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Intramolecular H Atom Transfer Reactions in Alkyl Radicals and the Ring Strain Energy in the Transition Structure

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Abstract: Ab initio calculations were performed on prototypical intramolecular H atom transfer reactions in alkyl radicals, namely, the identity reactions of 1,2-, 1,3-, 1,4-, and 1,5 intramolecular isomerizations in the ethyl, 1-propyl, 1-butyl, and 1-pentyl radicals, respectively. The equilibrium geometries and the transition structures have been optimized at the UHF/6-31G* and/or UMP2/6-311G** levels. The activation energies at 0 K were calculated with the MP-SAC2 and BAC-MP4 methods. The computed barrier heights (41.1, 41.6, 24.6, 17.2 kcal mol^{-1} at the MP-SAC2 and 43.1, 41.0, 25.1, and 18.8 kcal mol^{-1} at the BAC-MP4 level of theory) follow the trend expected and are in reasonable agreement with experimental data on related reactions. The differences between the ab initio barrier heights of alkyl isomerizations and that of the corresponding bimolecular reaction are in good agreement with the strain energies of the corresponding cycloalkanes.

I. Introduction

The isomerization of alkyl radicals by intramolecular H atom transfer plays an important role in various complex systems, especially in the pyrolysis and combustion of hydrocarbons.[1] The experimental determination of reliable Arrhenius parameters for a radical isomerization reaction, where a highly reactive free radical is converted into another radical, is rather difficult. One has to produce the reactant radical using a clean source and monitor the product in an environment where the reaction in question takes place in competition with a number of other processes. In view of these problems, only a limited number of such studies is available. The 1,4 and 1,5 isomerizations were studied very early,[2] but later the reported Arrhenius parameters were demonstrated to be too low.[3,4] Information of fundamental importance was derived from chemical activation studies of the isomerization of pentyl and hexyl radicals,[5] where the quantities of interest were obtained as fitting parameters in RRKM calculations. These results support the "high" values of the thermal Arrhenius parameters. Much less is known about 1,2 and 1,3 H atom transfers.[6,7] The activation energy of the isomerization depends on the types of the carbon atoms between which the H atom is migrating (i.e., primary, secondary etc.), and on the number of atoms in the chain connecting these atoms. The generally accepted value for the high-pressure limiting activation energy is 41 ± 4 kcal mol^{-1} for 1,2 H, 12−21.5 kcal mol^{-1} for 1,4 H, and about 12 kcal mol^{-1} for 1,5 H atom transfer reactions, depending on the type of the carbon atoms involved.[4]

The customary way of interpreting and calculating the activation energy is based on the fact that for these reactions to proceed formation of a cyclic transition structure is necessary.[2,8] The formation of a strained ring may require a significant amount of energy. As a result, the barrier for intramolecular H atom transfer is higher than that of the analogous intermolecular H atom transfer. The lower activation energy of the 1,4 and 1,5 H atom transfer as compared to the reactions involving a smaller ring in the transition structure can be interpreted in terms of a lower ring strain energy.

Several quantum chemical calculations were performed on the properties of the saddle point of the isomerization of ethyl radicals, but no studies were reported on the isomerization of higher alkyl radicals.[9−11] There are numerous theoretical studies concerning the related bimolecular H atom abstraction reactions,[12,13] among them those for several substituted methanes.[14−16] The reaction which is most closely related to the intramolecular H atom transfer in alkyl radicals

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$$^{\bullet}CH_3 + CH_4 \rightarrow CH_4 + {}^{\bullet}CH_3 \qquad (1)$$

has been extensively studied recently.[15−17]

