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On the Mechanism of Catalytic Isomerization of Xylenes. Molecular Orbital Studies

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On the basis of CNDO/2 molecular orbital calculations, we postulate the following detailed mechanism for the catalytic isomerization of xylenes which explains the initial product distributions and also our previous finding that the reaction is intramolecular: (i) adsorption of xylene on a surface acid site to form a Wheland-type complex; (ii) disrotatory cyclization of the protonated species into a bicyclo[3, 1, 0]hexenyl complex; (iii) migration of the methylene bridge to a new side of the pentagonal ring; (iv) change of the new bicyclic species back into the corresponding Wheland-type complex; (v) desorption of the xylene isomer from the surface of the catalyst.

The overall rate determining step can be either of the surface reactions (ii) or (iv).

INTRODUCTION

In a previous paper (*1*) we have shown that the isomerization of xylenes over silica–alumina proceeds via the consecutive and reversible steps,

$$\textit{ortho} \rightleftarrows \textit{meta} \rightleftarrows \textit{para} \qquad (1)$$

with hydrogenolysis and disproportionation as major competing reactions. Furthermore, the interconversion of the three isomers takes place almost exclusively by intramolecular 1,2 shifts of the methyl groups.

In this article we present some molecular orbital calculations carried out by the CNDO/2 method, within the valence shell approximation. Based on this information and on our previous work (*1*) a detailed mechanism for the intramolecular isomerization of xylenes is proposed, in which the rate determining step appears to be the disrotatory cyclization of an adsorbed Wheland-type complex around its protonated position.

MOLECULAR ORBITAL CALCULATIONS

For the CNDO/2 molecular orbital calculations (*2*), we have used the program written by Dobosh (*3*) with the same orbital parameterization described in the program. The geometric parameters of *ortho*- and *para*-xylene were taken from the literature (*4*, *5*) and for the *meta* isomer we have assumed somewhat similar values, as indicated in Fig. 1a.

The Wheland complexes, on the other hand, have been derived from the neutral molecules according to the following criteria: (i) The carbon atom bearing the

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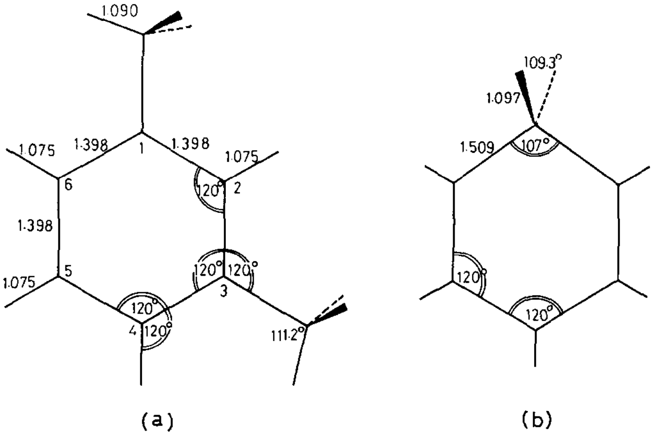

FIG. 1. Geometric parameters of xylenes: (a) isolated molecule; (b) adsorbed Wheland complex.

additional porton has a quasi-tetrahedral structure; (ii) the hexagonal six carbon ring in the protonated molecule is supposed to be planar, with the two C–H bonds of the protonated carbon atom symmetrically distributed with respect to that plane, as depicted in Fig. 1b.

In the transformation of the Wheland complex to the bicyclic form (see Fig. 2) the distance (*d*) between the two carbon atoms of the base of the triangle is considered to change gradually, with a simultaneous variation of the angle (θ) formed by the planes of the two rings. Other geometric parameters in the structure are considered to remain constant.

RESULTS AND INTERPRETATION

Adsorption of Xylenes

The need of an acidic catalyst for these isomerization reactions implies that the initial stage must be the interaction of each hydrocarbon molecule with an acid site, in our case most probably a SiOH group, as shown in Fig. 3a. The differences in the heats of adsorption of the three isomers should, therefore, be related to the stability of the adsorbed species on the surface of the catalyst.

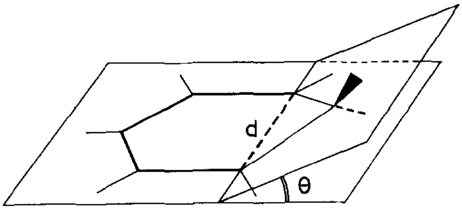

FIG. 2. Transformation of the Wheland complex to a bicyclo[3, 1, 0]hexenyl species.

Unfortunately, there is no direct experimental evidence on the nature of such adsorbed species, but we can reasonably assume that its conformation will be similar for the three isomers. Furthermore, we assume that upon adsorption the hybridization of one carbon atom of the aromatic ring changes from sp^2 to sp^3, by electrophilic aromatic substitution by an acid site of the catalyst. As a first approximation we shall assume that the acidic active site is a free proton, i.e., that the adsorbed species is always completely dissociated on the surface of the catalyst, as indicated in Fig. 3b.

