Molecular Orbital Studies on the Mechanism of Catalytic Isomerization of Xylenes

III. Protonation Channels

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The isoenergetic lines of the interaction energy between a bare proton and *ortho-*, *meta-*, and *para*-xylene have been calculated in order to detect both the best approaching channel and the preferred protonation positions. The channels found direct the protonation to the following ring positions: 4 and 5 for *o*-xylene, 4 and 6 for *m*-xylene, and 2 equivalents for *p*-xylene. The overall interaction energy determines the protonation positions on each isomer and the most important contributions to it are the electrostatic term in *o*-xylene, the polarization term in *p*-xylene, and both terms equally in *m*-xylene. These results are in agreement with the experimental findings and appear useful in the understanding of the heterogeneous catalytic isomerization mechanism of xylenes.

INTRODUCTION

A theoretical model for the isomerization mechanism of xylenes on solid acid catalysts has recently been proposed by some of us (*1, 2*). The adsorption of xylene molecules on the acid sites of the catalyst surface forming a Wheland-like complex would be the first step in such a mechanism. The ring positions at which the adsorption takes place will determine further reaction progress. Hanson and Engel (*3*), by means of the Hougen–Watson technique (*4*), have shown that the isomerization follows a single-site reaction model. Also, it has been shown that xylene isomerization is a unimolecular process (*5*) catalyzed by Brønsted rather than by Lewis acid sites (*6*).

The adsorption energy of a xylene molecule on a single catalyst active site can be written as the sum of the protonation energy of the xylene molecule on the adsorption position plus a term which is a constant for all the xylene isomers, whatever the

protonation position (*2*). This approach only holds when the adsorption process is referenced to the same active site of the same acidic catalyst.

The protonation energies for all the possible Wheland-like complexes as calculated by Corma *et al.*) (*1*) using the CNDO/2 method (*7*), and by Heidrich *et al.* (*8*) using the modified CNDO-FK method, indicate that for a given isomer there are several positions with similar basicity. From a thermodynamic point of view, the protonation process would proceed at these positions with equal probability. However, NMR studies of xylene solutions in superacid media (*9, 10*) have shown that the protonation only takes place at a single position for each isomer. In the isomerization mechanism (*1, 2*), the fact that the protonation only takes place at one position is crucial. For this reason, and also because the values of the protonation energies as calculated by CNDO methods do not find out the preferred single protonation position, we have calculated in this paper the minimal energy channels for the approaching of a proton to each of the three isomers. These

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calculations will unambiguously indicate that protonation position, if any among those with similar basicity are to form the Wheland-like complex. The catalyst active site is simulated by the bare proton, the simplest Brønsted acid.

METHOD

The interaction energy between a proton and a xylene molecule has been calculated following the method described by Bertrán

et al. (*11*) in their studies on aromatic substitution. They used a van der Waals-type approximation for the interaction energy, including electrostatic, polarization, and dispersion terms. These authors apply the first- and second-order Rayleigh–Schrödinger perturbation theory (*12*) with several simplifying hypotheses, all of them within the ZDO (zero differential overlap) approach (*7*). All these approximations yield Eq. (1), giving the interaction energy between two molecules I and II:

$$E = \sum_{A}^{S} \sum_{B'}^{S'} \frac{Q_A Q_{B'}}{R_{AB'}} + 2 \sum_{i=1}^{n} \sum_{j=n+1}^{\infty} \left(\frac{\left(\sum_{B'}^{S'} \sum_{p}^{M} C_{ip} C_{jp} (Q_{B'}/R_{B'p}) \right)^2}{E_0^{\mathrm{I}} - E_{i \to j}^{\mathrm{I}}} \right)$$

$$+ 2 \sum_{k'=1}^{n'} \sum_{l'=n'+1}^{\infty} \left(\frac{\left(\sum_{A}^{S} \sum_{p'}^{M'} C_{k'p'} C_{l'p'} (Q_A/R_{Ap'}) \right)^2}{E_0^{\mathrm{II}} - E_{k' \to l'}^{\mathrm{II}}} \right)$$

$$+ 4 \sum_{i=1}^{n} \sum_{j=n+1}^{\infty} \sum_{k'=1}^{n'} \sum_{l'=n+1}^{\infty} \left(\frac{\left(\sum_{p}^{M} \sum_{p'}^{M'} C_{ip} C_{jp} C_{k'p'} C_{l'p'} (1/R_{pp'}) \right)^2}{E_0^{\mathrm{I}} - E_{i \to j}^{\mathrm{I}} + E_0^{\mathrm{II}} - E_{k' \to l'}^{\mathrm{II}}} \right). \tag{1}$$