In this paper, we report on ab initio calculations of the transition structures of symmetrical isomerization reactions of ethyl, 1-propyl, 1-butyl, and 1-pentyl radicals. The reactions studied can be considered as prototypes of the classes of primary−primary 1,2-, 1,3-, 1,4-, and 1,5-intramolecular H atom transfer (often denoted as[4] 3pp, 4pp, 5pp, 6pp transfer, respectively) reactions in alkyl radicals:

$$CH_3CH_2^{\bullet} \rightarrow {}^{\bullet}CH_2CH_3 \text{ 1,2 H atom transfer} \qquad (2)$$

$$CH_3CH_2CH_2^{\bullet} \rightarrow {}^{\bullet}CH_2CH_2CH_3 \text{ 1,3 H atom transfer} \qquad (3)$$

$$CH_3(CH_2)_2CH_2^{\bullet} \rightarrow {}^{\bullet}CH_2(CH_2)_2CH_3 \text{ 1,4 H atom transfer} \qquad (4)$$

$$CH_3(CH_2)_3CH_2^{\bullet} \rightarrow {}^{\bullet}CH_2(CH_2)_3CH_3 \text{ 1,5 H atom transfer} \qquad (5)$$

These reactions themselves are identity reactions, but in principle, the energetic parameters can be expected to be characteristic for the class of which the reaction is a representative. The ab initio calculations were performed at various advanced levels, namely, MP-SAC2[17] and BAC-MP4,[18] because the empirical corrections applied in these methods make them equally accurate for all systems studied. This way we can also compare the performance of these two methods.

In the following, we first describe the methods, in section III we present and analyze the structures and energies of the transition structures of these reactions, and finally, we estimate the ring strain energy in the transition structures.

II. Computational Methods

Ab initio calculations were performed with the GAUSSIAN 92 program.[19] The *Z*-matrices for both the equilibrium and transition structures were constructed using the StrukEd molecular modeling software.[20] Equilibrium geometries of the radicals and of the saddle points were optimized at the UHF/6-31G* level for all systems (for ethyl isomerization also at the UMP2/6-311G** level). The low spin contamination ($S^2 = 0.797$, 0.819, 0.803 and 0.795 at the saddle point of reactions 2−5, respectively) indicates that the single-configuration UHF wave functions provide an acceptable description of the electronic structure of the radicals and the transition structures. This statement is further supported by the occupation numbers of the UHF natural orbitals: the orbitals below the singly occupied MO do not have an occupation number lower than 1.98, and those above it have smaller than 0.02 occupancy, indicating that no multiconfiguration treatment is necessary. It is clear, however, that for the "crowded" transition structure of reaction 2 an MC-SCF treatment is desirable,[9] but the empirical corrections in the MP-SAC2 and BAC-MP4 calculations are expected to correct for this deficiency.

Analytically calculated harmonic vibration frequencies were obtained at the same level as the optimizations. The saddle points on the potential energy surfaces were characterized by the vibrational frequencies: only one imaginary frequency was obtained in each case, proving that we found first-order stationary points. Intrinsic reaction coordinate (IRC) calculations confirmed that these saddle points do in fact separate the minima corresponding to the (identical) reactants and products.

We used several methods to obtain reliable values for the barrier height: UMP2/6-311G** calculations and the MP-SAC2[17] and the BAC-MP4[18] methods. The latter two methods, especially the BAC-MP4 method, ensure that the accuracy of the calculations is comparable for all systems involved in our study.

The basic idea behind the MP-SAC2 (Møller−Plesset second-order scaling all correlation energy) method of Gordon and Truhlar[17] is that one acknowledges that the available level of quantum chemical calculations (MP2 in the present case) does not accurately determine the correlation energy. The latter is defined as the difference between the accurate energy and the value obtained at the Hartree−Fock level (which, as an independent particle approximation, does not take into account the correlation of the motion of different electrons). Truhlar *et al*. suggested that the measure of the inaccuracy of the given method with limited inclusion of electron correlation can be calculated from the goodness of the dissociation energy provided by the method for a bond important in the reaction studied. More precisely, the difference between the experimental and the Hartree−Fock dissociation energy is taken to be the correlation energy. Calculating the difference between the MP2 and the Hartree−Fock bond energies, one can determine what fraction of the correlation energy is accounted for in the MP2 calculation:

$$F_2 = \frac{D_e(\mathrm{MP2}) - D_e(\mathrm{SCF})}{D_e(\exp) - D_e(\mathrm{SCF})}$$

