Effect of Temperature on Quantitative Structure/Reactivity Relationships for Hydrocracking Polynuclear Aromatics

by

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Introduction

The increased interest in the molecular modeling of hydrocarbon conversion processes is motivated by the need to predict both the performance and environmental properties of the products. A molecular description of the hydrocarbon mixture is the logical starting point for these predictions, which has motivated considerable interest in the development of molecular reaction models.

The construction of such models is complicated by the enormous need for rate, adsorption and equilibrium parameters. This staggering need can be reduced considerably when the homologous patterns of both compound types and their reactions in these mixtures can be recognized. This has motivated the development of a lumping approach that organizes the kinetics information in potentially thousands of rate, adsorption and equilibrium constants into the parameters of a handful (O(10)) of Quantitative Structure/Reactivity Relationships (QSRR) using the formalism of Linear Free Energy Relationships.

The application of these ideas to hydrocracking is quite recent. For example, Landau (1991) verified the applicability of the QSRRs to dealkylations of butyl tetralins. Neurock (1992) showed that the standard enthalpy of reaction of the controlling elementary step could be used to correlate the kinetics of both dealkylations and isomerizations. Korre (1995) developed QSRRs for hydrogenation of polynuclear aromatics using the same principles. All of the foregoing work was limited to a set of "isothermal correlations", i.e., one correlation was developed for each temperature. Clearly, a more universal, temperature-independent correlation would be desirable.

The present work aimed to exploit this concept and explore 1) the applicability of QSRRs to the acid center transformations during hydrocracking, and 2) the dependence of QSRRs on temperature for both metal- and acid- catalyzed reactions. The tangible result of such correlations would be the organization of energetic and entropic quantities for both overall reaction and activation for a wide range of hydrocracking reactions.

Experimental Results

A batch autoclave equipped with reactant injection and sample procurement systems was used. Naphthalene and phenanthrene hydrocracking were studied over the temperature range of 300-370°C. The reactant mixture consisted of 30 g of a 50% wt mixture of naphthalene and phenanthrene, dissolved in 15 g of cyclohexane. The reactant mixture was introduced in 400 g of cyclohexane as a solvent at the arbitrary t=0 time with hydrogen back pressure. The solvent was in a supercritical phase at all conditions, and the hydrogen pressure was varied from 62 atm (300°C) to 70 atm (370°C) in order to ensure constant hydrogen concentration of 1.33 gmol/l during all experiments.

The evolution of phenanthrene and naphthalene conversion with time is presented in Fig. 1. Conversion rates for both reactants were accelerated with increasing temperature. The effect of temperature was more pronounced at temperatures lower than 350°C. At the temperatures of 350°C, 365°C and 370°C, the influence of thermodynamic equilibrium on the hydrogenation rates began to appear.

Naphthalene and phenanthrene hydrocracking product yields vs. reactant conversion are presented in Fig. 2. Fig. 2f indicates that virtually all naphthalene was converted to tetralin at all temperatures, up to naphthalene conversion of approximately 0.6. At higher naphthalene conversions, the maximum in tetralin yield decreased with increasing temperature. This implies that tetralin consumption rates had a stronger temperature dependence than its formation rate from naphthalene hydrogenation. For irreversible reactions, a stronger temperature dependence is associated with a higher activation energy.

The effect of temperature on the yields of di- and tetra- hydrophenanthrene with respect to phenanthrene conversion is presented in Fig. 2a and Fig. 2b, respectively. The maximum yields for di- and tetra- hydrophenanthrene did not significantly diverge from 0.08 and 0.14 respectively, for all reaction temperatures. This indicates that their production and consumption reactions had similar temperature dependence.

These experiments led to the reaction network of Fig. 3. This allowed parameter estimation to the dual-site LHHW (Langmuir-Hinshelwood-Hougen-Watson) rate expression of Eq. 1.

$$-\frac{dC_i}{dt} = \frac{\sum_j k_{ij}(C_i - C_j / K_{ij})}{D_H} + \frac{\sum_l k_{il}(C_i - C_l / K_{il})}{D_A} \qquad (1)$$

In Eq. (1), C_i, C_j, C_l were component concentrations (mol l^{-1}), k_{ij}, k_{il} were combined numerator rate parameters (l kg_{cat}^{-1} s^{-1}), and K_{ij}, K_{il} were the equilibrium ratios (mol $_i$/mol $_j$/P_{H2}^n). D_H, D_A were the adsorption groups for the metal (hydrogenation, $_H$) and zeolite (acid, $_A$) sites respectively, defined in Eq. (2).

$$D_H = 1 + \sum_i K_i^H C_i, \quad D_A = 1 + \sum_i K_i^A C_i \qquad (2)$$

In Eq. (2), K_i^H, K_i^A (l mol^{-1}) represented individual component adsorption constants on the metal and acid sites, respectively.