Q_A is the net charge over the atomic center A; C_{ip} is the coefficient of the atomic orbital χ_p in the LCAO expansion of the molecular orbital ϕ_i; $E_{i \to j}^{\mathrm{I}}$ is the energy of the excited state of molecule I, as described by the configuration built by promoting an electron from the doubly occupied molecular orbital i to the empty j; E_0^{I} is the ground-state energy of molecule I; R_{ab} is the distance between the atomic centers a and b, or the atomic centers to which the atomic orbitals a and/or b are referred; the indices S, M, and n are, respectively, the total number of atomic centers, atomic orbitals, and doubly occupied molecular orbitals on molecule I. Indices with a prime always refer to molecule II.

The applicability of Eq. (1) is restricted to intermediate and long distances because it neglects the exchange repulsion term between the two molecules I and II, as it is derived from an unperturbed product of

isolated molecule wavefunctions: $\Psi = \Phi_A \Phi_B$. Notwithstanding this, we have used it in this work since molecule II is a bare proton and we are only concerned with distances greater than 2 Å from the xylene molecular plane. Introduction of such a contribution would be necessary for nearer approaches in the perturbative scheme.

The first term in Eq. (1) comes from first-order perturbation energy and it represents the electrostatic contribution to the interaction energy between molecules I and II. The remaining terms come from second-order perturbation energy, with the second and third terms representing the polarization energy, and the fourth term the dispersion energy.

In the case with which we are concerned, molecule II is a bare proton and consequently the third and four terms vanish, the interaction energy calculation being reduced to the electrostatic term and the one
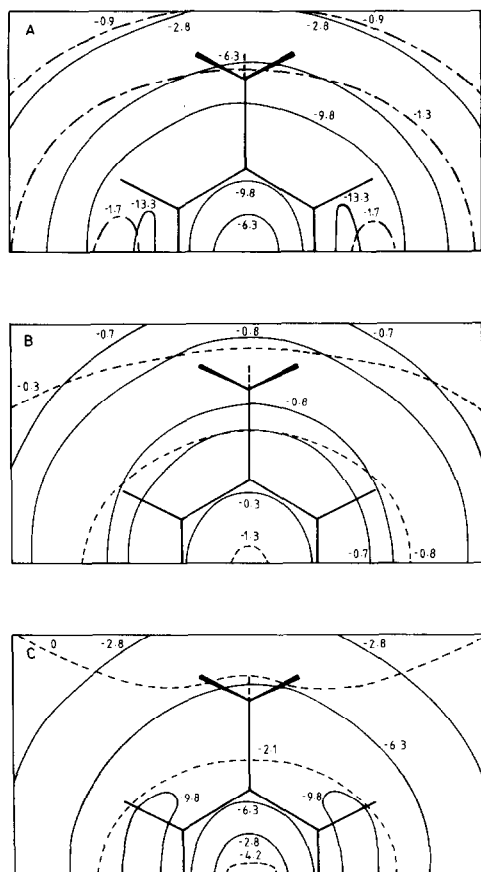
corresponding to the polarization of the xylene molecule (I) by the bare proton (II). For the calculation of LCAO coefficients and excitation energies in Eq. (1), the CNDO/S method of del Bene and Jaffé (*13–16*) has been used because this method includes the best approximations and parametrizations for the calculation of electronic transitions within the CNDO formalism. The program of Jaffé *et al.* (*17*) was used, and excited states were constructed with the VO approach. The summation over excited states in Eq. (1) is restricted to the first 30 monoexcited configurations. No significant improvement appears when a greater number of configurations is used.

FIG. 1. Interaction energies between *ortho*-xylene and a bare proton: (A) (– – –) Total energy at 4 Å; (——) total energy at 2 Å. (B) (– – –) Electrostatic term at 4 Å; (——) polarization term at 4 Å. (C) Same as (B) at 2 Å.

