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Ab initio calculations on the isomerization of C_4H_6 radical cations

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Abstract

Ab initio calculations on the potential energy surface for isomerization and dissociation of C_4H_6 give a reasonably consistent picture. In the competition between isomerization of different C_4H_6 radical cation structures to the 1,3-butadiene structure and fragmentation, tunneling appears to be of vital importance. An unsolved problem remains the difference between the calculated barriers for an isomerization of the butyne ions to the 1,3-butadiene structure and the experimental values obtained previously by Bunn and Baer from a combination of PEPICO measurements and photodissociation. (Int J Mass Spectrom 208 (2001) 119–125) © 2001 Elsevier Science B.V.

Keywords: C_4H_6 radical cations; Ab initio calculations; Fragmentation; Isomerization; Tunneling

1. Introduction

The isomerization and dissociation of C_4H_6 radical cations has been reported in many articles both by experimental methods and by quantum chemical calculations (see [1–5], and references cited therein). It is now clear that the dissociation of C_4H_6 radical cations by methyl loss proceeds by way of an isomerization to the 3-methylcyclopropene structure [1,2]. Also known are the barriers for the isomerization of the butyne radical cations to the 1,3-butadiene structure which were determined directly by Bunn and Baer [3] using a combination of photoelectron photoion coincidence (PEPICO) measurements with photodissociation.

Especially the ring opening of the cyclobutene radical cation to the 1,3-butadiene structure has been an important topic in theoretical work. For recent elaborate studies of this process see [4] and [5]. Hrouda et al. [2] did extensive calculations on the reaction of the ethylene radical cation with acetylene and calculated the barriers to form many of the possible C_4H_6 radical cation structures. The purpose of the present study is to obtain a more complete picture of the potential energy surface for the isomerization of C_4H_6 radical cations and, especially, to compare the barriers for the isomerization of the butyne ions, as measured by Bunn and Baer, with ab initio calculations.

2. Methods

Ab initio calculations using the double zeta plus polarization basis set of Dunning and Huzinaga [6]

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were performed with both the GAMESS-UK [7] and the GAUSSIAN98 [8] program packages. In previous calculations on the isomerization of radical cations we 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. Because the same will apply for unrestricted MP2 calculations, 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 of the vibration corresponding with the single negative force constant by use of VIBRAM [9]. For the optimized structures, multireference configuration interaction (MRCI) calculations with single and double excitations were done with the Table CI (and references cited therein) option of GAMESS-UK. In these calculations excitations involving the lowest 4 occupied (core) and the highest 14 virtual molecular orbitals were not included. 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 [10] was set at 4.0 μHartree. This implies that the number of configurations in the final diagonalization was in the order of 45 000. In Table CI calculations the contribution of the remaining configurations is calculated by perturbation theory. The final MRCI values given in the tables include a generalized Davidson size-consistency correction [11].

Rice-Ramsperger-Kassel-Marcus calculations including tunneling (RRKMT) were performed with a FORTRAN version of a Quick Basic program written by Baer and co-workers [12–14]. This latter program is based on an APL program without tunneling from Forst [15].

3. Results

The reaction scheme considered is shown in Fig. 1. This scheme is mainly based on a semiempirical exploration of possible connections between all more or less acceptable C_4H_6 radical cation structures and, in some cases, on 4-31G calculations of reaction paths. In the scheme we have not included the $CH_2CH_2CCH_2$ radical cation structure **13**, which can be obtained from the 1,3-butadiene ion structure by a 1,2 hydrogen shift and can isomerize further to the methylenecyclopropene structure **7**. The calculations produced two different geometries **13A** and **13B** for this ion (see Fig. 2). **13A** has an energy only slightly below the transition state from the 1,3-butadiene ion and **13B** an energy slightly above the methylenecyclopropene ion (see Table 1). For this reason it is assumed that **13A** and **13B** are not more than local minima on the route from the 1,3-butadiene ion **1** to the methylenecyclopropene ion **7**. A similar conclusion was reached in [2]. Despite numerous attempts using both ROHF and complete active space self-consistent field, optimizations and reaction path calculations, we could not find a transition state for an isomerization by a 1,2 hydrogen shift from **13A** or **13B** to the 1,2-butadiene structure **4** or in the opposite direction. This is also in agreement with the results in [2], where the authors could find a transition state for the reaction from **13A** at the unrestricted second order Møller-Plesset level but not from restricted calculations. Because the energy of **13A** is of the same order as the barrier $T_{1,10}$ for a direct reaction of the 1,3-butadiene ion **1** to structure **4** by way of structure **10** and the barrier $T_{1,7}$ for the isomerization of structure **1** to the methylenecyclopropene ion **7** by way of the hypothetical ions **13A** and **13B** (see Fig. 1 and Table 1), we have not considered this reaction any further. In Fig. 1 we have also included a ring opening of the cyclobutene radical cation **8** by way of the three-membered ring structure **14**. This pathway was originally suggested by Belville et al. [16] but Wiest [4] recently concluded that it is an artefact of the quantumchemical methods used previously. Following Sastry et al. [5] we conclude from the present results that the pathway by way of structure **14** is not an artefact and that the barrier for this reaction is almost equal to that for a direct ring opening of the cyclobutene radical cation **8** to the 1,3-butadiene structure **1**. The final results are summarized in Table

