J. Phys. Chem. A **1998,** *102,* 10777−10786

Ab Initio Studies of the Isomerization and Decomposition Reactions of the 1-Butoxy Radical

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Received: May 22, 1998

The unimolecular reactions of the 1-butoxy radical, a prototype of atmospherically important alkoxy radicals, are studied. The structures of the isomers of the C_4H_9O radical and the transition structures of the isomerization and main decomposition reactions of 1-butoxy are determined by ab initio quantum chemical methods. The energy-dependent rate coefficients of the unimolecular reactions involved were obtained in RRKM calculations. The threshold energy for the fastest channel, the 1,5 intramolecular H-atom transfer is 8.12, 9.23, 9.16, and 9.51 kcal mol^{-1} according to the MP-SAC2, BAC-MP4, DFT, and an additively corrected MP4 method, respectively. For the β-C−C dissociation reaction we found a barrier of 16.03, 13.34, and 12.39 kcal mol^{-1} at the BAC-MP4, DFT, and additively corrected MP4 level. The barrier height for the 1,4 isomerization is close to that of the C−C bond rupture. The fastest reaction of the radical is isomerization involving a six-member transition structure, converting the alkoxy radical into an OH-substituted alkyl radical. The decomposition reaction can compete with the 1,5 isomerization step at high excitation or at combustion temperatures.

I. Introduction

The alkoxy radicals are some of the key intermediates in the chemistry of the atmosphere[1−9] as well as in combustion.[10,11] In the atmosphere, the alkoxy radicals are formed from alkyl radicals, as the products of the oxidation of hydrocarbons initiated by OH radicals. Their major reactions[1,3,5,8] are the bimolecular reaction with oxygen molecules, producing HO_2 radicals and leading finally to aldehydes or ketones; the unimolecular decomposition, also yielding unsaturated compounds (mostly aldehydes) and an alkyl radical; and isomerization, which converts the oxygen-centered radical into a carbon-centered hydroxyalkyl radical. The relative rates of these processes determine the role of the alkoxy radicals in the ensemble of chain reactions, as the reactivity of the products of these reactions is different. At the elevated temperatures of combustion systems the importance of the decomposition processes may be increased. Successful modeling, essential to the understanding of atmospheric and combustion processes, requires the knowledge of the rate coefficients of the reactions involved in the system. However, very few of the rate coefficients of the major classes of reactions of alkoxy radicals have become known at a satisfactory accuracy despite two decades of research.[1] Especially little is known about the general importance of the unimolecular processes: decomposition and isomerization. The decomposition reactions of small alkoxy radicals were extensively studied by Batt and coworkers[7,8,12−17] and by others.[18−23] The decomposition rate is close to the high-pressure limit at atmospheric pressure and room temperature.[17,21,22] The activation energy was originally thought to follow a linear free energy relationship. Choo and Benson, however, suggested that the linearity is modified because the properties of the alkyl leaving group do influence the rate.[24] The expression they suggested to quantify the effect of the leaving group contains the ionization potential of the alkyl radical. Recently, Atkinson[1] has reevaluated the parameters of the equation based on the most recent experimental data.

There are only a few experimental investigations in the literature on alkoxy radical isomerization reactions.[19,20,25−30] The isomerization is fast only if formation of a six-member transition structure is possible, i.e., there is a linear chain fragment involving at least four carbon atoms next to the O atom of the alkoxy radical. The radical center is shifted from an oxygen to a carbon atom. The δ-hydroxyalkyl radical formed will react with O_2 molecules similarly to an alkyl radical, and a hydroxy-substituted peroxy radical is formed that follows the pathways of peroxy radical reactions. Atkinson[1] has evaluated the available experimental data and recommended some formulas for the calculation of the rate coefficient under tropospheric conditions. The evaluation shows that the rate of alkoxy isomerization exceeds that of the reaction with oxygen in butoxy, pentoxy, and hexoxy radicals as well as in some β-hydroxyalkoxy radicals.

The prototype of alkoxy radicals in which 1,5 H atom transfer is possible is the 1-butoxy radical. This radical has attracted significant recent attention as the smallest alkoxy radical in which 1,5-H atom transfer resulting in a 4-hydroxyalkyl radical is possible.[16,17,20,21,24,25] Due to the difficulties of the experimental determination of the absolute rates and branching ratios of alkoxy radical reactions, a theoretical approach is warranted. The 1,5 H atom transfer in this radical has been studied earlier by Houk et al.[31] at an approximate level (geometries not fully optimized, energies calculated at low level). Recently, Jungkamp et al.[32] performed an extensive set of ab initio and density functional theory calculations on a large number of reactions involved in the atmospheric degradation of *n*-butane,

10.1021/jp9823547 CCC: $15.00

including some reactions of 1-butoxy radicals. The barrier heights, reported by these workers, however, having been calculated with relatively low-level ab initio methods, cover such a wide range that the calculated rate coefficients differ by more than 3 orders of magnitude if derived from one or another barrier height. As they also concluded, more accurate calculations are needed to obtain reliable barrier heights required by quantitative modeling of these processes.

In this work, using several ab initio methods, we calculated the barrier height for the following unimolecular reactions of the 1-butoxy radical:

$$CH_3CH_2CH_2CH_2O$$

$$\xrightarrow{\beta\text{-C}-\text{C dissocn}} CH_3CH_2CH_2 + H_2CO \qquad (1)$$

$$\xrightarrow{\text{1,2 H atom transfer}} CH_3CH_2CH_2CHOH \qquad (2)$$

$$\xrightarrow{\text{1,3 H atom transfer}} CH_3CH_2CHCH_2OH \qquad (3)$$

$$\xrightarrow{\text{1,4 H atom transfer}} CH_3CHCH_2CH_2OH \qquad (4)$$

$$\xrightarrow{\text{1,5 H atom transfer}} CH_2CH_2CH_2CH_2OH \qquad (5)$$

$$\xrightarrow{\beta\text{-C}-\text{H dissocn}} CH_3CH_2CH_2CHO + H \qquad (6)$$

For comparison with the corresponding bimolecular reactions in which a H atom is transferred from an oxygen to a carbon atom, we also studied the following reactions:

$$CH_3O + CH_3CH_2OH \rightarrow CH_3OH + CH_3CHOH \qquad (7)$$

$$CH_3O + CH_3CH_2CH_3 \rightarrow CH_3OH + CH_3CH_2CH_2 \qquad (8)$$

$$CH_3O + (CH_3)_2CH_2 \rightarrow CH_3OH + (CH_3)_2CH \qquad (9)$$

Similarly to the work we have completed on the isomerization reactions of alkyl radicals,[33,34] we performed high-level ab initio calculations to locate the transition structures occurring in the possible isomerization and decomposition processes of this radical, and used RRKM theory to calculate the rates under different conditions. In the remainder of the paper we first sketch the theoretical methods (section II), then discuss the properties of the radicals and the transition structures (section III), and analyze the rate coefficients and the relative importance of the different channels under atmospheric conditions in section IV.

