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Carbon-14 Rearrangement in the Alkylation of Benzene with [1-^{14}C]Ethanol over ZSM-5 Catalyst

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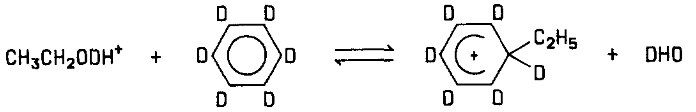
[α, β-^{14}C]Ethylbenzene produced from benzene and [1-^{14}C]ethanol using an acidic zeolite catalyst, HZSM-5, at 300°C had ^{14}C activity equally distributed between the α- and β-positions of the ethyl side chain. Thus, the carbon label in [1-^{14}C]ethanol was 100% scrambled in the ethylbenzene product. The same reaction at 200°C produced [α, β-^{14}C]ethylbenzene with approximately 18% excess ^{14}C activity at the α-position; this result corresponds to 82% scrambling of the carbon-14 label. Under these reaction conditions, the nearly equal α and β activity make it appear that little exchange of carbon between the ring and side chain of ethylbenzene occurred.

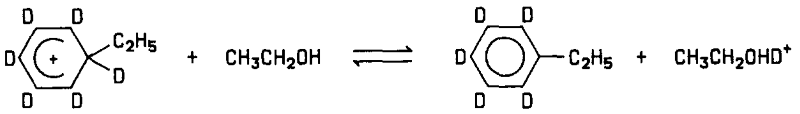
INTRODUCTION

Zeolites have been known for 2 centuries or more. Their ability to dehydrate (reversibly) without change in the sharpness of their crystal form was demonstrated by at least 1840 (*1*). Recognition of their ability to serve as molecular sieves by excluding molecules larger than the pore diameter dates to at least 1925 (*2*). However, the widespread use of zeolites as catalysts did not occur until the 1960's when Plank and Rosinski (*3*) discovered that these materials were more active and stable cracking catalysts than the amorphous silica–alumina cracking catalysts in use at that time. Zeolite cracking catalysts quickly gained widespread commercial acceptance (*4*) and are now the most important catalysts used in the petroleum industry (*5*). The technological importance of zeolite catalysts has led to widespread study of these materials and the synthesis of many new zeolites.

One of the important synthetic zeolites, ZSM-5 (*6*), has the property of selectively producing high yields of gasoline-range hydrocarbons from methanol (*7*). Alkylation of initial aromatic rings by an alcohol molecule is one important reaction in the gasoline synthesis. As part of a more extensive study, Anderson *et al.* (*8*) alkylated perdeuterobenzene with undeuterated ethanol. They interpreted their data to support a mechanism in which only the carbinol carbon becomes bonded to the ring as illustrated in the reaction scheme.

$$CH_3CH_2OH + DO\,Zeol \rightleftharpoons CH_3CH_2ODH^+ + O^-\,Zeol \quad (1)$$


(2)


(3)

$$CH_3CH_2OHD^+ + O^-\,Zeol \rightleftharpoons CH_3CH_2OH\ (\text{or } D) + D(\text{or } H)O\,Zeol \quad (4)$$

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This result is important since it would restrict, or even eliminate, many of the mechanisms proposed for the methanol-to-gasoline conversion (7). Another experimental approach to determine the validity of a mechanism comprised of reactions (1)–(4) utilizes ^{14}C tracer; this paper details results obtained from the alkylation of benzene with [1-^{14}C]ethanol.

EXPERIMENTAL

Materials. [1-^{14}C]Ethanol was supplied by New England Nuclear Corporation. Other chemicals used in the study were commercially available materials of reagent grade and were used without further purification. The catalyst was prepared by calcining an ammonia exchanged material at 500°C. The ZSM-5 catalyst, after calcination, had an X-ray diffraction pattern that was identical to the one obtained from a similarly treated sample of ZSM-5 supplied by Mobil Oil Corporation.

Methods. A plug-flow reactor contained a mixture of 1.1 g ZSM-5 and 2.1 g α-alumina at its midpoint where the mixture was in contact with a thermowell. The reactor had gas and liquid inlets and the upper portion of the reactor was filled with glass beads that served as a preheater. The reactor was attached to a condenser, maintained at 10–15°C, which in turn led to a sample receiver also maintained at 10–15°C. The effluent from the first receiver passed through a second receiver kept at -50 ± 5°C, then a condenser also at -50 ± 5°C, and finally through a drying tube to a gas burette.

Prior to a reaction run, the catalyst was activated in a slow air flow at 480–500°C for 4 or more hours. After air calcination, the apparatus was flushed with nitrogen prior to initiating reactant flow.

