HZSM-5-Catalyzed Isomerization of [1-^{13}C]Toluene

INTRODUCTION

The isomerization of alkyl aromatics is a topic important from both a scientific and a technological viewpoint. Early work on this reaction utilized homogeneous catalysts; aluminum chloride is an example of a widely used catalyst. The results from most kinetic studies with numerous alkyl aromatic reactants were consistent with a reaction mechanism in which alkyl groups migrate around the ring by a series of 1,2-alkyl shifts (for example, see Refs. (1–4)); however, there were exceptions to this mechanism (for example, see Ref. (5)). With the availability of carbon isotopes, the applicability of a 1,2-methyl migration mechanism was demonstrated for toluene. Steinberg and Sixma (6) isomerized [1-^{14}C]toluene with an aluminum bromide–hydrogen bromide catalyst and found that migration of ^{14}C from 1 position in the ring to other ring positions proceeds via a series of consecutive 1,2 shifts of the methyl group. Roberts and Roengsumran (7) carried out similar isomerization studies with ^{13}C rather than ^{14}C; these workers' ^{13}C data supported the elegant ^{14}C studies. They (7) found that isomerization with ethyl and n-propyl side chains was more complex than the simple 1,2-methyl migration case.

There is ample evidence to support the view that xylene isomerization follows a simple 1,2-methyl migration scheme with an aluminum chloride catalyst (1–4, 8) and that the contribution of 1,3 migrations is immeasurably small. With heterogeneous catalysis, diffusional influences may impart a kinetic disguise so that 1,3-methyl migration may appear to make a significant contribution even though in the correct mechanism, 1,2-methyl migration is the dominant, or even only, reaction pathway. At higher reaction temperatures with acidic silica–alumina heterogeneous catalysts, the 1,2-methyl migration mechanism dominates but not to the extent that it does with the homogeneous metal chloride catalyst (9). When an even smaller-pore heterogeneous catalyst, a LaY zeolite, is used for xylene isomerization, methyl shifts other than 1,2 migrations appear to make a significantly larger contribution to the overall conversion than for the amorphous, larger-pore silica–alumina catalyst (10, 11). When the even smaller-pore zeolite ZSM-5 was used, the products had essentially the equilibrium composition (12). Thus, the results with heterogeneous catalysts could be viewed as supporting, on the one hand, a diffusion disguise in which a series reaction mechanism of 1,2-methyl migrations appear experimentally as a coupled three-component reaction network or, on the other hand, to involve an isomerization mechanism that proceeds by a transalkylation mechanism (13).

It was therefore of interest to learn whether ZSM-5-catalyzed isomerizations followed the typical mechanism of a series of 1,2-methyl shifts. Toluene, since it has a considerably smaller kinetic diameter than o- or m-xylene, should have the least diffusional resistance of any aromatic compound suitable for isomerization studies. Consequently, toluene in which the ring was labeled with ^{13}C was converted with a portion of the same ZSM-5 used by Collins et al. (12) in their xylene isomerization studies in which the products were near their equilibrium value.

EXPERIMENTAL

A sample of ammonium ZSM-5 was calcined at 550°C. After calcination the sample had an X-ray diffraction pattern identical to the one obtained from a similarly treated sample of ZSM-5 supplied by Mobil Oil Corp. The ZSM-5 catalyst (0.8 g) was diluted with low-surface-area alumina (2 g) that had been calcined at 1200°C. A plug flow reactor contained the catalyst powder at its midpoint; a thermowell extended to the middle of the catalyst bed. The upper part of the reactor was filled with glass beads to serve as preheater. Products were collected after being passed through a water-cooled condenser. The catalyst was activated at 450°C *in situ* in ca. 25 ml/h air flow for 24 h; prior to use it was flushed with flowing nitrogen at 450°C and cooled to reaction temperature (225°C) in a nitrogen flow. *o*-Xylene was then pumped into the reactor and the nitrogen flow was terminated. Xylene samples were collected at intervals and analyzed for xylene isomer composition with a DB-5 or Bentone–diisodecylphthalate column. When the xylene conversion attained a predetermined level, (1) the xylene flow was terminated, (2) the reactor system was flushed with nitrogen to remove xylene vapors and the sample collector was drained of xylenes and cleaned, (3) ^{13}C-labeled toluene flow was initiated, and (4) the ca. 6 to 10 ml toluene product sample was collected. Since the amount of ^{13}C-labeled toluene was limited, it was necessary to evaluate the catalytic activity with unlabeled xylene isomerization. Following collection of the toluene, the reactor system was flushed with nitrogen and an *o*-xylene flow initiated. Since the xylene conversion undergoes a steady decline, we were able to ensure that no unusual activity changes resulted when the reactant was changed from *o*-xylene to toluene. Following termination of the reactant feed, the system was flushed with nitrogen and then air flow as initiated with the reactor at 220°C. The reactor temperature was gradually increased to 450°C and held at this temperature for 24 h. Following this regeneration, the above procedure was repeated, except in this case the toluene reactant was the toluene that had been collected as a product during the previous run. This regeneration and reaction cycle was repeated to provide the conversion range shown in the next section.

