ELSEVIER International Journal of Mass Spectrometry 210/211 (2001) 13–20 www.elsevier.com/locate/ijms

# Ab initio calculations on the isomerization of alkene radical cations. 2. Ring opening of cycloalkane radical cations

W.J. van der Hart

*Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Received 26 October 2000; accepted 5 February 2001

## Abstract

Ab initio calculations on the ring opening of the cyclopentane and cyclohexane radical cations do not give an explanation of previous experimental findings that, upon electron ionization, the cyclopentane ion ring opens whereas the cyclohexane ion is stable. The main difference between the two cases is that the cyclohexane ion first has to isomerize to the methylcyclopentane structure before ring opening. The barrier heights for ring opening in the two cases are comparable and significantly lower than the difference between the vertical and adiabatic ionization energies. The results suggest that, for an explanation of the experiments, accurate theoretical studies of the ionization process itself will be needed. (Int J Mass Spectrom 210/211 (2001) 13–20) © 2001 Elsevier Science B.V.

*Keywords:* $C_5H_{10}^{\cdot+}$; $C_6H_{12}^{\cdot+}$; ring opening; ab initio calculations

## 1. Introduction

The radical cations of cyclobutane and cyclopentane have been studied in a large number of articles, both by experimental methods, such as electron spin resonance and mass spectrometry, and by ab initio calculations (see [1–6] and references cited therein). In solid matrices these ions are stable. Upon ionization in a mass spectrometer, however, both cyclobutane and cyclopentane ring open whereas cyclohexane and cycloheptane remain cyclic (see, e.g. [5] and [6]). The ring opening of the cyclobutane radical cation is well understood. According to the ab initio calculations in [1] and [4] the reaction between ethylene and the ethylene radical cation to the 1-butene ion structure proceeds by way of a $(C_2H_4)_2^{\cdot+}$ complex cation and this ion complex is also the intermediate in the ring opening of the cyclobutane radical cation to the 1-butene cation structure [4]. A similar ion complex structure has been obtained from ab initio calculations on the reaction between the 1-butene radical cation and the ethylene molecule [7].

In the present work possible pathways for the ring opening of the cyclopentane and cyclohexane radical cations are studied by ab initio calculations.

## 2. Methods

Ab initio calculations using a split valence basis set [8] with one set of polarization functions (SVP) were

---

* E-mail: w.hart@chem.leidenuniv.nl

Dedicated to Nico Nibbering after almost 25 years of a very pleasant cooperation, joint workshops, and many useful discussions.

*PII* S1387-3806(01)00407-9

Table 1
ROHF, ZPE, and MRCI energies of the different radical cation structures and transition states in Fig. 1 and relative MRCI energies in kcal/mol$^{-1}$ corrected for the ROHF ZPE energy scaled by a factor of 0.89

| | ROHF | ZPE | MRCI | $\Delta E$ |
|---|---|---|---|---|
| Cyclopentane **1** | | | | |
| $C_2$ symmetry | | | | |
| Minimum | −194.863 195 | 0.146 512 | −195.199 499 | 2.0 |
| Vertical | −194.805 847 | | −195.146 799 | |
| $C_s$ symmetry | | | | |
| Minimum | −194.867 035 | 0.146 740 | −195.202 826 | 0 |
| Vertical | −194.787 904 | | −195.147 469 | 34.7[a] |
| **2A** | −194.864 483 | 0.141 483 | −195.194 040 | 2.6 |
| **2B** | −194.854 846 | 0.140 718 | −195.192 099 | 3.4 |
| 1-Pentene **3**[b] | −194.887 646 | 0.144 942 | −195.216 344 | −9.5 |
| Trans-2-pentene **4**[b] | −194.906 070 | 0.144 527 | −195.236 550 | −22.4 |
| **5** | −194.842 872 | 0.143 536 | −195.177 932 | 13.8 |
| **6** | −194.873 996 | 0.144 348 | −195.210 344 | −6.1 |
| $T_{1,2}$ | −194.839 949 | 0.140 827 | −195.170 826 | 16.8 |
| $T_{1,3B}$ | −194.782 841 | 0.142 647 | −195.133 912 | 41.0 |
| $T_{2,3A}$ | −194.837 939 | 0.141 334 | −195.176 974 | 13.2 |
| $T_{2,3B}$ | −194.850 820 | 0.141 355 | −195.188 294 | 6.1 |
| $T_{2,4}$ | −194.840 768 | 0.142 528 | −195.174 827 | 15.2 |
| $T_{2,6}$ | −194.856 250 | 0.139 636 | −195.183 750 | 8.0 |
| $T_{6,3B}$ | −194.861 141 | 0.139 964 | −195.192 891 | 2.5 |
| $T_{3,4}$[b,c] | −194.835 989 | 0.138 728 | −195.182 167 | 8.5 |

