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# On the Question of Aromatic Ring Expansion–Contraction for Conversions with a ZSM-5 Catalyst

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Toluene, labeled with $^{14}C$ in either the methyl position or uniformly in the aromatic ring, did not undergo a measurable amount of either ring expansion–contraction or ring degradation to produce ethene at temperatures up to 350°C. Ethylbenzene dealkylation and disproportionation and xylene isomerization occur to produce equilibrium mixtures of diethylbenzenes or xylenes under these reaction conditions; hence, ring expansion–contraction must be much slower than these isomerization reactions.

The mechanism of the isomerization of alkylaromatics has received wide interest for several decades. During this period, the migration of a methyl group has been convincingly demonstrated to occur by a series of 1–2 shifts (e.g., *1–5*). Steinberg and Sixma (*6*) utilized [1-$^{14}C$]toluene and a hydrogen bromide–aluminum bromide catalyst and found data to indicate 1,2-shifts of the methyl group. Roberts and Roengsumran (*7*) converted [1-$^{13}C$]toluene under similar experimental conditions and reached the same conclusion. Recently, Dabbagh *et al.* (*8*) isomerized [1-$^{13}C$]toluene over HZSM-5 and concluded that methyl migrates by a series of 1,2 shifts, and is nearly as free of diffusional disguise as the homogeneous acid-catalyzed reaction.

The nature of the intermediate by which the alkyl group migrates around the ring has not been well studied or understood. Brown and Smoot (*9*) suggested that a $\sigma$-complex is in rapid equilibrium with a localized high energy $\pi$-complex. Unseren and Wolf (*5*) isomerized ethylbenzene using $AlBr_3$–HBr at 0° and found that after partial disproportionation there is no rapid equilibrium between ethylbenzene and its localized $\pi$-complex. They further suggested that isomerization of ethylbenzene occurs by a series of rapid, stepwise carbonium ion rearrangements, and that this cannot be faster than disproportionation. Lien and McCaulay (*10*) proposed the formation of a resonance stabilized sigma complex when a proton is added to the ring.

Mole and co-workers (*11*) observed monolabeled [$^{13}C$]ethylene and $C_3$-labeled hydrocarbons when methanol and $^{13}C$-labeled benzene or toluene were passed over a ZSM-5 catalyst. They also reported the deuteration of toluene and xylene by $D_2O$ in which some of deuterium was in the methyl groups. The deethylation of ethylbenzene to benzene and ethylene was considered to be involved in the isomerization of xylene to ethylbenzene by an unlikely 1,3-carbon–carbon methyl shift.

Included among the proposed mechanisms is a ring contraction–ring expansion scheme (*11–16*). This mechanism has appealing features but there is little, if any, experimental evidence to support its operability for alkyl benzenes.

Our data for ZSM-5 catalyzed isomerization of [1-$^{13}C$]toluene clearly indicate that the methyl group migrates around the ring by a series of 1,2-shifts (*8*). At the longer

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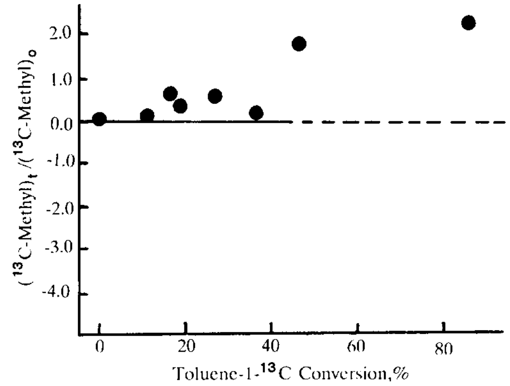


FIG. 1. The ratio ([$^{13}$C]methyl)$_t$/([$^{13}$C]methyl)$_0$, where subscripts $t$ and 0 refer to the amount of [1-$^{13}$C]toluene present at time $t$ and to start (0), respectively, versus the extent of isomerization of $^{13}$C from the ring $-1$ position to other ring positions.