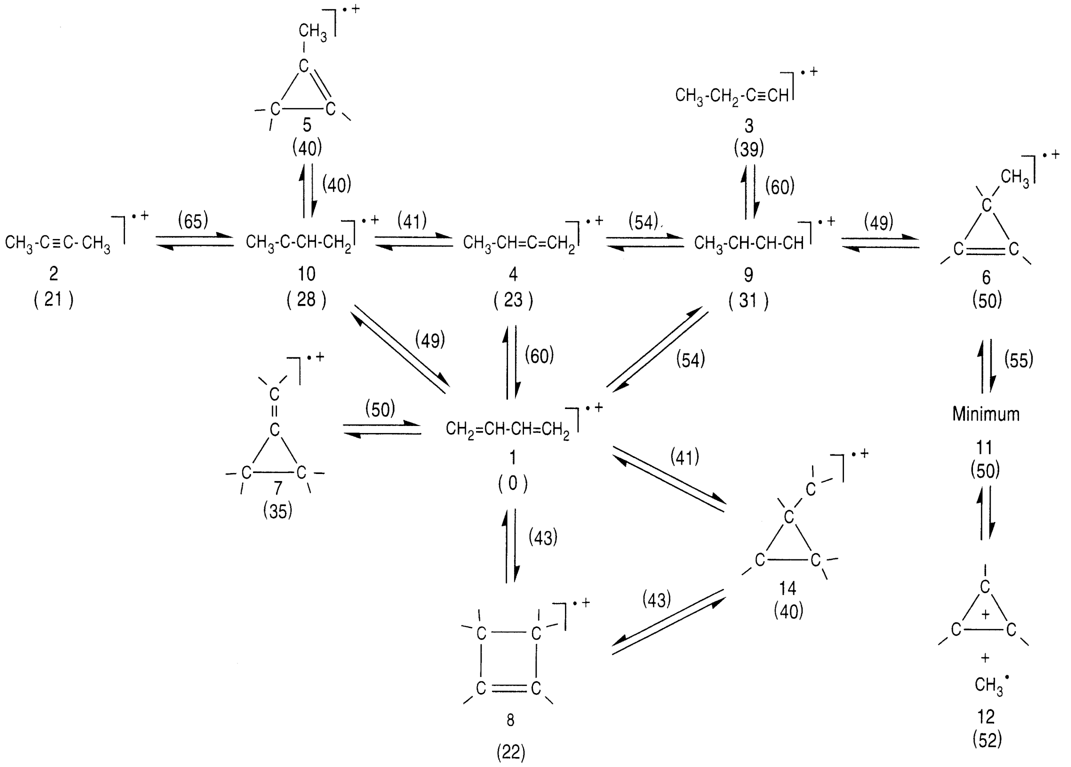


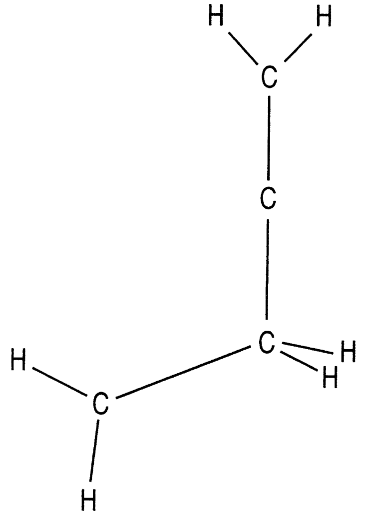
Fig. 1. Reaction scheme considered. Values in parentheses are the energies in kcal mol^{-1} relative to the 1,3-butadiene ion **1**.

1 and the relative energies in kcal mol^{-1} are included in Fig. 1.