II. Methods

The ab initio calculations were performed using the Gaussian 94 program suite.[35] The structure of the radicals and the decomposition products was determined at the UHF/6-31G* (for BAC-MP4 calculations) and at the MP2/6-31G* level. The nature of the stationary structures was justified by calculating the vibrational frequencies. All transition structures reported in this work are saddle points characterized by one imaginary frequency. The vibrational mode corresponding to the imaginary frequency involves motion that transforms the reactant of the reaction in question into the corresponding product. For the statistical mechanical calculation of the thermodynamical properties, the zero-point energies and vibrational frequencies were scaled by the factors recommended by Pople et al.[36] The energies of the stationary structures were calculated at the BAC-MP4,[37] MP2/6-311G**, and MP-SAC2[38,39] level of theory, as well as with density functional theory[40] (with the B3LYP functional[41] and the 6-311+G(2d,p) basis set). The SAC method was used to derive the barrier heights of the isomerization reactions 2−5 only, when the mean, $F_2 = 0.855$, of the correlation scale factors determined by Truong and Truhlar[38] for the O−H ($F_2 = 0.87$) and C−H ($F_2 = 0.84$) bonds was adopted. The application of the SAC procedure, based on the following reasoning, seems to be inapplicable for the dissociation reactions. The basic idea of the procedure is that one should know the dissociation energy of the critical bonds in the reaction. While in the isomerization processes the number and nature of the bonds remain the same, in the dissociation of the radicals in question a radical and a stable molecule are formed. During this process, in addition to the bond rupture, a C−O single bond is transformed into a C═O double bond and the dissociation energy of the radicals involves not only the energy needed to break the C−C or C−H bond but also the energy gain due to the formation of the double bond. It is probably not straightforward to include the corresponding complex correlation picture into one single scaling factor so that we do not use this method to calculate energetic data for reactions 1 and 6. It is worthwhile noting that during our initial attempts to apply the SAC method to the dissociation processes, at the MP2/6-311G** level we encountered a serious problem. We tried to derive the appropriate SAC factors for the MP2/6-311G** level from calculations on the dissociation of ethane to two methyl radicals and for the dissociation of butane to two ethyl radicals. The MP2/6-311G** dissociation energy, in both cases, exceeded the experimental one. Strictly speaking, this would mean that the MP2/6-311G** calculation "overestimates" the electron correlation resulting in a scaling factor larger than unity.

The calculations show that the lowest barriers correspond to reactions 1, 4, and 5. As the importance of reaction 1 is critical in certain cases, and the MP-SAC2 method proved to be inapplicable for the calculation of the barrier height of this reaction, we performed calculations at higher levels. G2-MP2 calculations proved not to be available using our resources. In the open-shell systems like the one in this study, a major source of error is the significant spin contamination. In our studies on bimolecular H-atom transfer reactions, we have observed that the energy correction that can be obtained using the QCISD(T) step of the G2 procedure can be very well reproduced in projected MP4 calculations.[42] Applying the additivity principles of the G2 method, we simulated PMP4/6-311+G(3df,2p)//MP2/6-31G* energies by performing MP2 and PMP4 calculations with the 6-311G** basis set and MP2 calculations using the 6-311+G(3df,2p) basis set. The PMP4/6-311G** energy was corrected by the energy improvement when the basis set was increased in the MP2 calculation. In the tables we refer to this method as "additively corrected MP4".

The specific rate coefficients $k_i(E)$ for each channel were calculated using RRKM theory.[43] For the calculation of the thermal rate coefficients of the simultaneous reactions at various pressures we used the techniques described in ref 34.

III. Results and Discussion

IIIA. Geometries of the Isomers of Butoxy. The most important parameters of the equilibrium geometries of the isomers of the butoxy radical are listed in Table 1. There are characteristic differences between the bond lengths of the C−C and C−H bonds, depending on their "distance" from the radical center and from the O substituent. In alkyl radicals the C−C bond involving the radical center (the α-C−C bond) was

TABLE 1: Selected Bond Lengths of the C_4H_9O Radicals

	bond length/Å						
radical	O−H	α-C−H	β-C−H	(O−)C−H	α-C−C	β-C−C	C−O
butoxy	N/A	N/A	N/A	1.103 1.103	N/A	1.523	1.390
1-hydroxybutyl	0.973	1.086	1.104	N/A	1.495	1.529	1.381
1-hydroxybut-2-yl	0.972	1.088	1.103	1.102 1.099	1.493	1.529	1.430
1-hydroxybut-3-yl	0.972	1.087	1.106	1.102 1.092	1.493	1.525	1.427
4-hydroxybut-1-yl	0.972	1.086	1.103	1.101 1.094	1.492	1.530	1.428

observed to be shorter than the C−C bonds in the unperturbed parts of the molecule,[33,34] suggesting that this bond is relatively strong. At the same time, the C−C bond involving the neighbor of the radical center and the carbon atom next to it (a β-C−C bond) is always longer in alkyl radicals than the C−C bonds in the spectator parts of the molecule,[33,34] indicating a relatively weak bond. The same observations can be made in the OH-substituted alkyl radicals. The α-C−C bond length is between 1.492 and 1.495 Å, while the unperturbed C−C bond length is about 1.525 Å (both essentially the same as in the unsubstituted alkyl radicals). The β-C−C bond, being between 1.523 and 1.530 Å, is the longest C−C bond in all alkoxy radicals, irrespective of whether the radical center is a carbon or an oxygen atom.

The C−H bonds also behave the same way as it was observed in alkyl radicals. The α-C−H bond length is between 1.086 and 1.088 Å while the β-C−H distance is between 1.103 and 1.106 Å. The former is shorter and the latter is longer than the unperturbed C−H bonds (around 1.095 Å at the MP2/6-31G* level). Interestingly, in the hydroxy-substituted isomers one of the C−H bonds that are in the β-position to the O atom of the OH substituent is also significantly longer than an unperturbed C−H bond.

The length of the C−O bond is 1.390 Å. As expected, this bond is shorter than an alcoholic C−O bond (about 1.43 Å) but longer than the carbonyl bond in butyraldehyde (1.224 Å). Interestingly, in the 1-hydroxybutyl isomer, where the oxygen atom is connected to the radical center, the C−O bond is also short (1.381 Å), in contrast to the other isomers where the C−O bond behaves as in alcohols. It is probably generally true that the bonds in the α-position to the radical center are shorter and probably stronger than the other bonds in the radical. An investigation of the lengths of bonds in the α- and β-positions with respect to the C═O double bond of butyraldehyde also shows that the α bonds are shorter and the β bonds are longer than the C−C and C−H bonds in the unperturbed alkyl chain of the aldehyde, just as in olefins. The possible reasons are generally the same as the shortening of the C−C bonds vicinal to carbon−carbon double bonds, as discussed in detail in ref 34.

IIIB. Reaction Enthalpies. The relative enthalpies of the isomers of the butoxy radical and its decomposition products, calculated with various methods, are listed in Table 2. The standard reaction enthalpy and so the heat of formation is more negative if the radical center is on a carbon atom. The least stable isomer is the oxygen-centered 1-butoxy radical, the most stable is the 1-hydroxybutyl radical, lower than the former by 14.5 kcal mol^{-1} at the MP-SAC2 and 12.3 kcal mol^{-1} at the BAC-MP4, and 7.7 kcal mol^{-1} at the DFT level. The isomers with a secondary carbon atom as a radical center are less stable (they are about 8 or 10 kcal mol^{-1} more stable than the butoxy radical at the MP-SAC2 and BAC-MP4 levels and by around 4 kcal mol^{-1} at the DFT level).