reaction times it appeared that some ring carbons could have exchanged with the methyl group of toluene (Fig. 1). However, the NMR peak-area/carbon corrections for the various ring and methyl positions in toluene may vary by nearly a factor of 2. Hence, the apparent increase in the $^{13}$C content above the natural abundance amount may be due to errors in the experimentally determined constants needed to correct the measured areas for each ring position and the methyl group. It was of interest to obtain additional data concerning this question. In this study, $^{14}$C was used as the label because of the expense involved for the amount of toluene needed to obtain the high conversions in our experiments using the HZSM-5 catalyst.

[*methyl*-$^{14}$C]Toluene was synthesized through the following series of reactions (Ph, phenyl; (*C, $^{14}$C):

$$\mathrm{PhMgBr} + {}^*\mathrm{CO_2} \xrightarrow{\mathrm{H+}}$$

$$\mathrm{Ph^*CO_2H} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Ph^*CH_2OH}$$

$$\xrightarrow{\mathrm{SOCl_2}} \mathrm{Ph^*CH_2Cl} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Ph^*CH_3}$$

Toluene (UL-$^{14}$C) was synthesized by the following procedure (UL-$^{14}$C represents each ring carbon uniformly labeled):

$$\mathrm{Ph(UL\text{-}^{14}C)} \xrightarrow[\text{reflux}]{A}$$

$$\mathrm{Ph(UL\text{-}^{14}C)CH_2Cl} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{Ph(UL\text{-}^{14}C)CH_3}$$

($A$: $(H_2CO)_n$, HCl, $H_3PO_4$, $CH_3CO_2H$)

A plug flow reactor with a catalyst bed at its midpoint was filled with ZSM-5 (0.8 g) mixed with 1.0 g alpha-alumina. The upper portion of the reactor was filled with glass beads to preheat the incoming reactants. The catalysts were activated at 450°C *in situ* with air flow of ca. 25 cc/h for 24 h followed by a flow of nitrogen for 1 h. The reactor then was cooled to the reaction temperature (220°C). Since the amount of labeled toluene was limited, it was necessary to evaluate the catalytic activity with isomerization of unlabeled xylene. When the desired catalyst activity was obtained the flow of *o*-xylene was replaced by nitrogen to remove xylenes; this was followed by the addition of labeled toluene without carrier gas. After the addition of toluene was completed, the system was flushed with nitrogen and then with an air flow at 220°C. The reactor temperature was gradually increased and held at 450°C for 24 h. Following this regeneration, the above procedure was repeated, except, in this case the toluene that had been collected as a product during the previous run was used as feed. This regeneration and reaction cycle was repeated to provide a conversion that should be greater than that required for the near equilibrium of $^{13}$C in the ring of toluene (Fig. 2, * represents estimated conversion for [$^{14}$C]toluene to give a statistical distribution).

The resulting toluene was then converted at higher temperatures (350°C for toluene (UL $^{14}$C) and 400°C for methyl labeled toluene) to produce benzene, xylenes, and ethylbenzene as major components in the liquid reaction products and very small amounts of $C_1$–$C_4$ gases. Liquid product compositions were obtained by gas chromatographic analysis using one or more of the following columns: 10% OV-101 (12 ft), 5% OV-101, 1.8% BENTONE 34 (6 ft), and

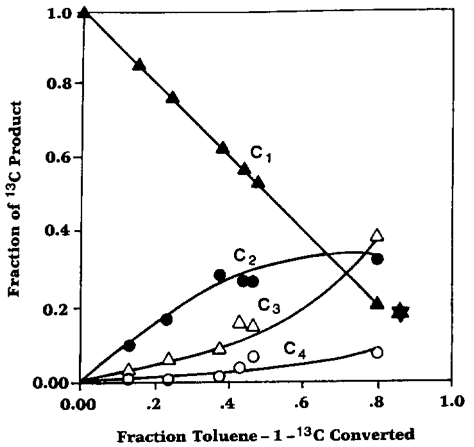


FIG. 2. Isotope distribution in the ring in the products for increasing reaction times for the conversion of [1-$^{13}$C]toluene with a HZSM-5 catalyst at 220°C (from Ref. (*8*)) and the extent of isomerization of [$^{14}$C]toluene (* based upon ring isotope equilibration).

