Ab Initio Barrier Heights and Branching Ratios of Isomerization Reactions of a Branched Alkyl Radical

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The factors influencing the rate of isomerization of alkyl radicals is investigated using ab initio calculations on the example of the 2-methylhexyl radical. The equilibrium geometries of the isomers and the transition structures of 16 isomerization channels connecting them are determined at the UHF/6-31G* level. The isomerization energies and barrier heights are calculated at the MP-SAC2/6-311G** level. The most stable isomer is the tertiary radical, less stable are the secondary isomers, and the least stable are the primary isomers of the 2-methylhexyl radical, the largest energy difference being about 3.5 kcal mol^{-1}. The heights of the barriers separating the isomers depend on the relative location of the radical center before and after the reaction. The barrier height for 1,2 as well as 1,3 H atom transfer is about 37−40 kcal mol^{-1}, that for the 1,4, 1,5, and 1,6 isomerizations is lower, about 20, 13, and 15 kcal mol^{-1}, respectively. The height of the barrier, and, accordingly, the activation energy vary by about 2 or 3 kcal mol^{-1} depending on the substitution in the ring of the cyclic transition structure and the concomitant change of the reaction enthalpy. Our RRKM calculations show that the fastest isomerization reaction is the 1,5 H atom transfer taking place through a six-membered cyclic transition structure. The relative importance of 1,4 and 1,6 H atom transfers to that of 1,5 isomerization, however, being dependent on the pressure and temperature, may not be negligible, and they together may exceed 30%.

I. Introduction

Isomerization reactions of alkyl radicals are important in the chemistry of free radicals for two reasons. First, these reactions occur in the pyrolysis and combustion of hydrocarbon fuels,[1] and second, they are prototypes of the intramolecular H atom transfer reactions in radicals derived from saturated compounds. Determination of the rate coefficients of the individual isomerization reactions is a prerequisite of the accurate modeling of systems such as engines and furnaces operating with hydrocarbon fuels. Knowledge of the rate coefficients and activation energies of the various isomerization channels of alkyl radicals allows one to derive the general rules that govern the changes in a series of such reactions. Experimental determination of such rate coefficients, however, is rather difficult. Not only are the concentrations of the reactants and products difficult to monitor, but also the assignment of the changes of concentrations to individual chemical processes requires extreme care. As a result, the number of such reactions studied experimentally is limited.[2−12] Because of the experimental difficulties, the Arrhenius parameters were also subject of discussion until the 1980s.[13]

Theoretical studies of the alkyl isomerization performed at a high level yield valuable information on the individual reactions and on the general features of related reactions. Recently, we have calculated the activation barriers of the 1,2, 1,3, 1,4, and 1,5 H atom transfer reactions of ethyl, propyl, butyl, and pentyl radicals,[14] respectively, with the BAC-MP4 and the MP-SAC2 ab initio quantum chemical methods. The calculations show that the barrier height decreases as the number of atoms in the ring of the cyclic transition structure increases. Comparison of the barrier heights with those of the corresponding bimolecular reactions indicates that the ring strain energy in the transition structures is large for the 1,2 and 1,3 H atom transfer and small for the 1,5 H atom transfer. The reactions studied in that work, however, were thermoneutral identity reactions for which essentially no experimental data are available, and the size of the radical itself changed in the series. The identity reactions do not change the concentration of the radical in question and so do not influence the kinetics of complex systems. In a general alkyl radical, however, many isomerization reactions are possible. The stability of the isomers in which the radical center is a primary, secondary, or tertiary carbon atom is generally different. As a result, the isomerization reactions are not thermoneutral, and the height of the barrier may be influenced not only by the number of carbon atoms in the alkyl chain between the donor and acceptor carbon but also by the nature of the radical center in the reactant and product. With this in mind, we have chosen to study the channels connecting the various isomers of the 2-methylhexyl radical. In this radical, all general types of isomerization are feasible from 1,2 to 1,6 H atom transfer including almost all combinations of primary, secondary, and tertiary donor and acceptor carbon atoms.

In the remainder of this paper, we first briefly describe the methods. In section III the equilibrium geometries of the alkyl radicals and the transition structures are presented. Section IV deals with the energetics of the reactions. In section V the kinetics of various channels is compared.

II. Computational Methods

The ab initio calculations were performed with the GAUSSIAN 92 and GAUSSIAN 94 packages.[15,16] The equilibrium

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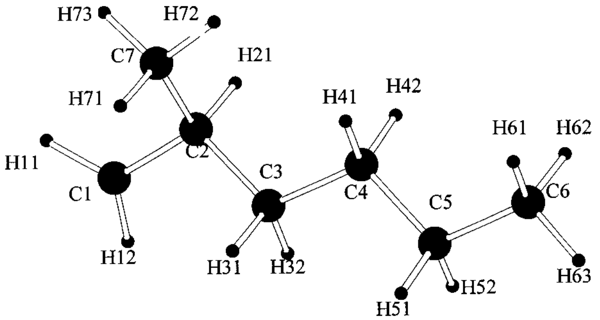


Figure 1. Numbering of atoms in the 2-methylhexyl radical.

geometries of the radicals and of the saddle points as well as the harmonic frequencies were calculated at the UHF/6-31G* level. The barrier heights were obtained at the UMP2/6-311G** level with inclusion of the MP-SAC2[17] type correction suggested by Gordon and Truhlar. In this method, we assume that the fraction of correlation energy accounted for in the MP2 calculations is essentially the same in all isomers and transition structures. We used the SAC scaling factor for C−H bonds, $F_2 = 0.84$, taken from the work of Truong and Truhlar.[18] We have tested the sensitivity of the final energy differences to the value of this parameter. A change of 0.01 in F_2 will modify the barrier heights by 0.14−0.16 kcal mol^{-1}. The value of $F_2 = 0.84$ suggests that the MP2/6-311G** calculation accounts for approximately 84% of the correlation energy. It seems to be reasonable to believe that the real value would not differ from this by more than a few percent, so that the error of the barrier heights due to the SAC correction would not exceed 0.5−0.9 kcal mol^{-1}.

The spin contamination in the isomers and the transition structures is generally low ($S^2 = 0.75-0.81$). The occupation numbers of the UHF natural orbitals do not differ significantly from two or zero below and above the Fermi level, respectively, indicating that the single-configuration UHF wave functions provide an acceptable description, except for the transition structure of the 1,2 H atom transfer reactions, where an MC-SCF treatment is desirable.[19] We expect, however, that the empirical corrections in the MP-SAC2 calculations correct for this deficiency.