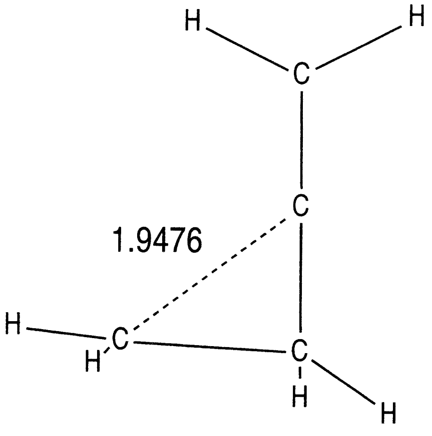
4. Discussion

Before discussing the results presented in Table 1 and Fig. 1, we first will make a comparison of the final relative energies with those obtained in [1] and [2]. This is shown in Table 2. In many cases there is a clear agreement between these results but there are also some exceptions where the relative energy calculated in the present work is higher than that in [1] and [2]. In part, this may be due the fact that, in the present work, the geometry optimizations were done with a more flexible basis set including polarization functions on the hydrogen atoms but this does probably not explain why on the average our relative energies are some 3–4 kcal mol^{-1} higher than those obtained in [2]. This could indicate that, for some reason, especially the final energy of the 1,3-butadiene radical cation is relatively lower in the present work. More interesting, however, are some other aspects of the results presented in Table 1 and Fig. 1.

Most of the isomerizations in Fig. 1 involve hydrogen shifts. This implies that tunneling may play a role. For example, Booze et al. [12] showed that tunneling has a very large effect on the barrier for HCl loss from ethyl chloride ions as obtained from photoelectron photoion coincidence measurements. Tunneling rates depend on the depths of the wells on both sides of the transition state and the direction of the reaction and are largely determined [13] by the value of the imaginary frequency in the transition state. In Table 3 we have collected the calculated values of the imaginary frequencies for the transition states in Fig. 1. It is clear that especially for the isomerization of structure **9** to the 1,3-butadiene ion **1**, one may expect a significant effect of tunneling. Table 4 shows the



13A



13B

Fig. 2. Projection of two different minimum geometries obtained for structure **13**.

RRKMT rates as a function of the energy with respect to the transition state for the isomerization of structure **9** to **1** and vice versa and for the isomerization of **3** to **9**. In PEPICO experiments the threshold for observation of an isomerization is a rate in the order of 10^4–10^5. If we take this as a criterion, then it follows from Table 4 that the experimental threshold for an isomerization of structure **9** to the 1,3-butadiene ion will be lowered by about 0.5 eV = 12 kcal mol^{-1} and for an isomerization of the 1-butyne ion **3** to structure **9** by at most 0.1 eV = 2 kcal mol^{-1}. These results yield a different picture of the competition between the dissociation of C_4H_6 radical cations by way of structures **9** and **6** and the isomerization of structure 9 to the 1,3-butadiene ion **1** than one should expect from a consideration of the calculated energies in Fig. 1 and in [1] and [2] (Table 2) alone.

As mentioned in sec. 1, Bunn and Baer [3] determined the isomerization barriers of the 1- and 2-butyne ions by a combination of PEPICO and photodissociation. Their values are 0.21 eV = 4.8 kcal mol^{-1} for the 1-butyne ion **3** and 1.03 eV = 23.8 kcal mol^{-1} for the 2-butyne ion **2**. The measurements were done on thermal ions which leads to a possible correction for the average thermal energy of about 0.1 eV = 2.3 kcal mol^{-1} [17]. The corrected values of 7 and 26 kcal mol^{-1} are significantly lower than the calculated barriers of 21 and 44 kcal mol^{-1} (Fig. 1 and Table 1). For this reason the barrier for the isomerization of the 1-butyne ion was recalculated by an optimization at the configuration interaction with singly and doubly excited states CISD level. The resulting barrier (Table 5) has the somewhat lower value of 18 kcal mol^{-1}. As discussed above, tunneling lowers this value further but by not more than 2 kcal mol^{-1}. The final value of 16 kcal mol^{-1} is still about 10 kcal mol^{-1} higher than the experimental isomerization barrier. If we apply the same correction of 5 kcal mol^{-1} to the barrier for isomerization of the 2-butyne ion, then its relative energy in Fig. 1 drops to 60 kcal mol^{-1}. This is still some 5 kcal mol^{-1} above the calculated dissociation limit which is also in contrast with the conclusions reached by Bunn and Baer. It is difficult to say how accurate calculations of transition barriers in radical cations really are but the barriers calculated for the 1- and 2-butyne ions seem to be consistent with the value obtained previously for a 1,2 hydrogen shift in the propyne radical cation [18]. A comparison can be made by looking at Fig. 3. In the 2-butyne radical

