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Dehydrocyclodimerization

V. The Mechanism of the Reaction

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Dehydrocyclodimerization proceeds through several consecutive steps: (1) dehydrogenation to monoolefins and diolefins; (2) dimerization of the olefins over the acidic sites; (3) aromatization of the dimerized olefins and diolefins. (4) Isomerization, transalkylation, and dealkylation of the primary aromatics to produce a large number of C_8–C_{10} alkylbenzene isomers.

Dehydrocyclodimerization converts light paraffins to aromatics. The reaction is catalyzed by dual-functioning catalysts having acid and dehydrogenation activities. The first three parts of this series described the reaction of C_3–C_4 and C_5 paraffins over various catalysts (*1–3*). The related reactions of olefins were discussed in Part IV (*4*). Here we propose a mechanism for the reaction.

DISCUSSION

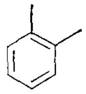
Dehydrocyclodimerization is the result of several consecutive and parallel reactions. Some of these are catalyzed by dehydrogenation components, some by acids, and some by both. The following reaction steps can be distinguished in dehydrocyclodimerization, using the reactions of butane as an example.

1. Dehydrogenation of butane to butenes and butadiene is the first step of dehydrocyclodimerization. This may be the only reaction which is not catalyzed by acids.

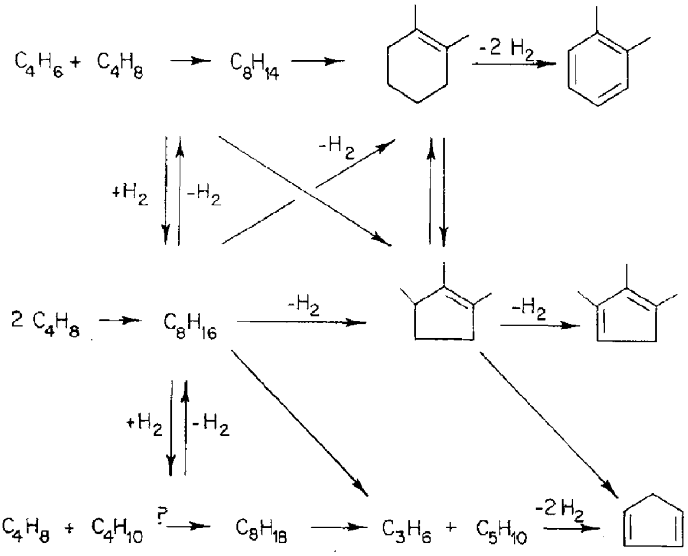
$$C_4H_{10} \rightleftharpoons C_4H_8 \rightleftharpoons C_4H_6.$$

2. Dimerization of olefins can proceed by several mechanisms. Acid-catalyzed polymerization is the most important way to produce dimers. Dimers identified by GLC-MS technique are 2,3- and 2,5-dimethylhexadienes, methylheptenes and dienes, and naphthenes with polyalkylcyclopentane and cyclohexane skeletons. Another possible dimerization route is thermal, involving conjugated diolefins. At very short residence times, vinylcyclohexene is one of the predominant naphthene produced from butene (*4*). Vinylcyclohexene can be produced by thermal dimerization of butadiene.

3. The dimers—C_8 olefins or naphthenes—may be converted to aromatics over either catalyst component. Aromatization over the dehydrogenation component is many times faster than over the acidic one. However, acid sites are needed to convert five-membered rings to six-membered ones before aromatization can take place. Over acidic catalysts, the distribution of xylenes and ethylbenzene is at or near thermodynamic equilibrium. The structures shown above do not differentiate between isomers which differ only in the position of double bonds or alkyl substituents; e.g., represents all three xylenes combined.