DB-5. The separation of toluene from all other aromatic products was obtained either on high performance liquid chromatography using a LC PAH column or collection of each individual compound as they eluted from the outlet of the thermal conductivity detector at dry ice temperature in a commercially available scintillation cocktail for $^{14}$C radioassy. The LC or GC peak area was used to calculate the amount of each aromatic compound collected for counting.

The analysis for the gas portion of the products was performed on a GC with Carbosive-2 (6 ft) or SP 1700 (15 ft) column connected in series to a Packard Model 894 gas proportional counter. The amount of gases produced was very small; hence, a considerable amount of air was also withdrawn into the sampling syringe. This, together with the multiple isomerization runs, prevented us from determining the specific activity of the gases produced.

At 270°C the amount of disproportionation to benzene and xylene is barely detectable under conditions where the methyl migration has essentially attained equilibration. Isomerization of *o*-xylene to an equilibrium xylene composition before and after the runs with the $^{13}$C- or $^{14}$C-labeled toluene support the view of near equilibrium methyl migration around the ring had occurred in both cases. The product from the final isomerization at 220°C (* in Fig. 2) was then passed over the HZSM-5 catalyst at a higher temperature to increase the amount of disproportionation; obviously, the migration of the methyl group around the aromatic ring at this temperature would occur even more rapidly than at 220°C.

Ethylbenzene could be converted directly to xylenes. However, the conversion of ethylbenzene over this HZSM-5 catalyst shows that dealkylation occurs at higher temperatures in contrast to the direct conversion of ethylbenzene to xylenes. At the higher temperatures, dealkylation is in competition with transalkylation. Thus, at 200°C the benzene/diethylbenzene ratio is ca. 1.0 as expected for transalkylation; at higher temperatures this ratio becomes larger than 1.0 (Fig. 3). Furthermore, at these higher temperatures ethylene produced by dealkylation undergoes secondary reactions to form higher molecular weight products.

Consider the case of uniformly ring-labeled toluene. Ring expansion–contraction can proceed to isotopic equilibration by the

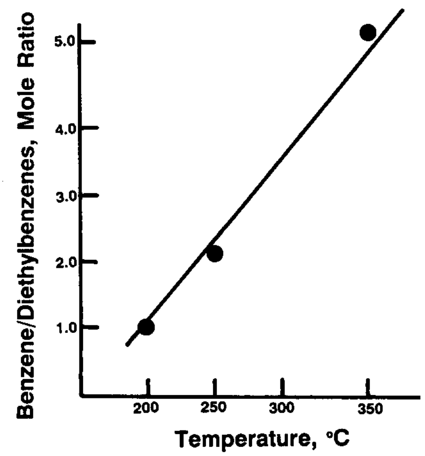
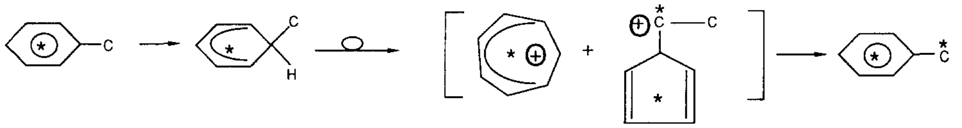
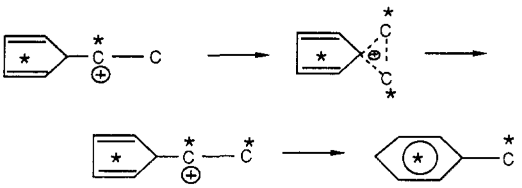


FIG. 3. Extent of toluene disproportionation (as benzene/diethylbenzene) with increasing reaction temperature.

