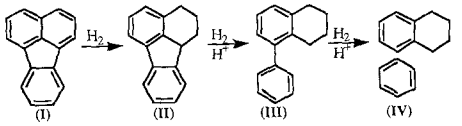
JOURNAL OF CATALYSIS 137, 504–509 (1992)

Cleavage of Biphenyl Moieties: An Efficient New Reaction Pathway in Catalytic Hydrocracking

Catalytic hydrocracking is a flexible process for the production of a wide range of upgraded products from heavy gas oils. Its key distinction from catalytic cracking is the production of valuable distillate products, in addition to gasoline, as a result of the consumption of hydrogen. Efficient use of the process hydrogen is an important economic goal that motivated our work (*1*, *2*) on the hydrocracking pathways, kinetics, and mechanisms of polynuclear aromatics (PNA's).

The catalytic hydrocracking of PNA's that contain only six-carbon-membered-rings, such as anthracene, phenanthrene, and naphthalene, proceeds by the classical pattern (*3–5*) of terminal ring saturation followed by isomerization, ring opening, and dealkylation to yield lower molecular-weight aromatic products and light gases (e.g., C_4). This pathway represents a poor utilization of process hydrogen and feed, and it poses a challenge for researchers to discover alternatives.

The hydrocracking of the five-carbon-membered-ring-containing PNA fluoranthsene (I) is qualitatively different from the classical pattern (*1*). A major reaction pathway involves hydrogenation to give tetrahydrofluoranthene, center ring opening to give phenyl tetralin, and biphenyl cleavage to give tetralin and benzene:



(1)

The remarkable selectivity of this pathway (giving no light gases) and reduced hydrogen consumption led to the mechanism proposed in Fig. 1. This mechanism includes protonation of (III) followed by an internal 1,5-hydride shift to afford the carbenium ion III^+, of III, represented in the benzylic form. A 1,3-hydride shift of a resonance form of III^+ affords benzene and a carbenium ion IV^+, the deprotonation of which leads to an intermediate, dialin, which is rapidly hydrogenated to yield tetralin. The noteworthy reaction in the sequence of Fig. 1, which is a net 1,5-shift of the benzylic hydride to the ring bearing the positively charged carbon, evidently takes place (not necessarily as an elementary step) along a molecular topology that includes a strong biphenyl linkage. This suggests an apparent structural moiety for efficient cleavage of strong biphenyl linkages, which otherwise would require prior hydrogenation. Thus, we have investigated the catalytic hydrocracking of molecules that either contain this structural moiety, or can react to form it.

Experiments were done to determine the hydrocracking pathways and kinetics of 9-ethyl fluorene, 9-phenyl anthracene, and 2-phenyl naphthalene in the presence of an equilibrated Ni-Mo/Al_2O_3-catalyst-containing ultra-stable Y-Zeolite (*2*) at 310–380°C and 153 atm. Experimental methods are reported elsewhere (*1*, *2*). In brief, hydrocracking reactions took place in a batch autoclave or in batch agitated tubing bombs. Experiments conducted in the stirred batch autoclave were in the presence of hexadecane solvent. No solvent was used

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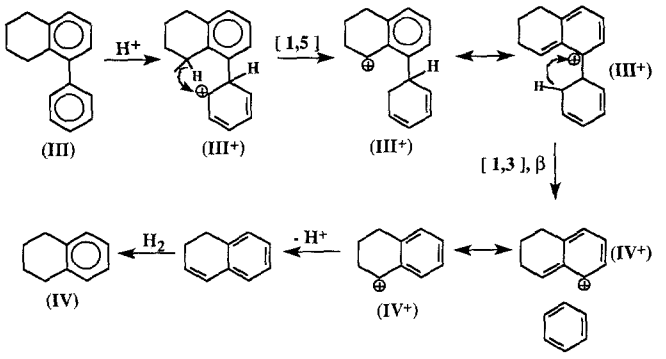

FIG. 1. Proposed mechanism for the efficient cleavage of biphenyl linkages; some of the reactions may not be elementary steps.

in the 10-cm^3 agitated tubing bombs. For both types of experiments, the catalyst was ground to 80–100 mesh. It was presulfided with 90% H_2/10% H_2S flowing at 30 cm^3(STP)/min for 2 h at 400°C and 1 atm. Gas chromatography and gas chromatography/mass spectrometry were used to identify liquid-phase reaction products.

