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LETTERS TO THE EDITORS

Stereochemistry and the Mechanism of Hydrogenation of Aromatic Hydrocarbons: Cycloalkene Intermediates

The ratio of *cis* and *trans* disubstituted cyclohexanes which is obtained from the hydrogenation of the isomeric xylenes and *p-tert*-butyltoluene, dissolved in acetic acid and in contact with reduced platinum oxide, is a function of the structure of the substrate and the pressure of hydrogen (*1*, *2*). A comparison of these data with the stereochemistry of the hydrogenation of the related cycloalkenes suggests that the latter are set free as intermediates in the reduction of the aromatic cycle. Quite a contrary view is common, attributable in part to the work of Balandin (*3*, *4*) as well as the classical stereochemical studies of Linstead and his students (*5*). More recently, however, Madden and Kemball observed cyclohexene during the early stages of the vapor phase hydrogenation (flow system) of benzene over nickel films at 0° to 50°C (*6*). The ratio of cyclohexene to cyclohexane diminished with time, and little or none of the alkene was detected if the films were annealed at 50°C in a stream of hydrogen. Also A. W. Weitkamp has isolated the octalins formed in the hydrogenation of methylnaphthalene, or naphthalene, over a platinum supported on alumina catalyst at about 100–150°C (*7*).

The publication by Hartog and Zwietering (*8*) on the formation of cycloalkenes during the hydrogenation of alkylbenzenes on several supported metallic catalysts prompted this preliminary report. In general, our results agree with their findings, however, a gas chromatograph fitted with a Beckman hydrogen flame ionization detector permitted us to detect the small concentrations of cycloalkenes formed when reduced platinum oxide was the catalyst although these olefins escaped detection by their bromometric or coulometric method. Research grade *m*- and *p*-xylenes (99.92 mole %) were obtained from the Phillips Petroleum Company. The studies were conducted as before with platinum oxide as catalyst and in the solvent glacial acetic acid (*1*, *9*). Control experiments established that no impurities which might interfere with the detection and quantitative estimation of the dimethylcyclohexenes were present in the reagents or introduced inadvertently. Results are presented in Table 1 and Fig. 1.

TABLE 1
OLEFINS FORMED IN THE HYDROGENATION OF *m*-XYLENE

Compound formed	Experiment[a] I	Experiment[a] II
cis-1,3-Dimethylcyclohexane	0.59	1.09
trans-1,3-Dimethylcyclohexane	0.17	0.30
1,3-Dimethylcyclohexene	0.00097	0.0021
2,4-Dimethylcyclohexene	0.00097	0.0021

[a] Composition: mole percent of hydrocarbon mixture.

Starting with *p*-xylene (1 atm, 25°C), 1,4-dimethylcyclohexene attains a steady state concentration of approximately 6×10^{-6} moles/liter (0.002 mole % of the hydrocarbon mixture) after about 2% of the aromatic hydrocarbon has been reduced. The same concentration is reached when 0.1% of the alkene is added initially with the xylene. Likewise the hydrogenation of *m*-xylene yields both 1,3- and 2,4-dimethylcyclohexenes in approximately equal amounts and at the same concentration level

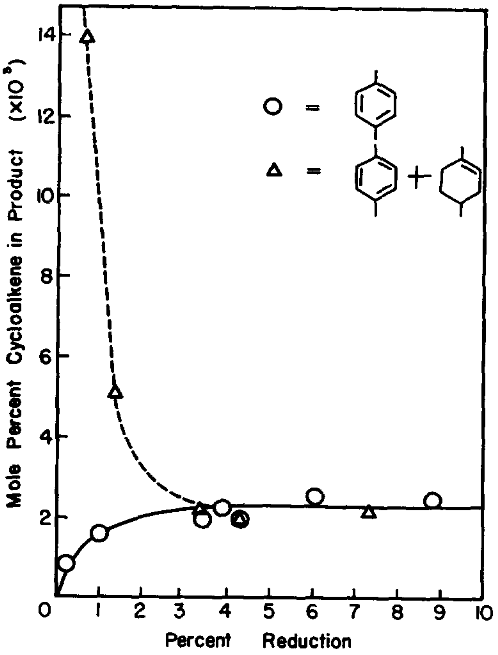

FIG. 1. Formation of 1,4-dimethylcyclohexene during the hydrogenation of *p*-xylene (○) and *p*-xylene containing initially 0.1% of the cycloalkene (△) over platinum oxide catalyst.

as in the preceding example. *p*-Xylene yields 68–70% and *m*-xylene 78% of the *cis* saturated stereoisomer under these conditions.

