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# The Mechanism of Catalytic Isomerization of Xylenes: Kinetic and Isotopic Studies

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The vapor-phase isomerization of xylenes over a silica–alumina catalyst containing 4 wt% nickel has been investigated in the presence of excess hydrogen at 400°C and pressures up to 15 atm. The results clearly indicate that the three isomers are interconverted via the consecutive reaction,

*ortho* ⇄ *meta* ⇄ *para.*

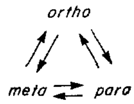
Hydrogenolysis to toluene and disproportionation to trimethylbenzenes are the two major competing reactions. Additional experiments carried out with deuterium-labeled *p*-xylene show that the isomerization proceeds almost exclusively by intramolecular 1,2 shifts of the methyl groups around the aromatic ring.

## INTRODUCTION

A substantial number of publications and patents dealing with catalytic systems for the gas-phase isomerization of xylenes involve the use of hydrogen and acidic or dual functional catalysts. There is still some controversy as to whether the reaction takes place consecutively (*1*, *2*),

ortho ⇄ meta ⇄ para,

or through the mutual interconversion of the three isomers (*3*, *4*):



Furthermore, to our knowledge, it has not been conclusively proven whether the isomers are really formed by transalkylation (*5*), i.e., by intermolecular displacement reactions of the $\text{s}_\text{n}2$ type, or by intramolecular 1,2 shifts of the methyl groups as suggested by others, both for the liquid (*6*) and the gas phase (*7*).

We have recently studied this catalytic reaction (*8*) and have obtained some additional data concerning the above mechanistic considerations, which we now report.

## EXPERIMENTAL METHODS

All experiments were conducted in a conventional fixed-bed stainless steel tubular reactor, heated electrically and equipped with a minipump for feeding the liquid hydrocarbon and a fine metering valve to regulate the hydrogen flow. The desired working pressure was adjusted by means of a back-pressure regulator and the temperature in the catalyst bed was measured with a chromel–alumel thermocouple located in a coaxial thermowell.

Reaction products were condensed at 15°C and analyzed by gas chromatography at 80°C in a column of 16 wt% silicone oil DC-200Me and 3 wt% Bentone on Chromo-

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TABLE 1

Isomerization of *o*-Xylene on SiANi-4 at 400°C with $H_2/HC = 4$ mole/mole

| Catalyst weight (g) | $W/F^a$ (g·hr/mole) | Pressure (atm) | Product analysis (mole%)[b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | *m*-X | *p*-X | T | B | TMBs |
| 5.000 | 2.52 | 0.93 | 3.0 | — | 0.2 | 0.1 | 0.1 |
| 0.500 | 5.38 | 0.93 | 5.4 | 0.1 | 0.4 | 0.1 | 0.2 |
| 2.000 | 11.31 | 0.93 | 14.1 | 0.9 | 1.0 | 0.2 | 0.7 |
| 2.000 | 15.08 | 0.93 | 17.6 | 1.6 | 1.2 | 0.2 | 1.2 |
| 2.000 | 22.62 | 0.93 | 24.9 | 3.0 | 2.0 | 0.2 | 1.3 |
| 2.000 | 30.16 | 0.93 | 30.1 | 4.9 | 2.8 | 0.3 | 1.8 |
| 4.000 | 45.24 | 0.93 | 38.1 | 8.6 | 4.3 | 0.4 | 2.4 |
| 0.100 | 0.24 | 14.93 | 2.1 | 0.1 | 0.1 | — | 0.03 |
| 0.100 | 0.29 | 14.93 | 2.3 | 0.2 | 0.1 | 0.06 | 0.03 |
| 0.100 | 0.73 | 14.93 | 5.2 | 0.8 | 0.2 | 0.06 | 0.1 |
| 2.000 | 5.80 | 14.93 | 18.7 | 4.5 | 1.5 | 0.1 | 1.4 |
| 2.000 | 14.71 | 14.93 | 21.8 | 6.9 | 2.7 | 0.2 | 2.2 |

[a] $F$ = Hydrocarbon feed.