TABLE 1

Product Selectivities (yield/conversion) for Hydrocracking of 2-Phenyl Naphthalene (2-PN), 9-Phenyl Anthracene (9-PA), and 9-Ethyl Fluorene (9-EF) with NiMo/Al_2O_3-USY-Z, 350°C and 153 atm

Reactant	2-PN	2-PN	2-PN	2-PN	9-PA	9-PA	9-PA	9-PA	9-EF	9-EF	9-EF	9-EF
t, min	10	23	30	61	5	10	32	62	119	167	249	388
Conversion of reactant	0.031	0.313	0.392	0.719	0.625	0.875	0.982	1	0.331	0.332	0.434	0.659
Biphenyl cleavage products												
1,2,3,4-tetrahydroanthracene	—	—	—	—	0.016	0.019	0.063	0.045	—	—	—	—
1,2,3,4-tetrahydronaphthalene	0.355	0.121	0.158	0.295	—	—	—	—	—	—	—	—
n-propyl benzene	—	—	—	—	—	—	—	—	0.060	0.060	0.069	0.127
benzene	0.323	0.153	0.176	0.292	0.090	0.142	0.360	0.572	0.045	0.060	0.069	0.121
Center ring cleavage products												
2-*n*-propyl biphenyl	—	—	—	—	—	—	—	—	1.076	0.738	0.244	0.127
Isomerization products												
1-phenyl naphthalene	0.419	0.089	0.092	0.057	—	—	—	—	—	—	—	—
5-phenyl-1,2,3,4-tetrahydronaphthalene	0.000	0.000	0.036	0.058	—	—	—	—	—	—	—	—
9-ethyl iso-hexahydrofluorene	—	—	—	—	—	—	—	—	0.039	0.105	0.203	0.058
Hydrogenation products												
6-phenyl-1,2,3,4-tetrahydronaphthalene	1.677	0.482	0.564	0.498	—	—	—	—	—	—	—	—
2-phenyl-1,2,3,4-tetrahydronaphthalene	0.387	0.128	0.138	0.067	—	—	—	—	—	—	—	—
9-phenyl-9,10-dihydroanthracene	—	—	—	—	0.666	0.509	0.193	0.029	—	—	—	—
9-phenyl-1,2,3,4-tetrahydroanthracene	—	—	—	—	0.157	0.142	0.153	0.062	—	—	—	—
9-phenyl octahydroanthracenes	—	—	—	—	0.000	0.007	0.031	0.030	—	—	—	—
9-ethyl hexahydrofluorene	—	—	—	—	—	—	—	—	0.106	0.123	0.166	0.058
Other products												
9,10-dihydroanthracene	—	—	—	—	0.032	0.055	0.066	0.025	—	—	—	—
octahydroanthracenes	—	—	—	—	0.016	0.029	0.091	0.205	—	—	—	—
ethyl benzene	—	—	—	—	—	—	—	—	0.027	0.060	0.046	0.111
toluene	—	—	—	—	—	—	—	—	0.027	0.060	0.046	0.109
Overall mass balance	1.067	0.992	1.064	1.192	0.985	0.914	0.958	0.968	1.126	1.069	0.932	0.810

