation of the butyl side chains.

Reasonable structure/reactivity correlations were obtained for the rate parameters of the dealkylation of butyl tetralins produced from phenanthrene hydrocracking. The heat of formation of the leaving alkyl carbenium ion ($\text{CH}_3^+ - \text{C}_5\text{H}_{11}^+$) as used from Mochida and Yoneda (1967) was established as a suitable reactivity index.

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