

# Molecular Orbital Studies on the Mechanism of Catalytic Isomerization of Xylenes

## II. The Photochemical Process

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The feasibility of an intermediate step in the mechanism of photochemical isomerization of xylenes in acidic media is explored by using CNDO molecular orbital methods. Along the reaction path from 2,6-dimethylbenzenium ion to dimethylbicyclo[3.1.0]hexenyl cation, the energy surfaces for this intermediate step have been drawn both for the first singlet  $S_1$  and triplet  $T_1$  excited states. The energies of these excited states have been calculated by adding to the ground-state energy calculated by CNDO/2 method the excitation energy calculated by CNDO/S-CI method. An optimization of the saddle point energy is achieved by introducing the angle between methyl groups and the ring plane as an additional parameter. The optimized energy results indicate that the cyclization process occurs with no energetic barrier from the first singlet excited state, while the calculated energy barrier for the cyclization in the ground state (thermal route) is about 46 kcal · mole<sup>-1</sup>.

### INTRODUCTION

Previous studies on the catalytic isomerization mechanism of *meta*-xylene (1) and *ortho*- and *para*-xylene (2) indicate that the internal disrotatory cyclization of the Wheland-like complexes is the predominant step. However, the Woodward-Hoffmann rules (3) on the orbital symmetry conservation state that such a process is strongly hindered for the thermal reaction, as reflected by the high energy barriers calculated (1, 2), and also by the low yield of conversion detected (4, 5). However, being thermally impeded, the process of disrotatory cyclization of the Wheland-like complexes must be favored in a photochemical route, as can be derived from the experimental work of Childs *et al.* (6, 7) and Berson *et al.* (8-12) on the photochemistry of benzenium and some polymethylbenzenium ions in strongly acidic solutions.

In the present paper the photoisomeriza-

tion process of the *meta*-xylene protonated complex, which relates to the adsorbed state found in heterogeneous catalysis, is studied theoretically. In order to estimate the energetic barriers for the possible cyclization steps, the evolution of the position-2 protonated complex in its lower excited states is followed. The calculations have been performed for the position-2 complex because its symmetry remains along the reaction coordinate, simplifying the great number of calculations performed.

### METHODS

As already pointed out (1), the cyclization process during *m*-xylene isomerization starts from the 2,6-dimethylbenzenium ion (I in Fig. 1) and ends in the dimethylbicyclo[3.1.0]hexenyl cation (III in Fig. 1). This ion, after rearranging, yields the 2,3-dimethylbenzenium ion which releases *o*-xylene on desorption.

The calculations have been performed by using the CNDO (complete neglect of differential overlap) formalism, with various

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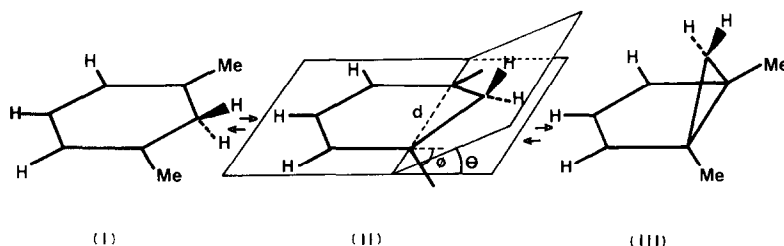


FIG. 1. Cyclization reaction scheme of the 2,6-dimethylbenzenium ion.

parametrizations to be detailed later. All the properties of the ground state have been calculated with the CNDO/2 method (13–15) by using the QCPE 141 (16) program with its implicit parametrization. The magnitudes corresponding to the excited states, as well as the electronic transition energies, have been calculated with the CNDO/S-CI method (17–20) by means of the QCPE 174 (21) program with its implicit standard parametrization. As is well known, the distinction between magnitudes referring to electrons in  $\sigma$  and  $\pi$  orbitals together with specific parametrization implicit in the CNDO/S makes the method suitable for the calculation of excitation energies of aromatic and related compounds.