The overall reaction energy would then be

$$\Delta E = \Delta E_x + \Delta E_c,$$

where ΔE_x is the difference in energy between the protonated complex and the neutral xylene, and ΔE_c the change in energy of the acid site after the transfer of its proton to the complex. The term

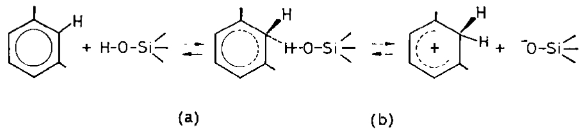

FIG. 3. Protonation of a xylene molecule on the surface of the catalyst.

ΔE_c will clearly remain constant as long as we work with the same catalyst, so that the adsorption energies can be related in this case to the energy of formation of the protonated Wheland complexes for the three isomers, ΔE_x.

The values of ΔE_x calculated by the CNDO/2 method are given in Table 1, from which we can see that the preferred positions for protonation are 2, 4, and 6 for *m*-xylene, and 3 and 6 for *o*-xylene, while in *p*-xylene all six carbons of the aromatic ring are almost equivalent. We can reasonably believe that the hydrocarbon molecules will preferentially adsorb by these carbons, and also that *m*-xylene, which has the greater protonation energy, should be more strongly adsorbed, in agreement with its greater basicity (*6*).

In order to check that these values of protonation energy are not merely a consequence of the geometric model adopted, we have changed the C–H distance between 1.07 and 1.12 Å, and the angle H–C–H between 105 and 118°, in the protonated carbon. We have found that the minimum of energy of the protonated species is obtained within these intervals, and that the protonation energies of Table 1 were only modified by ±0.0015 a.u.

We have also modified the value of the Mulliken–Wolfsberg–Helmholtz factor, K, (*3*) between 0.8 and 1.2, and found that the protonation energies of *meta*- and *para*-xylene remain constant, while that of the *ortho* isomer only changes by ±0.003 a.u. with respect to the value of 0.464 a.u. reported in Table 1, for $K = 1$.

Formation of the Activated Complex

The next step after the hydrocarbon is adsorbed on the surface of the catalyst is the transformation of such an adsorbed Wheland-type complex to another intermediate form, the nature of which will depend on the electronic charge distribution within the hydrocarbon molecule, particularly around its point of adsorption. We have calculated this charge distribution using the CNDO/2 method, and, in all

TABLE 1

Protonation Energies of Xylenes

Molecule	Position of protonation[a]	ΔE_x (atomic units)[b]
o-xylene	(1), (2)	−0.432
	(3), (6)	−0.464
	(4), (5)	−0.444
m-xylene	(1), (3)	−0.447
	(2)	−0.475
	(4), (6)	−0.478
	(5)	−0.445
p-xylene	(1), (4)	−0.465
	(2), (3), (5), (6)	−0.460

[a] The ring carbons have been numbered in the usual manner, so that *ortho*-, *meta*-, and *para*-xylene correspond to 1,2-, 1,3-, and 1,4-dimethylbenzene.

[b] 1 a.u. = 628 kcal/mole.

TABLE 2

Energy and Relative Population of the Vibration Levels along the Reaction Coordinate at 733°K

V	E_v (kcal/mole)	Population (%)
0	1.43	85.9
1	4.29	12.1
2	7.15	1.7
3	10.01	0.24
4	12.87	0.05

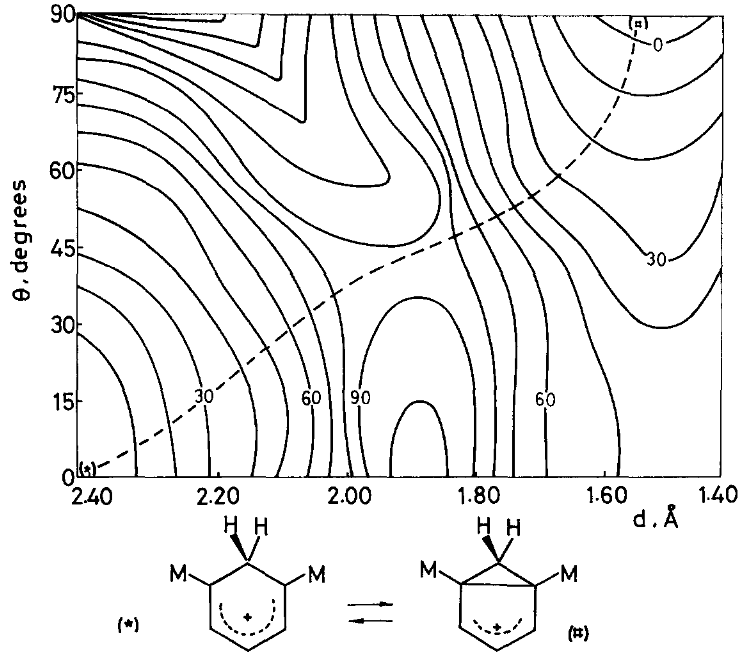

FIG. 4. Potential energy surface for the disrotatory cyclization of a *meta*-xylene protonated complex. The energy is given in kcal/mole and the broken line represents the reaction pathway.

cases, the *ortho* and *para* positions with respect to the point of adsorption appear to have significant electronic deficiencies (ρ between +0.15 and +0.25), which may be relevant for the formation of the intermediate activated complex.