Then, one assumes that the MP2 method describes the correlation effects with the same accuracy at all geometries in the system so that the accurate energy can be obtained by a scaled correction of the UHF energy:

$$E_{\mathrm{MP\text{-}SAC_2}} = E_{\mathrm{UHF}} - \frac{E_{\mathrm{MP2}} - E_{\mathrm{UHF}}}{F_2}$$

We used the value of $F_2 = 0.864$ obtained by Truong and Truhlar for C−H bonds using the 6-311G** basis set.[13]

The BAC-MP4 (bond additivity correction at MP4 level) method developed by Melius *et al*.[19] is based on the observation that the error of an ab initio calculation of the heat of formation of a compound can be composed of bond-wise additive error terms. The error due to a bond is related to its length. Introducing these terms as corrections, the heats of formation of many compounds and radicals can be obtained with remarkable accuracy (within a few kcal mol^{-1} for compounds containing as many as 10 carbon atoms). Melius *et al*. developed formulas and parameters for the calculation of the correction terms. The ab initio calculations needed are as follows: geometry optimizations and frequencies at the (U)HF/6-31G* level and single-point energy calculations at the (U)MP4/6-31G** level. We used our own code for the calculation of the BAC terms based on the prescriptions in ref 18.

III. Results and Discussion

Transition Structures. The equilibrium geometries of the radicals we obtained are identical with those reported by Pacansky *et al*.[21] The geometries at the saddle point are shown in Figure 1 of the supporting information (TSj denotes the transition structure for reaction j). The cyclic structures of TS2, TS3, TS4, and TS5 belong to the C_{2v}, C_{2v}, C_2, and C_s point groups, respectively (the *Z*-matrices of all optimized structures are available upon request).

As can be seen, the transition structure[22] is most strained in the case of the 1,2 H atom transfer, and it is more and more relaxed as the number of atoms in the ring increases. The distances between the moving H atom and the two bridgehead

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Table 1. Bond Orders in the Transition Structures between the Bridgehead C and the Transferred H atom, between the Two Bridgehead C Atoms, as Well as the Free Valences on These Atoms As Obtained at the UHF/STO-3G Level

reaction	B_{C-H}	B_{C-C}	F_H	F_C
1	0.46	0.14	0.07	0.39
2	0.46	1.10	0.07	0.40
3	0.44	0.12	0.11	0.44
4	0.45	0.12	0.08	0.40
5	0.46	0.13	0.07	0.39

carbon atoms are in the range 1.28−1.42 Å. The C−H bond length is smaller in the three-membered cyclic structure of reaction 2 than at the saddle point of the methyl + methane reaction (1.357 Å), while it is close to that reference value in the five- and six-membered cyclic transition structures. Interestingly, the C−H separation in the four-membered ring in the transition structure of reaction 3 is larger than in any of the other systems. This is probably a consequence of the high ring strain. A measure of the strain can be the C−H−C angle: it is small in the transition structure of reaction 2 (reflecting that this ring is highly strained) and gets closer and closer to the "optimum" collinear C−H−C arrangement of reaction 1 with the increase of the number of atoms in the ring. The triangular structure is responsible for the fact that the C−H distance is not larger in TS2 than in TS3: should it be larger, the H−C−H angle would be extremely small. The carbon atoms and the migrating H atom are necessarily in the same plane in TS1 and also in TS2. The ring in the other transition structures, however, also tends to be planar: in the four-membered TS3 it is strictly planar, and in TS4 it is somewhat twisted. The ring in TS5 is similar to the chair conformation of cyclohexane, but the migrating H atom hardly folds out of the plane of the four nearest carbon atoms (the C−H−C−C torsion angle is 23.5°). The energetic consequences of the observed features of the saddle point geometry will be discussed later.