The detection of the dimethylcyclohexenes formed during the hydrogenation of *m*- and *p*-xylene, under conditions identical to those employed in our previous stereochemical studies, lends support to our conclusions that the cycloalkenes, desorbed from the surface of the catalyst, are intermediates in this reaction. The concentration of the cycloalkene attained after about 2 to 4% of the aromatic hydrocarbon has been reduced is a steady state value which, as demonstrated, may be quickly reached when a higher concentration of the alkene is introduced initially.

Although we have postulated that all of the possible dimethylcyclohexenes are desorbed from the surface (*1*), only 1,4-dimethylcyclohexene was detected in the reduction of *p*-xylene; and *m*-xylene yielded only 1,3- and 2,4-dimethylcyclohexene. Indeed such a result should be expected since it has been shown that in competitive reductions over this catalyst, isomeric cycloalkenes which differ in the degree to which the double bond is substituted, react at greatly different rates (*9*, *10*). Thus the competitively *more* reactive alkenes should have steady state concentrations in the order of 1%, or less, of the alkenes observed and would therefore be outside of the sensitivity of our present measurements. Furthermore, the equal concentrations of 1,3- and 2,4-dimethylcyclohexenes observed in the reduction of *m*-xylene corresponds to the near equality in reactivity observed in competitive experiments performed at the usual range of substrate concentrations (*11*).

Although Hartog and Zwietering conclude that less than 10% of the aromatic hydrocarbon which is reduced does so via a desorbed cycloalkene, this conclusion does not account satisfactorily for the large amounts of *trans*-dimethylcyclohexanes which are formed. Probably the facts can be resolved by recognizing that the cycloalkene which is found in the phase which can be sampled is that fraction which not only desorbs from the surface but also escapes by diffusion from the pores of the catalyst before it can be readsorbed and reduced.

A 5% rhodium-on carbon catalyst yields much higher concentrations of cycloalkenes (*8*), consequently the stereochemistry is more readily studied. Details of this work will be reported elsewhere.

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A π-Complex Mechanism for Catalytic Exchange Reactions

The importance of π-complex intermediates has already been discussed in connection with the catalytic deuteration and tritiation of aromatic compounds (*1*, *2*). The existence of π-bonded species has also been proposed during the exchange of aliphatic hydrocarbons with deuterium (*3*). Extensive work involving typical π-electron systems, namely the monosubstituted benzenes (*1*), polycyclic aromatic hydrocarbons (*4*), and heterocyclics (*5*) has indicated that the exchange mechanism does not proceed by a *simple* π-complex substitution mechanism. The essential difficulty with such an interpretation is the failure to explain adequately ring orientation effects (*1*) and the ready exchange between two aromatic species. This conclusion is further substantiated by the results of exchange between deuterium and 7 alkylbenzenes on nickel (*6*) where ring hydrogens exhibit similarly drastic ortho deactivation effects.

In an extension of our monosubstituted benzene work, we have exchanged 12 alkyl aromatics and benzotrifluoride with deuterium oxide in the presence of active platinum (*7*, *8*), which differs from nickel in that aromatic and not aliphatic hydrogens are preferentially exchanged. Significant features of the results (Table 1)* indicate that: (a) The alkylbenzenes do not appreciably poison benzene exchange (*8*). (b) "Complete" ortho deactivation occurs when the ortho position is adjacent to a very large inert group or "flanked" by two methyl groups (*tert* butylbenzene, benzotrifluoride, mesitylene, and *m*-xylene). (c) "Severe" but incomplete *ortho* deactivation occurs when the *ortho* position is adjacent to only one methyl group. Isopropylbenzene is the one molecule which does not belong to either category, but appears to occupy a position midway between the two extremes. The relative reactivity of the alkylbenzenes in terms of active aromatic hydrogens is benzene > ethylbenzene > *c*-xylene > cumene > toluene > benzotrifluoride > *m*-xylene > *p*-xylene > hemimellitene > *tert* butylbenzene > mesitylene (no observed deuteration in the ring hydrogens of the last compound).

From these results and previously reported data (*1*, *2*, *4*, *5*), it is now possible to distinguish between two new mechanisms which the authors are postulating for catalytic exchange and propose to call the Associative and Dissociative π-Complex Substitution Mechanisms. Both mechanisms involve a π-complex-chemisorbed aromatic hydrocarbon which occupies a horizontal position on the catalyst surface [Eq. (1)]. When water or another aromatic is the other exchanging reagent, then π-complex bond

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* A more detailed account of this work will be published in the immediate future (*8*).