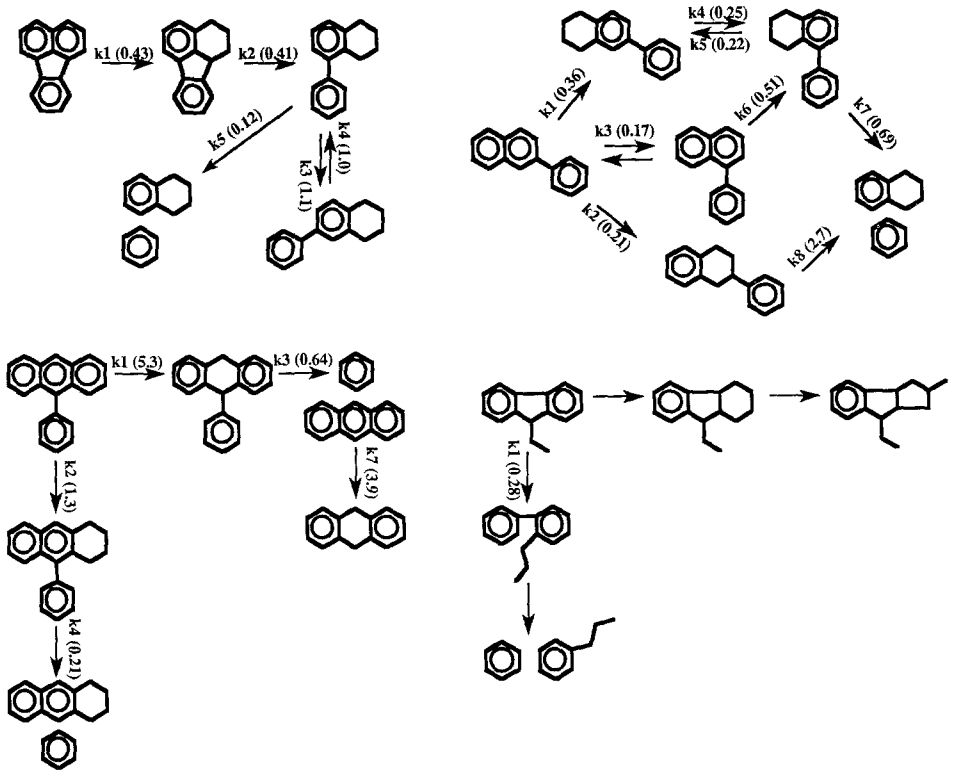

FIG. 2. Hydrocracking pathways of fluoranthene, 2-phenyl naphthalene, 9-phenyl anthracene, and 9-ethyl fluorene catalyzed by $NiMo/Al_2O_3$-USY-Z. The pseudo-first-order rate constants shown in parentheses are for reaction at 350°C. The rate constants have dimensions of cm^3 solution/(g of catalyst · s).

The results are summarized in Table 1, which lists product selectivities at various conversions. The products are organized into groups representing those resulting from formal biphenyl cleavage, center ring cleavage, isomerization, hydrogenation, and other reactions. Inspection of Table 1 reveals that 2-phenyl naphthalene, 9-phenyl anthracene, and 9-ethyl fluorene each underwent the biphenyl cleavage pathway.

The importance of the apparent 1,5-shift pathway leading to biphenyl cleavage is most clearly shown by the reaction networks and kinetics. These are summarized in Fig. 2, parts a–d, for fluoranthene, 2-phenyl naphthalene, 9-phenyl anthracene, and 9-ethyl fluorene, respectively. Comparison of the quantitative reaction network for fluoranthene with that for 2-phenyl naphthalene illustrates an important point: The 1,5-shift is kinetically more significant in the fluoranthene network, presumably because of its high hydrogenation selectivity to 5-phenyl tetralin, which incorporates the crucial moiety for the 1,5-shift. In the hydrocracking of 2-phenyl naphthalene, however, the hydrogenation includes a significant route to 2-phenyl tetralin, which can crack via protonation of the phenyl ring and dealkylation of a secondary alkyl carbenium ion, which ultimately affords tetralin. This pathway is akin to that of cumene dealkylation and competes with the 1,5-shift. Similarly, the hydrogenation of 9-phenyl anthracene to give 9-phenyl-9,10-dihydroanthracene is faster than the hydrogenation to give tetrahydro-9-phenyl anthracene. The former allows the classical route