TABLE 2: Standard Reaction Enthalpies (kcal mol^{-1})

no.	HF/ 6-311G**	MP2/ 6-311G**	MPSAC2	BACMP4	DFT	expt
1	16.19	7.59	N/A	3.25	9.48	13.21
2	2.68	−11.91	−14.49	−12.29	−7.67	N/A
3	4.88	−7.23	−9.37	−7.55	−4.14	N/A
4	4.18	−7.81	−9.92	−8.34	−4.40	N/A
5	7.13	−6.27	−8.63	−5.35	−0.11	N/A
6	26.24	7.43	N/A	15.70	19.03	18.25
7	2.47	−11.66	−14.15	−12.86	−8.30	N/A
8	6.9	−4.5	−6.51	−5.02	−0.76	−3.17
9	4.3	−7.09	−9.1	−8.65	−4.83	−5.74

The decomposition reactions were not studied at the MP-SAC2 level. The breakage of the β-C−C bond, leading to formation of a propyl radical and formaldehyde, is slightly endothermic (by 3.3 kcal mol^{-1}) at the BAC-MP4 level and endothermic by 9.5 kcal mol^{-1} at the DFT level. The "experimental" (see later) reaction enthalpy is 13.2 kcal mol^{-1}, closer to the theoretical value obtained at the DFT level. The other decomposition reaction we studied, the H-atom elimination from a β-position, is an endothermic process. The reaction enthalpy is 15.7 kcal mol^{-1} at the BAC-MP4 level and 19.0 kcal mol^{-1} from the DFT calculation. The experimental value is 18.3 kcal mol^{-1}, closer again to the DFT result.

On the basis of a global comparison of the relative enthalpies obtained with the two empirically corrected ab initio methods we can conclude that the MP-SAC2 method results in the most negative reaction enthalpies. The BAC-MP4 results are more positive by about 2 or 3 kcal mol^{-1}, while the DFT data are shifted further in the positive direction by about 5 kcal mol.$^{-1}$ The possibility for comparison of the calculated data with the experimental reaction energies is limited. On the basis of the heats of formation taken from the literature[44−46] (propane, methanol, butyraldehyde, 1-butoxy: ref 44; H, formaldehyde, ethanol: ref 45; CH_3O, $(CH_3)_2CH$: ref 46), we calculated the reaction enthalpies also listed in Table 2. Although the calculations reproduce the general behavior, none of them reproduces well *each* of the reaction energies. One should, however, consider the "experimental" data with due caution as the "experimental" heat of formation of the 1-butoxy radical is an estimated value. Unfortunately, the comparison with the experimental data is not satisfactory to judge which theoretical level is more reliable.

IIIC. Geometries of the Transition Structures. Table 3 lists some of the characteristics of the geometries at the saddle points corresponding to the nine reaction channels (the MP2 unimolecular transition structures are also visualized in Figure 1). The bond lengths of the forming O−H and breaking C−H bonds in the series of three-, four-, five-, and six-member cyclic transition structures of the isomerization reactions show characteristic changes. The changes are similar to those observable in the analogous cyclic TS's in alkyl radicals.[33,34] The C−H−O triangle in TS2, characterized by small bond angles, is highly

TABLE 3: Selected Geometrical Parameters of the Transition Structures of Reactions 1−9[a]

transition structure	breaking bond C_a−H	forming bond O−H	C−H−O angle	C−O	α-C−H	*β*-C−H	(O)-C−H	α-C−C	*β*-C−C
TS1	N/A	2.069	N/A	1.221	1.086	N/A	1.108	1.499	1.536
TS2	1.249	1.209	69.0	1.392	1.096	1.101	1.096	1.498	1.528
TS3	1.323	1.262	105.3	1.448	1.091	1.099	1.095	1.507	1.528
TS4	1.257	1.291	132.1	1.425	1.095	1.097	1.100	1.507	1.527
TS5	1.245	1.268	150.2	1.408	1.095	1.098	1.102	1.514	1.530
TS6	1.604	N/A	N/A	1.224	1.113	1.096	1.113	1.516	1.534
TS7	1.216	1.315	161.1	1.407	1.099	1.094	1.098	1.504	N/A
TS8	1.234	1.264	168.8	1.408	1.093	1.096	1.098	1.512	1.530
TS9	1.217	1.294	175.7	1.407	1.095	1.097	1.098	1.514	N/A

[a] Bond lengths in Å, angles in deg, obtained at the MP2/6-31G* level. C_a is a C atom at the reaction center.

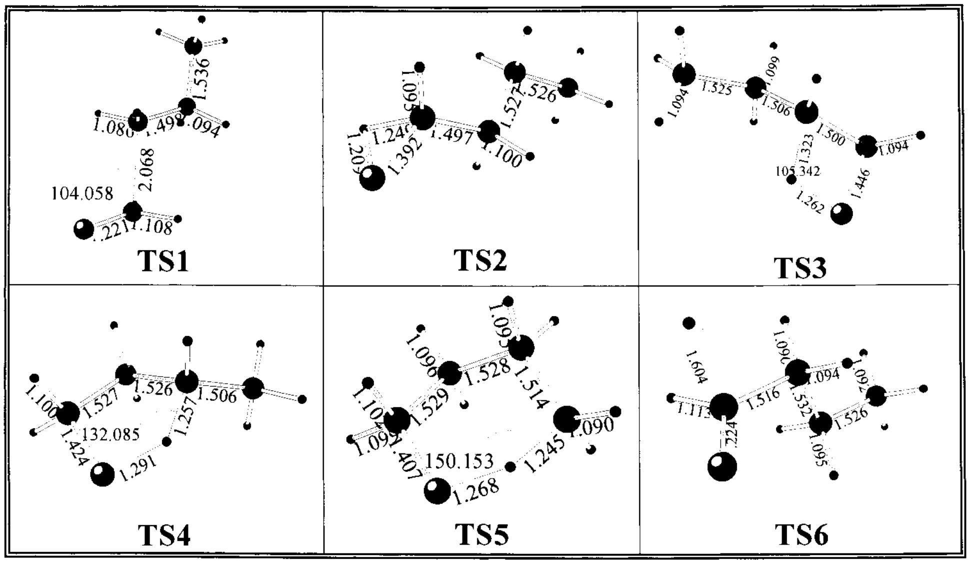

Figure 1. Transition structures for the unimolecular reactions of the 1-butoxy radical.

strained. The four-member ring in TS3 contains relatively long C−H and O−H bonds but is still very strained. In TS4 and TS5 the strain relaxes and the bond angles approach the equilibrium values, and the bond lengths of the breaking C−H and forming O−H bonds the values obtained in the related bimolecular reactions. The extension of the C−H bond is always larger than that of the O−H bond. There are some characteristic differences if one compares the bond lengths with those of the corresponding alkyl radicals. In the four-, five-, and six-member cyclic transition structures of the 1-pentyl radical we found that the C−H bond lengths at the reaction center are always larger by 0.05−0.09 Å than in the corresponding transition structures of 1-butoxy. In addition, the C−C bond lengths in the rings of the alkyl TS's are also shorter than in those of the alkoxy radical, the difference decreasing from 0.05 Å in the four-member ring through 0.015 Å in the five-member ring to essentially zero in the six-member ring. The angle at the reaction center, namely, the C−H−C angle in the TS's of 1-pentyl, is generally larger than the O−H−C angle in the corresponding TS's of 1-butoxy, but the difference is smaller than 1°. In the transition structures a main source of strain might be that the atoms at the reaction center are forced to a bent geometry while in an analogous bimolecular reaction the angle between the breaking and forming bond is relaxed. We found that the angle in question is very close to 180°, (within 2°) when an alkyl radical abstracts a H atom from an alkane, while in the studied bimolecular reactions involving H atom transfer by the methoxy radical the O−H−C angle is between 165° and 175°. As a result, the difference between the C−H−C angle in the intra- and bimolecular H abstraction transition structures of alkyl radicals is larger than the analogous difference in the TS's of the alkoxy radicals. This might be an indication that the latter TS's are less strained than the ones in which there is no oxygen atom in the ring.