[a] Value without ZPE correction.
[b] Values from [10].
[c] Not included in Fig. 1.

performed with both the GAMESS-UK [9] and the GAUSSIAN 98 [10] program packages. In our previous work it was found that at crucial points on the potential energy surface an unrestricted Hartree-Fock calculation may produce unacceptable values for the spin angular momentum ($S^2$) as high as 1.0. For this reason stable ion structures and transition states were optimized at the restricted open shell Hartree-Fock (ROHF) level.

Starting geometries for transition state optimizations were obtained from semiempirical or 4-31G ab initio calculations of the assumed reaction path. The results were tested by a calculation of the vibrational frequencies and by a visualization of the vibration corresponding with the single negative force constant by use of VIBRAM [11]. For the optimized structures, multireference configuration interaction (MRCI) calculations with single and double excitations were done with the Table CI ([12] and references cited therein) option of GAMESS-UK. In these calculations for $C_5H_{10}^{\cdot+}$ excitations involving 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). For $C_6H_{12}^{\cdot+}$ these numbers were 14 and 50, respectively. All configurations having 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 selection threshold used in Table CI of [12] was set at 2.5 $\mu$Hartree, which leads to about 50000 configurations in the final diagonalization. In Table CI calculations the contribution of the remaining configurations is calculated by perturbation theory. The MRCI values given in Tables 1 and 2 include a generalized Davidson size-consistency correction [13].

Rice-Ramsperger-Kassel-Marcus calculations including tunneling (RRKMT) on the rates of the first step in the isomerizations were performed with a FORTRAN version of a QUICK BASIC program

Table 2
ROHF, ZPE, and MRCI energies of the different radical cation structures and transition states in Fig. 5 and relative MRCI energies in $\text{kcal/mol}^{-1}$ corrected for the ROHF ZPE energy scaled by a factor of 0.89

| | ROHF | ZPE | MRCI | $\Delta E$ |
|---|---|---|---|---|
| Cyclohexane **7** | | | | |
| Minimum | −233.919 444 | 0.177 903 | −234.224 734 | 0 |
| Vertical | −233.867 004 | | −234.178 921 | 28.7[a] |
| Methyl-cyclopentane **8** | −233.925 990 | 0.176 840 | −234.225 679 | −1.2 |
| **9** | −233.912 200 | 0.171 916 | −234.204 440 | 9.4 |
| **10** | −233.912 291 | 0.171 511 | −234.197 692 | 13.4 |
| 1-Hexene **11** | −233.927 273 | 0.175 012 | −234.231 621 | −5.9 |
| 2-Hexene **12** | −233.951 124 | 0.175 093 | −234.239 603 | −10.9 |
| 3-Hexene **13** | −233.951 652 | 0.175 527 | −234.240 803 | −11.4 |
| $T_{7,8}$ | −233.885 252 | 0.171 913 | −234.191 129 | 17.7 |
| $T_{8,9}$ | −233.887 552 | 0.171 490 | −234.192 564 | 16.6 |
| $T_{8,10}$ | −233.903 489 | 0.170 384 | −234.194 552 | 14.7 |
| $T_{9,11}$ | −233.897 116 | 0.172 343 | −234.202 443 | 10.9 |
| $T_{9,12}$ | −233.898 759 | 0.171 945 | −234.192 854 | 16.7 |
| $T_{10,11}$ | −233.896 989 | 0.171 820 | −234.188 912 | 19.1 |
| $T_{10,12}$ | −233.883 098 | 0.172 095 | −234.193 080 | 16.6 |
| $T_{10,13}$ | −233.887 252 | 0.172 590 | −234.189 690 | 19.0 |

[a] Value without ZPE correction.

written by Baer [14,15]. This latter program is based on an APL program without tunneling from Forst [16].