Liquid product compositions were obtained by gas chromatographic analysis using one or more of three columns: 10% OV-101 (12 ft.); 5% OV-101 plus 1.8% Bentone 34 (6 ft.), and 10% Carbowax 20M (10 ft.). Relative ^{14}C activities of some samples were obtained by passing the effluent from the GC to a Packard Model 894 gas proportional counter. Gas mixtures were analyzed using a Carle Model 311H analyzer.

Carbon-14 radioassay was accomplished on distillation fractions enriched in the ethylbenzene fraction. Aqueous permanganate was used to oxidize a portion of each ethylbenzene fraction to benzoic acid which was purified by two recrystallizations. Liquid scintillation counting, using commercially available scintillation cocktail, was used for ethylbenzene fractions and for benzoic acid.

RESULTS

Several preliminary runs with unlabeled compounds were made to determine reaction product patterns so that the selectivity properties of the ZSM-5 catalyst used in the present work can be related to results reported by other investigators.

Ethylene over ZSM-5 at 200°C and higher temperatures gave liquid hydrocarbons in high conversion. At 225°C and WHSV 1.5 hr^{-1} ethylene was more than 90% converted to liquid hydrocarbons with production of approximately equal weight fractions of gasoline-range and C_4/C_5 hydrocarbons. The gasoline-range liquid consisted mainly of aromatics, approximately 70 wt%, distributed as shown in Table 1.

In another experiment, a mixture of ethylene and benzene was reacted over ZSM-5 at 200°C and WHSV 12 hr^{-1}, with benzene in slight molar excess over ethylene. For the initial period of this experiment the feed was composed of ethylene only. During this time ethylene was converted to liquid hydrocarbons in high yield, and 10 to 15% of the final gasoline-range liquid was produced from ethylene before benzene was included in the feed. The total gasoline-range mixture produced consisted of 85 wt% aromatics, distributed as shown in Table 1.

Ethanol was converted over ZSM-5 at temperatures of 150, 175, and 200°C, in succession, and at WHSV 6 hr^{-1}. At each reaction temperature the rate of gas production

TABLE 1

Distribution of Aromatics in the Gasoline-Range Liquids Formed from Ethylene and an Ethylene–Benzene Mixture

Aromatic	Aromatic, mole% formed from	
	Ethylene, 225°C	Ethlyene/benzene, 220°C
Benzene	5	37
Toluene	24	7
Ethylbenzene	7	27
Xylenes[a]	32[b]	8[c]
C_3 Alkylbenzenes	23	11
C_4 Alkylbenzenes	10[d]	10[d]

[a] Equilibrium xylene composition; $o:m:p$ = 1.0:2.6:1.1 at 225°C.

[b] Xylene, $o:m:p$ = 1.0:2.4:1.2.

[c] Xylene, $o:m:p$ = 1.0:2.8:2.0.

[d] At 225°C less than 40% of C_4 alkylbenzenes were diethylbenzene but at 200°C more than 80% of the C_4 alkylbenzenes were diethylbenzenes.

decreased during the run of 0.5 h duration. The yields of product types collected at each temperature are summarized in Table 2.

The benzene plus [1-^{14}C]ethanol reaction was carried out with a mole ratio of benzene/ethanol of 2.5 and a WHSV of approximately 7 hr^{-1}. For the conversion of this mixture at 200°C about one third of the starting ethanol was present in the form of ethylbenzene and one third was present in the diethylbenzene product. Ethylene, the major component of the gaseous products, contained about 12–13% of the radiolabel of the ethanol reactant.

TABLE 2

Conversion of Unlabeled Ethanol over ZSM-5 (1 g diluted in 2 g of α-alumina) at 150–200°C

Production	Products, wt%		
	150°C	175°C	200°C
Hydrocarbon gas[a]	9	16	9
C_4–C_5 hydrocarbons[b]	5	34	46
C_5 plus hydrocarbons	None	Low	45[c]

[a] Essentially ethylene (80–90% of total gas).

[b] Contents of the −50°C receiver; contaminated with small amounts of higher boiling hydrocarbons, propane and propene.

[c] By difference; ethanol was 100% converted at temperatures above 180°C for our reaction conditions.

TABLE 3

Gasoline-Range Hydrocarbon Distribution for the Conversion of Benzene/[1-^{14}C]Ethanol with ZSM-5

Component	Products, mole%	
	200°C	300°C
Aliphatics	0.7	0.4
Benzene	71.5	69.6
Toluene	0.1	2.0
Ethylbenzene	15.4	24.6
Xylenes	0.1[a]	1.1[b]
C_3 Alkylbenzenes	4.4	0.6
C_4 Alkylbenzenes	7.9	1.8

[a] p-Xylene, 0.05%; m- plus o-xylene, 0.05%.