Bond order and valence indices can also give some information on the nature of the transition structures.[23] For this purpose, we calculated the bond orders of the C−H bonds at the reaction center as well as the free valences on the H and C atoms from the ab initio wave functions using the formulation suggested by Mayer.[24,25] For these calculations we used the UHF/STO-3G wave function as proposed earlier.[26] The bond order (B_{C-H}) between the H atom being transferred and the bridgehead carbon atoms is almost the same, between 0.44 and 0.46 in the transition structures of reactions 1−5. The free valence corresponding to the radical center is distributed along the C−H−C sequence in the TS, and it is larger on the carbon atoms. Table 1 shows the actual figures. A clear correlation can be observed between the ring size and the free valences assigned to the carbon (F_C) and hydrogen (F_H) atoms. The values in the transition structure of the 1,5 H atom transfer exactly match those found in the transition structure of the methyl + methane reaction, reflecting the fact that, in the chemical sense, the two transition structures are very similar. In the direction reaction 5 to reaction 3, the C−H bond order decreases and the free valence on the bridgehead carbon and the H atoms increases. This indicates that in the transition structures these atoms are less and less tightly connected to each other and the structure, in the chemical sense, shifts toward a biradical + a free H atom setup. In the transition structure of reaction 2, the observed tendencies are not continued. The reason is probably that the ring is so small that the carbon atoms between which the H atom is transferred are directly connected to each other.

Table 2. Threshold Energies, E_0 (Activation Energies at 0 K) (in kcal mol^{-1}) for Reactions 1−5 As Obtained from ab Initio Calculations[a]

no.	E_0 HF/ 6-31G*// HF/6-31G*	E_0 MP2/ 6-31G*// HF/6-31G*	E_0 MP2/ 6-311G**// HF/6-31G*	E_0 MP-SAC2	E_0 BAC-MP4
1[a]	30.1	21.3[a]	19.9	18.0	15.2
2	55.3	46.5[b]	42.6[b]	41.1	43.1
3	54.3	46.3	43.1	41.6	41.0
4	38.3	29.3	26.4	24.6	25.1
5	31.9	21.9	19.1	17.2	18.8

[a] See ref 16, UMP2/6-31G** result. [b] UMP2/6-311G**//UMP2/6-311G**.

Energies at the Saddle Points. The threshold energies, *i.e.*, the activation energies at 0 K (in other words, the zero-point energy corrected barrier heights) derived from the energies of the reactants and saddle points obtained at various levels of theory are presented in Table 2. The largest threshold energy was found for the 1,2 H atom transfer and the lowest for the 1,5 transfer. This is in agreement with the expectation and the experimental observations. Generally, the HF calculations give the highest activation energies compared to the other ab initio data. Inclusion of MP2 corrections results in a significant lowering of the barrier height, by about 9 kcal mol^{-1}. Improvement of the basis set at the MP2 level from 6-31G* to 6-311G** further lowers the calculated barrier by about 2−4 kcal mol^{-1}.

Correlation effects are more accurately taken into account in the calculations at the MP-SAC2 and BAC-MP4 levels. The activation energy for reaction 1 at these levels is 18.0 and 15.2 kcal mol^{-1}, respectively, in better agreement with the experiment (14−15 kcal mol^{-1} see ref 27) than obtained recently[27] using more expensive (MP4, large basis set) calculations. In the series of isomerization reactions studied, the difference between the MP-SAC2 and BAC-MP4 data is the largest for reaction 2 (2.0 kcal mol^{-1}), which falls within the error limits of the corrected ab initio calculations at this level. The relative order of the activation energies at 0 K is the same as observed in the case of the uncorrected ab initio results: the 1,2 H atom transfer has the highest barrier, and the activation energy gradually decreases from about 43 to about 19 kcal mol^{-1} as the chain length of the radical increases.