The activation energies at 0 K were calculated from the classical barrier heights (obtained as the ab initio energy differences) by adding the difference of the vibrational zero-point energies. The latter were calculated from the UHF/6-31G* frequencies and multiplied by the zpe scaling factor of 0.9135.[20] For the calculation of vibrational densities of states, number of states, partition functions, and activation energies at 298 K the ab initio frequencies were scaled by the frequency scaling factor 0.8929.[20] The unimolecular rate coefficients were obtained in standard RRKM calculations.[21]

III. Isomers of the 2-Methylhexyl Radical

The 2-methylhexyl radical has six isomers according to the six possible locations of the radical center (see Figure 1, also indicating the numbering scheme of the atoms.) We denote them by the acronym *n*XR, where *n* is the number of the carbon atom carrying the unpaired electron, and X is P, S, or T if the radical center is a primary, secondary, or tertiary carbon atom, respectively. The bond lengths in the six isomers are listed in Table 1. The radical center resembles the structure of the methyl radical and is generally closer to planar than to tetrahedral.[22,23] The largest deviation from planarity occurs in the tertiary radical 2TR, where the sum of the C−C−C angles around the radical center is 353.4° instead of 360° corresponding to the planar arrangement. The pyramidality angle (the angle of a α-C−C bond and the bisector of the other two α bonds) is between 151.0° and 151.6°. The pyramidality angle at the saturated, tetrahedral carbon in other parts of our radicals is between 117° and 125°. The slightly distorted planar geometry at the radical center corresponds to an sp^2 carbon atom.

TABLE 1: Bond Lengths in the Isomers of the 2-Methylhexyl Radical (in Å)

	1PR	2TR	3SR	4SR	5SR	6PR
C1−C2	1.505	1.505	1.532	1.531	1.532	1.531
C2−C3	1.538	1.510	1.507	1.536	1.535	1.536
C3−C4	1.529	1.531	1.501	1.501	1.530	1.529
C4−C5	1.530	1.529	1.531	1.502	1.502	1.531
C5−C6	1.528	1.527	1.527	1.528	1.500	1.500
C2−C7	1.533	1.506	1.539	1.531	1.532	1.533
C1−H11	1.077	1.086	1.087	1.085	1.085	1.086
C1−H12	1.076	1.092	1.086	1.086	1.086	1.086
C1−H13		1.086	1.085	1.087	1.086	1.086
C2−H21	1.094		1.089	1.089	1.089	1.089
C3−H31	1.089	1.095	1.081	1.090	1.090	1.090
C3−H32	1.088	1.087		1.094	1.087	1.089
C4−H41	1.086	1.087	1.094	1.078	1.091	1.087
C4−H42	1.089	1.089	1.089		1.090	1.088
C5−H51	1.088	1.089	1.088	1.090	1.079	1.093
C5−H52	1.088	1.087	1.087	1.093		1.088
C6−H61	1.087	1.086	1.086	1.085	1.092	1.076
C6−H62	1.086	1.086	1.086	1.087	1.087	1.075
C6−H63	1.085	1.085	1.085	1.085	1.084	
C7−H71	1.084	1.084	1.086	1.087	1.084	1.083
C7−H72	1.085	1.085	1.086	1.085	1.086	1.086
C7−H73	1.086	1.093	1.086	1.086	1.087	1.088

Table 1 shows that the α bonds, involving the carbon atom which is the radical center, are shorter as compared to the length of the same type of bond in the other parts of the radical. The α-C−H (in which the H atom is directly connected to the radical center) bond lengths (about 1.077 Å) are the smallest among the C−H bonds in these radicals, the other C−H bond lengths being between 1.087 and 1.089 Å at the UHF/6-31G* level. Similarly, the α-C−C bond lengths (about 1.501−1.510 Å) are also smaller than the C−C distances in the other parts of the radical (being around 1.53 Å). This holds not only in primary alkyl radicals where the radical center is at the end of the chain as observed by Pacansky et al.[24] but also in secondary and even tertiary radicals (see also refs 22 and 23). In the 2-methylhex-2-yl radical (2TR), for example, where the radical center is localized at the tertiary carbon atom, the distances to the neighboring terminal methyl carbon atoms are 1.505 and 1.506 Å, while the distance to the next carbon inside the chain is 1.510 Å (the latter is the longest α-C−C distance in all the isomers of 2-methylhexyl). As the carbon atom carrying the unpaired electron is in an sp^2 hybrid state, one expects some similarity between the geometries of the radicals and the olefins containing a C(sp^2)−C(sp^3) bond. The bond lengths of the single bonds are 1.506, 1.506, 1.511, and 1.512 Å in propene,[25] 2-butene,[26] toluene,[27] and xylene,[28] respectively. These bond lengths are essentially identical with those observed in the alkyl radicals, suggesting that the reason for the contraction of this bond as compared to a single C−C bond is probably the same in all these compounds. The shorter C−C distance can be explained as a consequence of the smaller overlap repulsion between an sp^2 and an sp^3 carbon as compared to two carbon atoms in the sp^3 hybrid state. Another possible explanation is the hyperconjugation between the p orbital and the methyl groups. The bond orders calculated from the wave function[29,30] reflect the existence of the latter interaction and a smaller observable effect of the first one. The bond order of the contracted C−C bond (1.00−1.01 in the various isomers) is somewhat higher for the α-C−C bond than for the other C−C bonds in the chain (0.98−

1.00). This small difference only partially reflects the significant contraction of the α-C−C bond due to a partial double-bond character. On the other hand, there is always a nonzero bond order between the radical center and some of the H or C atoms connected to the neighboring carbon, especially those which are eclipsed with the p orbital on the radical center, indicating the existence of a partial chemical bond. In other parts of the molecules, the bond order in similar geometrical arrangements is zero.

In contrast to the α-C−C bonds, the bond length of the β-C−C bonds (between a carbon atom adjacent to the radical center and its next neighbor) is generally longer by about 0.005−0.010 Å than the length of the unperturbed C−C bonds. In agreement with this observation, the β-C−C bond orders (0.98−0.99) are found to be somewhat smaller than those of the unperturbed C−C bonds, always being the smallest in the radical. These features indicate that the β-C−C bonds are the weakest bonds of the alkyl radicals and are the most probable sites for scission.

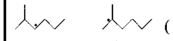
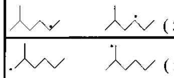
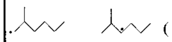
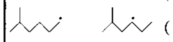
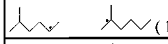
The conformation of the alkyl chains in the radicals is similar to that in alkanes. The most stable conformation of the chain in the radicals is also the most extended one, i.e., the one in which the carbon atoms of the backbone of the chain are in a plane, just like in alkanes. One of the methyl carbon atoms at the branching of the chain is, of course, out of this plane. The regular alkane structure is perturbed at the radical center where the sp^2 hybrid is located. We found that the stable conformations of the radicals are generally those, in which a β-C−H bond is perpendicular to the quasi-plane of the radical center, i.e., the p-orbital is eclipsed with an H atom, and the C−C bonds or other C−H bonds are just slightly out of the quasi-plane at the radical center. Chen et al.[23] and Pacansky et al.[24] also found that the β-C−H eclipsed conformers are the most stable in *n*-alk-1-yl radicals. In the secondary isomers of 2-methylhex-1-yl, 4SR and 5SR, the p orbital of the carbon atom, carrying the unpaired electron, is eclipsed with both β-C−H bonds, thus retaining the planar arrangement of the chain. The geometry of the other isomers is similar. In the tertiary isomer, 2TR, where there are three carbon atoms connected to the radical center, the p orbital is eclipsed with one of the β-C−H bonds on each of these carbon atoms. An exception is the 3SR isomer, in which both methyl carbons connected to carbon C2 are out of the molecular plane in the most stable conformer. The reason for this is that if the H atom on carbon C2 is forced into eclipse with the p orbital on carbon C3, and one of the methyl groups is driven into the plane of the remaining part of the chain, the latter will be in the cis position with carbon C4, a less favorable conformation than the one in which, instead of a C−C cis arrangement, the H atom on carbon C2 is in-plane, cis position with carbon C4. The energy difference between the potential minima corresponding to these two conformers is 1.2 mhartree = 0.75 kcal mol^{-1}, larger than the energy differences between some pairs of isomers. The barrier for the hindered rotation about this axis should still exceed this value, so that one can expect that under equilibrium conditions the gauche conformer is dominant, i.e., the one in which the p orbital is eclipsed with the C atom of the methyl carbon.

