Ab Initio Calculations on the Isomerization of the 1,3-Hexadien-5-ynyl Radical Cation to the Benzene Structure and to Nonclassical Ion Structures

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Ab initio calculations at the MRCI//ROHF/6-31G** level show that the barrier for isomerization of the 1,3-hexadien-5-ynyl radical cation to nonclassical structures with a five-membered ring and an exocyclic CH bond is about 15 kcal mol⁻¹. The barrier for a subsequent isomerization to the benzene structure is calculated to be slightly higher. (*J Am Soc Mass Spectrom* 1996, 7, 731-736)

It is well known that (collisionally induced dissociation) mass spectra of benzene and many of its isomers show highly similar fragmentation patterns (see ref 1 for a review). In addition, studies of ion-molecule reactions of C₆H₆ radical cations from different neutral precursors [2-5] and of their photodissociation and/or charge exchange ionization mass spectra [6-8] have shown that, depending on the internal energy, these ions may isomerize to the benzene structure without decomposition.

In a recent paper [9] from this laboratory, it was shown that semiempirical calculations give a clear, qualitative picture of the processes involved, which is in very good agreement with the experimental results. The conclusions from that work are now used as a starting point for ab initio calculations. In a previous article [10], we reported the results for the first processes studied: hydrogen scrambling via consecutive 1,2-hydrogen shifts and carbon scrambling via an isomerization to the fulvene structure. The semiempirical calculations [9] indicate that the lowest barriers that can be reached directly from the structures involved in these scrambling processes are those that lead to the 1,3-hexadien-5-ynyl structure and to nonclassical ion structures with a five-membered ring and an exocyclic CH bond and from these latter structures to the 1,3-hexadien-5-ynyl structure (see Schemes 4 and 7 in ref 9 and Figure I herein). This conclusion is in very good agreement with the experimental results. According to the photodissociation experiments [6] about 40% of the C₆H₆ radical cations obtained from 1,3-hexadien-5-ynyl by electron ionization at 16-eV isomerize to nonphotodissociating ions, which were assumed to have the benzene structure (see, however, subsequent text).

From further experiments with charge exchange ionization [7] it was concluded that the barrier for this isomerization is at most 1 eV.

In the present work the isomerization reactions involved and their connection with the intermediate structures in carbon and hydrogen scrambling reactions of the benzene radical cation [10] are studied by ab initio calculations.

Methods

Ab initio calculations that used the 6-31G** basis set were performed with both the GAMESS-UK [11] and the Gaussian 94 [12] program packages. In previous calculations [13] on the isomerization of C₃H₄ radical cations, it was found that at crucial points on the potential energy surface an unrestricted Hartree-Fock calculation may produce unacceptable values as high as 1.0 for the spin angular momentum (*S*²). For this reason stable ion structures and transition states were optimized at the restricted open shell Hartree-Fock (ROHF) level. Transition states were tested by a calculation of the vibrational frequencies and by a visualization, by use of VIBRAM [14], of the vibration with the single negative force constant. As a further test of some of the transition states, an intrinsic reaction coordinate (IRC) calculation was done by using Gaussian 94 to verify that the obtained transition state connects the correct ion structures.

For the optimized structures, multireference configuration interaction (MRCI) calculations with single and double excitations were done with the Table CI (ref 15 and references cited therein) option of GAMESS-UK. In these calculations, excitations that

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involved the lowest 10 occupied and the highest 40 virtual molecular orbitals were not included (these latter orbitals have an orbital energy higher than 2 hartree). All configurations that had a coefficient squared higher than 0.0025 in the final ground state wave function or higher than 0.0030 in the wave function for the second root (of the same symmetry) were used as reference configurations. The extrapolation threshold that is used in Table CI calculations was set at the lowest value compatible with the maximum number of 30,000 configurations in the final diagonalization (the contribution of the remaining configurations is calculated by perturbation theory). In most cases, the extrapolation threshold was 5 μ hartree, but for some structures a somewhat higher value was needed (see Table 1). The MRCI values given in Table

1 include a generalized Davidson size-consistency correction [16]. The final values in Figure 1 are relative to the benzene radical cation energy calculated with the same extrapolation threshold.