Carbon-13 NMR spectra were recorded for the toluene sample collected following each run. A total of 500 transients were acquired for each spectrum. The integral of each carbon signal was recorded three times and the average of these values was used in calculating the isotope distribution. The absolute intensity per carbon varies with ring position; to compensate for this, correction factors were determined for unenriched toluene and our values were very close to those in Ref. (7). The conversion was based on the loss of ^{13}C enrichment at ring position 1; that is, the amount of ^{13}C-enriched toluene reactant was the total ^{13}C at ring position minus one-half the total ^{13}C at the ring position 2 (or 3) of the reactant. The conversion was then the fraction of ^{13}C enrichment at position 1 that was lost when the reactant was passed over the catalyst. The amount of product labeled at a specific ring position was then the increase in ^{13}C at each ring position divided by the total enrichment at ring position 1 in the original toluene feed.

RESULTS AND DISCUSSION

The data obtained by Steinberg and Sixma in their classic isomerization experiment is reproduced in Fig. 1 as the fractional approach to equilibrium. The data in Fig. 1 show the ^{14}C distribution during the time course of the reaction that is expected for the series mechanism

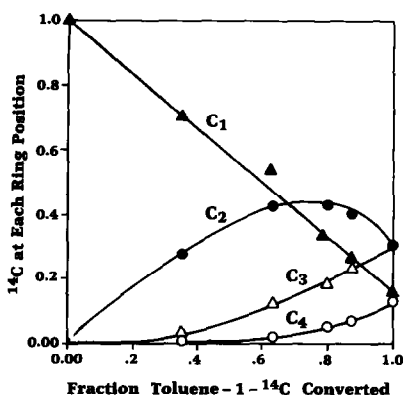The data obtained with a ZSM-5 catalyst are shown in Fig. 2. The experimental

FIG. 1. Isotope distribution in the products for increasing reaction times for the conversion of [1-^{14}C]toluene with AlBr$_3$/HBr (data estimated from figure in Ref. (6)).
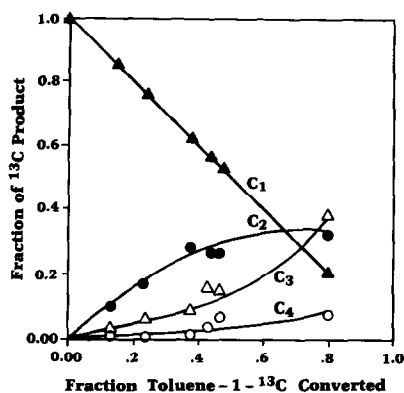

FIG. 2. Isotope distribution in the products for increasing reaction times for the conversion of [1-^{13}C]toluene with a HZSM-5 catalyst at 220°C.

problems encountered in operating with a small quantity of [1-^{13}C]toluene in a plug flow reactor introduces uncertainties in the cumulative reaction time; hence the comparison is based upon fractional conversion of [1-^{13}C]toluene rather than by reaction time as was done in Ref. (6).

The ^{13}C distribution in Fig. 2 is very similar to that presented in Fig. 1 for the homogeneous catalyst; the only difference is that with the homogeneous catalyst the amount of the initial isomerization product, [2-^{13}C]toluene, from a mechanism involving a series of 1,2-methyl shifts attains a slightly higher maximum value. For both catalyst systems, the initial product as conversion time approaches zero is the product labeled at ring position 2; the concentration of products labeled at ring positions 3 and 4 appears to approach zero as time approaches zero.

The data for ZSM-5 conversion of [1-^{13}C]toluene strongly supports a conventional mechanism by a series of 1,2-methyl shifts. The toluene "isomerization" appears to be nearly as free from diffusional disguise as the homogeneous acid-catalyzed reaction. Thus, even though there is apparently severe diffusional disguise in the kinetics of xylene isomerization with a por-

tion of this ZSM-5 catalyst, toluene follows an isomerization mechanism consistent with a simple acid-catalyzed series of 1,2-methyl shifts.

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