The most stable conformers of the isomers are very close in energy. Their energies are listed in Table 2. The tertiary isomer is the most stable. The least stable are the primary isomers, 1PR and 6PR, whose heats of formation at 0 K, compared to the tertiary isomer, are larger by 3.53 and 3.00 kcal mol^{-1}, respectively, at the MP-SAC2 level. The secondary isomers 3SR, 4SR, and 5SR are less stable than the tertiary isomer by almost the same amount, namely, 1.29, 1.12, and 1.13 kcal mol^{-1}, respectively. The differences in the heats of formation calculated at the HF/6-31G* level are somewhat larger than the MP-SAC2 values, the largest shift being 1.09 kcal mol^{-1} (cf. Table 2). The largest heat of reaction among all the isomerization processes is relatively small, about 3.5 kcal mol^{-1}, and many of these reactions are essentially thermoneutral.

TABLE 2: Relative Energies of the Isomers of the 2-Methylhexyl Radical Calculated at the HF and MP-SAC2 Levels (in kcal mol^{-1})

radical	HF/6-31G*	MPSAC2/6-311G**
2-methyl-hex-1-yl (1PR)	4.32	3.53
2-methyl-hex-2-yl (2TR)	0.00	0.00
2-methyl-hex-3-yl (3SR)	1.32	1.29
5-methyl-hex-3-yl (4PR)	1.64	1.11
5-methyl-hex-2-yl (4PR)	1.76	1.12
5-methyl-hex-1-yl (4PR)	4.09	3.00

TABLE 3: Threshold Energies (ZPE-Corrected Barrier Heights, in kcal mol^{-1}), Activation Entropies (cal mol^{-1} K^{-1}), Arrhenius Preexponential Factors and Standard Entropies of Reaction (T = 298.15 K, in kcal mol^{-1}) for the Isomerization Processes Studied in the 2-Methylhex-(*n*)-yl Radicals

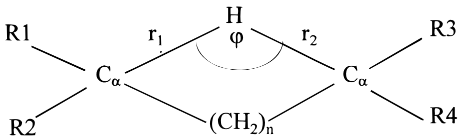
Reaction	E_0 HF/6-31G*	E_0 MP-SAC2 /6-311G**	$\Delta S_0^{\ddagger}$	lg(A / s^{-1})	ΔH^0_{r298} HF/6-31G*	ΔH^0_{r298} MP-SAC2 /6-311G**
 (1)	51.10	36.46	−1.12	12.98	-4.32	-3.53
 (2)	53.51	38.56	−1.59	12.88	-1.32	-1.29
 (3)	53.11	38.59	−2.00	12.79	-2.34	-1.88
 (4)	53.10	38.32	−4.73	12.19	-0.32	0.18
 (5)	53.30	38.38	−2.84	12.61	-0.11	-0.01
 (i)	52.58	39.90	-2.48	12.69	0.00	0.00
 (6)	50.62	38.12	−1.9	12.90	-3.00	-2.24
 (7)	52.56	38.17	−2.28	12.73	-2.45	-1.89
 (8)	52.64	39.02	−4.02	12.35	-0.43	0.17
 (9)	50.90	37.37	−5.55	12.01	-1.64	-1.11
 (10)	35.26	20.59	−5.64	11.99	-2.68	-2.42
 (11)	36.84	21.51	−6.23	11.87	-2.77	-1.71
 (12)	35.96	19.53	−6.91	11.72	-1.76	-1.12
 (13)	28.59	12.11	−7.98	11.58	-4.09	-3.00
 (14)	28.85	13.43	−7.52	11.48	-2.56	-2.41
 (15)	30.09	15.14	−9.51	11.15	-0.23	-0.53

IV. Geometries of the Transition Structures and the Barrier Heights

Geometries. There are 16 possible isomerization reactions which interconnect the six isomers of the 2-methylhex-1-yl radical, namely, one 1,6, two 1,5, three 1,4, five 1,3, and five 1,2 H atom transfer reactions. They are listed in Table 3, grouped according to the "distance" of the carbon centers between which the H atom is transferred. Among them, H transfers between different types of carbon atoms (such as primary to secondary etc.) are especially interesting. The transition structures of all these reactions are cyclic. Their properties, both the geometries and the energies, are very similar within a group of reactions involving the same number of atoms in the ring in the transition structure.

The parameters characterizing the reactive site of the transition structures calculated at the HF/6-31G* level are shown in Table 4. The distances between the moving H atom and the two bridgehead carbon atoms are very close to each other in the transition structures of reactions belonging to the same group. It is common to all the reactions that the migrating H atom

TABLE 4: Bond Lengths and Bond Angles Characterizing the Reaction Centers in the Transition Structures[a]



no.	n		r_1	r_2	φ	$C_\alpha-C_\alpha$	$C_\alpha-C_\beta$	$C_\alpha-H$	$C_\beta-H$
1	0	pt	1.304	1.302	69.8	1.491	1.506	1.074	1.092
2	0	st	1.309	1.306	69.8	1.496	1.507	1.079	1.092
3	0	ps	1.300	1.300	69.9	1.487	1.506	1.074	1.092
4	0	ss	1.304	1.303	69.7	1.488	1.505	1.078	1.091
5	0	ss	1.303	1.303	69.7	1.489	1.504	1.077	1.092
i	1	pp	1.421	1.420	102.7	2.219	1.530	1.078	1.085
6	1	ps	1.427	1.424	102.8	2.227	1.510	1.080	1.092
7	1	ps	1.432	1.428	102.6	2.232	1.511	1.078	1.092
8	1	ss	1.432	1.435	102.7	2.238	1.509	1.082	1.089
9	1	st	1.439	1.433	103.0	2.246	1.511	1.082	1.091
10	2	ps	1.394	1.379	131.2	2.526	1.516	1.082	1.091
11	2	ps	1.395	1.382	131.8	2.534	1.521	1.079	1.089
12	2	st	1.398	1.386	132.7	2.549	1.514	1.081	1.091
13	3	pt	1.382	1.349	153.6	2.658	1.517	1.080	1.091
14	3	ps	1.375	1.352	152.1	2.646	1.513	1.081	1.088
15	4	pp	1.354	1.349	165.0	2.679	1.515	1.081	1.089

[a] r_1 refers to the breaking and r_2 to the forming bond. The letters in column three indicate the types of the donor and acceptor carbon atoms (p, s, t for primary, secondary, and tertiary, respectively) Distances in angstroms, angles in degrees.

being transferred is closer to the carbon that carries more carbon substituents. The length of the C−C bonds involving the bridgehead carbon atoms is generally about 1.51 Å, i.e., somewhat longer than in the parent radicals but still close to that characteristic for a C(sp^2)−C(sp^3) bond. The pyramidality of the bridgehead carbon atoms also indicates that in the transition structures both are close to an sp^2 hybrid state. In the following, we briefly summarize the geometrical characteristics of the transition structures of each class of 1,*n* H atom transfer reactions.