Results and Discussion

The reaction scheme considered is shown in Figure 1. This scheme is based on the previous semiempirical results [9] with two extensions: the isomerization between structures 4 and 8 and the hydrogen shift from structure 8 to its mirror image. The reason for the inclusion of this latter process is its possible contribution to carbon and hydrogen scrambling. The ab initio results for the isomerizations between structures 1-5 were described in ref 10. The final self-consistent field

Table 1. SCF, MRCI, and ZPE energies (in hartrees) of the relevant ion structures and transition states

		SCF	MRCI	ZPE
Benzene 1		-230.421222	-230.870064	0.105319
			-230.868588 ^a	
2		-230.369397	-230.812758 ^a	0.104552
3	a' state	-230.365100	-230.812943 ^a	0.104318
	a'' state		-230.715670 ^a	
3A	a' state		-230.750085	
	a'' state	-230.306865	-230.764071	0.099966
4		-230.371634	-230.810205 ^a	0.104389
Fulvene 5		-230.401340	-230.849193 ^a	0.104267
1,3-hexadien-5-yne 6		-230.336125	-230.781256	0.101359
7	a' state	-230.357438	-230.796309	0.103563
	a'' state		-230.713083	
7A	a' state		-230.777961	
	a'' state	-230.304262	-230.747621	0.099575
8	a' state	-230.329295	-230.770054	0.102370
	a'' state		-230.692690	
8A	a' state		-230.755821	
	a'' state	-230.299955	-230.729327	0.099885
T ₁		-230.337993	-230.786505	0.101732
T ₂		-230.336971	-230.786555	0.102068
T ₃		-230.339736	-230.790783	0.102059
T ₄		-230.303401	-230.760790	0.102741
T ₅		-230.289201	-230.755454	0.099320
T ₆		-230.309322	-230.751755	0.100067
T ₇		-230.275304	-230.729562	0.098569
T ₈ ^b		-230.290666	-230.747879	0.100017
T ₉		-230.292347	-230.751372	0.100331
T ₁₀	a' state		-230.663421 ^a	
	a'' state	-230.295605	-230.749780	0.100004
T ₁₁	a' state		-230.593689	
	a'' state	-230.279074	-230.724991	0.099383
T ₁₂		-230.290164	-230.744660	0.100629

^a Extrapolation threshold is 7.5 μ hartree; in the other cases the threshold is 5.0 μ hartree.

^b See text.

Figure 1. Reaction scheme that was considered for the isomerizations considered and calculated relative energies in kilocalories per mole for the different reaction pathways at the MRCI//ROHF/6-31G** level including the ROHF zero-point energy scaled by a factor of 0.89.

(SCF), MRCI and zero-point energy (ZPE) values for the different ion structures and transition states are summarized in Table 1. The relative energies in kilocalories per mole, corrected for the (scaled) ZPE values, are included in Figure 1.

The structures of the transition states for the different 1,2-hydrogen shifts in Figure 1 are relatively easy to calculate and will not be discussed in detail. The same applies to the transition states T_9 that connect 2 and 7 and T_{12} between 4 and 8. As shown in Figure 2, these (nonplanar) transition states have relatively simple structures where the reaction takes place in one half of the molecule and the other half consists of a saturated carbon atom and a double bond. In both cases the calculation is straightforward. For T_{12} the calculations indicate that there is a possibility that in

Figure 2. Structures of the transition states T_9 and T_{12} .

the region of the transition state the system passes a minimum. Because the well depth of this minimum was calculated to be at most a few tenths of a kilocalorie per mole, which is within the accuracy of the calculations, we have paid no further attention to this possible minimum.

The remaining transition states are more difficult to find and will be discussed in the following text.

The Transition States T_{10} and T_{11}

The relatively simple structures shown in Figure 2 for the transition states T_9 and T_{12} are not possible for T_{10} and T_{11} that connect structure 3 with the five-membered ring structures 7 and 8, respectively. In these latter cases, the part of the molecule that is not involved in the ring contraction of structure 3 either consists of three unsaturated carbon atoms (T_{10}) or of a saturated carbon atom and two unconnected CH units (T_{11}); see Figure 3. It is, therefore, not surprising that the structures of these transition states appear to be essentially different from the structures of T_9 and T_{12} . As shown schematically in Figure 3 both T_{10} and T_{11} are planar (C_s), whereas their wave functions have a" symmetry (unpaired electron in a π orbital). Because the ground states of structures 3, 7, and 8 all have a' symmetry (unpaired electron in a σ orbital), it follows that both reactions should proceed via two (perhaps avoided) curve crossings.