A total of 21 numerator rate parameters (k_{ij}) and 17 equilibrium parameters (K_{ij}) were regressed for each of the eight reaction temperatures, corresponding to the naphthalene and phenanthrene hydrocracking networks of Fig. 3. Thus a total of 304 numerator rate parameters and equilibrium ratios were required to represent the kinetics of naphthalene and phenanthrene hydrocracking in the temperature interval 300–370°C. In this first-pass parameter estimate, the 34 adsorption constants for the metal and acid sites were not included; their addition for each temperature would have brought the total parameter number to 576. The overall agreement between experimental and calculated concentration profiles was very good. The sum-of-squares error on concentrations was less than 5.10^{-3} at all temperatures.

Reactivity Indices

The foregoing parameter estimation information shows that even the relatively simple hydrocracking networks of naphthalene and phenanthrene required 21 rate, 17 equilibrium and 34 adsorption constants at each temperature. Extrapolation to the demands of a heavy oil suggests that a lumping strategy aimed at representing this information in terms of fewer parameters would be very useful. To this end, it seemed cogent to attempt to organize the hydrocracking reactions into reaction families, which could in turn be characterized by quantitative structure/reactivity relationships.

The present development of QSRRs for each reaction family essentially is a model of the variation of the activation energies (E^*, kcal/gmol) and pre-exponential factors (A, $l/kg_{cat}/s$) within a reaction family. The concept of a reaction family exploits either a constant pre-exponential factor, or one that compensates with changes in E^*. The latter approach, adding flexibility, was used to relate changes in pre-exponential factors within a family to changes in activation energies. The activation energies for the acid center reactions were correlated with the enthalpy of formation of the carbocation intermediate (ΔH_c^+, kcal/gmol). The activation energies for the metal center transformations were correlated with the enthalpy of reaction (ΔH_R^0, kcal/gmol). Similarly, equilibrium constants for all reactions were correlated with ΔH_R^0, using the compensation notion to constrain the overall reaction and adsorption entropies. The adsorption constants for both metal and acid sites were correlated with the number of aromatic rings (N_{AR}) and the number of saturated carbons (N_{SC}). All thermochemical quantities were calculated with semi-empirical molecular orbital calculations (MOPAC/AM1).

Parameter Estimation Results

The parameter estimation was performed to the concentration vs. time experimental data from naphthalene/phenanthrene hydrocracking in the temperature interval 300-370°C. This represented approximately 1600 experimental concentration measurements. The quantitative structure/reactivity relationships were imposed for the relevant reaction family to summarize a total of 304 numerator rate and equilibrium constants and 272 adsorption constants on metal and acid sites. The final quantitative structure/reactivity relationships summarize the results. These are given in the following Eq. (3) – Eq. (12):

Hydrogenations:

Adsorption: $\ln K_{ads} = 1.324+(0.887N_{AR}+0.123N_{SC})/RT$ (3)

Equilibrium: $\ln K = -7.017\ n + (1/RT-0.54707)\ |\Delta H_r^0|$ (4)

Rate: $\ln k = \ln K_{ads} + n \ln P_{H2} + \ln A_H - E^*_H/RT$ (5)

$\ln A_H = -(6.613+5.767\ n);\ E^*_H = 0.228\ |\Delta H_r^0|$ (6)

Acid Center Transformations:

Adsorption: $\ln K_{ads} = 0.182+(1.934N_{AR}+0.187N_{SC})/RT$ (7)

Equilibrium: $\ln K = -1.775 + (1.469-1/RT)\ \Delta H_r^0$ (8)

Isomerization Rate:

$$\ln k = -2.89 - 305.\ (0.585-1/RT) + (1-1/0.585RT)\ \Delta H_c^+ \quad (9)$$

$$(E^*_i = -305. + 1.709\ \Delta H_c^+;\ \ln A_i = -2.89 + 0.585\ E^*_i) \quad (10)$$

Ring Opening Rate:

$$\ln k = \ln P_{H2} - 4.64 - 271\ (0.585-1/RT) + (1-1/0.585RT)\ \Delta H_c^+ \quad (11)$$

$$(E^*_{RO} = -271. + 1.709\ \Delta H_c^+;\ \ln A_{RO} = -4.64 + 0.585\ E^*_{RO}) \quad (12)$$

Fig. 2 summarizes these parameter estimation results in terms of a set of a yield-vs.-conversion plots for key products. The sum-of-squares error on concentrations was less than 0.05. The predictions follow the experimental data very closely, considering the reduction in the number of parameters from 576 to 17.

Summary

The number of parameters needed to describe hydrocracking kinetics was reduced by the development of temperature-independent quantitative structure/reactivity relationships for the activation and reaction enthalpies and entropies. This approach can be summarized in the quantitative structure/reactivity relationships of Eq. (3)–Eq. (12) for the calculation of rate, equilibrium, and adsorption constants. In turn this allowed the kinetics of naphthalene and phenanthrene to be represented very satisfactorily, over a wide temperature range, in terms of just 17 QSRR parameters. These 17 parameters summarized the chemical information in 576 rate, equilibrium, and adsorption constants, which shows that the QSRR approach reduced the number of modeling parameters by about 97%.