## 3. Results

### 3.1. Cyclopentane radical cation

It is well known that alkane radical cations generally have one very long (charged) C–C bond [17]. In the present case, the calculations give one C–C bond length of 2.054 Å in the cyclopentane radical cation (2.058 Å in [2]). In the following, it will be assumed that isomerization reactions of the cyclopentane radical cation take place in the neighborhood of this long bond (see Fig. 1). As remarked in Sec. 1, it has been shown in [1] and [4] that ring opening of the cyclobutane radical cation takes place by way of a $(C_2H_4)_2^{\cdot+}$ complex cation. One may assume that, in the same way, an isomerization of the cyclopentane radical cation to pentene structures will go via a propene/ethene ion adduct [structure **2** in Fig. 1(a)]. This ion geometry can, in principle, be reached in two

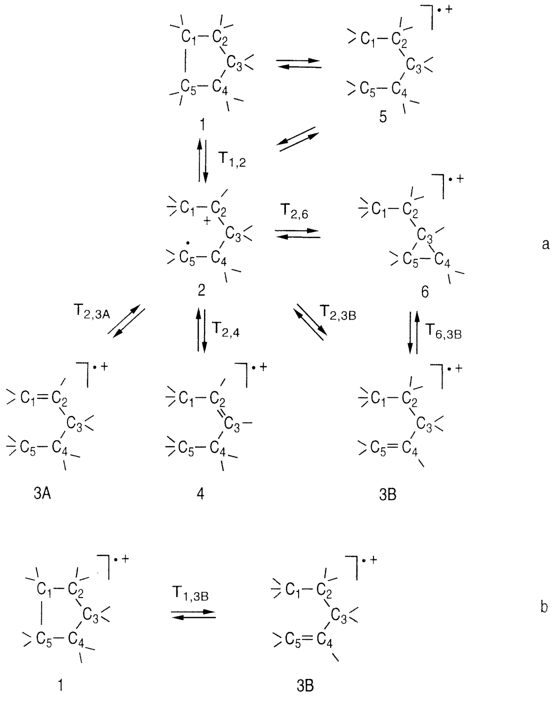


Fig. 1. Reaction schemes considered for the isomerization of the cyclopentane radical cation. The long bond (see text) is $C_1$–$C_5$.

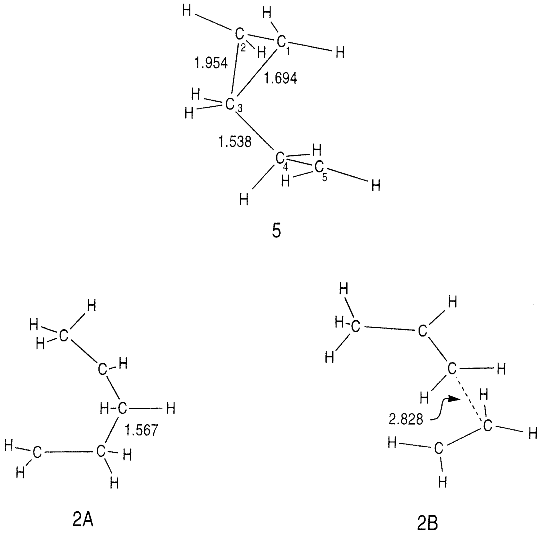


Fig. 2. Projected geometries of some relevant $C_5H_{10}$ ion structures.

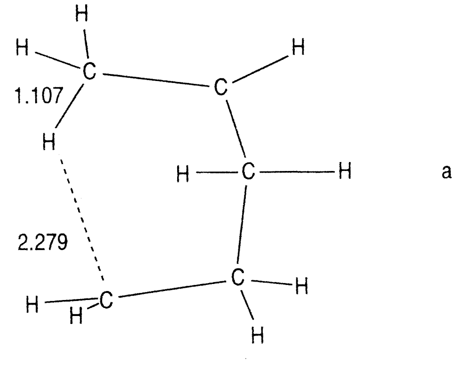
different ways. Either a direct reaction by a 1,2-hydrogen shift to one of the carbon atoms of the long bond simultaneously with a breaking of the long bond or by a breaking of the long bond to structure **5** followed by a 1,2-hydrogen shift. From structure **2**, the 1-pentene cation structure **3** can then be reached by either a 1,5-hydrogen shift [**3A** in Fig. 1(a)] or by a 1,3-hydrogen shift (**3B**) or by two successive 1,2-hydrogen shifts via the ethylcyclopropane radical cation **6** and the 2-pentene structure **4** by a 1,3-hydrogen shift from $C_3$ to $C_5$. An alternative isomerization pathway is a direct isomerization of the cyclopentane radical cation to the 1-pentene ion structure by a 1,4-hydrogen shift in combination with a breaking of the long bond [Fig. 1(b)]. In the following these possibilities will be discussed in more detail.