It is interesting to note that in the hydrocarbon transition structures the rings are unsymmetrical if there is a substituent at one of the bridgehead carbon atoms. The bonds connecting the unsubstituted carbon atom (which is in analogous position to the oxygen atom in the 1-butoxy TS's) to the neighboring C and to the transferred H atom in the ring are longer than the analogous bonds involving the branching point of the hydrocarbon chain. This means that the larger O−H bond extension is caused partially by the effect of branching in the alkyl part of the chain. The relatively small differences between the geometries of the transition structures occurring in the isomerization of alkyl and alkoxy radicals indicate that the ring strain is not much influenced by the substitution of a CH_2 group by an oxygen atom.

Interesting observations were made when we compared the bond lengths in the transition structures optimized at the HF/6-31G* as well as at the MP2/6-31G* level. All isomerization transition structures are reactant-like at both levels, which is in agreement with Hammond's principle as the reactions are exothermic. The bond lengths of the breaking C−H bonds in the isomerization TS's are closer to the equilibrium C−H bond length in the reactant than are the forming O−H bonds to the unperturbed O−H bonds of the corresponding products. The saddle point geometries obtained at the MP2/6-31G* level, however, seem to be more reactant-like than the HF/6-31G* geometries. Studying literature data on other reactions, we

TABLE 4: Bond Orders of the Breaking and Forming Bonds in the Unimolecular Reactions of 1-Butoxy Calculated from ab Initio Wave Functions

	B(C−H)		*B*(O−H)	
reaction	HF	MP2	HF	MP2
2	0.45	0.54	0.42	0.34
3	0.47	0.61	0.41	0.30
4	0.55	0.72	0.35	0.21
5	0.55	0.72	0.37	0.22

	B(C−C)		*B*(C−O)	
reaction	HF	MP2	HF	MP2
1	0.27	0.30	1.42	1.45

	B(C−H)		*B*(C−O)	
reaction	HF	MP2	HF	MP2
6	0.20	0.35	1.46	1.39

found that for exothermic reactions this tendency is quite general. In order to quantify the differences, we calculated the bond orders from ab initio wave functions using the definitions of Mayer.[47] As the calculation of bond orders requires a well-balanced basis set,[48,49] we derived the values listed in Table 4 from the HF/STO-3G wave functions. The data reflect the tendencies of the geometries. The advantage of bond orders is that it is easier to quantify the degree of bond formation in terms of them. In TS5, for example, the bond order of the breaking C−H bond is 0.72 at the MP2 and 0.55 at the HF geometry, roughly indicating that the bond rupture proceeded to some 30% and about 45%, respectively. The formation of the O−H bond is completed to about 20% at the MP2 geometry and nearly 40% at the HF geometry. In the other transition structures the tendencies are identical. The differences are large enough to conclude that it is advisable to use the geometries obtained with the inclusion of electron correlation. It is interesting to note that according to the reported parameters of the B3LYP/6-31G** saddle point geometries of Jungkamp et al.[32] the latter structures are between the HF and MP2 geometries we found.

In the cyclic transition structures of the isomerization reactions both bridgehead atoms (the oxygen from which and the carbon to which the H atom is transferred) cause contraction of α- and extension of the β-type bonds as observed in the free radicals, although the magnitude of the effect is smaller in the TS's. This means that they both influence their environment as a radical center. The reason is that these atoms are in a partial sp^2 hybrid state and the spin of the free electron is delocalized along the O−H−C fragment, as discussed again in ref 34.

In the transition structures of the dissociation processes (1) and (6) the breaking bond, the C−C and C−H bond, respectively, is significantly longer than an unperturbed single bond. The bond length of the C−O bond is between that of a single and a double bond, indicating that this bond is also in transition. These transition structures proved to be product-like when the bond order of the breaking bond is considered, as expected for an endothermic reaction. The bond order of the C−O bond which changes from a single to a double bond is smaller than 1.5, although the bond length is very close to that in the equilibrium geometry of the final aldehyde. Instead of assigning this result to an asynchronous mechanism, we think that the low C−O bond order reflects an inadequacy of the UHF wave function for the description of a distorted radical geometry with one extended bond. The relative “location” of the transition structures found at the HF and MP2 level is reverse to the relation observed in the isomerization reactions: in the exothermic direction (i.e., for the reverse process) the MP2 structure is slightly less reactant-like. It can be noted that in the transition structures of the dissociation reactions only one carbon atom of the breaking bond, the one which is connected to the remaining alkyl chain causes contraction of the α- and extension of the β-type bonds.

IIID. Barrier Heights. 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 5. The barrier heights obtained at the HF/6-31G*//HF/6-31G* level are very close (within about 1 kcal mol^{-1} to those at the HF/6-311G**//MP2/6-31G* level (note that there is a change in the geometry also)), and both are much higher than the results of the MP2 calculations. In the latter, in contrast to the HF calculations, the improvement of the basis set lowers the barrier generally by about 3 kcal mol^{-1}, irrespective of whether it was low or high. The empirical corrections in the MP-SAC2 and BAC-MP4 methods further decrease the barriers. The final results obtained at the two levels are very close to each other, in some cases the agreement is embarrassing. The largest difference is 1.6 kcal mol^{-1} except for reaction 7, which proved to be barrierless at the BAC-MP4 level. The DFT calculations also lead to similar results, the largest difference with respect to the farther of the BAC-MP4 or MP-SAC2 values being below 2 kcal mol^{-1} except for three cases. The additively corrected MP4 method was used to calculate the barrier height for reactions 1 and 5. For the former, it resulted in a lower barrier, and for the latter reaction in a higher barrier, than any other method.

The highest threshold energy was found for the 1,2 H atom transfer and the lowest for the 1,5 H-transfer reaction, similarly to the corresponding reactions of the alkyl radicals. The β-scission reactions fall between the two limits: their barrier height is lower than those of the 1,2 and 1,3 H atom transfer but higher than that of the 1,5 H atom transfer. The threshold energy of the 1,4 H atom transfer is very close to that of the β-C−C bond dissociation. This indicates that the fastest reaction is the 1,5 isomerization, in agreement with the experimental data, with the findings on the alkyl radicals, and with the theoretical results of others.[32]

The absolute magnitude of the barrier height is critical to the correct calculation of the rate coefficients. The theoretical calculations published earlier[31,32] resulted in a 5 kcal mol^{-1} scatter in the threshold energy of the fastest reaction, reaction 5. Such a large error leads to rate coefficients that differ by more than 3 orders of magnitude. The barrier heights we obtained using the high-level ab initio methods for this reaction are much closer to each other. The difference of the barrier heights is generally smaller than 2 kcal mol^{-1}, except for reaction 1 where the DFT and the additively corrected MP4 barrier is very low and the BAC-MP4 method yields a barrier that is about 3.6 kcal mol^{-1} higher than the lowest of the other two.