[b] p-Xylene, 0.3%; m-xylene, 0.5%; o-xylene, 0.2%.

The aromatic distributions obtained at 200 and 300°C with the benzene/[1-^{14}C] ethanol mixture are given in Table 3. A known amount of unlabeled ethylbenzene was added to the liquid product collected during the conversion of the benzene/[1-^{14}C]ethanol mixture at 300°C. Distillation of these samples produced fractions enriched in ethylbenzene; for the 300°C products distillation two fractions were collected and the compositions of these were similar (Table 4).

The ^{14}C activity of the ethylbenzene fraction and the benzoic acid was obtained from liquid scintillation measurements. There was a slight amount of self-quenching for the benzoic acid measurements; this is reflected in the data in Table 5 for the 300°C run data. Xylene was used as a solvent for the 200°C products scintillation measurements so that self-quenching was not a problem. The infinite dilution ratio was used for the following calculations with the 300°C data.

TABLE 4

Composition of Ethylbenzene-Rich Fractions Obtained from the Distillation of the Products, Diluted with Unlabeled Ethylbenzene, from the Conversion of Benzene/[1-^{14}C]Ethanol

Component	Composition, mole%		
	200°C	300°C, fraction 1	300°C, fraction 2
Benzene	2.2	5.0	1.4
Toluene	0.4	7.3	1.8
Ethylbenzene	76.5	83.3	89.8
Xylenes	0.9[a]	2.2[b]	4.0[c]
C_3 Alkylbenzenes	15.4	1.3	1.3
C_4 Alkylbenzenes	4.6	0.9	1.7

[a] *p*-Xylene, 0.6%; *m*-xylene, 0.3%; *o*-xylene, <0.1%.

[b] *p*-Xylene, 0.7%; *m*-xylene, 1.1%; *o*-xylene, 0.4%.

[c] *p*-Xylene, 1.1%; *m*-xylene, 1.9%; *o*-xylene, 1.0%.

TABLE 5

Ratio of the Molar ^{14}C Activities of Ethylbenzene [α, β-^{14}C]/[*carboxyl*-^{14}C]Benzoic Acid from [1-^{14}C]Ethanol Benzene Conversions with ZSM-5

Sample	Activity ethylbenzene/ activity benzoic acid		
	0.3 M	0.015 M	Infinite dilution
300°C, Ethylbenzene, fraction 1	1.85_5	1.81_5	1.80
300°C, Ethylbenzene, fraction 2	2.09_5	2.07_3	2.05_7
200°C, Ethylbenzene fraction	—	—	2.01[a]

[a] Self-quenching effects were small and approximately equal for labeled ethylbenzene and derived benzoic acid in the solvent used (xylene) and the activity ratio did not very with concentration, within experimental error.

From the radiochromatogram it is possible to calculate relative activities in the aromatic fractions and these are shown in Table 6. From some of the products the concentration is so low that a reliable relative activity was not obtained. For ethylbenzene and higher products the relative activity is that expected for benzene alkylation by radioactive ethanol.

For alkylation as shown in Eqs. (1)–(4), the ratio of specific activity in ethylbenzene to that of benzoic acid will be 1.0. If, on the other hand, the two carbons of ethanol equilibrated prior to, during or following alkylation the above ratio should be 2.0. It is clear that the data in Table 5 is inconsistent with the alkylation mechanism outlined in Eqs. (1)–(4) and is consistent with a mechanism that requires nearly, or complete, equilibration of the two carbons in the ethanol. The ratio in Table 5 would be 1.0 for any aromatics formed directly from ethanol and could, therefore, cause the activity ratio to be lower than the 2.0 expected for an equilibrated alklyation mechanism.

TABLE 6

Molar ^{14}C Activities of Various Aromatic Types Relative to that of Ethylbenzene Calculated from Proportional Counting of the Gas Chromatographic Effluent

Product	Relative ^{14}C activity[a]	
	200°C	300°C
Tolune	[b]	0.86
Ethylbenzene	1.00	1.00[c]
Xylenes	[b]	1.3–1.4[d]
C_3 Alkylbenzenes	1.5 ± 0.1	[f]
Diethylbenzene	1.8 ± 0.2[e]	[f]

[a] Determined using dual detectors in sequence; a thermal conductivity GC cell followed by combustion to CO_2 and detection by a proportional counter.

[b] Not determined due to low concentration of this product.

[c] Before dilution with unlabeled ethylbenzene.