In the transition structures of all 1,2 H atom transfer reactions the C−H distances r_1 and r_2 are between 1.300 and 1.309 Å. The rings are very strained, the C−H−C angles being about 70°. The C−C distances in the rings are about 1.49 Å. In the isomerization of the ethyl radical (an identity reaction) we found[14] a smaller C−H distance, 1.283 Å, but the C−C distance in that transition structure is very similar to those in the transition structure of the 1,2 H-atom transfers in 2-methylhexyl.

The transition structures corresponding to the 1,3 H atom transfer reactions contain a four-membered ring. The distance between the transferred H atom and the two bridgehead carbon atoms is between 1.420 and 1.439 Å. These C−H distances are the largest among all the reactions, in agreement with the observations made in the case of the *n*-propyl radical.[14] The actual values of the C−H distances are very close to each other in the four-membered rings of the transition structures of the isomerization of 2-methylhexyl isomers, of *n*-propyl, 2-methylbutyl, and *n*-pentyl (equal within 0.014 Å). In all transition structures the ring is planar, and the alkyl substituents assume a position expected based on chemical intuition: the largest possible C−C distances and open conformations.

The five-membered cyclic transition structures of the 1,4 H atom transfer reactions are nonplanar. The C−H distances at the reaction site vary between 1.379 and 1.398 Å (being 1.388 Å in the corresponding TS of the 1-butyl radical[14]), the length of the α-C−C bonds is about 1.515 Å in the ring, that of the *β*-C−C bond is around 1.545 Å.

In the six-membered transition structures corresponding to the 1,5 H atom transfer reactions, the C−H distances are between 1.349 and 1.382 Å (that in the corresponding reaction of *n*-pentyl[14] is 1.361 Å). It is in these structures among all 16 we studied that the difference between the distances of the H atom to the two bridgehead carbon atoms is the largest: in the TS of reaction 13 the primary carbon−H distance is 1.382 Å, that to the tertiary C is 1.349 Å, while in the TS of reaction 14 the H−*primary*-C distance is 1.375 Å compared to 1.352 Å of the H−*secondary*-C bond. The ring is in a chairlike conformation with the peculiarity that the H atom folds out of the plane of the two α and *β* carbon atoms by 3−5° only, because of the partial sp^2 hybrid state of the bridgehead carbon atoms.

The seven-membered ring in the 1,6 H atom transfer (reaction 15) is also nonplanar, and the position of C atoms is similar to that in the chair conformer of cyclohexane. The C−H distances at the reaction site are 1.354 and 1.349 Å, and the C−H−C angle is the largest here, 165°.

A general observation is that in the six- and seven-membered rings the geometry at the reaction site approaches that in the corresponding bimolecular reaction. With this similarity in mind, we have studied the transition structures of the prototypes of reactions in which methyl radical abstracts a primary, secondary or tertiary H atom from alkanes, namely, from ethane, propane and isobutane, respectively. In the transition structures corresponding to this series of reactions, the C−H distances between the abstracted H atom and the acceptor carbon atom are 1.346, 1.337, and 1.330 Å, respectively, and those between H atom and the donor carbon are 1.372, 1.385, and 1.396 Å, respectively. It can be seen that the H atom is always closer to the higher order carbon atom just as in the cyclic transition structures. The difference between the two C−H distances, however, is always larger in the TS of the bimolecular reactions than in the constrained cyclic ones. Among the cyclic transition structures, the six- and seven-membered rings contain the C−H distances which are closest to those in the bimolecular reactions, suggesting that these might be the least strained structures.

Energies. The reaction enthalpies and activation energies were calculated from the HF/6-31G* and the MP-SAC2 energies listed in Table 5. The results are summarized in Table 3. The activation energies and the classical barrier heights at the HF/6-31G* level are, as usual, higher than the more realistic MP-SAC2 results, by about 12−15 kcal mol^{-1}. We analyzed how the change of the basis set, the inclusion of electron correlation, and inclusion of SAC contribute to the large difference of the barrier heights. The results show that the absolute change of the barrier heights when the basis set is improved from 6-31G* to 6-311G** at the HF level is about −2.6, 1.4, 0.6, 0.25, and 0.1 kcal mol^{-1} for the 1,2, 1,3, 1,4, 1,5, and 1,6 H atom transfer reactions, respectively. When the electron correlation is taken into account at the MP2 level (using the 6-311G** basis set), the barrier height decreases by around 10.2, 9.9, 12.5, 13.2, and 12.6 kcal mol^{-1}, respectively, in the same series. The inclusion of the SAC correction causes an additional decrease of 1.6, 1.6, 2.0, 2.1, and 2.0 kcal mol^{-1}, respectively. It is obvious that the dominant contribution to the correction of the barrier height when the level of calculation is improved from HF/6-31G* to MP-SAC2 is the correlation energy, most of which is accounted for in the MP2 calculation. The reason is that the transition structure is more compact than the radical in an extended conformation, and, as the motion of the electrons is confined to a smaller space, it becomes more correlated. If, as in the MP2 calculation, we take into consideration the electron correlation, the energy as compared to the HF result decreases more for the transition structure than for the extended equilibrium conformation. A remarkable consequence of this observation is that if one is interested in the energies of compact

TABLE 5: Computed Total, Zero-Point and Thermal Energies for the Stationary Structures (in hartrees)