The potential energy surfaces of the excited states have been drawn according to Ellis and Jaffé (22). As these authors suggest, the energy of an excited state is well approached by adding to the ground-state energy, calculated by CNDO/2, the excitation energy from this state given by the CNDO/S-CI calculation. Such an approximation has proved to be satisfactory in several potential surface studies (23).

The geometrical parameters corresponding to the ring atoms and to the atoms close to the protonated atom are those from Part I of this series (1). The potential energy surfaces are defined in terms of the following geometrical variables: the distance  $d$  between the carbon atoms bonded to methyl groups, the dihedral angle  $\theta$  between the planes of the two rings (see II in Fig. 1). The configuration interaction in the CNDO/S-CI calculations has been ex-

panded to the lowest 30 monoexcited configurations. An expansion to a greater number of configurations, as tested in the more significant points of the surfaces, does not improve the results. The CNDO/S calculations have been performed with Mataga and Nishimoto's formula (24) for the bielectronic repulsion integrals,  $\gamma_{AB}$ , because we are mainly concerned with singlet states.

#### RESULTS AND DISCUSSION

The energy level diagram of the lowest excited states of 2,6-dimethylbenzenium cation is represented in Fig. 2. The energies of these states have been calculated for the ground-state equilibrium geometry; small changes in geometry do not change the order in energy of these states. As the electronic excitation is a "vertical" process, the diagram of Fig. 2 can be considered as an appropriate starting point for all of the subsequent deactivation pro-

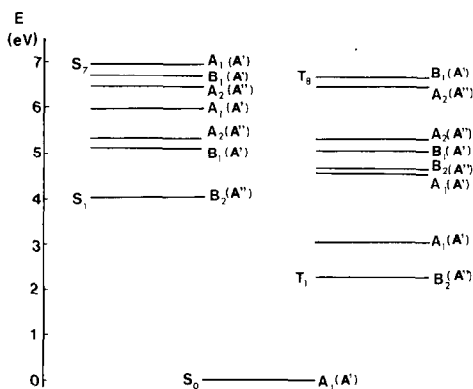


FIG. 2. Energy level diagram for the 2,6-dimethylbenzenium ion.

cesses. The irreducible representations of each state are quoted in Fig. 2, and it must be remembered that the molecule belongs to the  $C_{2v}$  symmetry point group. Also, quoted in parentheses are the representations corresponding to the  $C_s$  point subgroup in which are included all the symmetry elements remaining along the cyclization process.

The oscillator strength for the  $S_0 \rightarrow S_1$  transition, calculated by the CNDO/S-CI method, gives a mean lifetime of  $\tau_f^0 = 6.6 \times 10^{-9}$  s for the fluorescence process ( $S_1 \rightarrow S_0$ ). Then, in the absence of bimolecular quenching, the radiationless deactivation processes, the internal conversion (IC)  $S_1 \rightsquigarrow S_0$  to the ground state, and the intersystem crossing (ISC)  $S_1 \rightsquigarrow T_1$  to the corresponding triplet state, cannot compete with fluorescence. Thus, the photochemical reaction, if it takes place, must start from the first excited singlet  $S_1$ , in competition with fluorescence. The photochemistry starting from the first excited triplet  $T_1$  has a low

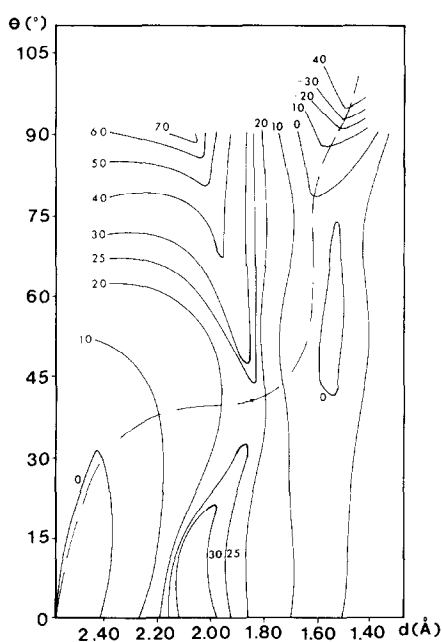


FIG. 3. Potential energy map for the  $S_1$  state of the 2,6-dimethylbenzenium ion. Isoenergetic line values are given in kilocalories per moles.