[b] The remainder up to 100% is the unreacted feed.

sorb W (80–100 mesh), with He as carrier gas (Perkin–Elmer F-990 with hot wire detector).

*Analysis of deuterated xylenes.* In the tracer experiments the mixtures of deuterated xylenes were analyzed with an AEI MS 30 mass spectrometer connected to a Pye Unicam gas chromatograph, Series 104. Conditions in the chromatograph were similar to those mentioned before, while for the spectrometer we used the following: ion source temperature = 150°C; filament current = 100 mA; accelerating voltage = 70 eV; mass span = 103 to 120; and variable sensitivity depending on the concentration of each isomer in the mixture.

We found in all cases that the distribution of deuterated species of each of the three xylenes changed along its corresponding chromatographic peak. That is to say, although we have only three peaks in the chromatogram for the $C_8$ fraction, the different deuteroderivatives of each isomer are not evenly distributed along the corresponding peak. It was then necessary to record 30 or more mass spectra in each chromatographic peak in order to obtain a good measurement of the true raw mass peak heights. The accuracy of this procedure was checked using known mixtures of *p*-$C_8H_4D_6$ and *p*-$C_8H_{10}$.

After this, the corrected mass peak heights were calculated following the usual corrections to allow for naturally occurring heavy carbon and deuterium and for fragmentation of the molecules (*9*) on the assumption that the energy required to break a C–H and C–D bond is the same, independent of the deuterium content in the molecule.

*Catalyst and chemicals.* The catalyst containing 4 wt% nickel (SiANi-4), was prepared by impregnation without excess solution using nickel nitrate (Riedel de Haën, cp, max. 0.01% cobalt) and commercial silica–alumina as support (Ketjen low alumina 3P, Test No. 14437; 13.1% $Al_2O_3$; surface area, 410 ± 10 $m^2/g$; pore volume, 0.47 ml/g). The silica–alumina was previously treated for 3 hr at 500°C in air. After impregnation the catalyst was dried at 120°C, then calcined in air for 3 hr at 500°C, and finally reduced in $H_2$ also for 3 hr at 500°C (surface area 420 ± 10

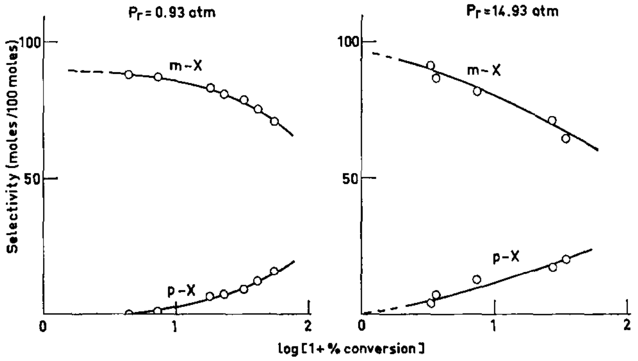


FIG. 1. Isomerization of o-xylene.

$m^2/g$; pore volume 0.48 ml/g). The average particle size was 0.105 mm, chosen in order to avoid diffusional limitations (*10*).

Reactants used in this work were high-purity hydrogen (Seo > 99.9%) and pure-grade xylenes (Scharlau, Ferosa 99% by gc). They were not further purified before use.

Hexadeuterated *p*-xylene ($CD_3$–$C_6H_4$–$CD_3$) was purchased from Merck, Sharp and Dohme of Canada, Ltd.

## RESULTS AND DISCUSSION

### *Kinetic Data*

Two series of experiments were carried out with *o*-xylene (*o*-X) at 400°C, constant hydrogen ($H_2$) to hydrocarbon (HC) ratio, and different values of weight of catalyst per hydrocarbon feed rate (*W/F*), the first series at 0.93 and the second at 14.93 atm of total working pressure.