	HF/6-31G*	HF/6-311G**	MP2/6-311G**	SAC2	ZPE	*E*(thermal)
2-methylhex-1-yl	−273.768 93	−273.838 05	−274.878 49	−275.042 26	0.216 36	0.225 92
2-methylhex-2-yl	−273.776 76	−273.845 15	−274.885 15	−275.048 85	0.217 09	0.226 92
2-methylhex-3-yl	−273.774 19	−273.842 87	−274.882 67	−275.046 34	0.216 89	0.226 45
2-methylhex-4-yl	−273.773 38	−273.842 16	−274.882 54	−275.046 30	0.216 34	0.226 10
5-methylhex-2-yl	−273.773 33	−273.842 01	−274.882 62	−275.046 42	0.216 57	0.226 25
5-methylhex-1-yl	−273.769 20	−273.838 25	−274.879 16	−275.043 01	0.216 23	0.225 82
TS1(12pt)	−273.683 61	−273.756 95	−274.813 44	−274.979 75	0.212 10	0.221 33
TS2(12st)	−273.684 46	−273.756 92	−274.813 56	−274.979 88	0.212 01	0.221 48
TS3(12ps)	− 273.680 64	−273.754 11	−274.8107 4	−274.977 06	0.211 92	0.221 04
TS4(12ss3)	−273.684 77	−273.757 71	−274.814 37	−274.9807 0	0.211 96	0.221 21
TS5(12ss5)	−273.684 09	−273.756 90	−274.814 01	−274.980 40	0.211 85	0.221 13
TSi(13pp)	−273.676 84	−273.748 62	−274.804 29	−274.970 46	0.211 39	0.220 36
TS6(13ps3)	−273.683 56	−273.755 02	−274.810 22	−274.976 32	0.211 20	0.220 23
TS7(13ps4)	−273.681 12	−273.752 42	−274.809 37	−274.975 74	0.211 51	0.220 38
TS8(13ss)	−273.684 87	−273.755 76	−274.812 76	−274.979 13	0.211 57	0.220 48
TS9(13st)	−273.687 78	−273.758 62	−274.815 38	−274.981 72	0.211 43	0.220 48
TS10(14ps4)	−273.709 31	−273.779 46	−274.838 67	−275.005 40	0.212 60	0.221 01
TS11(14ps3)	−273.707 44	−273.777 41	−274.838 08	−275.005 03	0.212 89	0.221 19
TS12(14st)	−273.712 25	−273.782 10	−274.843 71	−275.010 82	0.212 42	0.221 06
TS13(15pt)	−273.720 57	−273.790 05	−274.852 66	−275.019 92	0.212 86	0.221 02
TS14(15ps)	−273.719 72	−273.789 21	−274.849 97	−275.016 94	0.212 80	0.220 95
TS15(16pp)	−273.718 06	−273.787 27	−274.847 73	−275.014 66	0.213 27	0.221 03

conformations of alkanes or related molecules (for instance, when the molecule curls up to approach the geometry of the transition structure), it is necessary to take into account the electron correlation.

Barrier Heights. A study of the data in Table 3 indicates that the barrier heights of the reactions within a class (i.e., a group in which the number of the atoms in the ring in the transition structure is the same) are quite close to each other, generally within 3 kcal mol^{-1}. For example, the barrier heights of the 1,2 H atom transfers are between 36.5 and 40.5 kcal mol^{-1} (taking into account the reverse reactions also); those of the 1,4 H atom transfers are between 19.5 and 21.5 kcal mol^{-1}, etc. This suggests that if the H atoms of the carbon atoms in the ring in the transition structure are replaced by alkyl groups, the barrier height will change both due to the presence of the substituents and the change of the reaction heat. The mere fact that the ring in the transition structure carries substituents causes a decrease of the barrier heights. In the case of the isomerization of the unsubstituted parent radicals,[14] we found barrier heights of about 41, 42, 25, and 17 kcal mol^{-1} at the MP-SAC2 level for the 1,2, 1,3, 1,4, and 1,5 H atom transfer reactions, respectively. These barrier heights are close but generally higher than those calculated for the isomerization reactions of the 2-methylhexyl radical (even in the endothermic direction) where there are always alkyl substituents in the ring of the transition structure. The difference is generally smaller than 2 kcal mol^{-1}. One would expect that the lower barrier observed in the substituted systems is the result of a lower ring strain in the transition structures.

Very important may be, in some cases, the conformational effects. An interesting example for this is the transition structure for the identity reaction (i) of 2-methylhex-1-yl (a 1,3 H atom transfer from carbon 7 to carbon 1, see Figure 1). There are two conformers of the TS, both with one imaginary frequency: one in which the C4 atom of the *n*-butyl chain and the H atom connected to the tertiary carbon atom are in cis and one in which they are in trans position. The energy difference is 2.0 kcal mol^{-1} and the lower barrier belongs to the trans conformer in which the carbon atoms C1 and C2 are farther apart from C4.

The comparison of the barrier heights characterizing the different classes of H atom transfer reactions shows that the 1,2 and the 1,3 H atom transfer is the least favorable type of reaction. The barrier height in both classes is about 38 kcal mol^{-1}. For a general 1,4 H atom transfer to take place, a barrier of about 20 kcal mol^{-1} must be surpassed. The most favorable reactions are those in which the ring in the transition structure is six-membered, i.e., the 1,5 H atom transfers: the barrier height is about 12−15 kcal mol^{-1} depending on the direction of the reaction. The height of the barrier corresponding to a seven-membered cyclic transition structure is somewhat higher, between 15.1 kcal mol^{-1} for reaction 15 and 15.7 kcal mol^{-1} for the reverse reaction.

The relative magnitude of the barrier heights characterizing the different classes are in good agreement with chemical intuition and the previous calculations. We obtained the same tendencies for the identity reactions of the parent radicals (i.e., 1,*n* H atom transfer in *n*-alkyl radicals C_nH_{2n+1}).[14] This means that the heat of reaction resulting from the different relative stability of the isomers of an alkyl radical modifies the barrier height, but its influence does not overcome the effect of the ring strain. The barrier heights within a class are generally lower for those reactions in which the reaction is more exothermic. The correlation, however, is not strict. In many cases, the conformational differences in the "spectator" part of the molecule cause changes in the barrier height that amount to a few kcal mol^{-1}, comparable to the differences discussed above.

Ring Strain in the Transition Structures. According to the picture suggested by Benson,[31] the barrier separating the reactants from products in an isomerization reaction is determined by two additive contributions. One is the intrinsic barrier characterizing the atom transfer itself, which is "measurable" for a bimolecular reaction. The other is the strain energy needed to form the ring in the transition structure. An estimate of the ring strain then will be given by the difference of the barrier heights characterizing the intra- and intermolecular H atom transfer reactions. In our earlier study,[14] we used the barrier height characterizing the $CH_3 + CH_4$ reaction (18 kcal mol^{-1}) as the reference bimolecular barrier height, and obtained ring strain energies of about 23, 24, 7, and −1 kcal mol^{-1} for 1,2, 1,3, 1,4, and 1,5 H atom transfer, respectively, at the MP-SAC2 level. In the present case the reactant and product radical is different and it is desirable to take into consideration that the reaction is not thermoneutral. This can be done by using barrier heights for unsymmetrical bimolecular reactions as references, namely, those of the $CH_3 + H(CH_2)_4H$, the $CH_3 + HCH(CH_3)_2$, and the $CH_3 + HC(CH_3)_3$ reactions. Calculated at the MP-SAC2//HF/6-31G* level, the obtained barriers are 12.5, 14.9, and 10.1 kcal mol^{-1}, respectively. Each of these is lower than