A reaction path for breaking of the long bond, calculated at the 4-31G level, showed a steady increase of the energy but also passed a (local) minimum. An optimization of this minimum at the SVP level produced the geometry shown in Fig. 2 as a possible geometry for structure **5**. This geometry more or less looks like a trimethylene/ethene ion/molecule complex. From previous work [18], it is known that the trimethylene radical cation is unstable and isomerizes to the propene structure with a negligible barrier. This, however, does not work in the present case. A Mulliken population analysis showed that in structure **5** the charge is localized in the three-membered ring and the unpaired electron on $C_5$. As was found from 4-31G calculations of the reaction paths a shift of a hydrogen from $C_4$ to $C_5$, therefore, is unfavourable while a hydrogen shift from $C_4$ to $C_3$ did not produce structure **2** but appeared to lead to fragmentation. For this reason no further attention was paid to structure **5**.

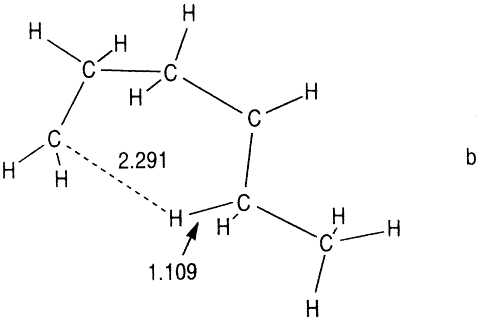
As shown in Table 1, a direct isomerization of the cyclopentane radical cation to the 1-pentene ion is possible but the energy of the transition state $T_{1,3B}$ is much higher than that of the other transition states considered.

It thus follows that isomerization of the cyclopentane radical cation takes place via $T_{1,2}$ to structure **2** and from **2** to the pentene structures by way of successive 1,2, 1,3, or 1,5 hydrogen shifts. For structure **2** we found two different ion geometries. **2A** has a normal bond length between the propene and ethene units and **2B** a very long bond length (see Fig. 2). This latter structure is comparable to the ion/molecule complexes in [1,4, and 7], although the bond length is much longer than the values given in these articles. According to the present calculations, **2A** has a slightly lower energy than **2B** (Table 1). The potential energy surface between **2A** and **2B** is rather flat. A reaction path calculation at the 4-31G level showed a maximum energy below 6 kcal $mol^{-1}$ above the energy of **2A**.

Optimization of the transition states $T_{2,3B}$, $T_{2,4}$, $T_{2,6}$, and $T_{6,3B}$ was straightforward. This, however, was not the case for $T_{2,3A}$. The reason is that, starting with structure **2**, a hydrogen has to move from $C_1$ to $C_5$ where, according to a Mulliken population analysis, the unpaired electron is localized [see Fig. 1(a)]. A complete active space self-consistent field (CASSCF) optimization with three electrons in four orbitals showed that the potential energy surface in the region of the transition state is rather flat: during a variation of the distance of the moving hydrogen to $C_5$ from 1.61 to 3.12 Å the energy changed by only 3.4 kcal $mol^{-1}$. An optimum geometry, however, was



$T_{2,3A}$



$T_{8,10}$

Fig. 3. Projected geometries of the transition states (a) $T_{2,3A}$ and (b) $T_{8,10}$.

not obtained. A subsequent ROHF optimization, starting with one of the points from the complete active space self-consistent field CASSCF calculation, finally produced an optimized geometry [Fig. 3(a)] with one negative force constant. The corresponding vibration and the Mulliken spin and charge distribution agreed with the expected nature of the transition state.

The final energy diagram is presented in Fig. 4. In this diagram we did not include $T_{2,3A}$ and the isomerization by way of the ethylcyclopropane radical cation which have higher energies than $T_{2,3B}$ (Table 1) but added the barrier for a direct isomerization of the 1-pentene radical cation to the 2-pentene structure as obtained in [19].