Because the reaction paths involved are clearly rather complicated, the geometries of the lowest a" states of 3, 7, and 8 also were optimized. The final geometries (3A, 7A, and 8A) together with those of 3, 7, and 8 are shown in Figure 4. As expected, the main difference between the a' and a" geometries for the different ion structures is found in the bond angle for

Figure 3. Structures of the transition states T_{10} and T_{11} .

the carbon atom that carries the unpaired electron in the a' geometries and the charge in the a'' geometries (compare Figures 5 and 6). Additional MRCI calculations on the a' states of 3A, 7A, and 8A showed that for 7A and 8A the a' state still has the lowest energy (Table 1). For 3A, however, the a'' state has the lowest energy. Calculations of the vibrational frequencies showed that 3A is not a stable structure but a transition state between two nonplanar mirror image structures. We have not tried to optimize these latter structures because we may expect that a further optimization without symmetry constraints should go to geometry 3.

The reaction paths from T_{10} and T_{11} were followed by intrinsic reaction coordinate (IRC) calculations by using Gaussian 94. The results showed the expected connection between 3A and 7A for T_{10} and between 3A and 8A for T_{11} . To save computer time, these calculations were done at the 3-21G level. Additional 3-21G state-averaged complete active space SCF (CASSCF) calculations on the two lowest states for a number of points along the reaction paths between T_{10} and 7A and between T_{11} and 8A showed that the assumed curve crossings do exist and have a geometry and an energy not much different from those of 7A and 8A, respectively. These kinds of curve crossings in isomerizations of radical cations presumably are of general importance. A previous highly comparable example was found in the isomerization of the allene radical cation to the CH_2CHCH ion structure [13].

The final set of energy diagrams at the MRCI//6-31G** level are given in Figures 5 and 6. The results in Table 1 and Figure 5 show that, although T_{10} is the

Figure 4. Difference between the a' and a'' geometries of structures 3, 7, and 8.

transition state between the a'' states of 7A and 3A at the SCF level, the a'' energy of T_{10} after the MRCI calculation is lower than that of 7A. This picture again is highly comparable to that obtained for the hydrogen shift in the allene radical cation [13]. Because the potential surface involved is almost flat and the curve crossing is close to the a'' state of 7A, it will be

Figure 5. Energy diagram at the MRCI//ROHF/6-31G** level of the isomerization between structures 7 and 3. The values are in kilocalories per mole relative to the ground state of the benzene radical cation without correction for the zero-point energies.

Figure 6. Energy diagram at the MRCI//ROHF/6-31G** level of the isomerization between structures 8 and 3. The values are in kilocalories per mole relative to the ground state of the benzene radical cation without correction for the zero-point energies.

assumed that the actual energy of the real transition state can be set equal to the energy of the a'' state of 7A. It is of course possible that this value is slightly too high because there may be an avoided crossing between 7A and T_{10} . In that case the energy of the real transition state should at least be equal to the energy of T_{10} , which is only 1.3 kcal mol⁻¹ lower than that of 7A and 1.1 kcal mol⁻¹ lower after correction for the ROHF ZPE. These differences are within the accuracy of the calculations.

