JOURNAL OF CATALYSIS 2, 79–81 (1963)

LETTER TO THE EDITORS

Olefins as Intermediates in the Hydrogenation of Aromatic Hydrocarbons

In a recent paper S. Siegel *et al.* (*1*) present indirect evidence for the occurrence of cyclohexene derivatives as intermediates in the liquid-phase hydrogenation of aromatic hydrocarbons. In connection with this we should like to report our experiments in which these intermediates were measured directly.

These experiments were performed at temperatures of 0–60°C and atmospheric pressure. The olefin concentration was determined either by titration with a bromide-bromate mixture or by a coulometric method.

As is to be expected, the olefin content of the reaction mixture first rises, then goes through a maximum, and decreases again to zero when the hydrogenation is completed.

As can be seen from the following table, olefins were easily observed with ruthenium and rhodium as catalysts, and to a lesser degree with nickel. On platinum and palladium the cyclohexene derivatives were not observed, as they are reduced much faster than the aromatic compounds.

TABLE 1

Catalyst	Substrate	Temp (°C)	Maximum olefin concentration (mole %)
Raney nickel	*o*-Xylene	25°	0.04
5% Rh/C	*o*-Xylene	25°	1.4
5% Ru/C	*o*-Xylene	25°	3.4
5% Ru/C	*o*-Xylene	60°	3.1
5% Ru/C	*m*-Xylene	60°	0.27
5% Ru/C	*p*-Xylene	60°	0.5
5% Ru/C	Toluene	60°	0.3
Ru black	Benzene	25°	0.18

It is also clear that methyl groups, especially if they are in the *ortho*-position with respect to each other, produce higher maximum amounts of olefins.

In Fig. 1 the result is given of a hydrogenation of *o*-xylene with a 5% Ru/C catalyst. The olefin content is plotted versus the amount of *o*-xylene converted. The kinetics conform to the following scheme (*2*):

$$\begin{tikzcd}
\mathrm{X} \arrow[r, shift left] & \mathrm{X_a} \arrow[l, shift left] \arrow[r, "k_1"] & \mathrm{Y_a} \arrow[r, "k_2"] \arrow[d, shift left, "k_d"] & \mathrm{Z} \\
& & \mathrm{Y} \arrow[u, shift left, "k_a"] &
\end{tikzcd}$$

where X is the aromatic compound, Y the intermediate tetrahydro derivative, Z the fully hydrogenated compound, and the subscript a means "adsorbed."

A steady state treatment based on the assumption that X_a is in equilibrium with X results in—after elimination of the time and integration (*2*):

$$Y = \frac{S}{(r-1)}(\mathrm{X} - \mathrm{X}^r)$$

where

$$r = \frac{k_a k_2}{k_1 K_x (k_2 + k_d)}$$

$$S = \frac{k_d}{k_2 + k_d}$$

X and Y are the mole fractions of the aromatic compound and the cycloalkene in the reaction product.

The curve drawn in the figure is the one calculated for $r = 0.9$ and $S = 0.08$. The fraction of the aromatic compound that leaves the surface as a cycloalkene during

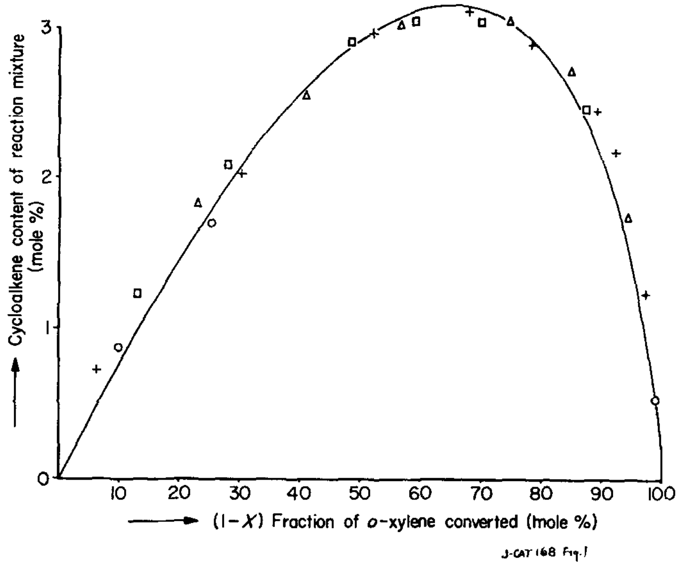

FIG. 1. Hydrogenation of o-xylene over a Ru catalyst; temp.: 0°C; pressure: 1 atm. (Symbols △, □, +, ○ refer to four separate experiments.)

hydrogenation is given by S. In all cases investigated so far S turned out to be of the order of 0.1.

In the case of o-xylene the intermediate cycloalkene is 1,2-dimethylcyclohexene, as shown by mass spectrometry and nuclear magnetic resonance. No other cycloalkenes were found, but experiments with mixtures of ruthenium and palladium catalysts suggest that they are nevertheless formed.

Table 2 gives the results of these experiments. The amount of palladium catalyst added was in both cases insufficient to cause by itself any measurable hydrogenation of the o-xylene.

TABLE 2
HYDROGENATION OF o-XYLENE AT 25°C BY MIXTURES OF RU AND PD CATALYSTS

Expt.	Catalyst	Maximum amount of 1,2-dimethyl-cyclohexene (mole %)	Fraction of *trans*-dimethyl cyclohexane in end product (%)
a	5% Ru/C (1 g)	3.4	7.6
b	5% Ru/C (0.5 g) + 5% Pd/C (0.5 g)	1.7	14.7
c	5% Ru/C (0.5 g) + 5% Pd/C (1.5 g)	1.0	18.9

The influence of the paladium added on the maximum amount of cycloalkene and the *trans*-content of the end product shows that part of the 1,2-dimethylcyclohexene which desorbs from the ruthenium catalyst is further hydrogenated on the palladium.

As found by Siegel and Smith (*3*), hydrogenation of 1,2-dimethylcyclohexene over Pd yields 75.6% *trans*-1,2-dimethylcyclohexane.

When it is assumed (a) that all the cycloalkene desorbing from the ruthenium catalyst (10% at this temperature) is further hydrogenated on the palladium, and (b) that all the *trans*-product formed with the ruthenium catalyst alone comes from the o-xylene that is totally hydrogenated during one sojourn on the surface, we would expect the maximum *trans*-content in the presence of Pd to be: $7.6 + 0.10 \times 75.6 = 15.2\%$.

Experiment c yields a higher amount of *trans*-product, however, although only part of the 1,2-dimethylcyclohexene is reduced on the palladium. These results suggest that also other isomeric cycloalkenes are desorbed from the ruthenium surface, but are hydrogenated too fast to be detected analytically. Further details of these investigations will be reported in a forthcoming publication.

References

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Received June 11, 1962