TABLE 6: Difference of the Barrier Heights of the Intra- and Intermolecular H Atom Transfer, $E_s = E_0(i) - E_0(\text{bimol})$, as a Measure of the Ring Strain in the Cyclic Transition Structures (Energies in kcal mol^{-1})

ring size	E_s	no.	reference reaction and its barrier height	
3-member	26.4	(1)	$CH_3 + i\text{-}C_4H_{10} \rightarrow CH_4 + t\text{-}C_4H_9$	10.1
	25.9	(3)	$CH_3 + C_3H_8 \rightarrow CH_4 + i\text{-}C_3H_7$	12.7
4-member	25.4	(6)	$CH_3 + C_3H_8 \rightarrow CH_4 + i\text{-}C_3H_7$	12.7
	26.4	(7)	$CH_3 + C_3H_8 \rightarrow CH_4 + i\text{-}C_3H_7$	12.7
	27.3	(9)	$CH_3 + i\text{-}C_4H_{10} \rightarrow CH_4 + t\text{-}C_4H_9$	10.1
5-member	7.9	(10)	$CH_3 + C_3H_8 \rightarrow CH_4 + i\text{-}C_3H_7$	12.7
	8.8	(11)	$CH_3 + C_3H_8 \rightarrow CH_4 + \text{i- }C_3H_7$	12.7
	9.4	(12)	$CH_3 + i\text{-}C_4H_{10} \rightarrow CH_4 + t\text{-}C_4H_9$	10.1
6-member	0.73	(13)	$CH_3 + C_3H_8 \rightarrow CH_4 + i\text{-}C_3H_7$	12.7
	2.0	(14)	$CH_3 + i\text{-}C_4H_{10} \rightarrow CH_4 + t\text{-}C_4H_9$	10.1
7-member	0.04	(15)	$CH_3 + n\text{-}C_4H_{10} \rightarrow CH_4 + 1\text{-}C_4H_9$	15.1

the barrier height for H-abstraction from methane by methyl. When comparing the barrier heights of the intra- and intermolecular reactions, we used these values as references for primary to primary, primary to secondary, and primary to tertiary H atom transfer. The differences between the intra- and intermolecular barrier heights are summarized in Table 6. If the difference is considered to be a measure of the ring strain, the latter is about 27, 27, 9, 1, and 0 kcal mol^{-1} for the three-, four-, five-, six, and seven-membered rings, respectively. These values are in good agreement with the ring strain energies for cycloalkanes recommended by Benson.[31] For 1,2 and 1,3 H atom transfer reactions the energy differences calculated in this way are higher than the ones obtained for the isomerization of the parent radical (1,*n* H atom transfer in *n*-alk-1-yl radicals), while for the 1,4 and 1,5 H atom transfers the strain is smaller if the ring carries substituents. If we use the barrier height of the $CH_3 + CH_4$ reaction as the reference bimolecular barrier height for these reactions, we obtain ring strain energies of about 20, 20, 2, −5, and −3 kcal mol^{-1} which seem to be much less reasonable. These results indicate that this way of estimating the ring strain energy is clearly highly sensitive to the barrier height of the reference bimolecular reaction. One can conclude that if one wants to estimate the magnitude of the ring strain, it is necessary that the bimolecular reaction with the proper nature of the donor and acceptor carbon atoms be used. The discrepancies observed can also be interpreted as an indication that the assumed additivity of the intrinsic barrier height for atom transfer and the ring strain may not be strictly valid. The dependence of the bimolecular barrier height on the substitution of the carbon atoms near the radical center and on the conformation means that the "intrinsic barrier height" of a H atom transfer reaction cannot be defined accurately and the calculation of the ring strain will always carry an error of a few kcal mol^{-1}. A decisive answer requires further studies.

Comparison with Experiments. Relatively little experimental information is available on the rate of H atom transfer reactions in alkyl radicals. Gordon et al.[10] studied the isomerization of the ethyl radical using isotopic substitution and obtained an activation energy of 41 ± 4 kcal mol^{-1}. This is in good agreement with the calculated value of 38−40 kcal mol^{-1} we obtained for various substituted ethyl radicals. We are not aware of any experimental information on the rate and activation parameters for 1,3 H atom transfer. 1,4 and 1,5 H atom transfers were the subject of detailed experiments by Rabinovitch and co-workers.[7,32] Most 1,4 H atom transfer reactions were found to proceed through a barrier of about 20 kcal mol^{-1}, which is consistent with the calculated ones.

The activation energy of 1,5 H atom transfer in hex-1-yl and oct-3-yl radicals was found to be 11.6 and 11.2 kcal mol^{-1}, respectively.[12] The barrier heights for 1,5 H-atom transfer found in the present study vary between 11.7 and 15.4 kcal mol^{-1} depending on the substitution and the direction of the reaction. The lower values correspond to the more exothermic reactions. The closest to the experimentally studied reactions in our work is reaction 14 in the forward direction, for which the calculated barrier height is 13 kcal mol^{-1}, and the agreement between theory and experiment can be considered good.

For 1,6 H atom transfer Rabinovitch et al.[7] suggested an activation energy of 16 kcal mol^{-1} which is higher than that for the 1,5 H atom transfer reactions. This value is in very good agreement with the calculated threshold energy of 15.1 kcal mol^{-1} for reaction 15 and 15.7 kcal mol^{-1} for its reverse reaction.

From the vibrational frequencies and moments of inertia we calculated the entropies of activation and the preexponential factors of the high pressure limiting rate coefficients of each reaction channel (see Table 3). The formation of the cyclic transition structures of the 1,2 and 1,3 H atom transfer reactions is accompanied by a relatively small entropy change and the preexponential factor approaches 10^{13} s^{-1}. The entropy loss at the formation of the ring in the TS of the 1,4, 1,5, and 1,6 H atom transfer processes gradually increases and, concomitantly, the preexponential factor decreases.

The generally good agreement between the experimental and theoretical activation energies and preexponential factors is encouraging and supports our belief that the relative magnitude of the barrier heights obtained for the different reactions with the MP-SAC2 method will also be reliable.

V. Kinetics of Isomerization: Importance of 1,2-, 1,3-, 1,4-, 1,5-, and 1,6 H Atom Transfer Channels in Complex Kinetic Systems

The knowledge of the theoretically obtained properties of the transition structures for the isomerization reactions in the 2-methylhexyl radical enables us to estimate the relative importance of the different isomerization processes of alkyl radicals in a complex system like hydrocarbon pyrolysis or combustion. The large difference of the barrier heights of the isomerization channels with different ring size in the transition structure indicates that the relative importance of the various channels is significantly different.

To estimate the actual branching ratios, we calculated the rate coefficients of the 1,2, 1,3, 1,4, 1,5, and 1,6 isomerization reactions of the 2-methylhex-6-yl radical (6PR), namely, reactions 3, 7, 11, and 13, and the reverse of reaction 15. The energy dependence of the microcanonical rate coefficients $k_i(E)$ obtained in RRKM calculations[21] for the selected isomerization channels is shown in Figure 2. The largest rate coefficient characterizes the 1,5 H atom transfer which also has the lowest threshold energy.