The Ring Closure of the 1,3-Hexadien-5-yne Radical Cation

Figure 7 shows the results of a semiempirical (modified neglect of differential overlap) grid calculation of the reaction paths that connect the 1,3-hexadien-5-yne ion structure 6 with structures 3 and 7 that have six- and five-membered rings, respectively. In these calculations the C_1-C_5 and the C_1-C_6 distances in Figure 7 were varied, whereas the other geometrical parameters were optimized. Figure 7 suggests that during a ring closure, the 1,3-hexadien-5-yne radical cation reaches a nearly flat part of the potential energy surface whence it may go to two valleys that have slightly different barriers; the barrier to the six-membered ring 3 is a few kilocalories per mole higher than that to the five-membered ring 7. The geometries of these semiempirical transition states were used as starting points for ab initio calculations on T_5 and T_8 . The optimization of T_5 appeared to be straightforward and will not be discussed in detail. This, however, does not

apply to T_8 that connects the 1,3-hexadien-5-yne radical cation structure with the six-membered ring structure 3. ROHF transition state optimizations that used the 3-21G and 6-31G basis sets produced geometries similar to that obtained from the semiempirical calculation. In these geometries the $C_4-C_5-C_6$ bond angle was about 170°, whereas a visualization of the vibration that corresponds to the single negative force constant by using VIBRAM [14] agreed with the expected reaction coordinate. Also an additional 3-21G IRC calculation showed the connection between structures 3 and 6. After addition of polarization functions, the $C_4-C_5-C_6$ bond angle increased to a value of 176° for the 6-31G** basis set. The energies obtained by using this basis set are given as the values for T_8 in Table 1. At the SCF level, the final energy obtained is slightly lower (0.9 kcal mol⁻¹) than the energy of T_5 , but after the MRCI calculation it is significantly higher (4.8 kcal mol⁻¹). In the vibration that corresponds to the single negative force constant, the distances between C_1 and C_5 and between C_1 and C_6 changed in a similar way and a visualization was not sufficient to determine whether the obtained transition state connected structures 6 and 3 or structures 6 and 7. In contrast to the results at the 3-21G level, additional IRC calculations finally showed a connection between structures 6 and 7.

A 6-31G** transition state optimization that started with a semiempirical geometry slightly below the barrier within the valley that leads to structure 3 in Figure 7 produced structure T_{10} , the transition state between 3 and 7.

These results together indicate that a ring closure of the 1,3-hexadien-5-yne radical cation essentially leads to the five-membered ring structure 7 and that the six-membered ring structure 3 can be obtained only by ring expansion of 7. The energy differences between the different transition states are at most slightly higher

Figure 7. Semiempirical (MNDO) potential energy surface that connects structures 3, 6, and 7. The difference between the contour lines is 5 kcal mol⁻¹.

than the accuracy of the present calculations. It is, therefore, possible that a somewhat different picture may be obtained from calculations at a higher level. This, however, will not change the major conclusions.

Conclusions

The final results are summarized in the reaction scheme in Figure 1. For the reasons discussed in the foregoing text, the energy for the transition state T_8 between the 1,3-hexadien-5-yne radical cation **6** and the six-membered ring **3** is omitted from this scheme. From the values in this scheme we arrive at the following conclusions.

1. In the isomerization of unsaturated hydrocarbon radical cations, nonclassical structures are of vital importance. These ion structures are characterized as consisting of an odd-membered charged π -electron system with the unpaired electron in a localized σ orbital (charge-delocalized distonic ions?). The prototype of such a nonclassical ion structure is the CH_2CHCH radical cation, which is best described as an allyl cation with one of the terminal hydrogen atoms removed [13]. Structure **8**, which has a branched π -electron system, has a relatively high heat of formation, but in all other cases the heat of formation of these ions is significantly below that of the classical 1,3-hexadien-5-yne radical cation.
2. As discussed in ref 10, the transitions between structures 1-5 and their relative energies explain the independence of hydrogen and carbon scrambling in the benzene radical cation. At an energy some 5-10 kcal mol⁻¹ above the barrier for carbon scrambling by isomerization to the fulvene structure, there exist several barriers for ring contraction to structures **7** and **8**. These barriers open a number of additional pathways for (independent) carbon and hydrogen scrambling.
3. The barrier for ring closure of the 1,3-hexadien-5-yne radical cation is about 15 kcal mol⁻¹. This is in excellent agreement with the experimental results mentioned in the introduction. Interestingly, the

barrier for further isomerization to the benzene structure is calculated to be a few kilocalories per mole higher. It is therefore quite possible that upon ionization of 1,3-hexadien-5-yne, a (small) ion fraction does not isomerize to the benzene structure but to the five-membered ring structure **7** or even to structure **8**.

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