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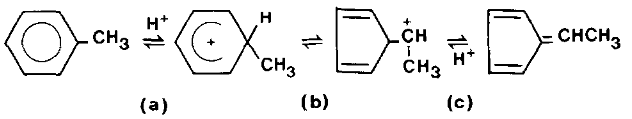
Further Comments on Aromatic Hydrocarbon Participation in Methanol Conversion: Reply to Pines

Pines, in his comments (*1*) on the interpretation of our study (*2*) of the role of aromatic hydrocarbons in methanol conversion, points out that a 6,5-ring expansion may account for the observed appearance of the ^{13}C label of benzene in ethylene product and for deuteration (by D_2O) of xylene in its methyl groups. The comments are pertinent to, but do not refute, the interpretation previously offered (*2*). The relevance of Pines' mechanism was noted in an earlier discussion of the ^{13}C-label results (see page 443 of Ref. (*2*)), but we should like to make the following comments:

(a) The 6,5-ring contraction, postulated by Pines, can be written in such a form as to make clear that it involves rearrangement of an aromatic ring to an *exo*ethylidine-cyclopentadiene.



(1)

The overall sequence (a)–(c) leading to an *exo*ethylidine-cyclopentadiene can be compared with our sequence (4) and (5) leading to an *exo*methylene-cyclohexadiene. Sequence (a)–(c) is obviously as thermodynamically difficult as (4)–(5); both involve loss of benzenoid conjugation, and (a)–(c) involves an additional skeletal rearrangement. The free-energy change from toluene to *exo*methylene-cyclohexadiene has been estimated (*3*) as 1.4 eV, indicating an activation energy >32 kcal for the sequence (4)–(5), and an *exo*methylene-cyclohexadiene/toluene ratio $<10^{-10}$ at equilibrium at 400°C. The *exo*ethylidine-cyclopentadiene mechanism must be as difficult (or more so).

(b) Aromatic rearrangement by ring contraction appears to be accepted wisdom, but there are very few examples which demonstrate such a mechanism unambiguously. The notable exception is Balaban and Farcasui's (*4*) demonstration of rearrangement of ^{14}C-labeled naphthalene. Mainly, however, the mechanism is assumed but not proven, for example, by Sullivan *et al.* (*5*) who converted hexamethylbenzene over silica/alumina at 344°C to products in which *penta-* and *tetra*-methylbenzenes, propane, *iso*butane, and *iso*pentane were dominant.

(c) Despite the present (*1*) and previous (*2, 6*)[1] discussion of xylene/ethylbenzene isomerization (2), it is important to recognize that such reaction is not facile over simple solid-acid catalysts.

$$C_6H_4(CH_3)_2 \rightleftharpoons C_6H_5(C_2H_5) \qquad (2)$$

For example, isomerization of xylenes over ZSM5 zeolite is facile under methanol-to-gasoline conditions (350–460°C; 1–10 h^{-1} W.H.S.V.), but the ethylbenzene component mainly undergoes (intermolecular)

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[1] Reference (*6*) is probably based on the work of Boedeker and Erner (*7*).

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transethylation and deethylation (see, for example, Ref. (*8*)). Ethylene so produced may undergo secondary reactions. Similarly in cracking of cumene (*9*), minor products such as ethyltoluenes may arise from secondary reactions (see, for example, Ref. (*10*)) of propylene, produced by reaction (3), rather than from 6,5-ring contraction (*11*) of cumene itself.

$$(CH_3)_2CH\ C_6H_5 \rightleftharpoons CH_3CH{=}CH_2 + C_6H_6 \quad (3)$$

In summary, we acknowledge that Pines' suggestion provides an explanation of [^{13}C]ethylene being produced from [^{13}C] benzene and methanol. However, we point out that: (i) there is no reason to regard Pines' rearrangement as energetically preferable to *exo*methylene-cyclohexadiene formation; (ii) the course of reaction giving [^{13}C]ethylene is inadequately defined; and (iii) scrambling of carbon label between aromatic ring and side chain has not been adequately demonstrated (even though our results can be so interpreted.

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