The lowest barrier among the unimolecular reactions of the 1-butoxy radical, corresponding to the 1,5 H atom transfer (reaction), is characterized by a barrier height of 8.12, 9.23, 9.16, and 9.51 kcal mol^{-1} according to the MP-SAC2, BAC-MP4, DFT, and additively corrected MP4 methods, respectively. Heiss and Sahetchian[29] reported an activation energy of 9.7 kcal mol^{-1} for this reaction, which is very close to the calculated ones. The scatter of the calculated barrier heights is much smaller than that of the previous calculations, leading to a possibility of calculating rate coefficients with a significantly improved accuracy. We can conclude that the earlier estimate

TABLE 5: Threshold Energies (Activation Energies at 0 K) for Reactions 1−9 Obtained from ab Initio Calculations (kcal mol^{-1})

	E_0									
reaction	HF/ 6-31G*	MP2/ 6-31G*	HF/ 6-311G**	MP2/ 6-311G**	MP4/ 6-311G**	B3LYP/ 6-311+G(2d,p)	MP-SAC2	BAC-MP4	corrected MP4	expt
1	28.92	22.76	27.45	20.66	19.98	13.34	N/A	16.03	12.39	16.6,[a] 15.1[b]
2	51.75	32.19	48.04	28.53	N/A	28.77	25.09	25.23	N/A	N/A
3	51.53	31.62	48.62	28.34	N/A	26.66	24.77	24.80	N/A	N/A
4	39.95	23.13	37.74	20.04	N/A	16.88	16.92	15.27	N/A	N/A
5	33.17	15.23	30.92	11.54	11.86	9.16	8.12	9.23	9.51	9.7[c]
6	33.93	24.10	32.95	24.35	N/A	20.60	N/A	22.73	N/A	N/A
7	25.88	8.64	24.40	5.72	N/A	1.91	2.42	−0.61	N/A	N/A
8	31.15	13.74	29.15	10.03	N/A	7.56	6.65	6.11	N/A	6.5[d]
9	28.01	11.00	26.25	7.66	N/A	4.54	4.37	5.61	N/A	4.6[d]

[a] Reference 2. [b] Reference 28. [c] Reference 29. [d] Reference 50.

of Baldwin and Golden,[23] $E_A = 7.7$ kcal mol^{-1}, is probably lower by 1 or 2 kcal mol^{-1} than the actual barrier height.

The next lowest barrier characterizes the 1,4 H atom transfer, reaction 4, with calculated barrier heights of 15.27, 16.88, and 16.92 kcal mol^{-1} at the BAC-MP4, DFT, and MP-SAC2 level, respectively (no additively corrected MP4 data are available for this reaction). One can expect a strong competition between the C−C rupture, reaction 1, and the 1,4 H atom transfer. The barrier height for the latter is 16.03, 13.34, and 12.39 kcal mol^{-1} at the BAC-MP4, DFT and additively corrected MP4 level (no MP-SAC2 data are available for this process due to the reasons discussed in section 2). The competition between decomposition and 1,4 isomerization depends not only on the threshold energy but also on the number of states at the barrier, and the latter favor the dissociation. This means that it is the actual energy in the radical that determines which reaction is faster. The barrier height is slightly lower for the isomerization at the BAC-MP4 level, while the DFT barrier height is much lower for the bond scission than for the isomerization. The barrier heights obtained at the MP-SAC2 level for reaction 4 and at the additively corrected MP4 level for reaction 1 are close to each other and fall in the higher part of the range spanned by the other calculations. The gas-phase experiments at relatively high pressures performed with radicals where both processes are possible (but the 1,5 isomerization is not) recorded the bond dissociation only. The barrier heights reported for the decomposition reactions are between 13.9 and 18.3 kcal mol^{-1} (see ref 2 for a compilation). This range overlaps with the values we found. Jungkamp et al.[32] obtained barrier heights between 9.8 and 15.6 kcal mol^{-1}, lower in general than the measurements and our data. The lower values were obtained by the simplified CBS calculations that are the highest level calculations in their study. The barrier height they obtained at the B3LYP/6-311+G-(3df,2p) level, 12.9 kcal mol^{-1}, is very close to our DFT and additively corrected MP4 value.

The next fastest channel is probably the β-C−H scission, as the barrier height for this process is around 21−22 kcal mol^{-1} according to the BAC-MP4 and DFT calculations. This channel probably cannot compete with the previous three reactions.

The 1,2 and 1,3 isomerization processes are not probable to take place in alkoxy radicals except the former in methoxy, as the barrier height for these processes, being around 25 kcal mol,$^{-1}$ is significantly larger than for other possible reactions.

IIIE. Ring Strain Energies. According to the picture suggested by Benson, the barrier separating the reactants from products in an isomerization reaction is determined by two additive contributions, the intrinsic barrier characterizing the atom transfer itself, and the strain energy needed to form the ring in the transition structure. The intrinsic barrier height can, in principle, be obtained from a bimolecular reaction. When studying the isomerization reactions of alkyl radicals,[33,34] we have estimated the magnitude of the ring strain energy as the difference of the barrier heights characterizing the intra- and intermolecular H atom transfer reactions. This procedure, however, is not straightforward in the reactions of alkoxy radicals. The problem is that if the reaction enthalpy of the intramolecular and bimolecular H atom transfer is different, two different ring strain energies will be obtained if calculated in the manner described above: one as the difference of the forward and one as the difference of the reverse barrier heights. The unequivocal solution to the problem is that one uses as reference reaction the bimolecular reaction corresponding to identically same reactants and products, i.e., in the present case the reactions in which a H atom is abstracted from different carbon atoms of 1-butanol by the 1-butoxy radical. (In this case one reactant and one product is 1-butanol and the reaction energy is identical to the isomerization energy of the alkoxy radical.) Unfortunately, we were unable to calculate the TS's for these reactions as the high-level ab initio calculation becomes prohibitively expensive for a TS involving 10 "heavy" atoms. We attempted the estimation of the ring strain using three other related reactions that are expected to be good representatives of the H atom transfer from C to O, namely, H abstraction by methoxy from ethanol and from the primary and secondary carbon atoms of propane (reactions 7−9). As listed in Tables 2 and 5, the reaction energy and the barrier height for these three processes are different from each other. Reaction 7 takes place through a very low barrier. The attack of a primary C−H bond (reaction 8) has a barrier of over 6 kcal mol^{-1}, while the secondary carbon atom yields its H atom more easily. Tsang[30] has listed experimental activation energies of 6.5 and 4.6 kcal mol^{-1} for reactions 8 and 9, respectively, which are very closely matched by the MP-SAC2 barriers (6.7 and 4.4 kcal mol^{-1}) and closely matched by the BAC-MP4 values, the agreement being within the expectable range of accuracy of the corrected ab initio schemes. In the chemical sense, reaction 7 is closest to reaction 2 as the H atom is abstracted from a carbon that is connected to an O atom, and really, the reaction energies (both at the BAC-MP4 and MP-SAC2 level) are quite close for these two processes. In reaction 8 the H atom is transferred from a primary carbon atom in a hydrocarbon environment and may serve as a reference for reaction 5. The reaction heats for these two reactions are the same at the BAC-MP4 level and within 2 kcal mol^{-1} at the MP-SAC2 level. The H abstraction from a secondary C atom, reaction 9, is the analogue of reactions 3 and 4, and they are also close in reaction energy (within about 1 kcal mol^{-1} at any level).