The results, summarized in Table 1, show that at both pressures the isomerization is the major reaction, with *m*-xylene (*m*-X) as primary product and *p*-xylene (*p*-X) as secondary product. On the other hand, minor products formed by disproportionation and hydrogenolysis include toluene (T), benzene (B), and the trimethylbenzenes (TMBs). The fact that *m*-xylene is the only primary isomerization product is better shown in Fig. 1, in which we have

TABLE 2

Isomerization of *m*-Xylene on SiANi-4 at 400°C with $H_2/HC$ = 4 mole/mole

| Catalyst weight (g) | $W/F^a$ (g·hr/mole) | Pressure (atm) | Product analysis (mole%)[b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | *p*-X | *o*-X | T | B | TMBs |
| 0.300 | 1.09 | 0.93 | 1.1 | 0.5 | 0.1 | — | 0.04 |
| 1.000 | 4.73 | 0.93 | 4.7 | 2.8 | 0.7 | 0.02 | 0.4 |
| 1.000 | 10.30 | 0.93 | 9.1 | 6.0 | 1.1 | 0.03 | 0.6 |
| 6.000 | 13.76 | 0.93 | 12.1 | 8.7 | 1.1 | 0.03 | 0.6 |
| 6.000 | 21.74 | 0.93 | 15.1 | 11.2 | 1.2 | 0.04 | 0.8 |
| 6.000 | 44.12 | 0.93 | 22.0 | 18.2 | 7.8 | 0.4 | 3.6 |
| 0.100 | 0.75 | 14.93 | 2.2 | 1.0 | 0.1 | — | 0.03 |
| 0.100 | 1.02 | 14.93 | 2.7 | 1.4 | 0.1 | 0.02 | 0.03 |
| 0.400 | 2.94 | 14.93 | 7.6 | 5.4 | 0.7 | 0.1 | 1.1 |
| 2.000 | 5.78 | 14.93 | 14.6 | 11.1 | 1.9 | 0.1 | 2.2 |
| 2.000 | 7.27 | 14.93 | 15.4 | 11.9 | 1.9 | 0.1 | 2.2 |
| 2.000 | 14.60 | 14.93 | 16.2 | 12.9 | 3.7 | 0.3 | 4.6 |

[a,b] See footnotes to Table 1.

TABLE 3

Isomerization of *p*-Xylene on SiANi-4 at 400°C with $H_2$/HC = 4 mole/mole

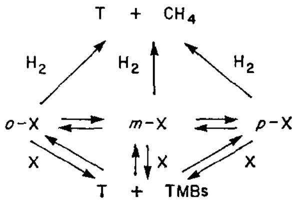
| Catalyst weight (g) | $W/F$[a] (g·hr/mole) | Pressure (atm) | Product analysis (mole%)[b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | *m*-X | *o*-X | T | B | TMBs |
| 0.300 | 1.09 | 0.93 | 1.8 | — | 0.3 | — | 0.2 |
| 0.300 | 3.09 | 0.93 | 4.9 | 0.06 | 0.6 | — | 0.4 |
| 0.300 | 4.54 | 0.93 | 7.1 | 0.2 | 0.7 | 0.1 | 0.6 |
| 6.000 | 13.95 | 0.93 | 22.4 | 1.9 | 1.8 | 0.1 | 1.7 |
| 6.000 | 17.34 | 0.93 | 25.9 | 2.8 | 2.4 | 0.2 | 1.9 |
| 6.000 | 44.12 | 0.93 | 32.0 | 5.6 | 5.5 | 0.2 | 2.8 |
| 0.050 | 0.14 | 14.93 | 3.0 | 0.2 | 0.2 | — | 0.1 |
| 0.100 | 0.29 | 14.93 | 5.9 | 0.6 | 0.4 | — | 0.4 |
| 0.100 | 0.74 | 14.93 | 11.0 | 0.8 | 0.8 | 0.02 | 0.8 |
| 2.000 | 5.78 | 14.93 | 25.8 | 5.9 | 4.4 | 0.1 | 4.0 |
| 2.000 | 14.71 | 14.93 | 35.8 | 9.2 | 5.4 | 0.2 | 5.1 |

[a,b] See footnotes to Table 1.

plotted the selectivity to the *meta* and *para* isomers as a function of log [1 + percentage conversion]. This is a modified Schneider and Frolich selectivity diagram (*11, 12*) in which the percentage conversion abscissa is plotted on a logarithmic scale in order to expand the data at low conversions and compress the less significant high-conversion points.