4. Transmethylation, isomerization, and dealkylation of the primary aromatic products may form almost all possible C_6–C_{10}



aromatics (Fig. 1). Isomerization and transmethylation are catalyzed by acids. Thermal-, base-, and acid-catalyzed routes are known for dealkylation. Aromatics with six, seven, or nine carbon atoms may also result from combinations such as $C_3 + C_3$, $C_3 + C_4$, and $C_4 + C_5$. C_4 trimers and higher polymers can produce alkylnaph-

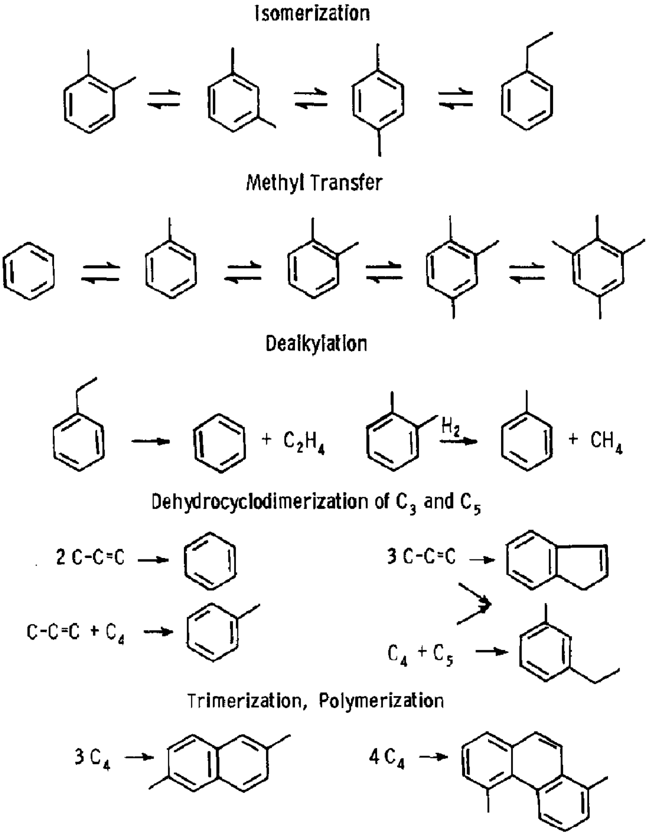


FIG. 1. Secondary reactions of aromatics in dehydrocyclodimerization.

thalenes and other polycyclic aromatic compounds. Table 1 shows C_{12}–C_{24} polycyclics which represent up to 2.4% of the aromatics produced.

5. Propane, propylene, and the corresponding C_5 hydrocarbons result from acid-catalyzed cracking of butene dimers.

6. Methane, ethane, and propane might be formed by hydrogenolysis over platinum or metal oxide sites.

7. Coking may occur over both the acid and the dehydrogenation components. Likely coke precursors are dienes, naphthenes with five-membered ring structures, and polycyclic aromatics.

TABLE 1

POLYCYCLIC AROMATICS IN THE REACTION PRODUCT OF ISOBUTANE DEHYDROCYCLODIMERIZATION AT 560°C WITH AN LHSV OF 1 OVER A 1:3 MIXTURE OF Pt (0.8%) ALUMINA AND ALUMINA

Aromatic class	Relative concentration (relative MS peak heights of the low voltage mass spectrum)[a]			
	Unsubstituted	Monomethyl	Dimethyl	Trimethyl
Anthracene and Phenanthrene	5	10	7	2
Pyrene	10	13	8	2
Benzanthracene and chrysene	8	4	2	
Benzpyrene	10	6	3	
Anthanthrene (dibenzpyrene)	7			
Dibenzanthracene (pentacene)	3			

[a] Mass spectrum of a $CHCl_3$ solution of the high boiling fraction (about 0.1 ml) of the liquid product.

The combination of dehydrogenation and acid components giving the best dehydrocyclodimerization catalyst has the following characteristics:

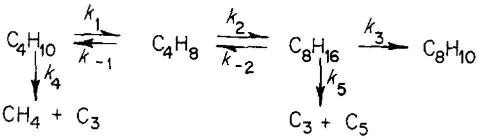
Butene formation over the dehydrogenation component is somewhat faster than butene dimerization over the acid component ($k_1 > k_2$; see the reaction scheme below).

The acidic component is active enough to convert five-membered ring naphthenes to six-membered rings.

Aromatization of the dimers over the dehydrogenation component is substantially faster than dimer cracking over the acid component ($k_5 \ll k_3 \gg k_{-2}$). The aromatization rate should be faster than the rate of dimerization ($k_3 > k_2$).

The dehydrogenation component should have low hydrogenolysis activity compared to its dehydrogenation activity ($k_1 \gg k_4 \ll k_3$).

Both components should function well at 550°C or higher temperatures. Equilibrium is unfavorable below this temperature.



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