The rates of unimolecular reactions depends on the pressure. As a first approximation, one can calculate the rate coefficients of the individual channels at various pressures (within the framework of the strong collision approximation) using the RRKM expression

$$k_i(T) = \int_{E_{i,0}}^{\infty} \frac{k_i(E)\omega}{k_i(E) + \omega} P(E)\, \mathrm{d}E \qquad \text{(A)}$$

where $\omega = Z_{LJ}[M]$ is the collision frequency and $P(E)$ is the Boltzmann distribution of energy levels of the reactant. To estimate the effect of the environment, we used the parameters of heptane, a strong collider to calculate Z_{LJ} and the collision frequency at a given pressure. Heptane was chosen to be the heat bath molecule because its properties match those of the

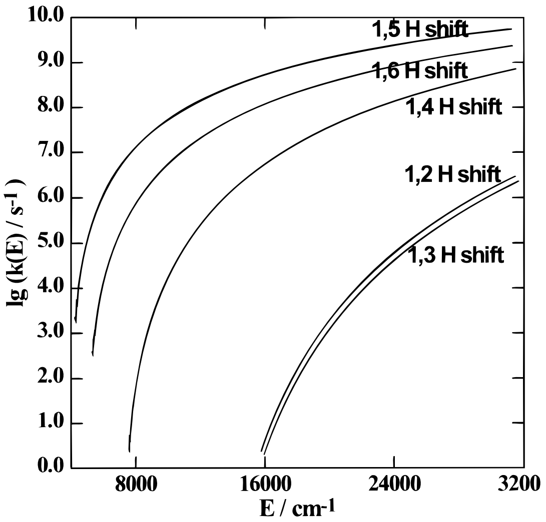


Figure 2. Energy-dependent specific rate coefficients $k_i(E)$ for the isomerization reactions of the 2-methylhex-1-yl radical, reactions 3, 7, 11, 13, and −15.

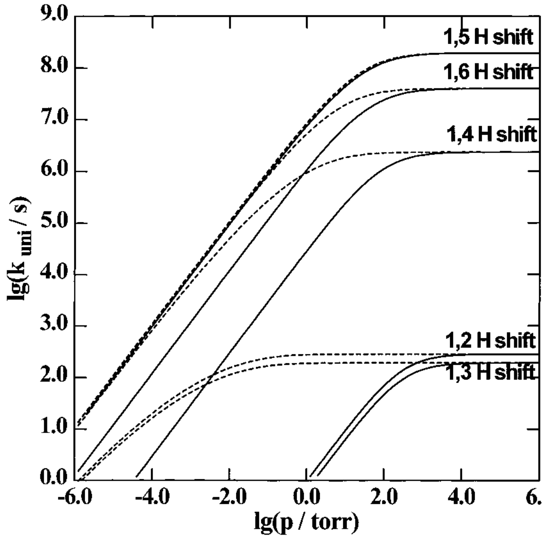


Figure 3. Pressure dependence of the thermal unimolecular rate coefficients for reactions 3, 7, 11, 13, and −15 at $T = 800$ K. Dashed lines from model A; continuous lines from model B.

main components both of the chemical activation experiments where the parent olefin is the main component and of the combustion systems based on gasoline.

The falloff curves obtained using this model (designated as model A) are shown as dashed lines in Figure 3. The slowest reactions are the ones that have the highest activation barrier. The pressure-dependent range, as in general, is shifted to lower pressures for the slower reactions. This picture, however, does not reflect the real rates of the reaction. The reason is that the various isomerization processes take place in competition with each other at each energy level and not as reactions of different species at thermal equilibrium. As a result, the relative importance of the slower channels is overestimated in model A. A naive refinement of this model is that one explicitly takes into account the existence of the competing channels when calculating the thermal pressure-dependent (but still strong collision) rate coefficient for each isomerization channel:

$$k_i(T) = \int_{E_{i,0}}^{\infty} \frac{k_i(E)\omega}{\sum_j k_j(E) + \omega} P(E)\, \mathrm{d}E \qquad \text{(B)}$$

TABLE 7: Branching Factor $\rho(i) = k_i/\sum k_i$ for the Three Most Important Isomerization Channels of the 2-Methylhex-1-yl Radical

T/K	log(p/Torr)	$\rho(11)$	$\rho(13)$	$\rho(-15)$
500	1.0E−02	0.000	0.978	0.022
	1.0E+00	0.000	0.952	0.048
	1.0E+02	0.000	0.933	0.066
	1.0E+04	0.000	0.932	0.068
800	1.0E−02	0.003	0.887	0.110
	1.0E+00	0.003	0.873	0.124
	1.0E+02	0.007	0.835	0.158
	1.0E+04	0.010	0.821	0.169
1200	1.0E−02	0.033	0.745	0.222
	1.0E+00	0.033	0.744	0.223
	1.0E+02	0.037	0.731	0.231
	1.0E+04	0.046	0.711	0.243
1500	1.0E−02	0.052	0.698	0.249
	1.0E+00	0.052	0.698	0.249
	1.0E+02	0.054	0.694	0.251
	1.0E+04	0.060	0.684	0.257

As a second approximation to reality, we used this modified RRKM equation to obtain the continuous lines in Figure 3. (Note that the possible decomposition channels are not taken into account.) As can be seen, the rates of the slow channels decreases at low pressures as compared to their apparent rate obtained if the existence of the other channels is disregarded. The pressure-dependent range also shifts to the range characteristic to the most important channel, the 1,5 H atom transfer. The falloff curves are parallel on the log−log plot, so that the relative importance of the individual channels is constant in the second-order range. The importance of the 1,5 H atom transfer is somewhat larger at low than at high pressures. It is important to note that the presence of the other channels hardly modifies the shape of the falloff curve characterizing the 1,5 H atom transfer. This means that the pressure dependence of the rate coefficient of this channel is not very sensitive to the conditions. As this is the dominant channel, its properties will determine the characteristics of the overall reaction. Under strong-collision conditions this channel is close to, but not in the pressure-dependent range at atmospheric pressure. The pressure where the rate coefficient is one-half of the high-pressure limiting value is 792 Torr at 1500 K, 446 Torr at 1200 K, and 46 Torr at 800 K. The analogous pressures for the other channels are higher and also increase with the temperature. The branching fractions for the three most important channels (the ratios of the rate coefficient of a channel to the sum of those for all channels) are shown in Table 7 at various conditions. At high temperatures the 1,5 isomerization is responsible for over 70% of the isomerization at 1 Torr, while at high pressures this fraction decreases by a few percent. The second most significant channel is the 1,6 H atom transfer in this system, its contribution to the total rate amounts to 10−25% at high temperatures. Under the conditions of a high-temperature burner, even the 1,4 H atom transfer may gain some importance (at 1500 K the branching ratio for this channel is about 5%). At decreasing temperatures the 1,5 H atom transfer becomes more and more dominant.

The actual numbers presented in the previous discussion, however, must be treated with caution, because model B is still approximate. There are a number of conditions implicitly assumed to be satisfied for the model to be correct. We list the most important ones:

(1) The model works if the product molecules are not present, for example, they are removed by other reactions so that the back reaction will not play a significant role. Such a situation may emerge in complex combustion systems or in kinetics experiments at low conversion.

(2) The precise description of the isomerization of alkyl radicals requires the accurate description of collisional energy transfer. This way the effects due to weak collisions can also be estimated. The extension of model B then involves the treatment of all channels simultaneously with each other and with collision energy transfer at the energy-resolved level. This means that the complete master equation for the system must be solved (in the most precise form, including back reactions also). In a bath of weak colliders, in such a model, especially at low pressures, the relative importance of the slow channels will be even lower than in model B, because the reactions with lower threshold energy will empty the relatively low levels and the stepwise collisional activation will not be able to populate the levels from which the slow reactions could take place.