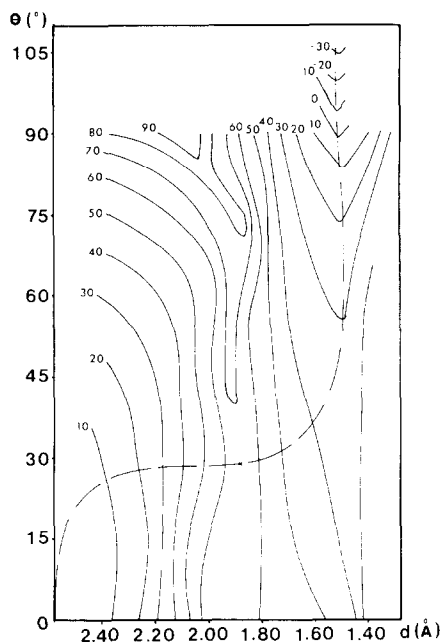


FIG. 4. Potential energy map for the  $T_1$  state of the 2,6-dimethylbenzenium ion. Isoenergetic line values are given in kilocalories per mole.

probability because of the difficulty in populating it.

By looking into the feasibility of the photochemical process, the potential energy maps for the change from 2,6-dimethylbenzenium ion to dimethylbicyclo [3.1.0]hexenyl cation have been drawn. In Figs. 3 and 4, the energy surface maps for the first singlet  $S_1$  and first triplet  $T_1$  excited states, respectively, are represented. The energy values quoted are given in kilocalories per mole, and refer to the energy of the conformation of the starting point as zero. The most favoured reaction paths are represented by broken lines.

The potential energy barrier in  $S_1$  (see Fig. 3) turns out to be about  $23 \text{ kcal} \cdot \text{mole}^{-1}$ . This value is quite high and it is not far enough from the one reported for the thermal reaction on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  catalysts which is about  $37 \text{ kcal} \cdot \text{mole}^{-1}$  (4, 5, 26-29). Such a large value may arise from the anomalously high value estimated for the energy of the saddle point in the ground state (1, 2). The calculation of the potential

energy surfaces in terms of only two parameters  $d$  and  $\theta$  must be reviewed. During the cyclization process it is evident that some other geometrical parameters will not remain constant, and the energy is also a function of those parameters. Special attention must be directed to the methyl substituents in the 2 and 6 positions. During the cyclization process the two C-CH<sub>3</sub> bonds will not remain coplanar to the five-membered ring as was supposed in the drawings of Figs. 3 and 4.

In order to improve the calculation of energy surfaces we have introduced a third geometrical parameter  $\phi$ , the angle between the C-CH<sub>3</sub> bond and the plane of the five-membered ring (see II in Fig. 1). An overall recalculation of the maps represented in Figs. 3 and 4 introducing the angle  $\phi$  is cumbersome. Notwithstanding this, we have recalculated the potential energy values along the reaction coordinates outlined in the maps, but optimizing the value of  $\phi$  for each point, and making a wider search about the saddle point in the ground state. The general features of the maps do not change significantly, and the saddle point for the ground state remains around the values of  $d$  and  $\theta$  estimated without considering the parameter  $\phi$ , which for such a saddle point gives a minimum energy

for  $\phi \approx 70^\circ$ , reducing the barrier height to 46 kcal · mole<sup>-1</sup> for the ground state, this calculated value lying inside the order of experimental values quoted in the literature (4, 5, 26-29).

In order to gain a better characterization of the geometrical structure of the saddle point, further work is in progress on this and other related structures using force-constant-based methods referring to all of the internal degrees of freedom except the ones involved in the reaction path.

The optimized energy levels for the  $S_0$ ,  $S_1$ , and  $T_1$  states of the 2,6-dimethylbenzenium cation, the intermediate saddle point, and the dimethylbicyclo[3.1.0]hexenyl cation are represented in Fig. 5. The most important feature derived from this diagram is the absence of any significant potential barrier for the cyclization process in the first excited singlet state  $S_1$ . Such an absence shows that the photoreaction is possible and that it can compete with fluorescence in the deexcitation of the 2,6-dimethylbenzenium ion  $S_1$  state.

