The C_6H_6 Potential-energy Surface: Automerization of Benzene

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High-level *ab initio* calculations are reported, which provide insight into the mechanism of the uncatalysed automerization of benzene.

Scott *et al.*[1] have shown that [1,2-$^{13}C_2$]benzene automerizes in a quartz flow system (2.0 s contact time) at *ca.* 1110 °C to give an 1,2 : 1,3 : 1,4 product ratio of 72 : 24 : 4. This automerization reaction is related to that of other aromatic hydrocarbons,[2] and as with the others the mechanism of this deceptively simple process is still a matter of some conjecture.[1] Scott *et al.*[1] presented four plausible mechanisms that can be used to explain the observed experimental facts for the automerization process: the 1,2-carbon shift mechanism, the dyotropic shift mechanism, the benzvalene mechanism, and the 1,2-hydrogen shift mechanism (Scheme 1). Herein, we have used *ab initio* quantum mechanical methodologies to elucidate the mechanism of the thermal automerization of benzene (AB).

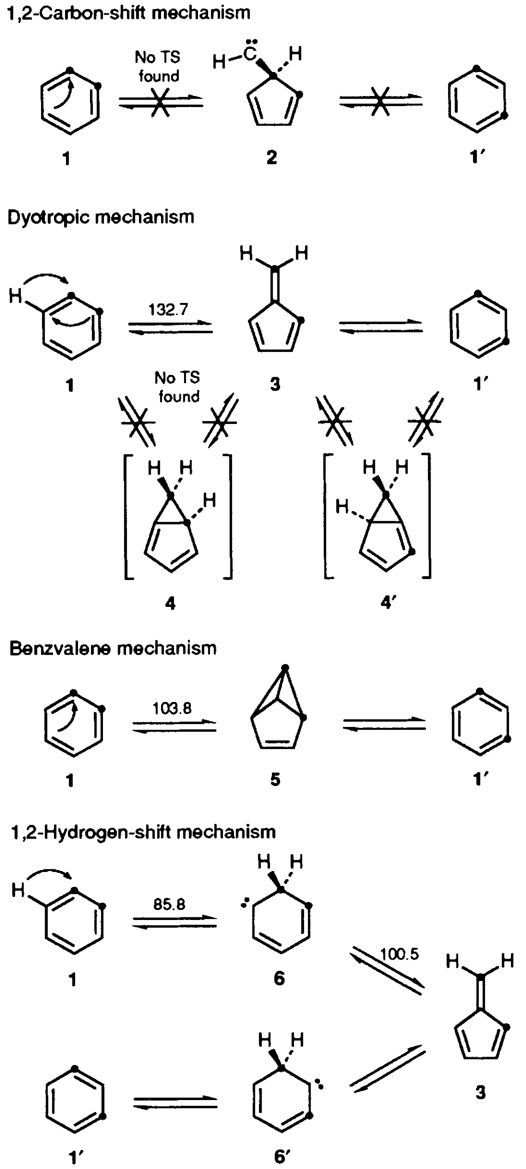
The *ab initio* calculations were carried out using GAUSSIAN 88 and the STO-3G, 3-21G, 6-31G* and 6-31G** basis sets,[3] but only the results from the latter two are reported. Correlation was included up to the MP3/6-31G**//6-31G** level and all energies reported were obtained at this level unless otherwise noted. Geometries were optimized with respect to all geometric variables without making any assumptions besides symmetry (at the uncorrelated levels only) and all stationary points were characterized by calculating force constants (up to the 6-31G*//6-31G* level only).[4] Thermodynamic corrections (at 1383 K only) were evaluated using standard procedures at the 6-31G*//6-31G* level.[5]

We first investigated the 1,2-carbon shift and the dyotropic mechanisms (Scheme 1). Recently, Scott *et al.* have demonstrated that a naphthalene-based carbene analogous to **2** is not involved in the automerization of naphthalene.[6] Nevertheless, we investigated the role that this pathway might play in the AB for the sake of completeness. After a thorough search of the potential energy surface we found no evidence for a transition state (TS) that corresponds to the direct formation of the carbene **2** from benzene by a 1,2-carbon shift. We did find,

Table 1 Relative energies and relative thermodynamic corrections (1383 K) for **1**–**6** and transition states[a]

Compound	6-31G*/kcal mol^{-1}	6-31G**/kcal mol^{-1}	MP2/kcal mol^{-1}	MP3/kcal mol^{-1}	H/kcal mol^{-1}	S/e.u.
1	0.0	0.0	0.0	0.0	0.0	0.0
2	114.1	113.7	128.9	120.4	−1.6	11.4
3	36.8	36.7	38.0	34.6	−0.1	8.6
4	89.9	89.9	75.5	77.8	−0.6	7.4
5	83.0	82.6	74.3	73.9	−0.6	3.6
6	89.3	89.5	103.6	93.4	−0.9	10.6
TS **1** → **4**[b]	165.1	162.7	143.0	146.7	−4.9	6.6
TS **1** → **5**	124.4	124.3	114.5	115.1	−3.8	5.4
TS **1** → **6**	98.8	97.6	99.4	96.8	−4.5	4.7
TS **6** → **4**[b]	109.7	109.8	115.6	110.6	−3.6	4.7
TS **4** → **3**	90.8	90.7	75.8	79.4	−3.3	3.9
TS **2** → **5**	122.6	122.4	113.4	115.8	−4.0	5.5
TS **2** → **3**	121.2	119.6	124.0	119.1	−4.8	7.3

[a] $\Delta_aG = [E(\mathrm{TS}) - E(\mathrm{GS})] + [H(\mathrm{TS}) - H(\mathrm{GS})] - \mathrm{T}^*[S(\mathrm{TS}) - S(\mathrm{GS})]$. Note that $E_a = \Delta_aH + RT$ where RT is equal to 2.748 at 1383 K and $\Delta_aH = [E(\mathrm{TS}) - E(\mathrm{GS})] + [H(\mathrm{TS}) - H(\mathrm{GS})]$. Other thermodynamic parameters can be determined in an analogous way (*e.g.* Δ_rH). [b] These represent transition states connecting **1** and **4** and **6** and **4** in the absence of thermodynamic corrections. Species **4** is found to be unstable on the free energy and enthalpy surfaces and, therefore, these transition states will lead directly to **3** in these cases.