(3) Model B assumes that the population of the energy levels follows the Boltzmann distribution. This will clearly be not satisfied in a weak-collision system mentioned above. The other definitive factor is the energy distribution of the radical at formation. In a combustion system the alkyl radicals are most probably formed by abstraction reactions. Then, the radical will probably not be formed at high internal excitation so that thermal activation is the vehicle through which reactive levels are populated. In such cases the model we applied (especially if the bath contains large molecules acting as strong colliders) is relatively close to reality. On the other hand, in chemical activation experiments the steady-state energy distribution may be far from thermal and the correct description of the reactive system requires the solution of the full master equation.

(4) Due to the lack of information about the decomposition channels, our model does not take into account that in a real system the isomerization takes place simultaneously with decomposition.

(5) In the high-pressure limit when collisions are expected to maintain a Boltzmann distribution of internal energies, the only important factor model B is missing is the presence of dissociation reactions.

Despite the approximate nature of our model, we think that the numbers that are calculated this way can also be used at least as semiquantitative indicators of the actual rate coefficient and of the relative importance of the various channels. As the discussion of the conditions of applicability shows, the model is closest to reality in a combustion system at or above atmospheric pressure. More complete model calculations can also be performed if the data from our calculations are supplemented by information on energy transfer and on the competing dissociation reactions.

As the high-pressure limiting Arrhenius parameters do determine the individual high-pressure rate coefficients, the knowledge of the height of the activation barriers for the isomerization channels enables us to refine the conclusions drawn by Pacansky et al.[24] These workers, based on reaction energies, tried to estimate the relative importance of isomerization to dissociation. According to their results, the dissociation along the β-C−H bond is endothermic by about 33 kcal mol^{-1} while the β-C−C bond scission (formation of an olefin and a smaller alkyl radical) requires 19.2−19.8 kcal mol^{-1}. Comparing these energies with the barrier heights we calculated, one can conclude that the β-C−H rupture could, at most, compete with the 1,2 and 1,3 H atom shifts. The β-C−C rupture, however, can be faster than the 1,4 H atom transfer. At lower temperatures it will probably not compete with the 1,5 and 1,6 H atom transfers but at higher temperatures its importance may increase.

As a conclusion, we think—in agreement with that of Walker[33]—that in the isomerization of small alkyl radicals where 1,5 and 1,6 H atom transfer is not feasible, the dissociation into an olefin and a small alkyl radical is the fastest unimolecular reaction. In radicals in which formation of six- or seven-membered cyclic transition structure is possible, the fastest step is the isomerization.

VI. Conclusion

We have chosen the 2-methylhexyl radical for a study of the factors governing the kinetics of the isomerization of alkyl radicals. This radical has six isomers: two primary, three secondary, and one tertiary radical. There are 16 possible isomerization reactions connecting them. These reactions include 1,2, 1,3, 1,4, 1,5, and 1,6 H atom transfer processes in which the H atom is transferred from a primary to a secondary, a primary to a tertiary carbon, etc.

In the equilibrium structures of the radicals the most important features are the following: (a) the radical center is an sp^2 type carbon atom with close to coplanar bonds; (b) the length of the α-C−C bonds is shorter than the regular single C−C bond, similarly to that in alkenes or the methyl−ring distance in toluene type aromatic molecules; (c) the length of the β-C−C bonds is longer than that of the regular single bond, reflecting the fact that this is the weakest, i.e., the most vulnerable bond in the chain; (d) in the most stable conformations the p orbital of the radical center is eclipsed with a C−H bond.

The isomerization barriers are found to be the highest for the 1,2 and 1,3 H atom transfer reactions which take place through highly strained three- and four-membered cyclic transition structures, respectively. The barrier height for these reactions is between 37 and 42 kcal mol^{-1}. The barrier for the 1,4 H atom transfer is significantly lower, between 19 and 22 kcal mol^{-1}, in agreement with the smaller ring strain needed when the five-membered ring is formed. The most favorable barrier height corresponds to the six-membered cyclic transition structure of the 1,5 H atom transfer reactions, the height being between 11 and 15 kcal mol^{-1}. We obtained a barrier height of 15 kcal mol^{-1} for the 1,6 H atom transfer process we studied (or 16 kcal mol^{-1} for the reverse reaction).

The actual height of the barrier for a reaction involving a given number of atoms in the ring of the transition structure depends on the direction on the reaction due to the nonzero reaction energy. The number of the substituents also influences the height of the barrier, generally decreasing it, but the difference (not exceeding 5 kcal mol^{-1}) caused by substitution is smaller than the difference between the barrier height characteristic for a given number of ring atoms in the transition structure. The only exception may be the 1,5 as well as the 1,6 H atom transfer reactions: in a relatively large alkyl radical the relative importance of these two types of reactions may depend on the actual substitution.

According to the picture generally accepted, the barrier height of an intramolecular atom transfer process is the sum of the intrinsic barrier of the atom transfer observable in a strain-free bimolecular system and the ring strain needed for the formation of the cyclic transition state. We have decomposed the ab initio barrier heights by subtracting the barrier height of the most similar bimolecular reaction to get the ring strain energy. The latter proved to be around 27 kcal mol^{-1} for the 1,2 and 1,3 H atom transfer, about 8 kcal mol^{-1} for the 1,4 and below 2 kcal mol^{-1} for the 1,5 and 1,6 H atom transfer. These values are very similar to the "strain energies" we observed in the parent reactions of 1,n H atom transfer in *n*-alk-1-yl radicals and to the ring strain in cycloalkanes. It should be noted that the concept of the "intrinsic barrier characterizing the given atom-transfer reaction" is an abstract quantity that never appears without distortions caused by the characteristics of the given reaction, namely, steric effects, nonzero reaction heat, etc., so that the ring strain cannot be precisely determined by comparison of the uni- and bimolecular barrier heights.

The relative importance of the competing isomerization reactions follows the order of the barrier heights. If there is no possibility for 1,5 and 1,6 H atom transfer, the β-C−C rupture is probably faster than the isomerization, because the barrier height for isomerization reactions involving cyclic transition structures with five or less atoms in the ring exceeds the dissociation energy into an olefin and a smaller alkyl radical. In alkyl radicals where the 1,5 and 1,6 H atom transfer is possible, the latter dominate over dissociation at lower temperatures, but the dissociation may become more important at high temperatures. We have discussed the possibilities of describing the pressure dependence of the system of competing isomerization reactions. As generally the 1,5 isomerization is the dominant isomerization channel, its pressure dependence determines taht of the overall process. In the isomerization of the 2-methylhex-6-yl radical (6PR) the reaction is in the pressure-dependent range at atmospheric pressure, a fact that combustion models including this reaction might need to involve.

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Supporting Information Available: Cartesian coordinates of the transition structures of intramolecular H atom transfers (8 pages). Ordering information is given on any current masthead page.

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