References

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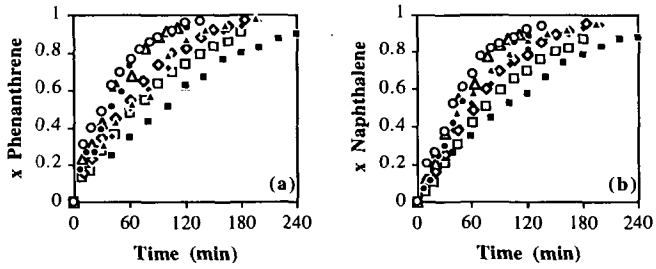

Fig. 1 Evolution of phenanthrene (a) and naphthalene (b) hydrocracking conversion with time as a function of reaction temperature.
(■): 300°C; (□): 310°C; (◆): 320°C; (◇): 330°C; (▲): 340°C; (△): 350°C; (●): 365°C; (○): 370°C.

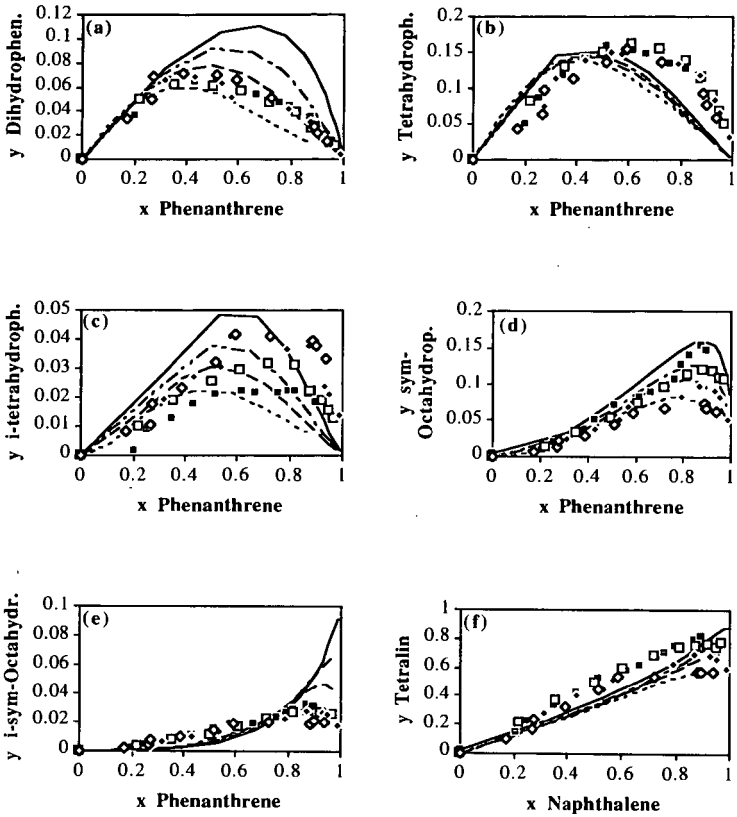

Fig. 2 Comparison between experimental and QSRR calculated yields of phenanthrene and naphthalene hydrocracking products.
(a) Dihydrophenanthrene. (b) Tetrahydrophenanthrene.
(c) *sym*-octahydrophenanthrene. (d) i-tetrahydrophenanthrene.
(e) i-*sym*-octahydrophenanthrene. (f) Tetralin.
Lines represent parameter estimation results (Eq. (1) – Eq. (12)).
(■): 300°C; (□): 320°C; (◆): 340°C; (◇): 365°C.

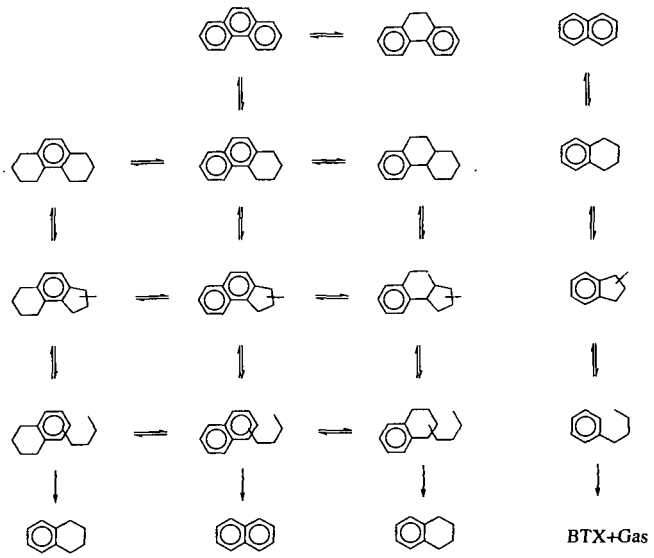

Fig. 3 Proposed network for phenanthrene and naphthalene hydrocracking.