Table 1
ROHF, zero point vibrational (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 zero point vibrational energy scaled by a factor of 0.89

	ROHF	ZPE	MRCI	ΔE
Trans-1,3-butadiene **1**	−154.666415	0.092233	−155.177214	0.0
2-Butyne **2**	−154.632939	0.087189	−155.139150	21.1
1-Butyne **3**	−154.604071	0.087952	−155.111383	38.9
1,2-Butadiene **4**	−154.633392	0.087064	−155.136118	22.9
1-Methylcyclopropene **5**	−154.609254	0.087520	−155.110034	39.5
3-Methylcyclopropene **6**	−154.589866	0.087876	−155.094045	49.8
Methylenecyclopropane **7**	−154.619686	0.088799	−155.118057	35.2
Cyclobutene **8**	−154.637821	0.090988	−155.140464	22.4
$CH_3CHCHCH$ **9**	−154.627080	0.088241	−155.123692	31.4
CH_3CCHCH_2 **10**	−154.633606	0.088502	−155.129542	27.8
Dissociation minimum **11**	−154.595479	0.081557	−155.087581	50.3
Fragments at 15 Å **12**	−154.591088	0.079780	−155.084028	51.5
13A	−154.597177	0.083498	−155.093490	47.7
13B	−154.604600	0.087225	−155.115381	36.0
14	−154.605511	0.089462	−155.107465	42.2
$T_{1,4}$	−154.558826	0.084367	−155.075212	59.6
$T_{1,7}$	−154.587580	0.083406	−155.090055	49.8
$T_{1,8}$	−154.604096	0.090131	−155.107149	42.6
$T_{1,9}$	−154.560328	0.083462	−155.083349	54.0
$T_{1,10}$	−154.582107	0.083966	−155.092087	48.8
$T_{1,14}$	−154.599686	0.088109	−155.108197	41.0
$T_{2,10}$	−154.563142	.083756	−155.066903	64.5
$T_{3,9}$	−154.565292	.083961	−155.073776	60.3
$T_{4,9}$	−154.579485	.082869	−155.082140	54.4
$T_{4,10}$	−154.600896	.082284	−155.102937	41.1
$T_{5,10}$	−154.596504	.086484	−155.109174	39.5
$T_{6,9}$	−154.584378	.085928	−155.094184	48.6
$T_{6,11}$	−154.575457	.085900	−155.084263	54.8
$T_{8,14}$	−154.604097	.090178	−155.107145	42.8

cation there is a stabilizing interaction between the charge and two alkyl substituents, which is one more than in the propyne radical cation. In the transition state, however, the number of stabilizing alkyl groups directly bonded to the “charged three-membered ring” is equal in both cases. In agreement with results obtained before for the alkene radical cations [19], the relative height of the transition state, therefore, is some 12 kcal mol^{-1} higher than in the propyne case. In an opposite way, the relative height of the transition state in the 1-butyne radical cation is about 12 kcal mol^{-1} lower than in the propyne case (see Fig. 3). Similar arguments hold for the relative energies of the isomerization products. For both the propyne and 2-butyne radical cations, the number of alkyl substituents on the charged part of the ion diminishes by one, leading to roughly equal relative energies, but, relative to propyne, it increases by one in the case of the 1-butyne ion.

5. Conclusions

The results of the present ab initio calculations seem to give a consistent picture of the dissociation and isomerization of C_4H_6 radical cations provided tunneling is taken into account. The calculated barriers for isomerization of the butyne ions are in agreement with results, obtained previously for the propyne ion, but the difference with the experimental results of Bunn and Baer remains unclear. The results of the RRKMT calculations suggest that deuteration should have a large effect on the competition between the dissociation of C_4H_6 radical cations by way of struc-

Table 2
Comparison of the calculated relative energies with previous results at the RCCSD (T) /cc-pVTZ//UMP2/6-31G* [2] and UMP2/6-311G**//UMP2/6-31G* [1] levels

