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Reply to "On the Possible Reaction Scheme of Aromatization in Catalytic Reforming"

The letter by Z. Paál (*1*) extends the bifunctional reaction scheme for C_6 hydrocarbon transformations to benzene and coke in our previous paper (*2*) to a more general scheme including other possible routes, but it must be emphasized that those routes operate under particular conditions.

Since the main reason for studying this reaction is the commercial importance of the naphtha reforming process, in our paper (*2*) we refer to the reaction scheme we suppose as operating under conditions similar to the commercial ones. The direct n-C_6 cyclization was not ignored; as quoted from page 45, "Paál and Tetényi (*3*) described their results for the dehydrocyclization of n-C_6 over Pt, Ni, and metal oxides by analogous mechanisms via the intermediates hexene-hexadiene-hexatriene," and on page 46 it is stated that "there are other reactions that can be added; for instance, the dehydrogenation of n-hexene to n-hexadiene on the metallic site, which can then produce MCPe on the acid sites, as proposed by Sinfelt" (*4*). But, under commercial conditions it is considered that the bifunctional mechanism through MCP as intermediate is very rapid compared to the only metallic mechanism through hexatriene.

In the references quoted in Paál's letter for direct n-C_6 cyclization involving dehydrogenation of n-C_6 to hexatriene, low total pressure and very low or zero hydrogen pressure were used, and only the metallic function was operating—which are very different from commercial catalysts and operational conditions. Also Paál's "industrial samples" (Refs. (*9, 10*)) are monofunctional Pt on a nonacidic support, and his Ref. (*11*) suggests that stepwise dehydrogenation of n-C_6 to hexatriene may be important *only near atmospheric pressure.*

In Ref. (*2*, p. 45) it is said that "according to Sinfelt (*5*), under commercial reforming conditions dehydrocyclization and isomerization on the metallic sites are negligible compared with the bifunctional mechanism. Vestiges of S are enough to poison the reaction mechanisms involving only the metal. These are the reasons why only the bifunctional mechanism will be considered here." In this mechanism—as quoted in Paál's letter (*1*)—the metallic function maintains its dehydrogenation activity. This activity is decreased by the increase in hydrogen pressure, and at high hydrogen pressure it is not possible to dehydrogenate n-C_6 up to hexatriene. Working under conditions similar to the commercial ones and with the bifunctional catalyst, hexadiene and hexatriene were never detected, but most of the intermediates of the classical bifunctional scheme (as MCP) were detected.

Then, Ref. (*2*), according to its purpose, presents the reaction scheme that can be considered operable in the proximity of the operational conditions of the commercial processes, and Paál adds in his letter (*1*) routes that can be operating under other particular conditions—such as, low total pressure, low hydrogen pressure, and absence of the acidic function.

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J. M. PARERA

INCAPE
Santiago del Estero 2654
3000 Santa Fe
Argentina

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