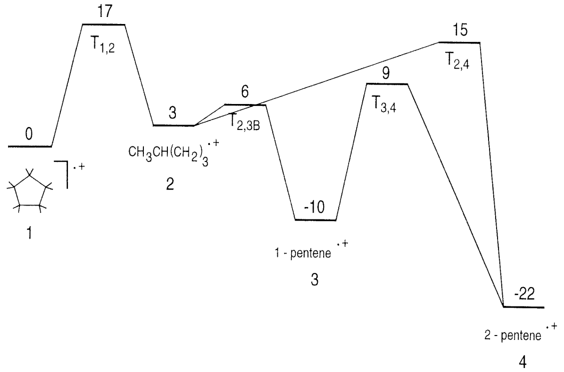


Fig. 4. Energy diagram for the isomerization of the cyclopentane radical cation.

### 3.2. Cyclohexane radical cation

A pathway as described for the cyclopentane radical cation by a 1,2 hydrogen shift to an acyclic ion structure which can be described as an alkene/alkene ion adduct is not possible for the cyclohexane radical cation **5**. One might suppose that this could explain the relative stability of the cyclohexane radical cation. Calculations on 1,2 hydrogen shifts, however, showed the existence of an alternative pathway: a direct isomerization to the methylcyclopentane structure **6** by a 1,2 hydrogen shift simultaneously with a ring contraction. Structure **6** again has one very long (2.089 Å) bond length from the substituted carbon $C_2$ to one of the neighboring carbon atoms, e.g. $C_2$–$C_6$ (see Fig. 5). Then two different reactions, comparable to the reaction from the cyclopentane radical cation **1** to structure **2**, are possible, one leading to structure **7** and one to structure **8** (Fig. 5). Structure **7** is reached by a hydrogen shift from $C_5$ to $C_6$ together with a breaking of the $C_2$–$C_6$ bond and structure **8** by a hydrogen shift from $C_3$ to $C_2$ and, again, a breaking of the $C_2$–$C_6$ bond. Structure **7** can be considered as a propene/propene ion adduct and structure **8** as a 1-butene ion/ethene adduct. In both cases we obtained quite normal bond lengths between the alkene units: 1.614 Å for **7** and 1.538 Å for **8**.

Further isomerizations of **7** and **8** to hexene structures are comparable to the reactions of structure **2** to the pentene ions. The 1-hexene radical cation **9** can be

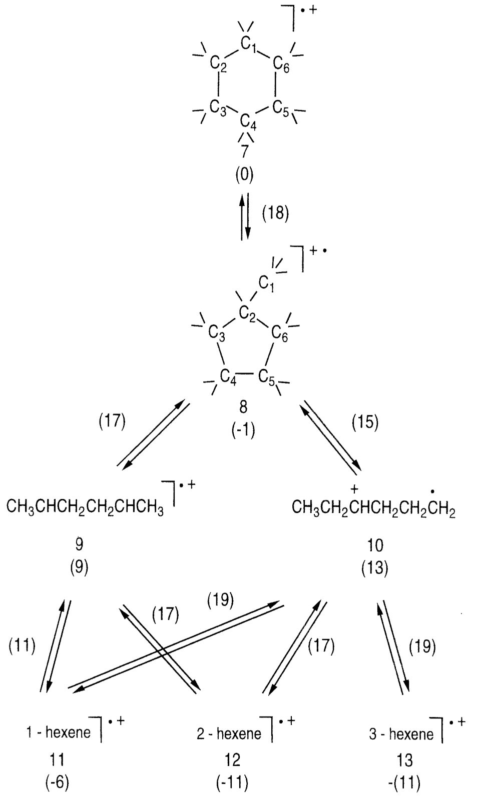


Fig. 5. Reaction schemes considered for the isomerization of the cyclohexane radical cation. The long bond in structure **8** (see text) is $C_2$–$C_6$.

obtained by a 1,5 hydrogen shift from **7** and by a 1,3 hydrogen shift from **8**, the 2-hexene radical cation **10** by a 1,3 hydrogen shift from **7** and a 1,5 hydrogen shift from **8** and, finally, the 3-hexene radical cation by a 1,3 hydrogen shift from **8**. The total reaction scheme is shown in Fig. 5 and the calculated energies are given in Table 2. Fig. 5 also shows the final relative MRCI energies corrected for the zero-point energy.

The same problem as mentioned in the cyclopentane case for $T_{2,3A}$, was observed here for the transition state $T_{8,10}$ [Fig. 3(b)] but, also in this case, an optimized geometry could be obtained at the ROHF level.

