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LETTERS TO THE EDITORS

On the Possible Reaction Scheme of Aromatization in Catalytic Reforming

The possible pathway(s) of aromatization of alkanes have been much disputed during the 50 years since the first discovery of the reaction (*1*), and especially since the development of catalytic reforming (*2*). An ingenious and instructive two-dimensional scheme has been developed by Mills *et al.* (*3*) to describe how bifunctional catalysts in reforming operate: this chart attributed dehydrogenation reactions to metallic, isomerization reactions (including ring closure) to acidic functions. Although this reaction scheme can be found in most textbooks and is claimed to be the most probable mechanism under industrial conditions which provides the best matching with kinetic studies and industrial observations (*4*), continuous work on the mechanism of reforming indicates that the scheme may not be perfect and comprehensive. The possible reactions have been critically reviewed and evaluated by Parera *et al.* (*5*) in a recent issue of the *Journal of Catalysis*. The authors propose an extended version of the original chart of Mills *et al.* So far this represents the most extensive mechanism for reforming, including such reactions as hexane skeletal isomerization, methylcyclopentane ring opening, etc., which were conspicuously missing from the original version. A remarkable novelty of the improved scheme is that it proposes a new reaction for C_6 ring formation, namely the ring expansion of methylcyclopentadiene to cyclohexadiene.

However, we feel that even the improved scheme has a serious shortcoming, the complete disregard of direct C_6-cyclization of open chain hydrocarbons. Increasing evidence suggests that this may be the major pathway of aromatization on laboratory (*6–8*) and industrial (*9–10*) samples. The most recent example (using conditions simulating those of commercial reforming) has just been published in the same issue of the *Journal of Catalysis* (*11*). The reaction sequence hexane → hexene → hexadienes → hexatriene → cyclohexadiene → benzene was supported by radiotracer experiments (*12*) and by reacting hexenes, hexadiene, and hexatriene isomers in the presence of various amounts of hydrogen on Pt-black (*13*) as well as on alumina-supported Pt and Pd (*14, 15*). *Cis*-hexatriene always transformed into benzene very rapidly. The formation of small amounts of cyclohexadiene was confirmed by radiotracers (*12d*). Other C_6-cyclics (cyclohexane, cyclohexene) must have been formed by hydrogenation of the latter. In the presence of gas phase or surface hydrogen more hydrogenation products (hexadienes, hexenes, and hexane) than benzene (*13, 15*) are formed from *trans*-hexatriene. Small amounts of hydrogen in the system promotes *trans* $\rightleftarrows$ *cis* isomerization (via half-hydrogenated intermediates). Without this process, polyenes would be stuck to the surface in geometries as they were produced and their further dehydrogenation and polymerization/condensation would give coke. There is only one triene geometry favorable for cyclization (cisoid conformation of *cis*-hexatriene), therefore, the statistical probability of coke precursor formation is much higher than that of benzene precursor formation. This is reflected by the deactivation rate of a Pt-catalyst by various hydrocarbons: this is almost nil with the *cis*-hexatriene reactant and considerable with all other n-C_6 feeds (*13*). That is why elongated polyenes have

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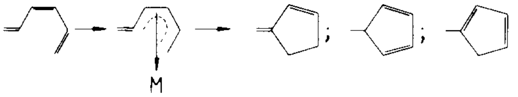
been suggested as possible coke precursors (*7*). This carbonization pathway was further experimentally verified (*16*): the rate of carbon accumulation on the surface was higher with any open-chain C_6 reactant than with benzene (*16*). Adding a second metal like Sn to Pt/Al_2O_3 enhanced its relative rate.

We see one serious logical error in the reasoning of Parera *et al.* (*5*): They regard the metallic function as being poisoned by sulfur, therefore, they consider bifunctional reactions only. However, the function of the metal is *dehydrogenation*, and they regard (in our view, correctly) dehydrogenation of cyclopentanes and cyclohexanes on the metallic function as unhindered processes. If, however, these hydrocarbons are able to be hydrogenated and dehydrogenated, then the hexane → hexenes → hexadienes → hexatriene reaction sequence must also be operative. Adding an inactive alloying element (such as gold) to platinum stops the aromatizing entirely while its dehydrogenation activity still exists (*17*). Thus, we feel that alkane dehydrogenation [either without desorption of its unsaturated products or with their appearance in the gas phase (*18*)] cannot be neglected.