The calculated barrier heights cannot be directly compared with experimental results. The reactions studied in this work are identity reactions and are accessible to experimental investigations *via* isotope labeling. The only experiments utilizing isotope labeling in which Arrhenius parameters are derived is that of Gordon *et al.*[6] on the isomerization of ethyl radicals. These authors obtained $E_A = (41 \pm 4)$ kcal mol^{-1}. Both the MP-SAC2 and BAC-MP4 activation enthalpies (41.5 and 43.5 kcal mol^{-1}, respectively) are equal to this value within the reported experimental error. The direction of change of the theoretical barrier heights for reactions 3−5 is in agreement with the recommended experimental activation energies[4] whereas the latter are generally lower. We do not think that this difference should be taken as a significant deficiency of the ab initio calculations. The 1,4 and 1,5 H atom transfers, for which experimental Arrhenius parameters are available, are not the identity reactions studied here. The major difference between the identity reactions and the experimentally studied ones is that the latter are not thermoneutral because the reactant and

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Table 3. Difference of the Height of the Barrier of the Cyclic Transition Structures and That of the Bimolecular H Atom Transfer, E_0(i) - E_0(1), Compared with the Strain Energy in the Corresponding Cycloalkanes As Suggested by Benson (in kcal mol^{-1})

reaction	HF/6-31G*//HF/6-31G*	MP2/6-31G*//HF/6-31G*	MP2/6-311G**//HF/6-31G*	MP-SAC2	BAC-MP4	cycloalkane
2	25.2	25.2	22.7	23.1	27.9	27.6
3	24.2	25.0	23.5	23.6	25.8	26.6
4	8.2	8.0	6.5	6.6	9.9	6.3
5	1.8	0.6	−0.8	−0.8	3.6	0.2

product radicals are not identical. This is expected to influence the height of the barrier. We will perform further studies in order to see how the methods applied here reproduce the results for systems that were studied experimentally.

The Effect of the Ring Strain on the Barrier Height. The barrier heights increase as the size of the ring in the transition structure decreases. Even from the geometries at the saddle point it is obvious that the rings are more and more strained in the series reaction 5 to reaction 2. The higher ring strain is reflected in the height of the barrier. The generally accepted procedure for estimating the barrier height for intramolecular atom-transfer reactions is based on the reasoning that, in such reactions, the atom transfer must proceed through a transition structure similar to that of the corresponding bimolecular reaction but distorted so that the fragment is forced into a strained ring. As a result, the height of the barrier to the intramolecular reaction is higher than that of the bimolecular reaction, approximately by the ring strain energy. The differences between the barrier heights of the isomerization reactions 2−5 and reaction 1 are presented in Table 3. For comparison, we listed the ring strain energy in the cycloalkanes with the same ring size.[28] The difference between the barrier height of reaction 2 and reaction 1 is between 23 and 28 kcal mol^{-1} as obtained at various ab initio levels which compares very well with the ring strain in cyclopropane, 27.6 kcal mol^{-1}. The increase of the barrier height due to the cyclic nature of the other transition structures is also in very good agreement with the strain energies in the corresponding cycloalkanes. On the basis of any of the ab initio calculations the strain energy values are very similar for a given transition structure, the largest difference being 5 kcal mol^{-1}, which indicates that the strain energy is, to a good approximation, separable from the other factors determining the barrier height.

Conclusion

The ab initio calculations predict activation energies that are the highest for 1,2 and 1,3 H atom-transfer reactions and the lowest for 1,5 H atom transfer, in good agreement with the experimental trend. The actual numerical values are hard to compare directly with the experiments, but they are close to the activation energies obtained for isomerization of similar radicals. The results support the assumption that the increase of the barrier height for the intramolecular isomerizations as compared to those of the corresponding bimolecular reaction is caused mostly by the ring strain so that the barrier height is approximately the sum of the contribution from the bimolecular reaction and the strain energy.

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Supporting Information Available: Figure 1 (geometries of the transition structures) and total energies and zero-point energies of the equilibrium and transition structures obtained at various levels of theory (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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