The results of the calculations, as given in Table 2, lead to the energy diagam shown in Fig. 6.

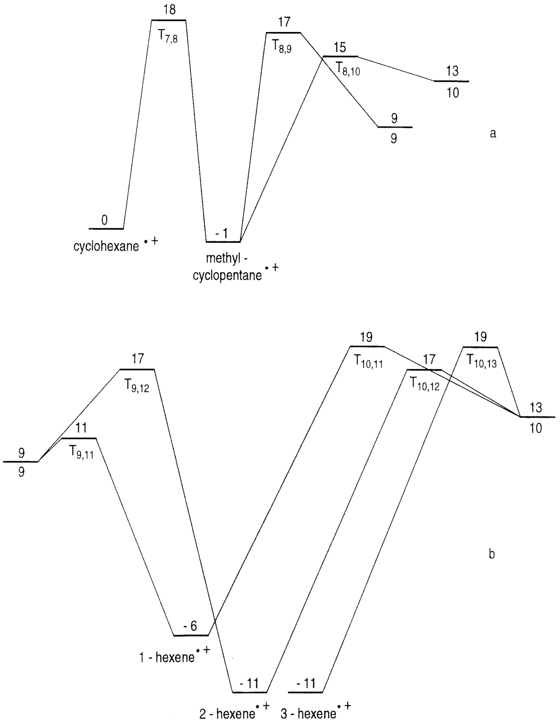


Fig. 6. Energy diagram for the isomerization of the cyclohexane radical cation.

## 4. Discussion

From the energy diagrams in Figs. 4 and 6, it is clear that the calculated barrier heights for the ring opening of the cyclopentane and cyclohexane radical cations are highly comparable and of the order of 17–18 kcal $mol^{-1}$. The main difference, in fact, is that the cyclohexane ion first has to isomerize to the methylcyclopentane structure which implies that there are two instead of one relatively high barriers to pass. The barriers obtained are not significantly different from that suggested for the ring opening of the cyclobutane radical cation in the revised potential energy surface in [4]. There is, however, a difference with the results of the photoelectron–photoion coincidence experiments on $C_5H_{10}$ radical cations in [20], where the authors conclude that the barrier for the ring opening of the cyclopentane radical cation to the 1-pentene structure is lower than the barrier for a subsequent isomerization to the 2-pentene structure.

Table 3
Calculated rates in $s^{-1}$ including tunneling for the first step in the isomerization of the cyclopentane and cyclohexane radical cations; $\Delta E$ gives the energy of the ion in eV relative to the transition state

| $\Delta E$ | $C_5H_{10}^{++}$ | $C_6H_{12}^{-+}$ |
|---|---|---|
| −0.3000 | $0.2528E-07$ | $0.1581E-03$ |
| −0.2500 | $0.3263E-04$ | $0.1974E-01$ |
| −0.2000 | $0.2152E-01$ | $0.2000E+01$ |
| −0.1500 | $0.8353E+01$ | $0.8203E+01$ |
| −0.1000 | $0.2437E+04$ | $0.6313E+03$ |
| −0.0500 | $0.7695E+04$ | $0.3696E+05$ |
| 0.0000 | $0.1522E+07$ | $0.1402E+07$ |
| 0.0500 | $0.3124E+08$ | $0.7733E+07$ |
| 0.1000 | $0.1018E+09$ | $0.2516E+08$ |
| 0.1500 | $0.2449E+09$ | $0.6618E+08$ |
| 0.2000 | $0.4988E+09$ | $0.1452E+09$ |

In addition, it is important to note that the experiments reviewed in [5] and [6] were performed in ion cyclotron resonance (ICR) spectrometers at low pressures where the time needed for relaxation of the internal energy of the ions is of the order of a few tenths of a second. This means that tunneling through the barriers may have a significant effect on the actual experimental barrier heights. For example, Booze et al. [14] showed that tunneling has a very large effect on the barrier for HCl loss from ethylchloride ions as obtained from photoelectron photoion coincidence measurements where the residence time of the ions is many orders of magnitude shorter than in ICR spectrometers. For this reason the RRKMT were calculated for the first step in the isomerization of the cyclopentane and cyclohexane radical cations. The results are shown in Table 3. These show that isomerization due to tunneling should be possible in ICR spectrometers at energies close to 0.2 eV = 4.5 kcal $mol^{-1}$ below the calculated barrier thus lowering the expected experimental barriers to values in the order of 13 kcal $mol^{-1}$.