We believe that the next step in the reaction mechanism might be the disrotatory cyclization of the "adsorbed" Wheland complex, toward cationic forms of bicyclo[3,1,0]hexenyl type (Fig. 2), which involves the formation of a new bond between the two adjacent electron-deficient carbon atoms and the consequent folding of the three-membered ring over the plane of the molecule. According to the rules of Woodward and Hoffmann (*7*), a reaction like this would present a strong thermal barrier (*8*) but could be accomplished, however, via photochemistry as found by Childs and Winstein (*9*) working with similar kinds of compounds.

If we consider that in our case the reaction temperature is quite high, plus the fact that the true activated complex in the surface of the catalyst obviously is not an isolated Wheland complex, we cannot reject the possible formation of the above bicyclic species merely because of the energetic barrier. In order to estimate the magnitude of such a barrier, we have calculated, as a good representative example, the potential energy surface associated with the transformation of *meta*-xylene protonated at C-2.

The isoenergetic curves obtained by CNDO/2 (see Fig. 4), correspond to different molecular configurations designed by changing the geometrical parameters *d* and *θ* in Fig. 2. From these results it appears that the reaction proceeds in a concerted fashion, with an energetic barrier of about 85 kcal/mole. The calculations also indicate that the bicyclo[3,1,0]hexenyl

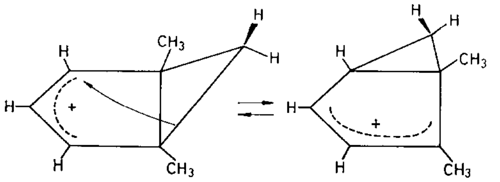

FIG. 5. Isomerization of the bicyclic hexenyl species.

compound is at least as stable as the starting Wheland complex, and hence the reverse reaction can be equally possible.

Now, although the experimental activation energy must be considerably lower than the estimated height of the energy barrier for the intermediate complex, this parameter should not actually be considered as the reference point for the activation energy, since the xylene molecules will not be exactly in the fundamental state of vibration at the reaction temperature. We have calculated approximately the energies of the first vibration levels as well as their relative populations at 733 K (see Table 2) on the assumption that the atomic displacements along the reaction coordinate are of the bending-type normal mode of vibration, with a vibration frequency of 1000 cm^{-1} (*10*). We can see that the energy of the fundamental level ($v = 0$) is much smaller than the height of the potential energy barrier, but there are a significant number of molecules in the next two levels of higher energies.

Despite this decrease in activation energy of these excited molecules, the height of the energy barrier still remains high, in our opinion due to the fact that the CNDO/2 method is not accurate enough for quantitative calculations and because each intermediate adsorbed species is not an isolated Wheland complex. The formation of the bicyclic compound would therefore be the rate determining step.

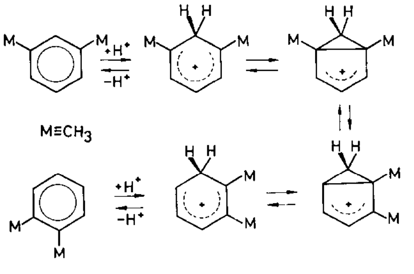

FIG. 6. Mechanism for the reversible isomerization of *meta-* to *ortho*-xylene.

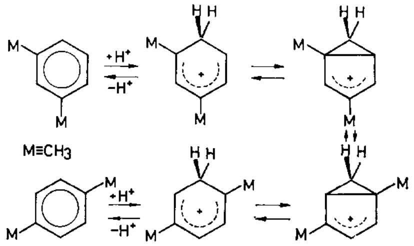

FIG. 7. Mechanism for the reversible isomerization of *meta-* to *para*-xylene.

Isomerization Step

Once the energetic barrier is surpassed and the bicyclic hexenyl complex attained, the next step in the isomerization mechanism will be the migration of the methylene group of the three-membered ring, as depicted in Fig. 5. The three-membered ring will now be located in one of the neighboring sides of the pentagon.

The work of Childs and Winstein (*9*) reveals that, under our isomerization conditions, there should be no appreciable energetic barrier for this migration step to occur. Once the new bicyclic complex is transformed back into the corresponding Wheland complex and the aromatic ring is regenerated (see Fig. 6) one obtains *ortho*-xylene. The formation of *p*-xylene can be explained in a similar way (see Fig. 7) starting from the *m*-xylene Wheland complex with the proton is positions 4 or 6. Finally, the formation of *meta*-xylene from both *ortho-* and *para*-xylene and the fact that these two isomers cannot be directly interconverted in each other, can now easily be explained on the basis of the above mechanism (see Figs. 6 and 7).

It is worth mentioning that all the intermediate steps we have postulated for the mechanism of xylene isomerization are reversible and consequently the reaction system should always transform toward equilibrium, as found in the long contact time experiments.

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