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[a]

ring size	O-containing rings			pure C rings		c alkane
	DFT	MP-SAC2	BAC-MP4	MP-SAC2	BAC-MP4	Benson[b]
3	27.0	22.7	25.8	23.1−26.4	27.9	27.6
4	22.1	20.2	19.2	23.6−27.3	25.8	26.6
5	12.3	12.4	9.7	6.6−9.4	9.9	6.3
6	1.9	1.7	3.1	−0.8−2.0	3.6	0.2

[a] Energies are in kcal mol^{-1}; data for the cyclic TS's of alkyl isomerization are taken from refs 33 and 34. [b] See Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: New York, 1976.

The differences between the intra- and intermolecular barrier heights using the reference bimolecular reactions listed above are summarized in Table 6. These quantities, due to the lack of the "absolute" intrinsic barrier height and the uncertainties sketched above, can serve as a rough measure of the ring strain. The source of error in the ab initio calculations is partly the intrinsic error of the barrier height coming from the corrected ab initio calculation, and partly that the reaction energies for the intra- and intermolecular processes are not identical. A worst-case estimate of this error is about 3 kcal mol^{-1}. The estimated ring strain energy is about 22−27, 19−21, 9−12, and 1−3 kcal mol^{-1}, respectively, for a three-, four-, five- and six-member cyclic transition structure containing an oxygen atom. For comparison, the corresponding values obtained earlier for alkyl isomerization reactions are also listed in Table 6. The estimated strain energy in the TS's of the alkoxy isomerization reactions are essentially the same as in those of alkyl isomerization. (E_s is somewhat lower at the corresponding level of calculation in the four-member and higher in the five-member oxygen-containing rings than in the corresponding alkyl rings, but the difference is comparable to the expected accuracy of the estimation of the ring strain.) The near equality of the respective strain energies in the TS's of alkoxy and alkyl isomerization indicates that the energetics does not reflect the virtually smaller geometrical strain observed in the alkoxy TS's. (As noted in Section IIIA, in the intramolecular TS's the O−H−C and C−H−C angles are very close. In contrast, the TS of the bimolecular H transfer from O to C takes place through a bent TS, especially for reaction 7, while the C-to-C H transfer is essentially collinear.) The comparison of the estimated ring strain energies for alkoxy isomerization with the values recommended by Benson for cycloalkanes shows that for the three- and six-member rings they are close to each other, while for the TS's of the 1,3 and 1,4 isomerization the ab initio estimate is 5−7 kcal mol^{-1} lower and 6 kcal mol^{-1} higher, respectively. As the estimation of the ring strain energy is not a definitive procedure (see also the discussion above and in ref 34), we think that this difference is within the range of uncertainty of the estimation.

IV. Studies of Reaction Kinetics

IVA. Microscopic Rate Coefficients. On the basis of the ab initio frequencies of the reactant and the transition structures as well as the barrier heights, we performed RRKM calculations to determine the microscopic rate coefficients corresponding to the various channels. As long as the assumption of intramolecular chaos is valid, the rates of the individual reactions are independent from each other and the regular RRKM formalism can be used for each of them separately. A very accurate treatment of the isomerization reactions would involve the back-reaction also, especially for the high-pressure limit (see, e.g., ref 51). The products of the isomerization reactions, however, are either unimportant (channels 2, 3, 4) or very probably disappear in the presence of oxygen or NO (channel 5), a condition common to most experiments and real occurrences of alkoxy chemistry. For this reason we disregarded the reverse reactions in this study. In the RRKM calculations we assumed statistical factors of 1, 2, 2, 2, 3, and 2 for reactions 1−6, respectively, so that the rate coefficients for the isomerization reactions on a per H atom basis can be obtained from our data by division with the corresponding factor. Figure 2 shows the microscopic rate coefficients $k_i(E)$ obtained using the BAC-MP4 ab initio data which represent one extreme set of barriers: the barrier of the C−C decomposition is much larger than for the 1,5 isomerization, and is comparable to that of the 1,4 H atom transfer. Having the lowest threshold energy, the fastest reaction at energies below ~45 kcal mol^{-1} is reaction 5, the 1,5 isomerization of 1-butoxy. The rates of reactions 1 and 4 are very close to each other at low excitation above the barrier, but at energies above ~18 kcal mol^{-1} the rate of the C−C dissociation, increasing faster, passes that of the 1,4 isomerization. The rate of increase of $k_1(E)$, due to the faster increase of the number of states at the TS, is so large that at high energies it exceeds $k_5(E)$. All the other channels are significantly less important in the entire energy range.

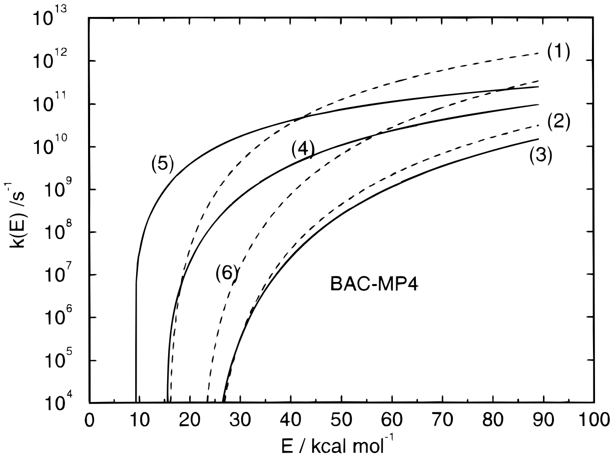

Figure 2. The microscopic rate coefficients for the six unimolecular channels (1)−(6) calculated based on the BAC-MP4 data.

While the BAC-MP4 calculations result in one extreme set of barriers, the other extreme is obtained when the barrier heights are taken from the expensive additively corrected MP4 calculations for the most critical reactions 1 and 5, and from the MP-SAC2 calculations for reactions 2−4 where this latter method is expected to be reliable (for the much less important reaction 6 we used the BAC-MP4 data). In these calculations the scaled MP2 frequencies are used. As expected, the importance of the decomposition is larger if calculated with these data, as shown in Figure 3. $k_1(E)$ becomes larger than $k_5(E)$ at about $E = 20$ kcal mol^{-1}. As the threshold energy for channel 4 is significantly higher than that of channel 1, the 1,4 isomerization is much less important than the C−C rupture at any energies. Similarly to the results based on the BAC-MP4 calculations, the rate coefficients for the other channels are also found to be much smaller if calculated with this set of ab initio data.

The branching factors calculated as the ratio of $k_i(E)$ to the sum of all microcanonical rate coefficients at energy E represent quantitatively the relative importance of the different channels. They were calculated using the rate coefficients based on the two sets of ab initio data listed above and are shown as a

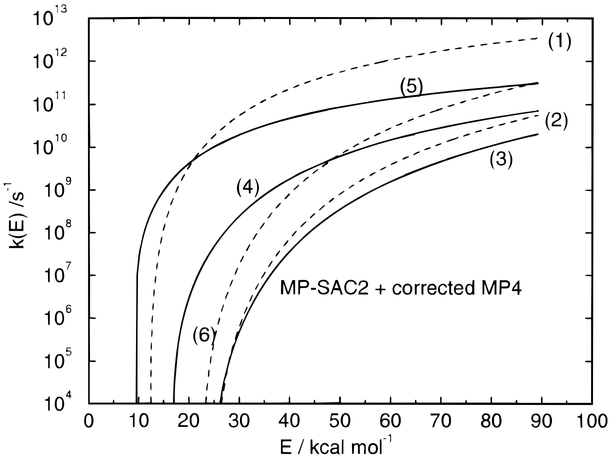

Figure 3. Microscopic rate coefficients for the six unimolecular channels (1)−(6) calculated based on additively corrected MP4 data for reactions 1 and 5, the MP-SAC2 data for reactions 2−4, and the BAC-MP4 data reaction 6.