The metal-catalyzed cyclization step: (*cis*-hexatriene or, eventually, *cis*-*cis*-2,4-hexadiene, giving cyclohexadiene) would occur on ensembles of up to three Pt-atoms (*19*). Sulfidation may deactivate these; then either thermal cyclization of trienes occur (*9*)—which is rather rapid even with *trans*-hexatriene above 450°C (*13*)—or, whenever possible, bifunctional cyclization steps will prevail. In addition to the step *n*-hexene → methylcyclopentane (Reaction (6) in Ref. (*5*)), other C_5 ring closure steps like hexadiene → methylcyclopentene may also occur. The formation of methylcyclopent-1-ene from hex-1-ene (*12a*), hexadiene isomers, and *trans*-hexa-1,3,5-triene (*20*) over Pt-black was shown earlier. Dienes and triene also gave methylcyclopentadiene(s). When catalyst deactivation decreased the benzene yield to about half of that observed on the fresh catalyst, the amount of C_5-cyclic unsaturated products was nearly doubled, their yield then being about 1/10 (with hexa-1,5-diene feed, 1/3) of the benzene yield. The formation of methylcyclopentadiene from hexatriene over Pd on—possibly acidic—alumina was reported (*15*). The yield of unsaturated vs saturated C_5-cyclics from toluene over Pt/Al_2O_3 increased with temperature (*21*). These may be produced, e.g., by the cyclohexadienyl route C_5-cyclization (*22*): which, perhaps, may take place on single metal atoms of a deactivated catalyst:



but they should be enormously accelerated by acidic sites.

In light of this, we propose a modified scheme for catalytic reforming (Fig. 1). Eleven more possible reactions were added to Parera's scheme (*5*). Reaction (18) represents direct dehydrogenation of cyclohexane to benzene (verified on both Re (*23*) and Pt (*24*); (19) and (20): two further steps of the stepwise dehydrogenation; (21) and (22): coke formation from elongated poly-

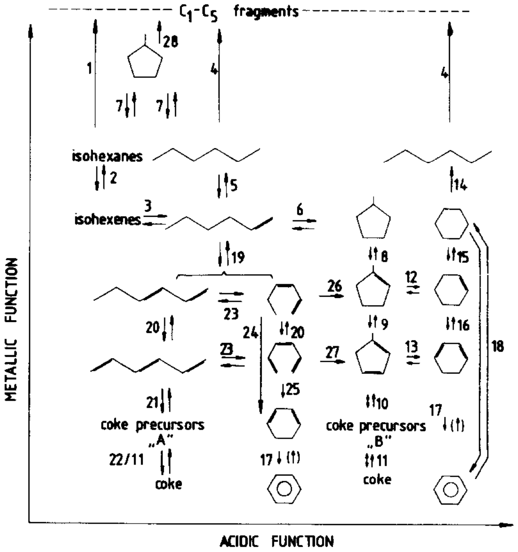


FIG. 1. Modified bifunctional reaction scheme for reforming of C_6 hydrocarbons. The reaction numbers are the same as in the work of Parera *et al.* (*5*).

enes; (23): the very important geometric isomerization of polyenes; (24)–(27): new ring closure steps, discussed in the present work; (28): hydrogenolysis of methylcyclopentane. We agree with Parera *et al.* (*5*) that ring opening on metal (Reaction (14)) is irreversible. It is practically absent on Pt (*12c, 22*) but considerable on Re (e.g., 5.5% fragments and 12% benzene were formed from cyclohexane on Re-black at 633 K). We modified the meaning of Reaction (7): this represents here the metal catalyzed alkane isomerization via C_5-cyclic intermediates (*25*). Reactions (24) and (25) represent the "direct" C_6 ring closure (which we believe takes place in reforming); (25) and (26) represent new C_5-cyclic reactions. Although the reactions may occur on metal (*14, 15, 20*), they were attributed here to the acidic function. These latter may couple the stepwise aromatization mechanism to the previously developed chart of bifunctional reforming as well as to the formation of C_5-cyclic coke precursors. Of the latter species, two types are distinguished ("A" and "B" in Fig. 1). We are not sure that they represent, indeed, different routes of carbonization. In fact, the denotation 22/11 under *trans*-hexatriene may indicate common steps with both precursors: Diels-Alder condensation of linear (*7*) or cyclopentanic (*26*) molecules or addition of cyclopentadienes to polycondensed aromatics with subsequent rearrangement of the network (*27*). The experimental evidence is insufficient for a final answer to this problem to be given.

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