Scheme 1 Mechanisms evaluated for the benzene automerization reaction. Calculated transition state free energies (Δ_aG) in kcal mol^{-1} (1 cal = 4.184 J) relative to benzene at 1383 K are shown above the arrows.

however, that **2** could collapse to **5** (TS **2** → **5**) or to **3** (*via* TS **2** → **3**) with total energy barriers (ΔE) obtained at the 6-31G**//6-31G** level of 8.7 and 5.9 kcal mol^{-1}, respectively (1 cal = 4.184 J). These barriers disappear at the highest correlated level suggesting that **2** will rearrange to **3** and **5** without activation. Analysis of the data in Table 1 reveals that this is also true on the enthalpy surfaces, while on the free-energy surfaces small barriers do appear (1.2 kcal mol^{-1} for both cases). Overall, these data are consistent with the recent results of Scott *et al.*[6]

We found a dyotropic shift TS from **1** to **4** and a second TS for opening of **4** to **3** on the 6-31G**//6-31G** energy surface, but no TS for a dyotropic shift directly from **1** to **3** could be located. When the thermodynamic corrections are taken into account, however, the shallow energy minimum for intermediate **4** disappears, and the dyotropic mechanism then proceeds concertedly from **1** to **3**. Regardless, the activation energy (E_a) and the free energy of activation (Δ_aG) for TS **1** → **3** are 144.5 and 132.7 kcal mol^{-1}, respectively. These activation parameters are much higher than those seen for subsequent reaction mechanisms. Hence, we feel that this mechanism and the 1,2-carbon shift mechanism are not important contributors to the AB reaction.

We next investigated the benzvalene mechanism. The ring opening of **5** has been studied previously using the MINDO/3 method[7] and was found to involve a rather unsymmetrical TS (a two-stage reaction[8]). This result is supported by our higher level calculations, which indicate that this TS is very unsymmetrical (1.72 and 2.41 Å distances for the bonds that are breaking at the 6-31G**//6-31G** level). The E_a, Δ_aS, Δ_aG and enthalpy of reaction (Δ_rH) for the formation of **1** from **5** have been determined experimentally[9] to be 26.7 kcal mol^{-1}, 1.6 e.u.,† 25.4 kcal mol^{-1} and −67.54 kcal mol^{-1}, respectively. The calculated E_a, Δ_aS, Δ_aG and Δ_rH for this reaction at 298 K are 39.9 kcal mol^{-1}, 3.2 e.u., 38.3 kcal mol^{-1} and −72.5 kcal mol^{-1}, respectively.‡ The agreement between theory and experiment is quite good for the Δ_rH, but the E_a, Δ_aS, Δ_aG are all too large. The E_a and Δ_aG for **1** → **5** (at 1383 K) are found to be 114.0 and 103.8 kcal mol^{-1}, respec-

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† 1 e.u. = 4.184 J K^{-1} mol^{-1}.

‡ The theoretical values quoted are for 298 K. The experimental activation parameters were determined in a temperature range of 313–330 K and the Δ_rH was obtained at 298 K. The relative H values for **1**, **5** and TS **1** → **5** are 0.0, −1.4 and −3.3, respectively, at 298 K. The relative S values for **1**, **5** and TS **1** → **5** are 0.0, 2.4 and 5.6, respectively, at 298 K.

tively, which are much more favourable than the activation parameters determined for the dyotropic pathway.

In our previous theoretical work on the automerization of naphthalene we discovered a new mechanism that was able to account for the experimental results[10] (the 1,2-hydrogen shift mechanism). In the present study we also explored the role that this mechanism might have in the AB reaction. From Table 1 (see Scheme 1) we find that ring contraction of **6** constitutes the rate-determining step for this reaction. The bicyclic structure **4** represents a bound intermediate on the pathway from **6** to **3** only before applying the thermodynamic corrections; the calculated E_a and $\Delta_a G$ (for **1** $\rightarrow$ **3**) are 109.7 and 100.5 kcal mol^{-1}, respectively. These activation parameters are lower than those found for the benzvalene mechanism and clearly suggest that this pathway is favoured over the benzvalene mechanism.

Based on our results we conclude that benzene automerizes by the 1,2-hydrogen shift mechanism. This conclusion is similar to that arrived at for the automerization of naphthalene.[10] The benzvalene mechanism, which was favoured by Scott *et al.*,[1] has activation parameters that are *ca.* 3–4 kcal mol^{-1} higher than those for the 1,2-hydrogen shift mechanism. The dyotropic shift mechanism is significantly higher in energy than either the benzvalene or the 1,2-hydrogen shift mechanism and the 1,2-carbon shift does not appear to be important because the carbene **2** is too high in energy. In this study we have used single determinantal methodologies, which may not handle some portions of this potential energy surface as well as a multi-determinantal (*e.g.* MCSCF) approach would. Regardless, it is still our expectation that either the 1,2-hydrogen shift or the benzvalene mechanism will be the favoured pathway. Further improvements in the theoretical approach will lead to a more definitive conclusion regarding which of the latter two pathways is the most favoured in the AB reaction.

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