These results combined lead to a problem. As shown in Tables 1 and 2, the calculated difference between the adiabatic and vertical ionization energy is 35 kcal $mol^{-1}$ for cyclopentane and 29 kcal $mol^{-1}$ for cyclohexane. Both values are clearly higher than the calculated isomerization barriers. A similar result was obtained before for $C_4H_5N$ radical cations [21]. In this case, calculations on cyclopropylcyanide also show that the difference between the vertical and the adiabatic ionization energy is higher than the barrier for isomerization to acyclic ion structures while the experimental results suggest that a large stable fraction of cyclopropylcyanide ions is formed upon electron ionization [22]. It thus seems that ab initio calculations of the isomerization barriers are insufficient to explain the difference in behaviour of cyclopentane and cyclohexane after electron ionization and that an accurate theoretical description of the ionization process itself is needed. In order to solve this problem, at least calculations of the Franck-Condon factors involved will be essential. Unfortunately, programs to do these calculations for molecules as large as cyclopentane and cyclohexane are not available at present.

## Acknowledgement

The author is very grateful to Professor Tomas Baer for sending a copy of his RRKMT program and for his help in the test of the derived FORTRAN version.

## References

[1] J.R. Alvarez-Idaboy, L.A. Eriksson, T. Fängström, S. Lunell, J. Phys. Chem. 97 (1993) 12737.
[2] S. Lunell, L.A. Eriksson, T. Fängström, J. Maruani, L. Sjöqvist, A. Lund, Chem. Phys. 171 (1993) 119.
[3] P. Jungwirth, P. Ĉársky, T. Bally, J. Am. Chem. Soc. 115 (1993) 5776.
[4] P. Jungwirth, T. Bally, J. Am. Chem. Soc. 115 (1993) 5783.
[5] R.C. Dunbar, in Gas Phase Ion Chemistry, Ions and Light Vol. 3, M.T. Bowers (Ed.), Academic, Orlando, 1984.
[6] W.J. van der Hart, Mass Spectrom. Rev. 8 (1989) 237.
[7] J.R. Alvarez-Idaboy, L.A. Eriksson, S. Lunell, J. Phys. Chem. 97 (1993) 12742.
[8] T.H. Dunning Jr., P.J. Hay, Modern Theoretical Chemistry, H.F. Schaefer III (Ed.), Plenum, New York, 1977, Vol. 3, p. 1.
[9] M.F. Guest, P. Fantucci, R.J. Harrison, J. Kendrick, J.H. van Lenthe, K. Schoeffel, P. Scherwood, GAMESS-UK User's Guide and Reference Manual, revision C.0, Computing for Science (CFS) Ltd., Daresbury Laboratory, Daresbury, UK, 1992.
[10] GAUSSIAN 98, revision A.5, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Bu-

rant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.

[11] J. Dillen, Program No. QCMP 12010, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47405, USA, 1992.

[12] R.J. Buenker, R.A. Philips, J. Mol. Struct. (Theochem) 123 (1985) 291.

[13] S.T. Elbert, E.R. Davidson, Int. J. Quantum Chem. 8 (1974) 857.

[14] J.A. Booze, K.M. Weitzel, T. Baer, J. Chem. Phys. 94 (1991) 3649.

[15] T. Baer, W.L. Hase, Unimolecular Reaction Dynamics. Theory and Experiments, Oxford University Press, Oxford, 1996, pps. 416 and 417.

[16] W. Forst, Theory of Unimolecular Reactions, Academic, New York, 1973, pps. 395–403.

[17] W.J. Bouma, D. Poppinger, L. Radom, Isr. J. Chem. 23 (1983) 21.

[18] P. Du, D.D. Hrovat, W.T. Borden, J. Am. Chem. Soc. 110 (1998) 3405.

[19] W.J. van der Hart, J. Am. Soc. Mass Spectrom. 10 (1999) 575.

[20] L.M. Duffy, J.W. Keister, T. Baer, J. Phys. Chem. 99 (1995) 17862.

[21] W.J. van der Hart, Int. J. Mass Spectrom. 198 (2000) 33.

[22] M.W.E.M. van Tilborg, J. van Thuijl, W.J. van der Hart, Int. J. Mass Spectrom. Ion Processes 54 (1983) 299.