Similar types of experiments were performed starting from *meta*- and *para*-xylene in order to determine product distributions with the advancement of the reaction. The results are summarized in Tables 2 and 3, and the corresponding selectivity diagrams for the isomerization appear in Figs. 2 and 3. We can see that *m*-xylene produces both *ortho* and *para* right from the beginning of the reaction, whereas *p*-xylene isomerizes initially to *meta* and then to the mixture of *meta* plus *ortho*.

On the basis of all this kinetic information we propose the following overall reaction scheme,



in which the isomerization steps are con-

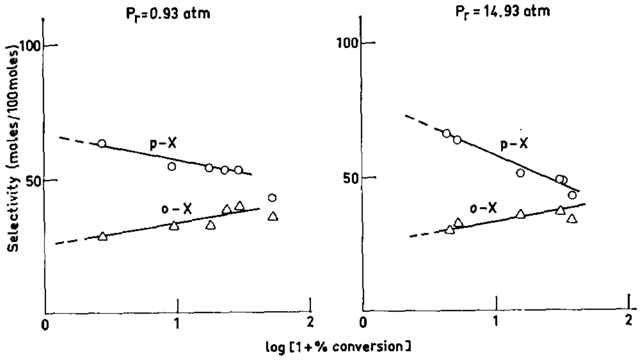


FIG. 2. Isomerization of *m*-xylene.

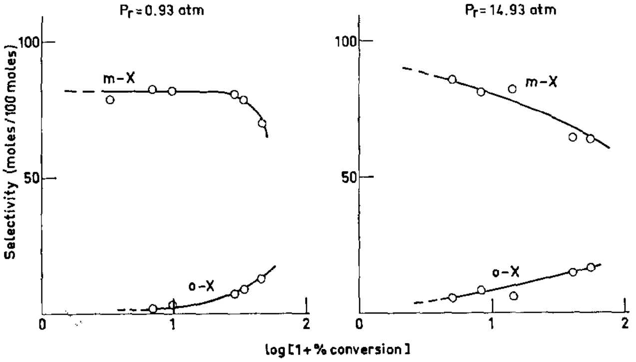


FIG. 3. Isomerization of *p*-xylene.

secutive, in agreement with the work of Hanson and Engel (*1*) and Okada *et al.* (*2*). Hydrogenolysis of the three xylenes to toluene and methane must be highly irreversible, as indicated by single arrows, and X in the metathesis reactions represents any of the three xylenes, thereby including cross-disproportionation.

Finally we made two isolated experiments with toluene over the same catalyst and under somewhat similar experimental conditions (Table 4) and found that benzene was being produced as expected by both hydrogenolysis and disproportionation of toluene. However, these minor secondary reactions have not been included in the above reaction scheme.

### *Isotopic Experiments*

The fact that the interconversion of the three xylenes proceeds in a consecutive manner does not tell us anything, however, about whether the individual steps involve two hydrocarbon molecules, i.e., intermolecular transalkylation, or, rather, 1,2 shifts of the methyl groups within each isolated molecule.

TABLE 4

Hydrogenolysis and Disproportionation of Toluene[a]

| $F_{HC}$ (mole/hr·10²) | Product analysis (mole%)[b] | | | |
|---|---|---|---|---|
| | B | *o*-X | *m*-X | *p*-X |
| 10.7 | 1.0 | 0.23 | 0.15 | 0.14 |
| 5.1 | 1.8 | 0.49 | 0.28 | 0.28 |

[a] Catalyst = SiANi-4; weight = 1.000 g; temperature = 465°C; pressure = 0.93 atm; $H_2$/HC = 3.6 mole/mole.

[b] The remainder up to 100% is unreacted toluene.