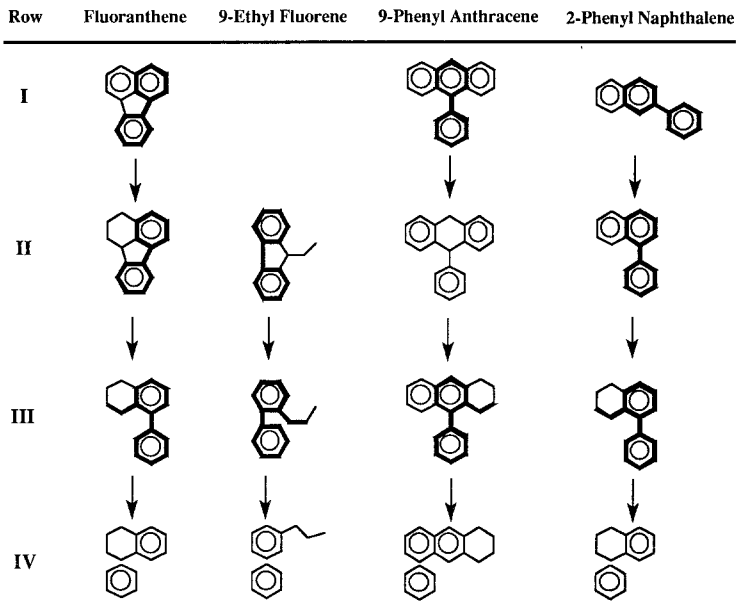

FIG. 3. Examples of efficient hydrocracking of biphenyl linkages: chemical moieties that are susceptible to the net 1,5-hydride shift are shown in boldface.

that is akin to the cumene dealkylation route, and the latter allows the 1,5-shift route. 9-Ethyl fluorene undergoes protonation and β-scission to open the center five-carbon-membered ring and then cleavage of the 2-propyl biphenyl intermediate.

The observed biphenyl bond cleavage pathways are organized by the grid of Fig. 3 in a hierarchical manner that aligns the members of each pathway according to their proximity to the biphenyl bond cleavage. Thus the rows of Fig. 3 correspond roughly to the molecules designated in Eq. (1) (I, II, III, and IV).

Inspection of Fig. 3 reveals the essential moiety for efficient biphenyl cleavage. The hydrocracking of 9-ethyl fluorene begins in row II, where center ring opening leads to propyl biphenyl, which cracks to give propyl benzene and benzene. The sequence is consistent with the reactions of Fig. 1, namely, phenyl ring protonation of III followed by a net 1,5-hydride shift from the propyl group. The resulting carbenium ion has several canonical forms, one of which is formally susceptible to the 1,3-hydride shift that affords benzene and a carbenium ion that can be deprotonated to give an olefin, which is rapidly hydrogenated to give propyl benzene.

The biphenyl cleavage pathway for 9-phenyl anthracene (9-PA) begins in row I. 9-PA is hydrogenated to give 9-P (9,10-DHA), which in turn is hydrogenated to give 9-P (THA). Highlighted in Fig. 3, in row III, is the essential moiety for efficient cracking of the biphenyl bond of 9-P-THA. The formation of THA and benzene is evidence of this efficient cleavage.

The efficient cracking of 2-phenyl naphthalene begins in row I with isomerization to give 1-phenyl naphthalene. Hydrogenation to give phenyl tetralin, in row III, creates the essential moiety for biphenyl bond cleavage, as described above for the reaction of fluoranthene.

A test of the generality of the observations summarized here is provided by results obtained in experiments with reactants that did not give evidence of the efficient bond cleavage pathway. Fluorene, for example, underwent ring opening to give 1-phenyl tol-