FIG. 2. Interaction energies between *meta*-xylene and a bare proton: (A) (– – –) Total energy at 4 Å; (——) total energy at 2 Å. (B) (– – –) Electrostatic term at 4 Å; (——) polarization term at 4 Å. (C) Same as (B) at 2 Å.

To carry out the calculations on a UNIVAC 1108 computer, a FORTRAN V program has been developed.

RESULTS

The van der Waals interaction energy for *o*-, *m*-, and *p*-xylene, as well as its components, are represented in graphic form in Figs. 1, 2, and 3, respectively. The isoenergetic lines correspond to the proton located on planes parallel to the aromatic ring. The protonation channel runs through the minimum energy of each plane. The values of the interaction energy, together with their electrostatic and polarization components, corresponding to the absolute

FIG. 3. Interaction energies between *para*-xylene and a bare proton: (A) (– – –) Total energy at 4 Å; (———) total energy at 2 Å. (B) (– – –) Electrostatic term at 4 Å; (———) polarization term at 4 Å. (C) Same as (B) at 2 Å.

minima for every calculated plane are given in Tables 1, 2, and 3.

The above calculations were performed by using the geometrical parameters of *p*-xylene taken from crystallographic data (*18*), similar values being assumed for the *ortho* and *meta* isomers. After Smeyers and Hernández-Laguna (*19*), the minimal energy conformation for *ortho*- and *meta*-xylene methyl groups has been selected. However, for *para*-xylene the eclipsed C_{2v} conformation with no hydrogen atoms on the ring plane has been selected instead of the more stable staggered C_{2h} conformation (*19*) because the calculations on planes parallel to the aromatic ring turn out to be

TABLE 1

Minimum Energy Values for *ortho*-Xylene–Proton van der Waals Interaction at Several Heights over the Ring Plane

Height (Å)	Energy (kcal · mole⁻¹)		
	Total	Electrostatic	Polarization
5	– 1.20	– 0.86	– 0.40
4	– 2.10	– 1.35	– 0.95
3	– 4.70	– 2.30	– 2.70
2	– 14.4	– 4.50	– 10.8
1	– 100.	– 10.0	– 94.0

easier in the former than in the latter conformation.

The maps in Fig. 1 referring to the interaction energy between *o*-xylene and the proton show a protonation channel which comes from a point outside the vertical of the C_4–C_5 bond (total energy: – 2 kcal · mole⁻¹) over the 4-Å plane and directs to a very near position (total energy: – 14 kcal · mole⁻¹) over the 2-Å plane. In summary, the protonation channel directs to the carbon atoms opposite to the methyl groups. Also, it can be seen from Fig. 1 that both electrostatic and polarization terms direct qualitatively to the same positions.

The interaction energy in the case of *m*-xylene (Fig. 2) outlines a branched protonation channel. At the 4-Å plane the channel directs to the vertical of C_5 (– 1.8 kcal · mole⁻¹) but when the proton approaches the molecular plane at 2 Å, the channel

TABLE 2

Minimum Energy Values for *meta*-Xylene–Proton van der Waals Interaction at Several Heights over the Ring Plane

Height (Å)	Energy (kcal · mole⁻¹)		
	Total	Electrostatic	Polarization
5	– 1.00	– 0.76	– 0.38
4	– 1.85	– 1.25	– 0.95
3	– 4.10	– 2.30	– 2.70
2	– 13.6	– 4.50	– 10.0
1	– 100.	– 10.0	– 90.0

TABLE 3

Minimum Energy Values for *para*-Xylene–Proton van der Waals Interaction at Several Heights over the Ring Plane

Height (Å)	Energy (kcal · mole⁻¹)		
	Total	Electrostatic	Polarization
5	−0.93	−0.80	−0.40
4	−1.75	−1.35	−1.70
3	−4.10	−2.30	−2.50
2	−13.0	−4.50	−10.0
1	−100.	−10.0	−94.0

bifurcates to the centers C_4 and C_6 (-13 kcal · mole⁻¹) with also a secondary minimum at C_2 (-11 kcal · mole⁻¹). The contributions of the two components, electrostatic and polarization, do not direct to the same positions in this case (see Figs. 2B and C). It can be seen that the secondary minimum over C_2 at the 2-Å plane is due to the polarization term.