A simple and quite straightforward way of discriminating between these two possible mechanisms is to isomerize a mixture of normal ($d_0$) and hexadeuterated ($d_6$) *p*-xylene, viz., *p*-$C_8H_{10}$ and *p*-$CD_3$–$C_6H_4$–$CD_3$, respectively. If $C_8H_7D_3$ ($d_3$) is formed

TABLE 5

Isomerization of 63.6% *p*-$C_8H_{10}$ plus 36.4% *p*-$CD_3$–$C_6H_4$–$CD_3$

| | Experiment | |
|---|---|---|
| | 1D | 2D |
| Reaction temperature (°C) | 465 | 465 |
| Catalyst | Silica–alumina | Silica–alumina |
| $W/F_{HC}$ (g·hr/mole) | 1.54 | 30.86 |
| $H_2$/HC (mole/mole) | 3.6 | 3.6 |
| Pressure (atm) | 0.93 | 0.93 |
| Product analysis (mole%)[a] | | |
| *o*-X | 0.6 | 14.2 |
| *m*-X | 5.2 | 43.3 |
| *p*-X | 92.0 | 25.5 |
| T | 0.9 | 8.6 |
| TMBs | 1.3 | 8.4 |

[a] Of liquid samples collected during the first half-hour.

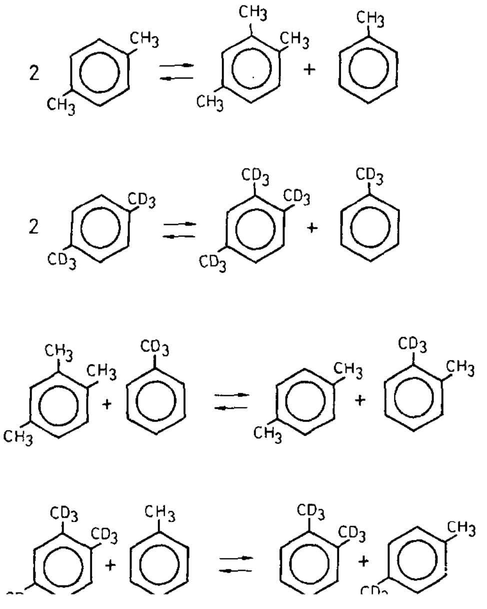
TABLE 6

Analysis of Deuterated Xylenes

| Experiment No. | Conversion (%) | Isomer | Isotopic distribution (mole%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ |
| 1D | 8.0 | *m*-X | 64.7 | 1.7 | 0.1 | 0.2 | 0.0 | 3.0 | 30.5 |
| 2D | 74.5 | *m*-X | 42.9 | 17.9 | 4.2 | 2.1 | 3.0 | 11.3 | 18.5 |
| 2D | 74.5 | *o*-X | 69.0 | 3.5 | 1.1 | 3.1 | 0.0 | 4.0 | 19.3 |

in increasing amounts, the intermolecular mechanism is playing a major role; otherwise, if $d_3 \simeq 0$, the reaction proceeds by internal 1,2 shifts of the methyl groups. In order to avoid the possibility of excessive hydrogen–deuterium exchange the experiments were done over the same silica–alumina catalyst without nickel and using helium as diluent, instead of hydrogen. The only real difference in doing this is that the catalyst deactivates more rapidly and the hydrogenolysis disappears (*8*), but the initial isomerization and disproportionation activities remain almost unchanged.

Another point to be aware of is the possible influence of the metathesis, which is a reversible reaction, in the final distribution of deuterated products. In this sense we must accept the possible occurrence, among others, of a set of reactions such as



which would justify the appearance of $d_3$ species, even on the assumption that isomerization is only intramolecular. This is why one should make at least one run at low conversion, where these secondary reactions are of minor significance.

The results obtained in the tracer runs are summarized in Table 5 and 6. We can see that the amount of $d_3$ is very small, both at low and high conversion, in comparison to the parent molecules $d_0$ and $d_6$ and the deuterated species $d_1$ and $d_5$ formed by hydrogen–deuterium exchange.

In conclusion we believe we have provided enough evidence to support a consecutive intramolecular type of mechanism for the catalytic isomerization of xylenes.

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