	[2]	[1]	Present work
1	0	0	0
2	. . .	. . .	21
3	39	. . .	39
4	16	. . .	23
5	. . .	. . .	40
6	40	35	50
7	30	. . .	35
8	21	. . .	22
9	33	32	31
10	. . .	. . .	28
11	51	46	50
12	54	48	52
13A	43	. . .	48
B	32	. . .	36
14	39[a]	. . .	42
$T_{1,4}$	55	. . .	60
$T_{1,7}$	42	. . .	50
$T_{1,8}$	39	. . .	43
$T_{1,9}$	48	51	54
$T_{1,10}$	. . .	. . .	49
$T_{1,14}$	39[a]	. . .	41
$T_{2,10}$	. . .	. . .	65
$T_{3,9}$	. . .	. . .	60
$T_{4,9}$	. . .	. . .	54
$T_{4,10}$	. . .	. . .	41
$T_{5,10}$	. . .	. . .	40
$T_{6,9}$	40	39	49
$T_{6,11}$	51	47	55
$T_{8,14}$	39[a]	. . .	43

[a] In [2] and [5], these structures are considered parts of a flat potential energy surface (called the "Bauld surface" by the authors) and only a single energy is reported.

Table 3
Absolute values in cm^{-1} of the imaginary frequencies of the transition states included in Fig. 1

$T_{1,4}$	638
$T_{1,7}$	665
$T_{1,8}$	135
$T_{1,9}$	2499
$T_{1,10}$	825
$T_{2,10}$	723
$T_{3,9}$	724
$T_{4,9}$	328
$T_{4,10}$	300
$T_{5,10}$	235
$T_{6,9}$	453
$T_{6,11}$	362

Table 4
RRKMT reaction rates as a function of the energy in eV with respect to the transition state involved

ΔE	$k_{9,1}$	$k_{1,9}$	$k_{3,9}$
−0.9000	0.2388*D*+03	0.1545*D*−03	
−0.8000	0.9704*D*+02	0.2759*D*−03	
−0.7000	0.1352*D*+04	0.1171*D*−01	0.7041*D*−15
−0.6000	0.4757*D*+04	0.1008*D*+00	0.7396*D*−13
−0.5000	0.3249*D*+05	0.1452*D*+01	0.4192*D*−08
−0.4000	0.2110*D*+06	0.1786*D*+02	0.1120*D*−05
−0.3000	0.5782*D*+06	0.8550*D*+02	0.1024*D*−01
−0.2000	0.2646*D*+07	0.6406*D*+03	0.5114*D*+02
−0.1000	0.8255*D*+07	0.3107*D*+04	0.4627*D*+04
0.0000	0.2968*D*+08	0.1663*D*+05	0.6164*D*+07
0.1000	0.8006*D*+08	0.6444*D*+05	0.5487*D*+08
0.2000	0.1756*D*+09	0.1969*D*+06	0.2253*D*+09
0.3000	0.3491*D*+09	0.5311*D*+06	0.6147*D*+09
0.4000	0.6302*D*+09	0.1271*D*+07	0.1360*D*+10
0.5000	0.1056*D*+10	0.2768*D*+07	0.2617*D*+10

Table 5
Energies in Hartree and relative energies in kcal mol^{-1} after CISD calculations

	CISD	ZPE	ΔE
1-Butyn **3**	−155.071476	0.086930	0
9	−155.087602	0.085977	−10.7
$T_{3,9}$	−155.037204	0.081587	18.2

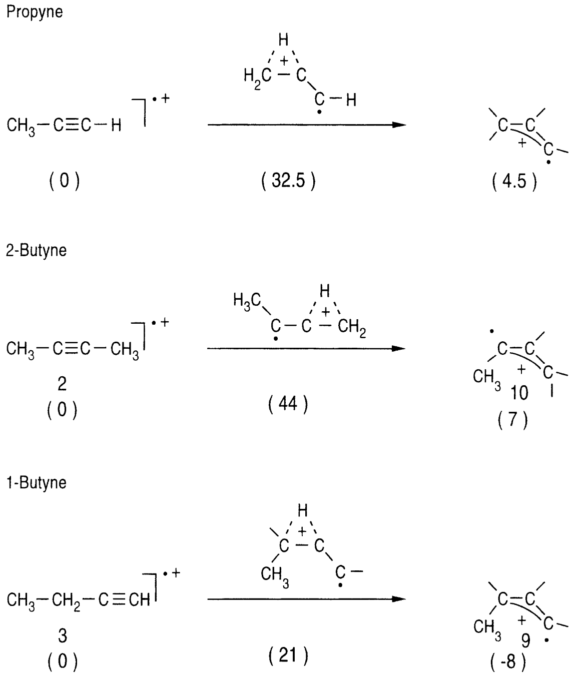


Fig. 3. Comparison of 1,2 hydrogen shifts in the propyne and butyne radical cations.

tures **9** and **6** and the isomerization of structure **9** to the 1,3-butadiene ion.

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