[d] Estimated indirectly as described in text.

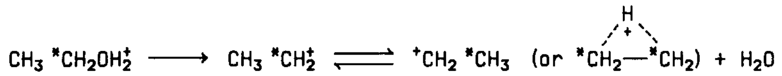
[e] Lower precision due to peak broadening in the proportional counter.

[f] Not determined because of low yield and number of these products.

DISCUSSION

The discovery of the methanol-to-gasoline (MTG) conversion elicited much interest in the mechanism for this complex reaction series (*7*). The mechanism involves, among others, formation of a C–C bond from a C_1 fragment generated at an acidic catalyst site, a chain growth mechanism, a mechanism for aromatics formation and alkylation of aromatics. There is a considerable diversity of opinion on most of these topics.

The validity of the mechanism outlined in reactions (1)–(4) would severely limit the mechanistic possibilities for one or more of the reactions listed in the above paragraph. However, the ^{14}C data clearly do not support such a mechanism. Rather, alkylation of benzene in the temperature range of Ref. (*8*) occurs, according to our ^{14}C results, with nearly complete carbon equivalency of the two carbons of ethanol. This result could occur by either reaction (5) or (6)



$$CH_3{}^*CH_2OH_2^+ \longrightarrow CH_3{}^*CH_2^+ \rightleftharpoons {}^+CH_2{}^*CH_3\ (\text{or}\ {}^*CH_2\overset{\overset{H}{+}}{—}{}^*CH_2) + H_2O \qquad (5)$$

$$CH_3{}^*CH_2OH_2^+ \longrightarrow CH_3{}^*CH_2^+ \xrightarrow{O^-Zeol} CH_2{}^*CH_2 + HO\,Zeol \qquad (6)$$

The ethylene formed in reaction (6) would then be utilized in acid-catalyzed alkylation of benzene.

The results for the conversion of ethylene with ZSM-5 in Ref. (*8*) and the present work are rather different since Ref. (*8*) reported that less than 1 mole% of higher hydrocarbons were formed at 187–232°C. Ethylene was almost completely converted to ethylbenzene (Ref. (*8*)) whereas nearly all ethylene was converted to higher carbon compounds at 200°C in the present study. Likewise, even at 238°C, benzene and ethylene were not appreciably (<2 mole%) converted to higher carbon number compounds, predominately ethylbenzene, in the earlier study (*8*). Since similar conditions were used, the differences between the results from the two studies is most likely due to differences in the catalyst or the reactor operation. The contact time in our studies was not longer than in Ref. (*8*) so that the difference is most likely due to differences between the ZSM-5 catalysts used in two studies.

The results obtained in the present study were not designed to determine the extent of exchange between the ring and alkyl carbons. However, any exchange of side chain ^{14}C into the ring would have been present in both ethylbenzene and benzoic acid; this would have reduced the ratio from the observed 100% scrambling. Hence, for the ethylbenzene product at 300°C it appears that essentially all of the ^{14}C is in the side chain and that ring expansion–contraction did not occur.

Aromatic co-catalysis has been advanced by Mole and co-workers (*9, 10*). The results from the present study support the view that the reaction of benzene with ethanol (or a product from ethanol) is more rapid than is the formation of higher weight products from ethanol. Ethanol, in the absence of added benzene, is converted at 300°C to higher hydrocarbon products in high yield. However, under similar conditions with excess benzene present, we calculate that only about 10% of the toluene produced was formed directly from ethanol (Table 6). Hence, benzene serves, under our reactions conditions, as an excellent trap for one or more precursors for chain growth. Since the predominate aromatic product is ethylbenzene it may be inferred that benzene trapping of a C_2 chain precursor is more rapid than is the first step of the chain growth mechanism.

In summary, alkylation of benzene with ethanol could occur by either an ethyl carbonium ion in which hydrogen migration occurs more rapidly than does addition to the ring or that ethylene was an intermediate in the reaction mechanism. The results obtained at 300°C are inconsistent with alkylation in which only the carbinol carbon adds to the ring to become the α carbon in the side chain. The results are in agreement with those mechanisms that provide for equivalency of the carbons in ethanol prior to the alkylation step.

Ethylbenzene produced in the alkylation of benzene with [1-^{14}C]ethanol at 200°C showed 17% excess ^{14}C activity at C_α (83 ± 2% scrambled). At this lower temperature a mechanism involving direct alkylation of benzene by ethanol appears to be in competition with the alternative reaction path(s) involving carbonium ion and/or ethylene formation from ethanol. However, more detailed studies at lower severities are required to elucidate the role of this possible direct alkylation mechanism.

ACKNOWLEDGMENT

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