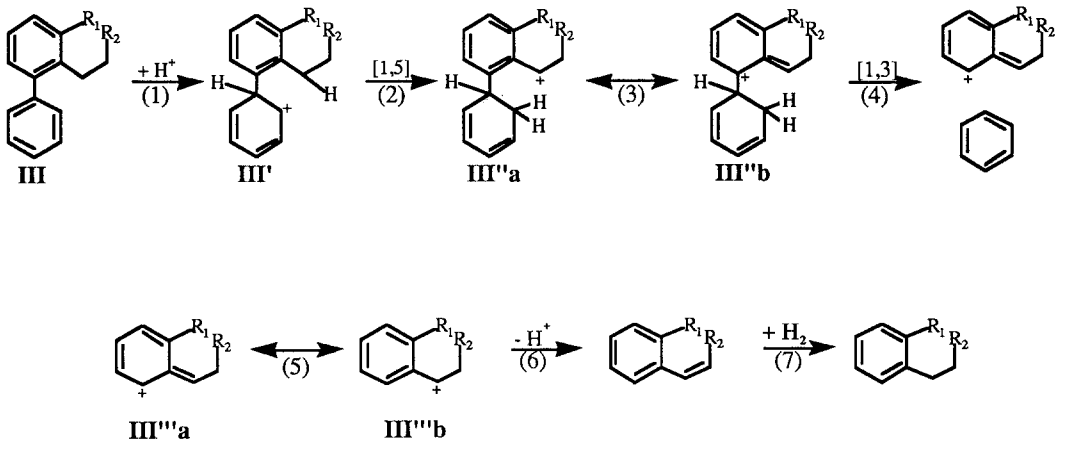

FIG. 4. Proposed mechanism illustrating the essential structural moiety for biphenyl cleavage via 1,5-hydride shift, β-scission, olefin formation, and hydrogenation.

uene, which contains the benzylic hydride but not the essential β saturated carbon at which deprotonation to give the olefin allows hydrogenation to the final alkyl-substituted product (*6*). Methyl biphenyl likewise suffers from the same structural deficiency, and was not converted by the cleavage pathway.

The foregoing mechanistic points are summarized in Fig. 4. All the molecules in row III of Fig. 3 share the essential moiety (III) of Fig. 4, which can be protonated (step 1) to give III'. This intermediate in turn can undergo the 1,5-hydride shift (step 2) to give III''_a[1]. Resonance form III''_b formally undergoes the 1,3-hydride shift that effects biphenyl cleavage to give the stable secondary benzylic carbenium ion III'''_a. Fragment III'''_a is then deprotonated in step 6, and the resulting olefin is hydrogenated in step 7 to afford the final observed product. The structural deficiencies of fluorene and methyl biphenyl deny them access to steps 6 and 7 and therefore the efficient biphenyl cleavage pathway.

The reaction paths of Eq. (1) and Fig. 3 have important implications for hydrocracking processes: They represent a selective and hydrogen-efficient cleavage of strong bonds to give highly aromatic products. They also confirm the need for a delicate balance of olefinic and paraffinic structural functionalities in the hydrocracked molecule (*5*); the balance in the reactivities is influenced by the balance of metal (hydrogenation, dehydrogenation) and acidic (isomerization, β-scission) functions of the catalyst. In addition, the results of this work suggest that controlled alkylation of feed stocks containing biphenyl linkages could improve process selectivity.

[1] Only one of the possible mechanisms for the migration of hydrogen is shown.

NOMENCLATURE

9-PA	9-phenyl anthracene
9-P(9,10-DHA)	9-phenyl,9,10-dihydroanthracene
9-P(THA)	9-phenyl-tetrahydroanthracene
THA	tetrahydroanthracene
2-PN	2-phenyl naphthalene
9-EF	9-ethyl fluorene
$NiMo/Al_2O_3$-USY-Z	industrial lined-out catalyst containing NiMo supported onto an alumina binder containing USY-Zeolite

ACKNOWLEDGMENT

We gratefully acknowledge the support of this work by Sun Refining and Marketing Company.

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MICHAEL T. KLEIN[2]
ARUNUS T. LAPINAS[3]
BRUCE C. GATES

CAROLE J. READ
JAMES E. LYONS

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

ARIS MACRIS

Sun Company
Technology Development
Refining and Marketing
P.O. Box 1135
Marcus Hook, Pennsylvania 19061

Received March 12, 1991; revised February 25, 1992

[2] To whom correspondence should be addressed.

[3] Present address: Corporate Research Laboratories, Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, NJ 08801.