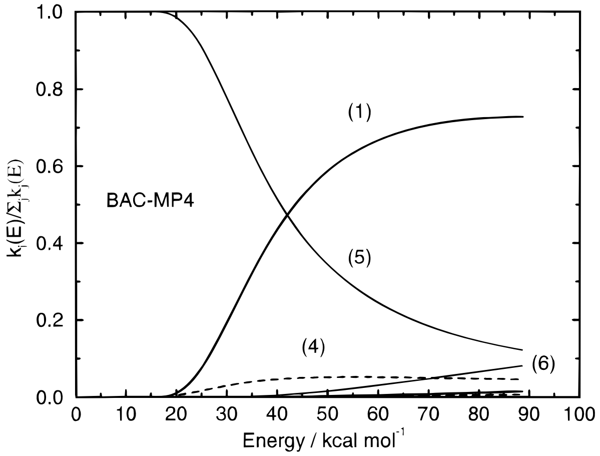

Figure 4. Branching factors, $k_i(E)/\sum_j k_j(E)$, calculated from the microscopic rate coefficients in Figure 2 (based on BAC-MP4 energetics), as a function of the energy in the 1-butoxy radical.

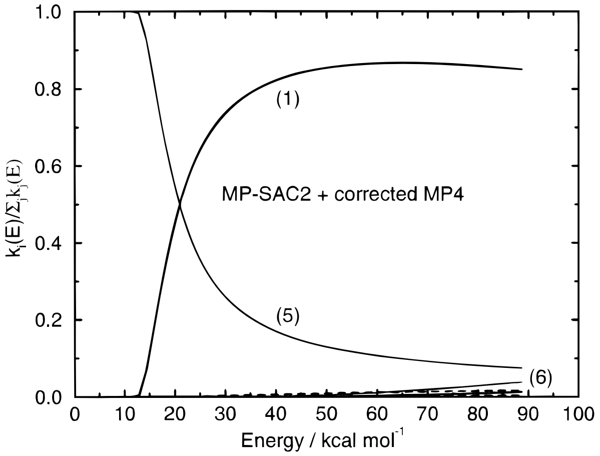

Figure 5. Branching factors, $k_i(E)/\sum_j k_j(E)$, calculated from the microscopic rate coefficients in Figure 3 (based on the corrected MP4 and MP-SAC2 energetics), as a function of the energy in the 1-butoxy radical.

function of the energy in Figures 4 and 5. At low energies 100% of the 1-butoxy radicals is consumed by 1,5 isomerization, while at high energies the C−C rupture, reaction 1 dominates. At medium energies the 1,4 H atom transfer may also participate up to a few percent, and at very high energies the C−H decomposition starts to be nonnegligible. In spite of the similar features, there is a qualitative difference between the two sets of curves. As the two sets of barrier heights represent two limiting cases, the difference may serve as a worst-case estimate of the error of the kinetics calculations based on the ab initio data. Based on the BAC-MP4 calculations, where the barrier height for the C−C decomposition is more than 5 kcal mol^{-1} higher than for the 1,5 H atom transfer, the isomerization and decomposition are equally important at about 40 kcal mol^{-1} excitation. On the other hand, as the barrier for decomposition is much closer to that of isomerization according to the additively corrected MP4 calculations, the rates of the two processes become equal at much lower energies (around 25 kcal mol^{-1}). The selection of the better set of ab initio data can be based on chemical activation experiments. If 1-butoxy is formed in a chemical activation reaction with a low energy (below 15 kcal mol^{-1}), 1,5 isomerization will dominate and all products will be formed from the 4-hydroxybutyl radical. The calculations based on both limiting sets of ab initio data predict the same outcome, so no distinction can be made between them. However, if the excitation in the chemically activated 1-butoxy radicals is large, around 40 kcal mol^{-1}, dominant C−C rupture can be expected if the threshold energy for the C−C rupture is low as in the corrected MP4 calculations. If, however, the barrier for C−C rupture is significantly higher than for 1,5 H atom transfer, as the BAC-MP4 data suggest, at this same energy the 1,5 isomerization is more significant although C−C rupture is not negligible, either. Interesting information can also be obtained from experiments with 1-butoxy activated into the range of very high energies. If the excitation energy is above 85−89 kcal mol^{-1}, and reaction 6, C−H decomposition, is found to be significant, it will indicate that the barrier for this channel is lower than in the BAC-MP4 calculations and might be similar to the results obtained with the DFT method. If the pattern of the actual barrier heights does not resemble the limiting cases we selected, the distinction and the experimental determination of the actual barrier heights will not be feasible based on one or a few “ultimate” experiments and the branching factors need to be measured at several energies.

IVB. Thermal Rate Coefficients. In contrast to microcanonical conditions, the macroscopically observable thermal rate coefficients of the multichannel reaction of 1-butoxy are not independent of each other. As discussed in ref 34 (model B), and using the notation of that paper, the approximate thermal rate coefficient for channel *i* can be obtained as

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

At low pressures the competition favors the faster channels more than that expected based on the ratio of the microcanonical rates because they empty the lower energy levels of the reactant, and the collisional energy transfer cannot fill up the higher levels where the slower channels could compete more efficiently (the quantitative description requires the solution of the master equation). The thermal rate coefficients at the high-pressure limit based on the BAC-MP4 and the combined MP-SAC2 + corrected MP4 set of barrier heights are listed in Table 7, and the falloff curves corresponding to 300 K are shown in Figures 6 and 7. The fastest isomerization reactions, (5) and (4), seem to be at or close to the high-pressure limit near 760 Torr. The C−C rupture, channel 1 and the slower isomerization channels are still in the falloff range at these pressures. At the reduced

TABLE 7: Limiting High-Pressure Unimolecular Rate Coefficients for Reactions 1−6 Based on the BAC-MP4 as Well as on the MP-SAC2 Barrier Heights for Reactions 2−4 and the Additively Corrected MP4 Data for Reactions 1 and 5

	reaction					
T/K	1	2	3	4	5	6
			$k_{i,\infty}$/s^{-1} (BAC-MP4)			
250	2.54E-02	1.63E-10	2.68E-10	3.30E-02	5.66E+03	2.92E-08
300	7.18E+00	9.21E-07	1.22E-06	5.99E+00	1.15E+05	7.40E-05
1000	4.12E+09	1.44E+07	7.93E+06	3.97E+08	4.38E+09	1.01E+08
			$k_{i,\infty}$/s^{-1} (MP-SAC2 + Corrected MP4)			
250	3.69E+01	2.62E-10	3.37E-10	1.33E-03	3.68E+03	2.97E-08
300	3.07E+03	1.48E−06	1.56E-06	4.06E-01	8.51E+04	7.59E-05
1000	2.29E+10	2.48E+07	1.05E+07	2.02E+08	4.95E+09	9.90E+07

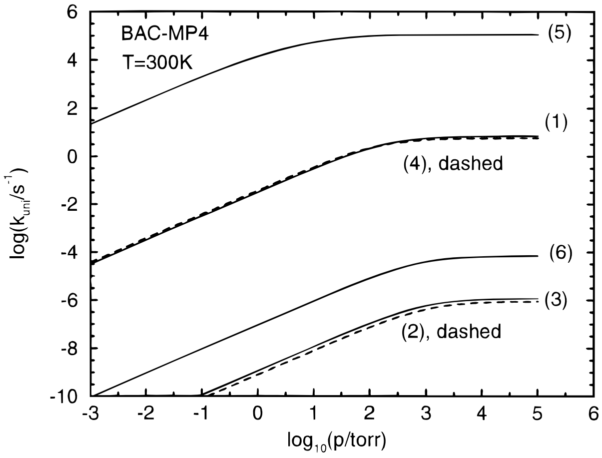

Figure 6. Unimolecular rate coefficients for reactions 1−6 as a function of pressure (T = 300 K), based on the microscopic rate coefficients calculated from the BAC-MP4 data.