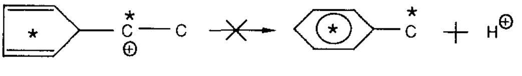
scheme shown below (in the following structures * is used to indicate positions where $^{14}C$ label may occur; the small number of labeled molecules used in $^{14}C$ tracer studies ensure that even the concentration of a doubly labeled molecule is insignificant):



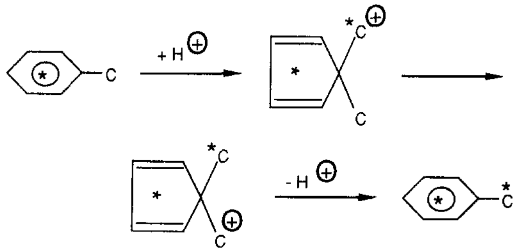
Likewise, a nonclassical ion provides the following reaction pathway:



However, the classical ion is not expected to contribute to the formation of methyl-labeled toluene through the following reaction:



Other isomerization pathways, such as:



involve primary carbocations and are considered unlikely.

For the uniformly $^{14}C$-labeled toluene, all six ring carbons are labeled and the methyl is unlabeled. When isotopic equilibration is attained the $^{14}C$ will become uniformly distributed so that 14.3% of the initial ring activity should be present in the methyl group. Likewise, the $^{14}C$ activity of the methyl-labeled toluene should have decreased from 100 to 14.3% at equilibration.

The data in Table 1 indicate that ring expansion–contraction is a minor reaction relative to methyl migration if, in fact, it occurs. For the ring-labeled toluene, benzene (0.996) and $C_8$ aromatics (1.03) have, within experimental error, the same specific activity as the toluene reactant (1.00). Thus, the maximum amount of $^{14}C$ lost from the ring in forming $C_8$ aromatics is less than 3% of the amount that would be lost if isotopic equilibration had occurred. The data with methyl-labeled toluene are also consistent with a small, if any, contribution of ring expansion–contraction during the period where migration of the methyl group around the aromatic ring has occurred to the equilibrium composition.

Toluene does produce a very small amount of gaseous products during the conversions over the catalyst; however, the small quantity prevented us from making a quantitative measure of the amount of gas produced.

TABLE 1

Carbon-14 Content of the Products of Dealkylation of [$^{14}C$]Toluene over ZSM-5 at 350°C

| Compound | Composition, mole%[a] | | CPM (Toluene = 1.00) | |
|---|---|---|---|---|
| | Methyl labeled | Ring labeled | Methyl labeled | Ring labeled |
| Benzene | 0.98 | 0.45 | [b] | 0.99 |
| Toluene | 97.6 | 99.1 | 1.00 | 1.00 |
| ET-benzene + xylenes | 1.4 | 0.45 | 1.8 | 1.03 |

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[a] Rounding off may cause percentages to differ from 100.

[b] Below detection limit (less than 0.01).

In summary, our results are consistent with the migration of alkyl substituents to their equilibrium composition being much more rapid than the aromatic ring expansion–ring contraction mechanism. The results also suggest that the aromatic ring, once formed in the methanol-to-gasoline conversion, remains intact during the time-scale of the synthesis reactions. While these data do not rule out the possibility of aromatic ring expansion–contraction, they do show that, if it occurs, it must be much slower than other catalyzed reactions—isomerization by alkyl migration or transalkylation—with HZSM-5 catalysts at temperatures up to 350°C. The data indicate that with a ZSM-5 catalyst aromatic ring contraction does not occur under reaction conditions up to 350°C where (1) ethylbenzene undergoes dealkylation and disproportionation to form essentially an equilibrium mixture of diethyl benzenes, (2) xylenes undergo isomerization to an equilibrium composition, (3) methyl migration of $^{13}C$ ring-labeled toluene occurs to produce a statistical distribution of ring label, and (4) methanol undergoes complete conversion to hydrocarbons, predominantly aromatics.

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