In addition, two points indicate that photochemistry starting from  $T_1$  is unimportant: (1) The low population of this state from the excited singlets, and (2) the quite high energy barrier shown in Fig. 5 (34 kcal · mole<sup>-1</sup>) which is of the order of mag-

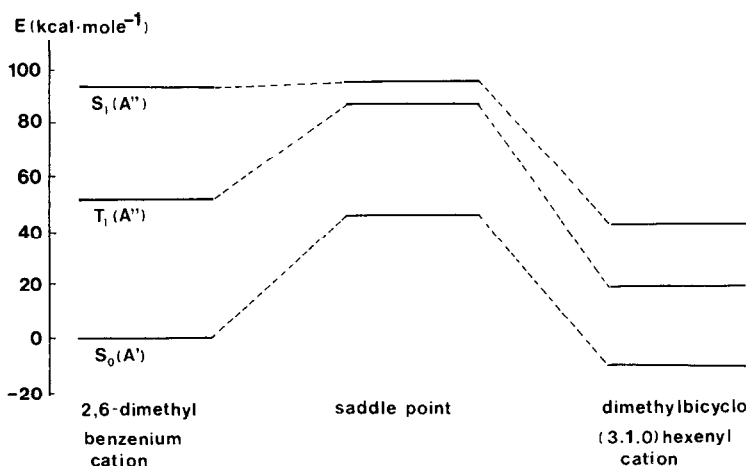


FIG. 5. Optimized correlation diagram of  $S_0$ ,  $S_1$ , and  $T_1$  states along the reaction path for the cyclization reaction of the 2,6-dimethylbenzenium ion.

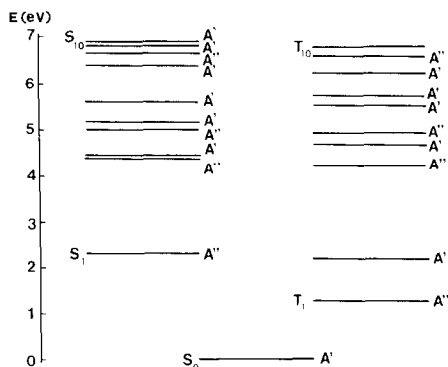


FIG. 6. Energy level diagram for the dimethylbicyclo[3.1.0]hexenyl cation.

nitude of the thermal barrier. However, the intersystem crossing between  $S_1$  and  $T_1$  around the saddle point must be considered. In this sense a more elaborate calculation introducing spin-orbital coupling is needed. In any case, the photochemical process must start from  $S_1$  driving to the  $S_1$  of bicyclo or  $T_1$  via ISC.

The energy level diagram for the electronic excited states of the bicyclic cation is given in Fig. 6. The fluorescence mean lifetime of this cation, estimated from the oscillator strength calculated for the  $S_0 \rightarrow S_1$  transition (25) is  $\tau_f^0 = 1.2 \times 10^{-7}$  s. This relatively high lifetime suggests that other decay processes such as ISC or IC may compete with fluorescence in the deactivation of the bicyclic cation from  $S_1$ . An important barrier, both from the ground and the excited states makes difficult the backward reaction to the benzenium cation.

#### CONCLUSION

The isomerization reaction from the 2,6-dimethylbenzenium cation to the dimethylbicyclo[3.1.0]hexenyl cation takes place without an apparent energy barrier through a mechanism involving the excitation of the former molecule by uv radiation with a wavelength less than 305 nm. This wavelength corresponds to the CNDO/S-CI transition energy calculated for  $S_0 \rightarrow S_1$ .

The photochemical reaction must occur via the  $S_1$  state directly, but ISC to  $T_1$  near the saddle point must not be discarded. The calculated energies for the  $S_1$  and  $T_1$  states of the bicyclic cation are very close, which suggests a fast radiationless relaxation to  $S_0$  for this cation.

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