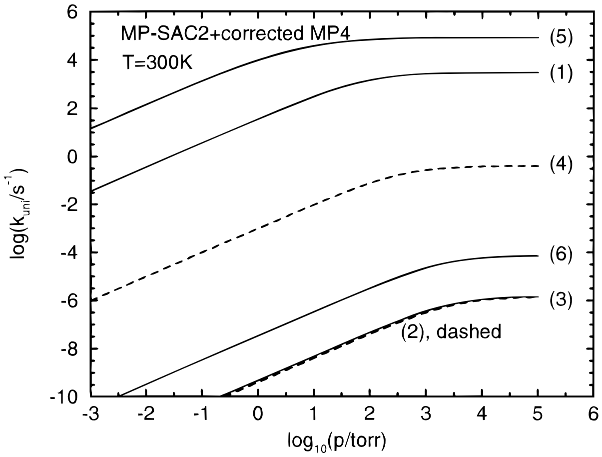

Figure 7. Unimolecular rate coefficients for reactions 1−6 as a function of pressure (T = 300 K), based on the microscopic rate coefficients calculated from the additively corrected MP4 data for reactions 1 and 5, the MP-SAC2 data for reactions 2−4, and the BAC-MP4 data reaction 6.

pressures of the troposphere, it is very probable that all channels are in the falloff range. As can be seen, the 1,5 isomerization is macroscopically also the fastest process at low temperatures. At lower temperatures its dominance is even more pronounced. With increasing temperature, however, the C−C rupture becomes more important, reflecting the changes of the specific rate coefficients with increasing energy. The calculated data can be compared with the experimental rate coefficient for reaction 5 at 300 K, found to be 1.2 × 10^5 s^{-1} by Heiss and Sahetchian,[29] while Atkinson recommends the value of 1.6 × 10^5 s.$^{-1}$ On the basis of the BAC-MP4, MP-SAC2, and corrected MP4 barriers used in RRKM calculations, we obtain for the high-pressure rate coefficient 1.15 × 10^5, 8.90 × 10^5, and 8.51 × 10^4 s^{1}, respectively. The calculated rate coefficient based on the BAC-MP4 barrier height for this reaction is very close to the experimental results. The low-temperature results indicate that the barrier height for this reaction is probably close to about 9 kcal mol.$^{-1}$ For the other reactions of 1-butoxy, clearly due to the dominance of the isomerization, no direct experimental data were found. The calculated rate coefficients, however, indicate that at higher temperatures the C−C decomposition will become more and more important, as the thermal populations of 1-butoxy sample the range of the higher energies where $k_1(E)$ is the largest.

V. Conclusion

We performed high-quality ab initio calculations for the unimolecular reactions of 1-butoxy radicals: 1,2-, 1,3-, 1,4-, and 1,5 H atom transfer leading to hydroxyalkyl radicals (reactions 2−5) as well as β-C−C (reaction) and β-C−H scission (reaction) processes. The barrier height obtained for the same reaction with the BAC-MP4 and MP-SAC2 methods and from additively corrected MP4 calculations differ by less than 2 kcal mol^{-1} except for a few cases. At the BAC-MP4 level the barrier heights are 16.0, 25.2, 24.8, 15.3, 9.2, and 22.7 kcal mol^{-1} for reactions 1−6, respectively. From the MP-SAC2 calculations we obtained 25.1, 24.8, 15.3, and 9.2 kcal mol^{-1} for the barrier height for the isomerization reactions 2−5, respectively. Our attempt to determine the barrier height at a higher ab initio level (using additive corrections as in the G2-MP2 method) yields 12.4 kcal mol^{-1} for the barrier height for the C−C decomposition and 9.5 kcal mol^{-1} for that of the 1,5 H atom transfer reaction 5. The results of our DFT calculations (B3LYP/6-311+G(2df,p)) are 13.3 kcal mol^{-1} for reaction 1 and 9.2 kcal mol^{-1} for reaction 5, indicating that the correlation energy is quite well described at this level. Comparing the barrier heights for the intra- and intermolecular H atom transfer processes, we found that the isomerization barrier can be estimated within about 4 kcal mol^{-1} from the barrier height of the proper bimolecular reaction by adding the ring strain energy recommended by Benson. The error of such an estimation is higher for the four-member cyclic transition structure where the apparent ring strain energy is about 5 kcal mol^{-1} lower than Benson's recommendation for cyclobutane.

The calculated microcanonical rate coefficients indicate, in agreement with the experiments, that the latter is the fastest reaction of 1-butoxy, except at very high excitation in a collision-free environment. The calculations are not conclusive concerning the importance of the 1,4 H atom transfer. At high energies the C−C decomposition is definitely faster than the 1,4 isomerization, but at low energies, due to tunneling, the latter may be the faster one. This competition does not influence the macroscopically observed kinetics at low temperatures as the 1,5 isomerization is much faster than either of these reactions.

In other systems, however, where 1,5 H atom transfer is not possible, its outcome may be very important. The thermal rate coefficient calculated from the BAC-MP4 data for the 1,5 H atom transfer is in very good agreement with the experimental observations. The rate coefficients at higher temperatures reflect the tendencies of the microcanonical ones: at combustion conditions, above 1000 K, the rate of the C−C decomposition is the highest.

The calculations allow us to estimate the relative importance of the various channels in general alkoxy radicals. In agreement with the generally accepted picture, if in an alkoxy radical 1,5 isomerization is possible, this will be the fastest reaction and the fate of the radical is determined by the kinetics of the formed hydroxyalkyl radical, most importantly, in the presence of oxygen, formation of hydroxyperoxy radicals and their further reactions. If an alkoxy radical is small or branched so that 1,5 isomerization is not feasible, probably the rupture of the β-C−C bond is the most important, but at low temperatures the 1,4 H atom transfer will not necessarily be negligible. In chemically activated systems, if the energy content of the radical is small, probably 1,5 isomerization will take place, while at high excitation the decomposition by the breakage of the β-C−C bond. The actual value of the relative rates, however, will also depend on the statistical factors, as in many cases there are several equivalent positions for H atom transfer or C−C rupture.

The question whether the barrier heights for a certain type of reaction are transferable is not yet clear. Several experiments (see, e.g., ref 2) indicate that in unsymmetrical alkoxy radicals the activation energy for C−C rupture varies with the reaction site. Work is in progress in our labs to answer this question by further ab initio calculations.

Acknowledgment. Financial support of our work by the Hungarian Scientific Research Fund (OTKA Grant T22824) and the use of the computational facilities made possible by a grant from CINECA (Bologna, Italy) are gratefully acknowledged. B.V. expresses thanks for a Magyary Zoltán postdoctoral fellowship (AMFK 535/2).

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