In the *p*-xylene case (Fig. 3) the energetics of the process direct the channel to the nonmethylated positions at both planes drawn. The specificity of the contributions of polarization and electrostatic terms can be inferred from Fig. 3 and it can be seen that the former is the determinant one for the directionality of the channels.

The electrostatic term gives the greatest contribution to the interaction energy at large distances in all three isomers. The contributions of electrostatic and polarization terms at medium distances are alike, the polarization term being the predominant one at van der Waals distances.

DISCUSSION

The protonation channels so far calculated distinguish between the protonation positions giving Wheland complexes of similar stability. Moreover, the calculated protonation channels go towards the same centers that are known as protonation positions from NMR spectra of protonated xylenes (*9*, *10*) in superacid media, which are C_4 in *o*-xylene, C_4 in *m*-xylene, and C_2

in *p*-xylene. Likewise, studies of xylene deuteration and dedeuteration reactions show that the protium/deuterium exchange is carried out at the same positions as the ones headed by the channels (*20–22*).

A model for xylene chemisorbed on Brønsted acid sites has been proposed by Takaya and co-workers (*23–25*). They assumed that the distance between the xylene molecule and the catalyst site is the sum of their van der Waals radii. Since the methyl group radius is 2.0 Å (*26*), and the aromatic-ring average half-thickness is 1.85 Å (*26*), the isoenergetic graphs at a plane 2 Å distant from the ring plane are the most appropriate for constructing an adsorbed complex model. Therefore, according to the mechanism proposed in previous papers (*1*, *2*), the isomerization reaction coming from the protonated complexes as calculated by the protonation channels, occurs in a direct way in the *m*-xylene–*p*-xylene case (Fig. 4), an additional step being, however, necessary in the *m*-xylene–*o*-xylene case because no *m*-xylene derivative seems to be formed when the starting point is position-C_4-protonated *o*-xylene, and because the secondary channel going to C_2 of *m*-xylene is necessary in order to form the protonated complex able to yield an *o*-xylene derivative (Fig. 5).

Consequently, both processes *o*-xylene ⇄ *m*-xylene are somewhat slower than the *p*-xylene ⇄ *m*-xylene ones, and no intermediate step is found in order to perform the direct *o*-xylene ⇄ *p*-xylene interconversion. Both conclusions are in agreement
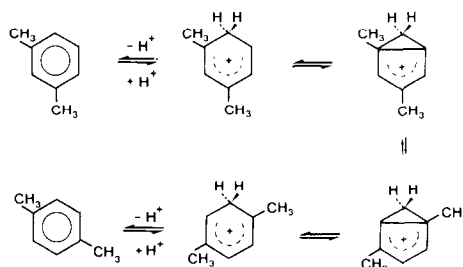

FIG. 4. *meta*-Xylene ⇄ *para*-xylene isomerization mechanism (Ref. (*1*)).
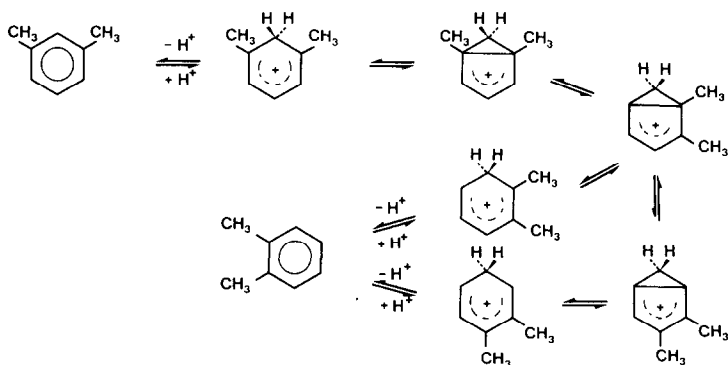
FIG. 5. *meta*-Xylene ⇌ *ortho*-xylene isomerization mechanism (Ref. (*1*)).

with experimental results on the kinetics of isomerization processes (5). It can therefore be concluded that the best approach channels for the proton are those which direct to appropriate adsorbed Wheland-like complexes, in order for the isomerization processes to follow.

ACKNOWLEDGMENTS

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